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THE TECHNOLOGY OF SCANDIUM, YTTRIUM, AND THE RARE EARTH METALS

A LITERATURE SURVEY

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FOREWORD

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ABSTRACT

A survey has been made of the unclassified literature relating to the rare earth elements. The best available data has been compiled for the abundance and distribution of the elements, the methods of recovery from ores, separation and purification techniques, and procedures for reduction to metal. The physical, chemical, and mechanical properties of the elements and their important compounds are presented.

PUBLICATION REVIEW

This report has been reviewed and is approved

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INTRODUCTION

This report constitutes a revision of the previously made literature survey reported in *Selection and Evaluation of Rare or Unusual Metals for Application to Advanced Weapons Systems* (461). Since publication of that report in 1958, significant advances have been made in rare earth metals technology. Scandium, yttrium, and the lanthanon elements have been prepared as high purity metals. Physical and mechanical properties have been investigated, and constitutional diagrams have been established for many metals with yttrium and the lanthanons.

Primary emphasis in this report will be placed on the properties of the rare earth metals and their alloys. As previously noted, however, utilization of these materials will ultimately depend on their cost as well as on their properties. For a better understanding of the economic factors involved, a preliminary discussion will be presented of sources of supply, methods of recovery from ores, methods of separation and purification of the individual rare earths, and procedures for the preparation of metals from the purified compounds. Since these processes are based upon chemical changes, a brief discussion will also be made of the more important chemical reactions and physical properties of the rare earth materials.

One of the most important economic considerations is the rate of overall production of rare earth materials, determined largely by demand for all types of products. Present and possible future uses of rare earths, in both the metallic and nonmetallic forms, will therefore also be considered.

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THE RARE EARTHS

Nomenclature and Terminology

The rare earths are defined as the group of elements of atomic number 57 through 71. Scandium, atomic number 21, and yttrium, atomic number 39, have properties which are similar to the rare earths, and they occur in nature together with the rare earths. These elements are therefore generally included in the term rare earths and will be so included in this report. For similar reasons, thorium, atomic number 90, is sometimes included. In this report, however. thorium will be omitted, except in so far as that its properties, especially in the metallic state, may offer clues as to the behavior of the rare earths.

The term "earths", when used in the strict chemical sense, refers to oxides. Through common usage, however, "rare earths" has come to have a generic sense, and is thus used to designate the group of elements irrespective of their chemical state. For example rare earth metals, rare earth ions, rare earth salts, or even redundantly rare earth oxides, are commonly used terms. It is further recognized that although the elements might well have been considered rare during the early period of discovery and chemical development, they are actually more abundant than many more commonly available, and better known, elements.

The term "lanthanons" has been proposed for the elements of atomic number 57 through 71 (517). Derived from lanthanum, the first member of the series, the suggestion is based on the similarity of the electronic structures of the rare earths to that of the transuranium elements. The latter are commonly called actinons after actinium, the first member of the series. Current literature makes use of all terms, and no clear cut acceptance has yet developed. There is considerable merit to the use of "lanthanons", but because "rare earths" is still the most widely used designation and because it is of a more general nature, including as it does scandium and yttrium, it will be most frequently used in this report.

The entire rare earth series is frequently divided into groups. The elements number 57 to 63; lanthanum, cerium, praseodymium, neodymium, promethium, samarium, and europium are called cerium group or light rare earths. The elements 64 through 71; gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium, and yttrium and scandium, are called yttrium group or heavy rare earths.

The terms "cerium group" and "yttrium group" are derived from the major element present in each group. The terms "light" and "heavy" rare earths are based on the relative atomic weights. Scandium, although light by virtue of its low atomic weight, behaves chemically more like lutetium than any other rare earth and is, therefore, included in the heavy group.

This division into groups is more than just an arbitrary one. The rare earths from any one natural source are usually found as one or the other major group. Also, many chemical properties show a gradual transition through the series. A break in these properties frequently seems to occur, however, at about element 63 or 64, europium or gadolinium, thus emphasizing division into two groups.

Occasionally gadolinium, terbium, and dysprosium will be referred to as a terbium group, or other groupings may be combined, but these terms will not generally be used in this report.

The term "didymium" has remained in usage from early in the history of the rare earths when it was believed to be a single element. It is now used primarily for the mixture of rare earths left after cerium is removed from cerium group earths. Some authors use "didymium" to identify the rare earths left after both lanthanum and cerium are removed. This latter mixture would contain mostly neodymium with praseodymium, samarium, and small percentages of the other elements. This mixture will be referred to in this report as "neodymium rich" or as "75% neodymium".

It may be appropriate at this point to note that precautions are particularly necessary with respect to interpretation of the terms "ceria" and "cerium" as used in the literature. As noted in the following section the entire cerium group of elements was at one time thought to be an individual element. Even after isolation, however, difficulties in separation and difficulties in analysis resulted in rather crude materials being identified as pure compounds. Of equal importance has been the general laxness in terminology as used by commercial suppliers of rare earth materials. Industrial mixtures were long identified as "ceria" compounds, and the mischmetal obtained from such mixtures as "cerium". More recently these have been generally properly identified, but "cerium" compounds are still of varying purity and may typically contain 80 - 98% cerium. It may be noted that both the United States Pharmacopeia and the Merck Index (533,856). indicate that ceric oxide and salts "may contain variable amounts of the other rare earth elements".

History

Discovery. The Finnish chemist, Johann Gadolin, in 1794 first discovered a new "earth" in a mineral which had been found at Ytterby, Sweden. Three years later, Ekeberg confirmed the discovery and suggested the name yttria for the oxide. Both Gadolin and Ekeberg considered yttria to be the oxide of a single element.

In 1803, Klaproth, and Berzelius and Hisinger, working independently, almost simultaneously discovered an oxide resembling yttria. The name ceria was proposed after the newly discovered planetoid Ceres.

Various investigators soon found that the oxides were in reality complex mixtures of many elements. The difficulties of separation and analysis led to a long and confusing history of discoveries, claims, and counter-claims, which did not end until the development of the ion-exchange method of separation, and the discovery of promethium as a fission product, during World War II. A brief outline of the historical development is given by Hopkins (323). Details of the discoveries, and intriguing personal notes on the discoverers, are well told by Weeks (897).

Technical Development. The development of the rare earth industry started with attempts during the nineteenth century to produce more light from flames. Berzelius in 1825 observed that thoria and zirconia emit an intense white light when heated in a non-luminous flame. Many attempts to develop a workable process were made during the next 60 years, including the use of rare earth mixtures as the illumination bodies. This work culminated in the discoveries of Dr. Carl Auer Von Welsbach, which were patented in the years between 1884 and 1893, of compositions and processes for the manufacture of gas mantles (897).

The process developed by Von Welsbach is still in use. A woven fabric framework is impregnated with a solution of thorium and cerium nitrates or acetates in the ratio of 99 parts thorium to one part cerium. Upon ignition the fabric burns away, and a coherent thoria residue is left which glows brightly when heated by a flame.

The need for thoria for the gas mantle industry led to the creation of a large monazite processing industry. Since monazite has approximately 10 times as much rare earths as thoria, large stockpiles of rare earth concentrates soon began to accumulate.

The second stage in the development of the rare earth industry was based upon the spread of applications for the rare earth mixtures, and a simultaneous decline of the mantle industry as electrification developed. Uses were developed for misch metal in pyrophoric alloys, for didymium and cerium in the glass industry, for rare earth fluorides as core materials in searchlight and arc lamp electrodes, and for specially prepared oxides as polishing materials replacing rouge.

The third stage of the rare earth industry is the current period since World War II. Thorium, upon capture of a neutron may fission, or may go through a decay chain eventually being converted to U_{233}, also a fissionable material. Thorium has consequently been classified by the United States Atomic Energy Commission as an atomic energy source material along with uranium. Production of thorium in the United States for potential use in atomic energy programs increased greatly during this period. Rare earth by-products from this thorium production were again available in larger quantities than needed for current commercial uses. Simultaneously, production of thorium from monazite was undertaken by both India and Brazil. This further increased the world's supply of rare earths, and created a situation of widespread over supply. The most recent mineral industry survey of the United States Bureau of Mines (451) indicates that domestic use of rare earths during 1959 was essentially the same as for 1958, and principally for the applications indicated above. Domestic production was about 40% of estimated consumption.

Abundance and Occurrence

It has often been repeated that the "rare earths are not rare". Estimates of the abundance of the rare earths in the earth's crust have been made by many geologists and geochemists, and an excellent summary of these estimates has been compiled by Michael Fleischer for the United States Geological Survey (209).

Fleischer tabulates the results of nine principal investigation sources as follows:

(1) Mason, Brian; 1952, Principles of Geochemistry, John Wiley and Sons, New York.
(2) Rankama and Sahama; 1950, Geochemistry, University of Chicago Press.
(3) Polanski; 1948, Soc. des Amis des Sci., Lettres de Poznan, Ser. B., Vol. 9.

(4) Anderson; 1945, Chemistry of the Earth, Royal Soc. New South Wales, Journal and Proceedings, Vol. 76.
(5) Goldschmidt; 1937, Norske Vidensk-akad., Oslo, Mat.-Nat. Klasse, No.4.
(6) Fersman; 1933, Quoted by Wells, 1937, USGS Bull. 878.
(7) Schneiderhohn; 1934, Metallwirtschaft, Vol. 13, Page 151-7.
(8) Berg; Vorkommen Und Geochemie der Mineralischen Rohstoff, Page 11, Leipzig.
(9) Clark and Washington; 1924, USGS Professional Paper 127, Page 1-117.

To this list has been added the work of: Rankama (664) and of Vinogradov (876).

Table I has been compiled from these references to give the best considered percentage range for the occurrence of the rare earths in the earth's crust. In addition, for comparative purposes, Table II indicates the occurrence of some of the more commonly known elements in approximately the same range of abundance.

It will be noted that total rare earths are about half as abundant as carbon or chlorine, in the same range of abundance as chromium, vanadium, or zinc, and more abundant than nickel, copper and many others. The more abundant individual elements are in the same range as bromine, tin, and molybdenum; even the scarcest are in the same range or more abundant than cadmium, mercury, bismuth, silver, or gold.

Mineralogically, the rare earth ores almost invariably fall into two classes, cerium and yttrium minerals.

Cerium minerals have a cerium content equal to approximately 50% of the contained rare earths. The balance is almost entirely the lighter rare earths of atomic number 57 to 64. Usually two percent or less of yttrium and two percent or less of the higher atomic numbered earths are present.

Yttrium minerals contain approximately 50 to 60% yttria (of the contained rare earths) with most of the balance being the intermediate and higher (64-71) atomic numbered rare earths. Only 1 to 10% of the lighter rare earths including cerium will be present.

Excellent summaries of the economic geology of the rare earth elements have been prepared by Heinrich (296) and Whitman (909). Particular emphasis is placed upon the chemical nature of rare earth minerals, the relationship between the various types of minerals and the geologic structures in which they occur, and the problems of mining and marketing.

Cerium Group Minerals. The cerium group ores have been of most commercial importance to date. Primarily this has been due to their greater availability and to the nature of the development of rare earth technology based upon the rare earths available as by-products of thorium production, almost all of which has been from the mineral monazite.

Monazite. Monazite is a phosphate of thorium (3 to 10%) and the light rare earth elements. It forms monoclinic crystals with a specific gravity of 5.0 to 5.5 and a hardness of about 5 (Moh's Scale). Small crystals are disseminated through many granites and pegmatites. Through weathering of these rocks and subsequent placer action, the heavy monazite is concentrated in stream and beach deposits together with the other heavy minerals present. Occasionally monazite is found in veins or massive deposits. Except as noted below, these are usually small and cannot be operated economically (534).

Production of monazite is based upon concentration of the heavy mineral fractions, followed by magnetic and sometimes electrostatic separation. Since monazite is weakly magnetic, the strongly magnetic minerals may first be removed by a weak magnet, and the monazite subsequently removed from non-magnetic minerals by a strong magnet (28,115).

Up to the time of World War II, almost all of the monazite processed in this country was imported. The principal sources were India and Brazil, where extensive placer deposits are located which are rich in monazite of high thorium content. Smaller imports were made from Korea and other parts of Asia, and from Australia.

Since the war, both India and Brazil have placed embargoes on the export of monazite. This has been done both to preserve fissionable thorium for their own future energy requirements and also in efforts to build domestic processing industries (116, 534,704).

The sudden cut-off of the major foreign sources led to an extensive exploratory program in the United States as well as abroad. Several large deposits were developed in the United States, and other potential sources were indicated.

In general, monazite deposits in the United States are not rich enough to be worked for the one mineral alone. The monazite is invariably associated with other commercially marketable minerals however. Monazite production is, therefore, dependent upon the establishment of very large scale operations for the separation of gold, ilmenite and/or rutile, garnet, zircon, and other minerals. Such operations are, or have been, conducted principally in Florida and South Carolina (450). In Idaho, stream placer deposits were developed and operated for several years, but the relatively low thorium content (3 to 5%) led to their abandonment in favor of other sources. These deposits remain, however, as potential future sources for monazite (28,116, 789,790,826). Some foreign sources produce monazite as a by-product of tin (cassiterite) mining (593).

Exploratory programs of the Bureau of Mines, and the prospecting of individuals and firms stimulated by government purchasing programs and exploration aid, have uncovered deposits of monazite in Idaho, Florida, North and South Carolina, Georgia, Alabama, Virginia, Montana, Wyoming, California, and Alaska. These discoveries provide monazite reserves for the future, and estimates of productive capacity range upwards from hundreds of thousands of tons (28,43,115,116,534,535,704,789,790,826).

The major new foreign source has been developed in the Union of South Africa, where monazite occurs in one of the rare massive vein deposits which is large enough and rich enough to be worked directly (475,593). It is believed that Australian sources have been developed to larger capacity, and monazite is also produced in Ceylon, Indonesia, Malaya, and Korea (593).

Bastnasite. Bastnasite, a rare earth fluocarbonate, was discovered in the Mountain Pass area of California in 1949. It had previously been known only as a mineralogical curiosity. The principal deposits occur in an area 3 miles wide by 7 miles long, although several near-by areas covering scores of square miles are reported to contain lesser deposits. The Sulphide Queen body alone, owned and operated by the Molybdenum Corporation of America, is estimated to contain more than one million tons of rare earths. This deposit is furthermore of particular value from a processing point of view since the mineral is largely carbonate with a minimum of fluoride, and thus lends itself to simplified process procedures (13,600, 601,659).

Bastnasite deposits have also been discovered in New Mexico, and some of these were reported to have produced bastnasite commercially for processing to rare earth compounds (100).

Allanite. Allanite (orthite) is a silicate of the rare earths with aluminum, iron, calcium, and sometimes beryllium. Allanite occurs rather commonly and is widely distributed in pegmatite bodies throughout the western United States, as well as in many other parts of the world. It may occur as small or large disseminated crystals throughout the pegmatite body, or as veins which may vary from a fraction of an inch to several feet in width. The rare earth content of allanites from various sources varies from 3 to 51% by weight as oxide, but it normally is 20 to 30%. It is this relatively low oxide content and the low thorium content (from a trace up to, perhaps, 3%) which has kept allanite from being processed on a large scale. Should a large demand for rare earths be created, however, the availability of very large quantities of allanite, which might be produced at a lower cost per ton than monazite, might overcome some of these disadvantages (593).

Cerite. Cerite is a rare earth, calcium, iron silicate. It contains from 50% to 70% cerium group earths, and may have 5 to 10% yttrium group earths, which is somewhat higher than present in monazite or bastnasite. Cerite occurs primarily in Sweden and in a few other localities, but is not abundant enough to be considered a principal source of rare earths.

Yttrium Group Minerals. The principal source of yttrium and the heavy rare earths in the past has been the mineral gadolinite and the "heavy" fractions from monazite. More recently, large quantities have become available from xenotime and euxenite.

Gadolinite. Gadolinite is a rare earth, iron, beryllium silicate. It usually has a rare earth content of about 40% as oxide. Most gadolinite comes from the Scandinavian countries. It is, however, a widespread although not very abundant component of pegmatites, and is found in small veins, lenses, or pockets in many states in the United States and in many foreign countries.

Xenotime. Xenotime, a phosphate of yttrium, the heavy rare earths, and thorium, has been found to occur along with its homolog monazite, in the placer deposits of Florida and the Carolinas. It is more strongly magnetic than monazite and thus can be separated from monazite by magnetic means. Since its magnetic properties approach that of ilmenite, it will concentrate with this fraction, but it is a poor electrical conductor and can therefore be separated from the ilmenite electrostatically (593).

The normal proportion of occurrence varies, but ranges from 1/2% to about 5% of the amount of monazite present. With recent emphasis on the discovery of rare materials, and improved methods of detection and analysis, reports of new discoveries of xenotime are occurring. Offerings of multi-ton quantities from Africa have been made. In California, recent discoveries have indicated the potential availability of monazite-xenotime mixtures in which the proportion of xenotime may be as high as 50% (676).

Euxenite. Euxenite is a complex tantalo-niobate of titanium, the rare earths, thorium, uranium, and minor elements. The mineral has been obtained from placer deposits in Idaho. After chemical processing, the uranium concentrates were sold to the Atomic Energy Commission, and the rare earth and niobium-tantalum fractions became the property of the General Services Administration.

Monazite Fractions. By-products from monazite processing yield fractions enriched in yttrium and the heavy rare earths (Table III). These fractions are obtained by processing mother liquors after separation of the cerium group as sodium double sulfates, or from the rare earths which accompany thorium in the initial thorium separations.

Scandium. Thortveitite is the only known mineral containing any significant concentration of scandium. It is a scandium silicate in which variable amounts of yttrium and rare earths, aluminum, iron, thorium, zirconium, and alkaline earths substitute for the scandium. Only two sources are known. Thortveitite was originally found in a granite pegmatite in southern Norway. A variety called befanamite is found in Madagascar.

The scandium content of these materials has been reported to be 33 to 45%. Analysis and processing recovery in the Research Chemicals laboratories indicate that material presently available is not always of such high grade.

Scandium is present as a minor element in many minerals (84,353,551,705,863). The development of solvent extraction processes for the recovery of uranium from its ores has provided a new source for this element. Although the scandium content of the ore is low, it gradually accumulates in the organic solvent and is eventually recovered as a greatly enriched concentrate.

Distribution of Individual Rare Earths in Rare Earth Concentrates. The availability of any individual rare earth element will depend upon its relative concentration in the mixed oxide as well as the availability of the oxide concentrates. Table III lists the relative abundancies of the elements in some typical ores and concentrates. These values are summarized and simplified in Table IV which indicates the approximate relative percentages of cerium group elements and yttrium group elements from their most probable sources.

Summary of Production and Availability

Cerium Group Earths. Accurate production figures for monazite are not available since they are classified secret under the Atomic Energy Act of 1946. The annual (United States) production capacity available to the principal processors, however, is estimated at 20,000-25,000 tons (422,431). It is probably a fair assumption that about 10,000 tons were processed annually during most of the 1950 decade. The potential available supply, as previously mentioned, is upwards of hundreds of thousands of tons from undeveloped domestic sources alone, in addition to the undisclosed reserves of currently operating deposits. The world's known reserves of monazite are estimated at three million tons (13).

Bastnasite, as indicated, is available in quantities upwards of one million tons. Present mill capacity at Mountain Pass is approximately 3,000-5,000 tons per year and can be rapidly expanded (659).

Allanite and other cerium group minerals will be available in very large, but unspecified, quantities should market conditions warrant.

Yttrium, Scandium, and Yttrium Group Earths. If we assume an average xenotime concentration of 1 to 2% in monazite deposits, the recent annual production of yttrium and yttrium group earths has been approximately 100-200 tons per year. The yttrium and heavy earths from processed monazite would provide an additional 100-200 tons per year. The General Services Administration has indicated an annual production rate of about 100 tons of rare earth oxides from euxenite.

Thortveitite production has been difficult to establish. A considered estimate based upon availability of material, and unconfirmed reports, indicates approximately 20 kilograms per year may be available from Norway. A reported 50 to 100 kilograms were produced in Madagascar. The latest indications are that no more is being produced there.

The market for yttrium and the heavy rare earths has been very modest until perhaps the last few years. The high cost of separation and purification has kept potential market demands down. Even in this situation, new deposits have been discovered.

One of the major sources of the future, in our opinion, will be the by-products of mineral processing for many other elements. Yttrium and the rare earths are present as minor constituents of many of the principal ores of columbium, tantalum, zirconium, and titanium. Almost all uranium and thorium ores contain small to moderate amounts of rare earths. References (58,123,551,641, 826,847,915,925) for example, are illustrative. Analyses are given indicating the presence of trace to major amounts of rare earths and yttrium, and traces of scandium, in many uranium and thorium ores in the United States.

Up to the present time, the limited market has mitigated against any development of these sources. Recent developments, however, have increased interest in potential by-product recovery, and as indicated above, scandium is now available as a by-product of uranium extraction processes. It may be emphasized that concentration factors of 50 to 100 fold may occur merely by recovery of major constituents. In many cases it may be possible to recover rare earth concentrates, essentially pure, by only one additional processing step.

Recovery of Rare Earths from Ores

Current procedures for extraction of the mixed rare earths from their ores are primarily based upon chemical cracking of the ores and precipitation of the rare earths.

Monazite is commonly processed by one of three procedures.

1. The ground monazite is heated with a slight excess of concentrated sulfuric acid. When the reaction mixture is poured into an excess of water, most of the rare earths go into solution. Thorium and some rare earths remain undissolved and are filtered off for further processing. The rare earths are recovered from the solution by precipitation with oxalic acid or with sodium sulfate.

2. By heating the monazite with a larger excess of sulfuric acid, all of the rare earths and the thorium may be kept in solution when the mix is added to water. Thorium, along with yttrium and some of the heavy rare earths, is then precipitated as a basic compound by careful partial neutralization. The thorium is filtered off for further processing and the cerium group rare earths are recovered as described above.

3. The ground monazite is digested at elevated temperatures with caustic soda. An exchange occurs; producing, upon dilution, insoluble hydrated oxides of the rare earths in a trisodium phosphate solution. The rare earths are recovered by filtration.

Upon careful partial neutralization of the hydrates with acid, most of the rare earths dissolve, leaving thorium and some of the heavy rare earths as insolubles. Recovery again is as above.

Procedures for xenotime are similar to those for monazite, except that the rare earths would not be recovered by precipitation with sodium sulfate, since yttrium and the heavy rare earth double sulfates are quite soluble.

Most of the bastnasite produced in this country is treated by the Molybdenum Corporation of America at its Mountain Pass mine and mill. The ore, as mined, contains 7 to 10% rare earth oxides. The ore is crushed, ground, and classified to -100 mesh. A flotation process floats the bastnasite and depresses quartz, barite, and calcite.

Separation gives a concentrate containing 63% oxide. Leaching with 10% hydrochloric acid dissolves the remaining calcite gangue, yielding a concentrate containing 72% oxide. Calcining finally yields an oxide concentrate containing 90% rare earth oxides (659). The concentrates may then be further treated with mineral acids, and the rare earths recovered as fluorides, oxalates, or other compounds by addition of the appropriate reagents (417).

Allanite, gadolinite, and most other rare earth silicate ores are easily cracked by digestion with mineral acid. Nitric or hydrochloric is commonly used. The rare earth solution is filtered away from the insoluble materials, and the rare earths are usually recovered by precipitation with oxalic acid.

Euxenite, fergusonite, pyrochlore and other niobates, tantalates, or titanates are generally quite resistant to attack by the ordinary mineral acids. They may be decomposed by fusion with potassium bisulfate. The fusion melt is digested in water precipitating niobium, tantalum, and, depending upon conditions, titanium as hydrous oxides. The rare earths are recovered from the solution as oxalates. Alternatively, the ore may be treated with hydrofluoric acid. After digestion with water, the rare earths remain as insoluble fluorides, most of the other constituents of the minerals being soluble. The rare earth fluorides are treated with concentrated sulfuric acid which volatilizes hydrofluoric acid and leaves the rare earths as soluble sulfates.

Although thortveitite is a silicate, it is not easily attacked by ordinary mineral acids. It may be fused with alkalies, the silica forming soluble silicates, and the scandium and rare earth remaining as insoluble basic compounds. There is danger of losing scandium, however, through the formation of soluble complexes. One alternative procedure is decomposition with hydrofluoric acid, recovery of the rare earths as fluorides, followed by conversion to sulfates by digesting with sulfuric acid as described above for euxenite. The scandium and rare earths are finally recovered by precipitation as oxalate.

Thortveitite may be treated in the dry way of heating to 1800°C with carbon to form a mixture of carbides. These may be extracted with dilute hydrochloric acid (354) or chlorinated directly (627,869). Spedding and co-workers (781) have treated thortveitite with ammonium bifluoride, volatilizing the silicon and forming crude anhydrous rare earth fluorides. These are reduced to the metal with calcium, and subsequently dissolved for separation and purification.

Other procedures have been proposed for the cracking of ores, but are not used on a commercial scale at present. These might prove useful, however, if other end products than those now produced were desired. Thus, for example, the direct chlorination of monazite has been proposed which would produce rare earth chlorides directly. This might be good cracking procedure if it were desired to go directly to the metal on a large scale. Chlorination of euxenite concentrates, followed by fractional distillation, effectively separates rare earth, titanium, and niobium plus tantalum fractions (298).

Similarly, the development of new separation techniques might simplify procedures for recovery of rare earths from the cracked ores. Thus, selection of proper solvents for solvent extraction procedures might minimize the need to recover rare earths as a group from the cracked monazite solutions, since solvents might be selected which would selectively strip thorium, and then individual rare earths from the cracked ore solutions.

Electronic Structure

All of the elements, both naturally occurring and artificially produced, can be arranged into a periodic system. The periodic system helped explain the properties of many little known elements and indeed predicted that unknown elements would exist. When the electronic structure of the rare earths became known, their position in the periodic table became clear. Most of the chemical and physical properties of the rare earths find logical explanation when viewed in the light of their electronic structure.

The periodic table is based upon the arrangement of the elements in order of ascending atomic weight. The most common periodic arrangement of the elements starts with an alkali metal as the first member of each row, and ends with a noble gas. Each successive element represents an increase of one, in atomic number, and a corresponding increase of one electron in the outer orbits of the atom. The electronic structure of a noble gas represents completed shells of electrons, an exceptionally stable arrangement.

The first two rows start with lithium and sodium, and progress by the addition of successive outer electrons to neon and argon respectively.

The third row starts with potassium and is followed by calcium, but starting with scandium, the next element, an inner shell of electrons is filled to form a transition series, which is completed after eight electrons are added at the element nickel. The row then resumes adding outer electrons with the element copper, and is finally completed with the krypton noble gas structure. Similarly the fourth row starts with rubidium, is followed by strontium, and then yttrium starts a transition series which is completed after eight electrons at palladium. The row is eventually completed with a stable xenon structure. In both of the above transition series the inner shell is only one or two electrons deep, and so the addition of electrons still produces significant changes in chemical properties.

The fifth row starts with cesium and is followed by barium and lanthanum. Lanthanum starts another transition series. The succeeding members of this series are hafnium, tantalum, tungsten, etc. Between lanthanum and hafnium, however, an inner transition sequence occurs. The filling of this inner shell (under several outer shells of electrons) constitutes the rare earth elements starting with cerium and concluding with lutetium.

Since the electronic structure which distinguishes one element from the other is deeply buried, and since chemical properties are determined by the outer electronic structure, it follows that the chemical properties of the rare earths are generally similar.

The strictly consecutive filling of the 4f quantum state by 14 electrons in direct numerical order is still open to question. Configurations have been proposed, for instance, in which most, but not all, of the rare earths have no electrons in the 5d quantum state and have this electron as an additional one in the 4f state, Yost (931). Several configurations are indicated in Table V.

In general, however, the important consideration is that the electrons are forming an inner transition sequence leading to relatively small changes in chemical properties. There are, however, definite physical effects as well as some important chemical effects.

Oxidation States of the Rare Earths. The normal oxidation state of rare earths is the tri-positive state created by removal of the three outer electrons. The resulting electronic configuration for the ions would then favor the 4f shell filling consecutively from one to fourteen, irrespective of which of the above discussed (or possible other) configurations hold for the neutral atom.

Three electronic states among the rare earth ions are particularly stable from atomic and quantum mechanical considerations. The first is the La^{3+} configuration which is the same as the extremely stable xenon configuration. The second is the half-filled 4f configuration of Gd^{3+}, and the third is the Lu^{3+} configuration which has completely filled subshells only.

Since these configurations are particularly stable, it might be expected that adjacent elements might have some tendency to form other oxidation states than three, and this is indeed the case. Thus cerium can rather easily lose a fourth electron to form Ce^{4+} which corresponds to the stable La^{3+}. Praseodymium can also form a higher oxidation state than three as the oxide, although only the trivalent state is stable in aqueous solution. Similarly terbium can exist as oxide in a higher valence state than three, the electronic structure approaching that of gadolinium.

Europium in the divalent state will have a half-filled 4f shell, and samarium in the divalent state also approaches the gadolinium structure if no electrons are in the 5d orbitals as discussed above. Ytterbium in the divalent state will approach the lutetium structure. All three of these elements; europium, samarium, and ytterbium, do exist as divalent ions in solution, and in various compounds. Archard and Tsoucaris (27) have also reported the preparation of ytterbium monoxide. The sesquioxide is reduced by carbon at elevated temperatures and reduced pressure.

Senderoff and Mellors (735) have proposed the formation of a reduced cerium state to account for the solution of cerium in $CeCl_3$(liq.). Druding and Corbett have investigated the systems neodymium and praseodymium with their respective chlorides and iodides (168). A number of new solid phases are reported in which the oxidation states of neodymium and praseodymium are less than three.

Color of Rare Earth Ions. The color of solutions of trivalent rare earth ions (and of rare earth salts) is due to sharply defined absorption bands in the visible portions of the spectrum. Sharp bands are also observed in the violet and infrared regions, and may be detected by instruments sensitive to these wavelengths.

Qualitatively, the relationship between color and electronic structure was first pointed out by Main-Smith (506) who noted that the color of the first seven ions are similar to the last seven in reverse order (Table VI). Electronically this means that an ion having N electrons more than lanthanum has the same color as one having 14-N electrons more than lanthanum. The spectra of divalent and quadrivalent ions, however, show broad, diffuse absorption bands rather than sharp narrow ones, and the colors do not match those of their isoelectronic trivalent ions. Yost (931) points out that a more sophisticated analysis is necessary, and that a detailed quantum mechanical interpretation of energy levels must be made to properly interpret the absorption spectra.

Paramagnetism. The paramagnetic properties of rare earth ions have provided important additional information towards the elucidation of the electronic structure of the rare earths. Calculations based upon the assumption of the filling of the orbitals have been markedly confirmed by experimental data: Hund (333), Van Vleck and Frank (859), Cabrera (107), Zernicke and James (933), Decker (154), Williams (192), Yost (931), and Vickery (864), Selwood (730) has found that the Curie-Weiss constants of divalent europous and trivalent gadolinium ions are very nearly equal, and concludes they must have the same electronic configuration.

The magnetic properties of the rare earths have been put to use in the attainment and measurement of very low temperatures through adiabatic demagnetization. The method was independently proposed by Debye (153) and by Giauque (238). Temperatures as low as 0.09° absolute have been obtained.

Lanthanide Contraction. It might ordinarily be thought that the addition of electrons would increase the ionic radius. The increased nuclear charge more than compensates for the added electrons, however, and produces a gradual decrease in radius. This is particularly true for the rare earths since the electrons are added to the inner 4f shell. The contractive effect is known as the "Lanthanide Contraction." It is sufficient in magnitude (lanthanum 1.22, lutetium 0.99)(871), so that at about the position of holmium the radius decreases to that of yttrium. The similar radii of yttrium and members of the rare earth series is one of the principal factors leading to similar chemical properties. It may be pertinent to note here that the atomic (metallic) radius also decreases with increase in atomic number, except for discontinuities at europium and ytterbium.

Chemical Properties

The chemical properties of the rare earths provide the basis for most methods of processing and separation. They are also the basis for methods of producing metals, compounds, and materials of industrial importance. The following discussion will consider the principal chemical properties of rare earths in solution, and some of the more important chemical and physical properties of the rare earth compounds. A discussion of the properties of the elemental metals and their alloys will be provided in the following sections of this report.

Oxides. All of the rare earths form sesquioxides (RE_2O_3). Cerium, praseodymium, and terbium normally form higher oxides of the general composition CeO_2, Pr_6O_{11}, and Tb_4O_7 when prepared at elevated temperatures in the presence of sufficient oxygen. The oxides are formed by combustion of the metal, or by ignition of the oxalate, hydroxide, carbonate, sulfate, nitrate, or many other salts. Cerium, praseodymium, and terbium sesquioxides can be formed by ignition in hydrogen or inert atmosphere, or by reduction of the higher oxides with hydrogen at high temperature, and in the case of cerium dioxide at high pressure.

The sesquioxides are basic and tend to absorb water vapor and CO_2 from the atmosphere. The order of basicity decreases with increasing atomic number; lanthanum sesquioxide is almost as basic as calcium oxide, while the oxides of the heaviest rare earths are fairly stable.

The very obvious moisture absorption of lanthanum and other cerium group oxides had previously led to generalizations that all of the rare earth oxides rapidly absorbed moisture, and that the most likely end products were the respective hydroxides. Love (462), however, has determined the rate of moisture absorption of eleven rare earth oxides at various temperatures and relative humidities. Marked differences were found in the rates of absorption and in the total moisture absorbed. Complete hydration occurred only for lanthanum, neodymium, samarium, and gadolinium oxides, and for the latter three this only occurred at elevated temperatures. Praseodymium oxide only absorbed one-half, and dysprosium and yttrium oxides only one-third of the theoretical amount for complete hydration; erbium, holmium, terbium, and cerium oxides absorbed much less.

The sesquioxides dissolve easily in the strong mineral acids. Those of the lighter rare earths dissolve readily even in weak acids such as acetic or formic. The heavy rare earths will dissolve in these acids, but much more slowly. The higher oxides of praseodymium and terbium are also soluble in mineral acids, but dissolve more slowly than the sesquioxides. Solution is aided by the presence of a reducing agent such as hydrogen peroxide. Ceric oxide, CeO_2, is much more stable, and if fully ignited, is extremely difficult to dissolve.

Some physical properties of the oxides are tabulated in Table VII. The crystal structures of the rare earth sesquioxides have recently been redetermined by Roth and Schneider (695). The three types originally proposed by Goldschmidt (250) were again confirmed and careful lattice parameter measurements were made (Table VIII).

Hydroxides. The hydroxides of all rare earths are insoluble, and may be formed by the addition of sodium, potassium, or ammonium hydroxide to rare earth solutions. The hydroxides formed under varying conditions of precipitation have been investigated by numerous workers (216,530,547,550,900). In general, it appears that the hydroxides precipitate as hydrated compounds with varying amounts of water. They easily form sols (399,545, 546), but if precipitated from hot, dilute solutions, a well coagulated, easily filterable precipitate may be obtained.

The hydroxides are one of the least soluble of rare earth compounds. They may be formed by direct metathesis, therefore, from other quite insoluble compounds such as oxalates, phosphates, or double alkali sulfates. The reaction is a useful method of converting these insoluble compounds into hydroxides which are readily soluble in acids.

The varying basicities of the elements are illustrated by the pH at which precipitation takes place. Moeller and Kremers (547,550) illustrate that precipitation pH's are a function of the solution conditions. The data in Table IX indicate the gradual change through the series for one particular system.

The differing pH's at which precipitation is initiated has been the basis for much of the early work in rare earth separations and will be discussed somewhat further in the separations section.

Cerous hydroxide in alkaline or neutral solution is readily oxidized by almost any oxidizing agent including air. A filtered cerous hydroxide precipitate will likewise be oxidized if exposed to air. The resulting basic ceric compounds have properties which are considerably different from the trivalent rare earths, and these properties are the basis for a method of separation and purification of cerium.

Carbonates. Rare earth carbonates form quite readily from almost all salt solutions. The degree of hydration varies with the method of preparation. Since the carbonates are easily removed from solutions, and since they are a convenient form for storage and use in industry, significant quantities are prepared in this form. The chemistry of carbonate formation is quite complex, however, with many possibilities of complex formation and double salt formation, as well as varieties of basic compound formation (217,528,864). Quill and co-workers (701) have extensively investigated these systems, and particularly the carbonates formed by the hydrolysis of the trichloro acetates.

Oxalates. Rare earths are precipitated from acid solution by oxalate ions. This is probably one of the most important reactions of rare earth ions, since it provides a convenient means of separating the rare earths from most other elements, and since it provides a convenient means of recovery of the rare earths even from dilute solutions. The resulting oxalate precipitates are readily filterable. They may be converted to hydroxides by metathesis with sodium hydroxide or may be ignited directly to the oxides.

In neutral solution, excess alkali oxalates tend to solubilize the rare earths somewhat due to the formation of complex double oxalates (133,200). This is most pronounced for the heaviest rare earths and has been used as a method of fractionation (931).

Halides. The halides have been extensively studied, both from a preparative and from a thermodynamic point of view, since they have been the most common starting materials for the preparation of the metals.

The chlorides and bromides may be prepared by the dissolution of the oxide, carbonate, or hydroxide with the respective hydrochloric or hydrobromic acid. All are very soluble in water. Evaporation of these solutions, cooling of a hot concentrated solution, or addition of the halogen acid gas to a saturated solution, will yield a crystal crop which may be filtered and dried in a vacuum or over a desiccant. Excess acid traces may be removed by drying over fused KOH which will absorb acid fumes as well as water. The resulting salts are hydrated and usually contain from 6 to 9 molecules of water of crystallization. They are, moreover, hygroscopic and absorb moisture from the air.

For the production of high purity metals, it is necessary that the halides have minimum oxygen content. The hydrated chlorides or bromides as prepared above cannot be dehydrated by simple heating in air, since decomposition occurs and oxyhalides are formed according to the reaction:

$$RECl_3.6H_2O \rightarrow REOCl + 2HCl + 5H_2O$$

They may, however, be fairly completely dehydrated by slowly heating in a stream of anhydrous acid (384).

Anhydrous chlorides may also be prepared directly from the oxides by reaction with ammonium chloride at elevated temperatures (671,672).

$$RE_2O_3 + 6NH_4Cl \rightarrow 2RECl_3 + 3H_2O + 6NH_3$$

The oxides may also be heated with carbon tetrachloride (537), sulfur monochloride vapor (310) or other chlorinating agents under reducing conditions.

The fluorides may similarly be prepared by the addition of hydrofluoric acid to a chloride or nitrate solution. The fluorides are insoluble and precipitate initially in a gelatinous form, but digestion at moderate temperatures helps effect coagulation. The fluorides contain one-half to one molecule of water of crystallization. The fluorides can be dehydrated to an oxygen content of one-half percent or less by slow careful heating in vacuum, in a stream of anhydrous hydrofluoric acid, or in purified helium (145,764).

Anhydrous fluorides may also be prepared from the oxides by heating the respective oxide with ammonium bifluoride, or by passing anhydrous hydrofluoric acid over the oxide at elevated temperature. Excellent summaries of methods of preparing anhydrous halides for metal production are presented by Love (462, 463), Smutz, Olson, and co-workers (754) and Spedding and co-workers (34).

Tetra- and Dihalides. Cerium tetrafluoride is the only halide of quadrivalent cerium which is stable.

Europium, samarium, and ytterbium trihalides are reduced by hydrogen to the dihalides at temperatures of 270 to 560°C. At higher temperatures (900 to 1000°C) partial reduction to the metal may occur.

Halates. Bromates have been used for the separation of the yttrium group elements by fractional crystallization. Along with the chlorates and iodates, they may be prepared by the addition of a barium halate solution to a rare earth sulfate solution, resulting in the precipitation of barium sulfate and the formation of the rare earth halate solution (282,934).

Nitrates. Aqueous solutions of nitrates may be prepared by dissolution of the oxide, hydroxide, or carbonate with nitric acid. Hot concentrated nitric acid will also decompose oxalate compounds to produce the nitrate. The nitrates, as the halides, are readily recovered in crystalline form by evaporation of solutions or cooling of saturated hot solutions.

The nitrates have played an important part in the history of rare earth separations. The simple nitrates may be crystallized from concentrated nitric acid, and have a minimum solubility at europium or gadolinium, the center of the series. Double nitrates may be formed with many other mono or divalent nitrates. The double ammonium nitrate $RE(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$ has long been used as the principal salt for the fractional crystallization of lanthanum and praseodymium. The double magnesium nitrate $2RE(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$ has been most commonly used for the purification by fractional crystallization of neodymium, samarium, europium, and gadolinium.

Sulfates. The chemistry of the sulfates is important since the principal processing of monazite is carried out in sulfuric acid solutions. The sulfates generally crystallize with eight waters of hydration. By careful heating to about 400 to 450°C they may be dehydrated. Heating to higher temperatures causes decomposition by loss of SO_3.

The hydrated sulfates are only slightly to moderately soluble. The minimum solubility occurs at europium with both the cerium group and yttrium group sulfates being more soluble. There is an inverse temperature effect, the sulfates being less soluble in hot solutions than in cold. The anhydrous sulfates as prepared above - or as probably exist in the hot concentrated sulfuric acid solution from the cracking of monazite - are considerably more soluble. They do not quickly transform to the hydrated salt, and the rare earths thus remain in solution long enough for further processing.

The addition of ammonium, potassium, or most commonly sodium sulfate will effect a group separation of the rare earths. The cerium group rare earths form quite insoluble double salts. The heavy rare earths may then be recovered by precipitation as oxalate or hydrate. The change in solubility is not extremely sharp, and there is also co-precipitation, so that the separation is not sharp. The procedure is quite effective, however, for the initial division of a mixture of rare earths into the two groups.

Interoxide Compounds. The availability of pure rare earth oxides and increasing interest in materials for high temperature applications has re-focused attention on the preparation and properties of ceramic type mixed oxide compounds. Titanates, niobates, zirconates, ferrites, and similar compounds have been prepared (232,233,234,243,380,402,572,634,673,698,718,872, 873,895,921,922). Particular interest has centered around yttrium and gadolinium iron garnet structures for their ferroelectric and magnetic properties.

Binary Metallic Compounds. Similarly, the availability of research quantities of pure metals, or the techniques for producing them, has renewed interest in the preparation and properties of compounds such as carbides, hydrides, nitrides, sulfides, etc. Many of these are most easily prepared from the metals themselves, and the unavailability of the metals in the past has hindered their preparation and evaluation. Selected references discussing preparation and properties include: 174,178,207,222, 337,338,387,404,541,640,702,773,825,874,894.

Compounds of the rare earths with other metals (i.e. iron, cobalt, magnesium, etc.) will be discussed in the chapters on alloys and constitutional diagrams.

Other Compounds. Many hundreds of other compounds of the rare earths have been prepared. Most of these were made many years ago in efforts to find better means of separation, some in efforts to find commercial applications.

Since the rare earths are metals with moderately strong basic properties, they form compounds with most anions and anionic groups of elements. Metallo-organics may be formed as well as strictly inorganic compounds.

Oxidized and Reduced States. Most of the chemical behavior discussed in this section has been based on the trivalent oxidation state of the rare earths.

Cerium, however, forms a quite stable tetravalent ion and much of cerium chemistry is based upon oxidation-reduction reactions. Cerium may be oxidized by electrolysis; by strong oxidizing agents such as nitric acid, permanganate ion, or peroxydisulfate in acid solution; or by hydrogen peroxide or air in neutral or alkaline media. In the tetravalent state it is a strong oxidizing agent when in dilute acid solutions.

Europium, ytterbium, and samarium form divalent ions in solution and divalent compounds if kept under reducing conditions. Europium is the most easily reduced (zinc in hydrochloric acid solution, or passage through a Jones Reductor) and europous compounds are the most stable. Yost (931, p. 66) reports less than 3% oxidation of europous sulfate after four months in a corked vial.

Nuclear Properties

The nuclear properties of materials have become increasingly important as our technology has advanced into the "atomic" age. Any use of rare earth metals or alloys as materials of construction in or near nuclear reactors must be considered in the light of these properties.

Neutron Cross Section. The thermal neutron absorption cross sections (801) of the rare earths are indicated in Table X. Complete cross section data as a function of neutron energy is reported in BNL 325 (331).

Radioactive Isotopes. Certain radioactive isotopes produced upon irradiation of rare earths may have industrial application, and may thus affect the economics of rare earth separations. These will be dealt with in a subsequent chapter, but we may here specifically mention scandium, europium, and thulium.

Effect of Irradiation Upon Structural Properties. No data has been found relating to the effects of irradiation on the mechanical properties of the rare earths.

Separation of the Rare Earth Elements

The separation of the mixed rare earths into the purified individual elements has been one of the most challenging chemical problems of the past hundred and fifty years. Literally hundreds of different compounds were prepared in efforts to find materials with varying properties so that separations could be effected.

Much of the presently known chemistry of the elements is based on this early work. In this respect, it must be recognized that much of the early work, even if performed carefully by competent investigators, is erroneous. This is due to the fact that mixtures of elements were originally believed to be individual elements, and that purities were difficult to determine with the techniques then available.

The following discussion will first cover the classical methods of separation developed up to the time of World War II. Several powerful new tools for separation have since been developed and will be discussed subsequently.

General Considerations. The separation of any two or more materials may occur by a process which is essentially complete in one step, or by a process which is fractional in character.

A complete process might be illustrated by an oxidation procedure in which one component only is oxidized, and after oxidation has properties sufficiently different from the other components so that it may be removed completely. The efficiency of this type of process is determined by the completeness of the removal of the oxidized component on the one hand, and the physical contamination of the removed oxidized material on the other.

A fractional process might be illustrated by a crystallization procedure in which one component is less soluble than the others. When the crystallization of this component is attempted, it does not separate completely, but is accompanied by other components in a rather closely fixed ratio which is determined by the particular conditions of the separation.

Another fractional process might be illustrated by a single stage distillation in which the distillate is enriched in one component, but in which complete separation does not occur.

Because of the close similarity of chemical and physical properties of the rare earths, most separation processes are of the fractional type. The processes must then be repeated until the desired degree of separation is achieved.

Separation Factor. One of the most useful concepts for the measurement of the effectiveness of a fractional process is the separation factor. If a mixture of two materials A and B is divided, by whatever means, into two groups, one and two; then the concentrations of A and B in group one will be A_1 and B_1, respectively. The concentrations in group two will be A_2 and B_2, respectively. The ratios of concentration in the two groups will correspondingly be A_1/B_1 and A_2/B_2. The separation factor is now defined as the ratio of these ratios:

$$\text{S.F.} = \frac{A_1/B_1}{A_2/B_2}$$

Since it is a ratio of ratios, it is a pure number and has no units.

The significance of the separation factor may be illustrated by two simple cases. Consider a solution initially containing 50% each A and B. This solution is divided into two equal fractions 1 and 2 in one case, and I and II in another, such that the final concentrations are as indicated below:

Fraction	1	2	I	II
Concentration of A	51%	49%	75%	25%
Concentration of B	49%	51%	25%	75%
Separation Factor Calculation	$\frac{51/49}{49/51}$		$\frac{75/25}{25/75}$	
Separation Factor	1.08		9.0	

Considering now the converse calculation, it is seen that a process with a separation factor of 9.0 increases the concentration of a 50% component to 75%. When the separation factor is 1.08, the increase is only from 50% to 51%.

It is obvious that procedures with small separation factors will require very many repeated operations to effect major changes in composition. It is further obvious that if there are sixteen components in a mixture, rather than only two, separations may indeed have to be repeated many thousands of times to effect purification of all components.

It may be noted that the separation factor is essentially a mathematical concept. As such it holds for any ratios of the relative percentages of A and B, and likewise for any ratios of quantities of the two resulting division groups. This is true providing that the conditions which create a particular separation factor are not in themselves changed by the division. Such a change in separation factor might occur at extremely low or extremely high concentrations, or might be due to simultaneous changes in other variables, such as acidity.

Fractional Crystallization. In fractional crystallization procedures a part of the salt in solution is precipitated, generally by a change in temperature or by evaporation of a saturated solution. If there is a difference in the solubility of the various components of the solution, the composition of the crystal crop will be different from that of the original solution, the less soluble components being enriched. The more soluble components will, of course, be simultaneously enriched in the liquor.

Where more than two components are present, fractionation is usually designed to first split the material into groups of two or at most three components. These may then be fractionated until material of requisite purity is obtained at both the most soluble and least soluble ends.

Many salts and double salts have been used for the separation of rare earth elements. The most commonly used are indicated in Table XI.

Selwood (731) gives data for the separation of lanthanum and neodymium by ammonium double nitrate crystallizations. Assuming the separation factor is constant between each pair of elements from lanthanum to neodymium, the average separation factor for adjacent elements is calculated as 1.15.

Fractional Precipitations. Fractional precipitation reactions involve the removal of part of the rare earths from solution by the addition of a chemical reagent to form a new, less soluble compound. The rare earths remaining in solution are recovered in some cases by further precipitation as the same compound, in other cases by complete precipitation as the oxalate, hydroxide, or other compound.

Since each precipitation forms a new material, this process does not lend itself to repeated operations as well as fractional crystallization processes. Before the precipitation can be repeated, the precipitate must be reconverted to the original solution form. Each complete cycle, involving as it does, chemical reaction, physical separation, and chemical or other method of reconversion, is time consuming and may lead to a significant loss of valuable material. Only significantly higher separation factors will therefore justify fractional precipitation over fractional crystallization methods.

Principal Precipitation Reactions. The double sulfates are most commonly precipitated by the slow addition of powdered sodium sulfate to the rare earth solution. Since the method is primarily used to separate the light from the heavy elements, a convenient indication of completeness of reaction is the disappearance of the neodymium absorption bands.

Moeller & Kremers (548) have extended the method to include splitting of an intermediate (terbium) group, and the enrichment of yttrium fractions.

Basicity separations have been useful for the separation of rare earths into groups, and as an aid in the purification of lanthanum and yttrium. Basicity changes may be effected by several procedures (547) among the most important of which are:

1. Addition of an alkaline reagent. Sodium or potassium hydroxide may be used, but create local excesses of hydroxyl ions. Magnesia or other metal oxides, reacting more slowly, are better. The slow addition of dilute ammonia (656,677) or, to prevent excessive dilution, introduction of an air stream containing ammonia

vapor (312,832,866) is especially effective.

2. Hydrolysis. Local excess of alkali is avoided by the slow decomposition of unstable compounds. The pH of solutions may be slowly increased by heating solutions containing urea (211,731) or thiosulfate. Electrolysis of solutions may also be effective (410,411,425,584).

The oxalates show a sequence of precipitation starting with europium as the least soluble element. If the rare earths are first divided into cerium and yttrium groups, subsequent fractional precipitations with oxalic acid will further subdivide these groups.

Cobalticyanides, ferrocyanides, and ferricyanides have been used for separations, especially of yttrium and the heavy elements around erbium. The ferricyanides (516) appear to be most effective.

From data by Selwood (731), the following average separation factors for several types of fractional precipitations have been calculated for individual rare earth pairs between lanthanum and neodymium:

Method	Separation Factor
Sulfate	1.2
Oxalate	1.6
Basic Magnesia	1.2
Basic Urea	1.4
Alkali Carbonate	1.7
Basic Electrolytic	1.7
Basic Ammonia	2.3

Comparison of Fractional Crystallization and Fractional Precipitation Methods. The principal advantages of fractional crystallization methods are the following:

1. Handling processes are minimized. The material processed is always in the same chemical form so that it is not necessary to convert and re-convert various compounds.

2. Cost of processing is usually low. No chemicals are needed for reaction purposes, most processes requiring only heat.

3. There is good conservation of material. The only losses will occur in filtrations if they are necessary. Since the materials filtered are soluble, they are easily recovered. In many cases it is possible to work so that filtration is not required at all, the liquors being quite effectively decanted from

the crystal crops.

The principal advantage of fractional precipitation methods lies in the greater separation factors available. Although generally used for group separations, two elements may be readily purified by fractional precipitation methods. The first is lanthanum. It is at one end of the series and thus must be separated from elements "on one side only". It is also the most abundant element in the cerium group raw materials after cerium is removed, and therefore needs less purification than the other rare earths. The second is yttrium which can be purified by a combination of two fractional precipitation methods. This is due to the fact that yttrium, in different separation procedures, does not always fall at the same point in the rare earth series. Thus, when rare earth sodium double sulfates are precipitated, yttrium behaves as though it were at about the position of holmium. When basic precipitations are made, yttrium behaves as though it were in the approximate position of neodymium or samarium. The use of both procedures, therefore, removes the elements from lanthanum to dysprosium by the first method, and over-lappingly, europium through lutetium by the second.

Oxidation Reactions. The separation of cerium from mixed rare earths by an oxidation procedure was reported by Bunsen in 1853 (106). Bunsen treated an alkaline rare earth suspension with chlorine. The cerium was oxidized to the ceric state and formed an insoluble basic oxide. Simultaneously a dilute acid solution was formed which dissolved the other rare earths.

Almost all methods subsequently developed for the rapid separation of cerium are based upon its initial oxidation by any of a number of reagents or processes. Chlorine, bromine, lead or bismuth oxides, sodium peroxide, bromate, permanganate and peroxydisulfate have been commonly used (203,864). Electrolytic oxidation has been recommended by Pearce (625), Smith (748), and others.

If the cerium is obtained as the tetravalent ion in solution, it may be precipitated at a low pH. The incipient precipitation pH of Ce^{4+} is 2, that of Lu^{3+} (the lowest trivalent rare earth) is 6.3 (547). If the cerium is obtained as ceric hydroxide, or a hydrated ceric salt mixed with other rare earth hydroxides, the other earths may be dissolved away by dilute acids.

A most important commercial method is described by Powell (651) in which the rare earth hydroxides are exposed to air at 100°C. The cerous hydroxide is oxidized to ceric hydroxide which is insoluble in dilute nitric acid. After a dilute acid extraction of the other rare earths, the insoluble residue is then dissolved in concentrated nitric acid from which it may be precipitated for additional purification.

Johnson and Olson (371) have recently investigated the separation of cerium from other rare earths by ignition of the nitrates. Close control of temperature of molten salt baths containing mixed rare earth nitrates resulted in almost complete separation of cerium as a high purity oxide.

Praseodymium and terbium may be concentrated by oxidation (electrolytically or by chlorate) in molten alkaline (KOH) baths (52,511,515). The precipitated PrO_2 or Tb_4O_7 is partially separated by gravity, since it drops to the bottom of the melt. Further separation from the other rare earths is by treatment with very dilute acids which dissolve away the melt but only attack the oxide very slowly. In contrast to ceric oxidation and separation, praseodymium and terbium are only fractionally enriched by these processes.

Reduction Reactions. Samarium, europium, and ytterbium may be reduced to oxidation states lower than plus three. In lower oxidation states chemical properties are different and the elements may be separated from the trivalent rare earths.

Yntema (929) first separated rare earths by a reduction method in 1930. Europous ion was formed by electrolytic reduction at a mercury cathode. In the presence of dilute sulfuric acid europous sulfate precipitates and is separated by filtration.

As in the case of oxidation techniques, the purification of rare earths by reduction procedures may be considered in two steps, first the method of reduction, and second the physical separation process.

Europium has been reduced by electrolysis (929,511,376,203 p. 66) by amalgamated zinc, or zinc dust in dilute hydrochloric acid (476-480) and by sodium or other amalgams (513). The reduced europium may be recovered as the almost insoluble sulfate (in dilute acid), or dichloride (in concentrated hydrochloric acid). When reduction is by electrolysis using a mercury cathode (481,482,604) or by sodium amalgam it is also possible to remove the europium as the amalgam, to be subsequently recovered by treatment with dilute hydrochloric acid.

Samarium (98,513,605) and ytterbium (376,512,483,549,655, 930) are more difficult to reduce, and the reduced ions are less stable. Processes similar to those for europium have been developed, however, and are effective for concentration and purification. Onstott (606) has effected electrochemical fractionation of yttrium and the lanthanons at a lithium amalgam cathode. Europium, ytterbium, and samarium are rapidly electrolyzed through reduction to divalent states. The other rare earths are electrolyzed more slowly.

It may be noted that both oxidation and reduction processes are effective, not only for the purification of the particular element concerned, but also for the purification of adjacent elements. Thus, if during a fractional separation process a fraction containing only thulium and ytterbium is obtained, the removal of the ytterbium will also provide pure thulium.

Spedding and co-workers (761) have noted this effect in another system. In their metallothermic reduction of anhydrous trihalides to metals it was observed that samarium, europium, and ytterbium are only reduced as far as the divalent state. If, therefore, gadolinium containing europium is reduced to metal, a separation is effected since the europium remains in the slag.

Fusion Reactions. Fusion reactions involving the oxidation and separation of cerium, praseodymium, and terbium have already been discussed.

Separations of rare earths have been made by partial fusion of mixtures. The method is based upon the partial decomposition of the fusion mixture, the decomposed material becoming insoluble. The most frequently used system was the nitrate. Except for cerium, the nitrates decompose in approximately inverse order of atomic number, with yttrium falling at about the position of samarium or gadolinium. Cerium is oxidized to ceric ion which decomposes at a much lower temperature than the other rare earth nitrates. The decomposed nitrates form basic salts or oxides from which the undecomposed materials may be separated by solution in water. The oxides or basic salts may then be dissolved in acid (152,157,514,547,864,876).

Volatilization. Distillation or volatilization processes are excellent separation methods provided systems can be found with satisfactory differences in vapor pressures or sublimation rates. Several such systems have been proposed.

1. Distillation of metallo-organic compounds. The acetylacetonates of the rare earths may be distilled at reduced pressures. Scandium and thorium have been separated by this method (558).

2. Sublimation of salts. Vickery (870) investigated the separation of rare earths by fractional volatilization of the chlorides, and obtained quite good results when dealing with small quantities.

Harrison (283) has determined vapor pressures and thermodynamic data for lanthanum, cerium, praseodymium, and neodymium chlorides, and lanthanum, cerium, neodymium, and samarium bromides. Temperature differences of about 20-30°C were observed for the boiling points of adjacent rare earths, and also for the temperatures at which the vapor pressures were 10^{-1}mm.

3. Sublimation of Metals. Spedding and Daane (763) have recently suggested the possibility of direct fractional volatilization of the elemental metals. A synthetic mixture was heated in a vacuum so that the vapors condensed in a tantalum fractionating column. Partial separations were achieved, and the order of decreasing volatility established (europium, ytterbium, lutetium, thulium, holmium, dysprosium, erbium, gadolinium) for the elements in the mixture.

Solvent Extraction. Principles. Two important considerations are necessary for complete understanding and systemization of solvent extraction systems.

The first is the phase rule, which relates the number of phases (P), the number of components (N), and the number of independent variables (F) necessary to completely define a system at equilibrium.

$$F = N - P + 2$$

The second is the distribution law, which relates the concentrations of various components in the various phases of a system at equilibrium.

For purposes of this discussion the phase rule is of minor importance. Complete derivations and discussions may be found in standard texts on physical chemistry or phase rule (205,245, 492).

The distribution law (also known as the partition law) states that when a substance is distributed, under equilibrium conditions, between two phases, the ratio of concentrations in the two phases will have a constant value. If A_1 and A_2 represent the concentrations of A in phase 1 and phase 2, then:

$$\frac{A_1}{A_2} = K$$

If, now, there are two substances, A and B, distributed, then:

$$\frac{A_1}{A_2} = K_A \qquad \frac{B_1}{B_2} = K_B$$

We note that these two relationships may be combined:

$$\frac{A_1/A_2}{B_1/B_2} = \frac{K_A}{K_B} \qquad \text{or} \qquad \frac{A_1/B_1}{A_2/B_2} = \frac{K_A}{K_B} = \text{S.F.}$$

and therefore that the ratio of distribution constants is the separation factor.

Solvent Extraction. Separation of the Rare Earths. The first suggestion that solvent extraction might be used to separate the rare earths was apparently made by Hopkins and Quill (324) in 1933, although previous workers (345,902) had noted that ceric and other rare earth nitrates were extracted into ether. Hopkins and Quill investigated the solubilities of some of the cerium group anhydrous chlorides in anhydrous alcohols. The systems were found to be markedly affected by traces of water and by the formation of various hydrates and alcoholates, but some separations were obtained.

Appleton and Selwood (25) investigated the solubilities of a number of neodymium and lanthanum salts in a wide variety of organic solvents. A separation factor of 1.06 was found for lanthanum-neodymium thiocyanate in an aqueous-butyl alcohol system. Although this separation factor is small, and for elements which are several atomic numbers apart, it was suggested that continuous counter-current extraction might be effective for separations.

Templeton and Peterson (812,813) studied the distribution of cerium group rare earth nitrates between water and n-hexyl alcohol. Separation factors of 1.29 - 1.55, depending upon experimental conditions, were obtained for lanthanum-neodymium.

During the past ten years increasing emphasis has been placed on the tributyl phosphate-nitric acid system for the separation of rare earths. The earliest described work is apparently that of Warf who first observed (893), and then investigated (892), the extraction of ceric ion from aqueous nitrate, and nitric acid solutions by tributyl phosphate. Petrow and co-workers (637), and Bauer and co-workers (44,45), have recently extended this work, and presented data to indicate that the preparation of pure cerium oxide by solvent extraction methods is competitive with the older chemical separations methods.

In 1952, Peppard, Faris, Gray, and Mason (629) observed that the extractability of the rare earths into tributyl phosphate from concentrated hydrochloric or nitric acid solutions increased with increasing atomic number. The order of extraction from dilute (0.3N) nitric acid was reversed.

Salting out effects were observed for ammonium nitrate and aluminum nitrate. Although these salting agents were effective for removing and separating the rare earths from impurities, the most effective separations of rare earths from one another was from the concentrated nitric acid solutions. Separation factors for adjacent rare earths were reported to be 1.6 for 12 N. nitric acid, and 1.9 for 15N. nitric acid, systems. These values were determined from single stage extractions using radioactive tracers. Later investigations indicated these values were reasonable for cerium group elements but somewhat optimistic for yttrium group elements. The system nevertheless turned out to be an effective one.

Peppard and co-workers subsequently continued investigations into the separations of the rare earths, thorium, scandium, protoactinium, uranium, and zirconium (628,630,631,632,633). Gray and Thompson (254) and Gray (253) have also continued this work.

Weaver and co-workers adapted the method to produce purified rare earths to be used as a source material for isotope separations at Oak Ridge. Weaver, Kappelmann, and Topp (896) reported the separation of the first kilogram of gadolinium oxide in 1952. Topp (823) reported on distribution coefficients and the separation factor (found to be 2.8) of neodymium and samarium. Topp and Weaver (824) then extended this work, determining the effect of variables on the separation factors for samarium, gadolinium, dysprosium, and yttrium. Their results indicated good separations should be obtained.

Bochinski, Smutz, and Spedding (68) investigated the separation of rare earths from monazite, employing tributyl phosphate in various concentrations. Very dilute nitric acid solutions were used. Starting with a mixture containing essentially 75% neodymium, 15% praseodymium, 6% samarium, and 4% gadolinium, a division was made into an aqueous phase containing 25% praseodymium, and 75% neodymium and an organic phase containing 48% samarium and 34% gadolinium. Variables influencing mass transfer were also investigated. The same authors (67), subsequently presented a mathematical method for calculating operating conditions necessary to effect a given separation.

Foos and Wilhelm (212) extended this work to investigate the separation of yttrium and some heavy rare earths. The starting materials were concentrates from gadolinite, fergusonite, and tailings from ion exchange separations. Single stage distribution coefficients were determined, and a 20-stage continuous countercurrent apparatus was used to follow up the more promising conditions. The results from one such multistage extraction are indicated below.

Component	Initial Percentage	Product Percentage	
		Aqueous	Organic
Pr_6O_{11}	2.0	3.4	N.D.
Nd_2O_3	7.6	22	N.D.
Sm_2O_3	5.7	16	N.D.
Gd_2O_3	8.4	22	N.D.
Dy_2O_3	4.0	4.4	2.4
Y_2O_3	66	24	91
Total	93.7	91.8	93.4

Gruzensky and Engel (262) processed a euxenite concentrate through a six stage extraction. The solvent phase was a solution of tri-n-butylamine in 3-methyl-2-butanone. The aqueous phase was 8 N. HNO_3. The final product contained 83% yttrium oxide compared to 47% in the starting material.

Studies of the solvent extraction of rare earths with tributyl phosphate systems have recently been reported by Soviet scientists (592,617). Their results are in general agreement with those indicated above.

Much of the above reported work was pragmatic in the sense that systems were investigated and found to either effect separations or not. Further investigations of those which did work, as the tributyl phosphate-nitric acid systems, examined the effects of variables on the separations achieved, but very little was actually known about the mechanism of transfer and the species involved.

McKay, Healy, Alcock, and co-workers at Harwell (6, 291,292, 494) have recently published a series of papers describing the results of their investigations. They found the following complexes formed and involved in rare earth transfers:

$$HNO_3 \cdot TBP$$
$$RE(NO_3)_3 \cdot 3TBP$$
$$Ce(NO_3)_4 \cdot 2TBP$$

Their work has materially aided in the interpretation and understanding of the effects of acid concentration and salting agents on mass transfer.

<u>Ion Exchange</u>. <u>Principles</u>. An ion exchange resin may be considered to be an ionic salt in which one of the ions is attached to an insoluble organic matrix. The charge on the attached ion determines whether the resin is an anion or cation exchanger.

If the ion exchange resin is brought into contact with a salt solution, the movable ion in the resin phase may be displaced. In general, the following principles govern the displacement.

1. An ion of higher charge displaces an ion of lower charge.

2. For similarly charged ions, the ion with larger (non-hydrated) radius displaces the smaller (821).

3. The displacement occurs according to the law of mass action, thus for cation exchange:

$$MR + A^{+}{}_{(aq)} = AR + M^{+}{}_{(aq)}$$

$$K = \frac{(AR)\ (M^{+})_{(aq)}}{(A^{+})_{(aq)}\ (MR)}$$

Where M is the cation originally attached to the resin,
R is the resin exchanger
A is the cation in solution
K is the equilibrium constant
( ) represents concentration

4. If the solution contains ions C which complex with one of the ions involved in the exchange, further equilibria occur:

$$A^{+}(aq) + C_{1}^{-}(aq) = AC_{1}(aq) \qquad K_{1} = \frac{(AC_{1})_{(aq)}}{(A^{+})_{(aq)}\ (C_{1}^{-})_{(aq)}}$$

$$A^{+}(aq) + C_{2}^{-}(aq) = AC_{2}(aq) \qquad K_{2} = \frac{(AC_{2})_{(aq)}}{(A^{+})_{(aq)}\ (C_{2}^{-})_{(aq)}}$$

$$\text{------} \quad \text{------} \quad \text{-------} \qquad \text{--} \quad \text{----------------}$$

$$A^{+}(aq) + C_{n}^{-}(aq) = AC_{n}(aq) \qquad K_{n} = \frac{(AC_{n})_{(aq)}}{(A^{+})_{(aq)}\ (C_{n}^{-})_{(aq)}}$$

and all such equilibria must be satisfied.

The above principles may be simply illustrated by considering the ordinary use of ion exchange resins for water softening. Thus:

1. An ion of higher charge displaces an ion of lower charge. In water softening, ions such as calcium or magnesium, of charge two, will displace ions such as sodium or hydrogen, of ionic charge one.

2. For similarly charged ions, the ion with larger radius displaces the smaller. Thus, ions such as potassium, of charge one, will displace ions such as sodium, of charge one.

3. The displacement occurs according to the law of mass action. Thus, in the regeneration of water softeners, the use of a concentrated solution of sodium chloride produces a high concentration of sodium ions which act by mass action to replace the ions which ordinarily adhere more tightly to the resin, such as potassium, calcium, or magnesium.

4. Although not normally a water softening practice, the fourth principle may be observed by adding a complexing agent such as EDTA (ethylene diamine tetraacetic acid) to the water before passage through the resin. In this case no exchange takes place at all, since all of the calcium and magnesium is bound by the complex and essentially no free cations are available for exchange.

Separation of Rare Earths by Ion Exchange. Consideration of the basic principles governing ion exchange phenomena as indicated above, indicated that good separation of the rare earth elements would not be obtained from ordinary solutions. This is evident since:

(a) All of the rare earth ions are ordinarily of the same charge (plus 3).

(b) Although there is a contraction of ionic radius with increasing atomic number this effect is relatively small as compared to that usual for those elements of the same charge, but which are located one above another in the periodic table.

The successful use of ion exchange techniques came as a result of the application of the important complexing phenomena which could be produced in the solution passing through the ion-exchange columns. Thus, by addition of a complexing agent to the solution, the environment around the ion exchange particles was drastically changed, some of the rare earth ions were more tightly complexed in solution than others. These were consequently not as available for exchange with the ions on the resins. The equilibria in solution became the principal determining factor in separations, and the ion exchange resins became essentially inert reservoirs of rare earth ions which acted as sites for repetitive re-equilibrations of the solution.

The process as developed, and essentially as practiced currently, is therefore one of loading a column of ion exchange resin with rare earth ions. An eluting solution containing the complexing agent is then permitted to flow through the loaded columns. The complexing agent strips the rare earths from the top of the column and then passes through the rest of the column. In doing so, however, the solution equilibria are disturbed, and a re-equilibration occurs. Those elements which tend to form tighter complexes leave the resin and enter the solution. The less tightly complexed elements which have been simultaneously released leave the solution and occupy the newly vacated sites on the resin.

The solution is now permitted to flow through a resin column equilibrated with ions (NH_4^+, H^+, Cu^{++}, etc.) which may be replaced by any rare earth ion. The rare earths accordingly are redeposited on the new resin, but, and most important, the first rare earths deposited are those which formed the most tightly formed complexes in solution, since the solution has been preferentially enriched with them. As the process is repeated over and over, the situation gradually develops wherein those elements which formed the strongest complex are now at the very leading edge of the rare earth band, and those which formed the weakest complex are at the trailing edge of the band with all the others in between.

Initially the boundaries between adjacent elements overlap greatly, but as the process continues, the boundaries sharpen. The process is continued until the desired degree of separation has occurred.

The effluent solution is now collected in fractions, which theoretically at least, contain only separated individual elements, and these are recovered from the solution by chemical means.

Advantages and Disadvantages. The principal advantage of ion exchange separation techniques as practiced today, is the ability to produce extremely high purity materials.

The disadvantages of ion exchange techniques are indicated below.

(a) The capacity of equipment used is limited relative to that used in most industrial chemical processes. An ion exchange column is mostly filled with ion exchange resin, and will at best (using currently available resins) contain only about five pounds of rare earth per cubic foot.

(b) Flow rates through the columns must be slow enough to permit satisfactory exchange of ions between solution and resins. In current practice this is about one linear centimeter per minute.

(c) Currently available complexing agents have limited maximum concentration ranges. The optimum concentration of rare earths in solutions of the most commonly used complexing agents at present is approximately one-quarter percent.

(d) The number of "column lengths" through which an original column load of rare earths must be passed for good separation ranges from four to eight depending upon the degree of separation desired. Coupled with dilute solutions and slow flow rates, this means a long residence period for the starting material, a large necessary inventory of ion exchange resin, and a large capital investment for the required equipment.

The development of ion exchange chromatography has been carried out in many laboratories both in the United States and abroad. Particular reference must be made to the initial reports of Tompkins, Khym, Cohn, Marinsky, Glendenin, Coryell, Harris, Ketelle and Boyd (280,382,510,820) who made the separations on a micro and tracer scale at the Clinton National Laboratories; and Spedding, Voigt, Gladrow, Sleight, Powell, Wright, Butler, Figard, Fulmer, Gobush and Porter from Iowa State College (770,785,786) who made the first effective macro rare earth separations. The first separation of promethium, element 61, was made by Marinsky, Glendenin, and Coryell (510). Simultaneous theoretical studies of the processes were made by Boyd, Schubert, Adamson, Bauman, Eichhorn, Myers, Tompkins, and Mayer (49,88, 89,821).

The work at Iowa State College was continued by Spedding, Powell, Wheelwright, and co-workers, and procedures were developed for the separations of the rare earths on a multikilogram scale (653,768,769,771,772,778,782,783,904). Contributions to the theory of separations were also made (519,652,779,780, 784,905).

Meanwhile, separations of fission products were continued at Oak Ridge by Pressley and Rupp (661) and Brooksbank and Leddicotte (97). At the University of California Radiation Laboratories, studies were made and procedures developed, for the accurate control of elution for analytic studies of radioactive rare earths (524,803). Various separations were developed at Los Alamos and Argonne National Laboratories (126,749, 795) and in the Bureau of Mines laboratories (453).

Abroad, Vickery (868) compared various eluting agents, and Cornish et al, and Topp reported on separations at Harwell, England (130,822). In France, Trombe, Lorier, and co-workers (845) reported extensively on their research. Andreeva and co-workers reported research in the Soviet Union (15,16,17, 454).

Separations From Non-Rare Earths. The rare earths may be separated from other elements by many processes. Basically these may be divided into two types; first, procedures in which other materials are removed from the rare earth solution, and second, procedures in which the rare earths are precipitated or otherwise removed from solution, leaving impurities behind.

When the rare earth content of a solution is low relative to the impurities present, it is generally a better procedure to remove the rare earths away from the impurities, providing suitable procedures are available. When the rare earth content is high and only small amounts of impurities are present, it is frequently better to remove the impurity if a suitable method is available. The most common methods are indicated below.

Recovery of Rare Earths. The rare earths may be precipitated from solution by a number of reagents which are quite selective.

Oxalic acid will precipitate the rare earths from acid solution. Elements which form soluble oxalates or oxalate complexes in acid solution (such as iron or titanium) are not precipitated.

Ammonia precipitation is effective for removal from soluble hydroxides and from elements forming ammonium complexes. Sodium hydroxide precipitation is likewise effective for removal from soluble hydroxides and amphoteric elements.

Fluoride precipitation with hydrofluoric acid will remove many soluble fluorides and complexes and also silica by volatilization.

Recent developments in solvent extraction techniques have indicated that it may be possible to separate the rare earths from almost all other cations and most anions by extraction with tributyl phosphate from a nitrate solution loaded with ammonium or aluminum nitrate. The rare earths are recovered by extracting the organic phase with water and precipitation as above (629).

Removal of Impurities. The removal of impurities from rare earth rich materials normally is carried out by classical solution chemistry.

Treatment of solutions with hydrogen sulfide is effective for the removal of the "sulfide group" elements (arsenic, mercury, copper, silver, antimony, bismuth, tin, cadmium, lead, zinc, cobalt, nickel) since the rare earths are not precipitated from nearly neutral or acid solutions (in alkaline solutions basic rare earth salts would precipitate).

Treatment with sulfuric acid will precipitate barium.

Small amounts of manganese may be removed by persulfate oxidation in dilute sulfuric acid. The hydrolyzed manganese is then removed by filtration.

Tantalum and niobium (and to a certain extend titanium) may be removed by boiling dilute acid solutions. The elements hydrolyze and are removed by filtration.

Summarizing the techniques of rare earth separation, it may be first noted that the separation methods used would depend upon the particular element or elements desired. For highest purities ion exchange would probably be used for most elements. Combinations of several other methods would be used for nominal purities. As production requirements increase, the use of solvent extraction techniques would become more important.

Methods of Analysis

General Considerations. Analysis of rare earths is subject to all of the usual problems of analytical chemistry plus the special problems introduced by the similarity of the elements. In general, chemical separations are used only for the determination of total rare earths. With the exception of cerium, europium, and to a limited extent yttrium, physical methods are used for the analysis of the individual rare earths.

Preliminary concentration procedures may be used when the concentration of rare earths in a matrix is very low. Such procedures have been especially important in the analysis of reactor materials, since some rare earths have very high neutron absorption cross sections, and analysis may be necessary at levels of parts per million or less. Thus, Hettel and Fassel (309) determine traces of rare earths in zirconium by forming the stable fluozirconate ion and passing the solution through a cation exchange column. The rare earths are retained and subsequently stripped with hydrochloric acid, while the fluozirconate anions pass through the column. Quite similarly, Feldman and Ellenburg (201) remove microgram quantities of rare earths from thorium nitrate or uranyl nitrate solutions onto cellulose. Peppard and coworkers (629) have shown that rare earths as a group may be efficiently extracted from nitric acid solutions by tributyl phosphate, especially if the solution is salted with ammonium or aluminum nitrate. Eberle and Lerner (177) describe the concentration of lanthanons in yttrium by solvent extraction.

Chemical Methods. Total rare earths are usually determined by precipitation as oxalate or hydroxide, followed by ignition to oxide. Standard analytical procedures are used for removal of impurities, and the precipitation of the rare earths will most usually provide an additional purification step. It is frequently necessary to repeat the precipitation due to co-precipitation or adsorption effects. It may be noted that although most rare earths form sesquioxides on ignition, cerium, praseodymium, and terbium form higher oxides.

Total rare earths may also be determined volumetrically by titration with a complexing agent, most commonly ethylene diammine tetraacetic acid (EDTA). Barnard, Broad, and Flaschka (38), have excellently summarized the EDTA titration methods.

Cerium may be easily oxidized to the quadrivalent state. In the quadrivalent state it may be separated from rare earths by precipitation as a basic salt or as the iodate (719). Since precipitation separations usually require re-precipitation and are time consuming, volumetric methods are preferable. Many such have been proposed, but the easiest and best seems to be oxidation with ammonium persulfate followed by titration with ferrous ion to an o-phenanthroline end point (748,911).

Europium may be determined volumetrically by passing the rare earth solution through a Jones reductor into a known excess of standard permanganate or iodine, and titrating the excess (477,480).

The determination of the average atomic weight was, and still is, useful for the determination of yttrium when spectrographic equipment is not available. If no foreign contaminants, scandium, or thorium are present, then the difference between the atomic weight of yttrium - 88.92 - and the other rare earths - 138.9 to 175.0 - is sufficient to permit fairly good estimates of yttrium purity. The presence of 1% of rare earths in yttrium affects the average atomic weight by approximately 0.5 units or 0.5%. One of the simplest methods of atomic weight determination is calculation of the ratio of rare earth oxide to rare earth oxalate (41,92).

Analysis by Color. Early workers in the rare earth field did not have available present day analytical facilities. Much of the progress of separations was visually established by changes in the appearance of oxides or solutions.

Table VII gives the color of the oxides prepared by ignition in air. It will be noted in particular that Pr_6O_{11} is black, and that Tb_4O_7 is dark brown. The presence of these elements, particularly in adjacent elements, is easily detected. Lanthanum oxide is white; approximately 0.01% praseodymium will produce an off-white, gray color, 0.1%-1% will produce a definite brown tint which becomes darker with increasing praseodymium content until the oxide becomes black when over 30-40% is present.

Pure neodymium oxide is light violet in color. The presence of a few hundredths of one percent of praseodymium will impart a definite gray tint which becomes brown with increased percentages.

Similarly the presence of 0.01% or less of terbium will impart a definite buff or light brown tint to gadolinium or yttrium, which becomes darker with higher concentrations of terbium.

The colors of rare earth solutions are described in Table VI. As fractionation proceeds, separations can frequently be followed by visual color observations. In a few cases, visual examination may indicate the presence of 1% or less in adjacent elements (praseodymium in lanthanum, neodymium in samarium), but in most cases only major changes can be observed. The general progress of fractional separations can, however, be nicely established, since many color differences are easily detectable.

Absorption Spectroscopy. The first instrumental approach to rare earth analysis came through the use of absorption spectroscopy. Those rare earths forming colored solutions have sharp absorption bands which are easily visible when light from an incandescent source is passed through the rare earth solution and diffracted by a spectroscope (658). The width of the dark absorption bands is proportional to the concentration of element present, and if standards are set up, visual comparison of the absorption bands will permit fairly accurate determinations. Alternatively, the length of light path through the solution may be varied to match the absorption band with that of a standard, and calculation of concentration may then be made (155, 218,928).

Visual spectroscopy is limited by the range of light radiation visible to the eye, roughly 4,000-7,000 Angstroms. Further difficulty may be encountered by the presence of absorption bands from different elements which are so close together that they cannot be differentiated by eye.

Spectrophotometry. The application of instrumental measuring devices reduces these difficulties. The range of wave lengths conveniently covered is extended to 2,000-10,000 Angstroms. This permits analysis of gadolinium, europium, and ytterbium which have no absorption bands in the visible region, and also permits the use of additional absorption bands of some of the colored elements.

The use of narrow slit widths provides better resolution of absorption bands, and minimizes interferences.

The major advantage introduced, however, is the ability to make quantitative measurements. Rodden (681,682) in the first definitive works, found general accuracies of the order of 1-2%. His work was subsequently extended by Moeller & Brantley (544) and others (793,794,796,926) who investigated the effects of various anions, adopted slightly varying techniques or used different instruments.

Spectrophotometric determinations are based upon the Beer-Lambert expression:

$$\log \frac{I_o}{I} = kcl$$

where k is the absorption coefficient
I_o is the intensity of incident light
I is the intensity of the transmitted light
c is the concentration of the element (grams/liter)
l is the light path (cm)

Provided that the Beer-Lambert law is obeyed, it may be seen that the ratio of intensity of incident light to transmitted light, which is the phenomenon measured, is directly proportional to the concentration and the length of the light path.

Under nominal analytic conditions, assuming a 1 cm. light path and an observed optical density difference of 0.01 between the intensities of incident and transmitted light, the absorption coefficients permit the following levels of detection:

Praseodymium	0.1 grams/liter
Neodymium	0.3
Samarium	0.5
Europium	0.5
Gadolinium	0.6
Dysprosium	0.4
Holmium	0.2
Erbium	0.4
Thulium	0.7
Ytterbium	1.0

If the solution contains 100 grams/liter of rare earth the above values are percentages. The limits of detection may be significantly lowered by increasing the light path length or improving photometric procedure to improve the sensitivity of detection.

Flame Spectrophotometry. Analysis of rare earths by flame spectrophotometry has been described by several investigators (171,532,647). The method has not as yet come into common use, presumably because very high flame temperatures are needed to obtain good excitation.

Emission Spectrography. Excitation of rare earths by an arc or spark results in a complex spectrum for most elements. Many of the lines are sensitive and persistent, and are useful for the detection of small percentages of rare earths.

During the period 1930-1941, Selwood (729), Bauer (46), Hopkins et al (474), Gatterer and Junkes (220), and Lopez 'de Azcona (460) investigated the analysis of rare earths by spectrographic means. The simpler methods described lacked accuracy and reproducibility. Those which were more accurate were lengthy and time consuming.

Starting in 1948 Fassel and co-workers (195,196,198,199,396) developed techniques which were both rapid and accurate. Analysis is based on the use of powdered graphite as a carrier and buffer, and the use of either the matrix rare earth, or an added rare earth such as cerium, as an internal standard. With these methods most rare earths may be determined when present at 0.01%, and some may be determined at 0.001% or less.

It must be emphasized that in common with spectrographic analysis generally, analysis of the rare earths is critically dependent upon the conditions used. Variables such as the type of diffraction apparatus, its speed and dispersion, the type and intensity of excitation used, the form of the rare earth (metal, oxide, salt, solution, etc.), the material and even the shape of the electrode, the wave length region covered, and the type of film and development used, all play a very important part in the ultimate sensitivity and accuracy attainable. In addition to the reports by Fassel, recent techniques for the spectrographic analysis of rare earths have been reported by Hirt and Nachtrieb (320), Smith and Wiggens (747), Norris and Pepper (595), White and co-workers (906), and Love (462) in the United States, and by several workers in the Soviet Union (4, 259,427,429,740).

The principal reference source for spectral line identification has long been the MIT Wavelength Tables (284). With the availability of very high purity rare earths from ion exchange columns, a number of errors have been found, apparently caused by the unrecognized presence of rare earth impurities in the materials initially examined. Kniseley, Fassel, and Lentz (395) have recently reported corrections for some 290 spectral lines in the MIT tables. Norris (594) has compiled a new wavelength table for rare earth and associated elements which should also prove valuable to the rare earth spectrographer.

X-Ray Spectrography. Recent developments and improvements in instrumentation have renewed interest in X-ray spectrography for rare earth analysis (294,472). The method thus far shows promise for the determination of major constituents in mixtures, but analysis at concentrations below 1% becomes increasingly difficult.

Neutron Activation. Many of the rare earth elements, as discussed under nuclear properties, have sizeable thermal neutron absorption cross sections. Where applicable, neutron activation techniques have proven successful for analysis. Two primary variations have been used.

1. Actual cross section measurement; in which the presence of neutron absorbing elements is determined by the increase in absorption cross section.

2. Analysis by determination of the type and energy of radiation produced after activation.

In general the neutron activation methods have the restriction of needing large activation facilities, such as a pile, and prolonged time intervals (from days to weeks). With such activation periods the detection of individual rare earths in minerals is of the order of parts per billion (917). In specific cases, where only a limited number of known impurities might be present, more rapid analysis is possible. Thus Jarrett and Berger (362) give data for the radioisotopes produced in one hour by a 1-watt reactor, which indicate that activation analysis in a small reactor would be possible for some rare earths; particularly europium, dysprosium, and lutetium.

Analysis for Non-Rare Earth Contaminants. Analysis for most other elements in rare earth materials may be performed by conventional methods. Chemical, spectrophotometric, and spectrographic methods are all applicable.

Particular attention must be placed upon the problem of analysis of the metals for contained gases. As in the case of other active metals, such as titanium and zirconium, the presence of oxygen, nitrogen, and hydrogen materially influence the properties of the metals. Nitrogen may be determined by standard Kjeldahl procedures. Hydrogen may be determined by high temperature combustion. Both of these gases and oxygen may be determined by vacuum fusion followed by gas analysis.

Fassel (197) has recently described an emission spectrographic method for the determination of oxygen in metals. Based upon excitation of the metal in a molten platinum bath in an argon atmosphere, followed by spectrographic comparison of oxygen and argon emission lines, it is much more rapid than previous methods available, but requires spectrographic and auxiliary equipment.

Love (462) combines portions of several methods to avoid expensive capital equipment. The metal is melted in a platinum bath in a graphite crucible. The liberated carbon monoxide is oxidized by iodine pentoxide and the equivalent iodine liberated is titrated.

Economics

The future cost of rare earth metals for direct use or alloying purposes will be a function of several variables:

1. Raw materials cost
2. Processing and separations cost
3. Cost of reduction to metal

All of these factors will be influenced by the general situation, at any time, with respect to the forces of supply and demand. The demand for rare earth compounds or metals may be considered in the light of present and potential future applications. At the present time the bulk of rare earth applications is for the mixed cerium group elements.

The metals industry uses misch metal, and mixed oxides or halides, for additions to iron, steel, stainless steel, nickel-chromium alloys, magnesium, and to a lesser extent, other metals. The production of lighter flints is a major use for misch metal.

The glass industry uses cerium as an absorber of ultraviolet light, and as an oxidizing agent for ferrous iron; and neodymium (in crude mixtures or didymium) to neutralize ferric color. Large quantities of mixed oxides or ceric oxide are used as a polishing agent for plate and optical glass, gem-stones, etc. Didymium is used in welders' goggles and special filters to absorb yellow light.

Electrodes for searchlights and illuminating arc lamps are cored and packed with rare earth compounds to increase the brilliance and luminosity of the light.

Metallic soaps and dryers are produced for use in a number of applications in paint, lubricating, plastic, and other industries.

The separated rare earths have found applications in a number of fields but on a much more limited scale.

In metallurgy, there has been some recent emphasis on the use of separated lanthanum and cerium metals as additions to ferrous alloys, and there is increasing interest in the use of separated rare earths in magnesium alloys.

The glass industry uses pure lanthanum oxide to make non-silicate glasses, with high index of refraction and low dispersion, for optical lenses. The light absorbing and color producing properties of cerium, praseodymium, and neodymium are used in other special glasses.

The ceramic industry uses small quantities of rare earths for special purpose ceramics. Ceria and some other rare earths are used as constituents of vitreous enamels for opacifying and color effects. Modest quantities of ceria are used in the gas mantle industry.

In the medical field, cerium oxalate is used as an anti-nausea and anti-seasickness agent. Research is underway with lutetium and yttrium for cancer treatment.

In the nuclear field, pilot quantities (up to perhaps several thousand pounds) of purified rare earths are being investigated as neutron absorbers. Limited quantities of rare earths, particularly thulium, samarium, and europium are activated for use as radiation sources.

In the electronics industry, small quantities are used as getters, as constituents of thermionic emitters, and as constituents or activators for phosphors. Gadolinium and yttrium oxides are used in the production of various types of ferrites.

A modest quantity of cerium is used as an analytical reagent.

The sum total of all usage amounts to some several thousand tons per year (the United States Bureau of Mines (451) estimates the apparent consumption in 1959 at about 1,500 tons of rare earths as oxides). Some of the applications will probably never increase to any considerable extent, but applications in some fields of interest are still in their infancy, and usage may increase tremendously.

In the metal industry, for example, it might be speculated that definite advantage might be established for the use of rare earths in steel. In this case, if we assume that 10% of the steel produced would have 0.1% rare earths added, 10,000 tons of rare earths would be needed annually. Similar speculations might be made for other metals.

In the ceramic field a growing potential seems to exist for special purpose ceramics for high temperature, and special electrical, magnetic, and electronic applications (semiconductors, masers, thermoelectric devices, etc.).

In the chemical field research is progressing, and many possible applications for rare earths as catalysts have been proposed in the literature and in patents. Some typical references are 131,237,325,400,517,679,809,855 respectively.

In the nuclear field, rare earths may find several applications. Samarium, europium, and gadolinium are the best thermal neutron absorbers, and their potential use for control materials has been well evaluated by Anderson (14) and by Ploetz (644) Dysprosium and erbium have attractive resonance absorption properties (372,665). Other rare earths have low cross sections and may find application as part of the structural materials in reactors. Several may be activated to form useful radiation sources.

In addition to those uses which are indicated above, and which are based on rare earth compounds which are now available, whole new fields may open up as an indirect effect of metal availability. Metals availability will permit the production and potential application of many other compounds such as carbides, nitrides, hydrides, sulfides, etc. which were previously unavailable.

Based on the above discussion we may reasonably assume that production and use of rare earths will steadily increase during the next few decades.

At the present time mixed rare earth chlorides are selling at approximately $0.20-0.35 per pound, oxides at $0.30-2.00 per pound, and misch metal at $3.00-4.50 per pound. Cerium and lanthanum metals are in the $15.00-30.00 per pound range for commercial grade materials.

Referring again to the basic variables influencing costs, and considering them in the light of possible production rates, it may be concluded that the cost of raw materials should not increase, and may decrease with increased production. The cost of processing and separations should definitely decrease with increasing scales of operations. The cost of reduction to metal may be roughly compared to that for titanium and zirconium. In general, therefore, it might be concluded that the cost of the more abundant elements in metallic form, would be in the range of $5.00-20.00 per pound, the moderately abundant elements would be somewhat higher, perhaps $25.00-100.00 per pound. The cost of the scarcer rare earths is more difficult to evaluate, since in addition to the above considerations, economic factors relating to large by-product volumes of the more abundant elements must be considered.

THE RARE EARTH METALS

Introduction

The stimulus of improved methods of rare earth separation, and the consequent production of larger quantities of pure materials, encouraged efforts to produce the pure metals. The rare earth compounds are difficult to reduce, and the metals are active materials when hot. Many have very high melting points. It is thus necessary to work at high temperatures in vacuum or inert atmospheres and with non-reactive materials of construction.

The following sections will discuss the preparation of the metals and their properties. Most of the physical properties (heat capacities, electrical resistivities, magnetic properties, etc.) have been determined in efforts to obtain a better understanding of basic physical and quantum mechanical structures. More recently mechanical properties of the metals and metal alloy systems have been determined, particularly by Love at the Research Chemicals Division of Nuclear Corporation of America and Carlson at Iowa State College.

Preparation of Metals

The first metals produced were yttrium by Berzelius in 1825 (60) and cerium by Mosander in 1827 (573). The metals were obtained in poor yields by the reduction of the chlorides with sodium or potassium. It must be recalled that these were not pure rare earths since most of the elements had not yet been identified and separated.

In 1875 Hillebrand and Norton (314) prepared lanthanum and cerium metals by the electrolysis of fused chlorides. This work was picked up, expanded, and improved by Muthmann and coworkers (581-583) in 1902-1907.

These two basic methods, metallothermic reduction and electrolysis of fused salt mixtures, have remained the principal, and indeed almost the only methods for metal preparation.

Metallothermic Reductions. Reduction with Alkali Metals. Starting with the aforementioned work of Berzelius and Mosander, many other investigators used sodium or potassium to reduce rare earth chlorides (385,410,413,414,56,509,910,920,938). Invariably, powdered metal was obtained, mixed with the alkali chloride slag.

Because of the reactivity of the metal, chemical separation was virtually impossible. Klemm and Bommer in 1937 (385), however, used the reaction to produce all of the rare earth metals, which they left suspended in the salt matrix and investigated by X-ray diffraction in the as-prepared state.

Power, Fox, and Otto (654) investigated the reduction of lanthanum bromide and chloride by potassium vapor. Working on a semi-micro scale, yields of approximately 99% were obtained.

Campbell and co-workers (848-854), have produced laboratory and pilot plant scale quantities of yttrium by reduction of the chloride with lithium or sodium. Higher purities were obtained than for reductions with calcium or magnesium.

Morrice and co-workers (559) report the preparation of cerium by reduction of cerium fluoride with lithium (and added lithium-iodine).

Reduction with Magnesium. The reduction of both oxides and halides by magnesium has been tried. Mahn (503) obtained dilute solutions (<5%) of rare earths in magnesium when he reacted the oxides with magnesium metal at 1050°C. Better success was had by Trombe and Mahn (846) who obtained cerium, neodymium, and gadolinium by reduction of the chloride with magnesium. A magnesium-rare earth melt was obtained. The magnesium was removed by vacuum distillation, and Trombe claimed rare earth purities of 99.5-99.8%.

Reduction with Calcium. Reduction of oxides by calcium was tried by Hirsch (319) and Winckler (918). Some reduction was obtained but a mixture was produced which could not be separated.

Reduction of the halide was effected by Moldenhauer in 1914 (552), then by Karl (377) and by Derge and Martin (157). More recently the preparation of the rare earth metals by calcium reduction was undertaken on a larger scale by Spedding and co-workers at the Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa.

The reductions were first carried out (787) in a steel bomb lined with jolt packed (and later sintered) lime or dolomite. A charge consisting of anhydrous rare earth chlorides and calcium metal was heated by placing the bomb in a furnace and initiating the reaction at 650-750°C. Once started, the reaction went to completion in a few seconds. The temperature reached in the reaction was not sufficient, however, to permit good separation of slag and metal. Further heating of the bomb did not materially improve the separation. Final success was achieved by adding a "booster" reaction which provided added heat. Several such reactions were tested, an iodine-calcium reaction being finally selected.

Clean ingots of lanthanum, cerium, praseodymium, and neodymium were prepared by this technique. Samarium and europium could not be reduced to metal, although a reaction (apparently reduction to the divalent state) took place as evidenced by the heat evolved. Yttrium metal could be produced but it was intimately mixed with slag, not enough heat being produced to melt the metal into an ingot.

The metals produced were purified of calcium and magnesium by vacuum melting and distillation of these impurities.

Part of the magnesium impurity was due to attack of the magnesia crucible by the molten rare earth metal. Spedding and Daane (761) found that tantalum metal was much more resistant to attack. They modified the procedure and found that the booster charge became unnecessary. The chloride and calcium were reacted in a tantalum crucible heated above the melting point of the metal by an induction furnace while in a vacuum or argon atmosphere. Lanthanum, cerium, praseodymium, neodymium, and gadolinium were prepared with 99% yields.

Preparation of yttrium and the heavier rare earths was accomplished by changing the rare earth halide salt from chloride to fluoride (145). The greater stability and lesser volatility of the calcium fluoride at high temperatures permitted carrying the temperature as high as 1600°C. Yttrium, erbium, holmium, dysprosium, terbium, and thulium were thus obtained as fused metals. Izhvanov (356) describes a similar procedure for yttrium.

More recently, for large scale preparation of yttrium metal, magnesium has been added to lower the melting point of the metal phase, and $CaCl_2$ has been added to lower the melting point of the slag (118). A complete summary of the methods used for the preparation of yttrium at Iowa State University of Science and Technology has recently been published (34).

Onstott (34) was able to reduce samarium oxide with calcium. Redistillation of the calcium-samarium fraction gave pure metal in about 40% yield. Onstott (602) also prepared samarium metal by the reaction of samarium bromide with barium at 1650-1700°C.

Petru (638) prepared scandium metal in a molybdenum crucible by reducing ScF_3 or $ScCl_3$ in an argon atmosphere with calcium. Final distillation, reportedly at 1500-1600°C, gave pure scandium.

Spedding and Daane report the preparation of scandium metal by reduction of scandium fluoride with calcium metal in a tantalum crucible (350). Zinc metal and lithium fluoride are added to the charge in order to reduce the melting points of the metal and slag phases. The zinc was removed by heating in a vacuum at 1000°C, and the resulting scandium sponge was consolidated by arc-melting.

Reduction with Rare Earths. In all of the above described procedures, the preparation of samarium, europium, and ytterbium proved to be extremely difficult or impossible. Reduction invariably only went as far as the divalent state. Daane, Dennison, and Spedding (143) provided a major breakthrough in the preparation of these materials in 1953.

Considering that lanthanum oxide has the highest heat of formation of the rare earth oxides, and that lanthanum metal appeared to be the least volatile of the rare earth metals, they concluded that the reaction:

$$La + Sm_2O_3 \rightleftharpoons La_2O_3 + Sm$$

might be driven to completion by distilling away the samarium metal.

The reaction does indeed proceed as postulated, and good yields of high purity samarium, europium, and ytterbium have been prepared by this method (142,143,775). Campbell and Block (108) have also reduced these metal oxides with zirconium in an analogous procedure.

Misch metal has also been used for the preparation of these metals. Its use for the preparation of other metals would be dependent on the purities desired, since the more volatile elements in the misch metal itself would also distill.

Electrolytic Reductions. Reduction from Molten Salts. Approximately one-fourth of the rare earths sold commercially are in the metallic state. Most of this metal is misch metal, a mixture consisting of the rare earth elements in approximately the same relative proportions as present in cerium group rare earth minerals.

The mixed rare earth chlorides (hydrated) are charged to iron pots and gently heated to drive off the water of hydration. A mixture of anhydrous calcium, sodium, and potassium chlorides (with perhaps barium chloride) is added, and the temperature is raised to produce a melt. For electrolysis, an iron or carbon rod is used as the anode, and the iron pot as the cathode. The misch metal collects as a molten pool and is then cast into plates, bars, or other shapes.

Electrolysis from molten salts has also been used to prepare the individual rare earth elements of the cerium group. The work of Hillebrand and Norton, and Muthmann, has been mentioned. Hirsch (319) and Thompson (815) prepared cerium in the period from 1910-20. In the next decade Kremers and co-workers (410,413,414, 910) and subsequently Schumacher and co-workers (726,727) prepared the cerium group metals using various materials for electrodes.

Schumacher and Harris (726) also reported the reduction of the heavy rare earths with aluminum, forming an aluminum alloy which was not attacked by short periods of contact with concentrated potassium hydroxide, and which could not be separated by volatilization.

In 1930 Urbain initiated a program to investigate the properties of rare earth metals. The metals were prepared by Trombe (827,828) by electrolysis, using a rotating cathode to promote agglomeration of metal. Paying particular attention to materials of construction and quality of reagents, metals reported to be 99.8% pure after re-fusion in vacuum were obtained.

In subsequent work, Trombe (830,831,833) produced metallic gadolinium, europium, and dysprosium, and Fischer (206) produced scandium by electrolyzing the chlorides using molten zinc or cadmium cathodes. The alloy formed was then heated in a vacuum and the zinc or cadmium distilled away from the rare earths.

Eastman and co-workers (175) prepared cerium by electrolysis of fused LiCl-KCl eutectic containing $CeCl_3$ or CeF_3, and CaF_2-LiF eutectic containing $CeCl_3$. The cerium-potassium-lithium system gave ingot metal, the cerium-calcium-lithium melt produced finely divided metal.

The principal sources of impurities in massive metals prepared by electrolytic reduction from molten salts are the impurities in the starting materials, contamination from the atmosphere, and reaction of the metal with container or electrode materials at the elevated temperatures involved.

Morrice and co-workers (559,560) have recently described work in the electrowinning of cerium as carried out at the Bureau of Mines Reno Metallurgy Research Center. Cerium of better than 99.9% purity has been produced by careful minimization of the sources of error described above. Anhydrous cerous fluoride is prepared by the reaction of cerium oxide with ammonium bifluoride. An electrolyte phase is prepared from 73% CeF_3, 15% LiF, and 12% BaF_2 powders. This is vacuum dried at 280°C. The electrolyte is charged to a graphite cell and the center portion melted by passage of an a-c current through an electrode assembly. After sufficient electrolyte has melted (the portion next to the graphite remains solid as a skull) vacuum dried cerium oxide is added, and the current changed to d-c for electrolysis. The cerium is deposited as nodules which do not come in contact with the graphite container since they come to rest on the solid electrolyte. The entire electrolysis assembly is encased in an inert atmosphere chamber to prevent atmospheric contamination.

Reduction from Solution. The molten zinc or cadmium cathode technique was a high temperature variation of mercury amalgam techniques developed for preparing metal from solution. Audrieth (with Jukkola, Meintz, and Hopkins) (29,322,374,525) electrolyzed anhydrous chlorides in alcoholic solution. Dilute rare earth amalgams were obtained, and the metals from them by vacuum distillation of the mercury.

McCoy (481) obtained europium and ytterbium amalgams by electrolyzing acetate solutions containing potassium citrate as a complexing agent. Attempts to prepare europium metal by distilling the mercury in a vacuum failed. Heating to "red heat" still left a europium-mercury compound. This decomposed suddenly when heated in vacuum by an induction coil, and no metallic europium could be recovered.

Moeller (543) has investigated the possibility of depositing rare earths from aqueous solutions containing various complexing agents, and from various protonic solvents. Electrolysis yields only very small quantities of metal at best unless a mercury cathode is used.

Howes (329) has reported the deposition of thin films of several rare earths onto copper, but no details are provided.

Reduction with Hydrogen. Direct reduction of the oxides or halides to metal cannot be effected by hydrogen. The trichlorides of samarium, europium, and ytterbium are reduced, however, to the dichlorides. These may dissociate to the metal and the trihalide if heated above the melting point.

$$3SmCl_2 \rightleftharpoons 2SmCl_3 + Sm$$

The reactions are not quantitative, however, and they cannot be combined since the hydrogen would react with the metal at elevated temperatures.

Purification of Metals

The metals prepared as discussed in the previous section contain various impurities, the type depending on the method of preparation. Many investigators have attempted purification of the metals, and several different techniques have been successfully applied.

Washing and Remelting. Metals prepared by electrolysis may have inclusions of soluble halides. Significant improvement can be effected by a rapid water wash followed by remelting under sodium chloride or a eutectic mix.

Remelting and Slagging. Investigators at Iowa State University of Science and Technology (34) have reported a slagging process for the purification of yttrium. The yttrium-magnesium alloy is remelted under fresh yttrium fluoride plus calcium chloride eutectic. Melting is in a tantalum crucible, and the mixture is stirred with a tantalum or titanium stirrer. The procedure is applied to the magnesium alloy rather than to the recovered yttrium in order to keep melting temperatures low and thus to minimize contamination from the container. The oxygen content of yttrium so treated is reported reduced from 1500-3000 ppm to 300-500 ppm.

Amalgam Formation. Some metals may be amalgamated by direct combination with mercury. Metallic compounds such as carbides, oxides, or unreacted halides do not amalgamate, and may then be skimmed off. The mercury is subsequently distilled away from the rare earth by heating in a vacuum. The rare earths are obtained as pyrophoric powders which must be remelted in an inert atmosphere. This technique has been used by Schumacher (726) who claimed to have obtained 99.8% pure rare earths. There seems to be some question, however, as to whether all of the mercury can be removed, or whether a small amount remains as a high temperature stable compound.

Vacuum Melting. Vacuum remelting of a rare earth metal, at temperatures below its volatilization point, is effective for the removal of volatile impurities such as calcium or magnesium.

Distillation. Many of the rare earth metals have significant vapor pressures at temperatures reasonably attained by induction heating. Vacuum distillation separates these metals from non-volatile metal contaminants such as molybdenum or tantalum, and from stable compounds such as oxides (351,463).

Other Methods. In addition to the above methods some procedures might be applicable to certain specific purifications. Thus tantalum will "scavange" nitrogen from rare earth metals, forming the extremely stable nitride (142).

The de Boer hot wire process has been tried (213) but poor yields were obtained even on a milligram scale of operations.

Yttrium zone refining investigations were reported by Huffine (330). The reactivity of molten yttrium with container materials necessitated the use of a floating zone technique. Although some improvement was observed, high purity metal was not obtained.

Carbon deoxidation studies have been made by Love (464) and by Spedding and Daane (349). Slight reduction in oxygen content was achieved, but carbon content, and hardness increased.

Attempts to purify rare earths by electron beam melting have also been reported (464,330). The method is only applicable to those rare earths which have low vapor pressure at the melting point. The concentration of volatile impurities was reduced in these elements.

Physical Properties of the Rare Earth Metals

Effect of Impurities. The early preparations of rare earth metals usually produced rather impure products. This was due in part to the impurity of the starting materials and in part to the methods used for preparation. Certain aspects of the influence of rare earth impurities on the behavior of rare earth oxides have been determined (302). In contrast, the influence of the rare earth metals on the physical properties of each other has not been well defined. Only a very few of the constitutional diagrams of the rare earth metals in each other have been determined.

The effect of some non-rare earth elements on the properties of metals is better known. The influence of iron on the physical properties of rare earths has been systematically studied by Henry La Blanchetais (300,302). Cerium must contain less than 5 ppm of iron in order to obtain the exact magnetic moment. Nevertheless, several per cent of iron does not modify the position of the magnetic abnormalities of cerium but only the general appearance of the curve of susceptibility as a function of temperature. The addition of magnesium to cerium containing traces of iron considerably modified the observed magnetic properties. Iron, initially in the form of a complex, seems to be precipitated in the free state when the magnesium content is high (502).

Carbon in the rare earth metals produces a carbide which can remain in solid solution in the metal under certain conditions. The magnetic properties and the coefficient of expansion appear to be little influenced by traces of carbon. In contrast, the mechanical properties may be notably modified.

One-tenth to one percent of silicon appears to influence the mechanical properties, but seems to have little influence on the magnetic properties and the several allotropic transformations of the rare earth metals. Silicon and iron have very low solid solubilities in cerium. This is in agreement with the fact that the atomic volumes of iron (7.1) and of silicon (12.04) are considerably different from that of cerium (20.8).

Systematic studies of the influence of magnesium on cerium and gadolinium have been carried out by F. Mahn (Gaume-Mahn), (221,223,224,500,502). These show that the expansion abnormality at low temperatures, which is a maximum for the pure metals, decreases regularly with the addition of magnesium, and disappears when the cerium or gadolinium contains only 1% of magnesium. The abnormal magnetic properties also disappeared for the same percentage of magnesium, and were influenced to a much greater extent by small percentages than were the expansion properties. Gadolinium too, has its magnetic properties completely modified by addition of 2% magnesium. The influence of calcium, though less studied at the present time, seems to be of the same order of magnitude. In particular, it appears that the allotropic transformations and magnetic properties are affected by a small amount of calcium or magnesium, and these must then be particularly eliminated from the rare earth metals to obtain accurate measurements (838).

Kleber and Vickery found that the Curie temperature of gadolinium is lowered slightly by the addition of small amounts of iron, then rapidly raised by larger additions. Nickel and cobalt markedly lower the Curie temperature of gadolinium (674).

Appearance. The rare earth elements have a metallic appearance, generally similar to iron. Slight differences in grayness and luster are apparent when the elements are closely compared. Samarium is the only metal having any other color, a definite golden tint being evident. Some of the metals corrode rapidly in air (see discussion below). The appearance of freshly cut surfaces may consequently change in a short time.

Crystal Structure. Table XII gives the crystal structures, summarized from various workers, of the rare earth metals. The greater proportion of the rare earth elements have hexagonal or face centered cubic structures at room temperature. Lanthanum, cerium, praseodymium, and neodymium have structures related to hcp, but due to interlayering of hcp and fcc layers, the C axis is twice as long as is normal for hcp (776). Europium has a body centered cubic structure (765) and ytterbium is face centered cubic. X-ray studies of samarium indicate that if the structure is hexagonal it has layers arranged ababcbcac, hence with a c:a ratio 4½ times normal (776). Since this is possible but not very probable, a more likely structure is the rhombic (Daane, et al; 139,144). The results confirm the work of Ellinger and Zachariason (180), who predicted a rhombic structure.

Several of the rare earth metals have allotropic transformations at elevated temperatures. For lanthanum, cerium, praseodymium, neodymium, samarium and yttrium, the transformations are to body centered cubic structures; the ytterbium transformation is to a hexagonal structure (493,350,351,776). Transformations have also been detected by thermal methods in gadolinium and terbium but the high temperature structures have not been established.

The Allotropic Transformation of Metallic Cerium. Cerium has four different crystalline allotropes, and most of the studies of crystallographic transformations have been made with this metal.

As previously indicated, various impurities can seriously impair the accuracy of measurement of some of these properties. In 1934, a thermal magnetic study of cerium containing only 0.1% silicon and 0.1% iron, consequently quite pure, showed an anomaly between 100° and 170°K. (62,827,829). This anomaly was not found again by different authors (791,862) who studied commercial samples of cerium of somewhat less purity. Klemm and Bommer again found the anomaly in their general study of the pure rare earths (386).

Trombe and Foex, in 1942, established the presence of three allotropic forms of cerium. They called the high temperature form "gamma", the lower temperature forms "alpha" and "beta". In pure cerium the "gamma" form had a face centered cubic structure, the "beta" form was hexagonal close packed. The alpha form was also face centered cubic (210,840). It must here be cautioned that various investigators have used the terms alpha, beta, gamma, and delta in the light of their own individual investigations and that these may refer to different structures in different references.

A comparative study of pure cerium and commercial cerium (844) enabled Trombe and Foex to observe the relative stabilities of these metals. The commercial cerium contained calcium. As noted above, calcium and magnesium are phase transformation inhibitors, and Trombe and Foex now noted this was particularly true for production of the "alpha" phase (see also ref. 225). In 1946 Schuch & Sturdivant studied the structure of a dense form at low temperature. X-ray studies by these authors (722) showed that the contracted phase is face centered cubic as is the generative phase, but the lattice dimension is not more than 4.82 Angstroms, whereas it was 5.14 Angstroms in the normal form at ordinary temperature (663). The change in volume for the contracted form was 6½%. In 1949, Lawson and Tang obtained complete transformation to the dense form at ordinary temperatures, by compressing cerium at a pressure of 15,000 atmospheres (434). X-ray study under pressure shows that one obtains the same crystalline form as at low temperatures.

The transformations in cerium are illustrated in Figures 1 and 2 (From Gschneidner (264). It may be noted in particular that the transformation temperatures and extent of transformation are dependant upon rate of cooling, previous thermal history (i.e. temperature cycling effects), pressure, amount of cold work and temperature of cold working, and the presence of impurities. The overall effect of these variables is essentially to produce wide temperature ranges and hysteresis loops, and wide variations in the rate of crystallographic transformations.

The transformation temperatures of the rare earths are indicated in Table XIII. Hysteresis effects are not included, temperatures being listed only for transformations from low temperature stable forms to forms stable at higher temperatures.

Density. Densities of the metals have been calculated from X-ray data, and are presented in Table XII. The measured densities which have been experimentally determined are in good agreement (264,675). Europium and ytterbium, whose metallic valency according to Pauling is two, have abnormally low densities compared with the other rare earths whose metallic valence is three. Samarium, which can also form bivalent salts, presents in the metallic state a normal density for the position it occupies in the group, and thus confirms its metallic trivalency.

Thermal Properties. Linear Coefficient of Expansion. Coefficients of expansion have been investigated by Trombe and Foex (841,842,843), and Jaeger, Bottema, and Rosenbohm (358), who were primarily interested in determining allotropic transformations. Barson, Legvold, and Spedding, (40) with larger quantities of high purity material available, redetermined these coefficients for the same purpose. In general, it was found that the coefficients are lower than for most other metals and are not linear except over relatively small temperature ranges. Because of the importance of the coefficient of expansion in engineering applications, and because of the wide irregularities in the shapes of the curves, the curves are reproduced directly (Figures 3-8). Additionally, the coefficient of thermal linear expansion has been reported (775) for europium between 20 and 780°C as being $26 \times 10^{-6} (^{\circ}C)^{-1}$.

Melting Point and Boiling Point. Melting point observations were made by many of the investigators who worked on the preparation of pure metals. Precise measurements were difficult to make because of the small amounts of metal available, and the results did not always agree due to variations of purity. The best of this early work was by Trombe (838), and by Fischer, Brunger, and Grieneisen (206).

Spedding and his collaborators (776) however, working with 200 to 300 gram samples carried out precise thermal analyses. The determinations were made in a tantalum crucible and the temperature was measured by a thermocouple in a tantalum sleeve.

Melting points of higher melting or scarcer elements were estimated by optical observations of the temperature at which the metal flowed (776). The metals were heated either in a vacuum of 10^{-5} mm. or in an atmosphere of purified argon. The cooling rate was about 10°C per minute. By this method, not only the melting points, but the high temperature transformation temperatures were obtained.

Subsequent measurements were reported for higher purity (distilled) yttrium, terbium, dysprosium, holmium, erbium, and lutetium (352). The melting points of yttrium and lutetium melted in tantalum were approximately 30°C higher than the same metals "as distilled".

Melting and boiling points are summarized in Table XIII. Boiling points are taken from published data of Daane, Spedding, and co-workers (146,775,776,760).

Thermal Conductivity of the Rare Earths. Only limited studies have been made of the thermal conductivity of rare earth metals (Legvold and Spedding (348). The conductivities are generally low compared to other metals. Values available are summarized in Table XIV.

Thermodynamic Properties. The availability of pure metals has stimulated investigations of their thermodynamic properties. Values for heat capacity at 0°C, heat of fusion, heat of vaporization, thermal conductivity and the temperatures at which the vapor pressures of the elements are 1 and 0.001 mm. are indicated in Table XIV.

Electrical Properties. Resistivity. The rare earth metals are poor conductors of electricity. James, Legvold and Spedding (360), Bridgman (94), and Spedding, Daane, and Herrmann (766), have reported resistivity values for groups of elements. Purity, heat treatment, crystal structure, and state of strain all influence the resistivity of the elements, and considerable variance in reported results are noted in the literature. Table XV presents the resistivity data reported by Bridgman, along with more recent data obtained by Spedding and co-workers (as referenced). Morrice has recently reported determinations of the resistivity of cerium of various purities. Values as low as 12×10^{-6} ohm·cm were obtained for electrorefined metal (559,560).

Resistance Anomalies. A study of resistance as a function of temperature shows a number of anomalies. In the pure metals these may be associated with allotropic transformations. Lanthanum, cerium, praseodymium, and neodymium (360), and gadolinium, dysprosium, and erbium (764) have been investigated. As with thermal expansion, the resultant plots of resistance vs. temperature are reproduced directly (Figures 9-19) (764).

Bridgman, working with metals prepared by Spedding and others, determined the variations in volume and electrical resistance under pressures up to 100,000 kg/cm^2 of the following rare earth metals: lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium (94). All of these elements except ytterbium show decreasing resistance as pressure is increased. This is a normal metallic behavior. Ytterbium, however, shows an increase of resistance by a factor of about 12 when the pressure is increased to 60,000 kg/cm^2 and then an initially abrupt and subsequently gradual decrease. Bridgman hypothesized that this abnormality of the conductance of ytterbium corresponds with transformation into a semi-conducting state under the influence of pressure. He therefore made measurements at pressures of 0 to 7000 kg/cm^2 as a function of temperature between 0° and 200°C. Results of these measurements show an inversion of the coefficient of temperature resistance between 0° and 100°C.

Superconductivity. Lanthanum is the only rare earth found to be superconductive. Originally not observed (495), superconductivity was first reported by Mendelssohn and Daunt (531), and Schoenberg (720), and subsequently by others (360,612,935,936). The observed properties were not related, however, to the crystal structure of the lanthanum and the values reported varied from 3.9 to 6.0°K. In 1953 Ziegler, Young, and Floyd (937) reported that alpha- and beta-lanthanum had different transition temperatures, and this was subsequently confirmed by others (11,57, 521,937). The best averaged values are 4.9°K for alpha-, and 5.9°K for beta-lanthanum.

Anderson, Legvold, and Spedding (11), investigated the effect of alloying lanthanum with yttrium and with lutetium. The superconductive transition temperature decreases for both alloy systems with increasing alloy addition (up to 40 atomic percent yttrium and 45 atomic percent lutetium). Compositions containing 15 percent or more of the alloying element were reported in the hexagonal lanthanum crystal state. Hein and coworkers (295) report that lanthanum alloys containing up to 0.98% gadolinium are superconducting, but alloys containing 1% or more gadolinium are not superconducting above 0.1°K. Matthias (520) reports that increasing percentages of both neodymium and erbium decrease the superconducting transition temperature of lanthanum. The decrease is associated with the spins of the solute atoms. Neodymium lowers the transition more than equal percentages of erbium. The difference is ascribed to the effect of the higher effective moment of erbium, contributing towards raising the superconducting transition temperature. It may be noted that both Hein (loc.cit.) and Matthias report rare earth containing compositions with indicated simultaneous occurence of superconductivity and ferromagnetism. Heat capacity measurements by Phillips have confirmed this phenomenon in the lanthanum-gadolinium system (639).

Superconductivity was not detected in cerium, praseodymium, and neodymium down to 0.25°K (251), yttrium to 0.10°K (251) and ytterbium to 1.24°K. (455).

Magnetic Properties of the Rare Earth Metals. The magnetic properties of materials are frequently defined by their susceptibilities. Susceptibility is a measure of the change in magnetic moment caused by a field (i.e. a measure of the induced moment). If the moment is increased, the susceptibility is positive and the material is said to be paramagnetic. If the moment is decreased, the susceptibility is negative, and the material is said to be diamagnetic.

Paramagnetic materials may be further subdivided into three groups. The first group consists of materials obeying the Curie-Weiss law (which relates the intensity of magnetization to the magnetic field and the absolute temperature), and having low atomic susceptibilities (10^{-1} to 10^{-6} cgs units). The other two groups involve ordering of atoms. If the atomic spins are aligned parallel, the materials have very high atomic susceptibilities (10^4 cgs units), and are known as ferromagnetic materials. If the spins are aligned antiparallel, the susceptibilities are again low (approximately 10^{-3} cgs units, more or less as for disordered atoms) and the materials are called antiferromagnetic.

All of these magnetic properties are temperature dependent, and a given material may show a transition from one behavior to another at a certain temperature. These transition temperatures are identified and defined as follows (9):

> Ferromagnetic Curie Temperature. (frequently simply "Curie Temperature" or "Curie Point"); "the point, as the temperature increases, at which the transition from ferromagnetic to paramagnetic properties is complete". (note that antiferromagnetism is a 'paramagnetic' property, and that the transition may therefore be from ferromagnetic to antiferromagnetic).
>
> Antiferromagnetic Curie Temperature or Neel Temperature. "Antiferromagnetism is characterized by the tendency of the magnetic dipoles of near-neighboring atoms to be arranged antiparallel. The temperature at which the heat motions destroy the spatial arrangement is called the antiferromagnetic Curie point or Neel point."
>
> Paramagnetic Curie Temperature. "At temperatures above the ferromagnetic (or antiferromagnetic if present) temperature, most paramagnetic materials obey the Curie-Weiss Law, usually written:

$$\chi = \frac{C}{T-\theta}$$

C is defined as the Curie-Weiss constant, T is the absolute temperature, and θ is defined as the paramagnetic Curie Temperature."

Paramagnetic Metals. All of the rare earth metals, with the exception of scandium, yttrium, lanthanum and lutetium are paramagnetic within a certain range of temperature. In addition, in a more narrow interval within this range, most follow the Curie-Weiss law. Generally, the best measurements on these metals indicate that except for europium, the paramagnetic moment of the metal is essentially the same as that of the trivalent ion. Europium shows a moment very close to that of gadolinium, which indicates that the metal europium might exist as the divalent europium ion. Such behavior may be explained by considering that the carriers of magnetic moments are found in a lower (4f) level.

Magnetic susceptibility measurements have been made and reported by many competent investigators. Much of this data is in reasonably good agreement, and selection of best values is probably academic. For some metals the values reported have varied by a factor of two or more. The magnetic data reported in Table XVI are generally the most recent data reported. Based on the availability of highest purity metals, and an increased awareness of the importance and effects of crystal structure, purity, work-stress condition, and thermal history, it is considered probably most accurate. Readers are also referred to the many excellent papers by Owen, Klemm and Bommer, Henry La Blanchetais, Trombe, Urbain, Weiss, Neel, Legvold, Spedding and co-workers, and others for complete details 182,183,300,302,303, 386,435,436,586,610,776,829,834,835,836,838,857).

Metals with Weak Paramagnetism. Scandium, yttrium, lanthanum, and lutetium should be diamagnetic since they have no unpaired electrons. All of these metals show weak paramagnetism, however, which varies little with temperature. They do not follow the Curie-Weiss Law (776,838).

Ferromagnetism. The magnetic properties of most of the rare earth metals have now been examined to very low temperatures (1-4°K). Saturation phenomena appear in many of the heavy metals at temperatures below the paramagnetic region.

The ferromagnetism of gadolinium was discovered in 1934 by Urbain, Weiss, and Trombe (857). The Curie temperature is 289°K, so that the transition falls in a temperature range that is especially suitable for accurate measurement. For gadolinium the value of the magnetic moment at saturation is 263.5 cgs units. Iron under the same conditions is 221 cgs. units. The corresponding atomic moment for gadolinium is 7.16 Bohr magnetons. There is therefore good agreement between the measured moment and the theoretical moment of the gadolinium ion (7 Bohr magnetons). The Gd^{+3} ion has a total moment equal to the sum of the spins of the seven electrons present in the 4f level. Klemm and Bommer (386) also determined the Curie point of gadolinium, and Spedding and his collaborators have studied the complete magnetic properties of this metal (182,435).

Thoburn, Legvold, and Spedding (814) have established the magnetic properties of terbium. The metal is ferromagnetic below 218°K. Above this temperature, and up to 230°K, the metal exhibits ferromagnetic properties in applied fields greater than 200 oersteds, but appears to be antiferromagnetic in lower fields.

In 1937, Klemm and Bommer (386) studying a mixture of dysprosium and potassium chloride at low temperature, determined the paramagnetic moment of the metal and concluded the absence of true ferromagnetism. A detailed study of the compact metal made by Trombe in 1945 led to very different conclusions however. Metallic dysprosium is paramagnetic at normal temperatures, and ferromagnetic at very low temperatures (834,835,836,843). The moment at low temperatures appears greater than that of gadolinium, which itself is greater than that of iron. The saturation moment at 0°K has not been unambiguously determined (183) but presumably is somewhere in the neighborhood of 273 to 295 cgs units corresponding to between 8 and 8.7 Bohr magnetons. Behrendt, Legvold, and Spedding (55), have examined the properties of a dysprosium single crystal. The metal is ferromagnetic below 85°K.

Rhodes, Legvold, and Spedding (677) found that holmium is ferromagnetic below 20°K.

Interpretation of the magnetic data for erbium has been more difficult. Neel (586) working with the magnetic data of Klemm and Bommer (386) had predicted a Curie point for erbium at about 40°K. Barson's work (435) on the electrical resistivity of erbium has shown an anomaly at about 80°K. This type of anomaly in the electrical resistivity has been shown to be closely associated with magnetic phenomena in gadolinium (435,857), and dysprosium (183,435,834). Studies by Elliott, Legvold, and Spedding (184) on the magnetic properties of erbium metal, have established the initial susceptibility, magnetic moment, and magnetization isotherms of erbium. One would expect an absolute saturation moment of 9 Bohr magnetons if all the spin and orbital angular momentum contributed to the ferromagnetism. The extrapolation, however, corresponds to 269 cgs units or only about 8.0 Bohr magnetons.

Koehler and Wollan (397) examined erbium metal by neutron diffraction. Magnetic transitions were reported near 80°K and near 35°K. The metal was definitely ferromagnetic at 4.2°K with a ferromagnetic moment at this temperature of 7.2 Bohr magnetons. The electrical resistivity vs temperature curve for erbium shows a break at 78°K (435). Heat capacity measurements indicate anomalies at 19.9°K, and near 84°K (744). In summary the data indicate a probable ferromagnetic transition at about 20°K, and an antiferromagnetic transition at about 80°K.

Thulium was investigated by Rhodes, et al along with holmium as described above (677). The metal was considered antiferromagnetic below 51°K, but no ferromagnetic transition was found. Davis and Bozorth, however, found thulium ferromagnetic below 22°K, and antiferromagnetic from 22° to 60°K (150).

Antiferromagnetism. Of the light rare earths, antiferromagnetism has been observed in cerium, neodymium, and samarium by Locke (456), and in europium by Bozorth and Van Vleck (90). The Neel temperatures for the first three metals were very low; 12.5°, 7.5°, and 14.8°K respectively, that for europium was approximately 90-100°K. None of these metals showed any ferromagnetic properties. Among the heavy rare earths, antiferromagnetism has been observed in terbium, dysprosium, holmium, and erbium. Terbium, as noted above, is antiferromagnetic at temperatures between 218 and 230°K in low fields (below 200 oersteds). Dysprosium, holmium, erbium, and thulium are antiferromagnetic in the temperature ranges 85-178°K, 20-133°K, 20-80°K, and 22-60°K respectively. They are ferromagnetic below the lower limit and paramagnetic above the upper limit.

Hall Effects. The Hall effect is "the production of a transverse potential gradient in a material by a steady electric current which has a component normal to a magnetic field" (9). It is of particular importance for the evaluation of band properties, since it is a measure of the number and nature of charge carriers.

Detailed studies of the Hall effect in rare earth metals have been made by Kevane (383), and Anderson (12), with Legvold and Spedding. The values obtained for the Hall coefficients at room temperature are reported in Table XV.

The Mechanical Properties of Rare Earth Metals

At the time of publication of the previous literature survey (461), the only data available concerning the mechanical properties of the pure rare earth metals were the compressibility data of Bridgman (94) and the elastic properties as determined from sonic velocities by Smith, Carlson, and Spedding (750). Since that time the mechanical properties of rare earth metals have been determined by direct measurement, principally in the laboratories of the Research Chemicals Division of Nuclear Corporation of America, Iowa State University of Science and Technology, and the General Electric Company - Aircraft Nuclear Propulsion Department.

Most of the data obtained has been of an exploratory nature since so little was previously known. Areas of promise have been found, and have served as focal points for concentration of effort. Again it must be emphasized that the effects of impurities, work induced stress, thermal history, etc., are important for the rare earths, as indeed they are for other metals. Limited efforts to evaluate some of these variables have been made.

The correlation of data obtained by various investigators is complicated not only by variations in the composition and states of the metals tested, but also by variations in the testing techniques used. The original reports should be examined for details of actual procedures. Further, since the units used by various investigators may not be directly equatable, the results compiled in this section are most frequently given in the units as reported.

Hardness. Table XVII presents hardness data, where this has been determined, for a number of elements under similar conditions. It is observed that, except for ytterbium, the heavy rare earths show higher hardness values than the light rare earths.

The effect of cold working is to increase hardness for all of the metals. The effect is very nearly linear with the extent of reduction up to approximately 50% reduction for dysprosium and erbium (464) and for yttrium (170,266,742). Hot swaging (1000°C) does not increase the hardness of erbium or yttrium (464).

A large number of different impurities may be present in the metallic rare earths. The most extensive investigations of the effects of impurities have been investigations of the relationship between hardness and the oxygen content of yttrium. Love

(464) reported that the hardness of a high oxygen content yttrium decreased proportionately with the decrease in oxygen achieved by carbon deoxidation. Carlson (170) found that the hardness of arc-cast yttrium varied linearly from 57-100 BHN for 500-4000 ppm oxygen, and that the hardness of annealed yttrium changed only slightly (from 48-53 BHN) over this same range of oxygen contents. Simmons (742) found the same relationship for cast yttrium, but found that the hardness was not changed by annealing.

The hardness of gadolinium and yttrium was reported as a function of temperature by Simmons (742). Values for gadolinium remain essentially constant from room temperature to approximately 250°C after which they drop rapidly. The hardness of high purity yttrium decreases almost linearly with temperature (63 to 5 BHN for room temperature to 900°C), but the presence of 0.2% oxygen plus 0.3% fluorine produces an initial slow decrease followed by a more rapid decrease above 400°C.

The effect of heat treatment on the hardness of yttrium is not clear. Carlson (57), reports that a specimen of yttrium with an as-cast hardness of 51 BHN decreased to a hardness of 31 BHN after annealing at 950°C followed by slow cooling; the same metal quenched from 950°C had a hardness of 51 BHN, unchanged from the as-cast state.

Carlson (170) has observed that yttrium shows considerable anisotropy of hardness with grain orientation. A single crystal cut into a parallelepiped showed hardness values of 67, 69, 72, 86 and 89 R_F on the various faces. The impressions on some faces were ellipsoidal, with the major axis parallel to the 001 plane of the crystal. The impressions in the faces lying parallel to the basal plane were round and smaller in diameter. Simmons (742) reports variations of hardness up to 50% on large columnar grains found in consumable arc-melted yttrium.

Simmons (742) reports the hardness of as-cast scandium metal produced by reduction of scandium fluoride with lithium was 78 BHN; that reduced with calcium was 100 BHN. Geiselman (23), reports the hardness of arc-melted scandium as varying between limits of 47-196 BHN. As-cast scandium increased in hardness from 127-136 (Reichert micro-hardness, 17 grams) when cold swaged 22%; after annealing, the hardness was still 136 (229).

Tensile Strength. Love (462) has determined the tensile strength of a number of rare earth metals in both the as-cast and worked conditions, and at room and elevated temperatures. The individual rare earths show large differences in ultimate tensile and yield strengths.

The lower atomic numbered elements have ultimate tensile strengths (as-cast) ranging from 12,000-20,000 psi. Yttrium and the higher atomic numbered elements (except ytterbium 10,000 psi) have ultimate tensile strengths ranging from 25,000 to 42,000 psi. Cold working (50% reduction in area by swaging) increased ultimate strengths by 50-75% for most metals. The higher strength metals showed quite good retention of tensile properties at temperatures up to 427°C (800°F); between 40 and 75% of the room temperature strength being retained at this temperature. The data obtained is summarized in Figures 20 and 21. Subsequent analysis of larger specimens prepared from arc-cast buttons indicated slightly lower room temperature ultimate tensile values for dysprosium and erbium, and somewhat lower room temperature yield values for yttrium, dysprosium, and erbium (464). Again, the cold swaging of dysprosium and erbium markedly increased both ultimate tensile and yield strengths. Moderate increases in strength were noted for erbium and yttrium when hot swaged.

The room temperature tensile properties of several rare earth metals have been reported by Savitskii (709). Values for lanthanum and neodymium were somewhat lower, and those for cerium and gadolinium were slightly higher than reported by Love (462,464). The value for erbium was very nearly the same. Simmons (742) in reporting the strength vs temperature relationship for gadolinium indicated the room temperature ultimate tensile strength as approximately 23,000 psi in good agreement with Love, although the room temperature yield strength was considerably lower. Simmons also found that gadolinium decreased only slightly in strength with increasing temperature to 400°F, and then decreased by approximately 50% at 800°F.

The tensile strength of as-cast scandium was determined at elevated temperatures by Geiselman (230). A specimen tested at 426°C (800°F) had an ultimate tensile strength of 32,200 psi with a yield strength of 25,100 psi. A specimen tested at 871°C (1600°F) had an ultimate tensile strength of 1780 psi with no evidence of plastic yield. Another sample tested at room temperature had a tensile strength of 23,000 psi in the as-cast condition and 37,000 psi after 22% reduction by cold swaging.

Carlson (170) determined the tensile properties of yttrium sheet; hot worked, fully annealed, and stress relieved. Ultimate tensile values of 18,800-22,100 psi, and yield strength values of 8,300-12,000 psi were considerably lower than those reported for the as-cast or arc-melted metals. Both ultimate tensile and yield strengths increased regularly with cold working.

Carlson also determined the effects of minor additions of impurities. At the 0.1 weight percent level, hydrogen increases, and fluorine decreases strength somewhat; while oxygen, nitrogen, and carbon have relatively minor effects. At somewhat higher concentrations, (0.34 weight percent) carbon increases ultimate tensile and yield strengths appreciably. Small additions of titanium, vanadium, chromium, iron, nickel, aluminum, and silicon have only minor effects on the tensile and yield strengths of the base yttrium metals.

Elongation. Ductility, as measured by percent elongation is greater for the lower strength, low atomic numbered elements than for the high strength elements. In general elongation increases with temperature, and decreases with amount of cold work (170,462,464,742). Carlson (170) also points out that hydrogen, nitrogen, and oxygen, which have severe embrittling effects on many metals, do not affect the uniform elongation of annealed yttrium significantly in compositions containing up to several tenths percent. It must be noted, however, (see discussion below) that the presence of impurities does affect ductility as measured by ease of working.

Tensile Modulus. The modulus of elasticity for the rare earth metals is presented in Table XVIII as determined by various investigators. The values of Love (464), calculated from stress-strain measurements, are in reasonable agreement with those of Smith (750) as determined from sonic measurements.

Tensile Fatigue Properties. Tensile fatigue properties were determined by Love (464) for dysprosium, erbium, and yttrium. Specimens were tested to one million cycles. The S-N curves obtained are illustrated in Figure 22. Extrapolation of the curves indicates the endurance limits for yttrium and erbium to be at a stress level equivalent to approximately 50% of the respective ultimate tensile strengths, and the endurance limit for dysprosium to be approximately 40% of its ultimate tensile strength.

Tensile Creep Data. Simmons (742) reports tensile creep data for yttrium metal at 590°C (1100°F). The elongation rate under 400 psi load was 0.005%/hr. At higher stress (1000 psi) the rate of elongation increased rapidly (0.135%/hr.), and the specimen broke after approximately 500 hours.

Compression Properties. The compression properties reported in the literature are indicated in Table XIX. Modulus calculations from sound velocity measurements and from high pressure measurements are in reasonable agreement except for samarium. There is very little area for comparison of mechanically determined properties. Savitskii (709) determined the ultimate and yield properties of yttrium. The yield value for erbium as determined by Love (464) is in nearly the same ratio to the ultimate value determined by Savitskii as the latter's ratio for yttrium.

The compression modulus obtained by Love (464) for erbium is higher than those obtained from sonic measurements by Smith (750) and high pressure measurements by Bridgman (94), but the corresponding values for dysprosium are in reasonable agreement. The effects of the various compositional and physical variables on the compression properties of rare earths have not been reported.

Impact Properties. Impact properties have been reported by Love (462,464). Although there is considerable variation between individual elements, all of the rare earths must be considered notch sensitive in the cast condition. The Izod values for arc-melted yttrium and erbium are somewhat higher at 204°C (400°F) than at room temperature, but the increases are not great enough to indicate a change from brittle to ductile behavior.

Recrystallization Studies. Love (464) has studied the recrystallization of swaged yttrium and erbium. Interpretation was based upon microstructure examination.

Specimens of yttrium which had been cold worked 20% (area reduction) after an initial hot swaging of 40% (area reduction) were annealed for four hours at temperatures of 900°C, 1000°C, and 1100°C. Recrystallization was essentially complete at 900°C within four hours. Annealing at 1000°C produced a similar structure with somewhat sharper grain definition. After annealing at 1100°C, marked grain growth occurred.

Recrystallization of erbium studies were performed on metal which had been cold swaged to 60% area reduction after initial hot swaging to 40% area reduction. Annealing times were again four hours at temperatures of 900°C, 1000°C, 1100°C, and 1200°C. The structure after annealing at 900°C was that of the cold worked metal. After annealing at 1000°C the microstructures still showed strong evidence of the previous cold working. The presence of a few sharp grain boundaries suggested that new grains had been nucleated and that the recrystallization process had begun. When the temperature was raised to 1100°C, the recrystallization process went almost to completion within the four hours holding time. The structure consisted principally of new, equi-axed grains. Some evidence for distortion produced by the previous working remained, principally in areas of high impurity (oxide) concentration. The structure resulting from annealing at 1200°C was completely recrystallized, with sharply defined grains and appreciable grain growth evident.

The data obtained in these studies indicated that the recrystallization characteristics of yttrium and erbium are appreciably different. Erbium recrystallizes at approximately 1100°C in four hours, whereas yttrium recrystallizes at or below 900°C in the same time. Further evidence was noted in the hot swaging operations which suggested a recrystallization temperature near 982°C (1800°F) for yttrium while this temperature produced a "cold" worked, strain-hardened structure in erbium.

Williams and Huffine (913) report recrystallization studies based on hardness measurements. Cold worked yttrium was annealed for one and for three hours at elevated temperatures then slow cooled. Very little decrease in hardness was observed below 540°C (1000°F). Recrystallization, as measured by decrease in hardness to approximately the original hardness, was essentially complete in one hour at 1200°C (2200°F) or in three hours at 980°C (1800°F). These values are in good agreement with those reported by Love.

Guidoboni and co-workers (266), however, also measuring recrystallization by decrease in hardness, report full recrystallization of yttrium metal, cold rolled from 11-31.5%, after a vacuum anneal for one hour between 540 and 600°C (1000-1100°F).

The Fabrication and Forming of Rare Earth Metals

The availability of rare earth metals as engineering materials has led to investigations towards determining suitable procedures for forming and fabricating into useful shapes. Aside from lanthanum and cerium, yttrium has been produced in greatest quantity, and has correspondingly been examined most completely. All of the metals, however, have been worked with to lesser extents.

General Precautions. The rare earth metals exhibit varying degrees of atmospheric and chemical reactivity (discussed more fully in the section: "Chemical Properties"). Their affinity for oxygen and water vapor is particularly important at the elevated temperatures frequently needed or encountered in various forming operations.

Some of the metals may be worked at room temperature without excessive work hardening (note that this again may be a function of purity), but many primary reduction procedures (rolling, swaging, etc.) may be best performed at elevated temperatures. In such cases cladding or jacketing procedures are desirable. Standard metallurgical techniques appear to be quite adequate in most cases, and several have been described in the literature. Love (464), has successfully used both mild steel and stainless steel tubing to jacket dysprosium, erbium, and yttrium for hot swaging (1800°F) operations. Brundige (99), used a double canning technique, with the inner container of tantalum, titanium, or zirconium, for the hot rolling of yttrium. Ray (666) reports that copper jacketed samarium, gadolinium, and dysprosium may be extruded at temperatures of 930°, 1200°, and 1200°F respectively, but that lanthanon-copper reactions occur at higher temperatures. Williams and Huffine (913) report extrusion of yttrium ingots clad with aluminum oxide and a copper jacket. Simmons (742) also reports successful hot extrusion of uncanned, but "Graphite Dag" coated, yttrium. Geiselman (231) reports triple cladding scandium with a coating of CaF_2, a tantalum foil liner, and a steel tube prior to hot forging. Klepfer and Snyder (388) forged thulium in copper at 1450°F. Some reaction was noted at 1550°F.

Extension of atmospheric corrosion to a limiting situation must consider the pyrophoric nature of the rare earth metals when in finely divided form. In cutting or machining operations the chips should be as large as possible, and the temperature kept as low as possible. Chips should not be allowed to collect around machines or in exhaust ducts. Storage is preferably in drums or metal containers under high flash point oil (913).

Melting. The rare earth metals may be melted in an inert atmosphere or vacuum, utilizing standard induction or resistance furnaces. Europium, samarium, ytterbium, and thulium are melted at or above atmospheric pressure because of their high vapor pressures. Yttrium has been consolidated from compacted sponge by consumable arc-melting. Ingots up to 7½ inches in diameter and weighing about 100 pounds have been produced. Non-consumable arc-melting has been used to consolidate many metals, and for the production of simple shapes, such as solid discs, bars, etc. The use of a water cooled hearth plate permits the melting of many metals with relatively high vapor pressures, although considerable loss is experienced with the more volatile metals ytterbium and samarium (575). The arc-melting of europium has not been reported. Some rare earths may be melted in an electron beam furnace, but since this furnace must operate in relatively high vacuum, melting is inherently limited to low vapor pressure metals.

Casting. Metals melted by induction, or in a resistance heated furnace, may be cast in graphite or copper chill molds. The rare earth metals will react with copper at elevated temperatures so these molds must either be cooled or have sufficient heat capacity to maintain relatively moderate temperatures.

Cutting. Metals may be cut with mechanical or hand saws, or by abrasive cut off wheels. Because of the heat generated in abrasive cutting, cooling is required, and the method is limited to those metals which do not react with the coolant liquid.

Work Hardening. The hardening of metals by cold working has been discussed in the section: "The Mechanical Properties of Rare Earth Metals". Work hardened metals may be softened by annealing, or metals may be worked above the recrystallization temperature with large reductions and no hardening.

Extrusion. The softer metals are easily extruded at room temperature. Thus, europium was extruded through a 0.0625 inch orifice at 80,000 psi (462). Bohlander (71), and Williams and Huffine (913) report extrusion of yttrium, gadolinium, and dysprosium by hot extrusion. Ingots of 2 to 6 inch diameter were extruded into rods 0.6-3.625 inch diameter at temperatures of 900-1650°F (475-900°C).

Forging. Forging is reported to refine grain size and improve structural properties. Large (6") diameter bars may be reduced in 1/8 inch steps at 1600°F with intermediate anneals at the same temperatures (913). Yttrium prepared at the Bureau of Mines, Albany, Oregon, has been hammer or press-forged through reductions of approximately 50-60% (849).

Rolling. Rare earth metals may be easily rolled or swaged, particularly when above the recrystallization temperature, The degree of reduction per pass, and the total reduction between anneals is particularly a function of the purity of the metal. Brundige and co-workers (99) rolled 1/8 inch yttrium to 0.050 inches at 600°C; successive light passes at 200°C, with intermediate high-vacuum anneals, reduced the metal to 0.002 inches. Guidoboni successfully cold rolled yttrium (after prior breakdown by extrusion) to 0.002 inches with reductions of 4-5% per pass and cumulative reductions of 25-50% before anneals. The extruded metal may also be hot rolled at 1000°F (540°C).

Campbell and co-workers (848) reduced high purity yttrium (approximately 99.8%) from 0.165 inch to 0.004 inch sheet. Reductions per pass were 0.003 inches to 0.005 inches and the overall reduction was 97%. Subsequently developed techniques (850) indicated that reductions of approximately 50% per pass produced less work hardening than equivalent smaller reductions per pass. Optimum results were obtained by first breaking up the cast structure by hammer forging to about 50% reduction, annealing at 500°C for five minutes and cold rolling (853). Geiselman (231) reports that scandium metal which could not be cold-rolled or swaged was successfully hot swaged 5% per pass at 1000°C for a total reduction of 55%. Klepfer and Snyder (388) report that after breakdown by hot forging thulium may be successfully hot rolled (copper jacketed), or cold rolled after vacuum annealing.

Swaging. Swaging, particularly at elevated temperatures is an effective method of reduction. Williams and Huffine (913) report swaging yttrium down to 0.022 inch wire for a 91% reduction in diameter. Love (462,464) has reported the mechanical properties of many elements both hot and cold swaged.

Machining (913). Yttrium and the rare earths (except europium, ytterbium, and possibly cerium) machine with approximately the same degree of ease. Yttrium is considered free machining with but minor tendency towards galling. High speed tool steel or carbide tipped tools may be used. In lathe work and milling, a 0.010 inch minimum chip load is suggested to minimize fire hazard. Dry cutting is preferred rather than the use of a lubricant. For drilling, flushing with a high flash point oil is advised to free chips which otherwise have a tendency to pack around the drill.

Yttrium and most metals may be ground with free cutting "crystalon" wheels. The softer metals tend to gall. A water-soluble or high flash point cooling oil should be used. The metals may be sanded through successively finer grit belts, again with liquid cooling (462,464).

Joining. Williams (913), reports a study on the inert-gas tungsten-arc welding process for joining yttrium to itself. The metal melted and fused but exhibited longitudinal cracks through the center of the weld on cooling. Less cracking occurred when filler metal was added during welding. Block (853) reports successful joining of yttrium by both inert-atmosphere tungsten-arc welding and resistance spot welding. Muir (575) reports successful resistance spot welding on several rare earth metals.

The Chemical Properties of Rare Earth Metals

Atmospheric Corrosion. Based on experience with misch metal, and to a lesser extent with cerium and lanthanum, the rare earth metals have long been considered as subject to rapid atmospheric attack. Love (462) has investigated the rate of atmospheric corrosion at room and elevated temperatures, and in both dry and moist air. The results are presented in Table XXI. It is evident that the various rare earth metals show significant differences in behavior.

Oxidation at room temperature and at 95°C is most rapid for the light rare earths lanthanum and cerium, followed by praseodymium and neodymium. The effect of water vapor is apparent, serving to increase the corrosion rate by approximately an order of magnitude. It is postulated that the effect of moisture may operate through either or both of two mechanisms. First, the water vapor may react directly with the metal, this rate being more rapid than oxidation, or second, the initially formed oxide film may react with the water vapor to form a hydroxide or basic oxide. The compound formed would have a different crystal structure than the oxide and a greater bulk volume. Expanding and sloughing away from the metal, it would overcome any tendency for protective oxide film formation, and continuously expose fresh metal surface for subsequent attack.

The corrosion rate of the heavy rare earth metals is low at moderate temperatures, even in the presence of moisture. The corrosion rate increases rapidly with increased temperature however; the rate for gadolinium, dysprosium, and holmium at 600°C becoming approximately the same as that for lanthanum and neodymium. The corrosion rate curves at 200, 400, and 600°C indicate that in many cases most of the weight gain occurred during the first few hours of test, indicating the possibility of protective film formation at these temperatures.

The very rapid increase in rate at elevated temperature for praseodymium and terbium is probably due to the ability of these metals to form oxides in more than one oxidation state. The mechanism of oxidation of cerium has been found to progress from an initial sesquioxide formation to a final dioxide formation; the latter having a greater volume, falls off and exposes fresh metal surface for oxidation.

The most unusual behavior observed was that of samarium which showed a very low rate of corrosion even at 600°C. This resistance to corrosion has been confirmed by Daane, (140) who reports that samarium metal does not ignite completely to oxide when heated for several hours in a furnace at 800-1000°C.

All of the metals corroding in the dry atmospheres first lost their luster, then acquired a very thin, dark coating. As corrosion continued, the typical oxide color appeared except for gadolinium which was yellow and cerium (at 400°C) which formed a shiny, light-brown scale. Terbium formed the dark brown oxide and praseodymium formed the black oxide (but formed a light green product in the presence of moisture).

Metallographic examination of corroded specimens indicated several different corrosion processes may occur. Observed were intergranular corrosion, attack along strain deformation bands within crystals, attack at oxide platelet inclusions within crystals, attack at impurity inclusions (particularly calcium), and attack along preferred crystallographic planes.

Carlson and co-workers (119) have reported a study of the high temperature oxidation of yttrium. The weight gain was found to be very small at 450°C, but increased rapidly as the temperature was increased to 700°C. After decreasing slightly at 750°C, the oxidation increased to a destructive rate at 925°C.

Europium corrodes rapidly when exposed to moist air, forming a yellow compound which becomes white on standing. The presence of moisture is apparently necessary for this reaction, since metal kept at 110°C overnight acquired only a dark coating (775).

The atmospheric corrosion rate for scandium has been determined by Geiselman (229,230). The corrosion rate in air was 0.45, 7.28, and 10.1 $mg/cm^2/24$ hours at 400, 600, and 800°C, respectively. The rate at 800°C in oxygen was 32.5 mg/cm^2 and in nitrogen was 3.96 mg/cm^2. The rate in air at 400 and 600°C is comparable to that obtained for yttrium by Love at these temperatures. The rate at 800°C is considerably lower than that obtained for yttrium by Carlson at this temperature.

Passivation. Love (462) reports a passivation procedure for metallographic specimens. Polished cerium is immersed in a 2-5% solution of nitric acid in ethanol. The dark colored corrosion film which starts forming immediately after polishing changes to a yellow deposit. This is removed by swabbing with alcohol, and the process is repeated until the yellow deposit no longer forms. A metallic luster is revealed which is stable for months. Lanthanum, praseodymium, and neodymium, passivated by the same treatment, remained lustrous for several days.

Reactions with Water. The rare earth metals react with water at varying rates. Europium reacts violently with cold water (775), liberating hydrogen and forming a compound identified as $Eu(OH)_2 \cdot H_2O$. The light rare earth metals react slowly with water at room temperature, vigorously at elevated temperature. The heavy rare earths are more stable, reacting very slowly.

The reaction of yttrium with water at 600-800°C has been studied at Iowa State College (351). X-ray examination of tested metal indicates the presence of yttrium hydride, YH_2, as well as yttrium oxide.

Reactions with Acids. Dilute mineral acids dissolve all rare earth metals readily. The metals are attacked somewhat more slowly by concentrated sulfuric acid. Daane has recently reported (352) that a mixture of equal parts of concentrated nitric acid and 48% hydrofluoric acid attacks most rare earths only superficially, and may be used for removing tantalum from these metals.

Reactions with Hydrogen. The rare earth metals combine readily with hydrogen at elevated temperatures. Hydrogenation of cerium has been reported even at room temperature if the metal surface is clean (540). Pressure-temperature relationships for cerium-hydrogen have recently been described by Mikheeva (540), and for neodymium-hydrogen and dysprosium-hydrogen by Yeamans, et al (927).

Reactions with Non-Metallic Elements. The rare earths will react with elemental nitrogen, phosphorus, carbon, boron, and sulfur, and with many compounds of these elements to form the corresponding nitrides, phosphides, carbides, borides, and sulfides. The preparation, structure, and properties of many of these compounds, and including silicides, has been reviewed by Binder (65). The metals burn readily in halogen vapors above 200°C (415).

Reactions with Metals. The rare earth metals react with many other metals to form compounds or extensive solid solutions. Many compounds are formed with the noble metals (128).

Reactions with Compounds. The rare earth metals react with many compounds such as refractory oxides, silicates, etc. customarily used in high temperature work.

Summary. It is noted that the rare earth metals are in general quite reactive, although there are wide extremes of reactivity in specific systems. Reactivity is especially pronounced at elevated temperatures. One consequence of this reactivity is the lack of suitable container materials for elevated temperature operations. Even solid metals, for example, react with silica above 1200°C. The molten metals react to some extent with all customarily used container materials. Above 1500°C the most useful materials appear to be tantalum, tungsten, and sintered beryllium oxide, with limitations imposed not only by reactivity but by the difficulty of fabricating these materials.

Metallography of the Rare Earth Metals

The metallography of rare earth metals was described by Love (462,464,465) and Lundin (469). Metallographic examination is complicated by the fact that sixteen elements, with different properties as indicated above, are subject to investigation. Extension of investigations to alloy systems may introduce further difficulties. The general approach indicated below is described as most suitable for a wide variety of materials.

Sectioning. Metals may be sectioned in an inert atmosphere, as in a glove box. Liberal amounts of coolant (mineral oil) are required to prevent overheating and excessive metal distortion.

High speed abrasive wheels may be used, but are applicable primarily for the less reactive metals, since a water-based oil emulsion must be used as a lubricant and coolant. Mineral oil is too viscous and kerosene may ignite.

The most practical method appears to be sectioning in air with a hacksaw. The metals cut rather easily, and slow cutting, particularly with mineral oil as lubricant, prevents excessive overheating and metal disturbance. Liberal use of mineral oil prevents excessive atmospheric oxidation, even for cerium and lanthanum.

Mounting. Specimens may be mounted in "lucite" or "bakelite" by conventional methods. Room temperature setting epoxy resins may be used if it is desirable to avoid excess pressure.

Grinding. Critical care must be exercised in grinding due to the following factors; although the metals vary in hardness all are quite soft, some metals are easily oxidized by air or corroded by water or aqueous solutions, and finally, the metals are easily disturbed mechanically to great depths. This latter effect may not become apparent until the metal has been polished and etched, at which time evidence of mechanical twinning may be observed. Kerosene was found to be an adequate lubricant and coolant. For moisture sensitive metals it may be dried over anhydrous calcium sulfate.

Polishing. Excessive polishing was avoided because of the ease of flow under slight pressure. Several polishing operations of short duration (approximately 2-3 minutes), using successively finer abrasives, were found most satisfactory. Silicon carbide abrasive is superior to alumina for rough polishing, since the latter has a greater tendency to smear the metal. Very fine alumina or diamond abrasive may be used for the final polish. Low wheel speeds (150-250 r.p.m. are preferred). Kerosene is used as the polishing vehicle and for rinsing between polishing steps.

Etching. Etching procedures take advantage of the rejection, by the metals, of most impurities into grain boundaries and along preferred crystallographic planes. Air may serve as a satisfactory etchant for the more reactive metals, revealing details of structure as well as do conventional etching solutions.

Liquid etchants found most suitable are generally based upon nitric or phosphoric acid solutions. The following are most commonly used:

Nital. 1-5% solutions of nitric acid in ethyl alcohol. The specimens are immersed, immediately rinsed with acetone or alcohol, and allowed to dry.

Nitric acid - Aqueous. Solutions of nitric acid, usually about 10-50% in water, followed by distilled water or acetone rinse.

Concentrated nitric acid. Very short time dips, followed by a water rinse, and alternating with repolishing steps.

Hydrofluoric acid-nitric acid-water. A solution containing 2.5 parts hydrofluoric acid and 12.5 parts nitric acid in 85 parts of water. Immersion is followed by water rinse and drying.

Chemical polish and etch. The specimen is immersed in a solution containing 15 parts phosphoric acid, 4 parts each of sulfuric, nitric, and acetic acids, and 0.02% "Tergitol" wetting agent. It is then water rinsed and dried.

Nitric acid - Non-aqueous. Lundin has successfully used a solution of 25 ml. concentrated nitric acid with 75 ml. glycerine for most of the rare earth metals, the yttrium-cerium system, and for yttrium binary alloys with up to 2% of some 16 other elements. The etchant is applied by swabbing the surface of the specimen with cotton saturated with the etchant. The etching time varies, the action being stopped after the first dark film has been removed and the structure revealed (a gold-to-green coloring will appear). The composition too was occasionally varied slightly; an immediate blue coloring was found to be an indication that the concentration of the nitric acid was too great, and dilution was necessary.

Phosphoric Acid, Non-Aqueous. For alloy system investigations Lundin prefers a solution of 42 ml. phosphoric acid (85%) with 48 ml. glycerine and 11 ml. ethylene glycol monoethyl ether. The most satisfactory method of employing this etchant is to apply a few drops on the specimen surface. It is essential that the etchant be allowed to react uniformly over the entire specimen surface. The etchant must not be swabbed over the surface, or the etching action will not be uniform, causing streaking and staining. The etching action is stopped after 10-12 seconds by flooding the surface with alcohol. The depleted etchant must be completely removed by rinsing before the specimen is dried, or staining and streaking will invariably occur. Water must never be used for rinsing. If the etching action is stopped too soon, the specimen must be lightly repolished before the treatment is repeated.

Microscopy and Photography. Standard metallographic procedures are used for examination of the polished and etched specimens. Illumination may be bright field or with polarized light.

RARE EARTH METALS SYSTEMS

Binary Constitutional Diagrams

Studies of the basic alloying behavior of some of the rare earth metals dates back many years. Much of the early work was with lanthanum, cerium, or praseodymium, these being most readily available in relatively pure condition. Phase diagrams, compound formation, and solubility data have been compiled and presented in reference form by Hansen (279), Haughton (286), Smithells (753), Love (461), and Gibson et al (240). Reference in the subsequent text to "early" or "older" literature is reference to work published essentially prior to 1950 and included in these compilations.

Summary diagrams of the early work are taken from Smithells (753) and are so referenced. In addition, references are provided to the original literature for each diagram. The more recent diagrams are credited directly to the respective authors.

The diagram and discussion are in alphabetical order of the non-rare earth element. This method is arbitrary and not in accordance with the general practice of arranging phase diagrams in alphabetical sequence of the two elements involved. It does, however, permit a more direct comparison of the alloying behavior of the various rare earths with the same element. Similarly, to permit better comparisons, and for uniformity, the various published diagrams have been redrawn where necessary, so that in each case the horizontal abscissa represents the weight percent of the non-rare earth element (except for hydrogen and plutonium which are given in atomic percent).

Aluminum. Phase diagrams for the systems lanthanum-aluminum, cerium-aluminum, and praseodymium-aluminum have been established (Figures 23,24,25). They are characterized by compound formation, eutectics at either end, and mutual insolubility in the solid state.

The diagrams are based in part on the work of Vogel. In the cerium-aluminum system Vogel first found the compound Ce_3Al present (881), but later (879) reported that Ce_3Al was not present and that Ce_3Al_2 was (also La_3Al_2 and Pr_3Al_2). Van Vucht (861) reinvestigated the cerium rich end of the cerium-aluminum system, and proposed the partial phase diagram shown in Figure 26.

Van Vucht found the compounds Ce_3Al and CeAl to be present, but not Ce_3Al_2. The compound Ce_3Al exists in two allotropic modifications.

The yttrium-aluminum system, as recently established by Lundin and Klodt (471), contains the same general features as the light rare earth metal systems (Figure 27). Savitskii (714) has presented a partial diagram for the aluminum rich end of the yttrium-aluminum system (Figure 28). He tentatively assigned the composition Al_5Y_2 to the aluminum rich compound while Lundin proposed YAl_3. Savitskii reports slight solubility (0.2-0.3%) of yttrium in aluminum at the eutectic temperature.

Antimony. The lanthanum-antimony system has been studied and a phase diagram presented (Figure 29). The lanthanum used was reported as only 97% pure. A series of high melting point compounds is formed. A eutectic is present at the lanthanum end of the system. No solubility is reported in the solid state.

Beryllium. The yttrium-beryllium system has been studied by Lundin and Klodt (471), and a phase diagram proposed (Figure 30). The principal feature is the formation of a high melting point compound, YBe_{13}. Lundin and Klodt assigned approximately 1920°C to the melting point, Chubb and Dickerson (125) found the melting point to be 1600°C. Solid solubility is negligible in the solid state.

A partial diagram of the ytterbium-beryllium system (Figure 31) has been presented by Love (463). The compound $YbBe_{13}$ is formed. Ytterbium was found insoluble in beryllium, and it has no effect on the beryllium transition temperature. Love(462) has also found the corresponding $ErBe_{13}$ compound in the erbium-beryllium system.

Bismuth. A phase diagram for the cerium-bismuth system has been published (Figure 32). A number of compounds are formed. There is a eutectic at the cerium end of the system, but the melting point of bismuth is not lowered. No solid solubility is indicated.

Pleasance (643) has recently examined the bismuth end of this system in greater detail (Figure 33). Positive identification was not made, but Pleasance believes the first bismuth rich compound to be Bi_3Ce. Again the melting point of bismuth was unchanged, and no solubility was detected.

Boron. A phase diagram is reported for the yttrium-boron system (Figure 34) by Lundin and Klodt (471). A number of intermetallic compounds are formed. The YB_4 compound is congruent melting at a very high temperature (2800°C). No solid solubility is reported, and the yttrium transition temperature is apparently not affected. Eutectics are formed at both ends of the system.

Calcium. The lanthanum-calcium binary system (Figure 35) has been constructed by Savitskii (712). The principal feature of the system is the presence of an extended liquid immiscibility region which results in layered microstructures. Solid solubilities at the eutectic temperature are reported not to exceed 3-5%. The lanthanum-1% calcium alloy is reported single phase, indicating restricted but measurable solubility of calcium in lanthanum.

Carbon. Carbides of most of the rare earths have been prepared and studied. Spedding, Gschneidner, and Daane present crystal structure data for the RE_3C compound for yttrium and the lanthanides of atomic number 62-71 except europium; for the sesquicarbides of lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium, and holmium; and for the dicarbides of yttrium and all of the lanthanides except europium. The phases present at selected compositions are given up to 20% carbon in the cerium-carbon system, to 7.9% carbon in the praseodymium-carbon system, and up to 7.7% in the neodymium-carbon system (773).

The same authors (774) present a partial phase diagram for the system lanthanum-carbon (Figures 36 and 37). Two compounds, La_2C_3 and LaC_2, are present; the compound La_3C was not detected. The lanthanum alpha-beta transformation is not affected, but the beta-gamma transformation is raised slightly. The solubility of carbon in lanthanum is low, the maximum being about 0.4% at 875°C.

Chromium. All of the reported phase diagrams for rare earth-chromium systems are of recent origin. Lundin and Klodt (471) propose a simple eutectic system, with no compounds, for the yttrium-chromium binary (Figure 38). The partial diagram for the same system as presented by Love (463) is of the same type, but includes a liquid immiscibility region at high temperatures in the chromium rich end (Figure 39). The solid solubilities are low. Epstein et al (188), investigating the solubility of yttrium and the lanthanides in chromium and chromium-iron alloys found the solubility at 1260°C to be 0.1-0.3% for dysprosium, erbium, and holmium, and 0.1% or less for the other elements. The solubility was slightly less at room temperature.

In the erbium-chromium system (Figure 40), the two liquid region is more extensive. Again no compounds are formed.

The cerium-chromium system (Figure 41) as proposed by Savitskii (709) contains an extensive liquid immiscibility region, and appreciable solid solubility of cerium in chromium. The solubility is not in agreement with the results of Epstein.

Cobalt. The cerium-cobalt phase diagram (Figure 42) was the only rare earth-cobalt binary available for many years. Critchley (132) made a check determination of this system and obtained results in close agreement with the published data.

More recently the phase diagram for the gadolinium-cobalt system (Figure 43) was established by Vickery, et al, (674) and partial diagrams for the yttrium-cobalt (Figure 44) and erbium-cobalt (Figure 45) systems were prepared by Love (463).

All of the systems are characterized by the presence of a number of incongruently melting compounds. A eutectic is formed near the rare earth end of each system with a melting point sharply lower than that of the respective rare earth. The solid solubilities are very limited.

Copper. Phase diagrams for the systems lanthanum-copper (Figure 46), cerium-copper (Figure 47), and praseodymium-copper (Figure 48) have been previously reported. Domagala (161) has recently published the phase diagram for the yttrium-copper system (Figure 49), and Love (463) has published partial diagrams of the rare earth ends of the yttrium- and erbium-copper systems (Figures 50,51).

Copper forms a series of compounds with the rare earths. Multiple eutectics are present, the first (rare earth rich) sharply depressing the melting point of the rare earth metal. Solubility is very restricted.

Gold. Constitutional diagrams have been established for lanthanum, cerium, and praseodymium with gold (Figures 52-54). A series of intermetallic compounds is formed with multiple eutectics. The melting point of the rare earth metal is sharply depressed at the first eutectic, but the melting point of the REAu compound is considerably higher than that of either constituent.

Gallium. Only one diagram (Figure 55) for the praseodymium-gallium system has been reported (336). A number of intermetallic compounds are formed. The compound richest in gallium, $PrGa_2$, has a melting point of approximately 1475°C compared with the melting point of gallium (30°C).

Hafnium. Lundin and Klodt (471) have determined the yttrium-hafnium system (Figure 56). No compounds are formed. Mutual solubilities at the eutectic temperature, although small, are nevertheless appreciable in comparison with most other systems.

Hydrogen. Although the hydrides of a number of rare earths have been studied for their chemical and physical properties, the only phase diagram reported is for the yttrium-hydrogen system (Figure 57) by Lundin and Blackledge (470). The stable hydrides are YH_2 and YH_3.

Indium. The phase diagram for the cerium-indium system (Figure 58) was established by Vogel and Klose (888). A number of intermetallic compounds are formed and several eutectics are present. The addition of cerium to indium raises the liquidus sharply to the first compound $CeIn_3$.

Iron. The only complete phase diagram for the cerium-iron system was established by Vogel many years ago (884). A partial phase diagram at the cerium end (Figure 59) has been prepared by Critchley (132), and the partial phase diagram at the iron end (Figures 60 and 61) has been established by Jepson and Duwez (364). These indicate that Vogel's original phase diagram was probably in error in several respects. Two intermetallics are present, Jepson reporting $CeFe_5$ and $CeFe_2$ from the iron end, and Critchley reporting $CeFe_2$ from the cerium end. The solubility of iron in cerium, and of cerium in both alpha- and gamma iron is limited.

A partial phase diagram for the system lanthanum-iron (Figure 62) also indicates low solubility of lanthanum in iron, and the compounds $LaFe_5$ and $LaFe_2$ (709). Daane (140), however, has tentatively reported the absence of compounds in the lanthanum-iron system.

A complete diagram for the yttrium-iron system (Figure 63) has been prepared by Domagala et al (161). A number of compounds are present, and several eutectics. The melting point of the first (yttrium rich) eutectic is considerably below that of the pure yttrium metal. A partial diagram of the iron end (Figure 64) has also been prepared by Farkas and Bauer (194). They report the first iron rich compounds as YFe_5 and YFe_4, while Domagala reports YFe_9, and YFe_4. Daane (140) has reported a tentative identification of YFe_9.

Kleber and Vickery (674) report the phase diagram for the system gadolinium-iron (Figure 65). Seven compounds are reported. $GdFe_4$ is congruent melting; the others decompose by peritectic reactions.

Lead. All of the phase diagrams of lead with rare earths are from the older literature. High melting point compounds are formed in the systems lanthanum-lead, cerium-lead, and praseodymium-lead (Figures 66-68). Solubility is negligible.

Magnesium. Phase diagrams for the systems lanthanum-magnesium, cerium-magnesium, and praseodymium-magnesium have been established, and are presented in Figures (69-71). The systems are characterized by the formation of a number of intermetallic compounds, only one of which, $REMg_3$, is congruent melting. Eutectics are formed at both ends of each system. The transformation temperature of each rare earth is lowered significantly.

The solid solubility of the rare earth metals in magnesium is quite limited. The best considered values as reported by Leontis (443) are 0.4, 0.9, 1.0-1.5, and 1.5-2.0 weight percent for lanthanum, cerium, praseodymium, and neodymium, respectively, at the eutectic temperature. The solubilities decrease with decreasing temperature, thus rendering the alloys amenable to precipitation hardening.

The yttrium-magnesium system (Figure 72) has recently been reported by Gibson and Carlson (239). A number of compounds are again reported, all formed peritectically. Magnesium is soluble in beta yttrium. The yttrium transition temperature is lowered and the beta field extended.

The solubility of yttrium in magnesium is reported as 9 weight percent at the eutectic temperature, considerably higher than the solubilities of the light rare earths as noted above.

Manganese. Phase diagrams for the lanthanum-manganese and cerium-manganese systems are presented in Figures 73 and 74) respectively. No compounds are formed. There is no significant solid solubility and there is no effect upon the manganese allotropic transformations.

A provisional partial diagram of the yttrium-manganese system was recently proposed by Hellawell (297)(Figure 75). The solubility of yttrium in gamma- and delta manganese is approximately 0.8 weight percent; the solubility in alpha- and beta manganese is very restricted. A eutectic is reported between gamma manganese and the first compound (or yttrium), not identified by the author.

Molybdenum. Only one rare earth molybdenum system has been reported. Lundin and Klodt (471) propose a simple eutectic system for the binary, yttrium-molybdenum. No compounds are formed, and solid solubility is very low (Figure 76).

Nickel. The lanthanum-nickel, cerium-nickel, and praseodymium-nickel diagrams (Figures 77-79) all appear in the older literature. They are characterized by a series of compounds with rare earth : nickel ratios of 3:1, 1:1, 1:2, 1:3, 1:4, and 1:5.

More recently Kleber and Vickery (674) presented the phase diagram for the gadolinium-nickel system (Figure 80), and Domagala et al (161), the diagram for the yttrium-nickel system (Figure 81). In the gadolinium-nickel system, compounds in addition to those indicated above, include the 3:2, 2:7, and 2:17 compositions. Domagala, for the yttrium system, includes the 3:2 and 1:9 compounds. Lundin and Klodt have proposed a system for yttrium-nickel which is the same in most essentials to Domagala's, except that the 2:7 compound is included and that the 2:17 compound is reported rather than the 1:9. The compounds reported by Lundin for yttrium-nickel are therefore the same as those indicated above for the gadolinium system.

For all rare earths, the $RENi_5$ and RENi compounds are stable and congruent melting. For lanthanum, cerium, and praseodymium, the RE_3Ni compounds are also reported congruent melting. All other compounds are formed peritectically. Solid solubility is limited in all systems.

Niobium. Partial phase diagrams for the systems lanthanum-niobium (Figure 82) and cerium-niobium (Figure 83) have been constructed by Savitskii. An extensive two-liquid region exists in both systems at high temperatures. The solid solubilities of lanthanum and cerium in niobium are negligible.

The complete phase diagram for the system yttrium-niobium (Figure 84) has been determined by Lundin and Klodt (471). Again, an extensive liquid immiscibility region occurs and solid solubility is low.

Plutonium. The cerium-plutonium system (Figure 85) has recently been reported by Ellinger and co-workers (179). Cerium is soluble in delta plutonium which it stabilizes. Plutonium is extensively soluble in (beta) cerium (defined as the room temperature stable fcc structure), and slightly soluble in gamma cerium. Restricted solubility is indicated in alpha cerium. No compounds are formed.

Rare Earths. A limited number of phase diagram studies have been made of rare earth metal systems with other rare earths. Vogel and Klose (888) investigated the cerium-lanthanum system. Complete solid solubility was found between the same crystallographic phases of the two elements. The phase diagram obtained is presented in Figure 86 to indicate the nature of the system. It must be noted that currently accepted transformation temperatures for lanthanum and cerium, and the melting point of lanthanum, are at some variance with the points indicated in the diagram. Recent work by Savitskii confirms the mutual unlimited solubility of lanthanum and cerium, and presents details of the solidus-liquidus region (Figure 87). The phase diagram is reported only for temperatures above 675°C. Savitskii reports phase transformations in lanthanum and cerium at 600°C and 360°C respectively, and therefore does not indicate such transformations in the phase diagram (Spedding and co-workers 766) reported the high temperature transformations at 864 and 730°C respectively).

Spedding and co-workers (351) have investigated systems of yttrium with lanthanum, praseodymium, and neodymium. Although complete phase diagrams have not been presented, extensive mutual solid solubility has been reported, and a new structure of the samarium type has been found at approximately the equiatomic composition.

Lundin and Klodt (471) have determined the phase diagram for the cerium-yttrium system (Figure 88). Cerium is extensively soluble (approximately 50 weight percent) in alpha yttrium. Several percent of yttrium dissolves in gamma-cerium. A single phase region extends between the high temperature (delta) form of cerium and the high temperature (beta) form of yttrium. This phase dissociates by peritectoid and eutectoid reactions to form alpha yttrium, a gamma phase with the samarium structure, beta cerium, and gamma cerium.

Rhenium. Lundin and Klodt (471) report the phase diagram for the yttrium-rhenium system (Figure 89). One peritectic compound, YRe_2, is formed, a eutectic is present at the yttrium end of the system, and solid solubility is very low.

Silicon. A partial phase diagram (Figure 90) for the cerium-silicon system has been presented (91, 882). One compound, CeSi, was identified. Krikorian (419) has reported additionally the presence of $CeSi_{0.35}$, $CeSi_{0.5}$, $CeSi_{0.75}$, and $CeSi_2$ in this system.

The yttrium-silicon system (Figure 91) has been reported by Lundin and Klodt (471). Four intermetallic compounds are indicated. Solid solubility is negligible.

Silver. Lanthanum-silver, cerium-silver, and praseodymium-silver phase diagrams have been reported (Figures 92-94). Three compounds are reported in each system with multiple eutectics present. No solid state solubility is reported. Ferro (204) reported NdAg, $NdAg_2$, and $NdAg_3$ similarly present in the neodymium-silver system.

Tantalum. The phase diagram for the yttrium-tantalum system (Figure 95) has been determined by Lundin and Klodt (471). It is characterized by an extensive high temperature liquid immiscibility region. No compounds are formed and solid solubility is very low.

Thallium. A partial phase diagram for the lanthanum-thallium system, and complete diagrams for the cerium-thallium, and praseodymium-thallium systems have been reported (Figures 96-98). The systems are apparently similar, with several compounds and one eutectic. No solid solubility is shown.

Thorium. The cerium-thorium system has been investigated by Weiner et al (899), and a simplified diagram was reported (Figure 99). Complete solid solution was found for the face centered cubic phase. Complete mutual solubility was also reported by Van Vucht (860).

Rough and Bauer (696), have reported that there is extensive solid solubility in the lanthanum-thorium system.

The yttrium-thorium system has recently been investigated by Eash and Carlson (172). The high temperature beta yttrium and beta thorium phases form a region of complete solid solubility. The beta phase dissociates eutectoidally into alpha thorium and alpha yttrium solid solutions. The solubility of thorium in alpha yttrium, and of yttrium in alpha thorium is extensive but not complete (Figure 100).

Tin. Phase diagrams have been reported for the lanthanum-tin, cerium-tin, and praseodymium-tin systems (Figures 101-103). A number of compounds are present, and multiple eutectics exist.

Partial tentative diagrams for the yttrium-tin (Figure 104) and erbium-tin (Figure 105) systems have been reported by Love (463). A eutectic exists between the rare earth metal and the first compound, RE_2Sn. Solubility is very low in all systems.

Titanium. The titanium end of the cerium-titanium system has been investigated by Taylor (810) and by Savitskii and Burchanoff (710). The phase diagram (Figure 106) proposed by Taylor indicates limited solubility of cerium in titanium, reaching a maximum of somewhat less than 1% at the peritectoid (titanium transformation) temperature. Savitskii, however, reports significantly greater solubility, reaching approximately 5% at the titanium transformation temperature, which incidentally is reported raised by some 33° to 915°C. The solubility at room temperature is reported as 2-2½% (Figure 107). Love (462) examined a 2% cerium alloy by X-ray and metallographic methods, and concluded that this was above the limits of solubility, in agreement with the results of Taylor.

The lanthanum-titanium system was also investigated by Savitskii (710). The phase diagram (Figure 108) is quite similar to that for the cerium-titanium diagram, differing primarily in the titanium transformation and eutectic temperatures reported. Love (462) reports the transformation temperature of titanium raised from 882°C to 905°C in reasonable agreement with Savitskii's value of 900°C, but again finds solubility to be only about 1% at the peritectoid temperature.

Phase diagrams for the yttrium-titanium system have been determined by Lundin and Klodt (471), Bare and Carlson (37), and Love (462). Similar results were reported (Figures 109-111). No compounds are formed. A eutectic occurs at the high yttrium end, and solid solubility is very limited. The alpha-beta transformation of titanium is essentially unaffected. The partial diagram for the erbium-titanium system (Figure 112) obtained by Love (463) is essentially similar to the yttrium-titanium system. A tentative phase diagram for the gadolinium-titanium system (Figure 113) as proposed by Armantrout, et al (852) is again essentially similar, although the eutectic temperature, 1220°C, is the lowest reported for any of the systems.

In summary it is noted that lanthanum, cerium, gadolinium, erbium, and yttrium all produce similar systems with titanium. Lanthanum and cerium are slightly soluble in titanium, and raise the transition temperature slightly. The solubility of the other rare earths is negligible. No compounds are formed, but a eutectic is present at the rare earth end of each system.

Tungsten. Lundin and Klodt (471) have proposed a binary diagram for the system yttrium-tungsten (Figure 114). The invariant temperature coincides with the melting point of yttrium. Solid solubility is severely limited and no intermetallics are formed.

Uranium. Constitutional diagrams for rare earth-uranium systems have not been constructed. Investigations of these systems, however, indicate very restricted solubility in the solid phases, and low solubility in the liquid phases at temperatures up to 1250°C. A large liquid immiscibility region is present. Monotectics were found in the cerium- and neodymium-uranium systems, and a eutectic in the yttrium-uranium system (270).

Vanadium. Komjathy, Read, and Rostoker (401) investigated vanadium systems with several rare earths. They proposed a generalized phase diagram of the type shown in Figure 115, characterized by a miscibility gap in the liquid region, and invariant temperatures close to the melting points of vanadium and the respective rare earth. The solubilities of cerium, lanthanum, praseodymium, neodymium, and gadolinium in solid vanadium were reported to be negligible.

Phase diagrams for the systems yttrium-vanadium (Figures 116, 117) have been reported by Love (463) and by Lundin and Klodt (471), and for the system erbium-vanadium (Figure 118) by Love (463). All show a two liquid immiscibility region, and invariant temperatures near the melting points of the metals. Solid solubility is very low at both ends of the diagram. A eutectic is present near the rare earth end of each system.

The lanthanum-vanadium system (Figure 119) is reported by Savitskii (709), and is essentially of the same form. A eutectic is reported at the vanadium end of the system, and there appears to be a small peritectic region at the lanthanum end.

Zinc. The lanthanum-zinc system has been investigated by Rolla and Iandelli (685). Five compounds, LaZn, $LaZn_2$, $LaZn_4$, $LaZn_8$, and $LaZn_{13}$ were reported. Schramm (721), however, reports that the compounds at the zinc end of the system are $LaZn_9$ and $LaZn_{11}$, and Nowotny (596) reported the crystal structure of a $LaZn_5$ compound. The location of thermal arrests as reported by Rolla and by Schramm are also markedly different. It is therefore difficult to construct a representative phase diagram, and none is presented in this report.

Zirconium. Phase diagrams have recently been constructed for zirconium with yttrium, and with several of the heavy rare earth metals.

The yttrium-zirconium system (Figures 120 and 121) has been investigated by Lundin and Klodt (471) and in part by Love (463) Their results are in general agreement. The system is simple eutectic with no intermetallic compounds. There is some solubility near the eutectic temperature at both ends of the system. Love indicates that there is several percent solubility of zirconium in yttrium at room temperature.

A tentative phase diagram for the gadolinium-zirconium system is given in Figure 122 after Armantrout, et al (851). The solubility of zirconium in gadolinium is about the same as in yttrium. The solubility of gadolinium in zirconium is somewhat greater, however, particularly in the beta phase.

A tentative phase diagram for the dysprosium-zirconium system (Figure 123) is reported by Armantrout, et al (850). This system is again similar to those of yttrium-zirconium and gadolinium-zirconium except for increased solubility of dysprosium in zirconium. The solubility of dysprosium in alpha zirconium at the peritectoid is approximately 13%, in beta zirconium at the eutectic approximately 30%.

The phase diagram for the erbium-zirconium system has also been determined by Armantrout, (850) and a partial diagram at the erbium end was established by Love (463) (Figures 124 and 125) The system is quite similar to those discussed above except for increased solubility. The solubility of zirconium in erbium is approximately 20% at the eutectic temperature. The solubility of erbium is approximately 30% in alpha zirconium at the peritectoid temperature, and apparently over 60% in beta zirconium at the eutectic temperature. The zirconium alpha-beta transformation is raised by somewhat over 100°C.

Ternary Constitutional Diagrams

Only limited work has been reported on determinations of ternary diagrams involving the rare earths.

Farkas and Bauer (194) studied the addition of yttrium to iron-chromium alloys. Tentative ternary isotherms were presented for 600°, 900°, 1100°, and 1250°C. The solubility of yttrium is low. The first yttrium compound formed is YFe_5, which is present in equilibrium with alpha iron-chromium. Epstein and co-workers (188), investigated the solubility of the lanthanides, as well as yttrium, in chromium and in chromium-iron compositions. The solubility was found to be low for all rare earths in all chromium-iron compositions.

The ternary systems cerium-cobalt-iron and cerium-cobalt-plutonium have been investigated and reported by Critchley (132). Vertical sections, isothermal sections and liquidus surface contours are presented.

Vogel and Klose have examined the ternary system silver-cerium-lanthanum (889). Continuous solid solutions were found between the systems silver-cerium and silver-lanthanum. The compounds Ag_3Ce and Ag_3La were reported to have the same melting point; as did the compounds Ag_2Ce and Ag_2La. The solid solutions between the respective compounds also had the same melting points as the compounds themselves.

Murray (579) studied the effects of the addition of small amounts of cerium to thorium-zirconium alloys. The thorium-zirconium system contains a solid state miscibility gap. The addition of 2 atomic percent of cerium causes the miscibility gap to disappear and a smooth beta decomposition curve is obtained.

Principles of Alloying Behavior as Applied to Rare Earth Metals

The lanthanons, because of their unusual electronic structures, have become elements of considerable interest to investigators working in the field of alloying behavior and the properties of metals as related to basic physical principles. The rules of Hume-Rothery, Raynor, Pauling, Mott, and others have been used as guides for the prediction of alloying behavior, and for the selection of alloy systems to be investigated (462,463,464). Conversely, experimentally established data on solubility, compound formation, melting point depression, etc., have been analyzed to establish agreement with first principles. The available phase diagrams and miscellaneous data, unfortunately, relate to scattered systems which were of interest to individual investigators, rather than to comprehensive evaluations for obtaining systematic, comparative data. Additionally, as previously noted, the accuracy of some of this data is suspect. Nevertheless efforts at correlation and evaluation have been made, notably by Gschneidner and Waber (265).

Solid Solubility. The solid solubility rules of Hume-Rothery (332) were found to apply reasonably well for rare earth metals, although most of the data available to the authors involved only the elements lanthanum, cerium, and praseodymium, and to a lesser extent yttrium and europium. Darken-Gurry maps, which combine size factor and electronegativity factors for the prediction of solid solubility were constructed for lanthanum, cerium, yttrium, and europium.

It may be noted that Love (462,463), Armantrout (850,851), and Lundin and Klodt (471) have since reported on zirconium systems with gadolinium, dysprosium, erbium, and yttrium. The atomic radius of alpha zirconium is 1.60 A^{o}. The radii of gadolinium, yttrium, dysprosium, and erbium are 1.79, 1.78, 1.77, and 1.76 A^{o}, respectively. Although the change in radius of the rare earths appears to be small, the larger radii are at the limits of size suggested by Hume-Rothery for solubility, and indeed it is found that solubility is limited. The radius for erbium, however, is within 10% of that for zirconium, suggesting significant solubility, and such is the case.

Compound Formation. Pauling (621) has formulated concepts of compound formation based upon bond orbital and electron availability of the elements. The rare earths were found (265) to form compounds in agreement with these principles.

Hypoelectronic (electron deficient) atoms do not form compounds with the rare earth metals. Stable and hyperelectronic (electron excess) atoms do form compounds. The buffer atoms of the 1A to 7A periodic groups do not form compounds, while those of the transition and 1B to 7B groups do.

Eutectic Composition and Temperature. Raynor plots (667) relating the melting points of the first compound to the eutectic temperature and to the eutectic composition were also made by Gschneidner and Waber (265) for cerium-, lanthanum-, and praseodymium rich alloys. In general, the eutectic temperature rises, and the eutectic composition decreases with increase of compound melting point: in agreement with theory.

Thermodynamic Considerations. Gschneidner and Waber (265) reviewed the thermodynamic considerations of Jones (373) and of Betterton and Frye (61) as applied to the liquidus and solidus curves for rare earth alloy systems. The methods show promise, but usefulness is limited by lack of accurate data.

Analysis of liquid phase solutions (mutual solubility) was based on the thermodynamic proposals of Hildebrand (313) and Mott (574). The Mott bonding numbers and the Hildebrand factor as calculated by Teatum, Gschneidner, and Waber (811) were reported. The authors concluded that Mott's analysis appeared more reliable.

Haefling and Daane (270) have determined the solubility of uranium in various rare earths, and of the various rare earths in uranium at temperatures from 1050° to 1250°C. The solubilities are low and an extensive immiscibility region exists. The authors report that calculations according to Hildebrand's rule indicate very high temperatures are necessary for complete solubility. The solubility values for some of the rare earths do not fall in line with calculations however. Yttrium and lutetium are farthest from theoretical, and the authors ascribe their behavior as possibly due to the fact that yttrium has no 4f electrons, and that in lutetium the 4f shell is completely filled.

METAL ALLOY SYSTEMS CONTAINING RARE EARTHS

Introduction

The most important alloy of the rare earths is that of the rare earths in each other, commercially referred to as misch metal, cerium misch metal, or even at times, as cerium metal. A typical composition contains 45% to 50% cerium, 22% to 25% lanthanum, 15% to 17% neodymium, 8% to 10% other rare earths, up to 5% of iron, 0.1% to 3% silicon, and lesser percentages of calcium, magnesium, aluminum, oxygen, nitrogen, and carbon. The rare earth metals, it is noted, are present in misch metal in about the same proportions as in the ore from which the misch metal was produced. The melting point of this alloy is approximately 750°C, and it is usually produced by electrolysis of the rare earth chlorides. Approximately one-fourth of the commercial production of rare earths is devoted to misch metal or misch metal alloy systems.

The largest use of rare earth alloys is in sparking flints for lighters. The flint material is an alloy of the rare earth misch metal and 18% to 30% of iron. It may contain small amounts of zinc, aluminum, magnesium, calcium, and silicon. These alloys, of course, are pyrophoric.

Metallurgically, rare earth alloys are frequently used as refining and cleaning agents. In steel, as deoxidizers, they are added as ferro-cerium or misch metal. The addition of 0.2% to hot short, high alloy stainless austenitic steels relieves the hot shortness condition. The addition of 0.75% of misch metal to cast iron produces nodular graphitic cast iron, which in some cases has replaced cast steel parts. Misch metal is added to aluminum and magnesium alloys to provide strength at high temperature. In aircraft applications, for example, 2% to 6% of misch metal may be added to magnesium used for structural applications; or 0.3% misch metal may be added to secondary aluminum for pistons for internal combustion engines. Misch metal is also used in nickel alloys for high temperature oxidation resistance, in copper alloys as a hardening agent, in rectifiers, and as getters in vacuum tubes. The application of rare earths to iron, steel, aluminum, and magnesium will be discussed in detail.

General reviews of the industrial uses of rare earth metals have been prepared by Trombe (828,837), Charrin (120,121), Vlasov and Kogan (877), Klicker and Gammill (389), Savitskii (715), Howes (329), Nijhawan (591), and Prochovnik (662).

Historical

Rare earth alloys were first produced in attempts to prepare rare earth metals by reduction of their oxides with magnesium or aluminum. Matignon (518) produced alloys (or compounds) of aluminum and cerium, or magnesium and cerium, in his attempts to reduce ceric oxide with aluminum or magnesium metal. Winckler (918)attempted to reduce cerium oxide with magnesium, and instead produced a pyrophoric alloy of cerium and magnesium. Schiffer (717)working in Muthmann's laboratory attempted to reduce cerium oxide with metallic aluminum and instead produced an alloy of cerium and aluminum.

Muthmann and Beck (580) undertook the first major study of the alloys of the rare earths. The salts were prepared by the Welsbach method of fractional crystallization; the metals were prepared by electrolysis. Cerium, lanthanum, praseodymium, and a number of other rare earth metals in various states of purity were produced. Muthmann found many intermetallic compounds between cerium and aluminum, and identified $CeAl_4$.

The American study of the rare earths was begun by Dr. Alcan Hirsch (319). Dr. Hirsch prepared quantities of pure metallic cerium, and studied the alloys of cerium with silver, gold, platinum, copper, tin, antimony, arsenic, carbon, silicon, sulfur, selenium, tellurium, lead, calcium, sodium, aluminum, zinc, cadmium, chromium, manganese, iron, nickel, tungsten, mercury, and magnesium.

The electrical conductivity of misch metal was investigated by McLennan, Howlett, and Wilhelm (496). According to these authors, misch metal gave no indication of becoming super-conducting at low temperature. This is in contrast with the results obtained with pure lanthanum, although the addition of other rare earths to lanthanum has been shown to lower the super-conducting transition temperature (36).

Patents have been granted for the production of misch metal (392,808). In general these patents are based upon the fusion electrolysis of rare earth salts (usually the halide), or the alkali metal reduction of the halide. Patents have also been granted for the casting of misch metal (95,96) and for the extrusion forming of cerium-iron alloy flints (102,248). Patents have also been granted for improvements to misch metal by heat treatment or chemical means (103,247).

Iron Alloys Containing Rare Earths

Rare earths have long been used as deoxidizers in the manufacture of cast iron. The earliest reference is the work of Damiens in 1913 (147). In 1919 Moldenke (553) reported the use of cerium bearing misch metal in cast iron, and in 1920 the trade journal Iron Age (19) reported the use of misch metal as a scavenger or deoxidizer in cast iron. Because of the availability of more economical deoxidizers, misch metal was never widely used in the production of cast iron. A great deal of experimental work was done in the ensuing years however (42,124,267,268,269,405,423,788,799, 805). During this period of investigation, it became apparent that the rare earths added were more than mere deoxidizers. That is to say, the properties of the cast iron produced were different from the properties of cast iron produced using the other types of deoxidizers which were available (42,47,66,173,562,563,564,642). The essence of this work is that the addition of up to 2% of misch metal, along with silicon, magnesium, and aluminum, desulfurizes, and increases the tensile strength, bending strength, and Brinell hardness of cast iron.

Nodular Cast Iron. In 1948, Morrogh reported the production of nodular graphitic structures in cast iron by the addition of cerium (561,565). The effect of the nodular graphitic structure on the properties of cast iron is much more pronounced than changes merely due to a lowering (scavenging) of the sulfur content. A number of simultaneous conditions which must be met in order to produce the nodular structure are indicated. These are quite critical, and it is not surprising that nodular cast irons had not been produced before. It should be noted again that Morrogh refers to cerium additions and has produced some laboratory scale melts with pure cerium.

After Morrogh's announcement of the production of nodular graphitic structures in cast iron by the addition of cerium, considerable work was begun in widely separated laboratories throughout the world (158,190,252,272,321,344,507,619,804). The effect of pure cerium alloy additions, in contrast to misch metal additions, on graphitic formation in alloy cast irons was investigated by E. A. Rowe and H. A. Johnson (697). The cerium used was 92.6% cerium, 1.1% iron and the balance other rare earth metals. Cerium alone tended to produce oriented graphite and had a chilling effect. Desulfurization was not as complete as reported with misch metal. Nodular structures were obtained, but at the expense of modifying the acicular pearlite matrix. Best results were obtained with 0.04% to 0.05% of cerium and 1% to 1.2% ferrosilicon.

In commercial production, the cerium additions have generally been made as cerium bearing misch metal. These cast irons prossess properties intermediate between gray and malleable cast iron. Properties are developed in the as-cast state by addition to the melt of controlled amounts of misch metal and a ladle graphitizer. There is no necessity for applying any heat treatment subsequent to the solidification of the castings (626).

The production of nodular graphite by the use of cerium or misch metal only is difficult, and as indicated above critically dependent upon a number of processing variables. Subsequent work was therefore undertaken to determine the effects of the other additives on the production of nodular graphitic cast iron.

Bogan (70) refers to the basic use of magnesium in nodular graphitic cast iron. Traces of titanium, bismuth, lead, antimony, aluminum, arsenic, and tin inhibit graphitization. But cerium, together with magnesium, overcomes the inhibition. Morrogh also investigated the influence of some of the residual elements in magnesium treated nodular cast iron (566). The cerium addition is valuable to neutralize some of the residual elements. Other elements which cause graphite to precipitate in a nodular form include boron, potassium, sodium, lithium, calcium, and barium (542).

Research by Lowhie (151)indicated that 0.05% cerium makes the magnesium addition more effective in producing nodular cast iron. This is in agreement with some of the previous work on the subject as regards neutralization of various impurities present in cast iron by cerium, so that the magnesium can produce the spheroidal graphitic structure required in nodular cast iron. The addition of misch metal or ferrocerium to cast irons has also been studied by Shkolnikov, et al (739). Ferrocerium plus magnesium was the preferred additive. Patents covering the use of magnesium and cerium together, for producing nodular cast iron, include those to Morrogh (571), Barnes and Dahm (39), and Steven and Lamb (792).

A high strength iron has been reported by Estes and Schindwind (189). A cast iron was produced using calcium carbide as a carburizing agent, and rare earth oxides. The properties produced were between those of gray iron and nodular iron. Otoya and co-workers (608,609), also describe the production of an improved hypoeutectic cast iron containing calcium and cerium. A process for the production of nodular cast iron using magnesium chips, calcium carbide, and rare earths has been patented by Spangler and Estes (759).

Snyder and Slowinski prepared nodular cast iron welding rods by the addition of sodium and cerium to cast iron (755).

Kusikawa effected spheroidization of graphite in cast iron by diffusion of misch metal in the solid state at elevated temperatures (428).

Kol (398) found that the addition of misch metal to cast iron increased the surface tension of the molten metal by about 50%. The increase in surface tension was accompanied by the formation of spheroidal graphite. These changes were attributed to the decrease in sulfur content of the cast iron from 0.03% to 0.01% which was brought about by the addition of the misch metal (227,379). It seems unlikely, however, that the decrease of sulfur content alone would effect such changes.

Hillerton and Lindblom have suggested a theory for the growth of graphite nodules (315). This theory suggests that the growth of such nodules is by means of screw dislocations generated by the inclusion of foreign atoms in the graphite lattices. It therefore implies a uniform distribution of the nodulizing agents in each graphite nodule.

Steel. The effect of rare earth additions to steel is subject to considerable controversy. Many investigators have reported dramatic improvement of properties, others have found no improvement or actual impairment of properties. Steels are complex alloys containing a large number of alloy and impurity elements. Their properties are further markedly affected by heat treatment and processing variables. Even the order of addition of ingredients to the melt may influence the final composition or properties of the metal. Thus, Bolkcom and Knapp (75) found that additions of rare earths are most effective when made after the oxygen content has been reduced to less than 0.007%, and further, that additions are more effective if made in the form of specified master alloys, than if made as rare earth metal directly (74,76). In consideration of the large number of experimental variables possible, it is perhaps not surprising that all results have not been in complete agreement.

Reviews of the uses of rare earths in steel processing have been presented by "Steel" Magazine (22,23).

One of the first important investigations of the effect of rare earths on the properties of steel was by Nekrytyi (587). An alloy of "cerium and the other metals of the rare earth group" (apparently misch metal), containing 51% of cerium, was added to steel in quantities of 0.5% to 2%. The fluidity of the melt increased up to additions of 0.75% of the rare earth alloy; beyond this, fluidity decreased. The carbon, silicon, manganese, and phosphorus were reportedly not affected by the addition of 2% of cerium. This research thus established the first of the basic reasons for rare earth additions to steel--increased melt fluidity. This effect was also investigated and confirmed by Pigott (642).

A second basic consideration for the addition of rare earths to steel was investigated by Post, Schoffstall, and Beaver (649, 650) and Berry, et al (59). The rare earths improve the forgeability of stainless steels. Some stainless steels which were desirable from a corrosion standpoint were not commercially available because they could not be hot forged. Additions of rare earths remedied this so that they could be produced on a commercial scale. In addition, where nickel is added to improve the hot workability, the rare earths allow a reduction in the quantity of nickel required. Recent British Patents (281,159), cover the use of rare earths to improve rupture strength and forgeability of stainless steels, and rare earth additions to welding rods for stainless steels.

Knapp and Bolkcom investigated the properties of rare earth additions to ferrous metals (394). The rare earth alloy used was a lanthanum rich misch metal in additions of 0.04 to 0.3%. It improved properties of stainless, tool, alloy, and electrograde steels. The rare earths were believed to work by complexing the nonmetallics carbon, oxygen, sulfur, nitrogen, hydrogen, etc., to a stable refractory form. It was reported that the transition temperatures were lowered, the hardness and impact strengths were increased, and ductilities were improved. The fluidity of the melts increased, and less grain coarsening occurred. Others reporting improved properties in steels as a result of rare earth additions include Lomas (459) Willners (914) and Lilliequist and Mickelson (452) who reported the results of a systematic survey which revealed that the addition of rare earths to cast steels had a beneficial effect on almost all the properties, and in no case was any detrimental effect noted. Improvements were found in ductility, impact strength, inclusions, hot tears, fluidity, sulfur reduction, porosity, weldability, and feedability. The addition alloys investigated contain various percentages of the rare earths and are known commercially as "Lanceramps". Other workers reporting improved qualities for steel include Post and Beaver (648) who reported on the use of rare earth metals in stainless steel production.

The addition of cerium and lanthanum overcomes hot shortness in steel alloys containing chromium, molybdenum, tungsten, nickel, and copper. Misch metal is added in various amounts from 0.02% to 0.18%, depending upon the kind and amount of alloying constituent present (616).

Hurlich (334) observed that the addition of two pounds of rare earth metals per ton of low alloy boron treated steel increased ductility and toughness. Boni and Buffum (80), noted that the addition of rare earths caused an increase in the impact strength of two experimental gun steels at the transition temperature. The effect was greatest on specimens with a bainite-martensite structure. Reed (670) found that the impact resistance of homogeneous armor steel plate was improved by rare earth metal additions, and that its weldability was improved by rare earth oxide additions. Recent patents have been granted for rare earth modified alloy steels with improved low temperature impact strength (75,538).

Wells and co-workers (901), on the other hand, made a statistical evaluation of the toughness of ordnance steels as deoxidized by various techniques including rare earth additions, and concluded that the effect of rare earths was not firmly determined. Stiles and Pierson, investigating the effects of rare earth and of boron additions to 18 medium carbon steels, reported no significant effect on impact properties from such additions (797). Gerken (235) reported further that lanthanum additions to manganese-molybdenum armor steels increased notch sensitivity.

Grain refinement is frequently claimed for rare earth additions to steels. U.S. Patent No. 2,683,661 was granted to Tisdale and Tisdale (818)covering the production of iron or low alloy or carbon steels treated with a composition containing rare earth metals, e.g. misch metal, for the production of fine grained iron and steel. An Austrian patent was granted to Bohler and Company A.-G. (72) for grain refinement in the casting of high-melting metals. The effect of a 3% addition of an alloy containing lanthanum and cerium is covered.

In stainless steels, however, Gautschi and Langenberg report inconsistent results. Lanthanum had a grain refining effect in 30 lb. ingots, but results with 200 lb. ingots were not consistent (228).

DeMastry and co-workers (156), added yttrium to 55Fe-22Ni-17Cr-3Mo-1Nb and 36Fe-38Ni-18Cr-3Mo-2Nb-1Al alloys, and found essentially no effect on fabricability by small additions (up to 1-1/2% to the first, up to 1/2% to the second). The ductility at elevated temperatures of the fabricable alloys was slightly increased.

One of the important effects of rare earth additions to steel is control of sulfur impurity. It is not yet completely clear whether this is accomplished through actual removal of sulfur, or through its effective removal by the formation of stable compounds.

Tageev and Smirnov (807) report the formation of high melting point sulfide constituents which aided in the prevention of segregation during solidification. Singleton (743) reported that sulfides stay in the ingot as inclusions (while oxides slag off), and Knapp and Bolkcom, as previously indicated (394) believe the sulfides are complexed to a stable form.

Gautschi and Langenberg, however, found that rare earth additions lowered the sulfur content of stainless steels when the original sulfur exceeded 0.015 per cent (228). Endebrock and co-workers found the sulfur content of stainless steel was reduced from 500 ppm to less than 80 ppm by yttrium (187). Russell (699) reported that additions of rare earth metals, either in the ladle or in the mold, effectively reduced the sulfur content of the steels to which they were added. Improvements in hot workability and surface condition were ascribed to an increase in the manganese to sulfur ratio. Mention has already been made (loc.cit.) that Tisdale believes the sulfur content to be lowered. Various additional reports have been made (21,50,418,432,670,916) but a definitive answer is not yet apparent.

Improvement by the addition of rare earth oxides, rather than metal, has also been reported (22,122,299,357,393,635,728,903). Patents have been issued to Tisdale and Tisdale (817,819) covering the addition of 0.05 to 0.25% of rare earth silicides or oxides, but especially the latter, to steels and stainless steels. Sulfur content was reduced, and a fine grained as-cast structure was obtained. The use of master alloys for the introduction of rare earths (74), and rare earths plus boron (76), has been previously noted.

The effect of rare earth additions on the corrosion properties of steels has not been extensively investigated. Beaver and Lamphier (51) discuss a new rare earth containing alloy "Carpenter 20", an austenitic stainless steel, whose mechanical properties, hot working qualities, and corrosion resistance are improved. Wright, Block, and Kato (923) modified type 304 stainless steel by arc-melting with up to 43% gadolinium. Alloys to 25% were homogeneous, workable, and showed good corrosion resistance in hot water and steam.

Collins (127) reported that the elevated temperature oxidation resistance of iron - 30% chromium alloys is remarkably improved by low yttrium additions. One percent of yttrium is equivalent in effectiveness to 5% of aluminum, and additionally produces a fine grained structure. The oxide coating which forms on a 25% chromium, 3% aluminum, 1% yttrium alloy is hard and enamel-like, in contrast to the flaky scale which normally forms on the yttrium free alloy.

Dubinin (169) reported improved heat resistance for steel after surface alloying with cerium.

The physical properties of iron alloys are also changed by the addition of rare earths. Savitskii (709) comments on shifts in magnetic properties of iron-aluminum alloys. Iron alloys containing nickel, aluminum, and rare earths have been described by Glaser (244) as having improved magnetic properties.

As has been noted, work on stainless steels, and steels in general, has primarily involved additions of rare earths as misch metal or mixed oxides. Lanthanum and cerium metals of various degrees of commercial purity have been used to a lesser extent, and a few investigations have been made with yttrium. There is no agreement as to which additive or method of addition is best; different investigators claiming various degrees of success or failure for their particular experiments. Little comparative work (for various rare earths) has been done, and almost all of this involves only lanthanum, cerium, or the mixed metals. The previous discussion of elemental properties, however, has indicated that the individual rare earths are not only dissimilar but have properties considerably different from those of misch metal.

Magnesium Base Rare Earth Alloys

The addition of rare earths to magnesium produces alloys with improved creep resistance and strength properties at elevated temperatures. Although experimental evidence indicates that yttrium and individual elements other than lanthanum or cerium may be the most effective additions, economic considerations have thus far limited usage to misch metal and didymium. A number of alloys have been developed and are in commercial production.

The growth of magnesium-rare earth alloys paralleled the interest in lighter-than-air craft in Germany prior to World War II. The earliest recorded reference to such alloys is a British patent issued to I. G. Farbin Industries (340), Austrian (408) and French (343) patents were issued at about the same time.

The binary alloys of magnesium with aluminum, zinc, calcium, cerium, cadmium, and manganese were reviewed by Dumas and Rochaert (170). The constitution, structure, and properties of these alloys; and the mechanical properties of twelve French alloys of magnesium in the sand-cast, chill-cast, and forged extruded states are tabulated. Lugaskov discussed the influence of alloying elements on aluminum and magnesium alloys (468). Beck edited a comprehensive volume outlining the development of rare earth and zirconium containing wrought magnesium alloys in Germany from 1926-1936 (53).

Haughton and Schofield, in a series of researches on the alloys of magnesium, investigated the constitution of the magnesium rich alloys of magnesium and cerium (289). They used pure cerium and pure magnesium, and their results are incorporated in the section of this report concerned with the phase diagrams of the rare earths. In 1939, Haughton and Prytherch reported on European developments in wrought magnesium alloys (287). McDonald (489) reported on the effect of various additions in magnesium alloys. Magnesium-cerium alloys were also investigated by the following researchers: Neklyudor (586), Pogodin (646), Mikheeva (539), and Bohme and Choulant (73). Some of these magnesium-cerium alloys have been extensively studied and the recrystallization and hardness diagrams have been constructed.

Leontis (437,438,446) has investigated different rare earth alloying agents in conjunction with magnesium. Neodymium (75% neodymium, balance other rare earths) has a relatively high solubility and lanthanum and cerium have relatively low solubility in magnesium. Better mechanical properties were obtained with the neodymium rare earth addition. Cerium and lanthanum are apparently less desirable because of their low solubility in magnesium, which increases greatly the amount of intermetallic compound present. Leontis has summarized the effect of the various light rare earths on the yield strength of cast magnesium alloys containing 6% of rare earth metals (443). The results are presented in Table XXII.

The work of McDonald (484,485) also suggests that thorium or neodymium gives better physical properties than misch metal. Lucien and Tetart, however, recommend rather specific lanthanum-didymium ratios for optimum properties (466). Mellor and Ridley (529) indicate that cerium may be used as an alloying agent if manganese is added. The manganese apparently restrains the coarsening of the Mg_9Ce intermetallic compound which then remains as a fine precipitate. Good creep resistance is reported.

The yttrium-magnesium alloy system has been studied by Gibson and Carlson (239) . The resulting phase diagram is presented in the previous section of this report (Figure72). Yttrium shows appreciable solubility in magnesium. The solubility is temperature dependent, and with the existence of intermetallic compounds in the system, there is good potential for the development of age hardening alloys. Although commercial magnesium alloys have not been announced, implications of active research are found in the literature (443,709).

The mechanism by which the rare earths increase the high temperature properties of magnesium is discussed by Patten (618), Grube (260), Leontis (438), Van Ewyk (193), McDonald (485), and Roberts (680). The rare earths are believed to impart high creep resistance at room and elevated temperatures by an especially potent precipitation hardening process, locally at the grain boundaries, and also generally within the grains. The primary effect of the grain boundary precipitate is the blocking of the cyclic grain boundary deformation which is characteristic of unalloyed magnesium.

The effect of zirconium on the solidification crystallization of magnesium alloys has been investigated. Zirconium is added to the cast alloys as a grain refiner to prevent the formation of the rather large grains which are common in cast magnesium alloys (577). While sand-cast, binary magnesium-cerium alloys containing approximately 3% rare earths (added as misch metal) possess good strength and resist creep at elevated temperatures, their mechanical properties at ordinary temperatures are poor. The addition of 0.5% of zirconium gives these alloys mechanical properties at room temperatures comparable to usual casting alloys, but still possessing a high order of resistance to creep at elevated temperature. Other researchers on this type of alloy include: Sauerwald (706,707), Sully (802), and Ball (31). Pashak and Leontis (615) have recently noted that in contrast to the significant improvement observed in cast properties, zirconium additions to magnesium-rare earth alloys have little effect on the properties of extrusions.

Substantial additions of zinc can be made to magnesium-misch metal and magnesium-misch metal-zirconium alloys without markedly affecting either room or elevated temperature strength properties (557, 445, 443, 589). The addition of zinc improves general foundry characteristics, and simplifies heat treatment procedures. It renders castings free of microporosity, and strength properties are maintained over longer periods of exposure at elevated temperatures (443). Leontis and co-workers (440, 443, 615) point out, however, that the addition of zinc to magnesium-didymium-zirconium alloys are in general detrimental, due to the suppression of the normal high response of these alloys to solution heat treatment plus precipitation hardening.

Payne and Bailey (623) and Leontis (442) have found that magnesium-didymium-zirconium alloys containing 1-3.5% silver exhibit an exceptional combination of properties, both in cast and wrought forms. Commercial alloys have been developed in both the United States and Great Britain.

The commercial development of magnesium alloys containing rare earth metals became active after about 1948. A large number of articles appeared during the following decade covering techniques used, and properties obtained, in relatively large scale commercial use (18,20,101,105,148,163,176,192,215,258,260,261, 273,403,439,444,445,486,487,488,497,508,523,529,557,618,624, 680,687,688,741,800,875).

The importance of these alloys in military applications is reflected in the number of service sponsored research programs involving these materials. Among others, reference is made to the technical reports of Park and Wyman (611), Pashak (614), Baker (30), and Johnson and Masteller (369), and to a number of more recent reports in the technical literature (18,202,406,440,588, 623,816).

A large number of patents have been issued covering compositions intended primarily for elevated temperature applications and improved corrosion resistance. Referenced are the following: 2,7,8,32,54,165,186,241,242,246,285,288,311,341,342,365,366,367, 368,381,447,448,466,467,490,491,498,499,505,556,567,568,569,570, 576,669,683,708,756,757,758,907,908.

The composition of commercial alloys as produced in the United States and Great Britain is given in Table XXIII. Extensive compilations of mechanical properties have been derived, and much information is provided in the following references: 69,166,443,753.

Recent reviews and summaries of the nature of magnesium-rare earth alloys, their metallography, heat treatment, properties and applications are given by Stonebrook (798), Emley (185), and Leontis (441,443).

Aluminum Base Rare Earth Alloys

The effect of rare earth additions to aluminum and aluminum base alloys has not been well established. Results reported by a number of investigators, almost all of whom used cerium as the alloying rare earth, are inconclusive or contradictory.

Schulte (723,724) investigated the effect of cerium on the properties of aluminum and light metal alloys. Some strengthening was observed, and was ascribed to the removal of impurity iron by scavenging. Kroll (420) reported on the effect of yttrium in aluminum alloys. While the yttrium addition somewhat increased the hardness of certain alloys, and maintained a higher level of hardness over the temperature range to 300°F, the effect was not impressive. Bosshard (86) found that cerium had no appreciable effect on the electrical, chemical, or mechanical properties of aluminum or aluminum-magnesium alloys, but had a deleterious effect on the properties of some of the other aluminum alloys. Savitskii (709) contrariwise, reports that rare earths improve electrical and thermal conductivity of aluminum alloys. Petri (636) reported that the addition of cerium increased the tendency for stress corrosion. Baukloh and Redjall (48) indicated that the addition of cerium noticeably increased the solubility of hydrogen in aluminum. Bowen and Bernstein (87) found that cerium had little effect on the grain size of cast aluminum-copper alloy. Kubicheck and Mal'tsev reported that lanthanum and cerium did not affect the surface tension of an aluminum - 10% magnesium alloy (426). Gaume-Mahn and Cohen (226) found that lanthanum improves strength, elongation characteristics and rupture resistance of aluminum.

Despite the lack of agreement among researchers, cerium has been, and is being, used as a component of alloys for aluminum pistons. A number of patents have been granted for this purpose (81,82,83,249,274,375,578,668,700,745,746).

Titanium Base Rare Earth Alloys

The titanium metal industry has developed primarily in the period since World War II. Investigations into titanium-rare earth systems, contingent upon the preliminary development of titanium metallurgy, has largely occurred only during the past decade.

One of the first investigations is described in a patent issued in 1950 to Kroll for the preparation of titanium-rare earth alloys (421). Rare earth chlorides are added to titanium chloride and the two are simultaneously reduced by molten magnesium.

The effect of rare earth additions on the mechanical properties of titanium has not been well established. As for other base metals previously reported, some investigators indicate improved properties, others report adversely affected properties.

Titanium-gadolinium alloys were investigated by Ogden and Jaffee (599). Gadolinium was added as Gd_2O_3. Two alloy series were prepared, one of 0.6% gadolinium and one of 5.2% gadolinium. The 5.2% gadolinium alloy showed an ultimate tensile strength of 74,000 psi compared with 43,000 psi for pure titanium. The 0.6% gadolinium alloy was intermediate. Other properties were influenced in a similar manner. The matrix was equiaxed alpha with a second phase in the grain boundaries and within the grains. This was thought to be Gd_2O_3 which had not decomposed on melting.

The work of Ogden and Jaffee was reported in 1950. For a number of years thereafter little investigation occurred in this field. The recent availability of rare earth metals, and increased interest in materials for use at elevated temperatures spurred resumption of research.

Titanium-cerium alloys were investigated by Antes and Edelman (24). The effect of cerium additions on the grain size and mechanical properties of cast Ti-6Al-4V was studied. Two heat treatments were used. Cerium up to 0.42% was added and was found to decrease strength and ductility due to the cerium-rich phase in the grain boundaries. Grain size was reduced, but no benefit from the reduction was apparent.

The tensile properties of commercially pure titanium were found to be essentially unaffected by small alloying additions of lanthanum, gadolinium, yttrium, or erbium (463). Wright and co-workers (923) prepared titanium-gadolinium alloys and found good corrosion resistance in hot water and steam.

Hiltz (317) investigated the precipitation hardening systems titanium-silver-cerium, titanium-copper-cerium, and titanium-silicon-cerium. All showed appreciable response to age hardening. Hot shortness was evidenced in the silver alloy, and there was no alleviation of the characteristic rapid aging and overaging cycle of the binary silver alloy. The copper alloy, however, showed pronounced precipitation hardening and a slow overaging reaction. The alloy was considered promising for potential commercial application.

Davies (149) investigated the effects of ternary additions on lattice parameters in the gamma phase of the titanium-aluminum alloy system. Substitution of yttrium for part of the aluminum reduces the c/a ratio, and it appears to approach 1.00 at between 3 and 5.5% yttrium substitution.

Jaffee and co-workers (359) investigated titanium-tin matrix alloys with a number of ternary element additions. Cerium was found to be a compound former, and compositions containing 0.1-3% were patented.

Several studies were made of internally oxidized systems. Dhosi (160) studied the high temperature properties of titanium-copper-cerium alloys, modified with zirconium and tantalum, and internally oxidized. Both aging and internal oxidation improved stress rupture properties, but the effects were not additive. Hiltz, and Hiltz and Grant (316,318) studied the high temperature properties of internally oxidized titanium-cerium alloys. Increases in strength over pure titanium were noted.

An important consideration in alloying studies with titanium is the possible presence of impurity elements and the scavenging effect of the rare earth metals. Bare and Carlson (37) have shown that yttrium, added to sponge titanium, lowers the hardness; possibly by oxygen gettering. When yttrium was added to crystal bar titanium of low oxygen content, however, the hardness was increased, which was attributed to possible solid solution hardening or second phase formation. The observation by Savitskii that the welding of titanium is improved by rare earth additions (709) may also be attributable to the scavenging of impurities. Love (462) investigated the addition of rare earths to electrorefined titanium, a grade intermediate in quality between sponge and crystal bar grades. Essentially no change was found in hardness or tensile properties by the addition of up to 1% of lanthanum, gadolinium, erbium, or yttrium.

Heat Resistant and Refractory Alloys

Rare earths have been added to a number of heat resistant and refractory alloys. Again, conflicting reports of the effect of these additions have appeared in the literature. Since the principal interest in heat resistant and refractory elements is in phenomena at elevated temperatures, thermal factors are of particular importance in test methodology. Atmospheric corrosion properties of alloys at elevated temperatures have also been investigated.

L. Horn and others (306,326,327) investigated the effects of added rare earth elements on the oxidation of nickel and nickel-chromium alloys, and found that the addition of less than 0.01% cerium gives a tenfold increase in the life of nickel-chromium electrical resistance wire operated between 1150° and 1200°C. Small additions of calcium behave similarly, but not nearly as well. The effect was believed to be due to formation of a strongly adherent oxide layer, the surface of the alloy thus being protected by a gas impermeable film consisting essentially of one or more of the oxides of the rare earth elements (33). Collins (127), however, reports that the elevated temperature oxidation resistance of "Inconel" and "Nichrome V" are not measurably improved by rare earth additions. A number of patents have been granted for heat resistant alloys containing rare earth metals (271,304,307,308,378,457,458,554,555,624,806). A Russian patent (5) has been granted for a similar alloy protecting exhaust valves of aircraft engines.

Cobalt based alloys have been investigated by Breen and Lane (93) and Pierce and Lucas (660). Rare earths were added as misch metal. The rate of oxidation was decreased materially in the region of 950°C. Rupture strength was increased with all additions tested, and the minimum creep rate was lowered by a large (2%) addition of the rare earths. McAndrew and Levinson (473) studied wrought cobalt alloys with cerium and misch metal additions to promote hot forgeability. A cobalt alloy containing 6% tantalum and 0.4% cerium showed high strength properties, but the rare earths did not improve oxidation resistance of the compositions studied.

The effect of rare earth additions to chromium and chromium alloy systems has recently been investigated in some detail. Smith and Seybolt (751) found that cerium was effective in lowering the bend transition temperature of as-cast chromium. The benefits were attributed to the action of cerium in removing nitrogen. Abrahamson and Grant found that cerium also lowered the transition temperature of commercial electrolytic chromium (1). Further studies of the transition temperature and mechanism at the Massachusetts Institute of Technology involved yttrium and cerium as addition agents (449), and Metcalf and co-workers studied the effect of cerium additions on the ductility of chromium (536). Fountain and Lamont (214) found misch metal to be an effective deoxidizer in high chromium-iron alloys. The improved oxidation resistance of high chromium steels has been previously discussed.

The ductility of vanadium is markedly improved by the addition of yttrium or the rare earths (127,401,463,711,733).

The ductility and workability of niobium, and of tantalum, is improved by arc-melting these metals with rare earth additions. A niobium-5% cerium alloy was found to be considerably stronger than commercial niobium (711,733).

Rare earth additions are effective in improving the ductility of molybdenum (732), although Klodt and co-workers report varying results with different individual rare earths, and with varying percentage additions (390,391,711).

Improved ductility has been reported (598) for tungsten with rare earth additions, although again Klodt reports no improvement with additions of yttrium or lutetium.

A number of patents have been issued for hard or wear-resisting alloys containing rare earths in tantalum, niobium, tungsten, molybdenum, and other matrix elements (129,191,409,678,716).

Miscellaneous Alloys Containing Rare Earths

Zirconium, with rare earth additions, has been examined by several research groups, generally with particular emphasis on applicability to nuclear reactor systems. Anderson and co-workers (10) reported the study of about 25 zirconium rich systems, one of which was the zirconium-cerium system, with respect to fabrication and mechanical and physical property determinations. Preliminary results were reported, but no conclusions were drawn. Armantrout and co-workers examined zirconium and zircalloy - 2 compositions with minor additions of dysprosium and erbium (848,854). Hardness values were unchanged or raised slightly. The alloys were found to be attacked by steam at elevated temperatures (to about 370°C) much more rapidly than were the base metals. Ray (666) reports that the yield strength of heat treated and quenched zirconium containing 1% dysprosium is significantly increased, but that other properties are essentially unchanged.

Hausner and Pinto have investigated powder metallurgical techniques for incorporation of gadolinium containing compounds in beryllium (290). Beryllium compacts containing 10% gadolinium carbide were hot pressed at 600° to 650°C and 25 tons per square inch. Sound compacts were obtained having densities within about 1% of theoretical and uniform microstructures. The alloys were reported to have good hot water corrosion resistance.

Seybolt alloyed boron with yttrium and with cerium. No appreciable ductility was imparted to the base metal and all of the alloys were brittle (737).

A number of patents have been issued for miscellaneous alloys containing rare earth metals, and their use as pyrophoric materials, getters, electron emitters, solders, etc. (104,255,293,424, 590,597,734,855,939).

BIBLIOGRAPHY

(1) Abrahamson, E.P., Jr., and Grant, N.J.; in High Temperature Materials ed. by Hehemann, R.F., and Ault, G.M., John Wiley & Sons (1957)

(2) Afanas'eva, L.A., Gazez'yan, L.N., Tikhova, N.M., Blokhina, V.A., Strizhevskaya, L.M., Fedorov, P.S., and Gapanov, G.P.; USSR 106,859 (1957)

(3) Ahmann, D.H.; Doctoral Thesis, Iowa State College (1948)

(4) Akimov, A.I.; Optikai. Spektroskopiya, 2, 271 (1957); 3 545 (1957)

(5) Akimov, G.V., and Kiselev; USSR 64,821 (1945)

(6) Alcock, K., Grimley, S.S., Healy, T.V., Kennedy, J., and McKay, H.A.C.; Trans. Faraday Soc., 52, 39 (1956)

(7) Altwicker, H., and Rosenkranz, W.; Ger. 742,684 (1943)

(8) Altwicker, H., and Rosenkranz, W.; U.S. 2,221,319 (1940)

(9) American Institute of Physics Handbook; McGraw Hill Book Co. Inc., New York, N.Y. (1957)

(10) Anderson, Kroll, Hays, and Robertson; U.S. Bur. Mines, Rept. Invest. No. 4658 (1950)

(11) Anderson, G.S., Legvold, S., and Spedding, F.H.; Phys. Rev., 109, 243 (1958)

(12) Anderson, G.S., Legvold, S., and Spedding, F.H.; Phys. Rev., 111, 1257 (1958)

(13) Anderson, R.J.; Presented at the joint ASM-AEC Symposium on Rare Earths and Related Metals, Chicago, Ill. (Nov. 1959)

(14) Anderson, W.K.; Nucleonics, 15, No. 1, 44 (1957)

(15) Andreeva, Z.F., and Lischenko, T.V.; Doklady Moskov. Sel'skokhoz. Akad. im. K.A. Timiryazeva, Nauch. Konf. 1958, No. 32, 485-90; C.A. 54, 7395

(16) Andreeva, Z.F., and Lischenko, T.V.; Doklady Moskov. Sel'skokhoz. Akad. im. K.A. Timiryazeva, Nauch. Konf. 1958, No. 34, 203-7; C.A. 54, 5318

(17) Andreeva, Z.F., and Rozhdestvenskaya, O.I.; Doklady Moskov. Sel'skokhoz. Akad. im. K.A. Timiryazeva, Nauch. Kong. 1958, No. 34, 266-30; C.A. 54, 5313

(18) Anon; Dow Chem Reporter (1954); WADC-TR-54-294, PB 134494 (June, 1954)

(19) Anon; Iron Age, 105, (1920)

(20) Anon; Mg. Alloys, BIOS Interrogation Rept, #299, (Nov. 6,1946)

(21) Anon; Steel, 134 (1954)

(22) Anon; Steel, 140, 149 (1957)

(23) Anon; Steel, 141, No. 11, 112 (Sept. 9, 1957)

(24) Antes and Edelman; Foundry, 85, 116-119 (1957)

(25) Appleton, D.B., and Selwood, P.W.; J. Am. Chem. Soc. 63, 2029 (1941)

(26) Arajs, S., and Miller, D.S.; J. Appl. Phy. 31, No. 5 Suppl, 325 S (1960)

(27) Archard, J.C., and Tsoucaris, G.; Compt. rend. 246, 285 (1958)

(28) Argall, G.O., Jr.; Mining World, 16,#2, 26 (1954)

(29) Audrieth, L.F., Jukkola, E.E., Meintz, R.E., and Hopkins, B.S.; J. Am. Chem. Soc., 53, 1805 (1931)

(30) Baker, H.; PB 131436 (Sept. 1957)

(31) Ball, C.J.P.; Metal Industry, 75, 152 (1949)

(32) Ball, C.T.P., and Fox, F.A.; Brit. 533,719 (1941)

(33) Ballay; Rev. Nickel, 21, (1955)

(34) Banks, C.V., Carlson, O.N., Daane, A.H., Fassel, V.A., Fisher, R.W., Olson, E.H., Powell, J.E., and Spedding, F.H.; *Studies on the Preparation, Properties, and Analysis of High Purity Yttrium Oxide and Yttrium Metal at the Ames Laboratory* IS-1, Iowa State Univ. of Science and Technology, *Ames, Iowa* (July 1959)

(35) Bannister, J.R., Legvold, S., and Spedding. F.H.; ISC-342 (1953)

(36) Barbezat, A., and Loriers, J.; Compt. rend. 234, (1952)

(37) Bare, D.W., and Carlson, O.N.; ASM Preprint No. 178 (1960)

(38) Barnard, A.J., Jr., Broad, W.C., and Flaschka, H.; Chemist Analyst, 45, 86, 111 (1956); 46, 18,46,76 (1957)

(39) Barnes, H.C., Jr., and Dahm, G.P.; U.S. 2,834,668 (1958)

(40) Barson, F., Legvold, S., and Spedding, F.H.; Phys. Rev. 105, 418 (1957)

(41) Barthauer, G.L., Russell, R.G., and Pearce, D.W.; Ind. Eng. Chem., Anal. Ed. 15, 548 (1943)

(42) Bastien, P.G., and Guillet, L., Jr., Iron Steel Inst. Carnegie Scholarship Memoirs, 27, 77 (1938)

(43) Bates, R.G., and Wedow, H., Jr., U.S. Geol. Surv. Circ. 202 (1953)

(44) Bauer, D.J.; U.S. Bur. Mines, Rept. Invest. No. 5536 (1959)

(45) Bauer, D.J., Rice, A.C., and Berber, J.S.; U.S. Bur. Mines Rept. Invest. No. 5570 (1960)

(46) Bauer, H.; Z. anorg. u. allgem. Chem., 221, 209 (1935)

(47) Baukloh, W., and Meierling, H.; Giesserei, 27, 337 (1940)

(48) Baukloh, W., and Redjall, M.; Metall. (1942) 683

(49) Bauman, W.C., and Eichhorn, J.; J. Am. Chem. Soc. 69, 2830 (1947)

(50) Beaver, H.O.; Metal Progress, 66, 115 (Oct. 1954)

(51) Beaver, H.O., and Lanphier, B.T.; Materials and Methods, 43, 96 (1956)

(52) Beck, A.; Angew. Chem. 52, 2782 (1939)

(53) Beck, A.; *The Technology of Magnesium and Its Alloys*, F.A. *Hughes and Co., Ltd., London (1940)*

(54) Beck, A., Siebel, G., and Vosskuhler, H.; U.S. 2,420,293 (1947)

(55) Behrendt, D.R., Legvold, S., and Spedding, F.H.; Phys. Rev. 109, 1544 (1958)

(56) Beringer, A.; Ann. 42, 134 (1842)

(57) Berman, A., Zemansky, M.W., and Boorse, H.A.; Phys. Rev. 109, 70 (1958)

(58) Beroni, McKeown, Stugard, and Gott; U.S. Geol. Surv., Circ. No. 239

(59) Berry, C.D., and Dorvel, A.A.; Am. Foundryman 20, 45 (1951)

(60) Berzelius, J.J.; Pogg. Ann. 4, 117 (1825)

(61) Betterton, J.O., Jr., and Frye, J.H., Jr.; Acta Met. 6, 205 (1958)

(62) Billy, M., and Trombe, F.; Compt. rend. 193, 421 (1931)

(63) Biltz, W., and Pieper, H.; Z. anorg. Chem. 134, 13 (1924)

(64) Biltz, W., and Weibke, F.; Z. anorg. u. allgem. Chem. 236, 12 (1938)

(65) Binder, I.; J. Am. Ceram. Soc. 43, 287 (1960)

(66) Bischof, F.; Giesserei 28 (1941)

(67) Bochinski, J., Smutz, M., and Spedding, F.H.; Ind. Eng. Chem. 50, 157 (1958)

(68) Bochinski, J., Smutz, M., and Spedding, F.H.; ISC-348 (1953)

(69) Bockrath, R.E.; Modern Metals (Sept. 1958)

(70) Bogan; Australasian Engr. Mar, 66; Apr, 46; May, 42,52 (1953)

(71) Bohlander, K.M.; Presented at the ASM-AEC Symposium on Rare Earths and Related Metals, Chicago, Illinois (Nov. 1959); Metal Progress 77, No. 3, 140 (1960)

(72) Bohler, G., and Co. A.-G.; Austrian 179,025 (1954)

(73) Bohme and Choulant; Z. Metalk. 33, 394 (1941)

(74) Bolkcom, W.T., and Knapp, W.E.; U.S. 2,810,640 (1957)

(75) Bolkcom, W.T., and Knapp, W.E.; U.S. 2,823,992 (1958)

(76) Bolkcom, W.T., and Knapp, W.E.; U.S. 2,850,381 (1958)

(77) Bommer, H.; Z. anorg. u. allgem. Chem. 241, 273 (1939)

(78) Bommer, H.; Z. Elektrochem. 45, 357 (1939)

(79) Bommer, H., and Hohmann, E.; Z. anorg. u. allgem. Chem. 241, 268 (1939)

(80) Boni, R.E., and Buffum, D.C.; WAL. Rept. No. 310/211, PB 134742 (Aug. 1957)

(81) Bonsack, W.; U.S. 2,357,449 (1944)

(82) Bonsack, W.; U.S. 2,357,450 (1944)

(83) Bonsack, W.; U.S. 2,357,451 (1944)

(84) Borisenko, L.F.; Izvest. Akad. Nauk. S.S.S.R. Ser. Geol. (1959), No. 4, 53

(85) Borisenko, L.F., and Shcherbina, V.V.; Trudy Geokhim. Simpoziuma. Moscow (1957), 9-19 (Pub. 1959)

(86) Bosshard, M.; Alluminio 3, 205 (1934)

(87) Bowen, H.J., and Bernstein, H.G.; Trans. ASM 40, 209 (1948)

(88) Boyd, G.E., Adamson, A.W., and Myers, L.S., Jr.; J. Am. Chem. Soc. 69, 2836, 2849 (1947)

(89) Boyd, G.E., Schubert, J., and Adamson, A.W.; J. Am. Chem. Soc. 69, 2818 (1947)

(90) Bozorth, R.M., and Van Vleck, J.H.; Phys. Rev. 118, 1493 (1960)

(91) Brauer, G., and Haag, H.; Naturwiss. 37, 210 (1950)

(92) Brauner, B., and Batek, A.; Z. anorg. Chem. 34, 103, 307 (1903

(93) Breen, J.E., and Lane, J.R.; Am. Soc. Test. Matls. Spec. Tech. Publ. No. 174, 57 (1956)

(94) Bridgman, P.W.; Proc. Am. Acad. Arts Sci. 83, No. 1, 1-22 (195 76, 63 (1948); 81, 211 (1952); 82, 83, 97 (1953); 84, 111 (195

(95) Broadhurst, H.M.; U.S. 2,396,636 (1946)

(96) Broadhurst, H.M.; Brit. 567,308 (1945)

(97) Brooksbank, W.A., and Leddicotte, G.W.; J. Phys. Chem. 57, 819 (1953)

(98) Brukl, A.; Angew. Chem. 52, 151 (1939)

(99) Brundige, E.L., MaGuire, J.C., and Taub, J.M.; LA2172 (1958)

(100) Buck, K.L.; U.S. Geol. Surv. Bull. No. 1019-F (1957) (Bibliography)

(101) Bulian, et al; F.I.A.T. Rev. Ger. Sci., 1939-1946 (1948)

(102) Bungardt, W.; U.S. 2,660,301 (1953)

(103) Bungardt, W.; U.S. 2,776,919 (1957)

(104) Bungardt, W.; U.S. 2,792,301 (1957)

(105) Bunn, E.S.; Metal Progress 48, 708 (1945)

(106) Bunsen, R.; Ann. 86, 285 (1853)

(107) Cabrera, B.; Compt. rend. 180, 668 (1925) J. chim, phys. 36, 237 (1939)

(108) Campbell, T.T., and Block, F.E.; J. Metals 11, 744 (1959)

(109) Canneri, G.; Aluminio 2 (1933)

(110) Canneri, G.; Metallurg. Ital. 23, (1931)

(111) Canneri, G.; Metallurg. Ital. 24, 99 (1932)

(112) Canneri, G.; Metallurg. Ital. 25, 250 (1933)

(113) Canneri, G.; Metallurg. Ital. 26, 832 (1934)

(114) Canneri, G.; Metallurg. Ital. 26, 869 (1934)

(115) Cannon; Symposium on Mineral Resources of the south eastern United States; Univ. Tenn. Proceedings, 202-210 (1949)

(116) Carlson, E.J., Keiser, H.D., and Sargent, J.D.; U.S. Bur. Mines, Minerals Yearbook 1 (1952)

(117) Carlson, O.N., Bare, D.W., Gibson, E.D., and Schmidt, F.A.; Survey of the Mechanical Properties of Yttrium and Yttrium Alloys. Presented at the ASTM National Meeting, San Francisco, California (October 1959)

(118) Carlson, O.N., Haefling, J.A., Schmidt, F.A., and Spedding, F.H.; J. Electrochem. Soc. 107, 540 (1960)

(119) Carlson, O.N., Schmidt, F.A., and Wells, R.L.; IS-115, Iowa State University of Science and Technology, Ames, Iowa (1960)

(120) Charrin, V.; Genie Civil 135, 15 (1958)

(121) Charrin, V.; Genie Civil 135, 108 (1958)

(122) Chetham; Iron-Coal Trades Rev. 171, #4551 (1955)

(123) Christman, R.A., Heyman, A.M., Dellwig, L.F., and Gott, G.B.; U.S. Geol. Surv., Circ. No. 290

(124) Chubb, W.F.; Metallurgia (1933)

(125) Chubb, W., and Dickerson, R.F.; BMI 1327 (1959)

(126) Coleman, J.S., Penneman, R.A., Keenan, T.K., La Mar, L.E., Armstrong, D.E., and Asprey, L.B.; J. Inorg. and Nucl. Chem. 3, 327 (1956)

(127) Collins, J.F., Calkins, V.P., and McGurity, J.A., AECU-4424 (Nov. 1959)

(128) Compton, V.B., and Matthias, B.T.; Acta.Cryst. 12, 651 (1959)

(129) Cormack, C.E.; U.S. 2,780,542 (1957)

(130) Cornish, F.W., Phillips, G., and Thomas, A.; Can. J. Chem. 34, 1471 (1956); AERE C/R 1224 (1956)

(131) Cremer, E.; Z. physik, Chem. 144, 231 (1929)
(132) Critchley, J.K.; AERE-M 488 (1959)
(133) Crouthamel, C.E., and Martin D.S., Jr.; J. Am. Chem. Soc. 72, 1382 (1950); 73, 569 (1951)
(134) Curry, M.A., Legvold, S., and Spedding, F.H.; Phys. Rev. 117, 953 (1960)
(135) Curtis, C.E.; J. Am. Ceram. Soc. 40, 274 (1957)
(136) Curtis, C.E., and Johnson, J.R.; J. Am. Ceram. Soc. 40, 15 (1957)
(137) Curtis, C.E., and Tharp, A.G.; J. Am. Ceram. Soc. 42, 151 (1959)
(138) Daane, A.H.; Doctoral Thesis, Iowa State College, AECD #3209 (1950)
(139) Daane, A.H.; J. Am. Chem. Soc. 75, (1953)
(140) Daane, A.H.; Iowa State University of Science and Technology, Ames, Iowa; Personal communication
(141) Daane, A.H.; Personal communication to Simmons, AECU 4423.
(142) Daane, A.H. and Dennison, D.H., personal communication to Spedding and Daane, in "Progress in Nuclear Energy" Vol. 1, Series V (1956) Pergamon Press, N.Y.
(143) Daane, A.H., Dennison, D.M., and Spedding, F.H.; J. Am. Chem. Soc. 75, 2272 (1953)
(144) Daane, A.H., Rundle, R.E., Smith H.G., and Spedding F.H.; Acta Cryst. 7, 532 (1954)
(145) Daane, A.H., and Spedding, F.H.; J. Electrochem. Soc. 100, 442 (1953)
(146) Daane, A.H., and Spedding, F.H.; Presented at Am. Chem. Soc. Meeting, Chicago, Illinois (Sept. 1958)
(147) Damiens, A.; Compt. rend. 157, 214,335 (1913)
(148) Danks, W.D.; Modern Metals 6, 34-6 (May 1950)
(149) Davies, F.C.; Air Force Institute of Technology, Rept. GAW 59-3 (Sept. 1959)
(150) Davis, D.D., and Bozorth, R.M.; Phys. Rev. 118, 1543 (1960)
(151) Davis, J.A., Deem. H.W., and Lownie, H.W., Jr.; Trans A.F.S. 64, (1956)
(152) Debray, H.; Compt. rend. 96, 828 (1883)
(153) Debye, P.; Ann. Physik 81, 1154 (1926)
(154) Decker, H.; Ann. Physik 79, 324 (1926)
(155) Delaunay, E.; Compt. rend. 185, 354 (1927)
(156) DeMastry, J.A.; Shober, F.R., Dickerson, R.F.; BMI 1420 (1960)
(157) Derge, G., and Martin, A.E.; CT 2276 (1944)
(158) De Sy, A.L.; Metal Prog. 59, 798 (1951)
(159) Deutsche Edelstahl-Werke Akt; Brit. 799,966 (1958)
(160) Dhosi, J.M.; WAL. TR 405.2/5. (Dec. 1959)
(161) Domagala, R.F., Rausch, J.J., and Levinson, D.W.; ASM Preprint No. 187 (1960)
(162) Donnay, J.D.H., and Nowacki, W.; Geol. Soc. Am. Mem. 60 (1954)
(163) Dornauf, J.; Z. Metallk. 48, 142 (Mar. 1957)

(164) Dow Chemical Co.; Summary Report, Part 1, June 30, 1955 Contract DA-11-022-ORD-1645, Project TB4-15

(165) Dow Chemical Co.; Fr. 692,240 (1930)

(166) Dow Chemical Co.; Room and Elevated Temperature Properties of Magnesium Casting Alloys, Bulletin No. 141-176 (1958)

(167) D.R.P. 39162, 41945

(168) Druding, L.F., and Corbett, J.D.; Presented at the Am. Chem. Soc. meeting, New York, N.Y. (Sept. 1960). Div. of Inorg. Chem. Abs. No. 50

(169) Dubinin; Vestnik Machinostroeniya 33, 74-9 (1953)

(170) Dumas, A., and Rockaert, F.; Rev. aluminium 9, 1717 (1932)

(171) Dvorak, J., and Rezac, Z.; Chem. listy 53, 1113 (1959)

(172) Eash, D.T., and Carlson, O.N.; Trans. ASM, 1097 (1960)

(173) Eash, J.T.; Trans. A.F.S. 49, 887 (1941)

(174) Eastman, E.D., Brewer, L., Bromley, L.A., Gilles, P.W., and Lofgren, N.L.; MDDC-1629 (1945) (Decl. 1948)

(175) Eastman, E., Fontana, B., Thurmond, C., and Wilmarth, W.; TID-5212, p. 14 (1955)

(176) Eastwood; Prod. Eng. 22, 158 (1951)

(177) Eberle, A.R., and Lerner, M.W.; AECD-4286 (Oct. 1957)

(178) Eick, H.A., Baenziger, N.C., and Eyring, L.; J. Am. Chem. Soc. 78, 5987 (1956)

(179) Ellinger, F.H., Land, C.C., and Cramer, E.M.; Extractive and Physical Metallurgy of Plutonium and its Alloys, p. 149, Interscience Publishers, New York

(180) Ellinger, F.H., and Zachariasen, W.H.; J. Am. Chem. Soc. 75, 5650 (1953)

(181) Ellinger, F.H., and Zachariasen, W.H.; LASL, AECU, 2595, LADC-1455

(182) Elliott, J.F., Legvold, S., and Spedding, F.H.; Phys. Rev. 91, 28 (1953)

(183) Elliott, J.F., Legvold, S., and Spedding, F.H.; Phys. Rev. 94, 1143 (1954)

(184) Elliott, J.F., Legvold, S., and Spedding, F.H.; Phys. Rev. 100, 1595 (1955)

(185) Emley, E.F.; British Foundryman 51, 501 (Oct. 1958)

(186) Emley, E.F.; U.S. 2,604,394 (1952)

(187) Endebrock, R.W., Chubb, W., Foster, E.L., and Dickerson, R.F.; BMI 1338 (Apr. 1959)

(188) Epstein, S.G., Bauer, A.A., and Dickerson, R.F.; BMI-1376 (1959)

(189) Estes, J.W., and Schneidewind, R.; Trans. A.F.S. 63, 541 (1955)

(190) Evans; Brit. Cast Iron Assoc., J. Res. and Dev., Res. Rept. #317 (1951)

(191) Evans, F.C.; U.S. 2,357,190 (1944)

(192) Ewijk, L.J.G., van; Metalen Cong. Boek (1949), 79

(193) Ewijk, L.J.G., van; Modern Metals 7, 48 (April 1951)

(194) Farkas, M.S., and Bauer, A.A.; BMI-1386 (Oct. 1959)

(195) Fassel, V.A.; J. Opt. Soc. Am. 39, 187 (1949)

(196) Fassel, V.A., Cook. H.D., Krotz, L.C., and Kehres, P.W.; Spectrochim, Acta. 5, 201 (1952)

(197) Fassel, V.A., Gordon, W.A., and Tabeling, R.W.; Am. Soc. for Test. Matl's., Spec. Tech. Pub. No. 221, 3 (1958)

(198) Fassel, V.A., Quinney, B., Krotz, L.C., and Lentz, C.F.; Anal. Chem. 27, 1010 (1955)

(199) Fassel, V.A., and Wilhelm, H.A.; J. Opt. Soc. Am. 38, 518 (1948)

(200) Feibush, A.M., Rowley, K., and Gordon, L.; Anal. Chem. 30, 1610 (1958)

(201) Feldman, C., and Ellenburg, J.Y.; Anal. Chem. 30, 418 (1958)

(202) Fenn, R.W.; Proc. ASTM 58, 826 (1958)

(203) Fernelius, W.C.; Inorganic Synthesis, Vol. II, McGraw-Hill Book Co. Inc., N.Y. (1946)

(204) Ferro, R.; Gazz. chim. ital. 85, 888 (1955)

(205) Findley, A., and Campbell, A.N.; The Phase Rule & Its Applications, Longmans, Green & Co. Inc., N.Y. (1946)

(206) Fischer, Brunger, and Grieneisen; Z. anorg. u. allgem. Chem. 231, 54 (1937)

(207) Flahaut, J., et al; Bull. soc. chim. France (1958) p. 990

(208) Flahaut, J., et al; Compt. rend 247, 1866 (1958)

(209) Fleisher, M.; U.S. Geol. Surv. Circ. No. 285 (1953)

(210) Foex, M.; Compt. rend. 219, 117 (1944)

(211) Fogg, H.C., and Hess, L.; J. Am. Chem. Soc. 58, 1751 (1936)

(212) Foos, R.A., and Wilhelm, H.A.; ISC-695 (July 1954)

(213) Foster, K.W., Pish, G., Schamp, H.W., Goode, J.M., and Eyles, T.E.; MLM 686 (April 4, 1952)

(214) Fountain, R.W., and Lamont, J.L.; Ductile Chromium, p.255, ASM (1957)

(215) Fox, F.A.; Metal Treatment 14, 169 (1947)

(216) Fricke, R., et al; Z. anorg, Chem. 254, 107 (1947); 259, 305 (1949); Z. Naturforsch. 3A, 62 (1948)

(217) Friend, J.N.; A Text Book of Inorganic Chemistry, Vol. IV, Charles Griffin & Co., London (1921)

(218) Friend, J.N., and Hall, D.A.; Analyst 65, 144 (1940)

(219) Fulling, Moeller, and Vogel; Z. Metallk. 34, 253 (1942)

(220) Gatterer, A., and Junkes, J.; Spectrochim Acta 1, 31 (1939)

(221) Gaume-Mahn, F.; Bull. soc. chim. France (1954) 569

(222) Gaume-Mahn, F.; Bull. soc. chim. France (1956) 1862

(223) Gaume-Mahn, F.; Compt. rend. 232, 815 (1951)

(224) Gaume-Mahn, F.; Compt. rend. 235, 352 (1952)

(225) Gaume-Mahn, F.; Congr. intern. chim. pure et appl., 16^{e}, Paris 1957. Mem. sect. chim. Minerale, 27 (pub. 1958); C.A. 54, 7481

(226) Gaume-Mahn, F., and Cohen, M.; J. Res. du C.N.R.S. No. 38, 64 (1957)

(227) Gautschi; Giesserei 41, 661 (1954)

(228) Gautschi, R.H., and Langenberg, F.C.; Trans. AIME 218, No. 1, 128, (Feb. 1960)

(229) Geiselman, D.; Second Progress Report, WADC Contract No. AF 33(616)-6262, Task No. 73517, Union Carbide Metals Co. (Dec. 1959)

(230) Geiselman, D.; Third Progress Report, WADD Contract No. AF 33(616)-6262, Task No. 73517, Union Carbide Metals Co. (March 1960)

(231) Geiselman, D.; Fourth Progress Report WADD Contract No. AF 33(616)-6262, Task No. 73517, Union Carbide Metals Co. (June 1960)

(232) Geller, S.; J. Chem. Phys. 24, 1236 (1956)

(233) Geller, S., and Miller, C.E.; Am. Mineralogist 44, 1115 (1959)

(234) Geller, S., and Wood, E.A.; Acta Cryst. 9, 563 (1956)

(235) Gerken, J.M.; Dissertation Abstr. 17 (3), 590 (March 1957)

(236) Gerstein, B.C., Griffel, M., Jennings, L.D., Miller, R.E., Skochdopole, R.E., and Spedding, F.H.; J. Chem. Phys. 27, 394 (1957)

(237) Ghosh, J.C., and Basak, N.G.; Petroleum 11, 131, 146 (1948)

(238) Giauque, W.F.; J. Am. Chem. Soc. 49, 1864 (1927)

(239) Gibson, E.D., and Carlson, O.N.; Trans. ASM 52, 1084 (1960)

(240) Gibson, J.A., Miller, S.F., Kennedy, P.S., and Rengsdorff, G.W.; The Properties of the Rare Earth Metals and Compounds, BMI, Columbus, Ohio (1959)

(241) Gide, R.; U.S. 2,512,493 (1950)

(242) Giesche's Erben, Gerog von; Brit. 504,602 (1939)

(243) Gilleo, M.A.; J. Chem. Phys. 24, No. 6, 1239 (1956)

(244) Glaser, L.; U.S. 2,813,789 (1957)

(245) Glasstone, S.; Elements of Physical Chemistry, D. Van Nostrand Co., N.Y. (1946)

(246) Gleave, W.W.; Brit. 562,776, 562,777 (1944)

(247) Goldfinger, S.; Fr. 641,940 (1927)

(248) Goldschmidt, T., A.-G.; Australian 203,762 (1956)

(249) Goldschmidt, T., A.-G.; Brit. 221,082 (1923); Ger. 479,528 (1922)

(250) Goldschmidt, V.M., Ulrich F., and Barth, T.; Skrifter Norske Videnskaps-Akad. Oslo I, Mat. Naturv. Kl., No. 5 (1925)

(251) Goodman, B.B.; Nature 167, 111 (1951)

(252) Grant; Brit. Cast Iron Res. Assn., J. Res. and Dev., 3 Res. Rpt. #273 (1950)

(253) Gray; UCRL-2455 (1954)

(254) Gray and Thompson; AECD-3524, UCRL-2069 (1952)

(255) Grenagle, J.B.; U.S. 1,831,241; 2,008,302

(256) Griffel, M., Skochdopole, R.E., and Spedding, F.H.; J. Chem. Phys. 25, 75 (1956)

(257) Griffel, M., Skochdopole, R.E., and Spedding, F.H.; Phys. Rev. 93, 657 (1954)

(258) Gris; Metaux 27, 458 (1952)

(259) Grishina, T.I.; Zhur, Anal. Khim. 14, 427 (1959)

(260) Grube; Iron Age 169, 102 (1952)

(261) Grube, K., Kaiser, R., Eastwood, L.W., Schwartz, C.M., and Cross, H.C.; Nat. Advisory Comm. Aeronaut., Tech. Notes, No. 2325; Metal Progr. 61, 140 (May 1952)

(262) Gruzensky, W.G., and Engel, G.T.; Trans. AIME 215, 738 (1959)

(263) Gschneidner, K.A., Jr.; A Compilation of the Physical Properties of the Rare Earth, Scandium, and Yttrium Metals, Los Alamos Scientific Laboratory, Los Alamos, N.M. (Feb. 1959)

(264) Gschneidner, K.A., Jr.; Crystallography of the Rare Earth Metals, presented at the joint ASM-AEC Symposium on the Rare Earths and Related Metals, Chicago, Ill. (Nov. 1959)

(265) Gschneidner, K.A., Jr., and Waber, J.T.; Principles of Alloying Behavior of Rare Earth Metals, presented at the joint ASM-AEC Symposium on the Rare Earths and Related Metals, Chicago, Ill. (Nov. 1959). To be published

(266) Guidoboni, E.S., Huntress, A.M., and Loewenstein, P.; NMI-1228 (Oct. 1959)

(267) Guillet, L.; Bull. assoc. tech. Fonderie 13, 292 (1939)

(268) Guillet, L.; Chimie et Industrie 41 (1939)

(269) Guillet, L.; L'Usine 27, (1939)

(270) Haefling, J.F., and Daane, A.H.; Trans. AIME 215, No. 2, 336 (April 1959)

(271) Hagglund, E.H.M., and Rehnqvist, N.G.; U.S. 2,580,171 (1951)

(272) Hajto; Banyasz. es Kohasz. Lapok 82, 425 (1949)

(273) Hall; Magnesium Rev. and Abstr. 8, 3 (1948)

(274) Hall, H.C., Gresham, H.E., Doyle, W.M., and Wilson, C.; U.S. 2,522,575 (1950)

(275) Hall, P.M., Legvold, S., and Spedding, F.H.; Phys. Rev. 116, 1446 (1959)

(276) Hall, P.M., Legvold, S., and Spedding. F.H.; Phys. Rev. 117, 971 (1960)

(277) Hammond; AIME Tech. Publ. 2037

(278) Hanaman, F.; Intern. z. Metallog. 7, 174 (1915); J. Chem. Soc. 110, II, 35

(279) Hansen, M.; Aufbau der Zweistofflegierungen, J. Springer, Berlin (1936); Constitution of Binary Alloys, 2nd Ed., McGraw-Hill, New York (1958)

(280) Harris, D.H., and Tompkins, E.R.; J. Am. Chem. Soc. 69, 2792 (1947)

(281) Harris, G.T., and Child, H.C.; Brit. 787,636; 787,637 (1957)

(282) Harris, J.A.; J. Am. Chem. Soc. 53, 2475 (1931)

(283) Harrison, E.R.; A.E.R.E. G/R., 695 (1951)

(284) Harrison, G.R.; M.I.T. Wavelength Tables of 100,000 Spectrum Lines, The Technology Press, J. Wiley & Sons, Inc., N.Y. (1939)

(285) Haughton, J.L.; Brit. 472,771

(286) Haughton, J.L., and Prince, A.; The Constitutional Diagrams of Alloys, Institute of Metals, London (1956)

(287) Haughton, J.L., and Prytherch, W.E.; Magnesium and Its Alloys, (1937); European Developments in Wrought Magnesium Alloys, (1939), HM Stationary Office, London

(288) Haughton, J.L., and Prytherch, W.E.; U.S. 2,121,292 (1938)

(289) Haughton, J.L., and Schofield, T.H.; J. Inst. Metals 60, 339 (1937)

(290) Hausner, H.H., and Pinto, N.P.; SEP-64 (1951)

(291) Healy, T.V., and McKay, H.A.C.; Trans. Faraday Soc. 52, 633 (1956)

(292) Healy and McKay; Rec. trav. Chim. 75, 730 (1956)

(293) Heany, J.A.; Can. 323,315; 323,318; 323,319; 323,320; 323,321, 336,645 (1932,1933)

(294) Heidel, R.H., and Fassel, V.A.; Anal. Chem. 50, 176 (1958)

(295) Hein, R.A., Falge, R.L., Jr., Matthias, B.T., and Corenzwit, C.; Phys. Rev. Letters 2, 500 (1959)

(296) Heinrich, E.W.; Economic Geology of the Rare Earth Elements Contr. No. 197, Dept. of Minerology, Univ. of Michigan, Ann Arbor, Mich.

(297) Hellawell, A.; J. of the Less Common Metals 1, 343 (Oct. 1959)

(298) Henderson, A.W., May, S.L., and Higbie, K.B.; Ind. and Eng. Chem 50, 611 (1958)

(299) Henke, R.H., and Lula, R.A.; J. Metals 6, 883 (1954)

(300) Henry La Blanchetais, C.; Compt. rend. 220, 313 (1945)

(301) Henry La Blanchetais, C., and Trombe, F.; Compt. rend. 243, 707 (1956)

(302) Henry La Blanchetais, C.; J. Res. du C.N.R.S. 28, 32 (1954)

(303) Henry La Blanchetais, C.; J. Res. du C.N.R.S. 29, (1954)

(304) Heraeus; Fr. 848,129 (1937)

(305) Herzberg, G.; Atomic Spectra and Atomic Structure, Prentice Hall, N.Y. (1937)

(306) Hessenbruch, W.; Zunderfeste Legierungen Springer, Berlin (1940)

(307) Hessenbruch, W.; U.S. 2,104,835 (1938)

(308) Hessenbruch, W.; U.S. 2,104,836 (1938)

(309) Hettel, H.J., and Fassel, V.A.; Anal. Chem. 27, 1311 (1955)

(310) Hicks, W.B.; J. Am. Chem. Soc. 33, 1492 (1911)

(311) Hiege; U.S. 1,915,932

(312) Hilal, O.M.M., and Sugden, S.; J. Chem. Soc. (1949) 135

(313) Hildebrand, J.H., and Scott, R.L.; The Solubility of Nonelectrolytes, Reinhold Publishing Co., N.Y. (1950)

(314) Hillebrand, W.F., and Norton, T.H.; Pogg. Ann. 155, 633 (1875)

(315) Hillert, M., and Lindblom, Y.; J. Iron & Steel Inst. (London), 176, 338 (1954)

(316) Hiltz, R.H., Jr.; PB 131,788, AD 146619, Watertown Arsenal Laboratory (1957)

(317) Hiltz, R.H.; WAL Rept. No. TR 401/285 (April 1958)

(318) Hiltz, R.H., and Grant N.J.; Trans. AIME 212, 383 (June 1958)

(319) Hirsch, A.; Trans. Am. Electrochem. Soc. 20, 57 (1911); J. Ind. and Eng. Chem. 3, 880 (1911); 4, 65 (1912)

(320) Hirt, R.C., and Nachtrieb, N.H.; Anal. Chem. 20, 1077 (1948)

(321) Homma, M., Minato, A., Meguro, H., and Abe, Y.; J. Japan Foundrymen's Society 30, 947 (Dec. 1958)

(322) Hopkins, B.S.; Trans. Electrochem. Soc. 89, 295 (1946)

(323) Hopkins, B.S.; Chapters in the Chemistry of the less Familiar Elements, Stipes Publishing Co., Champaign, Ill. (1939)

(324) Hopkins, B.S., and Quill, L.L.; Proc. Nat. Acad. Sci. U.S. 19, 64(1933)

(325) Hopkins, B.S., and Taebel, W.A.; Trans. Electrochem. Soc. 71, 397 (1937)
(326) Horn; Z. Metallk. 36, 142 (1944)
(327) Horn, L.; Z. Metallk. 40, 73 (1949)
(328) Houk, L.G.; U.S.Bur. Mines Inform. Circ. 7233
(329) Howes, R.B.; Metal Progress 75, No. 6, 108 (1959)
(330) Huffine, C.L.; Presented at the joint ASM-AEC Symposium on the Rare Earths and Related Metals, Chicago, Ill. (Nov. 1959)
(331) Hughes, D.J., and Schwartz, R.B.; Neutron Cross Sections, BNL 325 (July 1, 1958) and Supplement No. 1 (Jan. 1, 1960)
(332) Hume-Rothery, W.; The Structure of Metals and Alloys, Chem. Pub. Co. Inc., Brooklyn, N.Y. (1939)
(333) Hund, F.; Z. Physik 33, 855 (1925)
(334) Hurlich, A.; WAL R 710/930-6, PB 133390 (Aug. 1955)
(335) Iandelli, A.; Atti accad. nazl. Lincei. Rend. 13, 265 (1952)
(336) Iandelli, A.; Gazz. chim, ital. 79 (1949)
(337) Iandelli, A.; Gazz. chim, ital. 85, 881 (1955)
(338) Iandelli, A.; Z. anorg. u. allgem. Chem. 288, 81 (1956)
(339) Iandelli, A., and Botti, E.; Atti reale accad. naz. Lincei 25, 129, 498 (1937)
(340) I.G. Farbenindustrie, A.-G.; Brit. 342,586 (1929)
(341) I.G. Farbenindustrie, A.-G.; Brit. 511,137 (1939)
(342) I.G. Farbenindustrie, A.-G.; Brit. 513,627 (1939)
(343) I.G. Farbenindustrie, A.-G.; Fr. 693,544
(344) Iitaka; Rept. Castings Res. Lab., Waseda Univ., (Tokyo) 2, 41 (1951)
(345) Imre, L.; Z. anorg. u. allgem. Chem. 164, 214 (1927)
(346) Iowa State College, Ames, Iowa; ISC-404 (1953)
(347) Iowa State College, Ames, Iowa; ISC-484 (1954)
(348) Iowa State College, Ames, Iowa; ISC-508 (March 1954)
(349) Iowa State College, Ames, Iowa; ICS-976 (1958)
(350) Iowa State College, Ames, Iowa; ISC-1049 (1958)
(351) Iowa State College, Ames, Iowa; ISC-1116 (1959)
(352) Iowa State University of Science and Technology, Ames, Iowa; IS-15 (1959)
(353) Ivanov, V.V., Borisenko, L.F., and Lizunov, N.V.; Doklady Akad. Nauk S.S.S.R. 125, 608 (1959)
(354) Iya, V.K.; Compt. rend 236, 608 (;953)
(355) Iya, V.K.; J. Res. du C.N.R.S. No. 35, 91 (1956), C.A. 51, 4189d (1957)
(356) Izhvanov, L.A., and Vershinin, N.P.; Tsvetnye Metally 32, No. 1, 44 (1959)
(357) Jackson, W.J.; Metallurgia 54, 233 (1956)
(358) Jaeger, F.M., Bottem, J.A., and Rosenbohm, E.; Proc. Acad. Sci, Amsterdam 41, 120 (1938)
(359) Jaffee, R.I., Ogden, H.R., and Maykuth, D.J.; U.S. 2,797,996 (1957)
(360) James, N.R., Legvold, S., and Spedding, F.H.; Phys. Rev. 88, 1092 (1952)
(361) Jan. H., and Hofmann, W.; Z. Metallk. 33, 361 (1941)

(362) Jarrett, A.A., and Berger, S.; Nucleonics 13, 64 (1955)

(363) Jennings, L.D., Stanton, R.M., and Spedding, F.H.; J. Chem. Phys. 27, 909 (1957)

(364) Jepson, J.O., and Duwez, P.; ASM Preprint #47, (1954)

(365) Jessop, A.C.; Fr. 864,208 (1941)

(366) Jessup, A.C.; U.S. 2,604,396 (1952)

(367) Jessup, A.C., Emley, E.F., and Fisher, P.A.; U.S. 2,549,955 (1951)

(368) Jessup, A.C., and Petch, J.H.T.; U.S. 2,829,973 (1958)

(369) Johnson, H.A. and Masteller, R.D.; PB 131417 (Sept. 1957)

(370) Johnson, R.G., Hudson, D.E., Caldwell, W.C., Spedding, F.H., and Savage, W.R.; J. Chem. Phys. 25, 917 (1956)

(371) Johnson, R.W., and Olson, E.H.; ISC-1069, (1958)

(372) Johnston, H.F., Russel, J.L., Jr., and Silvernail, W.L.; Nucl, Sci. and Eng. 6, 93 (1959)

(373) Jones, H.; Proc. Phys. Soc. (London) 49,,243 (1937)

(374) Jukkola, E.E., Audrieth, L.F., and Hopkins, B.S.; J. Am. Chem. Soc. 56, 303 (1934)

(375) Kamps, O.; U.S. 1,892,840 (1933)

(376) Kapfenberger, W.; Z. anal. Chem. 105, 199 (1936)

(377) Karl, A.; Bull, soc. chim. (5) 1, 871 (1934)

(378) Kay, W.M.; U.S. 2,174,919 (1939)

(379) Kayama; Rept. Castings Res. Lab., Waseda Univ., (Tokyo) No. 5, 4 (1954)

(380) Keith, M.L., and Roy, R.; Am. Mineralogist 39, 1 (1954)

(381) Kent, H.; U.S. 2,642,358 (1953)

(382) Ketelle, B.H., and Boyd, G.E.; J. Am. Chem. Soc. 69, 2800 (1947)

(383) Kevane, C.J., Legvold, S., and Spedding, F.H.; Phys. Rev. 91, 1372 (1953)

(384) Kleinheksel, J.H., and Kremers, H.C.; J. Am. Chem. Soc. 50, 959 (1928)

(385) Klemm, W., and Bommer, H., Z. anorg. u. allgem. Chem. 231, 138 (1937)

(386) Klemm, W., and Bommer, H.; Z. anorg. u. allgem. Chem. 241, 264 (1939)

(387) Klemm, W., and Winkelmann, G.; Z. anorg. u. allgem. Chem. 288, 87 (1956)

(388) Klepfer, H.H., and Snyder, M.E.; Trans AIME 218, 765 (Aug. 1960)

(389) Klicker, E.E., and Gammill, A.M.; Chem. Processing 20, 38 (1957)

(390) Klodt, D.T., and Lundin, C.E.; Denver Res. Inst., Univ. of Denver, Denver, Colo. Monthly Letter Reports, NASA Contract No. NASw-8

(391) Klodt, D.T., Nachman, J.F., and Mueller, W.M.; Denver Res. Inst., Univ. of Denver, Denver, Colo., Quarterly Progress Report No. 1, NASA Research Grant No. NsG 61-60 (May 1960)

(392) Kloepfer, H.; Ger. 803,157 (1951)

(393) Knapp, Steel 134, (1954)

(394) Knapp, W.E., and Bolkcom, W.J.; Iron Age 169, No. 17, 129; No. 18, 140 (1952)

(395) Kniseley, R.N., Fassel, V.A., and Lentz, C.F.; IS-50 (1959)

(396) Kniseley, R.N., Fassel, V.A., Tabeling, R.W., Hurd, B.G., and Quinney, B.B.; Spectrochim. Acta (1959) 300

(397) Koehler, W.C., and Wollan, E.O.; Phys. Rev. 97, 1177 (1955)

(398) Kol; Metall. 9, 17 (1954)

(399) Kolthoff, I.M., and Elmquist, R.; J. Am. Chem. Soc. 53, 1217 (1931)

(400) Komarewsky, V.I.; Ind. Eng. Chem. 49, 264 (1957)

(401) Komjathy, S.A., Read, R.H., and Rostoker, W.; WADC TR 59-483 (July 1959)

(402) Komkov, A.I.; Doklady Akad. Nauk S.S.S.R. 126, 833 (1959)

(403) Korol'kov, A.M., and Sal'dau, P.Ya.; Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S.S.S.R. 16, No.2, 295 (1946)

(404) Kost, M.Y., and Gol'der, G.A.; Zhur. Neorg. Khim. 4, 1488 (1959)

(405) Kothny, E.; Giesserei 27, 323 (1930)

(406) Kovalev, I.G., and Lebedeva, T.V.; Byulleten' izobreteniy, No. 2, 70 (1958)

(407) Kovalev, I.G., and Lebedeva, T.V.; U.S.S.R. 111,184 (1958)

(408) Kratky, A.; Austrian 123,325 (1929)

(409) Kratky, A.; Fr. 805,985 (1936)

(410) Kremers, H.C.; Trans. Am. Electrochem. Soc. 47, 365 (1925)

(411) Kremers, H.C.; Trans. Am. Electrochem. Soc. 55, 199 (1929)

(412) Kremers, H.C.; Trans. Illinois State Acad. Sci. 22, 359 (1930)

(413) Kremers, H.C. and Beuker; Trans. Am. Electrochem. Soc. 47, 353 (1925)

(414) Kremers, H.C., and Thompson, A.P.; Trans. Am. Electrochem. Soc. 47, 345 (1925)

(415) Kremers, H.E., Rare Metals Handbook , Chapt. 16, Reinhold, N.Y. (1954)

(416) Kremers, H.E.; Presented at meeting of Electrochemical Soc. San Francisco (1956)

(417) Kremers, H.E., et al; U.S. 2,900,231 (1959)

(418) Kreshchanovskii, N.S., and Kraskovskii, S.S.; Liteinoe Proizvodstvo (June 1957) 22

(419) Krikorian. O.H.; UCRL-2888, p. 16 (1955)

(420) Kroll, W.; Metals and Alloys 10, 332 (1939)

(421) Kroll, W.J.; U.S. 2,522,679 (1950)

(422) Kruesi, P.R.; Production and Uses of the Rare Earths, presented at the AIME meeting San Francisco, Calif. (Feb 1959)

(423) Krupp, F., A.-G.; Fr. 716,821 (1931)

(424) Krupp, F., A.-G.; Ger. 607,975 (1935)

(425) Kruss, G.; Z. anorg. Chem. 3, 60 (1893)

(426) Kubichek, L., and Mal'tsev, M.V.; Izvest Vysshikh. Ucheb. Aavedenii, Tsuetnaya Met. 2, No. 4, 112 (1959); C.A. 54, 8546 (1960)

(427) Kul'skaya, O.A.; Dopovidii Akad. Nauk, Ukr. RSR No. 7, 766 (1959)

(428) Kusikawa, T., J. Casting Inst. Japan 29 (4), 239 (April 1957)

(429) Kustas, V.L. and Lazebnaya, G.V.; Zhur. Anal. Khim. 15, No. 1, 57 (1960)

(430) Lambertson, W.A., and Gunzel, F.H., Jr.; AECD-3465 (Oct. 1952)

(431) Lancey, R.C., and Ousterman, W.E., et al; A Business Approach to Rare Earths, Harvard Business School Student Report (May 1957)

(432) Langenberg, F.C., and Chipman, J.; Trans. AIME 212, 290, (1958)

(433) Laves, F.; Naturwiss. 31, 96 (1943)

(434) Lawson, A.W., and Tang, T-Y; Phys. Rev. 76, 301 (1949)

(435) Legvold, S., Spedding, F.H., Barson, F., and Elliotts, J.F.; Revs. Modern Phys. 25, 129 (1953)

(436) Leipfinger, H.; Magnetic Properties of Rare Earth Metals at Very Low Temperatures. Air Research and Development Command, USAF, European Office. AFOSR TN 57-561, ASTIA Doc. AD 136546 (1957)

(437) Leontis, T.E.; J. Metals 3, (1951)

(438) Leontis, T.E.; J. Metals 4, Trans. 287 (1952)

(439) Leontis, T.E.; J. Metals 4, Trans. 633 (1952)

(440) Leontis, T.E. and Feisel, D.H.; J. Metals 9, AIME 209, 1245 (1957)

(441) Leontis, T.E.; Metal Progress 76, 134 (Oct. 1959)

(442) Leontis, T.E.; Metal Progress 76, No. 5 (Nov. 1959)

(443) Leontis, T.E.; Rare Earth Metals in Magnesium Technology. Presented at joint ASM-AEC Symposium on Rare Earth and Related Metals, Chicago, Illinois (Nov. 1959). To be published.

(444) Leontis, T.E.; Trans. AIME I.M.D. Tech. Pub. No. 1995 (1946)

(445) Leontis, T.E.; Trans. AIME 180, 287 (1948)

(446) Leontis, T.E.; Trans. AIME 185, 968 (1949)

(447) Leontis, T.E.; U.S. 2,569,477 (1951)

(448) Leontis, T.E.; U.S. 2,659,131 (1953)

(449) Levingston, H., et al; Mass. Inst. of Tech. Contract Noa (s) 59-6049-C

(450) Lewis, W.E.; Rare Earth Minerals and Metals, in Bureau of Mines Minerals Yearbook (1958)

(451) Lewis, W.E., and Paone, J.; U.S. Bur. Mines, Mineral Market Report, MMS No. 3067 (June 1960)

(452) Lilliqvist, G.A., and Mickelson, C.G.; J. Metals 4, 1024 (1952); J. Electrochem. Soc. 100, 117 (1953)

(453) Lindstrom, R.E.; U.S. Bur. Mines, Rept. Invest. No. 5523 (1959)

(454) Lishchenko, T.V., and Andreeva, Z.F.; Izvest. Timiryazev. Sel'skokhoz. Akad. 1959, No. 1, 223-8; C.A. 54, 7286.

(455) Lock, J.M.; Proc. Phys. Soc. (London) 70B, 476 (1957)

(456) Lock, J.M.; Proc. Phys. Soc. (London) 70B, 566 (1957)

(457) Lohr, J.M.; U.S. 2,581,420 (1952)

(458) Lohr, J.M.; U.S. 2,687,954 (1954)

(459) Lomas; Eng. and Boiler House Rev. 67, 325 (1952)

(460) Lopez De Azcona; Bol. inst. geol. y minero, Espana (3) 15, 270 (1941)

(461) Love, B.; Selection and Evaluation of Rare or Unusual Metals for Application to Advanced Weapons Systems. A Literature Survey. WADC Technical Report TR 57-666 Part I. Wright Air Development Center, Wright-Patterson Air Force Base, Ohio (June 1958)

(462) Love, B.; Selection and Evaluation of Rare or Unusual Metals for Application to Advanced Weapons Systems. The Metallurgy of Yttrium and the Rare Earth Metals. WADC Technical Report TR 57-666 Part II. Wright Air Development Center, Wright-Patterson Air Force Base, Ohio (March 1959)

(463) Love, B.; The Metallurgy of Yttrium and the Rare Earths. Part I. Phase Relationships. WADD Technical Report TR 60-74 Part I. Wright Air Development Center, Wright-Patterson Air Force Base, Ohio (May 1960)

(464) Love, B.; The Metallurgy of Yttrium and the Rare Earths. Part II. Mechanical Properties. WADC Technical Report TR 60-74 Part II, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio (June 1960)

(465) Love, B.; Metallography of the Rare Earths, Presented at joint ASM-AEC Symposium on the Rare Earths and Related Metals Chicago, Ill. (Nov. 1959). To be published

(466) Lucien, R., and Tetart, E.; U.S. 2,801,166 (1957)

(467) Lucien, R., and Tetart, E.; U.S. 2,839,394 and 2,839,395 (1958)

(468) Lugaskov, A.S.; Legkie Metal. 4, No. 5, 32 (1935)

(469) Lundin, C.E.; Denver Research Institute, University of Denver, Denver, Colorado, personal communication

(470) Lundin, C.E., and Blackledge, J.P.; Presented at joint ASM-AEC Symposium on the Rare Earths and Related Metals, Chicago, Ill. (Nov. 1959). To be published

(471) Lundin, C.E., and Klodt, D.T.; Presented at joint ASM-AEC Symposium on the Rare Earths and Related Metals, Chicago, Ill. (Nov. 1959). To be published

(472) Lytle, F.W., Botsford, J.I., and Heller, H.A.; U.S. Bur. Mines. Rept. Invest. No. 5378 (Dec. 1957)

(473) McAndrew, J.B., and Levinson, D.W.; Armour Res. Found. Summ. Rept., Contract NOa(s)56-103-C, AD-144723 (Aug. 1957)

(474) McCarty, C.N., Scribner, L.R., Lawrenz, M., and Hopkins, B.S.; Ind. Eng. Chem., Anal. Ed 10, 184 (1938)

(475) MacConachie; Optima, (June 1957), Reviewed in the Mining Magazine (London) (July 1957)

(476) McCoy, H.N.; J. Am. Chem. Soc. 57, 1756 (1935)

(477) McCoy, H.N.; J. Am. Chem. Soc. 58, 1577 (1936)

(478) McCoy, H.N.; J. Am. Chem. Soc. 58, 2279 (1936)

(479) McCoy, H.N.; J. Am. Chem. Soc. 59, 1131 (1937)
(480) McCoy, H.N.; J. Am. Chem. Soc. 61, 2455 (1939)
(481) McCoy, H.N.; J. Am. Chem. Soc. 63, 1622 (1941)
(482) McCoy, H.N.; J. Am. Chem. Soc. 63, 3432 (1941)
(483) McCoy, H.N., and Hammond, R.P.; J. Am. Chem. Soc. 64, 1009 (1942)
(484) McDonald, J.C.; J. Metals 4, 242 (1952)
(485) McDonald, J.C.; Light Metal Age 9, Nos. 11/12, 13 (1951)
(486) McDonald, J.C.; Materials and Methods (1952) 1
(487) McDonald, J.C.; Metal Progr. 52, 243 (1947)
(488) McDonald, J.C.; Proc.ASTM 48, 737 (1948)
(489) McDonald, J.C.; Trans. AIME, I.M.D. Tech. Pub. No. 1247 (1940)
(490) McDonald, J.C.; U.S. 2,285,822 (1943)
(491) McDonald, J.C.; U.S. 2,302,968 (1943)
(492) MacDougall, F.H.; "Physical Chemistry" Chap. 14, The MacMillan Co., N.Y. (1936)
(493) McHargue, C.J., Yakel, H.L., Jr., and Jetter, L.K.; Acta Cryst. 10, 832 (1957)
(494) McKay, Alcock, and Scargill; A.E.R.E. C/R 1514
(495) McLennan, J.C., Allen, J.F., and Wilhelm, J.O.; Phil. Mag. 10, 500 (1930)
(496) McLennan, J.G., Howlett, L.E., and Wilhelm, J.O.; Trans. Roy. Soc. Can. 23,287 (1930)
(497) Mader, H., and Laves, F.; Aluminium 25, 157 (1943)
(498) Magnesium Elektron Ltd; Brit. 532,143 (1941)
(499) Magnesium Prod. Co. Ltd; Brit. 540,333 (1941)
(500) Mahn, F.; Ann. phys. (12), 3, 393 (1948)
(501) Mahn, F.; Compt. rend. 218, 509 (1944)
(502) Mahn, F.; Compt. rend. 223, 78 (1946)
(503) Mahn, F.; J. Res. du C.N.R.S. No. 10 (1950)
(504) Mahn, F.; Rev. Met. 46, 365 (1949)
(505) Mahn, F.; Fr. 987,541 (1951)
(506) Main-Smith, J.D.; Nature 120, 583 (1927)
(507) Mantani and Takase'; Repts. Osaka Ind. Research Inst., III, 21 (1951)
(508) Marande, R.F.; Materials and Methods 23 418 (1946)
(509) Marignac, J. de.; Ann. chim. et phys. (3), 38 148 (1853)
(510) Marinsky, J.A., Glendenin, L.E., and Coryell, C.D.; J. Am. Chem. Soc. 69, 2781 (1947)
(511) Marsh, J.K.; J. Chem. Soc. (1934) 1972
(512) Marsh, J.K.; J. Chem. Soc. (1937) 1367
(513) Marsh, J.K.; J. Chem. Soc. (1943) 531
(514) Marsh, J.K.; J. Chem. Soc. (1946) 17
(515) Marsh, J.K.; J. Chem. Soc. (1946) 20
(516) Marsh, J.K.; J. Chem. Soc. (1947) 118
(517) Marsh, J.K.; Quart. Revs. (London) 1, 126 (1947)
(518) Matignon, C.; Compt. rend. 131, 837,891 (1900)
(519) Matson, L.K., and Spedding, F.H.; ISC-1014 (1957)
(520) Matthias, B.T.; J. Appl. Phys. 31, No. 5 Suppl., 23S, (1960)

(521) Matthias, B.T., Suhl, H., and Corenzwit, E.; Phys. Rev. Letters 1, 92 (1958)

(522) Meggers, W.F.; Revs. Modern Phys. 14, 96 (1942)

(523) Meier, J.W.; Modern Metals 5, 26 (Jan. 1950)

(524) Meinke, W.W.; AECD 3084, UCRL 432 (1951)

(525) Meints, R.E., Hopkins, B.S., and Audrieth, L.F.; Z. anorg. u. allgem. Chem. 211, 237 (1933)

(526) Meisel, K.; Naturwiss 27, 230 (1939)

(527) Meissner, K.L.; Metall u. Erz 21, 41 (1924)

(528) Mellor, J.W.; A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 5, Longmans, Green and Co., London (1924)

(529) Mellor, G.A., and Ridley, R.W.; J. Inst. Metals 81, 245 (1953)

(530) Meloche, C.C., and Vratny, F.; Anal. Chim. Acta 20, 415 (1959)

(531) Mendelssohn, K., and Daunt, J.G.; Nature 139, 473 (1937)

(532) Menis, O., Rains, T.C. and Dean, J.A.; Anal. Chim, Acta 19, 179 (1958)

(533) The Merck Index, Merck and Co., Rahway, N.J. (1960)

(534) Mertie; Industrial Minerals and Rocks; Amer. Inst. of Mining and Met. Engineers, New York, Second edition (1949)

(535) Mertie; U.S. Geol. Surv. Circ. No. 237

(536) Metcalfe, A.G., Spachner, S.A., and Rostoker, W.; WADC TR 58-342 (June 1958)

(537) Meyer, L.; Ber. 20, 681 (1887)

(538) Mickelson, C.G., and Lillieqvist, G.A.; U.S. 2,861,908 (1958)

(539) Mikheeva, V.I.; Bull. acad. sci. U.R.S.S., Classe sci. chim. (1941) 661

(540) Mikheeva, V.I., and Kost, M.E.; Doklady Akad. Nauk. S.S.S.R. 115, 100 (1957)

(541) Miller, J.F., Reid, F.J., and Himes, R.C.; J. Electrochem. Soc. 106, 1043 (1959)

(542) Mitsche, R.; Austria 175,911 (1953)

(543) Moeller, T.; Presented at joint ASM-AEC Symposium on the Rare Earths and Related Metals, Chicago, Ill. (Nov. 1959)

(544) Moeller, T., and Brantley, J.C.; Anal. Chem. 22, 433 (1950)

(545) Moeller, T., and Krauskopf, C.; J. Am. Chem. Soc. 60,726 (1938)

(546) Moeller, T., and Krauskopf, C.; J. Phys.Chem. 43, 363 (1939)

(547) Moeller, T., and Kremers, H.E.; Chem. Rev. 37, 97 (1945)

(548) Moeller, T., and Kremers, H.E.; Ind. & Eng. Chem., Anal. Ed. 17, 44 (1945)

(549) Moeller, T., and Kremers, H.E., Ind. & Eng. Chem., Anal. Ed. 17, 798 (1945)

(550) Moeller, T., and Kremers, H.E., J. Phys. Chem. 48, 395 (1944)

(551) Moen, W.S.; RME-2061 (Pt. 1) (1957)

(552) Moldenhauer, M.; Chem. Ztg. 38, 147 (1914)

(553) Moldenke, R.; Trans. A.F.S. 28, (1919)

(554) Mond Nickel Co. Ltd.; Fr. 806,080 (1936)

(555) Mond Nickel Co. Ltd., and Pfeil, L.B.; Brit. 574,088 (1945)
(556) Morana, S.J.; U.S. 2,771,359 (1956)
(557) Morayumi; Rpts. Govt. Ind. Research Inst., Nagoya 2, 255 (1953)
(558) Morgan, G.T., and Moss, H.W.; J. Chem. Soc. 105, 196 (1914)
(559) Morrice, E., Darrah, J., Brown, E., Wyche, C., Headrick, W., Williams, R., and Knickerbocker, R.G.; U.S. Bur. Mines, Rept. Invest. No. 5549 (1960)
(560) Morrice, E., and Knickerbocker, R.G.; Presented at joint ASM-AEC Symposium on the Rare Earths and Related Metals, Chicago, Ill. (Nov. 1959)
(561) Morrogh, H.; Am. Foundryman 13, 91 (1948)
(562) Morrogh, H.; J. Iron Steel Inst. (London) 143, 195,207 (1941)
(563) Morrogh, H.; J. Iron Steel Inst. (London) 155, 321 (1947)
(564) Morrogh, H.; Paper #875, 44 ann. meeting Inst. Brit. Foundrymen (1947)
(565) Morrogh, H.; Trans. A.F.S. 56, 72 (1948)
(566) Morrogh, H.; Trans. A.F.S. 60, 439 (1952)
(567) Morrogh, H.; Brit. 645,862 (1950)
(568) Morrogh, H.; Brit. 649,946 (1951)
(569) Morrogh, H.; Brit. 718,177 (1954)
(570) Morrogh, H.; U.S. 2,488,511; 2,488,513 (1949)
(571) Morrogh, H.; U.S. 2,841,488; 2,841,489 (1958)
(572) Moruzzi, V.L., and Shafer, M.W.; Res. Rept. RC-209, International Business Machines Corp., Yorktown Heights, N.Y. (1960)
(573) Mosander, C.G.; Pogg. Ann. 11, 406 (1827)
(574) Mott, B.W.; Phil. Mag. 2, Ser. 8, 259 (1957)
(575) Muir, H.; Research Chemicals Division of Nuclear Corp. of America, personal communication (1959)
(576) Murphy, A.J.; U.S. 2,461,229 (1949)
(577) Murphy, A.J., and Payne, R.J.M.; J. Inst. Metals 73, 105 (1946)
(578) Murphy, A.J., and Wells, A.E.; Brit. 457,133 (1936)
(579) Murray, J.R.; J. of the Less Common Metals 2, No. 1, (Feb. 1960)
(580) Muthmann, W., and Beck, H.; Ann. 331, 46,58,60 (1904)
(581) Muthmann, W., Hofer, H., and Weiss, L., Ann. 320, 231 (1902)
(582) Muthmann, W., and Scheidemandel, J.; Ann. 355, 116 (1907)
(583) Muthmann, W., and Weiss, L.; Ann. 331, 1, 146 (1904)
(584) Neckers, J.W., and Kremers, H.C.; J. Am. Chem. Soc. 50, 950 (1928)
(585) Neel, M.L.; Z. Electrochem. 45, 378 (1939)
(586) Neklyudov, D.P.; Tsvetnaya Metal, 16, No. 14/15, 72 (1941); Chem. Zentr. 1943, II, 948
(587) Nekrytyi, S.S.; Stal. 3, No. 3/4, 47 (1943) C.A. 38, 319
(588) Nelson, K.E.; Modern Castings 36, 601 (1959)
(589) Nelson, K.E., and Strieter, F.P.; Trans. A.F.S. 59, 532 (1951)

(590) Nielsch, W., and Schirmer, W.; Ger. 946,076 (1958)

(591) Nijhawan, B.R.; Symposium on Rare Earth Metals. Indian Institute of Metals (1959)

(592) Nikolaev, A.V., and Sorokina, A.A.; Doklady Akad. Nauk, S.S.S.R. 129, 341 (1959)

(593) Nininger, R.D.; Minerals for Atomic Energy, D. Van Nostrand Company Inc., Princeton, N.J., (1954)

(594) Norris, J.A.; Wave Length Table of Rare Earth Elements and Associated Elements Including Zirconium, Thorium, Hafnium, Rhenium, and Tellurium. ORNL 2774 (1960)

(595) Norris, J.A., and Pepper, C.E.; Anal. Chem. 24, 1399 (1952)

(596) Nowotny, H.; Z. Metallk. 34, 22 (1942)

(597) Nowotny, H., Smetana, O., and Komarek, K.; Austria 194,620 (1958)

(598) Office of Ordnance Research; Conference on Research in Progress on Tungsten, Duke University, Durham, N.C., (May 1958)

(599) Ogden, H.R., and Jaffee, R.I.; BMI-RIJ-1, (1950)

(600) Olson, J.C., and Pray, L.C.; Calif. Div. of Mines, Bull. 170, Chap. 8 (1954)

(601) Olson, J.C., Shawe, D.R., Pray, L.C., and Sharp, W.N.; U.S. Geol. Surv. Profess. Paper 261 (1954)

(602) Onstott, E.I.; J. Am. Chem. Soc. 75, 5128 (1953)

(603) Onstott, E.I.; J. Am. Chem. Soc. 77, 812 (1955)

(604) Onstott, E.I.; J. Am. Chem. Soc. 77, 2129 (1955)

(605) Onstott, E.I.; J. Am. Chem. Soc. 78, 2070 (1956)

(606) Onstott, E.I.; J. Am. Chem. Soc. 81, 4451 (1959)

(607) Onstott, E.I.; LA-1622 (1954)

(608) Otoya, T.; Maruyama, M., Morooka, Y., and Kataura, K.; Japan 5254 (1959)

(609) Otoya, T., Morooka, Y., and Kataura, K.; Japan 5252 (1959)

(610) Owen, M.; Ann. Physik. 37, 657 (1912)

(611) Park, J.J., and Wyman, L.L.; Phase Relationship in Magnesium Alloys, Wright Air Development Center, Technical Report 57-504, Contract No. 33(616)-55-4, ASTIA Doc. No. AD-142110, PB 131622 (1957)

(612) Parkinson, D.H., Simon, F.S., and Spedding, F.H.; Proc. Roy. Soc. (London) 207A, 137 (1951)

(613) Pasek, J., Jost, F., and Petru, F.; Coll, Czech. Chem. Comm. 24, 1394 (1959) C.A. 54, 58 (1960)

(614) Pashak, J.F.; WADC Technical Report 58-218 (Nov. 1958)

(615) Pashak, J.F., and Leontis, T.E.; Trans. AIME 218, 102 (Feb. 1960)

(616) Pastonesi; Met. ital. 46 Suppl. No. 5, 37 (1953)

(617) Patkin, I.P.N.; Doklady Moskov. Sel'skokhoz. Akad. im. K.A. Timiryazeva, Nauch, Konf. 1958

(618) Patten; Iron Age 169 (1952)

(619) Patterson, W.; Werkstatt u. Betrieb 83, 18 (1950)

(620) Pauling, L.; The Nature of the Chemical Bond, Cornell University Press, Ithaca, N.Y. (1940)

(621) Pauling, L.; Proc. Natl. Acad. Sci. 36, 533 (1950)

(622) Pauling, L., and Shappell, M.D.; Z. Krist. 75, 129 (1930)

(623) Payne, R.J.M., and Bailey, N.; Metallurgia 58, 67 (1958)

(624) Payne, R.J.M., and Michael, A.D., and Eade, R.W.; Metal Ind. (Lon.) 80, 103 (1952)

(625) Pearce, D.W.; Chem. Revs. 16, 121 (1935)

(626) Pearce, J.G.; Soc. Chem. Ind. (London) Chem. Eng. Group, Adv. Copy (April 6, 1948)

(627) Pechiney-Compagnie de produits chimiques et electrometallurgiques; Brit. 770,138 (1957)

(628) Peppard, D.F., Asanovich, G., Atteberry, R.W., DuTemple, O., Gergel, M.V., Gnaedinger, A.W., Mason, G.W., Meschke, V.H., Nachtman, E.S., and Winsch, I.O.; J. Am. Chem. Soc. 75, 4576 (1953)

(629) Peppard, D.F., Faris, J.P., Gray, P.R., and Mason, G.W.; J. Phys. Chem. 57, 294 (1953)

(630) Peppard, D.F., Gray, P.R., and Markus, M.M.; J. Am. Chem. Soc. 75 6063 (1953)

(631) Peppard, D.F., Mason, G.W., and Gergel, M.V.; J. Inorg. and Nucl. Chem. 3, 370 (1957)

(632) Peppard, D.F., Mason, G.W., and Maier, J.L.; J. Inorg, and Nucl. Chem. 3, 215 (1956)

(633) Peppard, D.F., and Peppard, M.A.; Ind. Eng. Chem. 46, 34 (1954)

(634) Perez y Jorba, M., Collongues, R., and Lefevre, J.; Compt. rend. 249, 1237 (1959)

(635) Perkins, R.A., and Binder, W.D.; J. Metals 9, 239 (1957)

(636) Petri, H.J., et al; Aluminum 26, 2 (1944)

(637) Petrow, H.G , Rigopulos, P.N., and Fredrickson, J.B.; Presented at AIME meeting, San Francisco, Calif. (Feb. 1959)

(638) Petru, F.; Chem. Listy 50, 2025 (1956)

(639) Phillips, N.E.; UCRL-9093, p. 95 (Feb. 8, 1960)

(640) Picon, M., and Patrie, M.; Compt. rend. 243, 1769 (1956)

(641) Pierson, C.T., and Singewald, Q.D.; U.S. Geol. Surv. Circ. No. 321

(642) Pigott, E.C.; Iron and Steel (London) 20, 43 et. seq. (1947)

(643) Pleasance, R.J.; J. Inst. Metals 88, 45 (1959)

(644) Ploetz, G.L.; Cer. Bull. 39, 362 (1960)

(645) Ploetz, G.L., and Krystyniak, C.W.; J. Am. Ceram. Soc. 41, 551 (1958)

(646) Pogodin, S.A., and Mikheeva, V.I.; Ann. phys. chim., Inst. chim. gen. (USSR) 14, 283 (1941)

(647) Poluektov, N.S., and Nikonova, M.P.; Ukrain, Khim, Zhur. 25, 217 (1959)

(648) Post, C., and Beaver; Blast Furnace and Steel Plant 41, 627 (1953)

(649) Post, C., and Schoffstall, P.; U.S. 2,553,330 (1951)

(650) Post, C.B., Schoffstall, D.G., and Beaver, H.O.; Iron Age 168 (1951); J. Metals 3, 973 (1951); Steel 129, 88 (1951)

(651) Powell, A.R., and Johnson, Matthey & Company; Brit. 510,198 (1939)

(652) Powell, J.E., and Spedding, F.H.; Chem. Eng. Prog. Symp. Series 55, 101 (1959)

(653) Powell, J.E., and Spedding, F.H.; Trans. AIME 215, 457 (1959)

(654) Power, W.H., Fox. G.L., and Otto, J.B., Jr.; MLM-995 (1954)

(655) Prandtl, W.; Z. anorg, u. allgem. Chem. 209, 13 (1932)

(656) Prandtl, W., and Rauchenberger, J.; Ber. 53, 843 (1920)

(657) Prandtl, W., and Rauchenberger, J.; Z. anorg. u. allgem. Chem. 120, 120 (1922)

(658) Prandtl, W., and Scheiner, K.; Z. anorg. u. allgem. Chem. 220, 107 (1934)

(659) Pray, L.C.; Calif. Div. of Mines, Mineral Information Service, 10, #6 (June 1, 1957)

(660) Preece, A., and Lucas, G.; J. Inst. Metals 81, (1952)

(661) Pressly, R.S., and Rupp. A.F.; ORNL 1313 (1953)

(662) Prochovnick, A; Literature Search Relating to Metallurgical Applications of the Rare Earths, Davison Chemical Company (1958)

(663) Quill, L.L.; Z. anorg. u. allgem. Chem. 208, 59, 273 (1932)

(664) Rankama, K.; Isotope Geology, McGraw-Hill, N.Y. (1954)

(665) Ransohoff, J.A.; Nucleonics 17, No. 7, 80 (July 1959)

(666) Ray, W.E.; in Neutron Absorber Materials for Reactor Control, Ed. by Anderson, W.K., and Theilacker, J.S. To be published.

(667) Raynor, G.V.; Physical Metallurgy of Magnesium and Its Alloys, Pergamon Press, N.Y. (1959)

(668) Read, F.J.; U.S. 1,714,729 (1929)

(669) Recherches, etudes, production (R.E.P.); Fr. 1,109,909; 1,109,937 (1956)

(670) Reed, G.; American Car and Foundry Company, Major rept. No. 207B (July 1957)

(671) Reed, J.B., Hopkins, B.S., and Audrieth, L.F.; J. Am. Chem. Soc. 57, 1159 (1935)

(672) Reed, J.B., Hopkins, B.S., and Audrieth, L.F.; In Inorganic Synthesis Vol. 1, McGraw-Hill Book Co. Inc. (1939)

(673) Remeika, J.P.; J. Am. Chem. Soc. 78, 4259 (1956)

(674) Research Chemicals, Kleber, E.V., Vickery, R.C., et al; Ferromagnetic Gadolinium Alloys, Report for Contract NObs 77038 (1959), Research Chemicals Div., Nuclear Corp. of America, Burbank, Calif.

(675) Research Chemicals,Div. of Nuclear Corp. of America; Unpublished Data

(676) Research Chemicas Inc., Burbank, Calif.; Samples submitted for analysis

(677) Rhodes, B.L., Legvold, S., and Spedding, F.H.; Phys. Rev. 109, 1547 (1958)

(678) Rhodin, T.N., Jr.; U.S. 2,838,395; 2,838,396 (1958)

(679) Rienacker, G., and Birckenstaedt, M.; Z. anorg. Chem. 258, 280 (1949); 262, 81 (1950)

(680) Roberts, C.S.; J. Metals 6, 634 (1954)

(681) Rodden, C.J.; J. Research Nat. Bur. Standards 26, 557 (1941)

(682) Rodden, C.J.; J. Research Nat. Bur. Standards 28, 265 (1942)
(683) Rohden, C. de; Fr. 858,371 (1940)
(684) Rolla, L.; and Iandelli, A.; Ber. 75, 2091,2094 (1942)
(685) Rolla, L., Iandelli, A., Vogel, R., and Canneri, G.; Ricerca sci. 12, 1216 (1941)
(686) Rolla, L., Iandelli, A., Canneri, G., and Vogel, R.; Z. Metallk. 35, 29 (1943)
(687) Rose, K.; Materials and Methods 28, 66 (July 1948)
(688) Rose, K.; Materials and Methods 40, 87 (July 1954)
(689) Rossi, A.; Atti reale accad. naz. Lincei 17, 182, 839 (1933)
(690) Rossi, A.; Gazz. chim. ital. 64, 748 (1934)
(691) Rossi, A.; Gazz. chim. ital. 64, 832 (1934)
(692) Rossi, A.; Gazz. chim. ital. 64, 955 (1934)
(693) Rossi, A., and Iandelli, A.; Atti reale accad. naz. Lincei 18, 156 (1934)
(694) Rossi, A.; and Iandelli, A.; Atti reale accad. naz. Lincei 19, 415 (1934)
(695) Roth, R.S., and Schneider, S.J.; J. Research Nat. Bur. Standards 64A, No. 4, 309 (1960)
(696) Rough, F.A., and Bauer, A.A.; BMI-1300 (June 1958)
(697) Rowe, E.A., and Johnson, H.A.; Trans. A.F.S. 60, 312 (1952)
(698) Roy, R.; J. Am. Ceram. Soc. 37, 581 (1954)
(699) Russell, J.B.; J. Metals (April 1954)
(700) Russell, J.B.; U.S. 2, 656,270 (1953)
(701) Salutsky, M.L., and Quill, L.L.; J. Am. Chem. Soc. 72, 3306 (1950)
(702) Samsonov, G.V., Popova, N.M., and Tikhomirova, L.I,; Zhr. Priklad. Khim. 31, 153 (1958)
(703) Samuelson, O.; Ion-Exchangers in Analytical Chemistry, p. 34, John Wiley & Sons Inc., N.Y. (1953)
(704) Santmyers; U.S. Bur. Mines, Inform. Circ. 6321
(705) Sargent, J.D.; Scandium in U.S. Bureau of Mines, Bulletin 556
(706) Sauerwald, F.; Z. anorg. Chem. 258, (1949)
(707) Sauerwald, F.; Z. Metallk. 40, 41 (1949)
(708) Sauerwald, F.; Ger 725,170 (1942)
(709) Savitskii, E.M.; Rare Metals and Alloys, Technology House, Moscow, 1959. Reported in Simmons (742)
(710) Savitskii, E.M., and Burchanoff, G.S.; Acad. Nauk. SSSR 11, 2698 (1957)
(711) Savitskii, E.M., and Terekhova, V.F.; Tsvetnye Metally. 32, No. 1, 48 (1959)
(712) Savitskii, E.M., and Terkhova, V.F.; Zhur. Neorg. Khim 3, No. 3, 756 (1958)
(713) Savitskii, E.M., Terekhova, V.F., and Burov, I.V.; Zhur. Neorg. Khim. 4, No. 6, 1462 (1959)
(714) Savitskii, E.M., Terekhova, V.F., and Tsikalov, V.A.; Zhur. Neorg. Khim. 4, 1461 (1959)
(715) Savitskii, E.M., et al; Metalloved. i. Obrabotka Metal. p. 2 (Aug. 1958)
(716) Schafer, C.J.; U.S. 2,187,630 (1940)
(717) Schiffer; Lecture Munchen, 1900.

(718) Schneider, S.J., and Roth, R.S.; J. Am. Ceram. Soc. 43, 115 (1960)

(719) Schoeller, W.R., and Powell, A.R.; Analysis of Minerals and Ores of the Rarer Elements, Hafner Publishing Co., N.Y. (1955)

(720) Schoenberg, D.; Proc. Cambridge Phil. Soc. 33, 577 (1937)

(721) Schramm, J.; Z. Metallk. 33, 358 (1941)

(722) Schuch, A.F., and Sturdivant, J.H.; J. Chem. Phys. 18, 145 (1950)

(723) Schulte, J.; Metall. u. Erz 18, 236 (1921)

(724) Schulte, J.; Metall. u. Erz 22, (1925)

(725) Schulze, G.E.R.; Z. Krist. 104, 257 (1942)

(726) Schumacher, E.E., and Harris, J.E.; J. Am. Chem. Soc. 48, 3108 (1926)

(727) Schumacher, E.E., and Lucas, F.F.; J. Am. Chem. Soc. 46, 1167 (1924)

(728) Schwartzbart, and Sheehan; Iron Age 175, 103 (1955)

(729) Selwood, P.W.; Ind. Eng. Chem., Anal. Ed. 2, 93 (1930)

(730) Selwood, P.W.; J. Am. Chem. Soc. 55, 4869 (1933)

(731) Selwood, P.W.; J. Am. Chem. Soc. 55, 4900 (1939)

(732) Semchyshen, M., and Barr, R.Q.; Arc-Cast Molybdenum Base Alloys. Climax Molybdenum Company (1955)

(733) Semmel, J.W., Jr.; in Technology of Columbium (Niobium), ed. by Gonser, B.W., and Sherwood, E.M.; John Wiley & Sons, N.Y. (1958)

(734) Sempell, L.; Ger. 809,972 (1951)

(735) Senderoff, S., and Mellors, G.W.; J. Electrochem. Soc. 105, 224 (1958)

(736) Serres, A.; J. phys. radium 13, 46 (1952)

(737) Seybolt, A.U.; Trans. ASM 52, 971 (1960)

(738) Shafer, M.W., and Roy, R.; J. Am. Ceram. Soc 42, 563 (1959)

(739) Shkolnikov, E.M., Bondarenko, L.G., Zakharov, V.A., and Chichagova, N.P.; Liteinoe Proizvodstvo p. 36 (Feb. 1960)

(740) Shvangivadze, R.R.; Zhur. Anal. Khim. 14, 562 (1959)

(741) Siebel, G.; Z. Metallk. 39, 97 (1948)

(742) Simmons, C.R.; AECU-4423; Presented at joint ASM-AEC Symposium on the Rare Earths and Related Metals, Chicago, Ill. (Nov. 1959)

(743) Singleton, R.H.; Trans. AIME 215, No. 4, 675 (Aug. 1959)

(744) Skochdopole, R.E., Griffel, M., and Spedding, F.H.; J. Chem. Phys. 23, 2258 (1955)

(745) Skoda; Austria 136,265 (1934)

(746) Skoda; Brit. 388,109 (1933)

(747) Smith, D.M., and Wiggins, G.M.; Analyst 74, 95 (1949)

(748) Smith, G. Frederick; Cerate Oxidimetry, Published by G. Frederick Smith Chemical Co., Columbus, Ohio (1942)

(749) Smith, H.L., and Hoffman, D.C.; J. Inorg. and Nucl. Chem. 3, 243 (1956)

(750) Smith, J.F., Carlson, C.E., and Spedding, F.H.; J. Metals 9, No. 10, 1 (1957)

(751) Smith, W.H., and Seybolt, A.U.; J. Electrochem. Soc. 103, 347 (1956)

(752) Smith, W.L., Franck, M.L., and Sherwood, A.M.; Am. Mineralogist 42, 367 (1957)

(753) Smithells, C.J.; Metals Reference Book (Two Volumes) Interscience Publishers, Inc., N.Y. (1955)

(754) Smutz, M., Burnet, G., Walker, J., Tischer, R., and Olson, E.; ISC - 1068 (1959)

(755) Snyder, J.S., and Slowinski, M.F.; U.S. 2,819,502 (1958)

(756) Societe generale du Magnesium; Fr 845,843

(757) Societe de produits chimiques des terres rares; Brit. 671,265

(758) Societe de produits chimiques des terres rares; Fr. 864,221 (1941)

(759) Spangler, G.E., and Estes, J.W.; U.S. 2,863,764 (1958)

(760) Spedding, F.H., Barton, R.J., and Daane, A.H.; J. Am. Chem. Soc. 79, 5160 (1957)

(761) Spedding, F.H., and Daane, A.H.; J. Am. Chem. Soc. 74, 2783 (1952)

(762) Spedding, F.H., and Daane, A.H.; J. Metals 6, 504-10 (1954)

(763) Spedding, F.H., and Daane, A.H.; Presented at Annual Meeting of AIME, N.Y., (Feb. 1954)

(764) Spedding, F.H., and Daane, A.H.; in Progress in Nuclear Energy, Vol. 1, Series V, Pergammon Press, N.Y. (1956)

(765) Spedding, F.H., Daane, A.H., and Herrmann, K.W.; Acta Cryst. 9, 559-63 (1956)

(766) Spedding, F.H., Daane, A.H., and Herrmann, K.W.; J. Metals 9, Trans. AIME 209, 895 (1957)

(767) Spedding, F.H., Daane, A.H., Wakefield, G., and Dennison, D.H.; Trans. AIME 218, 608 (Aug. 1960)

(768) Spedding, F.H., and Dye. J.L.; J. Am. Chem. Soc. 72, 5350 (1950)

(769) Spedding, F.H., Fulmer, E.I., Ayers, B., Butler, T.A., Powell, J.E., Tevebaugh, A.D., and Thompson, R.; J. Am. Chem. Soc. 70, 1671 (1948)

(770) Spedding, F.H., Fulmer, E.I., Butler, T.A., Gladrow, E.M., Gobush, M., Porter, P.E., Powell, J.E., and Wright, J.M.; J. Am. Chem. Soc. 69, 2812 (1947)

(771) Spedding, F.H., Fulmer, E.I., Butler, T.A., and Powell, J.E.; J. Am. Chem. Soc. 72, 2349, 2354 (1950)

(772) Spedding, F.H., Fulmer, E.I., Butler, T.A., and Yaffe, I.S.; J. Am. Chem. Soc. 73, 4840 (1951)

(773) Spedding, F.H., Gschneidner, K., Jr., and Daane, A.H.; J. Am. Chem. Soc. 80, 4499 (1958)

(774) Spedding, F.H., Gschneidner, K., Jr., and Daane, A.H.; Trans. AIME 215, No. 2, 192 (1959)

(775) Spedding, F.H., Hanak, J.J., and Daane, A.H., Trans. AIME 212, 379 (1958)

(776) Spedding, F.H., Legvold, S., Daane, A.H., and Jennings, L.D.; Progress in Low Temperature Physics, Vol. II, Ch. XII, Ed. by Gorter (1956)

(777) Spedding, F.H., Mckeown, J.J., and Daane, A.H.; J. Phys. Chem. 64, 289 (1960)

(778) Spedding, F.H., and Powell, J.E.; Chem. Eng. Progr. Symposium Ser. 50, No. 14, 7-15 (1954)

(779) Spedding, F.H., and Powell, J.E.; J. Am. Chem. Soc. 74, 856, 857 (1952)

(780) Spedding, F.H., and Powell, J.E.; J. Am. Chem. Soc. 76, 2545, 2550 (1954)

(781) Spedding, F.H., Powell, J.E., Daane, A.H., Hiller, M.A., and Adams, W.H.; J. Electrochem. Soc. 105, No. 11, 683 (1958)

(782) Spedding, F.H., Powell, J.E., and Wheelwright, E.J.; J. Am. Chem. Soc. 76, 612 (1954)

(783) Spedding, F.H., Powell, J.E., and Wheelwright, E.J.; J. Am. Chem. Soc. 76, 2557 (1954)

(784) Spedding, F.H., Powell, J.E., and Wheelwright, E.J.; J. Am. Chem. Soc. 78, 34 (1956)

(785) Spedding, F.H., Voigt, A.F., Gladrow, E.M., and Sleight, N.R.; J. Am. Chem. Soc. 69, 2777 (1947)

(786) Spedding, F.H., Voigt, A.F., Gladrow, E.M., Sleight, N.R., Powell, J.E., Wright, J.M., Butler, T.A., and Figard, P.; J. Am. Chem. Soc. 69, 2786 (1947)

(787) Spedding, F.H., Wilhelm, H.A., Keller, W.H., Ahmann, D.H., Daane, A.H., Hach, C.C., and Ericson, R.P.; Ind. Eng. Chem. 44, 553 (1952)

(788) Spring, L.W.; Foundry 50, 542 (1922)

(789) Staley, W.W.; Idaho Bureau of Mines and Geology, Mineral Resources Rept. 5 (1948)

(790) Staley, W.W., and Browning, J.S.; Idaho Bureau of Mines and Geology, Pamphlet 87 (1949)

(791) Starr, C., and Kaufmann, A.R.; Phys. Rev. 58, 657 (1940)

(792) Steven, W., and Lamb, R.M.; U.S. 2,841,490 (1958)

(793) Stewart, D.C.; A.E.C.D. 2389 (1948)

(794) Stewart, D.C.; ANL 5624 (1956)

(795) Stewart, D.C.; J. Inorg. and Nucl. Chem. 4, 131 (1957)

(796) Stewart, D.C., and Kato, D.; Anal. Chem. 30, 164 (1958)

(797) Stiles, R.D., and Pierson, M.B:; WAL TR 325/1 AD 216,459 (June 1959)

(798) Stonebrook, E.E.; Foundry 87, 90 (Sept. 1959)

(799) Strauss; Metallwirtschaft 16, (1937)

(800) Strieter, F.P.; Metal Prog. 63, 75 (March 1953)

(801) Sullivan, W.H.; Trilinear Chart of Nuclides, Superintendent of Documents, U.S. Gov't. Printing Office, Wash, D.C. (1957)

(802) Sully, J.; Metal Ind. (London) 74, 367 (1949)

(803) Surls, J.P., and Choppin, G.R.; J. Inorg. Nucl. Chem. 4, No. 1, 62 (1957)

(804) Suzuki, Y.; Japan 2813 (1950)

(805) Swartz; Trans. Am. Foundrymen's Assoc. 33, (1925)

(806) Tagaya, Y.; Japan 173,789 (1946)

(807) Tageev. M., and Smirnov, Yu. D.; Stal', 17, No. 9, 823 (Sept. 1957) (Brutcher Translation #4060)

(808) Takeshi, T.; Japan 172,731 (1946)
(809) Taylor, H.S., and Diamond, H.; J. Am. Chem. Soc. 55, 2613 (1933)
(810) Taylor, J.; J. Metals 9, 94; Trans. AIME 209, (1957)
(811) Teatum, E., Gschneidner, K., Jr., and Waber, J.; LA 2345, to be published.
(812) Templeton, C.C.; J. Am. Chem. Soc. 71, 2187 (1949)
(813) Templeton, C.C., and Peterson, J.A.; J. Am. Chem. Soc. 70, 3967 (1948)
(814) Thoburn, W.C., Legvold, S., and Spedding, F.H.; Phys. Rev. 112, 56 (1958)
(815) Thompson, A.; Met. and Chem. Eng. 17, 213 (1917)
(816) Tikhova, N.M., and Afanas'eva, L.A.; Metallovedenie i Obrabotka Metallov, (March 1958) (Brutcher Trans. No. 4166)
(817) Tisdale, N.F., and Tisdale, N.F., Jr.; U.S. 2,643,949 (1953)
(818) Tisdale, N.F., and Tisdale, N.F., Jr.; U.S. 2,683,661 (1954)
(819) Tisdale, N.F., and Tisdale, N.F., Jr.; U.S. 2,799,575 (1957)
(820) Tompkins, E.R., Khym, J.X., and Cohn, W.E.; J. Am. Chem. Soc. 69, 2769 (1947)
(821) Thompkins, E.R., and Mayer, S.W.; J. Am. Chem. Soc. 69, 2859, 2866 (1947)
(822) Topp, A.C.; Chem. and Ind. (London) (1956) 1320
(823) Topp, A.C.; ORNL 1409 (1952)
(824) Topp, A.C.;and Weaver, B., ORNL 1811 (Oct. 1954)
(825) Towndrow, R.G.P.; AERE Inf./Bib. 115 (1958)
(826) Trites, A.F., Jr., and Tooker, E.W.; U.S. Geol. Surv. Bull. No. 988-H
(827) Trombe, F.; Ann. chim. 6, 349 (1936)
(828) Trombe, F.; Chim. & ind. (Paris) 77 (March, 1957)
(829) Trombe, F.; Compt. rend. 198, 159 (1934)
(830) Trombe, F.; Compt. rend. 200, 459 (1935)
(831) Trombe, F.; Compt. rend. 206, 1380 (1938)
(832) Trombe, F.; Compt. rend. 215, 439 (1942)
(833) Trombe, F.; Compt. rend. 220, 603 (1945)
(834) Trombe, F.; Compt. rend. 221, 19 (1945)
(835) Trombe, F.; Compt. rend. 236, 591 (1953)
(836) Trombe, F.; J. Phys. Radium 12, 222 (1951)
(837) Trombe, F.; Metal Treatment and Drop Forging 24, 421 (1957)
(838) Trombe, F.; Rev. Met. 53, 1 (1956)
(839) Trombe, F.; Trans. Am. Electrochem. Soc. 66, 57 (1934)
(840) Trombe, F., and Foex, M.; Ann. chim. 19, 417 (1944)
(841) Trombe, F., and Foex, M.; Compt. rend. 217, 501 (1943)
(842) Trombe, F., and Foex, M.; Compt. rend. 232, 63 (1951)
(843) Trombe, F., and Foex, M.; J. Res. du C.N.R.S. 23, 71 (1953)
(844) Trombe, F., and Foex, M.; Rev. Met. 44, 349 (1947)
(845) Trombe, F., Loriers, J., Carminati, D., and Iya, V.K.; Compt. rend. 236, 1567, 1670 (1953); 237, 1328, 1413 (1953); 240, 1537 (1955); 242, 261 (1956)
(846) Trombe, F., and Mahn, F.; Compt. rend. 217, 603 (1943)
(847) Umamaheswararao, G.V., and Krishnaswamy, R.; J. Sci. Ind. Res. (India) 15A, 401 (1956); Chem. Zentr. (1958) 3831

(848) United States Bur. of Mines; Metallurgical Progress Report No. 1, USBM-U-550, (Jan. 1959)

(849) United States Bur. of Mines; Metallurgical Progress Report No. 2, USBM-U-596, (April 1959)

(850) United States Bur. of Mines; Metallurgical Progress Report No. 3, USBM-U-623, (July 1959)

(851) United States Bur. of Mines; Metallurgical Progress Report No. 4, USBM-U-647 (Oct. 1959)

(852) United States Bur. of Mines; Metallurgical Progress Report No. 5, USBM-U-672 (Jan. 1960)

(853) United States Bur. of Mines; Metallurgical Progress Report No. 6, USBM-U-699 (April 1960)

(854) United States Bur. of Mines; Metallurgical Progress Report No. 7, USBM-U-745 (June 1960)

(855) U.S. Patents; 2,369,074; 2,377,113; 2,442,131; 2,448,211; Brit. Patents; 565,341; 580,612, 793,083; Can. Patent; 567,015

(856) United States Pharmacopeia, Mack Printing Co., Easton, Pa.

(857) Urbain, G., Weiss, P., and Trombe, F.; Compt. rend. 200, 2132 (1935)

(858) Van Vleck, J.H.; Theory of Electric and Magnetic Susceptibilities, Oxford University Press, Oxford, England (1932)

(859) Van Vleck, J.H., and Frank, A.; Phys. Rev. 34, 1494, 1625 (1929)

(860) Van Vucht, J.H.N.; Philips Research Repts. 12, 351 (1957)

(861) Van Vucht, J.H.N.; Z. Metallk. 48, 253 (1957)

(862) Vereshchagin, L.F., Shubnikoff, L.V., and Lazarev, B.G.; Physik. z. Sowjetunion 10, 618 (1936)

(863) Vickery, R.C.; Australian J. Sci. 16, No. 3, 112 (1953)

(864) Vickery, R.C.; Chemistry of the Lanthanons, Academic Press, N.Y. (1953)

(865) Vickery, R.C.; Electrical and Magnetic Properties of Rare Earth Elements Alloys and Compounds. First Quarterly Report for period Feb. 15 - May 15, 1960. WADD Contract No. AF 33(616)-7012, Task No. 73710, RC No. 146. Research Chemicals Div. of Nuclear Corp. of America, Burbank, Calif.

(866) Vickery, R.C.; J. Chem. Soc. (1949) 2506

(867) Vickery, R.C.; J. Chem. Soc. (1949) 2508

(868) Vickery, R.C.; J. Chem. Soc. (1952) 4357

(869) Vickery, R.C.; J. Chem. Soc. (1956) 3113

(870) Vickery, R.C.; J. Soc. Chem. Ind. (London) 65, 388 (1946)

(871) Vickery, R.C.; Research and Engineering 2, No. 4, Sect. 1, (April 1956)

(872) Vickery, R.C., and Klann, A.; J. Chem. Phys. 27, 1161 (1957)

(873) Vickery, R.C., and Klann, A.; J. Chem. Phys. 27, 1219 (1957)

(874) Vickery, R.C., Sedlacek, R., and Ruben, A.; J. Chem. Soc. 498 (1959)

(875) Vigers, T.W., Ball, C.J.P., and Haughton, J.L.; Metal Ind. (London) 69, 91-3 (1946)

(876) Vinogradov; Geokhimiya (1956), No. 1,1; AERE Lib/Trans 795, (Aug. 1956)

(877) Vlasov, K., and Kogan, B.; J. Sci. Ind. Research (India) 17A, 41 (1958)

(878) Vogel, R.; Metallforschung 2, (1947)

(879) Vogel, R.; Ricerca sci. 14, 147-55 (1943)

(880) Vogel, R.; Z. anorg. Chem. 72, (1911)

(881) Vogel, R.; Z. anorg. Chem. 75, (1912)

(882) Vogel, R.; Z. anorg. Chem. 84, (1913)

(883) Vogel, R.; Z. anorg. Chem. 91, 277 (1915)

(884) Vogel, R.; Z. anorg. u. allgem. Chem. 99, 25 (1917)

(885) Vogel, R., and Heumann, T.; Metallforschung 2, 1-8 (1947)

(886) Vogel, R., and Heumann, T.; Z. Metallk. 35, 29 (1943)

(887) Vogel, R., and Heumann, T.; Z. Metallk. 38, 1 (1947)

(888) Vogel, R., and Klose, H.; Z. Metallk. 45, 633 (1954)

(889) Vogel, R., and Klose, H.; Z. Metallk. 45, 670 (1954)

(890) Walker, J.W., and Olson, E.; IS-2 (1959)

(891) Wallbaum, H.J.; Z. Krist. 103, 147 (1940)

(892) Warf, J.C.; AECD-2524 (Aug. 1947)

(893) Warf, J.C.; CC-2402 (April 1945)

(894) Warf, J.C., Donohue, J., and Hardcastle, K.; PB 136,459 (1957)

(895) Warshaw, I., and Roy, R.; J. Am. Ceram. Soc. 42, No. 9, 434 (1959)

(896) Weaver, B., Kappelmann, F.A., and Topp, A.C.; J. Am. Chem. Soc. 75, 3943 (1953); ORNL-1408

(897) Weeks, M.E.; *Discovery of the Elements*, J. Chem. Educ. 1939, 1945, 1956

(898) Weibke, F., and Schmidt, W.; Z. Elektrochem. 46, 357 (1940)

(899) Weiner, R.T., Freeth, W.E., and Raynor, G.V.; J. Inst. Metals 86, Pt. 4, 185 (1957)

(900) Weiser, H.B., and Milligan, W.O.; J. Phys. Chem. 42, 673 (1938)

(901) Wells, C., et al; WAL rept. No. 310/204-1 (Oct. 1957)

(902) Wells, R.C.; J. Wash. Acad. Sci. 20, 146 (1930)

(903) Wells, C., Russell, J.V., and Poole, S.W.; Trans. ASM 46, 129 (1954)

(904) Wheelwright, E.J., and Spedding, F.H.; J. Am. Chem. Soc. 75, 2529 (1953)

(905) Wheelwright, E.J., Spedding, F.H., and Schwarzenbach, G.; J. Am. Chem. Soc. 75, 4196 (1953)

(906) White, L.A., Gerring, M., and de la Haba, D.S.; U.S. Bur. of Mines, Rept. Invest. No. 5454 (1959)

(907) Whitehead, D.J.; U.S. 2,823,115 (1958)

(908) Whitehead, D.J.;and Emley, E.F.; Brit. 822,451 (1959)

(909) Whitman, J.H.; *The Occurrence, Mining and Marketing of the Yttrium Rare Earths. Presented at the AIME Meeting, San Francisco, Calif.* (Feb. 1959)

(910) Wierda, J., and Kremers, H.C.; Trans. Am. Electrochem. Soc. 48, 159 (1925)

(911) Willard, H.H., and Young, P.; J. Am. Chem. Soc. 50, 1322, 1334, 1368, 1372, 1379 (1928)

(912) Williams, E.H.; Phys. Rev. 12, 158 (1918); 14, 348 (1919); 27, 434 (1926)

(913) Williams, J.M., and Huffine, C.L.; AECU 4427 (1959), Presented at Joint ASM-AEC Symposium on the Rare Earths and Related Metals, Chicago, Ill. (Nov. 1959); Metal Progr. 77, No. 3, 140 (1960)
(914) Willners; Jernkontorets Ann. 136, 445 (1952)
(915) Wilmarth, V.R.; U.S. Geol. Surv. Circ. No. 312
(916) Wilson, W.G.; Iron Age (Oct. 2, 1958) 78
(917) Winchester, John W.; Radioactivation Analysis in Inorganic Geochemistry. Dept. of Geology and Geophysics, Mass. Inst. of Tech. Cambridge, Mass. (1959)
(918) Winckler, C.; Ber. 23, 772 (1890); 24, 873 (1891)
(919) Wisnyi, L.G., and Pijanowski, S.; KAPL-1564, (1956)
(920) Wohler, F.; Ann. 144, 251 (1867)
(921) Wold, A., Post, B., and Banks, E.; J. Am. Chem. Soc. 79, 4911 (1957)
(922) Wold, A., Post, B., and Banks, E.; J. Am. Chem. Soc. 79, 6365 (1957)
(923) Wright, M.L., Block, F.E., and Kato, H.; A/CONF. 15/P/696 (June 1958)
(924) Wucher, J.; J. Phys. Radium 13, 278 (1952)
(925) Wyant, D.G.; U.S. Geol. Surv. Circ. No. 322
(926) Wylie, A.W.; J. Soc. Chem. Ind. (London) 69, 143 (1950)
(927) Yeamans, N.L., Schneider, S., and Creedon, J.E.; Properties of Hydrogen Reservoir Materials, U.S. Army Signal Res. and Dev. Lab., Fort Monmouth, N.J. (1960)
(928) Yntema, L.F.; J. Am. Chem. Soc. 45, 907 (1923)
(929) Yntema, L.F.; J. Am. Chem. Soc. 52, 2782 (1930)
(930) Yntema, L.F.; J. Am. Chem. Soc. 52, 4264 (1930)
(931) Yost, D.M., Russell, H., Jr., and Garner, C.S.; The Rare Earth Elements and Their Compounds, John Wiley, N.Y. (1947)
(932) Zachariasen, W.H.; Z. Phys. Chem. 123, 134 (1926)
(933) Zernicke, J., and James, C.; J. Am. Chem. Soc. 48, 2827 (1926
(934) Zernicke, J., and James, C.; J. Am. Chem. Soc. 48, 2871 (1926
(935) Ziegler, W.T.; J. Chem. Phys. 16, 838 (1948)
(936) Ziegler, W.T., Floyd, A.L., and Young, R.A.; ONR Tech. Rept. No. 2, Georgia Inst. Tech. State Eng. Exp. Sta. (1950)
(937) Ziegler, W.T., Young, R.A., and Floyd, A.L., Jr.,; J. Am. Chem. Soc. 75, 1215 (1953)
(938) Zintl, E., and Neumayer, S.; Z. Elektrochem. 38, 84 (1933)
(939) Zwicker, U.; U.S. 2,849,790 (1958)

TABLE I

NATURAL ABUNDANCE IN THE EARTH'S CRUST OF THE RARE EARTH ELEMENTS. BEST ESTIMATED VALUES

IN ORDER OF INCREASING ATOMIC NUMBER		IN DECREASING ORDER OF ABUNDANCE	
Element	Abundance (ppm)	Element	Abundance (ppm)
Scandium	10	Cerium	46
Yttrium	28	Yttrium	28
Lanthanum	18	Neodymium	24
Cerium	46	Lanthanum	18
Praseodymium	5.5	Scandium	10
Neodymium	24	Samarium	6.5
Samarium	6.5	Gadolinium	6.4
Europium	0.5	Praseodymium	5.5
Gadolinium	6.4	Dysprosium	5.0
Terbium	0.9	Erbium	4.0
Dysprosium	5.0	Ytterbium	2.7
Holmium	1.2	Holmium	1.2
Erbium	4.0	Terbium	0.9
Thulium	0.4	Lutetium	0.8
Ytterbium	2.7	Europium	0.5
Lutetium	0.8	Thulium	0.4
		Total	160

TABLE II

NATURAL ABUNDANCE OF SOME COMMON ELEMENTS

Element	Abundance (ppm)
Carbon	320
Chlorine	310
Zirconium	220
Chromium	200
Vanadium	150
Zinc	130
Nickel	80
Copper	70
Tungsten	60
Bromine	30
Tin	40
Molybdenum	15
Beryllium	6
Mercury	1
Cadmium	0.3
Silver	0.1
Bismuth	0.1
Gold	0.005
Platinum	0.005

TABLE III

TYPICAL COMPOSITION OF PRINCIPAL RARE EARTH ORES

Relative Percentages of the Individual Rare Earths

Element	Gadolinite		(1)	(2)	(3)	Bastnasite		Monazite	Allanite
(Ref.)	(212)	(778)	(212)	(416)	(416)	(659)	(328)	(277)	(752)
Lanthanum		1		↑		30	38	25.3	20
Cerium		2				50	48.5	49.4	40
Praseodymium	2.0	2	2.0	0.5	0.5	4	3.6	4.7	10
Neodymium	5.0	5	10.0	↓	1.5	14	8.8	17.0	20
Samarium	5.0	5	10.0	2	50-55	1	0.5	1.7	2
Europium	4.7**	Trace		Trace	1-1.5		↑	↑	.03
Gadolinium	5.2	5	11.0	2	25-30			1.2	1
Terbium		0.5		0.1	↑			↓	.1
Dysprosium	7.6	6	7.0	6.5				↑	.3
Holmium	1.1	1	<1.0	1			0.6		.1
Erbium		4	<2.0	5	9-16.5			0.1	.3
Thulium		0.6		0.6					.1
Ytterbium	4.6	4	<2.0	2					.3
Lutetium	2.7**	0.6		0.3				↓	<.1
Yttrium	61	60	50	80	↓		↓	0.6	3
Scandium									.1

(1) Fergusonite; a rare earth tantalo-niobate containing thorium, uranium, and titanium.

(2) Crude yttrium earths from monazite.

(3) Samarium-rich fraction from monazite.

** These values are probably too high. Values given by Spedding and Powell (778) are in better agreement with values determined by Research Chemicals.

TABLE IV

APPROXIMATE RELATIVE PERCENTAGES OF RARE EARTH ELEMENTS FROM THEIR MOST PROBABLE SOURCES

CERIUM GROUP	
Lanthanum	25
Cerium	50
Praseodymium	5
Neodymium	15
Samarium	2
Europium	Trace
Gadolinium	1
Yttrium	1

YTTRIUM GROUP	
Yttrium	60
Samarium	5
Europium	Trace
Gadolinium	8
Terbium	0.5
Dysprosium	7
Holmium	1
Erbium	5
Thulium	0.5
Ytterbium	4
Lutetium	0.5
(Cerium Group)	Balance

TABLE V

SUGGESTED OUTER ELECTRONIC STRUCTURES FOR THE RARE EARTHS

Quantum State	4f	5d	6s	4f	5d	6s	4f	5d	6s	4f	5d	6s
(Ref.)	(305)			(332)(620)(871)			(931)			(522)		
Lanthanum	0	1	2	0	1	2	0	1	2			
Cerium	1	1	2	1	1	2	2	0	2			
Praseodymium	2	1	2	2	1	2	3	0	2			
Neodymium	3	1	2	3	1	2	4	0	2			
Promethium	4	1	2	4	1	2	5	0	2			
Samarium	6		2	5	1	2	6	0	2	6	0	2
Europium	7		2	6	1	2	7	0	2	7	0	2
Gadolinium	7	1	2	7	1	2	7	1	2	7	1	2
Terbium	8	1	2	8	1	2	8	1	2			
Dysprosium	9	1	2	9	1	2	10	0	2			
Holmium	10	1	2	10	1	2	11	0	2			
Erbium	11	1	2	11	1	2	12	0	2			
Thulium	13		2	12	1	2	13	0	2	13	0	2
Ytterbium	14		2	13	1	2	14	0	2	14	0	2
Lutetium	14	1	2	14	1	2	14	1	2	14	1	2

TABLE VI

COLOR OF TRIVALENT RARE EARTH IONS

Trivalent Ion	Color	Color	Trivalent Ion
Lanthanum	Colorless	Colorless	Lutetium
Cerium	Colorless	Colorless	Ytterbium
Praseodymium	Green	Pale Green	Thulium
Neodymium	Red	Red	Erbium
Promethium	Pink	Brownish Yellow	Holmium
Samarium	Pale Yellow	Pale Yellow green	Dysprosium
Europium	Pale Pink	Very pale pink	Terbium
Gadolinium	Colorless		

TABLE VII

PHYSICAL PROPERTIES OF RARE EARTH OXIDES

Oxide*	Color	Density (gm/cc)	Melting Point (°C)	Index of Refraction	Sp.Ht. 0-1000°C (cal/gm/°C)
Sc_2O_3	White	3.86			
Y_2O_3	White	5.037		1.91	0.13
La_2O_3	White	6.51	2300		
CeO_2	White or Lt.Yellow		> 2600		
Pr_6O_{11}	Black				
Nd_2O_3	Lt.Blue	7.24	2270		
Sm_2O_3	V.Lt. Yellow	7.096	2350	1.82	0.09
Eu_2O_3	V.Lt.Pink	7.300	2050		
Gd_2O_3	White	7.608	2350	1.82	0.08
Tb_4O_7	Dark Brown				
Dy_2O_3	White	8.177	2340		
Ho_2O_3	Lt.Yellow	8.404			
Er_2O_3	Pink-Red	8.650			
Tm_2O_3	V.Lt. Green	8.880			
Yb_2O_3	White	9.226			
Lu_2O_3	White	9.425			

* Stable form as produced by high temperature ignition of oxalate in air.

TABLE VIII

UNIT-CELL DIMENSIONS OF RARE EARTH SESQUIOXIDES (1)

	A Type Hexagonal		B Type Monoclinic				C Type Cubic
	a	c	a	b	c	β	a
Lanthanum	3.93	6.12					
Cerium(2)	3.88	6.06					
Praseodymium	3.85	6.00					
Neodymium(3)	3.82	5.98	14.35	3.666	8.99	100.34°	11.080
Samarium			14.16	3.621	8.84	100.05°	10.934
Europium			14.06	3.601	8.80	100.15°	10.860
Gadolinium	3.76	5.89	14.06	3.572	8.75	100.10°	10.8122
Terbium							10.729
Dysprosium							10.6647
Holmium							10.6065
Erbium							10.5473
Thulium							10.4866
Ytterbium							10.4334
Lutetium							10.3907
Yttrium							10.6021
Scandium(4)							9.81

(1) Roth and Schneider (695) except as noted.
(2) Zachariasen (932).
(3) Calculated by Roth and Schneider from data by Shafer and Ray (738).
(4) Donnay and Nowacki (162).

TABLE IX

PRECIPITATION pH VALUES FOR RARE EARTH HYDROXIDES

Rare Earth	Nitrate Solution		Solubility
	pH at precipitation incidence	pH at $OH^-/R^{+++}=0.4$	gram moles per liter $\times 10^6$
Scandium	~ 6.3		~0.05
Yttrium	6.83	6.90	1.2
Lanthanum	7.82	8.23	7.8
Cerium (ous)	7.60	7.76	4.8
Praseodymium	7.35	7.67	5.4
Neodymium	7.31	7.40	2.7
Samarium	6.92	7.08	2.0
Europium	6.82	6.90	1.4
Gadolinium	6.83	6.94	1.4
Erbium	6.76	6.84	0.8
Thulium	6.40	6.70	0.6
Ytterbium	6.30	6.65	0.5
Lutetium	6.30	6.63	0.5

TABLE X

NEUTRON ABSORPTION CROSS SECTIONS OF THE RARE EARTHS

Element	Thermal Neutron Cross Section (Barns)
Scandium	24
Yttrium	1.27
Lanthanum	8.9
Cerium	0.7
Praseodymium	11.2
Neodymium	46
Samarium	5,500
Europium	4,600
Gadolinium	46,000
Terbium	44
Dysprosium	1,100
Holmium	64
Erbium	166
Thulium	118
Ytterbium	36
Lutetium	108

TABLE XI

PRINCIPAL COMPOUNDS USED FOR THE PURIFICATION OF VARIOUS RARE EARTHS BY FRACTIONAL CRYSTALLIZATION

Element	Method	Element	Method
Lanthanum	1, 2	Dysprosium	4, 5, 7, 8
Cerium	1, 2	Holmium	4, 5, 7, 8
Praseodymium	1, 2, 3	Erbium	4, 5, 7
Neodymium	2, 3	Thulium	4, 5
Samarium	2, 6	Ytterbium	4, 5, 6
Europium	2, 6	Lutetium	4, 5, 6
Gadolinium	2, 4, 6, 7	Yttrium	4, 6
Terbium	4, 5, 6, 7	Scandium	5

Methods

1. Double ammonium nitrate
2. Double magnesium nitrate
3. Double manganese nitrate
4. Bromate
5. Ammonium double oxalate
6. Nitrate
7. Dimethyl phosphate
8. Ethyl sulfate

TABLE XII

CRYSTAL STRUCTURE OF RARE EARTH METALS

Element	Crystal Structure		Density (gm/cc)		Lattice Constants				Atomic Radius (A°)		Atomic Volume (cc)	
					a_o(A°)		c_o(A°)					
Scandium	hcp	(765)*	3.02	(526)*	3.31	(765)*	5.27	(765)*	1.62	(764)*	14.1	(526)*
Yttrium	hcp	(765)	4.47	(776)	3.65	(765)	5.73	(765)	1.78	(764)	19.7	(764)
Yttrium	bcc	(351)			3.91	(351)						
Lanthanum	hex	(765)	6.19	(765)	3.77	(765)	12.16	(765)	1.870	(864)	22.43	(864)
Lanthanum	fcc	(776)	6.18	(864)	5.30	(776)			1.872	(864)	22.48	(864)
Lanthanum	bcc	(351)	5.97	(263)	4.26	(350)			1.90	(263)		
Cerium	fcc	(493)	8.23	(263)	4.85	(493)			1.71	(263)		
Cerium	hex	(864)	6.66	(263)	3.68	(493)	11.92	(493)	1.81	(864)	20.7	(864)
Cerium	fcc	(765)	6.77	(263)	5.16	(776)			1.817	(864)	20.58	(864)
Cerium	bcc	(351)	6.77	(263)	4.12	(350)			1.83	(263)		
Praseodymium	hex	(765)	6.77	(263)	3.67	(765)	11.84	(765)	1.824	(864)	20.79	(864)
Praseodymium	bcc	(350)	6.64	(263)	4.13	(350)			1.84	(263)		
Neodymium	hex	(386)	7.00	(386)	3.66	(765)	11.80	(765)	1.818	(386)	20.60	(386)
Neodymium	bcc	(521)	6.80	(263)	4.13	(350)			1.84	(263)		
Samarium	rhom	(346)	7.49	(607)	8.99	(346)	β=23°13'	(346)	1.804	(181)	20.0	(145)
Samarium	bcc	(351)			4.07	(351)						
Europium	bcc	(765)	5.245	(775)	4.58	(775)			2.042	(864)	29.00	(864)
Gadolinium	hcp	(35)	7.86	(776)	3.64	(765)	5.78	(765)	1.794	(864)	19.79	(864)
Terbium	hcp	(765)	8.25	(776)	3.60	(776)	5.69	(776)	1.773	(864)	19.11	(864)
Dysprosium	hcp	(79)	8.55	(776)	3.59	(35)	5.65		1.769	(864)	18.97	(864)
Holmium	hcp	(776)	6.79	(776)	3.58	(765)	5.62	(765)	1.759	(77)	18.65	(864)
Erbium	hcp	(35)	9.15	(776)	3.65	(765)	5.58	(776)	1.757	(765)	18.29	(864)
Thulium	hcp	(765)	9.31	(776)	3.53	(776)	5.55	(776)	1.746	(765)	18.12	(864)
Ytterbium	fcc	(143)	6.96	(776)	5.49	(765)			1.940	(765)	24.75	(864)
Ytterbium	hcp	(351)										
Lutetium	hcp	(776)	9.85	(776)	3.50	(776)	5.55	(776)	1.737	(864)	17.95	(864)

* References

TABLE XIII

THERMAL PROPERTIES OF RARE EARTH METALS

Element	Transition Temperature °C	Melting Point °C	Boiling Point °C
Scandium		1539 (767)	2730 (767)
Yttrium	1490 (172)	1509 (597)* 1540 (597)**	3030 (776)
Lanthanum		920 (776)	3470 (146)
alpha-beta	310 (40)		
beta-gamma	864 (766)		
Cerium		804 (776)	3470 (146)
alpha-gamma	-103 (493,722)		
beta-gamma	90 (493,722)		
gamma-delta	730 (766)		
Praseodymium	792 (766)	919 (370)	3020 (776)
Neodymium	862 (766)	1019 (370)	3180 (776)
Samarium	917 (764)	1072 (777)	1630 (776)
Europium		826 (775)	1489 (775)
Gadolinium	1264 (347)	1312 (351)	2730 (776)
Terbium	1317 (776)	1356 (352)* 1355 (352)**	2530 (776)
Dysprosium		1407 (352)	2330 (776)
Holmium		1461 (352)	2330 (776)
Erbium		1497 (352)	2630 (776)
Thulium		1545 (352)	1720 (760)***
Ytterbium	798 (764)	824 (776)	1530 (776)
Lutetium		1652 (351)* 1680 (352)**	1930 (776)

* Distilled Metal
** Metal melted in tantalum
*** Calculated from referenced data

TABLE XIV

THERMODYNAMIC PROPERTIES OF RARE EARTH METALS

Element	$C_p 0^\circ C$ Cal/mole/deg.	ΔH Fusion Kcal/mole	ΔH Vaporization Kcal/mole
Scandium	6.01 (764)	3.8 (776)	78.6 (767)***
Yttrium	6.01 (764)	4.1 (776)	80 (776)
Lanthanum	6.65 (764)	2.4 (776)	93.8 (146)
Cerium	6.37 (777)	1.24 (777)	92.9 (146)
Praseodymium	6.38 (350)	1.65 (350)	79.5 (138)
Neodymium	6.51 (777)	1.70 (777)	70.6 (370)
Samarium	6.27 (777)*	2.60 (777)	46 (776)
Europium	6.00 (764)	2.5 (776)	42.1 (775)**
Gadolinium	11.20 (257)	3.7 (776)	73 (776)
Terbium	7.08 (363)	3.9 (776)	70 (776)
Dysprosium	6.72 (256)	4.1 (776)	67 (776)
Holmium	6.45 (236)	4.1 (776)	67 (776)
Erbium	6.66 (744)	4.1 (776)	67 (764)
Thulium	6.45 (764)	4.4 (776)	57.4 (760)***
Ytterbium	6.00 (764)	2.2 (776)	40 (776)
Lutetium	6.45 (764)	4.6 (776)	59 (776)

Vapor Pressures

Element	Reference	1 mm.Hg	10^{-3}mm.Hg
Scandium	(767)	1797°C*	1247°C*
Lanthanum	(138,763)	2331	1535
Cerium	(3)	1748	1331
Praseodymium	(138,763)	1850	1275
Neodymium	(763)	1767	1193
Europium	(775)	~ 830*	~ 530*
Dysprosium	(763)	1463	1005
Thulium	(760)	~ 1100*	~ 770*

		Thermal Conductivity 28°C cal/cm²/cm/sec/°C
Yttrium	(348)	0.035
Lanthanum	(348)	0.033
Cerium	(348)	0.026
Praseodymium	(348)	0.028
Neodymium	(348)	0.031
Gadolinium	(348)	0.021
Dysprosium	(348)	0.024
Erbium	(348)	0.023

* Calculated
** At 25°C
*** Ht. of Sublimation

TABLE XV

ELECTRICAL PROPERTIES OF RARE EARTH METALS

Element	Specific Resistance at 25°C ohm-cm x 10^6		Coefficient of Resistance 0-25°C $°C^{-1}$ x 10^3		Hall Coefficient at 25°C $\frac{\text{Volt} \cdot \text{cm}}{\text{Amp} \cdot \text{oer}} \times 10^{12}$	
Scandium	61[a]	(231)	2.82	(231)		
Yttrium						
Polycrystalline	57	(275)	2.71	(94)	-0.77	(383)
along c axis	35	(275)				
along basal plane	72	(275)				
Lanthanum	57	(766)	2.18	(94)	-0.8	(383)
Cerium	75	(766)	0.87	(94)	1.8	(383)
Praseodymium	68	(766)	1.71	(94)	0.71	(383)
Neodymium	64	(766)	1.64	(94)	0.97	(383)
Samarium	88	(94)	1.48	(94)	-0.2	(12)
Europium	90	(134)				
	81	(775)				
Gadolinium	140.5	(94)	1.76	(94)	-4.48[b]	(383)
Dysprosium						
Polycrystalline	57	(275)	1.19	(94)	-2.7	(383)
18.2° from c axis	35	(275)				
42° from c axis	72	(275)				
Holmium	87	(94)	1.71	(94)		
Erbium	107	(94)	2.01	(94)	-0.34	(383)
Thulium	79	(94)	1.95	(94)	-1.8	(383)
Ytterbium	29	(134)	1.30	(94)	3.8	(383)
Lutetium	79	(94)	2.40	(94)	-0.54	(383)

a. Average value along zone refined bar at 22°C.

b. The magnitude of the Hall coefficient of gadolinium increases rapidly as the temperature is lowered near to the Ferromagnetic Curie temperature. It is approximately -24 at 80°C and -120 at 29°C. The value -4.48 is for 350°C.

TABLE XVI

MAGNETIC PROPERTIES OF RARE EARTH METALS

Element	Ref.	Atomic Susceptibility at 298°K emu x 10^6	Curie-Weiss Constants C (atomic)	Curie-Weiss Constants Θ °K	Effective Moment Exptl.	Effective Moment Theoretical[a] Valence 3^+
Scandium	355	8.1				0
Yttrium	78	191				0
Lanthanum	456	101				0
Cerium	456	2,310	0.776	-38[b]	2.51	2.56
Praseodymium	456	5,320	1.585	0	3.56	3.62
Neodymium	456[f]	5,370	1.37	4.3[c]	3.3	3.68
Samarium	456	1,260				1.6
Europium	90	40,600	8.53	88	8.3[d]	7.9[e]
	301	32,900	6.25	108	7.1	3.5
Gadolinium	385	Ferromag.	7.49	302	7.8	7.94
Terbium	814	191,000	11.6	237	9.7	9.72
Dysprosium	776	92,600	13.3	154	10.2	
	835	99,800	14.07	157	10.64	10.6
Holmium	677	70,200	14.8	87.0	10.9	10.6
Erbium	776	49,200	12.6	41.6	10.0	
	385	44,100	11.2	40	9.6	9.6
Thulium	677	26,100	7.26	20	7.65	7.6
Ytterbium	455	70				4.5
Lutetium	776	17.9				0

a. Van Vleck (858)

b. Value obtained after 100 cooling cycles. Θ = -46 on first cooling cycle

c. $\chi_{Nd} = C/(T-\theta) + 5.0 \times 10^{-6}$ emu

d. $\mu_{eff} = 8.2$ obtained by Klemm and Bommer (385)

e. Calc. for Eu^{2+} by Bozorth and Van Vleck (90)

f. Arajs and Miller (26) found atomic susceptibility values for neodymium, holmium, and erbium in good agreement at room temperature with the data indicated. Neodymium does not satisfy the Curie-Weiss law at elevated temperatures. Holmium and erbium do follow the Curie-Weiss law to 1500° and 1400°K respectively

TABLE XVI (cont.)

THE MAGNETIC PROPERTIES OF RARE EARTH METALS

Element	Ref.	Ferromagnetic Curie Temp. °K	Neel temp. °K	Paramagnetic Curie temp. θ(°K)
Scandium	355	None	None	
Yttrium	78	None	None	
Lanthanum	456	None	None	
Cerium	456		12.5	-38
Praseodymium	456	None	None	0
Neodymium	456		7.5	4.3
Samarium	456		14.8?	
Europium	90	None[a]	90-100	88
Gadolinium	776	289		302
Terbium	814	218[b]	230	237
Dysprosium	55	84	178	157
Holmium	677	20	133	87
Erbium	776	20?	80?	40
Thulium	150	22	60	20
Ytterbium	455	None	None	
Lutetium	776	None	None	

a. Bczorth and Van Vleck (90) report that europium is not ferromagnetic at low temperatures, but has an anomalously high susceptibility.

b. Terbium is ferromagnetic below 218°K. It is antiferromagnetic from 218-230°K, but becomes ferromagnetic in this region in an applied field > 200 oe.

TABLE XVII

THE HARDNESS OF RARE EARTH METALS

Reference	Daane (141)				Love (462)		Love (464)		Simmons (742)	
Condition Units	a BHN	b BHN	c BHN	d BHN	e VHN	f VHN	g R_E	h R_E	i BHN	j BHN
Lanthanum	37			37	51	150				
Cerium	24				31	48				
Praseodymium	37				43	76			49	65
Neodymium	35				83	76			27	47
Samarium		42		45	64					
Europium		17								
Gadolinium	52			57	66	97				
Terbium	88			46					69	89
Dysprosium			55	42	93	117	61	94	51	86
Holmium			49	42	90				76	93
Erbium			60	44	127	161	74	96	83	109
Thulium			53	48					79	100
Ytterbium			21						35	45
Lutetium			118	77					91	114
Yttrium					105	140	81		61	108
Scandium	85(1)									

a. As-cast
b. Distilled and cast
c. Distilled and arc-melted
d. Annealed
e. As-cast
f. Swaged, 50% reduction in area
g. Arc-melted
h. Arc-melted and cold swaged, 50% reduction in area
i. As-cast
j. "Cold worked"

(1) Hardness R_H scale, Daane (767)

TABLE XVIII

YOUNG'S MODULUS OF ELASTICITY FOR RARE EARTH METALS

	Modulus, psi x 10^{-6}		
Condition Reference	a (750)	b (462)	c (464)
Yttrium	9.62	17	7-9
Lanthanum	5.57	10-11	
Cerium	4.35	6	
Praseodymium	5.11	7-14	
Neodymium	5.50		
Samarium	4.95	8	
Gadolinium	8.16	8-14	
Terbium	8.34		
Dysprosium	9.15	10-14	7-9
Holmium	9.73	11	
Erbium	10.6	16	6-10
Ytterbium	2.58		

Modulus Values for Yttrium (742)[d]

Metal Preparation	Modulus, psi x 10^{-6}
arc-melted	8.6-10.2
as-cast	9.5-11.5
as-cast and cold rolled 20%	16-19

a. Calculated from measured sonic velocities in as-cast metals
b. Measured from stress-strain relationship on as-cast metal
c. Measured from stress-strain relationship on arc-melted metal
d. Peak resonance method

TABLE XIX

COMPRESSION PROPERTIES OF RARE EARTH METALS

	Ultimate Compression Strength psi	Compression Yield Strength 0.2% Offset psi	Modulus of Compression psi x 10^{-6}		
Condition Reference	a (709)	b (464)	c (750)	d (94)	e (464)
Yttrium	113,800	24,200^{g}	6.8		
Lanthanum	31,200		4.38	3.6	
Cerium	42,600		2.87	3.0	
Praseodymium	46,900		4.33	3.8	
Neodymium	35,500		4.72	4.7	
Samarium			5.56	4.1	
Europium				2.03^{f}	
Gadolinium			5.64	5.7	
Terbium			5.80		
Dysprosium			5.94	5.5	6.7
Holmium		18,400	6.64	5.7	
Erbium			6.74	5.7	12.0
Thulium	110,100	20,300		5.5	
Ytterbium			1.99	1.9	
Lutetium				6.2	

a. Determined on as-cast metal
b. Determined on arc-melted metal
c. Adiabatic data from sound velocity measurements on as-cast metal
d. Isothermal data from high pressure measurements on as-cast metal
e. Measured from stress-strain relationship on arc-cast metal

f. Reference (775)
g. Reference (709) percent offset not stated

TABLE XX

NOTCHED BAR IMPACT PROPERTIES OF CAST RARE EARTH METALS

	Izod Impact (Inch Pounds)		
	As-Cast (462)	Arc-Cast (464)	
	Room Temperature	Room Temperature	204°C(400°F)
Yttrium	18	13	21
Lanthanum	54		
Cerium	26		
Praseodymium	57		
Neodymium	100		
Samarium	6		
Gadolinium	16		
Terbium	38		
Dysprosium	20	27	27
Holmium	86		
Erbium	14	20	26
Ytterbium	64		

TABLE XXI

THE CORROSION RATES OF RARE EARTH METALS IN AIR

(Mgm/dm^2/day)

Temperature	35°C		95°C		200°C	400°C	600°C
Relative Humidity	1%	75%	1%	75%			
Lanthanum	80	950	510	21,000	30	3,200	13,000
Cerium						200,000	
Praseodymium	8	76	900	5,500	80	38,000	130,000
Neodymium	2	7	60	2,000	70	380	4,800
Samarium	0	0	0	100	15	17	35
Gadolinium	1	2	0	35	0	210	16,000
Terbium	0	0	0		0	1,600	40,000
Dysprosium	0	0	0	43		350	6,600
Holmium	1	1	1		11	110	5,400
Erbium	1	1	0		10	90	720
Ytterbium						170	
Yttrium	1	1	2	9	4	40	1,900

TABLE XXII

THE COMPARATIVE EFFECT OF RARE EARTH METALS ON THE YIELD STRENGTH OF MAGNESIUM ALLOYS (443)

Temperature	Tensile Yield Strength of Cast Magnesium Alloys Containing 6% Rare Earth Metals (1000 psi)				
	70°F			400°F	600°F
Condition	F	T4	T6	T6	T6
Magnesium-Lanthanum	14	11	11	7.5	4.5
Magnesium-Cerium	15	12	15	11	7
Magnesium-Praseodymium[a]			18	15	11
Magnesium-Neodymium[b]	18	15	21	20	14

F	As Fabricated
T4	Solution Heat Treated
T6	Solution Heat Treated plus Artificially Aged

[a] Plus Lanthanum

[b] 75% Neodymium, balance principally praseodymium and other rare earths

TABLE XXIII

THE COMPOSITION OF COMMERCIAL MAGNESIUM-RARE EARTH ALLOYS

Cast Alloys		Nominal Composition (%)			
American	British	Mischmetal	Didymium	Zinc	Zirconium
EK 41A		4.0			0.6
	MCZ	3.0			0.6
EK 30A		3.0			0.3
EZ 33A		3.0		2.7	0.7
	ZRE 1	2.7		2.2	0.6
	ZRE 0	2.7		0.5	0.6
ZE 41A		1.2		4.2	0.7
	RZ 5	1.2		4.0	0.7
EK 31XA			3.0		0.6
QE 22A[a]			2.0		0.7
Wrought Alloys					
ZE 41XA		0.6		4.25	0.55
EK 31XA			3.0		0.6
ZE 10A		0.17		1.25	

a. Contains 2.5% silver

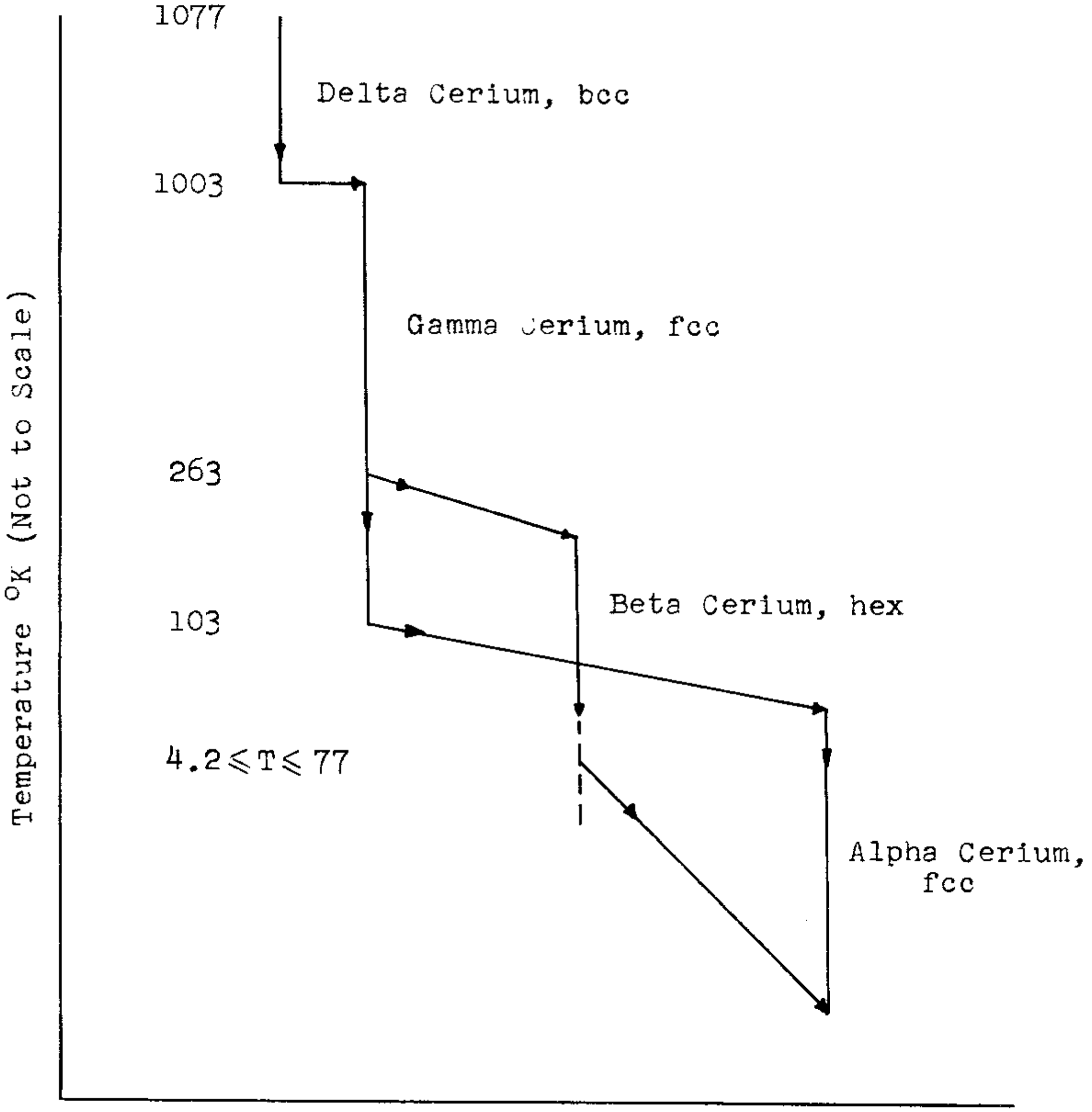

Figure 1. Schematic Diagram Showing the Behavior of Cerium Upon Cooling. After Gschneidner (264).

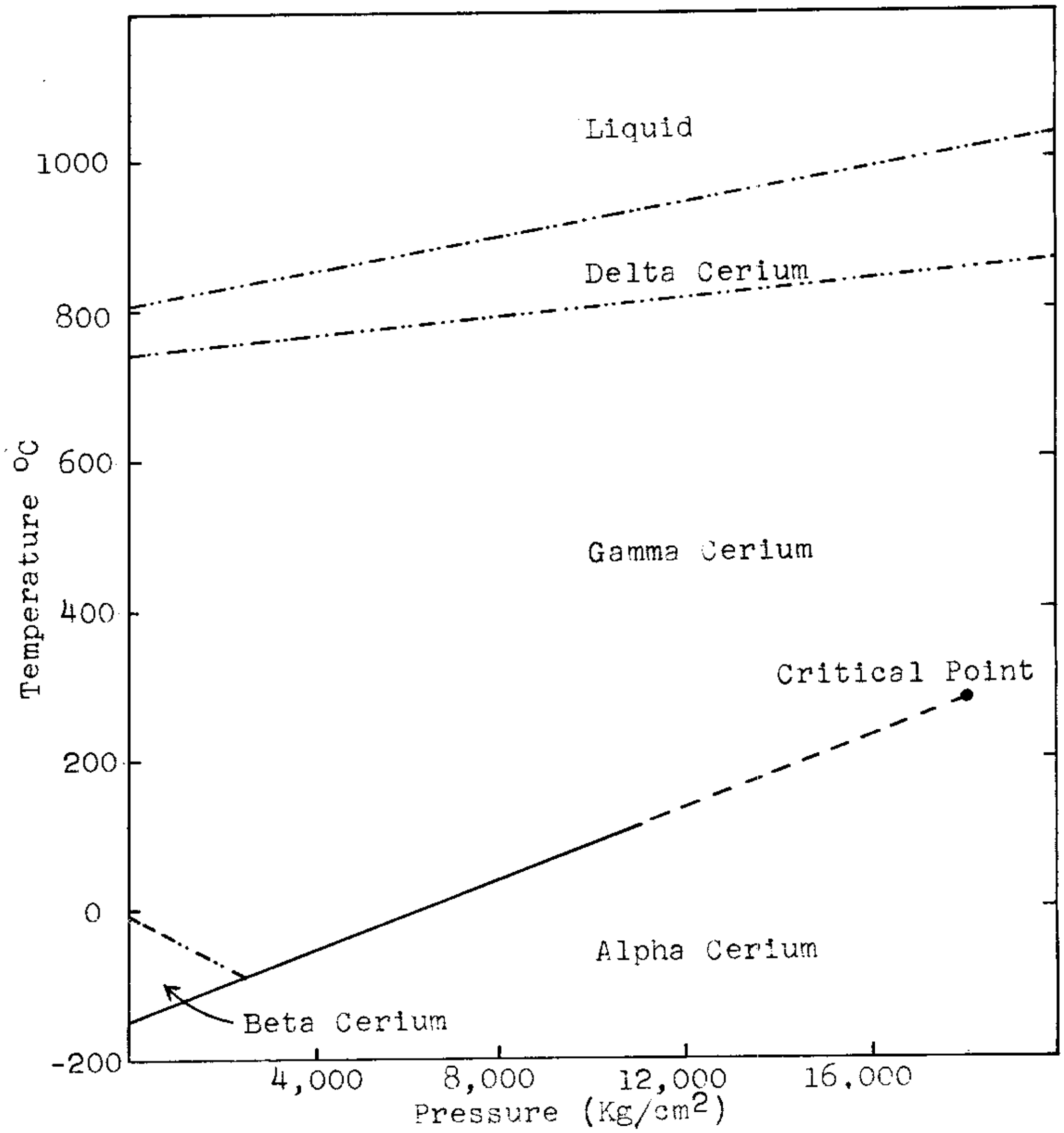

Figure 2. Proposed Cerium Temperature-Pressure Diagram. After Gschneidner (264).

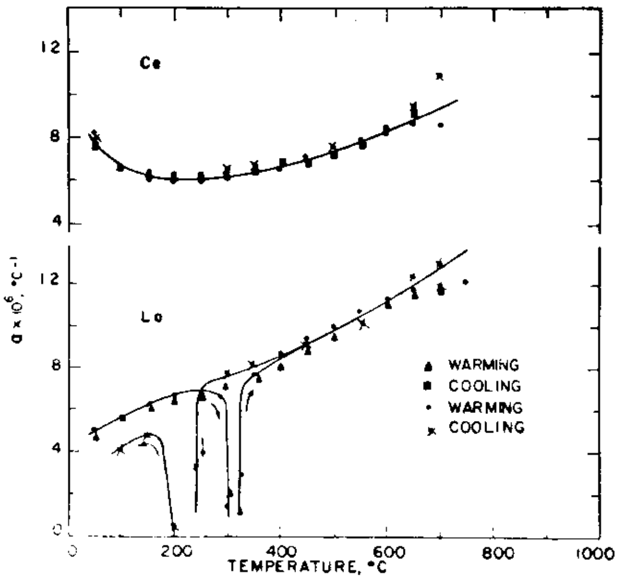

Figure 3. Thermal Expansion Coefficients of Lanthanum and Cerium

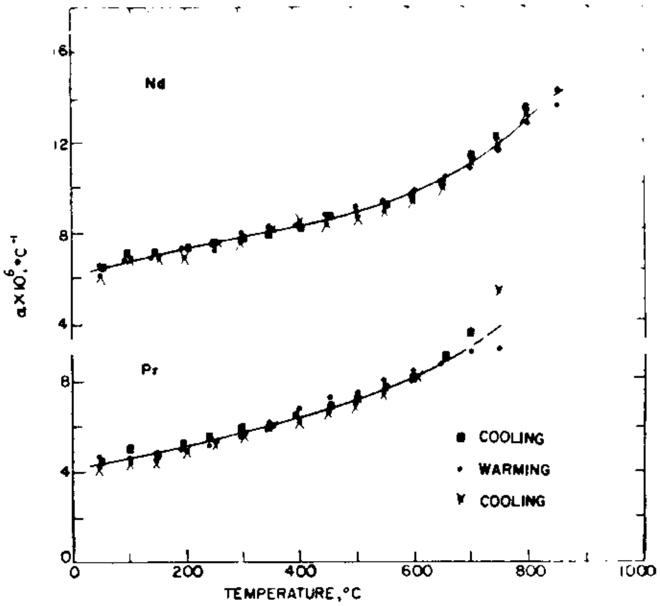

Figure 4. Thermal Expansion Coefficients of Praseodymium and Neodymium

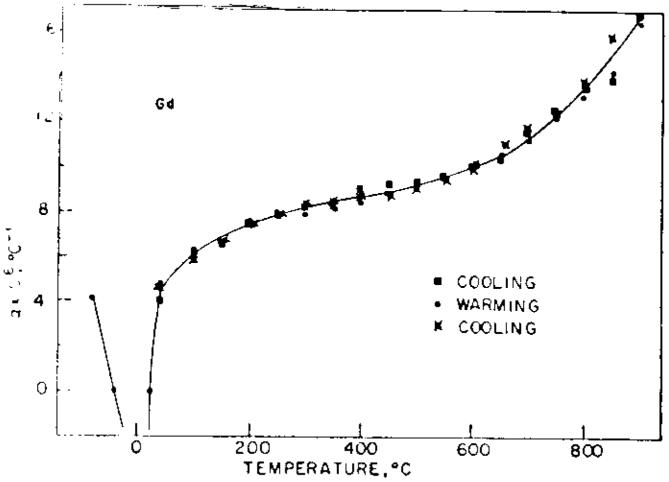

Figure 5. Thermal Expansion Coefficient of Gadolinium

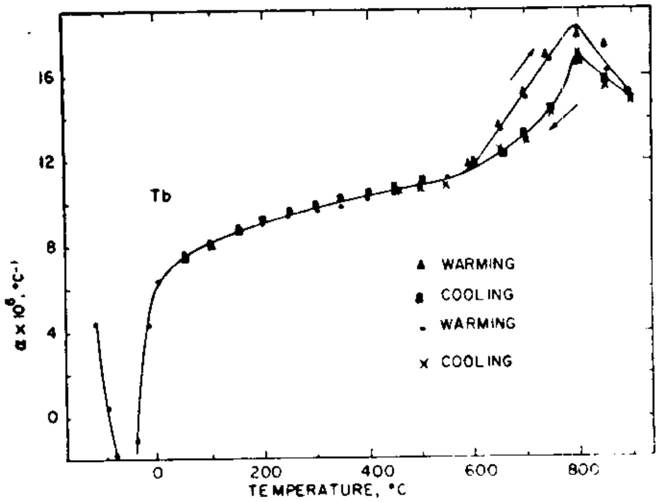

Figure 6. Thermal Expansion Coefficient of Terbium

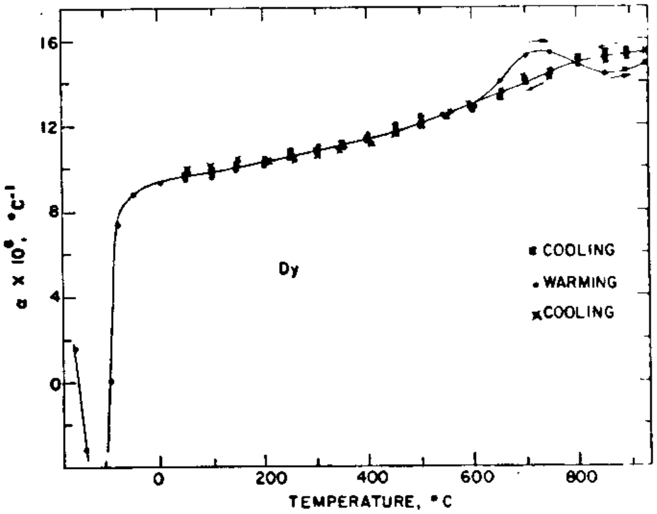

Figure 7. Thermal Expansion Coefficient of Dysprosium

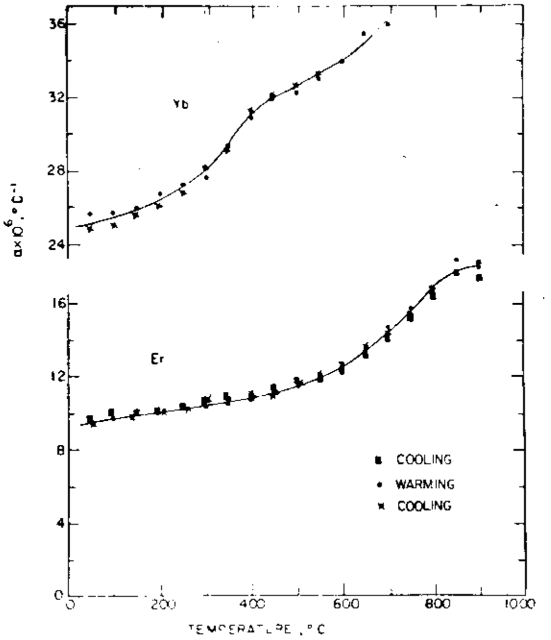

Figure 8. Thermal Expansion Coefficient of Erbium and Ytterbium

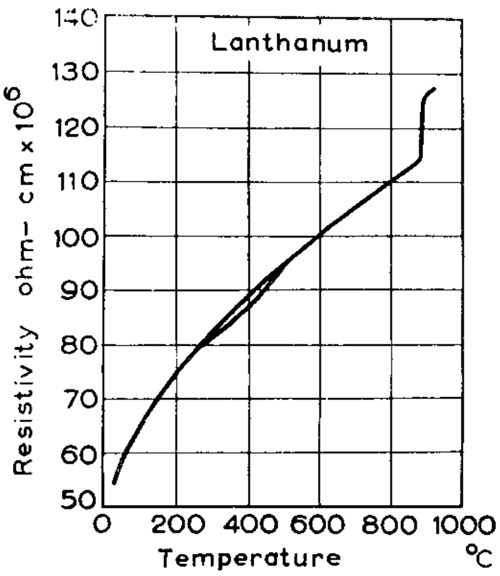

Figure 9.
Resistivity of Lanthanum

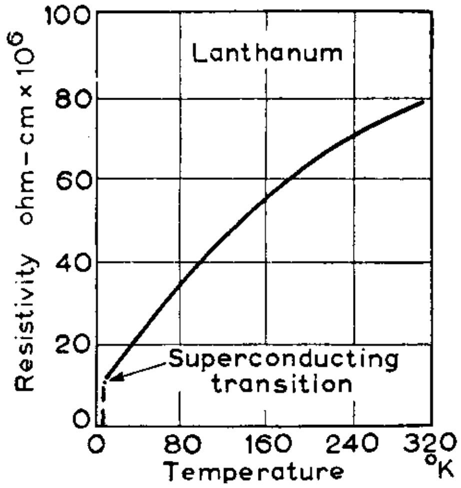

Figure 10.
Resistivity of Lanthanum

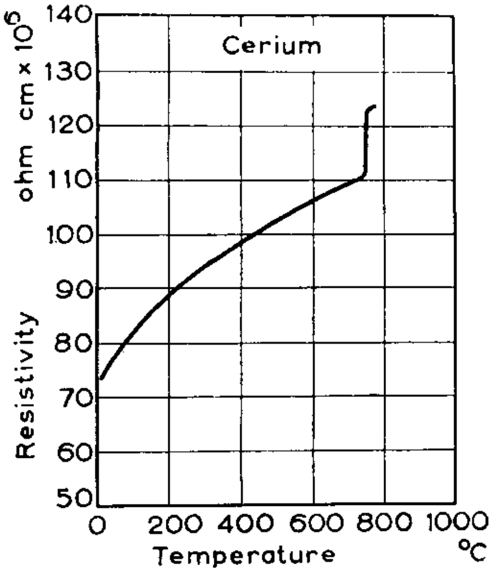

Figure 11.
Resistivity of Cerium

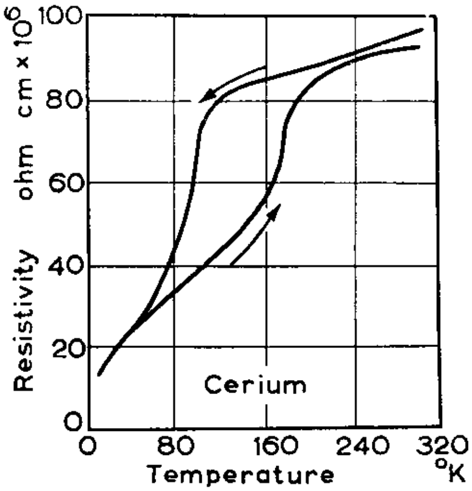

Figure 12.
Resistivity of Cerium

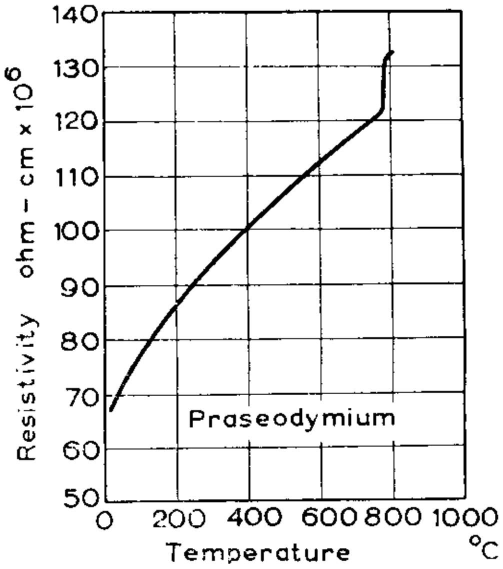

Figure 13.
Resistivity of Praseodymium

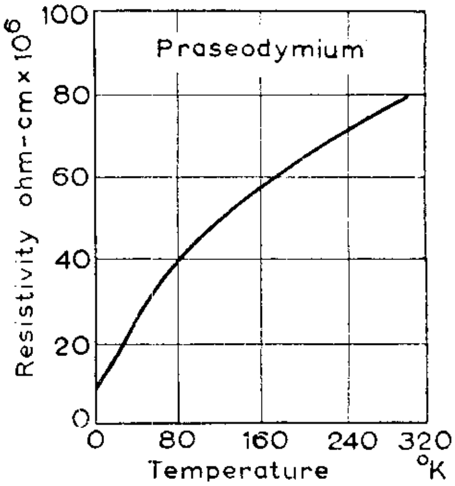

Figure 14.
Resistivity of Praseodymium

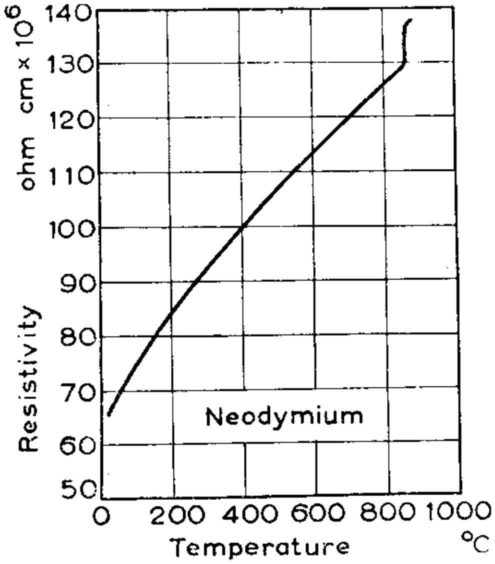

Figure 15.
Resistivity of Neodymium

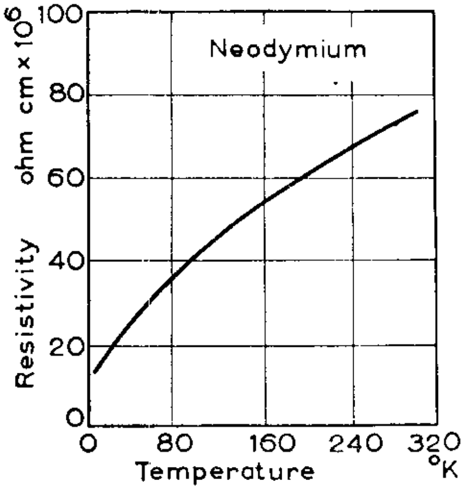

Figure 16.
Resistivity of Neodymium

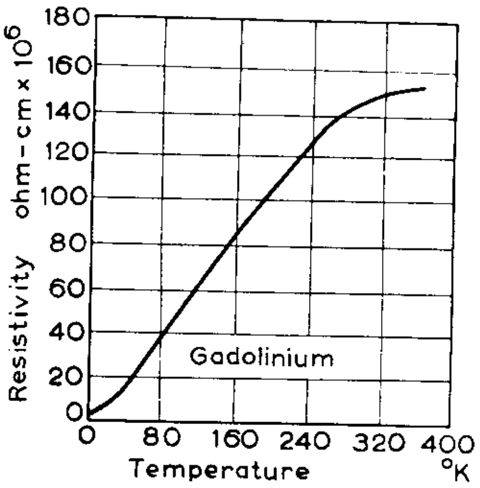

Figure 17.
Resistivity of Gadolinium

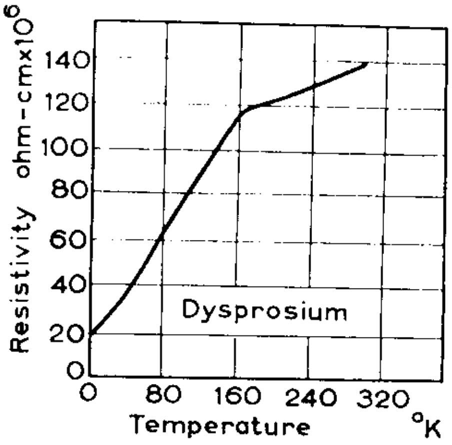

Figure 18.
Resistivity of Dysprosium

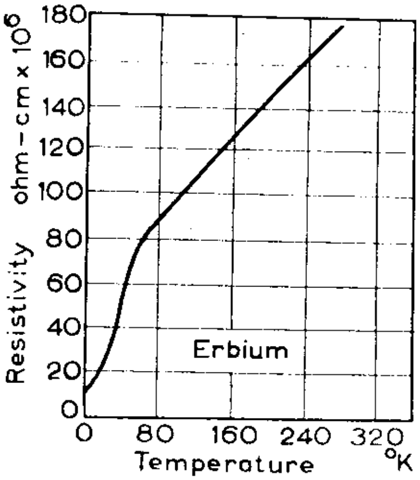

Figure 19.
Resistivity of Erbium

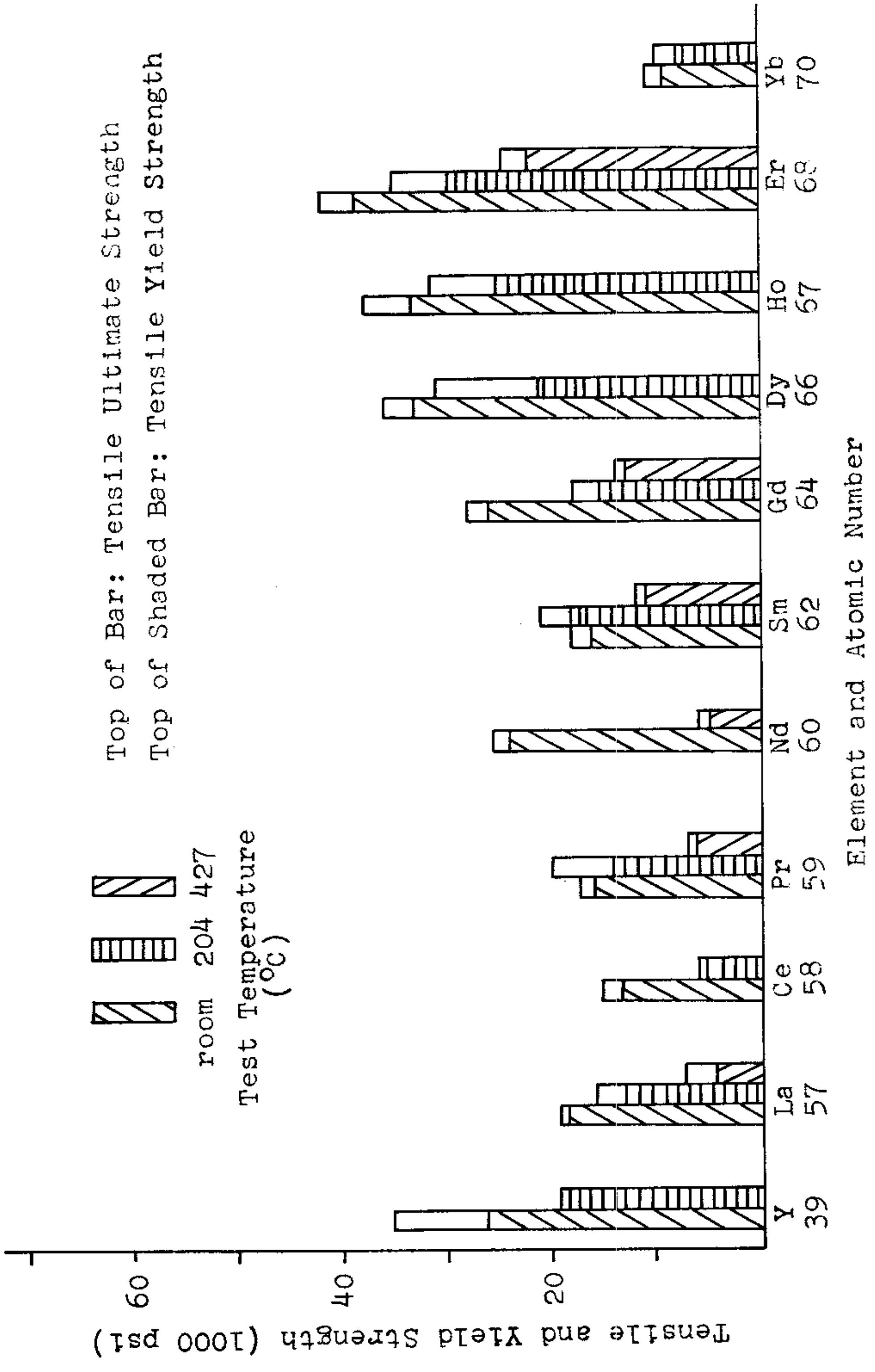

Figure 20. Tensile Properties of Rare Earth Metals: As Cast

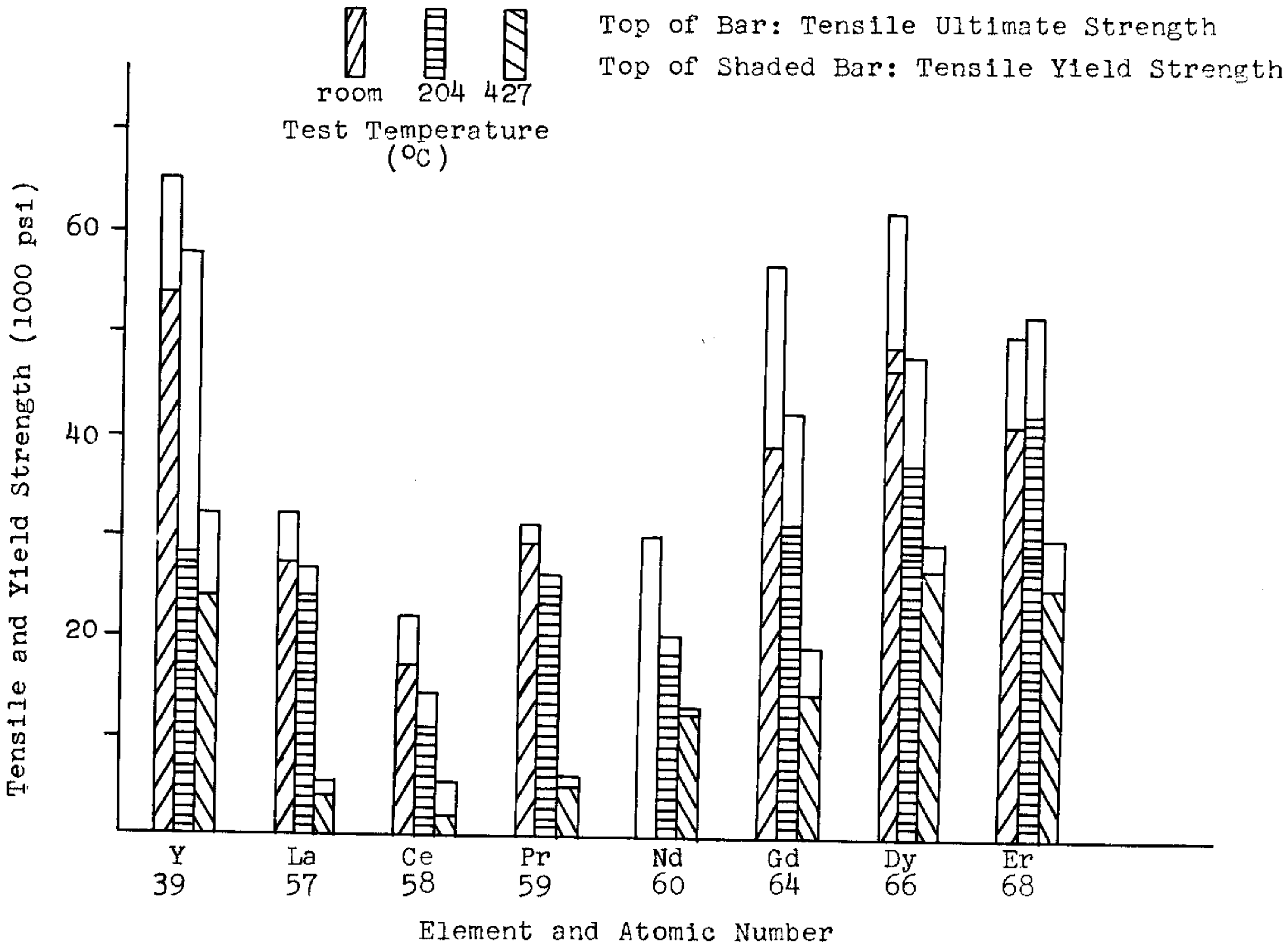

Figure 21. Tensile Properties of Rare Earth Metals: Worked

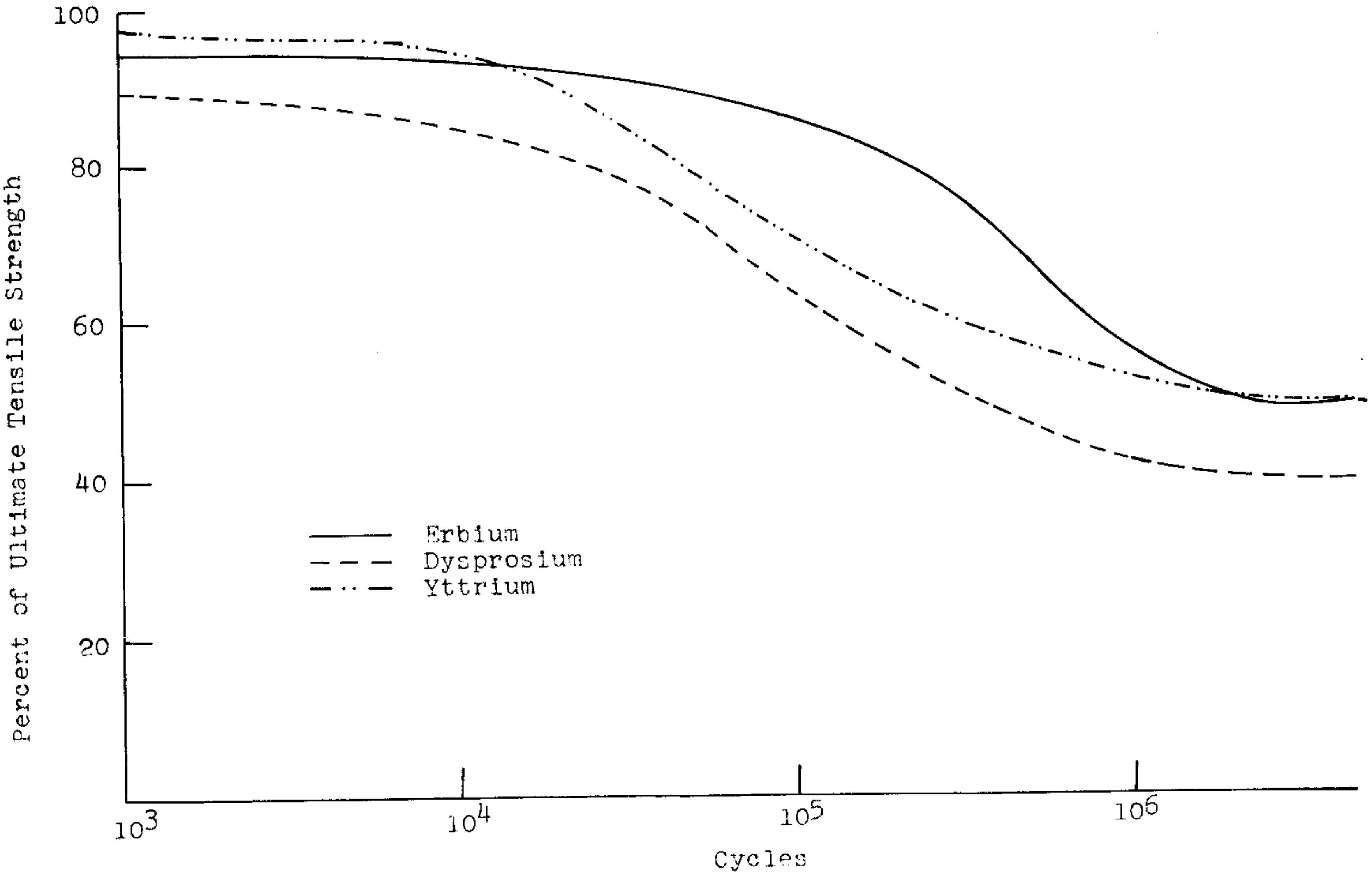

Figure 22. Tensile Fatigue Properties of Erbium, Dysprosium, and Yttrium

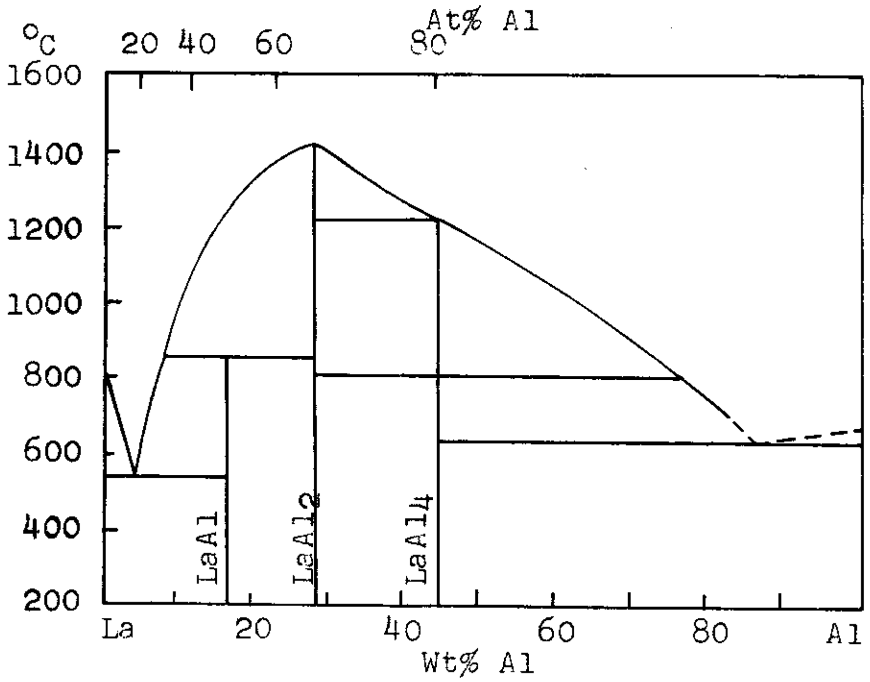

Figure 23. Lanthanum-Aluminum Constitutional Diagram (753). (111,596,689,725,879,886,898).

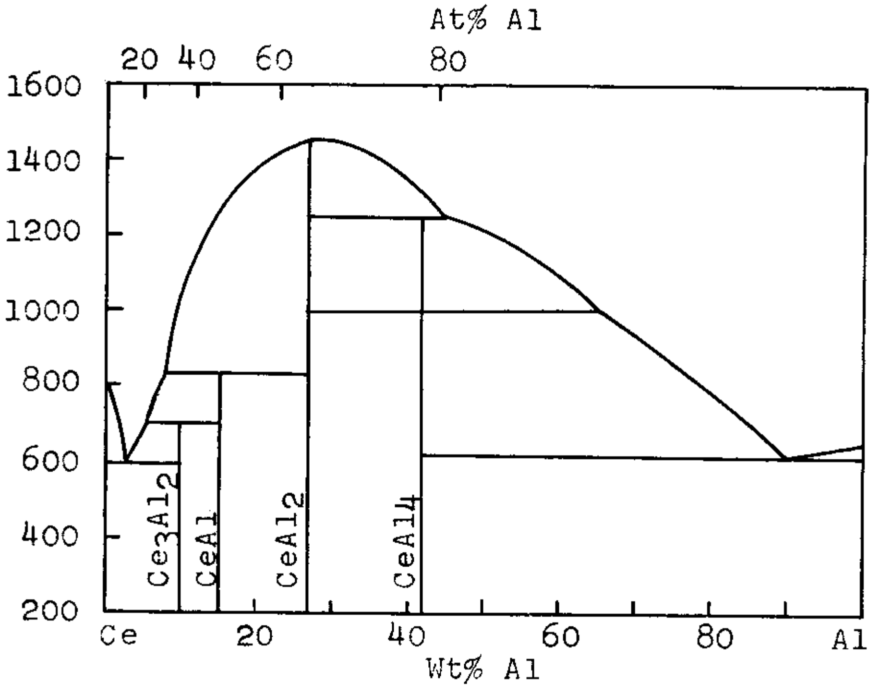

Figure 24. Cerium-Aluminum Constitutional Diagram (753). (63,527,596,723,879,881,886,891).

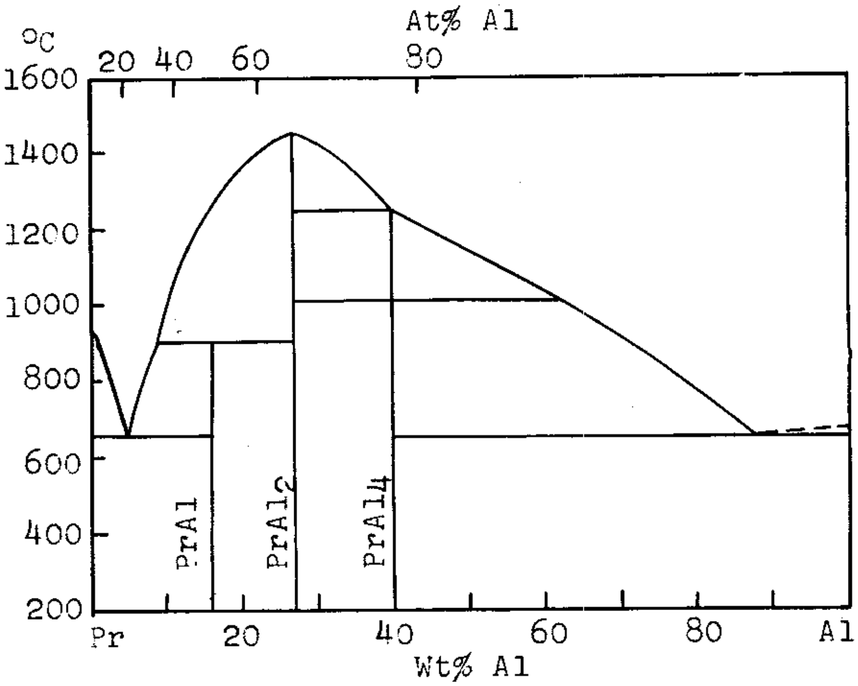

Figure 25. Praseodymium-Aluminum Constitutional Diagram (753). (109,879,886).

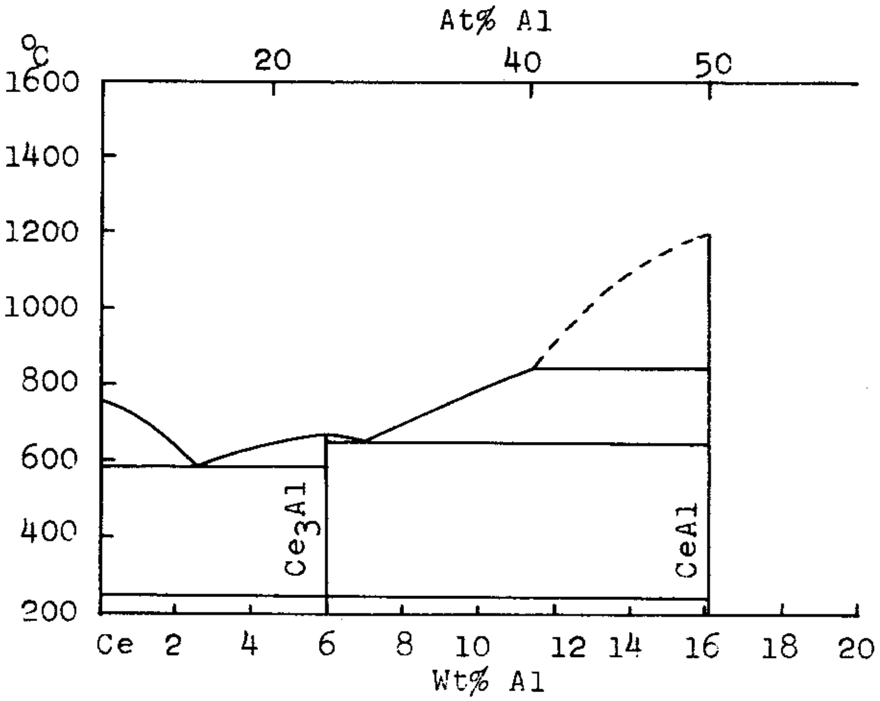

Figure 26. Cerium-Aluminum Partial Constitutional Diagram. Van Vucht (861).

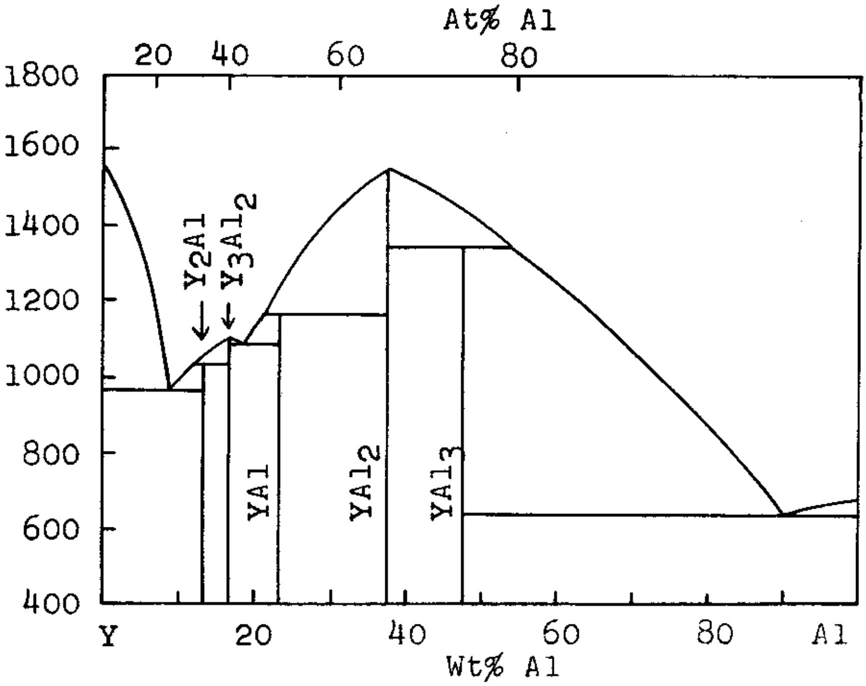

Figure 27. Yttrium-Aluminum Constitutional Diagram. Lundin and Klodt (471).

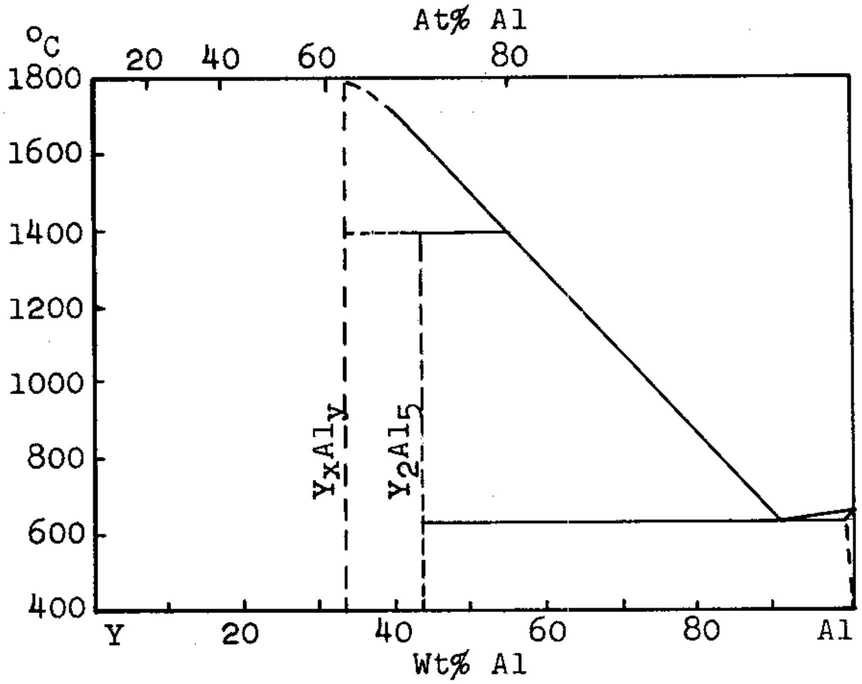

Figure 28. Yttrium-Aluminum Partial Constitutional Diagram. Savitskii (714).

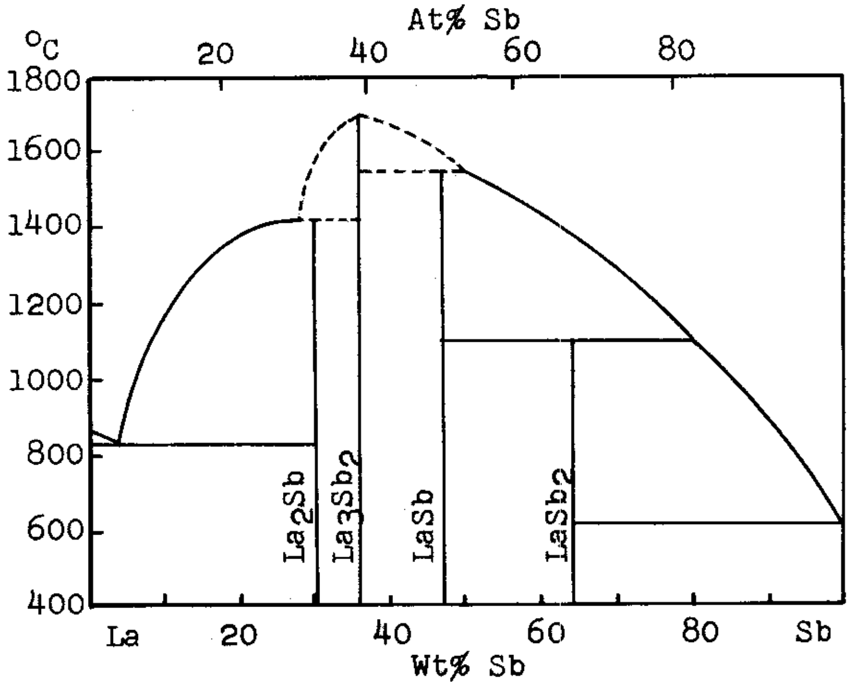

Figure 29. Lanthanum-Antimony Constitutional Diagram (753). (888).

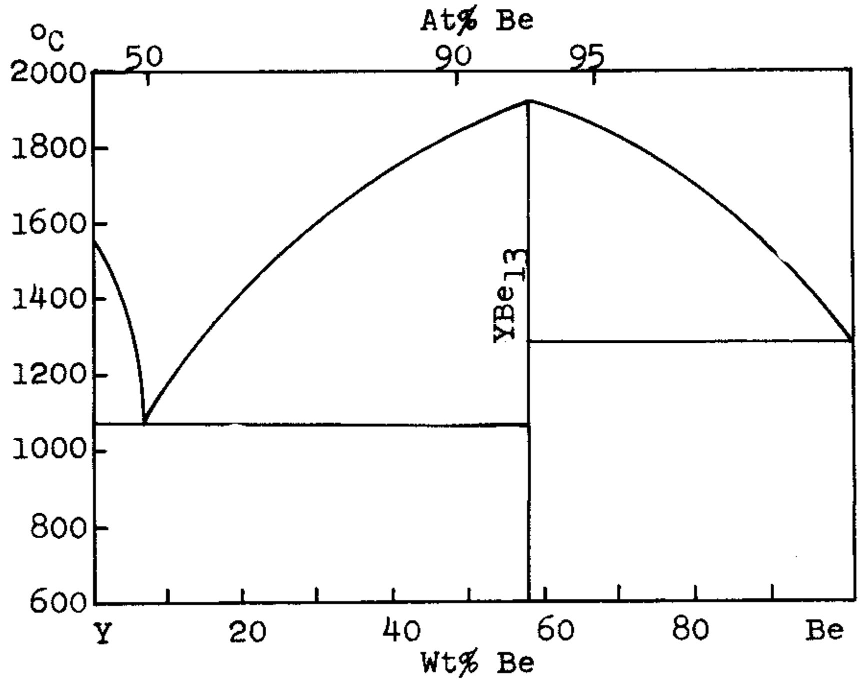

Figure 30. Yttrium-Beryllium Constitutional Diagram.
Lundin and Klodt (471).

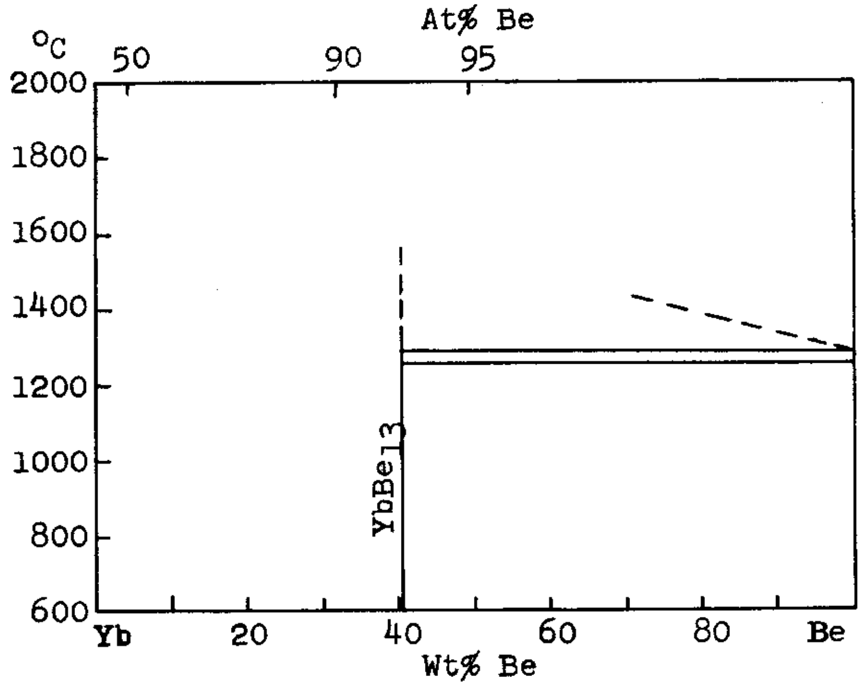

Figure 31. Ytterbium-Beryllium Partial Constitutional Diagram.
Love (463).

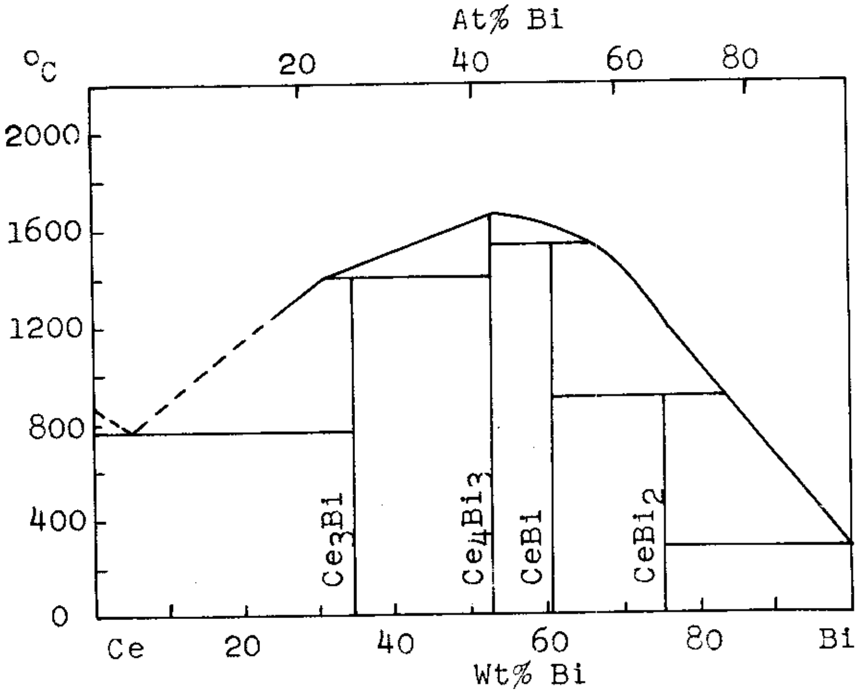

Figure 32. Cerium-Bismuth Constitutional Diagram (753). (339,882).

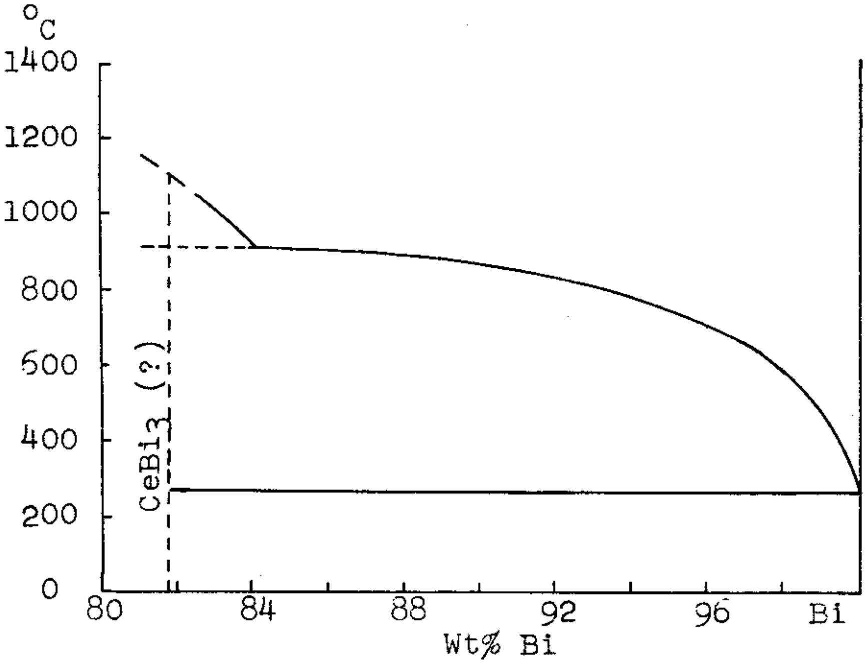

Figure 33. Cerium-Bismuth Partial Constitutional Diagram. Pleasance (643).

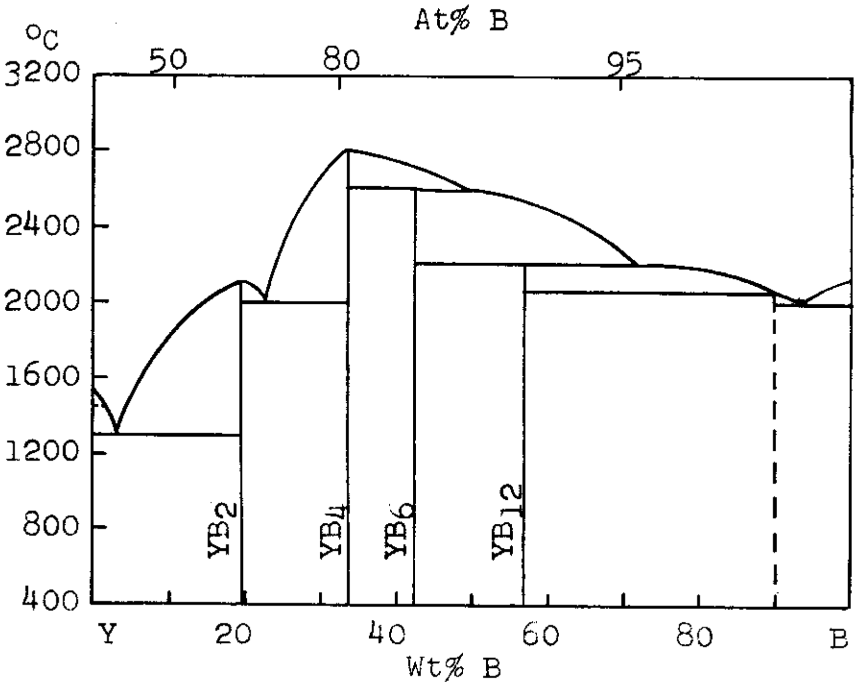

Figure 34. Yttrium-Boron Constitutional Diagram. Lundin and Klodt (471).

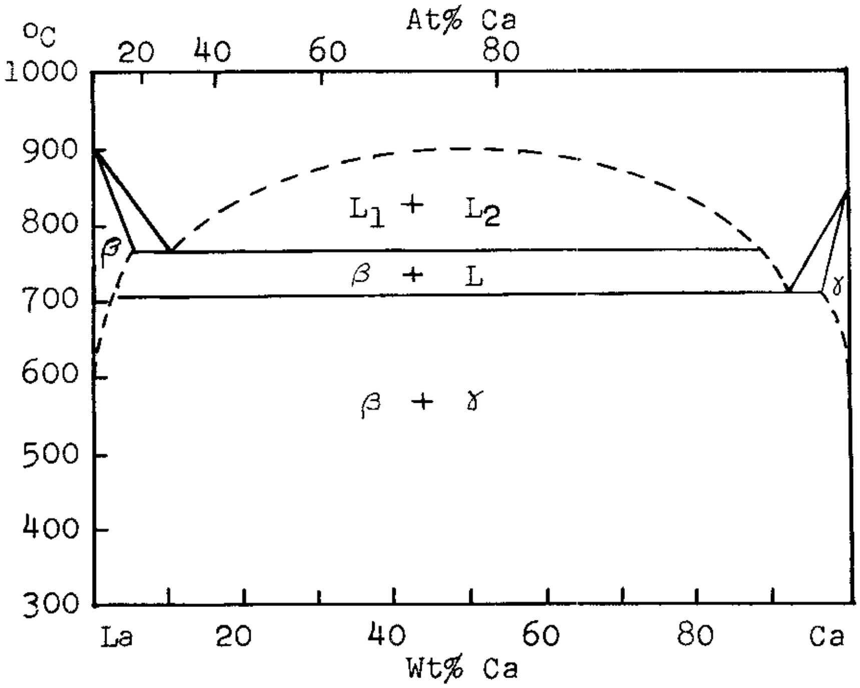

Figure 35. Lanthanum-Calcium Constitutional Diagram. Savitskii (712).

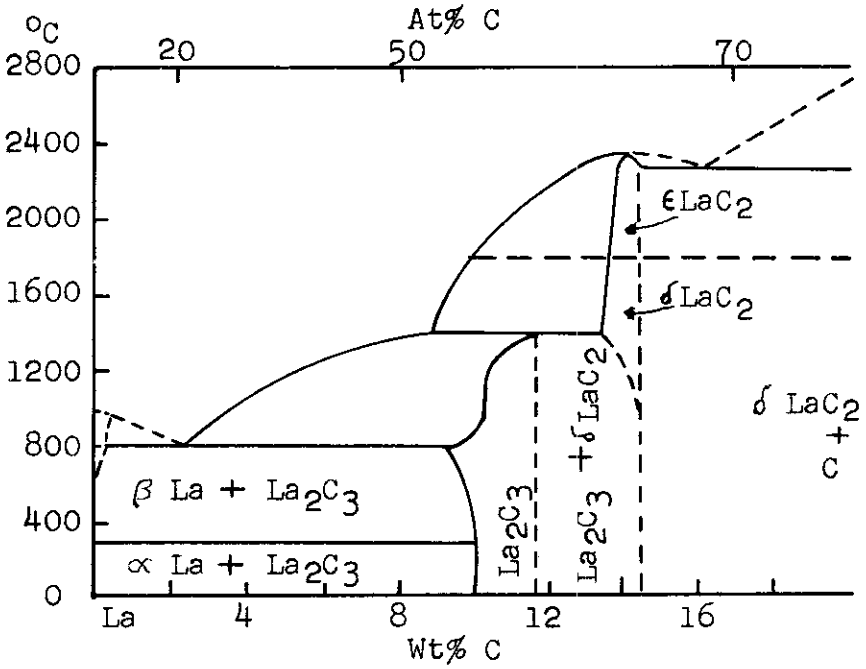

Figure 36. Lanthanum-Carbon Partial Constitutional Diagram. Spedding, Gschneidner, and Daane (774).

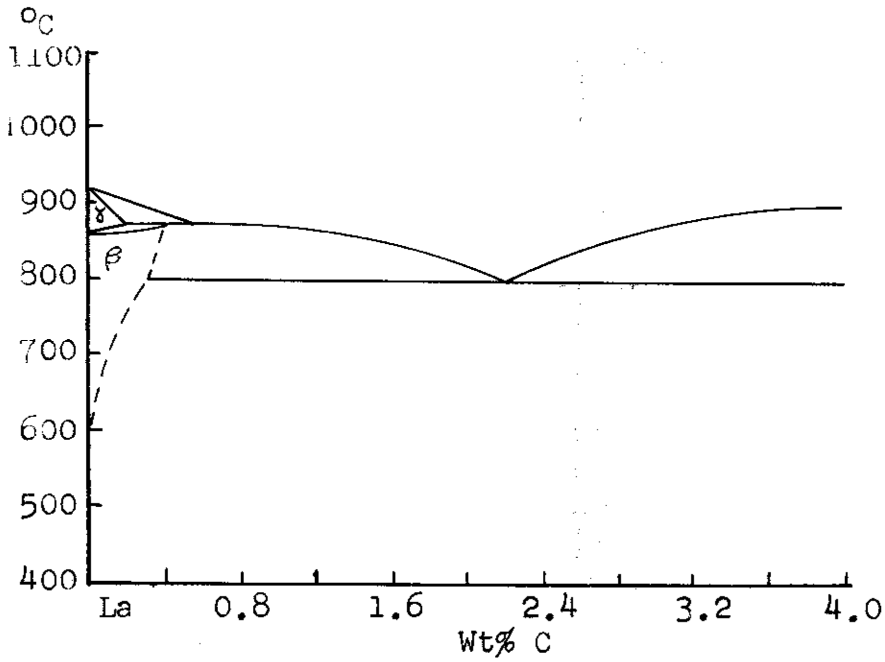

Figure 37. Lanthanum-Carbon Partial Constitutional Diagram. Spedding, Gschneidner, and Daane (774).

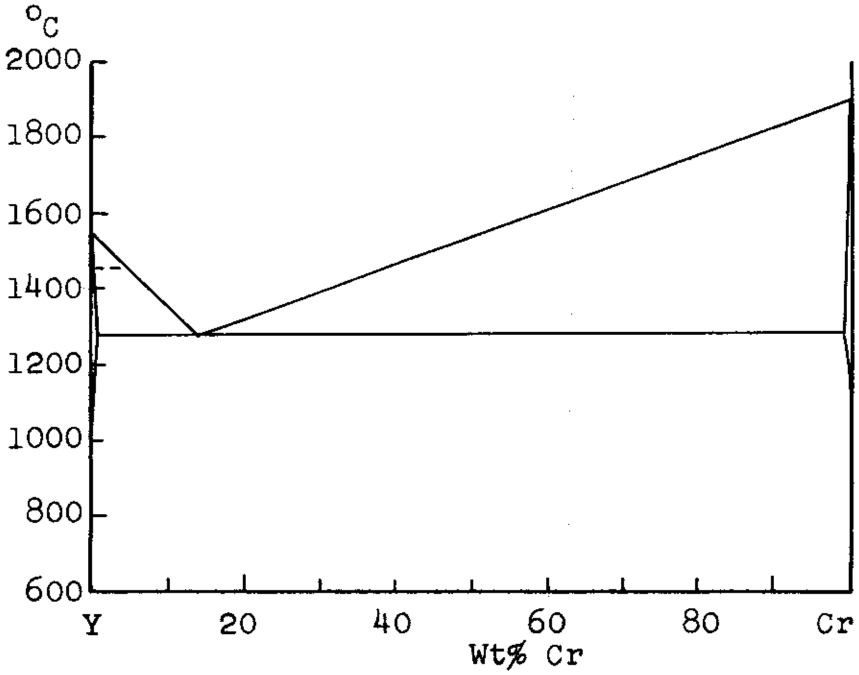

Figure 38. Yttrium-Chromium Constitutional Diagram. Lundin and Klodt (471).

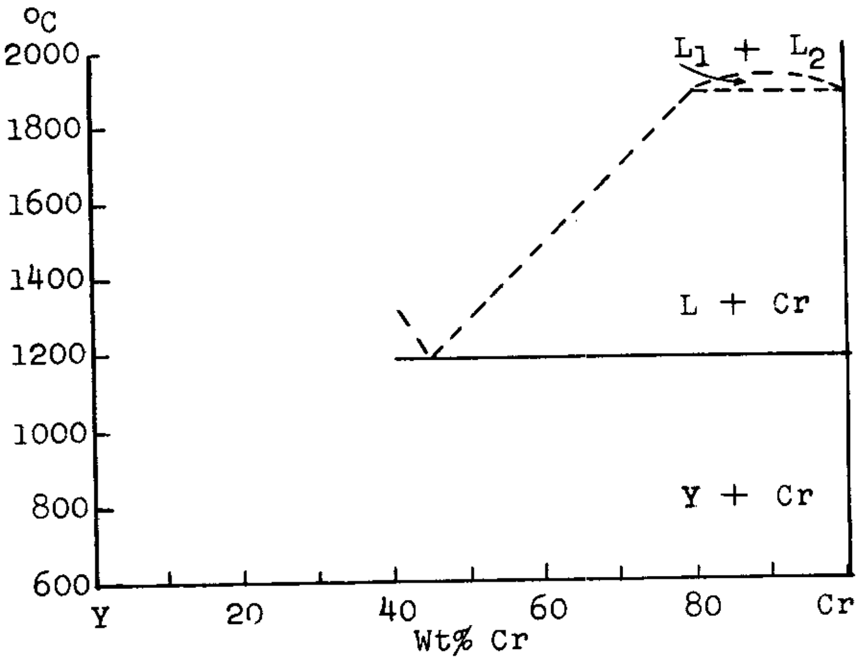

Figure 39. Yttrium-Chromium Tentative Partial Constitutional Diagram. Love (463).

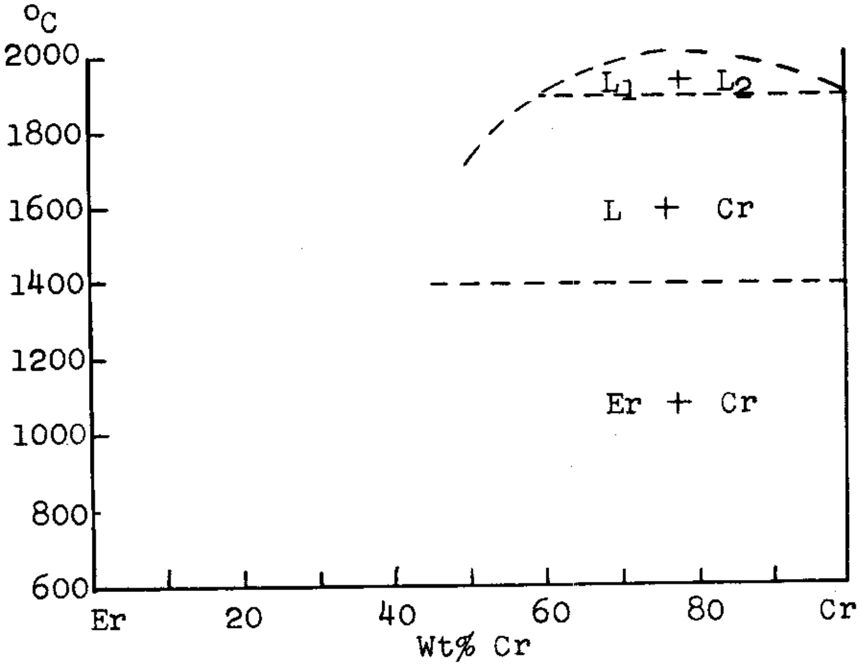

Figure 40. Erbium-Chromium Tentative Partial Constitutional Diagram. Love (463).

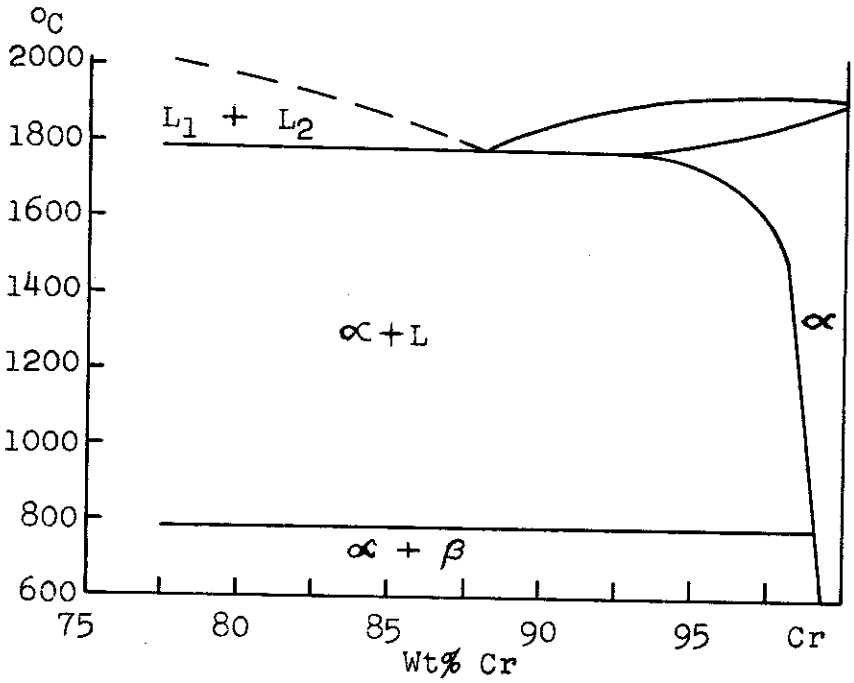

Figure 41. Cerium-Chromium Partial Constitutional Diagram. Savitskii (709).

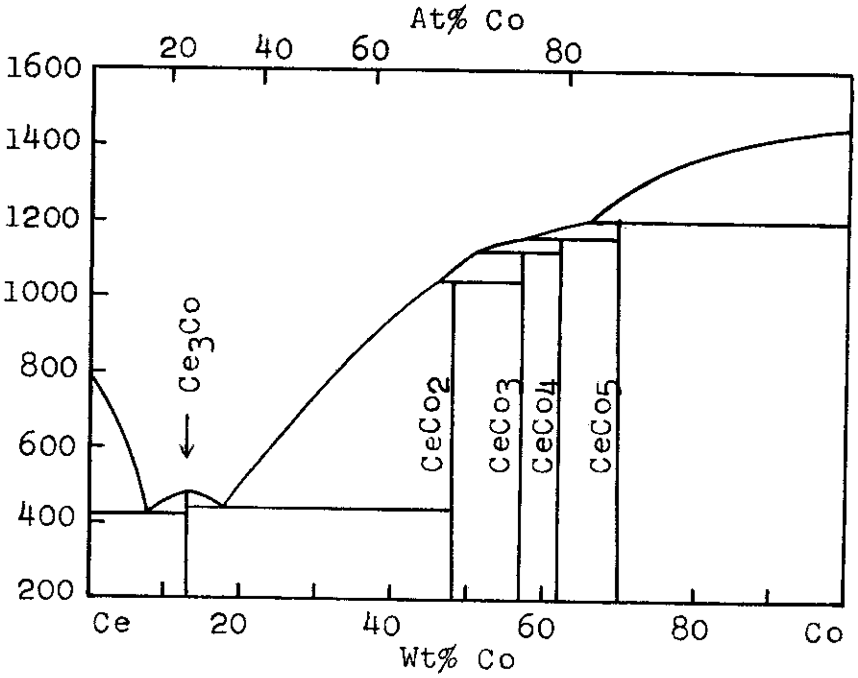

Figure 42. Cerium-Cobalt Constitutional Diagram (753). (219,878).

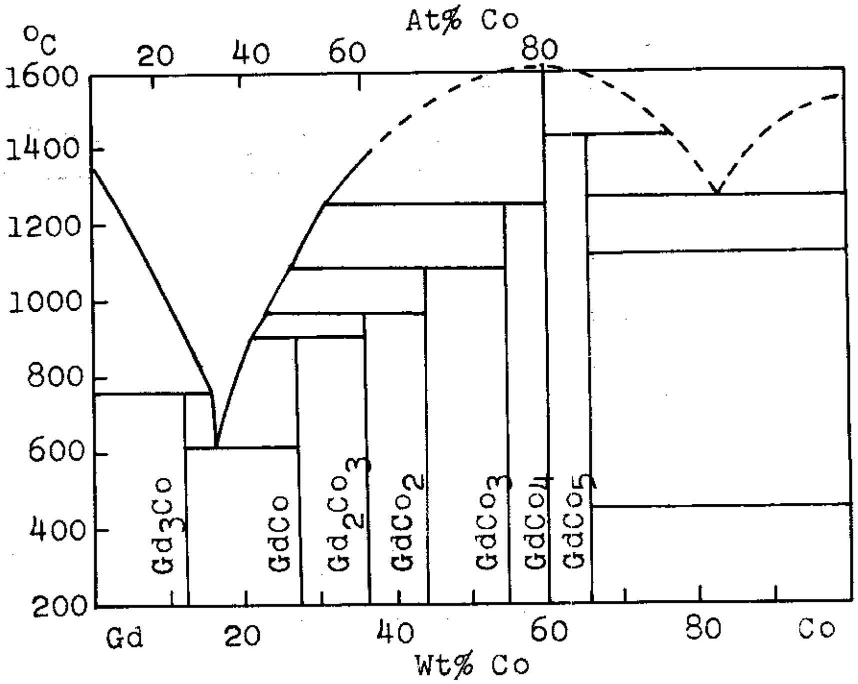

Figure 43. Gadolinium-Cobalt Constitutional Diagram. Vickery (674).

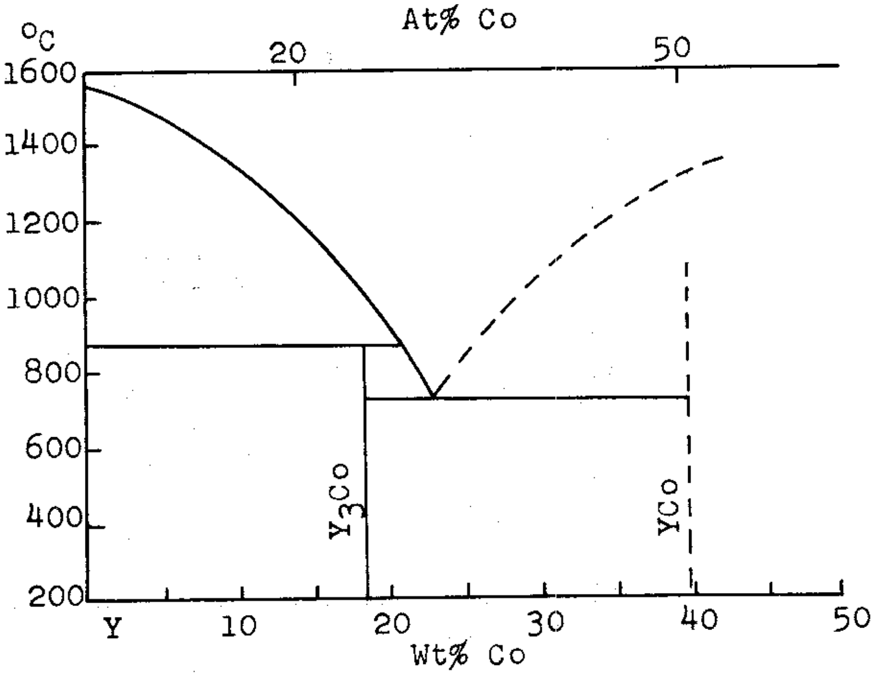

Figure 44. Yttrium-Cobalt Partial Constitutional Diagram. Love (463).

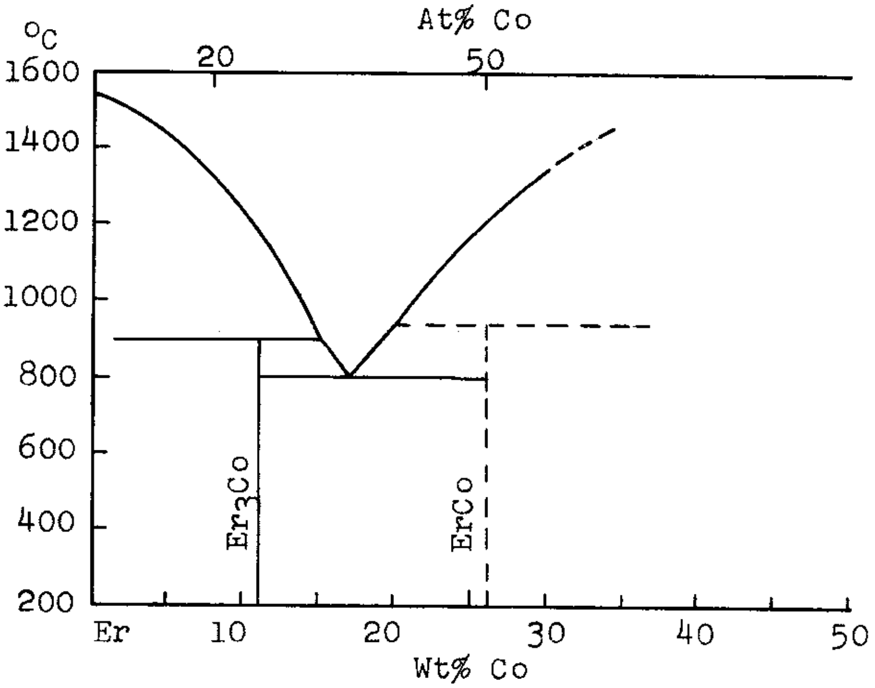

Figure 45. Erbium-Cobalt Partial Constitutional Diagram. Love (463).

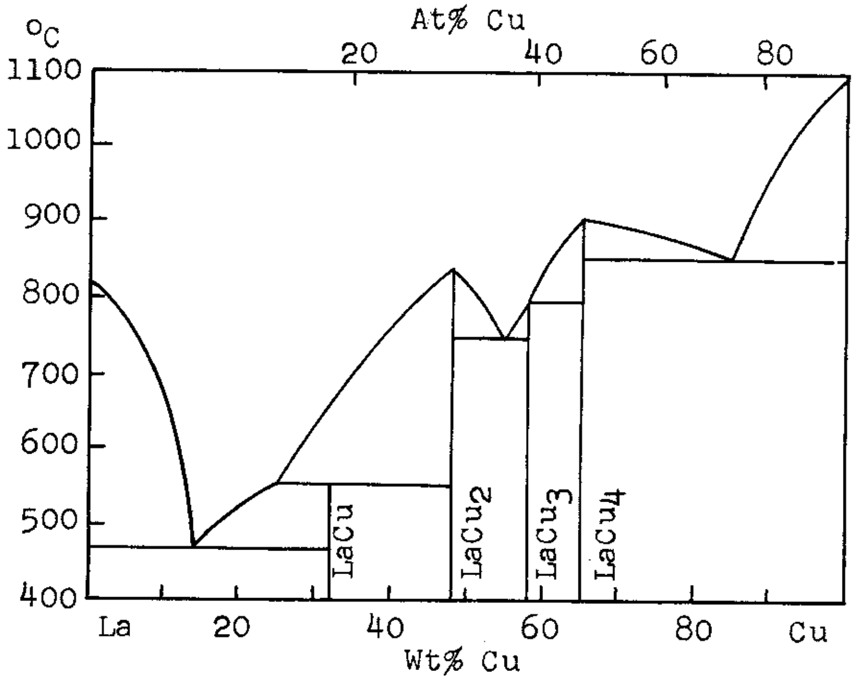

Figure 46. Lanthanum-Copper Constitutional Diagram (753). (110,596,879,886).

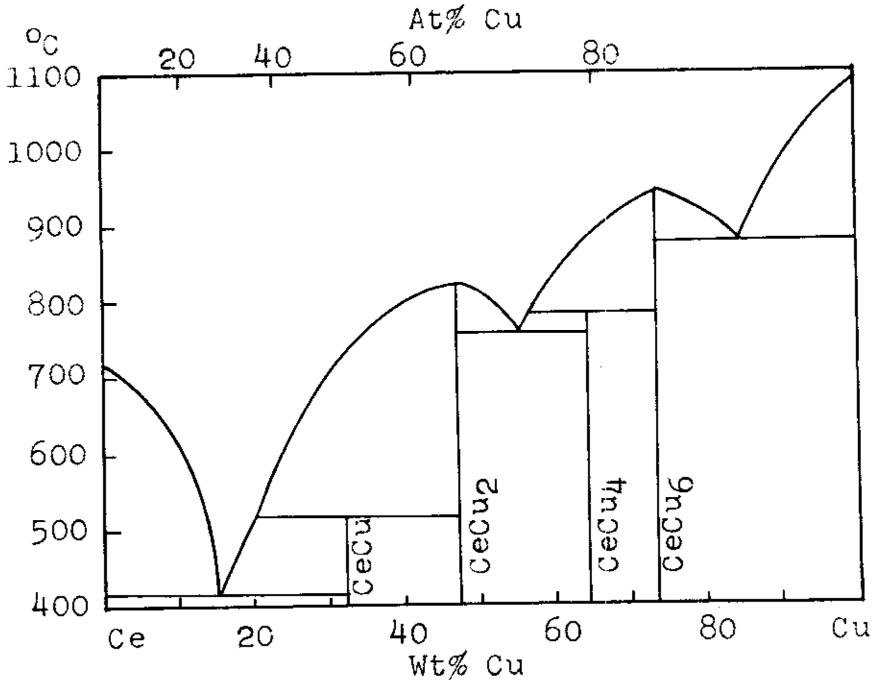

Figure 47. Cerium-Copper Constitutional Diagram (753). (287).

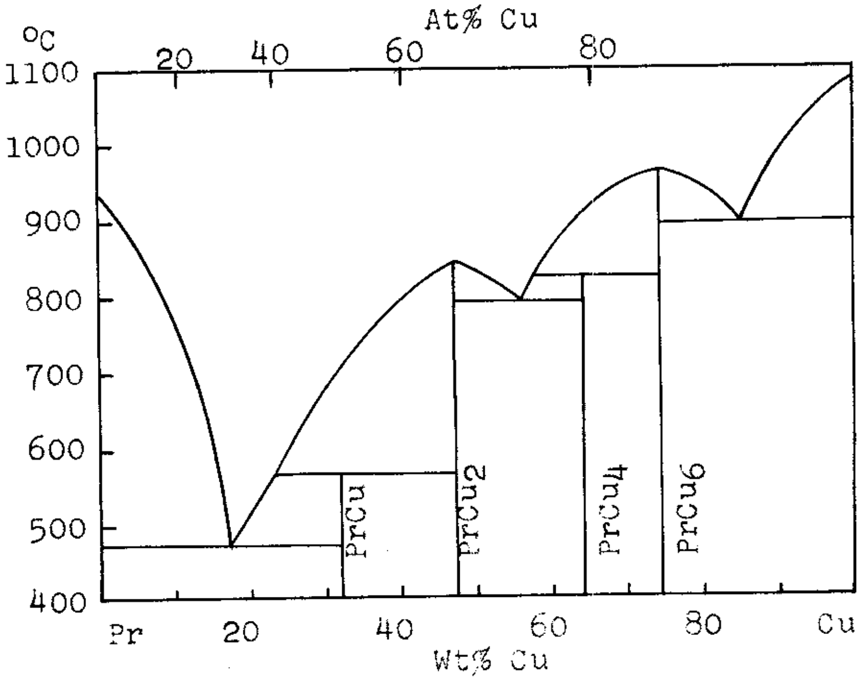

Figure 48. Praseodymium-Copper Constitutional Diagram (753). (114).

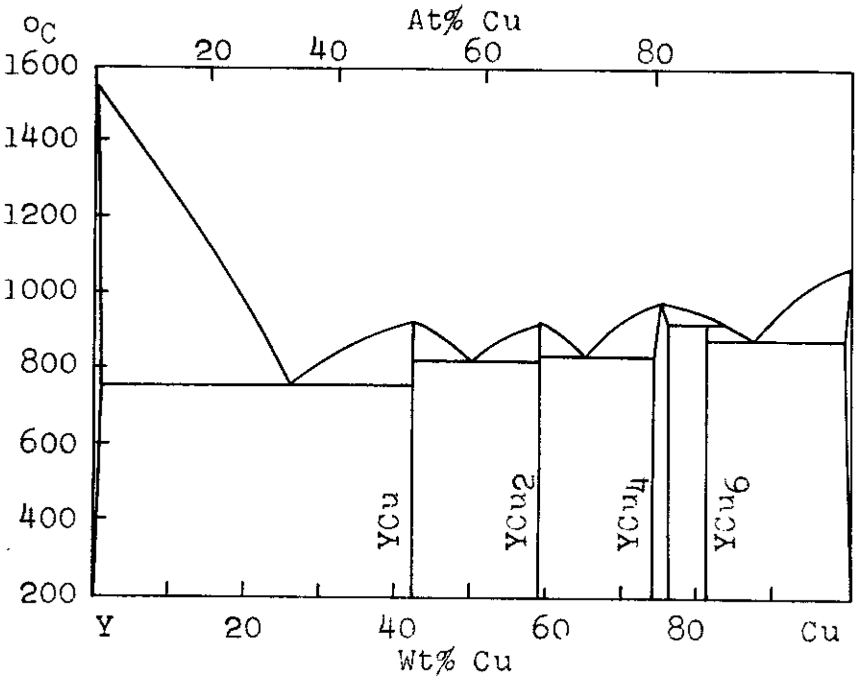

Figure 49. Yttrium-Copper Constitutional Diagram. Domagala, Rausch, and Levinson (161).

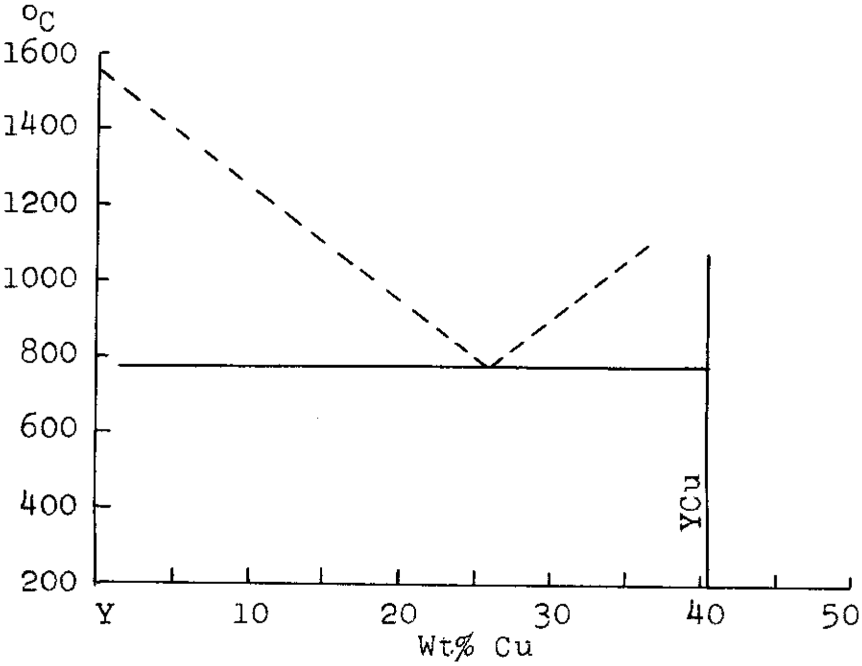

Figure 50. Yttrium-Copper Partial Constitutional Diagram. Love (463).

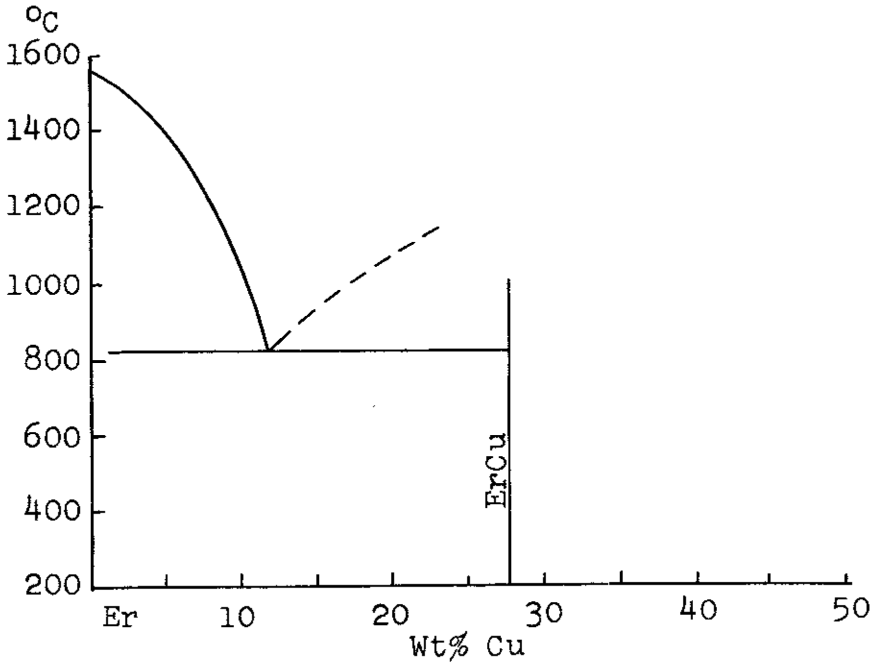

Figure 51. Erbium-Copper Partial Constitutional Diagram. Love (463).

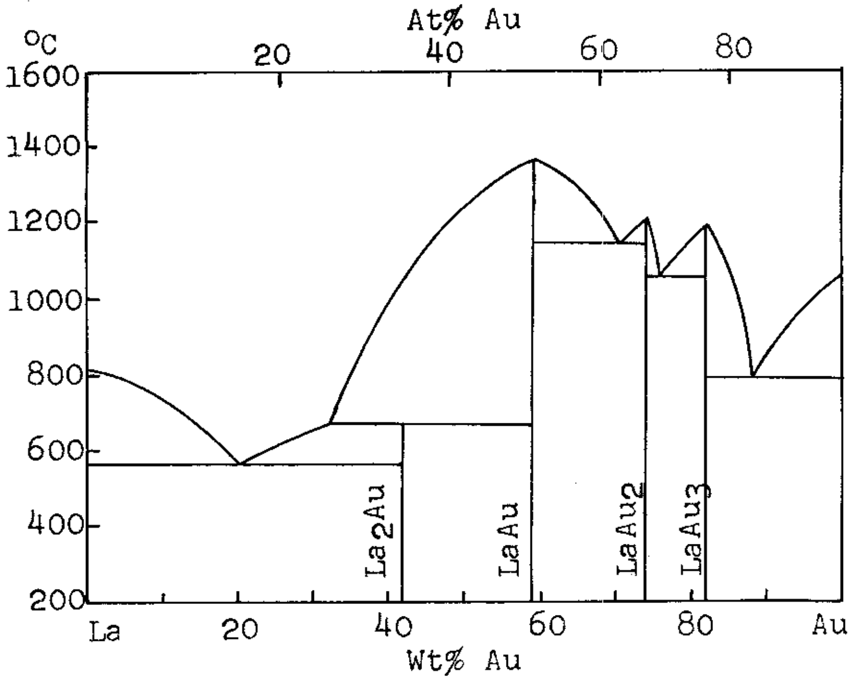

Figure 52. Lanthanum-Gold Constitutional Diagram (753). (64,110).

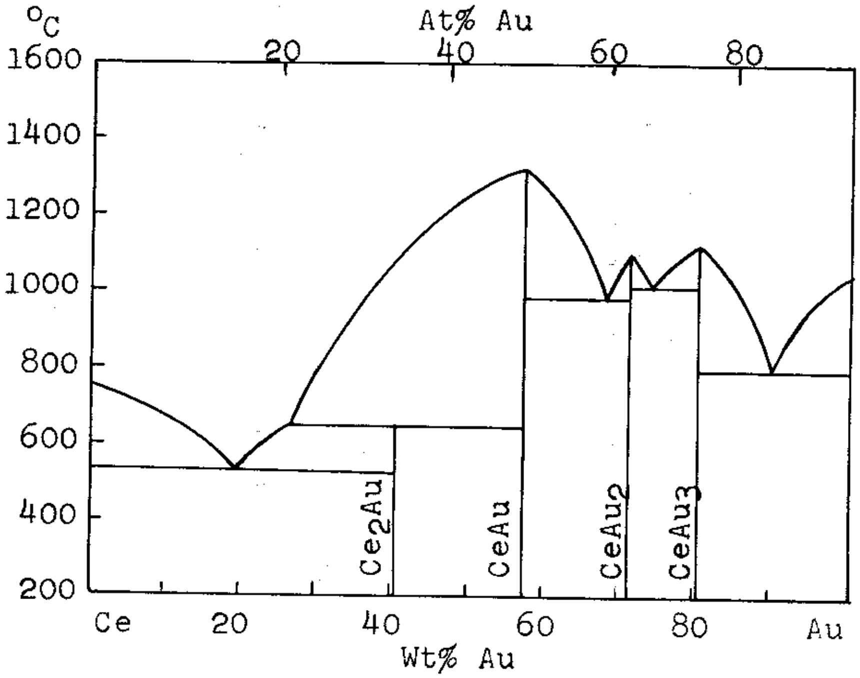

Figure 53. Cerium-Gold Constitutional Diagram (753). (879,886).

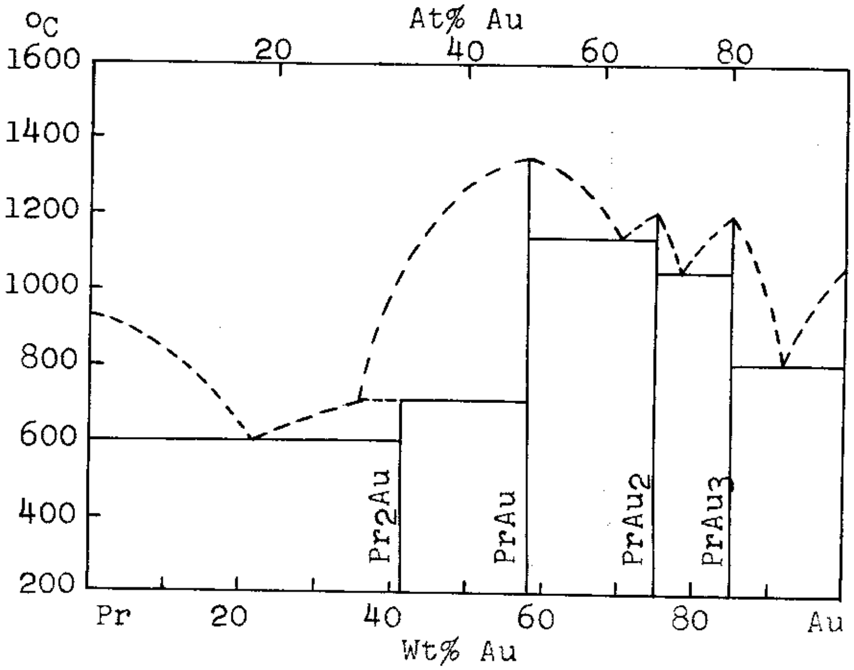

Figure 54. Praseodymium-Gold Constitutional Diagram (753). (690,879,886).

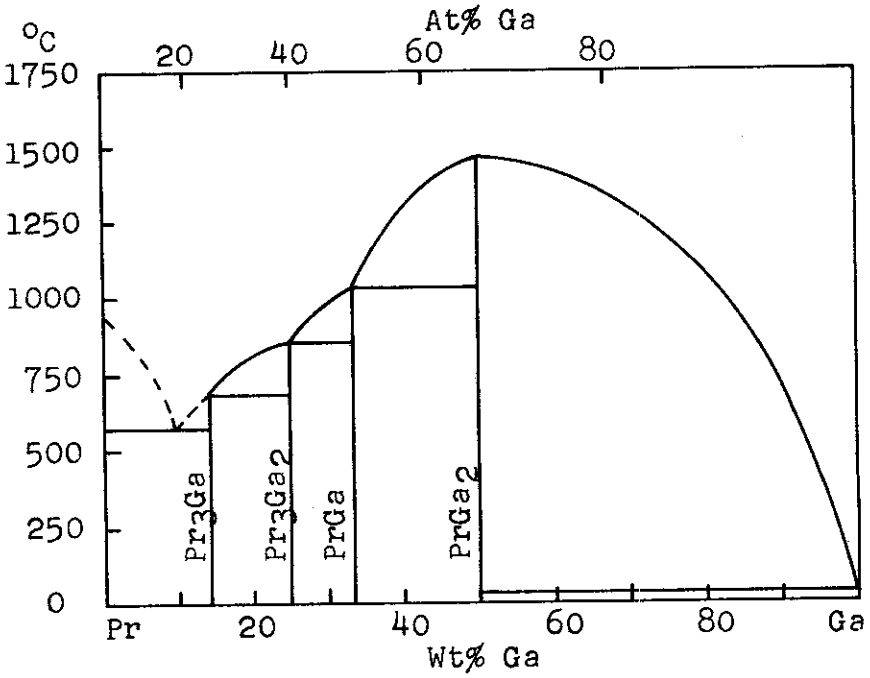

Figure 55. Praseodymium-Gallium Constitutional Diagram (753). (336).

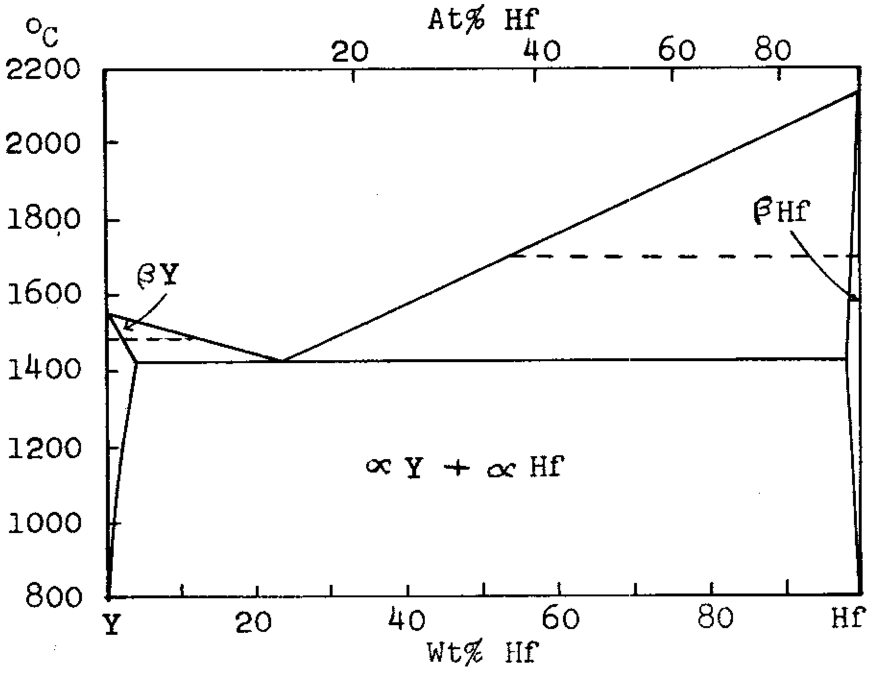

Figure 56. Yttrium-Hafnium Constitutional Diagram. Lundin and Klodt (471).

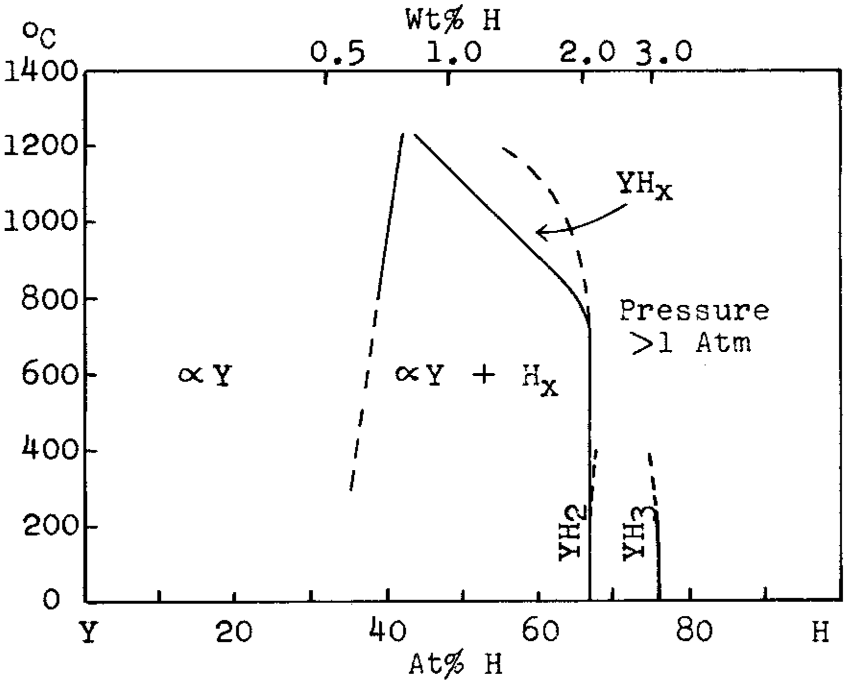

Figure 57. Yttrium-Hydrogen Constitutional Diagram. Lundin and Blackledge (470).

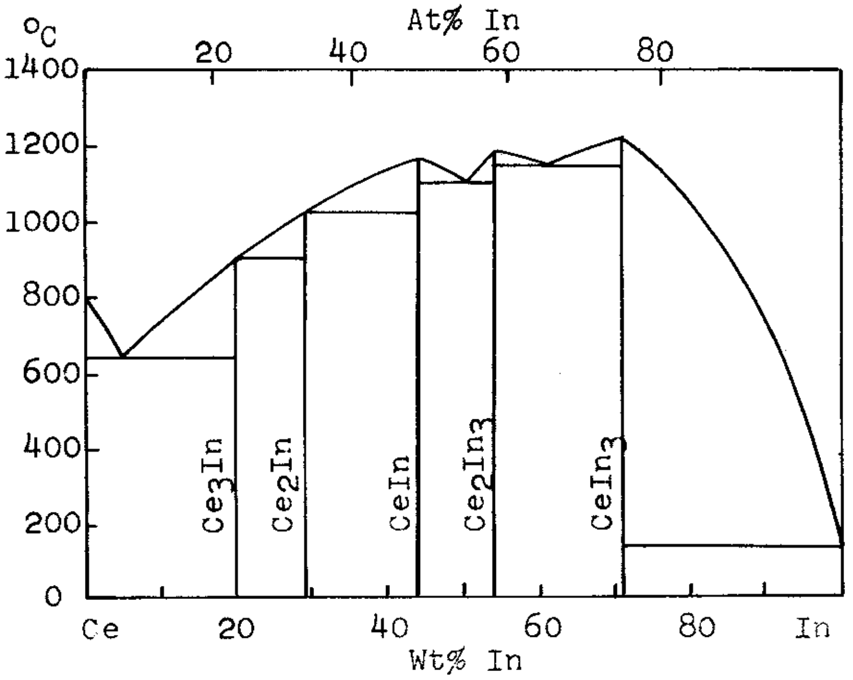

Figure 58. Cerium-Indium Constitutional Diagram (753). (888).

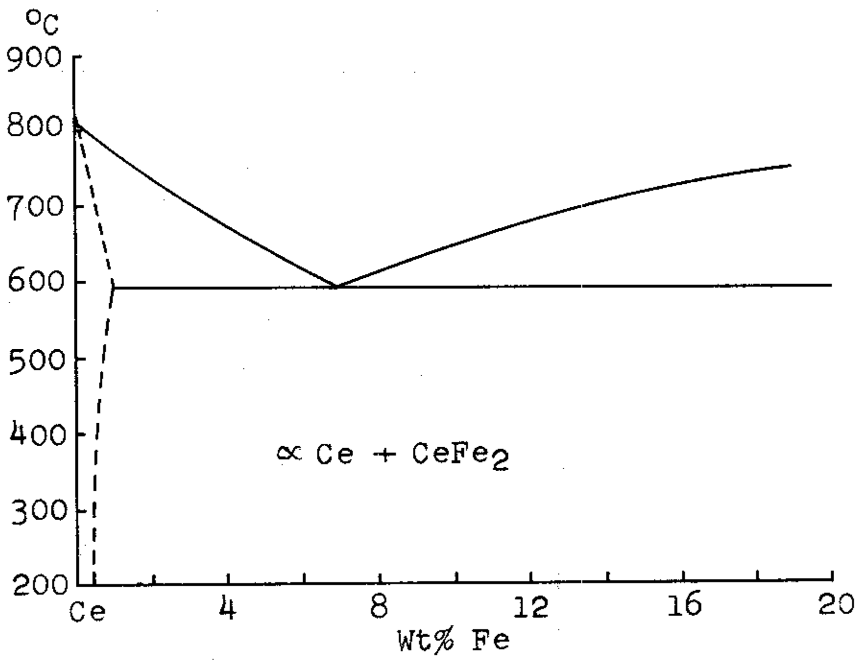

Figure 59. Cerium-Iron Partial Constitutional Diagram.

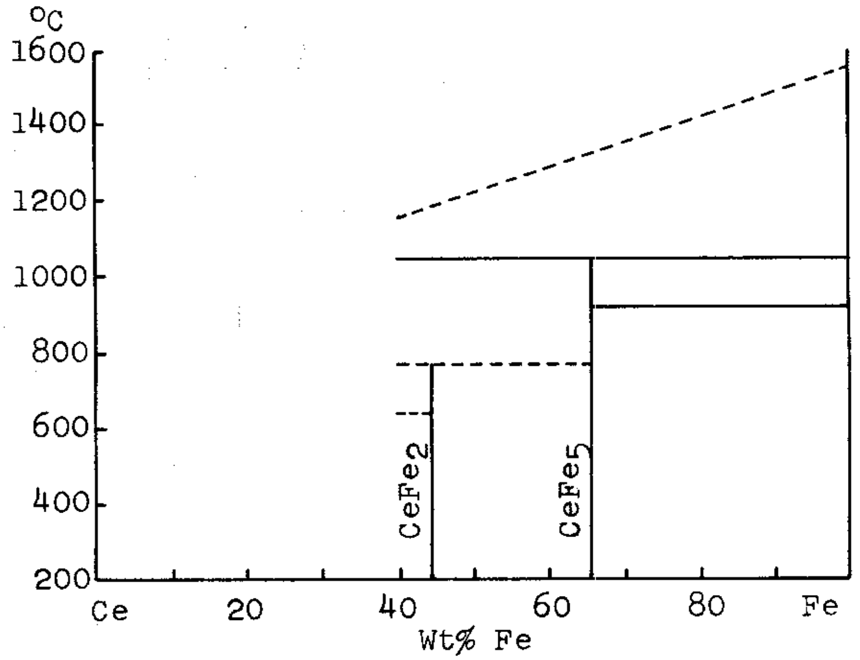

Figure 60. Cerium-Iron Partial Constitutional Diagram Jepson and Duwez (364).

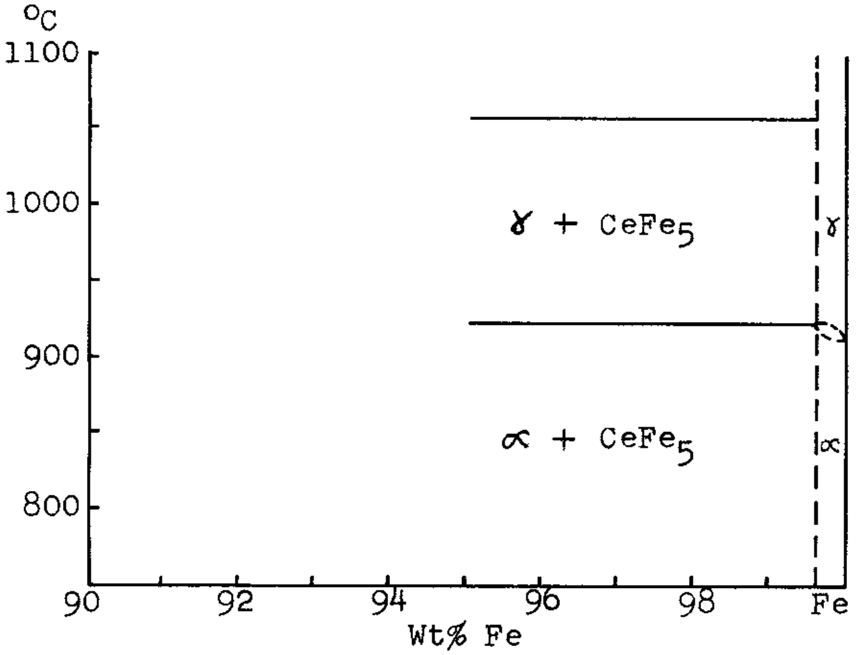

Figure 61. Cerium-Iron Partial Constitutional Diagram. Jepson and Duwez (364).

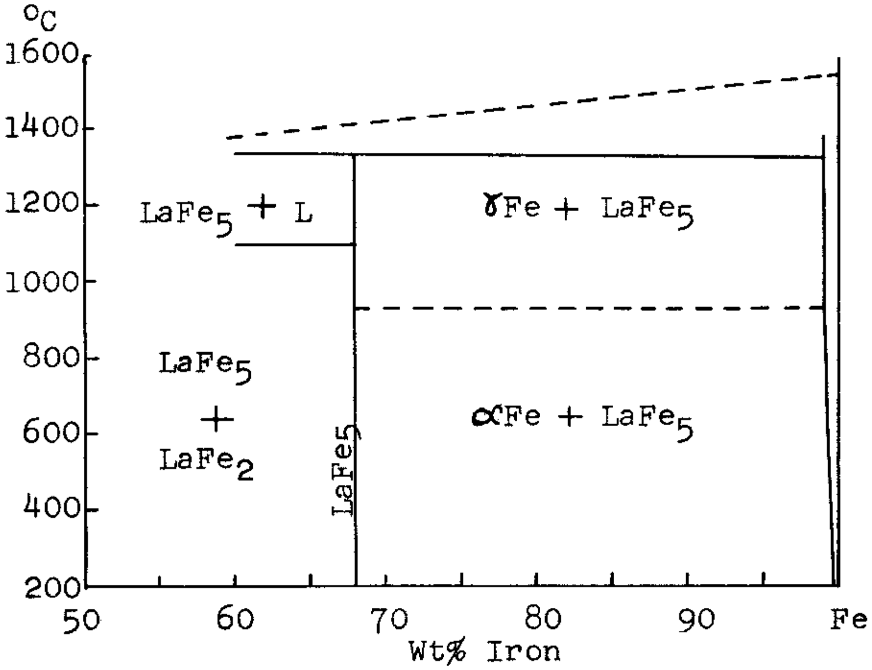

Figure 62. Lanthanum-Iron Partial Constitutional Diagram. Savitskii (709).

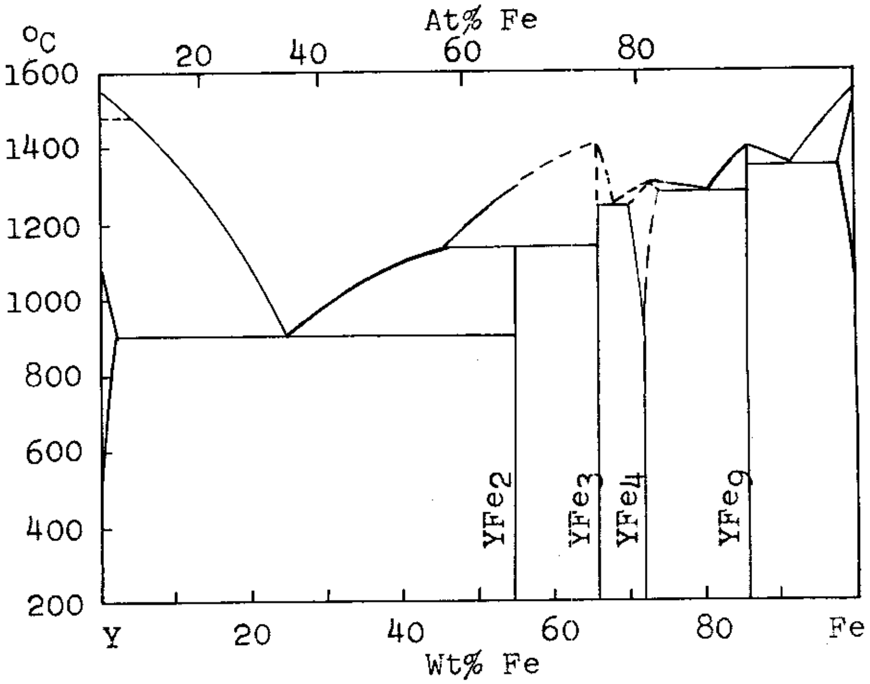

Figure 63. **Yttrium-Iron Constitutional Diagram.** Domagala, Rausch, and Levinson (161).

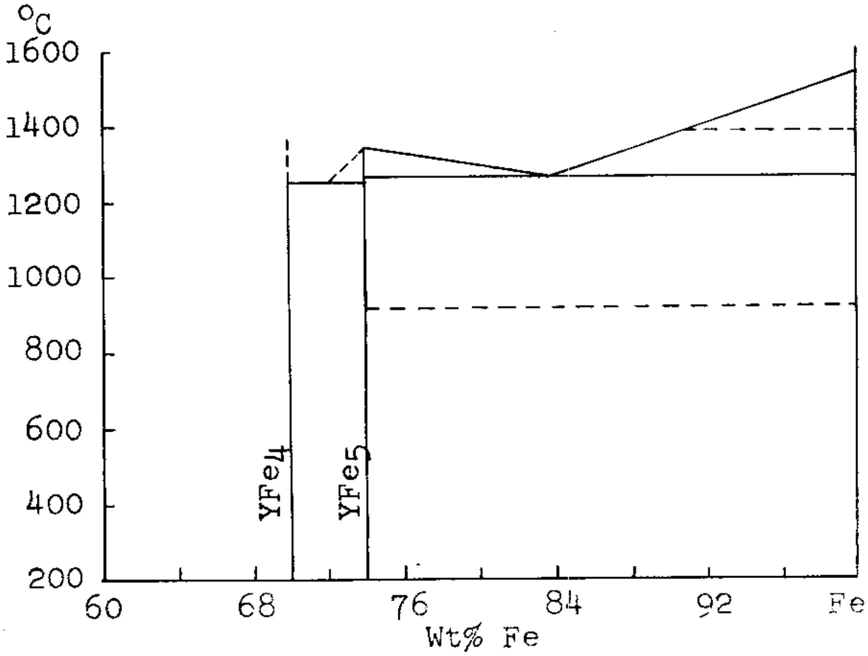

Figure 64. **Yttrium-Iron Tentative Partial Constitutional Diagram.** Farkas and Bauer (194).

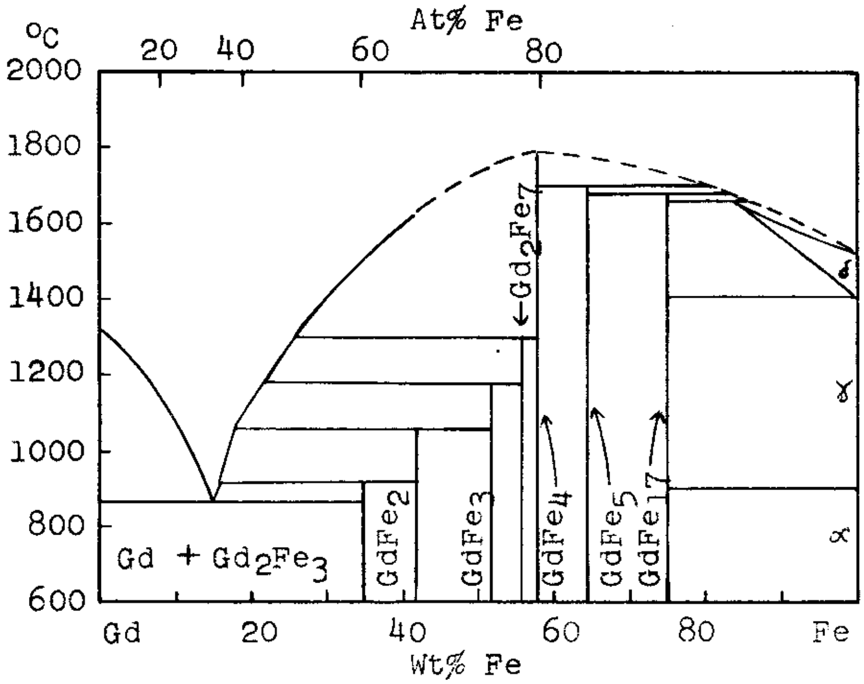

Figure 65. Gadolinium-Iron Constitutional Diagram. Vickery (674).

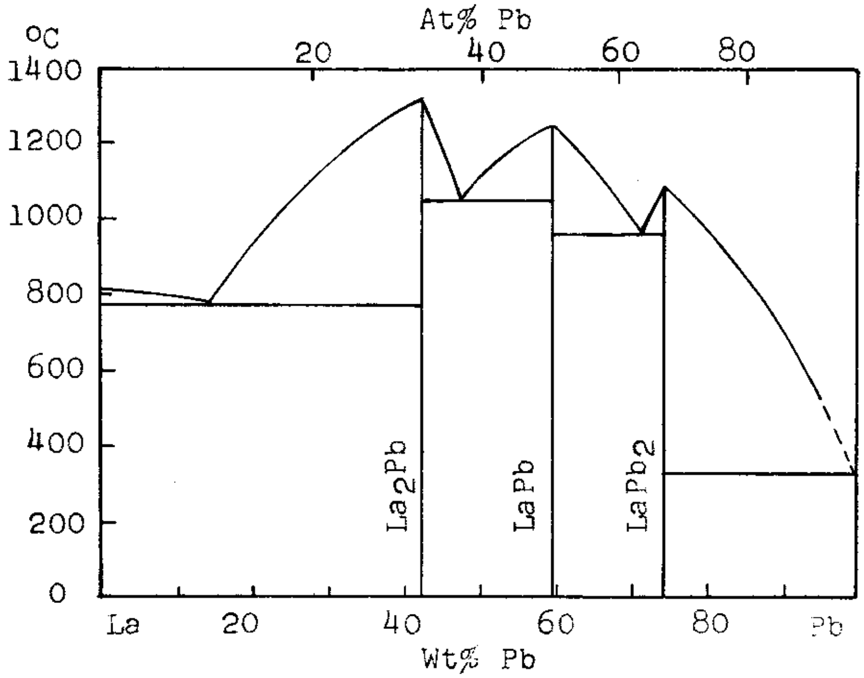

Figure 66. Lanthanum-Lead Constitutional Diagram (753). (110,689,691,879,886).

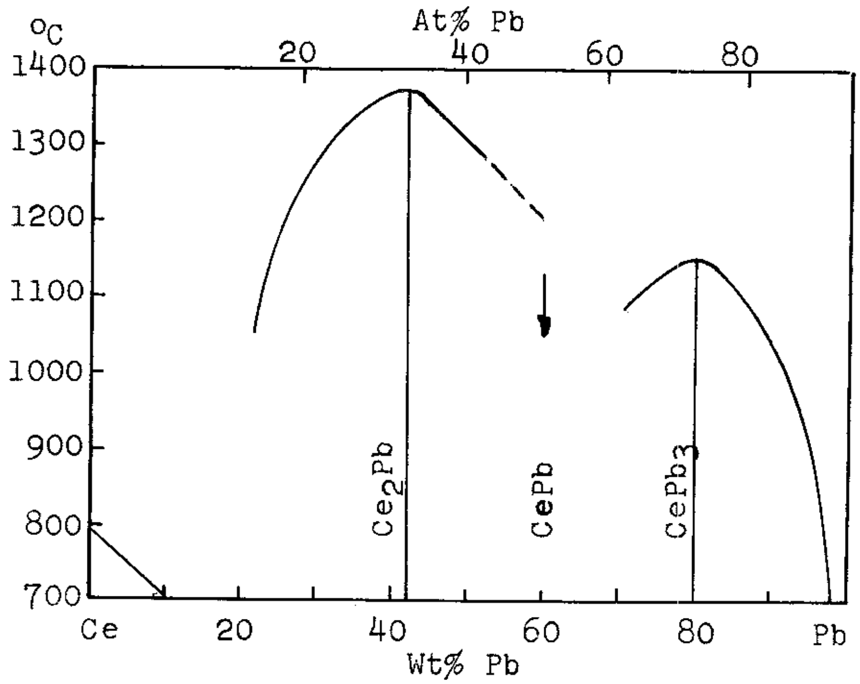

Figure 67. Cerium-Lead Partial Constitutional Diagram (753). (879,880,886,938).

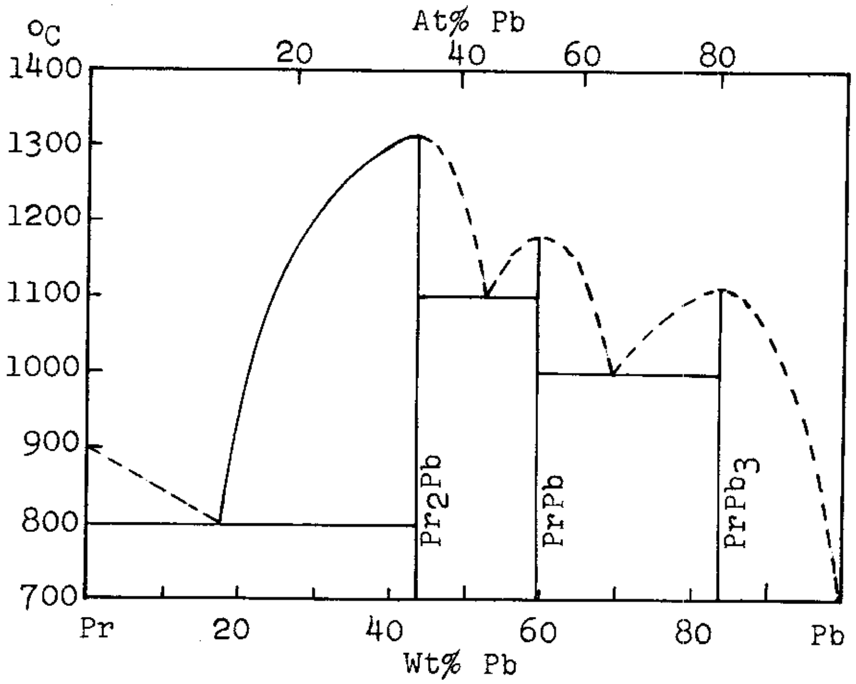

Figure 68. Praseodymium-Lead Constitutional Diagram (753). (691,879,886).

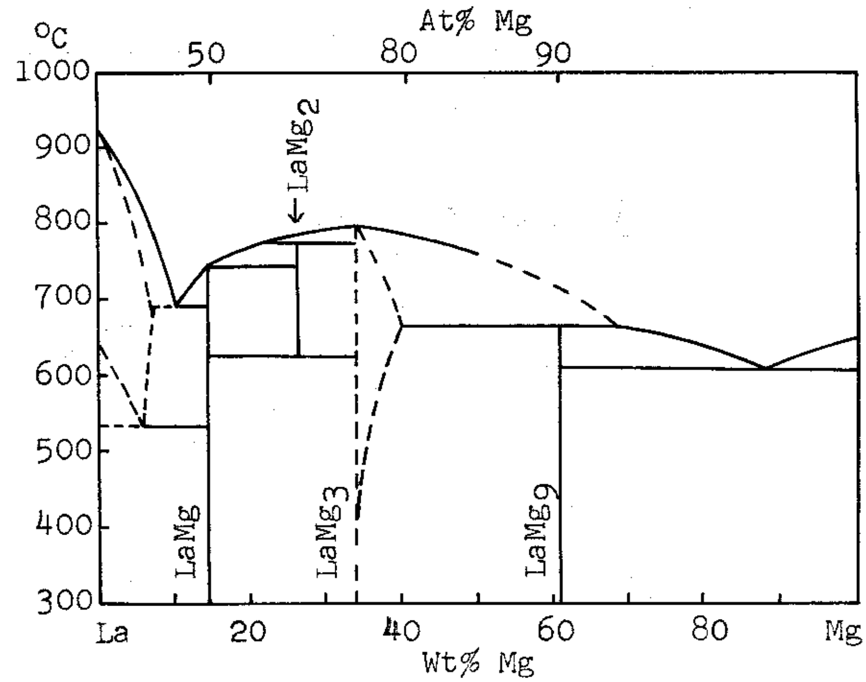

Figure 69. Lanthanum-Magnesium Constitutional Diagram (279). (433,446,886,887,898,101)

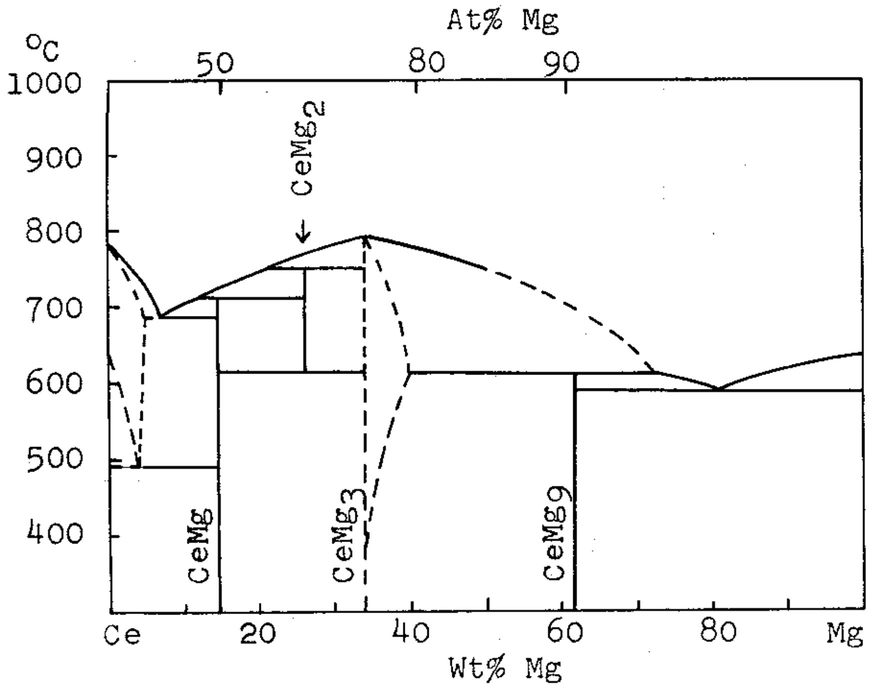

Figure 70. Cerium-Magnesium Constitutional Diagram (279). (164,289,443,500,504,883,887,898).

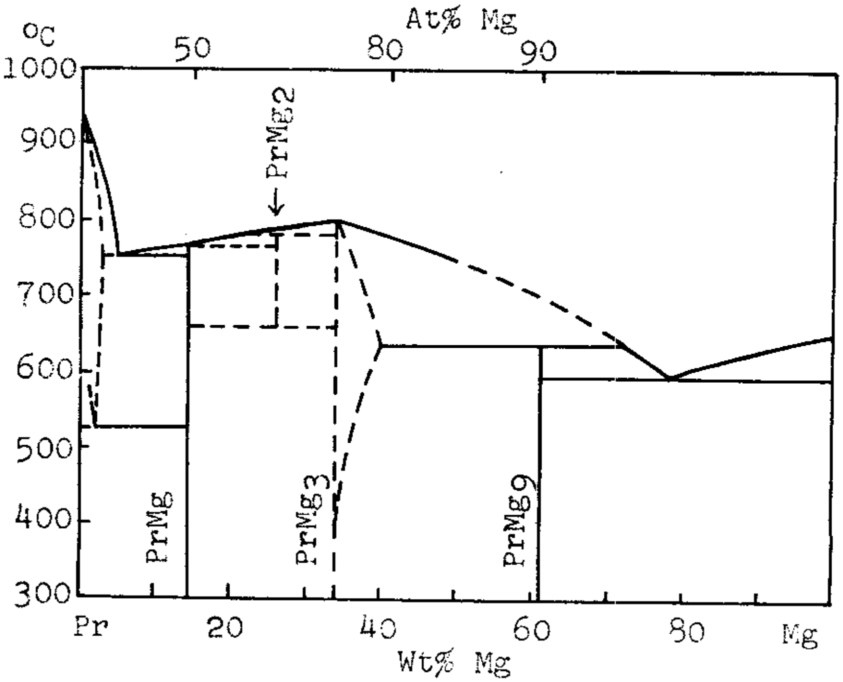

Figure 71. Praseodymium-Magnesium Constitutional Diagram (279). (112,886,887).

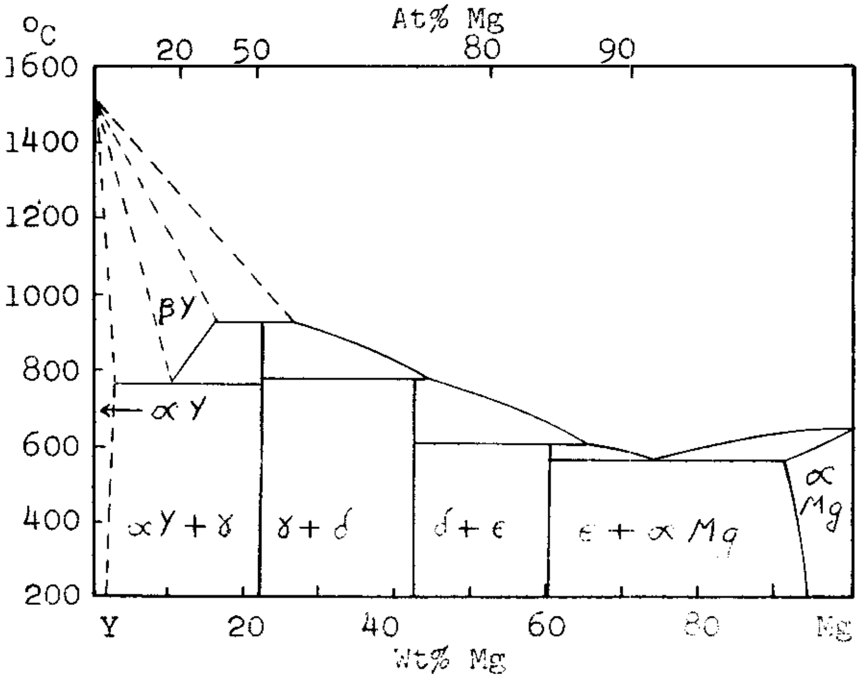

Figure 72. Yttrium-Magnesium Constitutional Diagram, Gibson and Carlson (239).

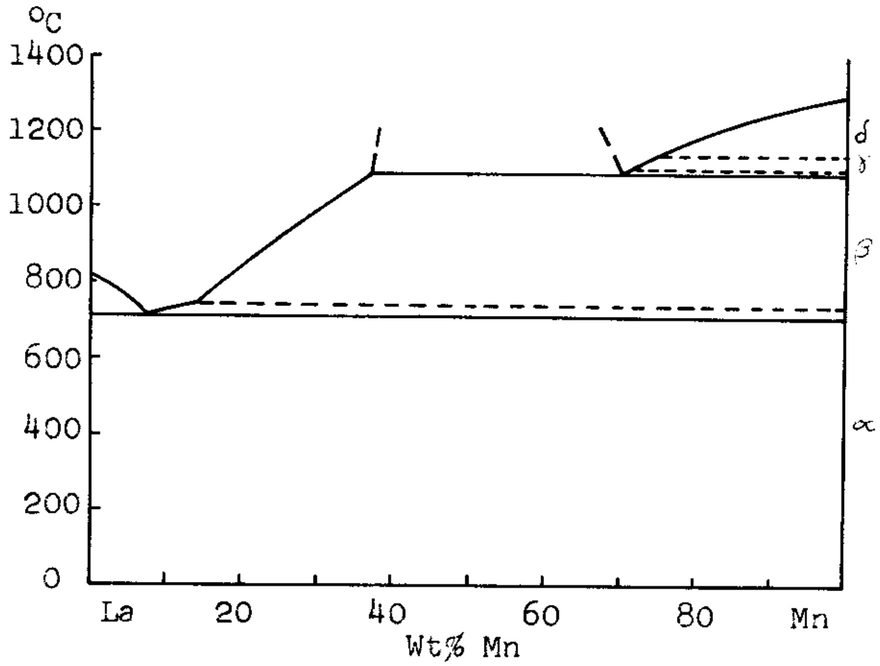

Figure 73. Lanthanum-Manganese Constitutional Diagram (279). (684,736).

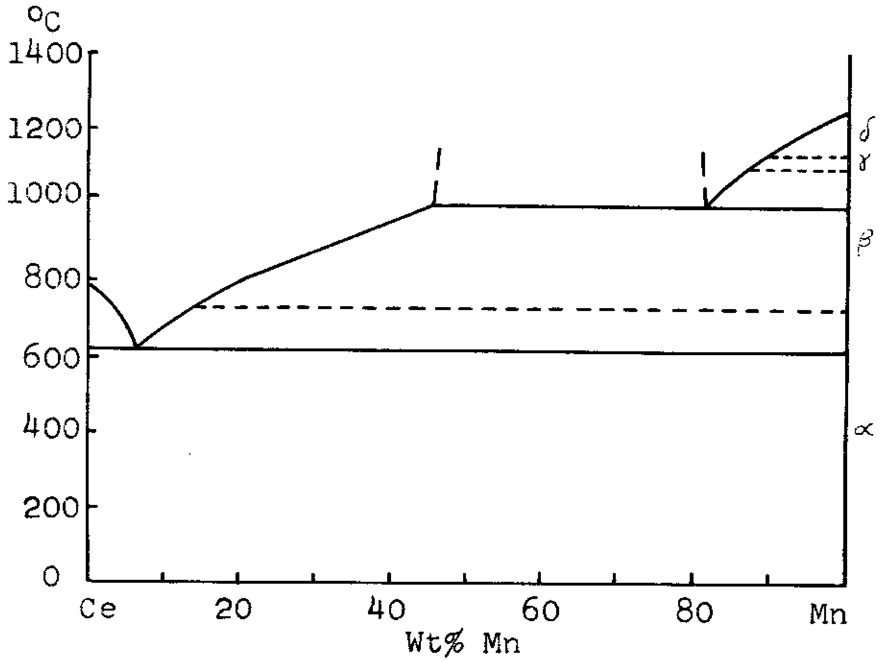

Figure 74. Cerium-Manganese Constitutional Diagram (279). (335,684).

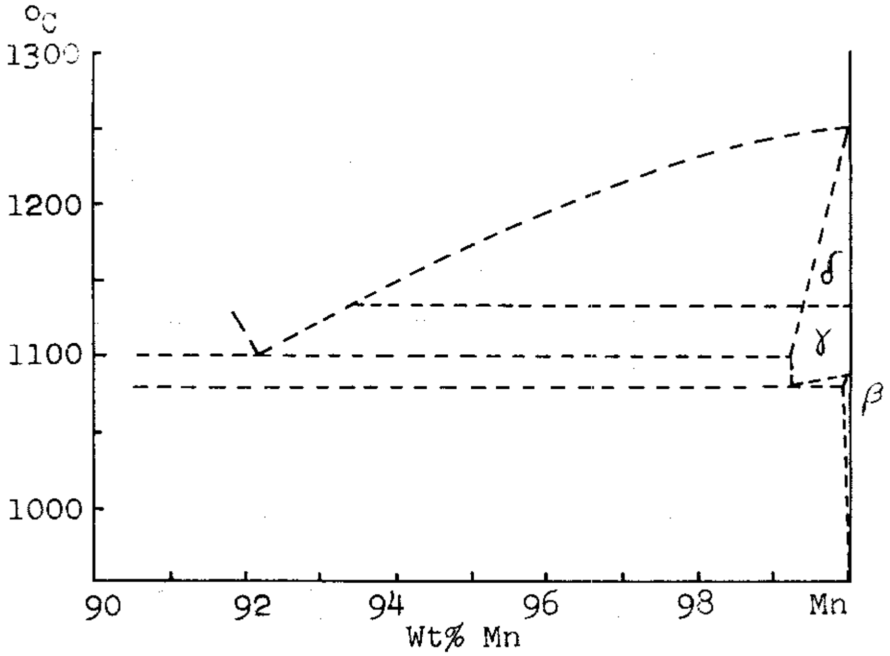

Figure 75. Yttrium-Manganese Partial Constitutional Diagram. Hellawell (297).

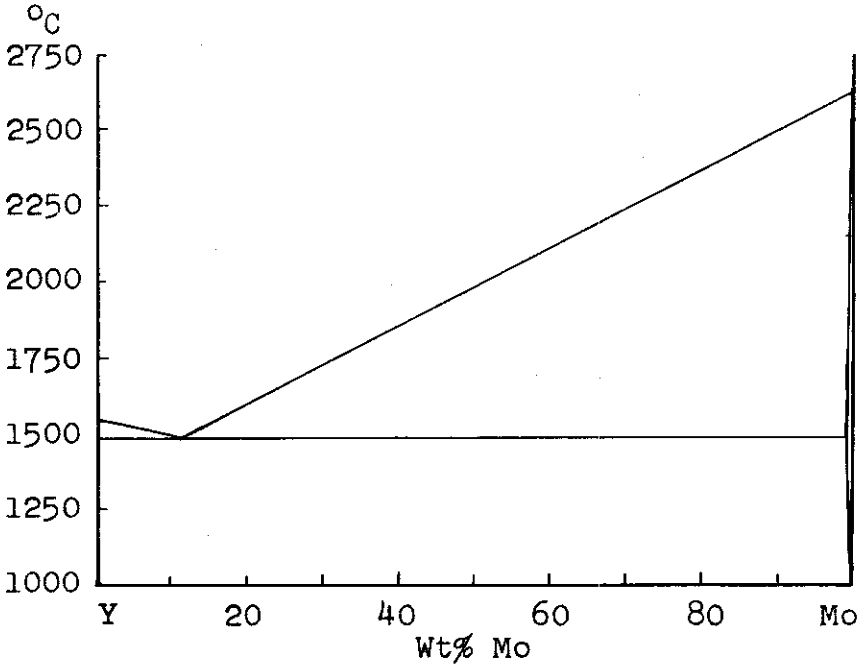

Figure 76. Yttrium-Molybdenum Constitutional Diagram. Lundin and Klodt (471).

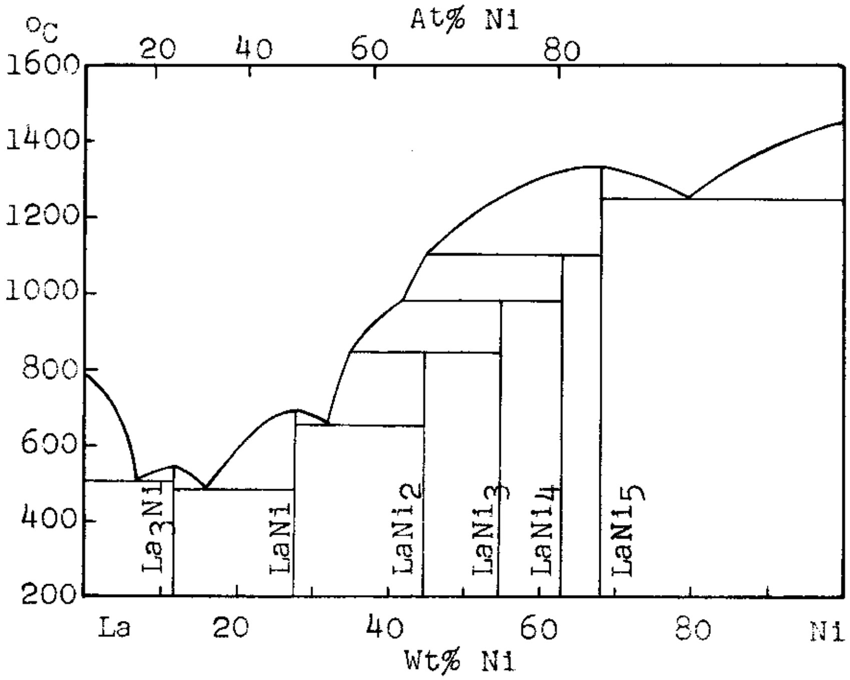

Figure 77. Lanthanum-Nickel Constitutional Diagram (753). (596,878,924).

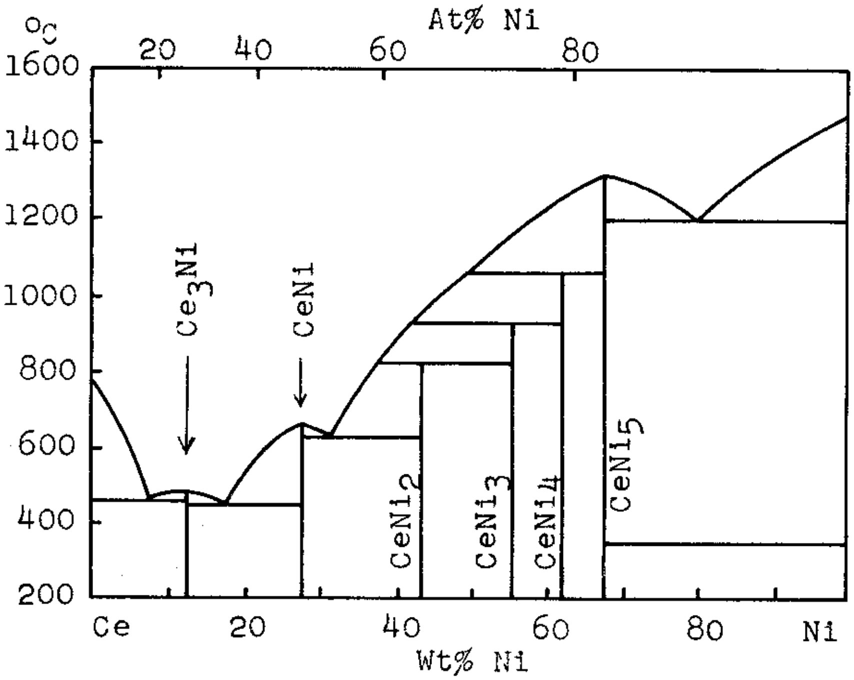

Figure 78. Cerium-Nickel Constitutional Diagram (753). (219,596,878).

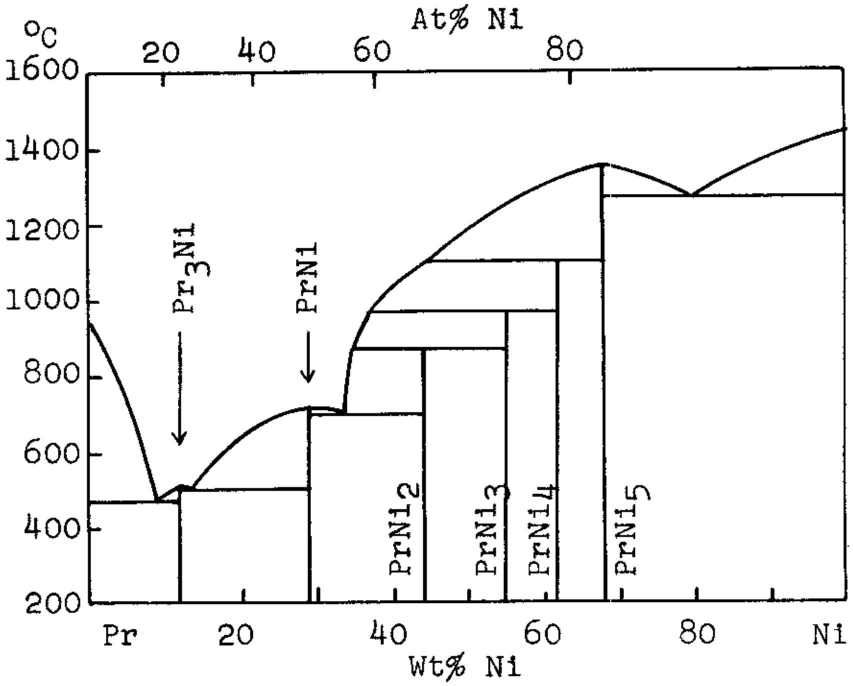

Figure 79. Praseodymium-Nickel Constitutional Diagram (753). (878).

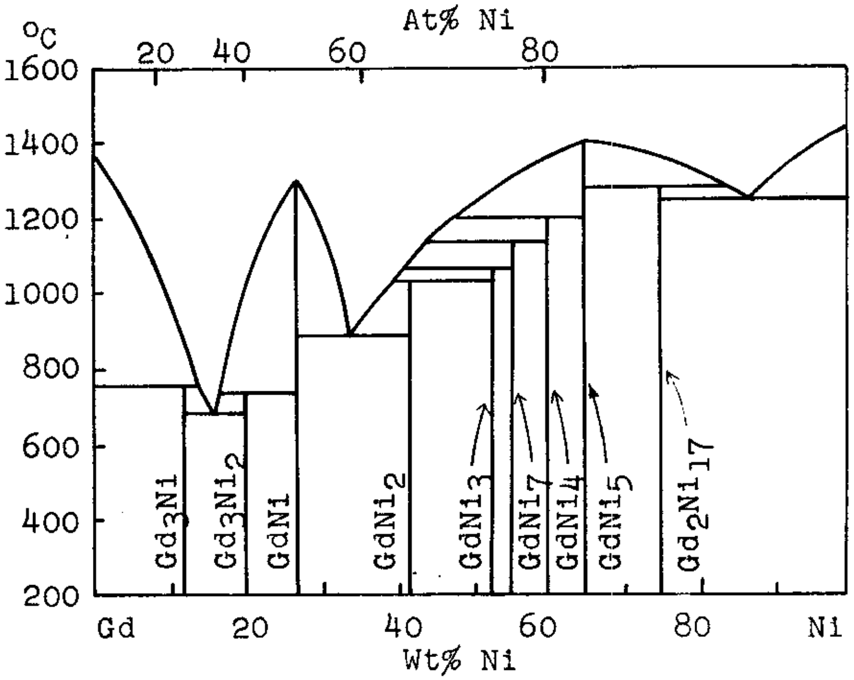

Figure 80. Gadolinium-Nickel Constitutional Diagram. Vickery (674).

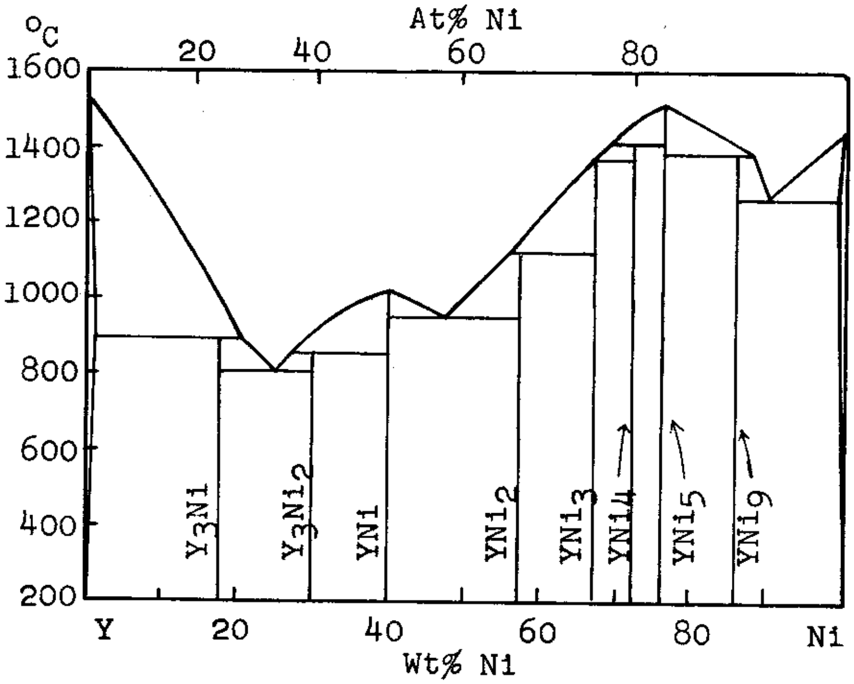

Figure 81. Yttrium-Nickel Constitutional Diagram. Domagala, Rausch, and Levinson (161).

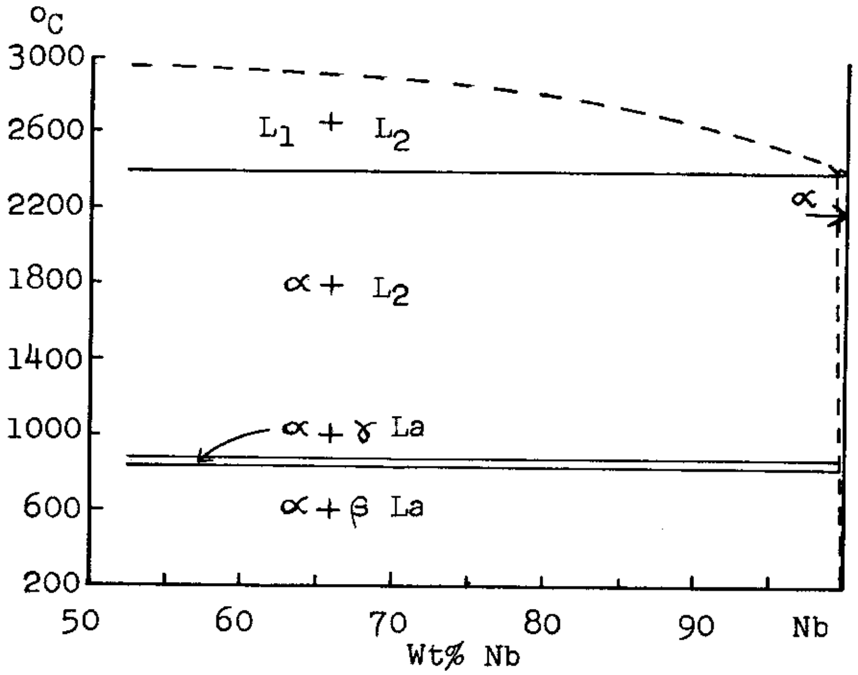

Figure 82. Lanthanum-Niobium Partial Consitutional Diagram. Savitskii, Terekhova, and Burov (713).

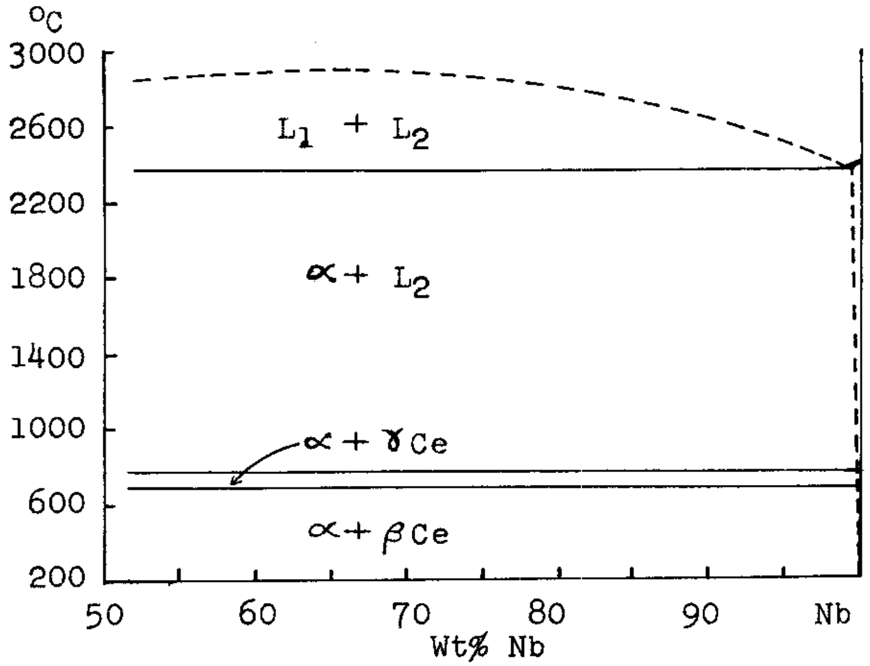

Figure 83. Cerium-Niobium Partial Constitutional Diagram. Savitskii, Terekhova, and Burov (713).

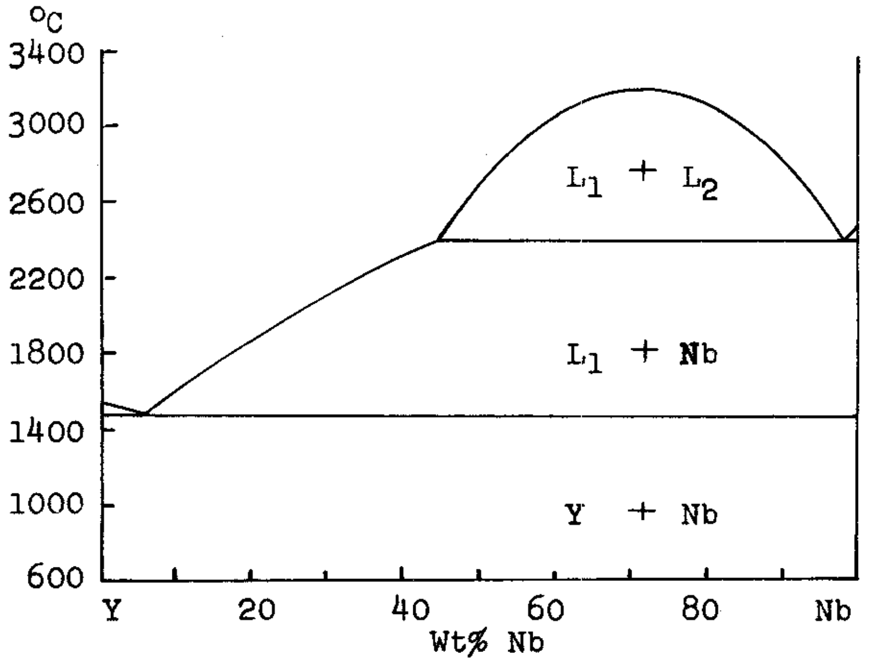

Figure 84. Yttrium-Niobium Constitutional Diagram. Lundin and Klodt (471).

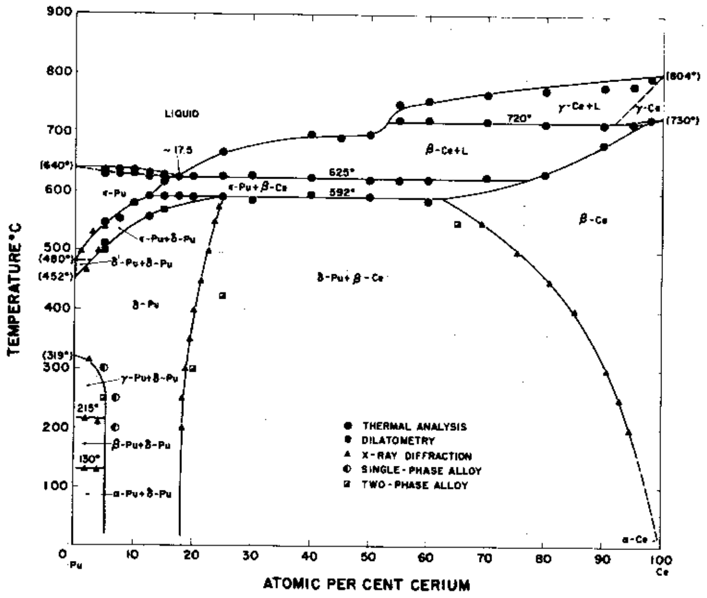

Figure 85. Cerium-Plutonium Constitutional Diagram.

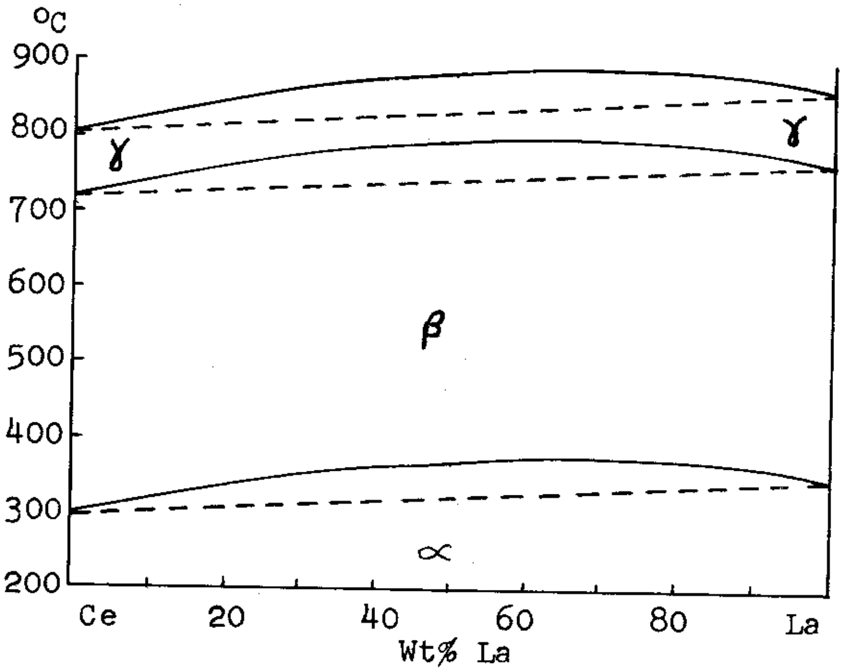

Figure 86. Cerium-Lanthanum Constitutional Diagram. Vogel and Klose (888).

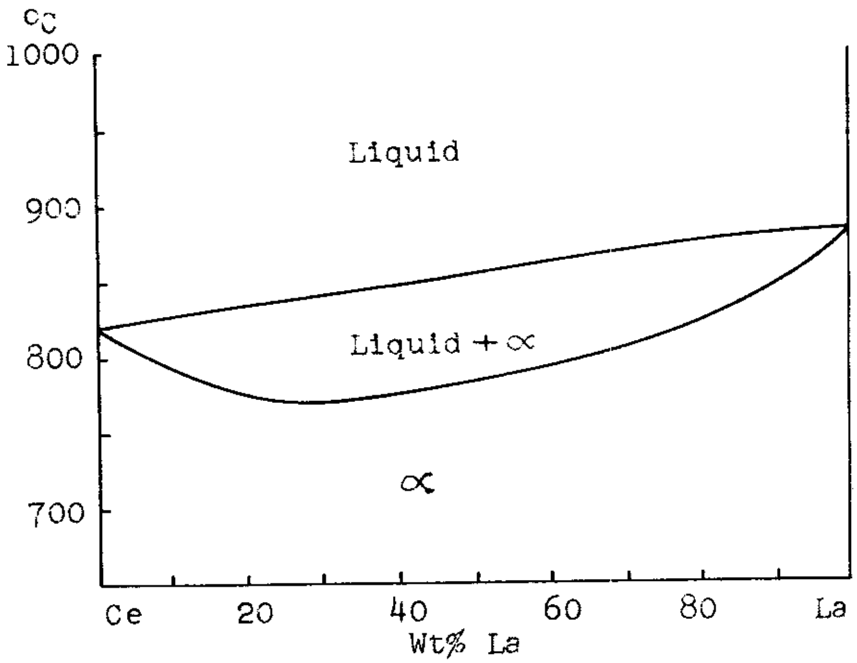

Figure 87. Cerium-Lanthanum Constitutional Diagram. Savitskii and Terekhova (712).

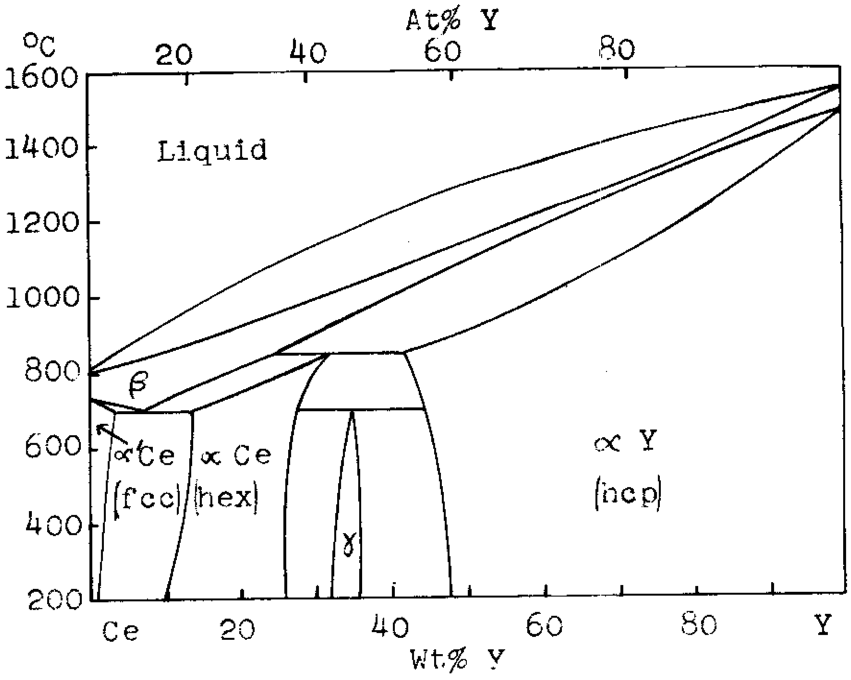

Figure 88. Cerium-Yttrium Constitutional Diagram. Lundin and Klodt (471).

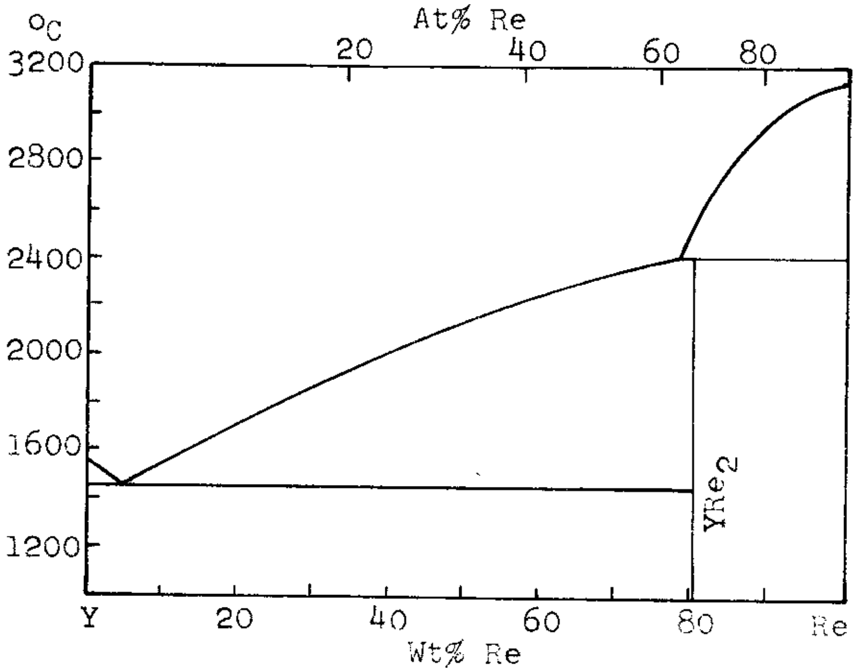

Figure 89. Yttrium-Rhenium Constitutional Diagram. Lundin and Klodt (471).

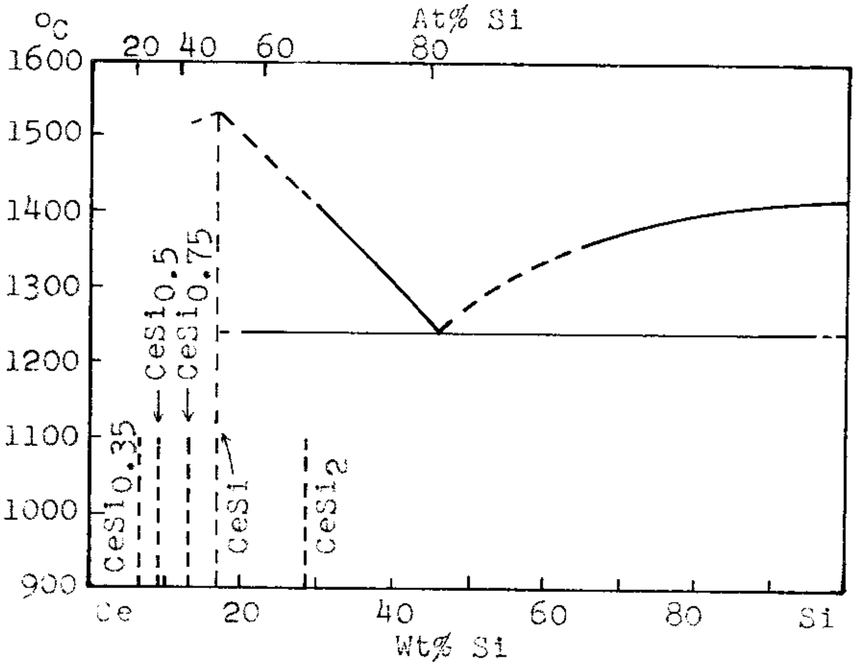

Figure 90. Cerium-Silicon Partial Constitutional Diagram (753). (91,419,882).

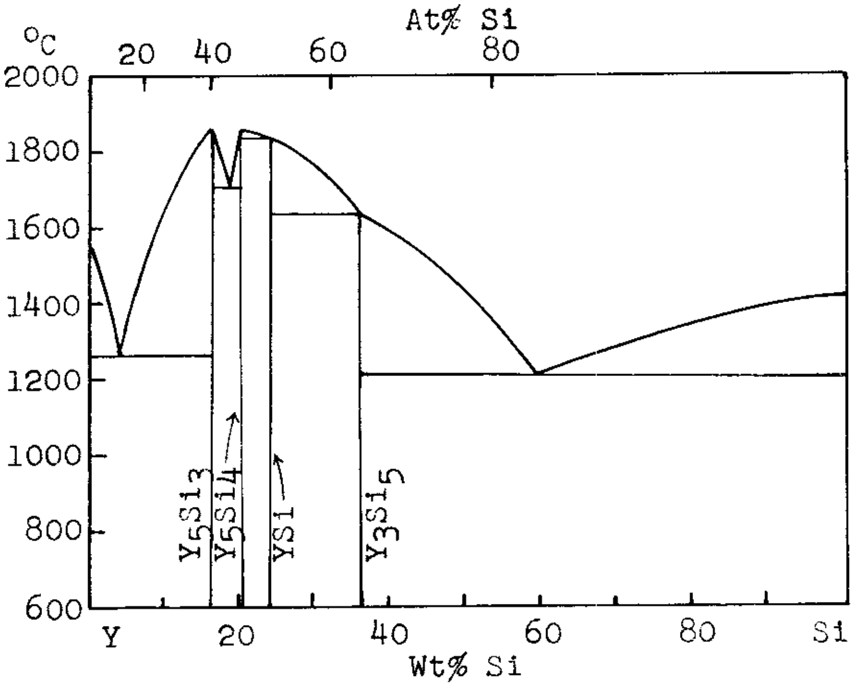

Figure 91. Yttrium-Silicon Constitutional Diagram. Lundin and Klodt (471).

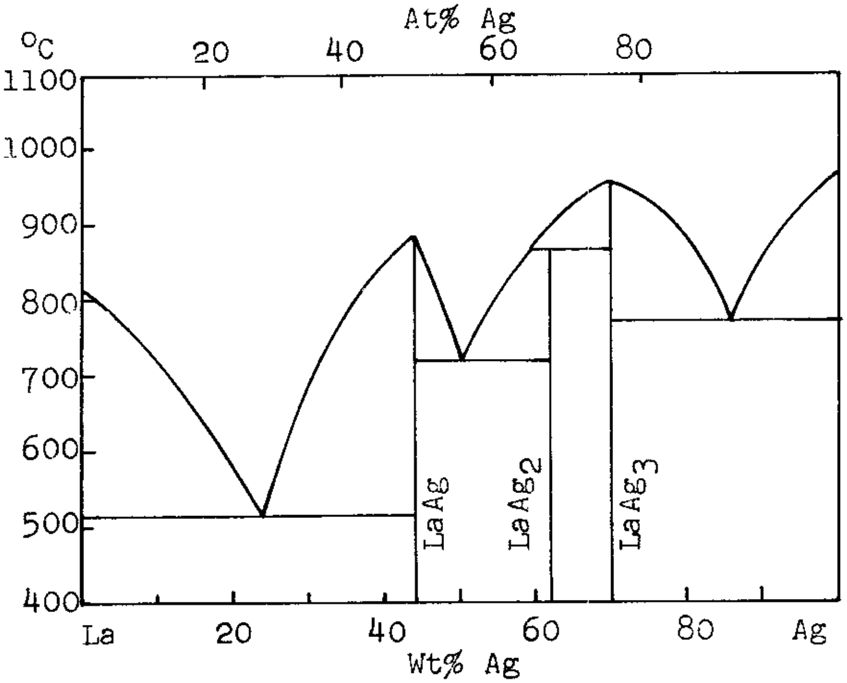

Figure 92. Lanthanum-Silver Constitutional Diagram (753). (111,596,689,725,879,886,898).

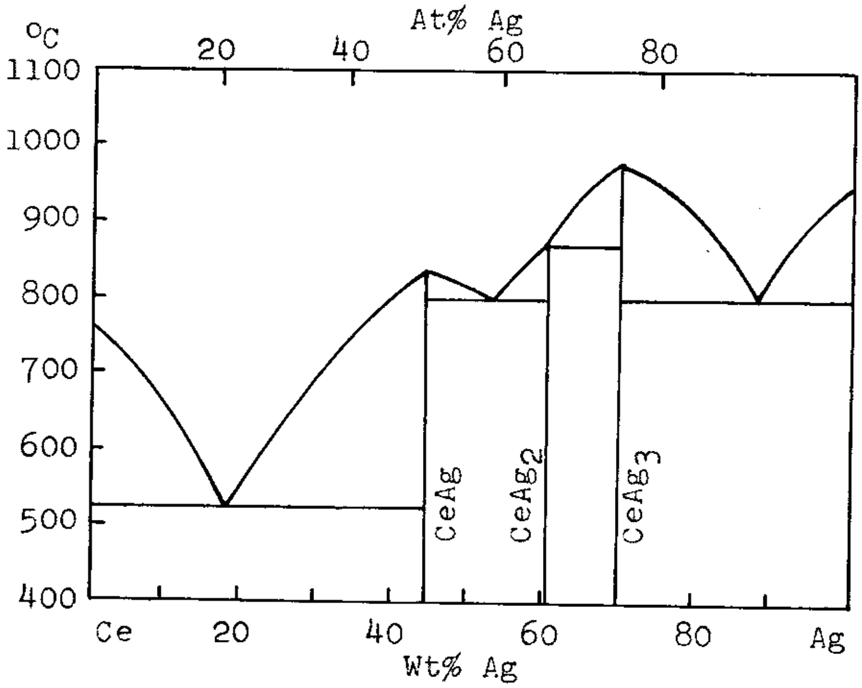

Figure 93. Cerium-Silver Constitutional Diagram (753). (879,886).

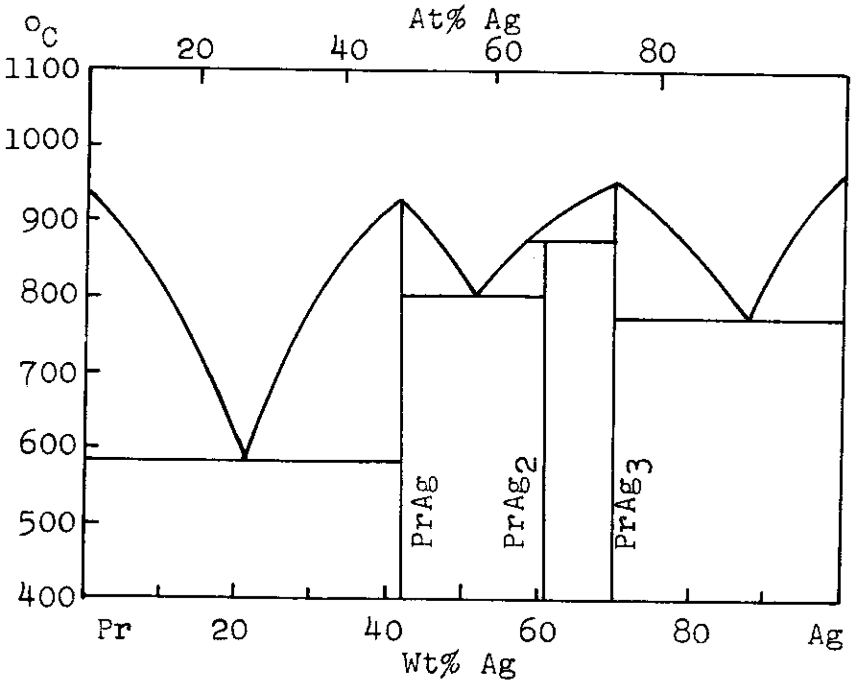

Figure 94. Praseodymium-Silver Constitutional Diagram (753). (113).

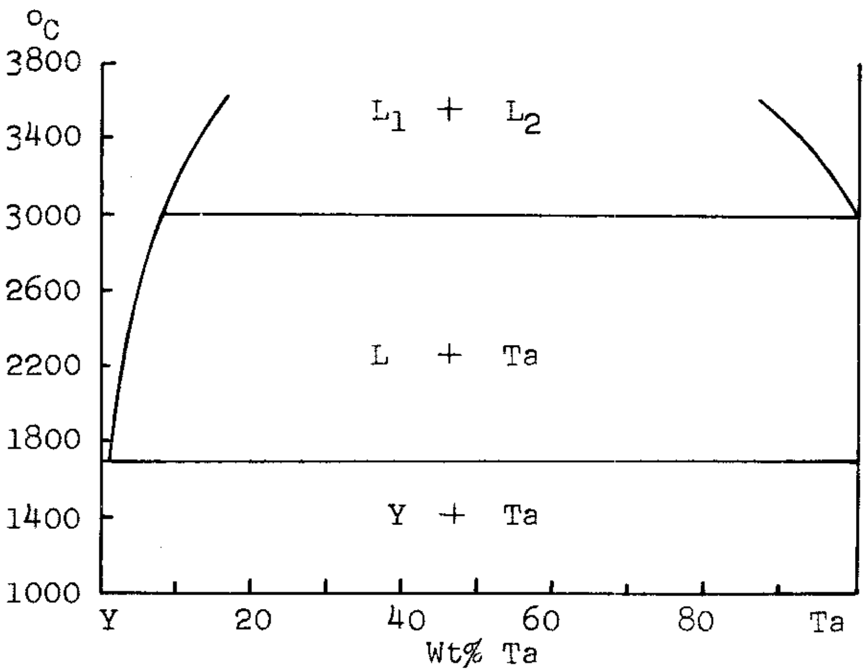

Figure 95. Yttrium-Tantalum Constitutional Diagram. Lundin and Klodt (471).

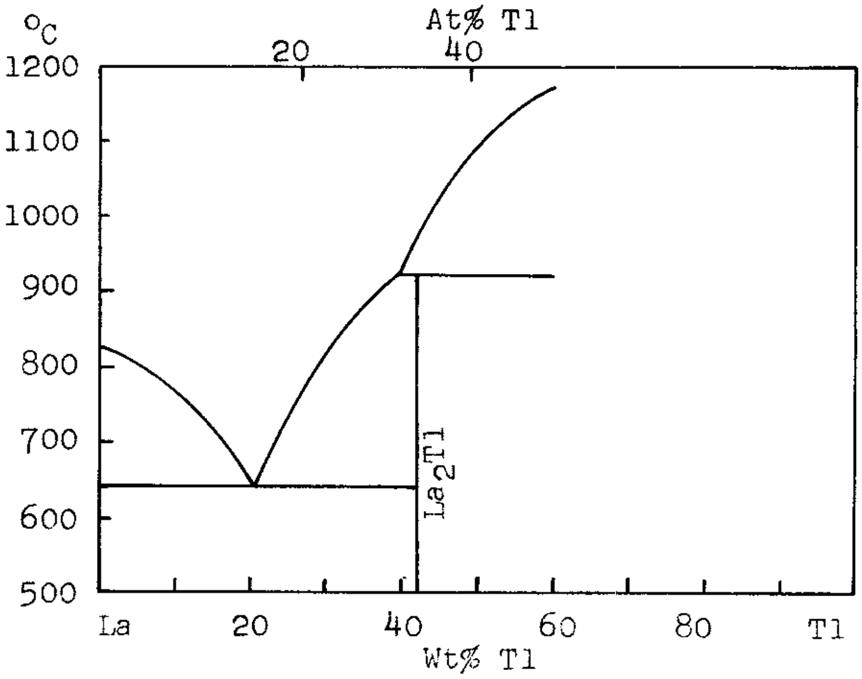

Figure 96. Lanthanum-Thallium Partial Constitutional Diagram (753). (879,886).

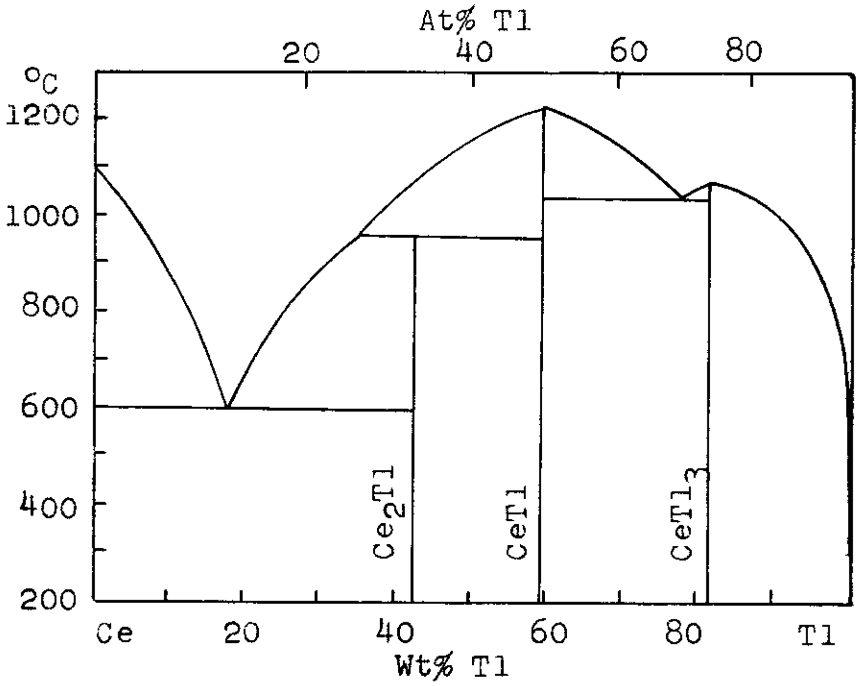

Figure 97. Cerium-Thallium Constitutional Diagram (753). (879,886).

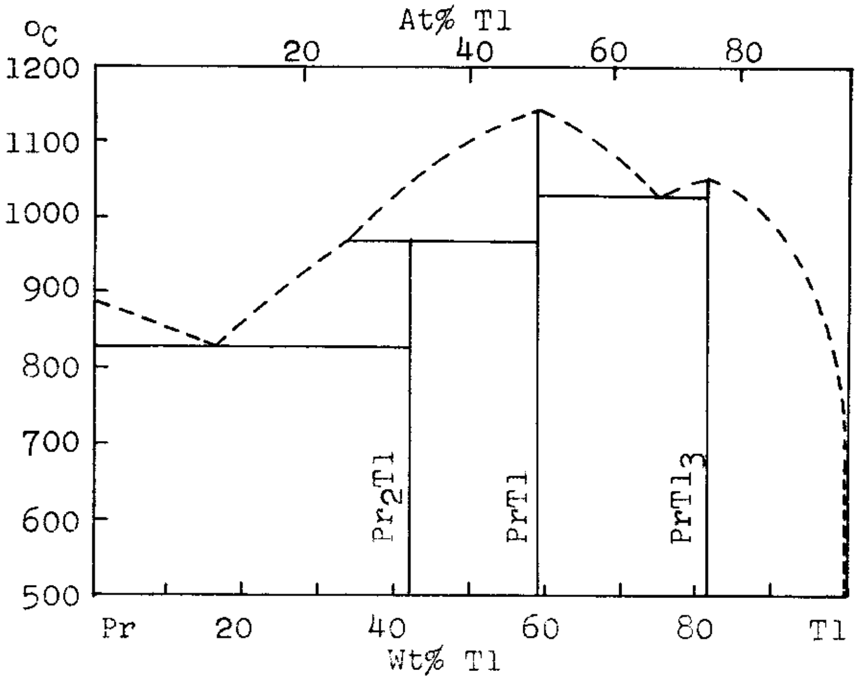

Figure 98. Praseodymium-Thallium Constitutional Diagram (753). (879,886).

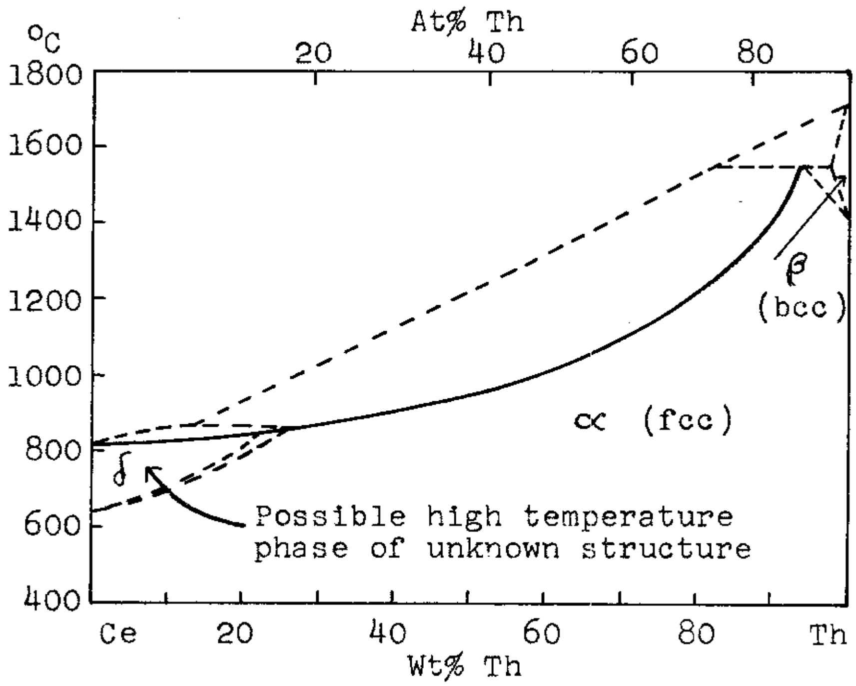

Figure 99. Cerium-Thorium Constitutional Diagram. Weiner, Freeth, and Raynor (899).

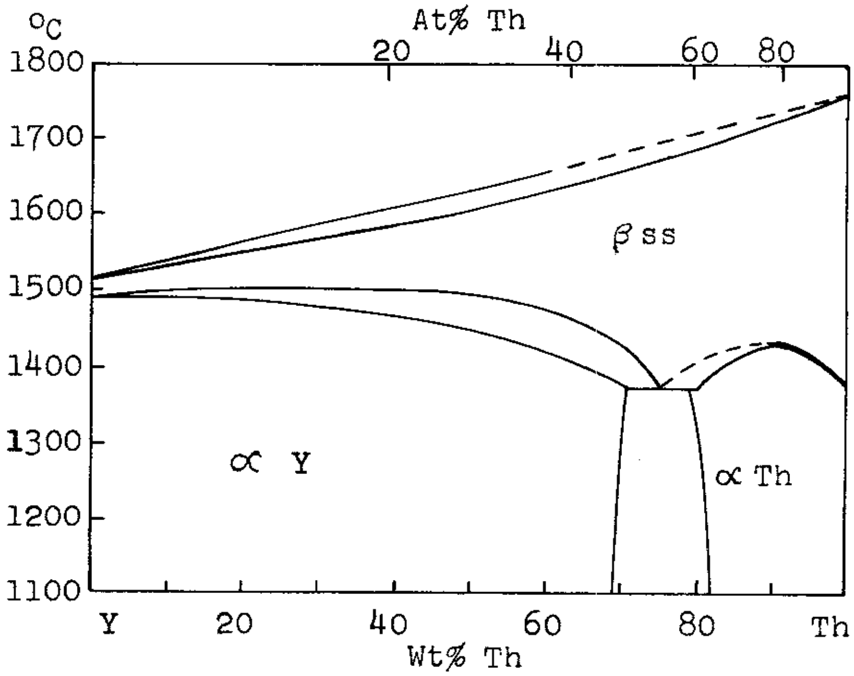

Figure 100. Yttrium-Thorium Constitutional Diagram. Eash and Carlson (172).

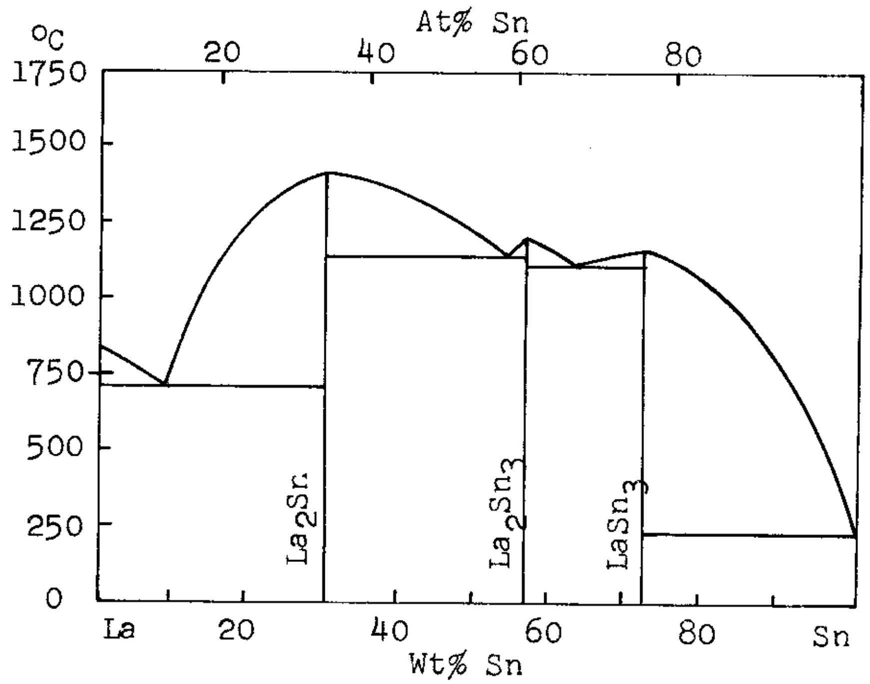

Figure 101. Lanthanum-Tin Constitutional Diagram (753). (110,689,691,879,886).

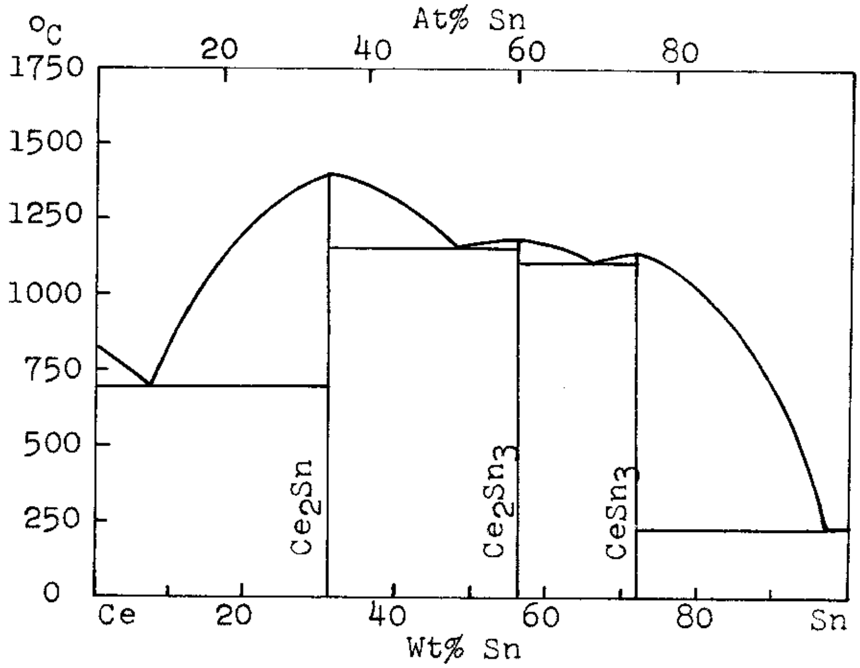

Figure 102. Cerium-Tin Constitutional Diagram (753). (879,880,886,938).

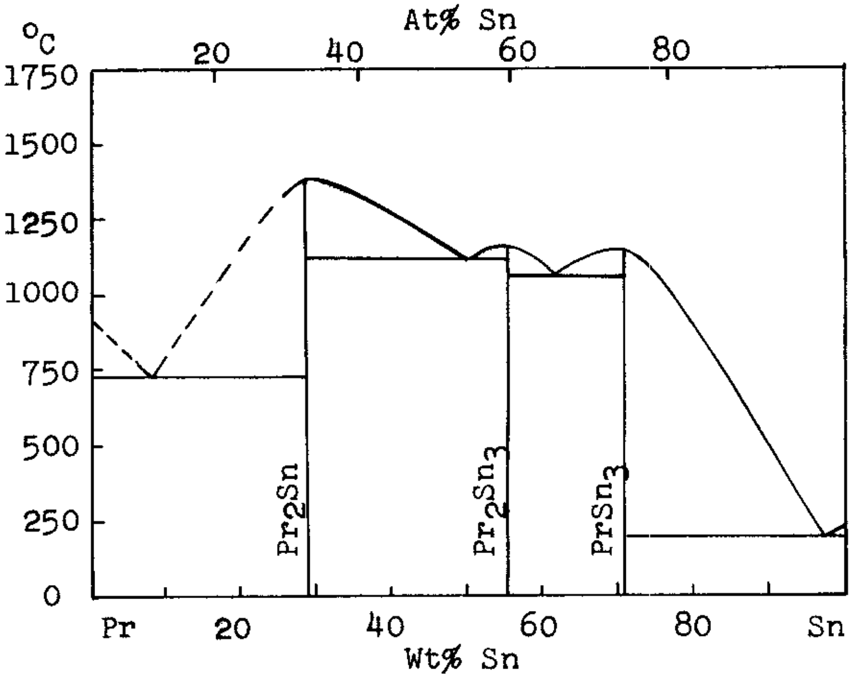

Figure 103. Praseodymium-Tin Constitutional Diagram (753). (691,879,886).

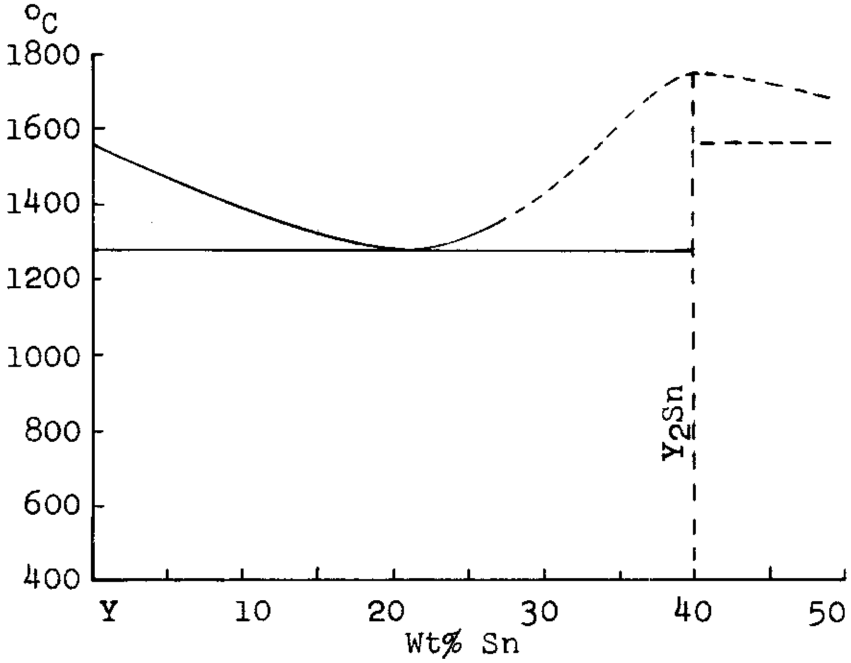

Figure 104. Yttrium-Tin Partial Constitutional Diagram. Love (463).

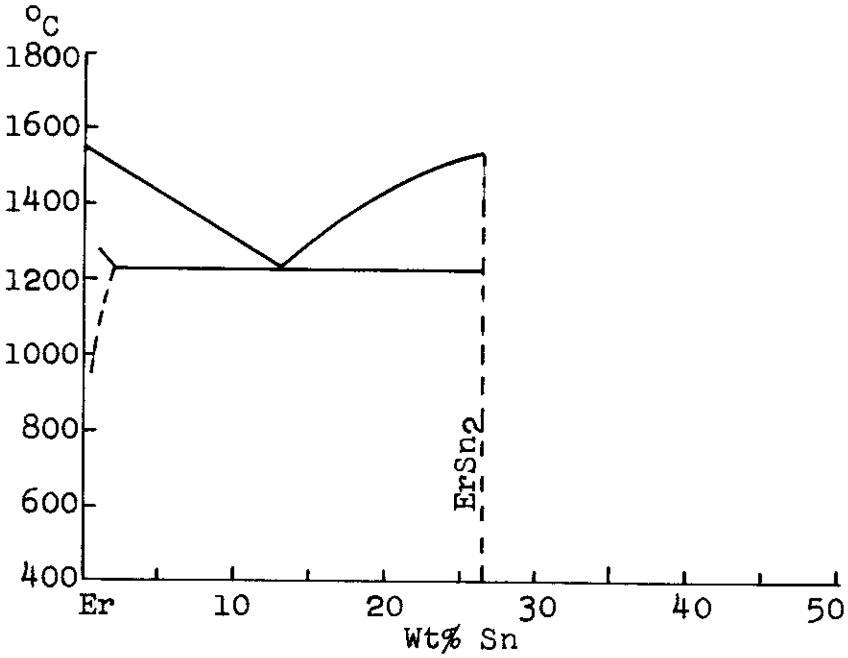

Figure 105. Erbium-Tin Partial Constitutional Diagram. Love (463).

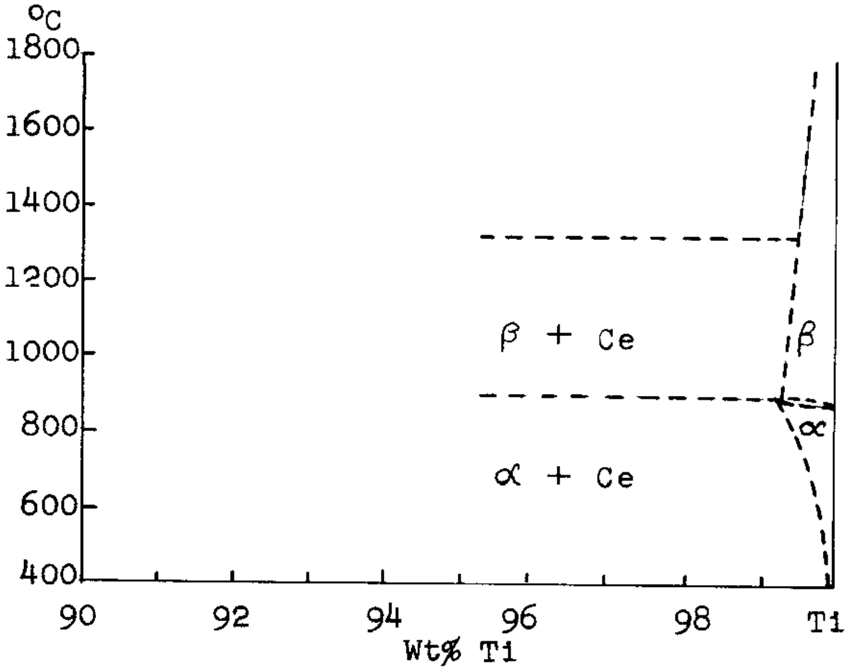

Figure 106. Cerium-Titanium Partial Constitutional Diagram. Taylor (810).

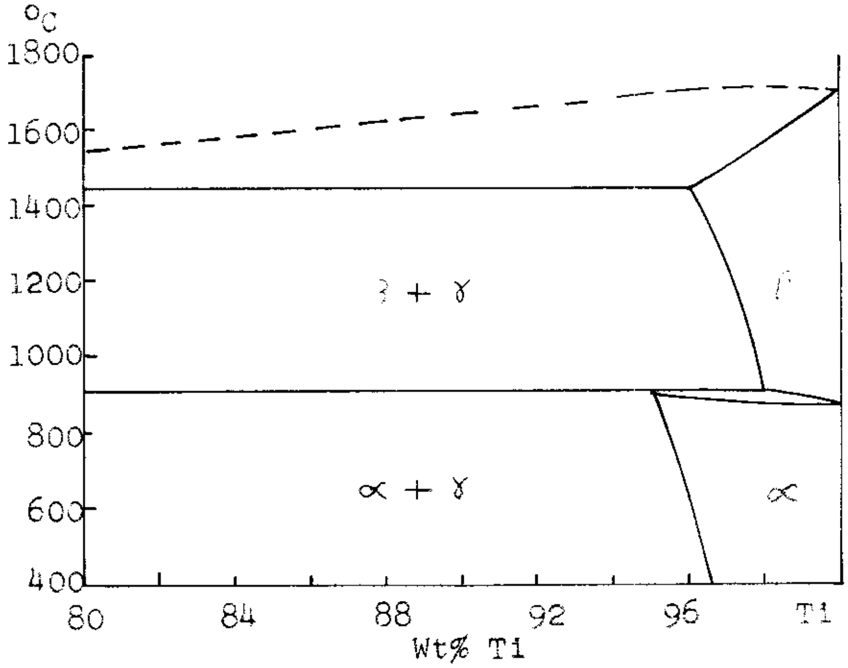

Figure 107. Cerium-Titanium Partial Constitutional Diagram. Savitskii and Burchanoff (710).

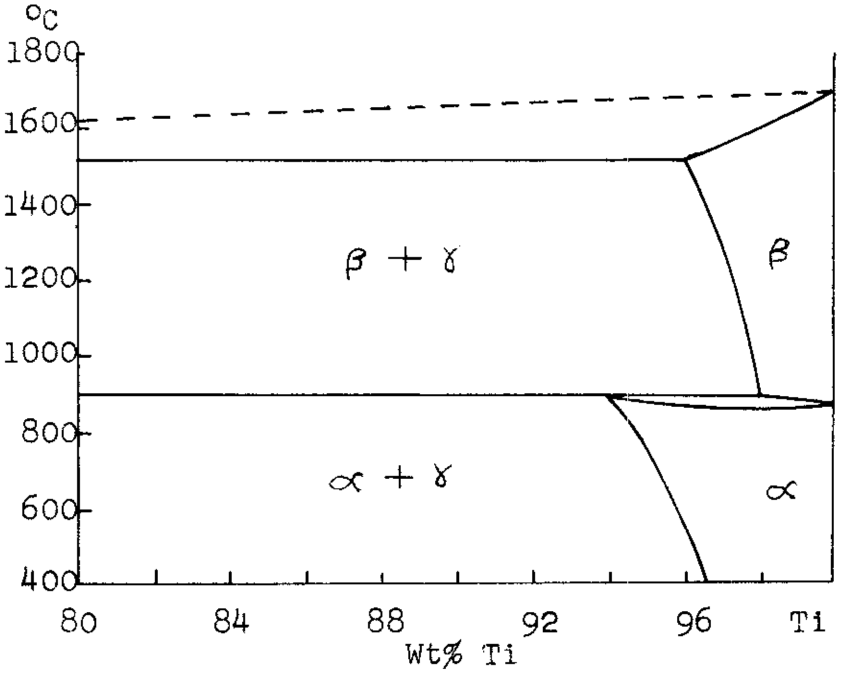

Figure 108. Lanthanum-Titanium Partial Constitutional Diagram. Savitskii and Burchanoff (710).

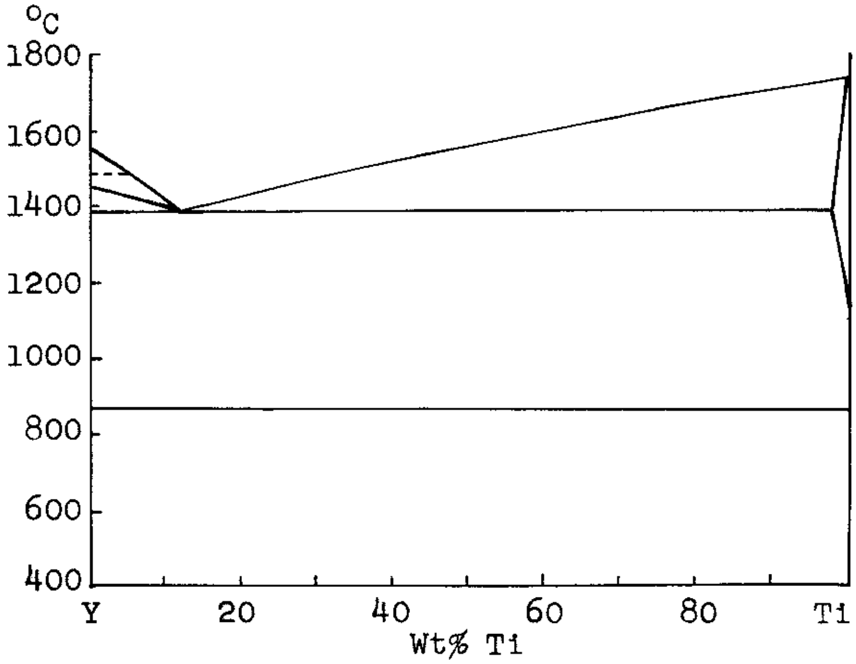

Figure 109. Yttrium-Titanium Constitutional Diagram. Lundin and Klodt (471).

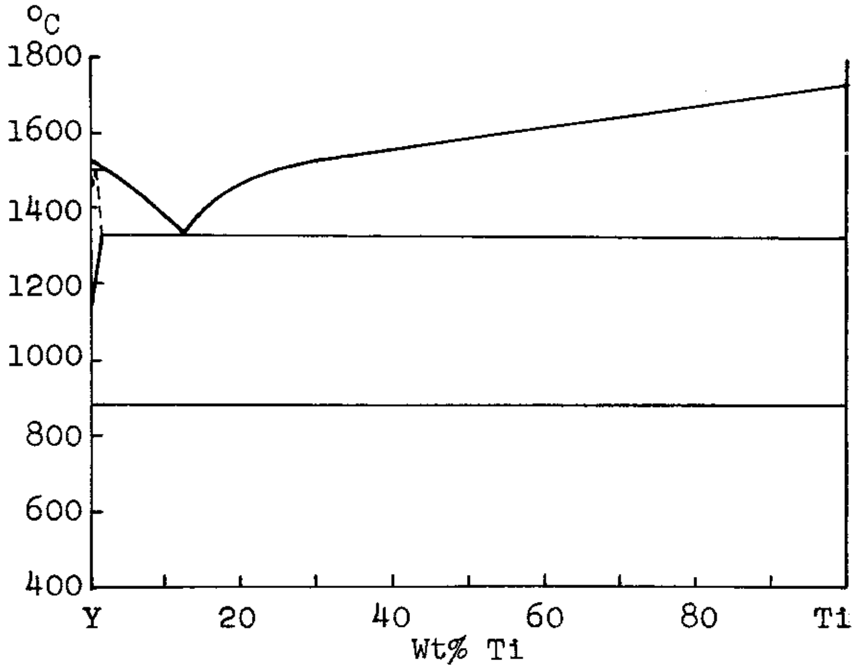

Figure 110. Yttrium-Titanium Constitutional Diagram. Bare and Carlson (37).

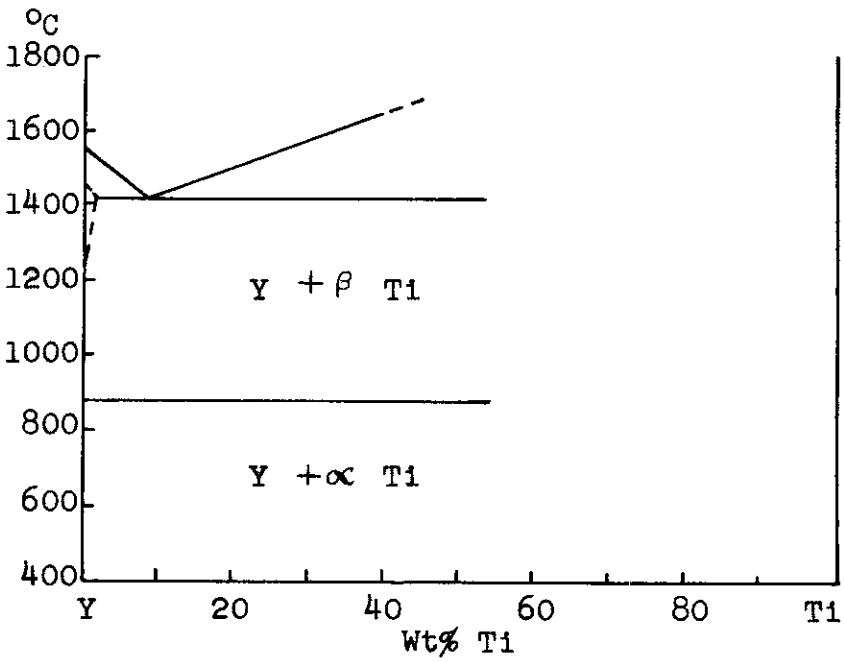

Figure 111. Yttrium-Titanium Partial Constitutional Diagram. Love (463).

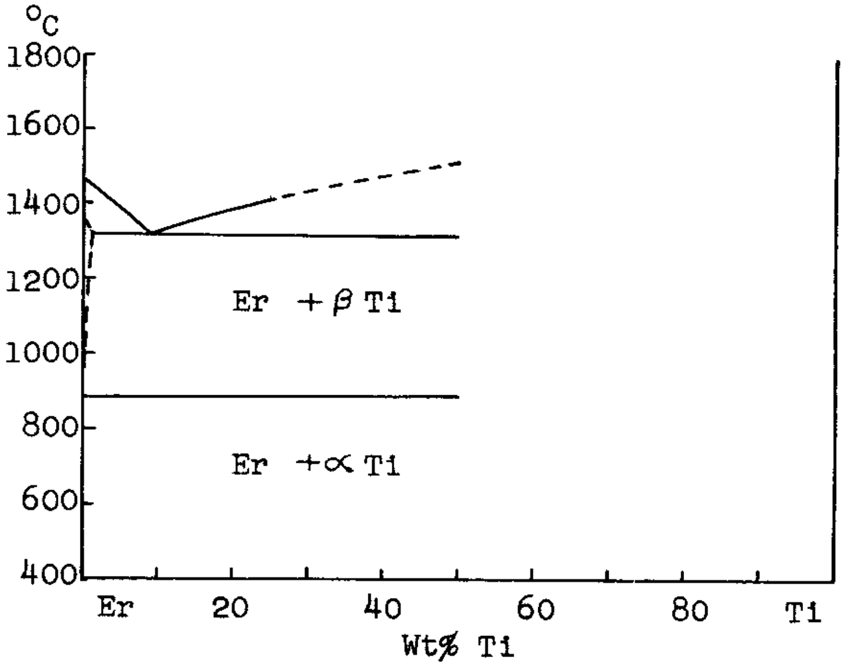

Figure 112. Erbium-Titanium Partial Constitutional Diagram. Love (463).

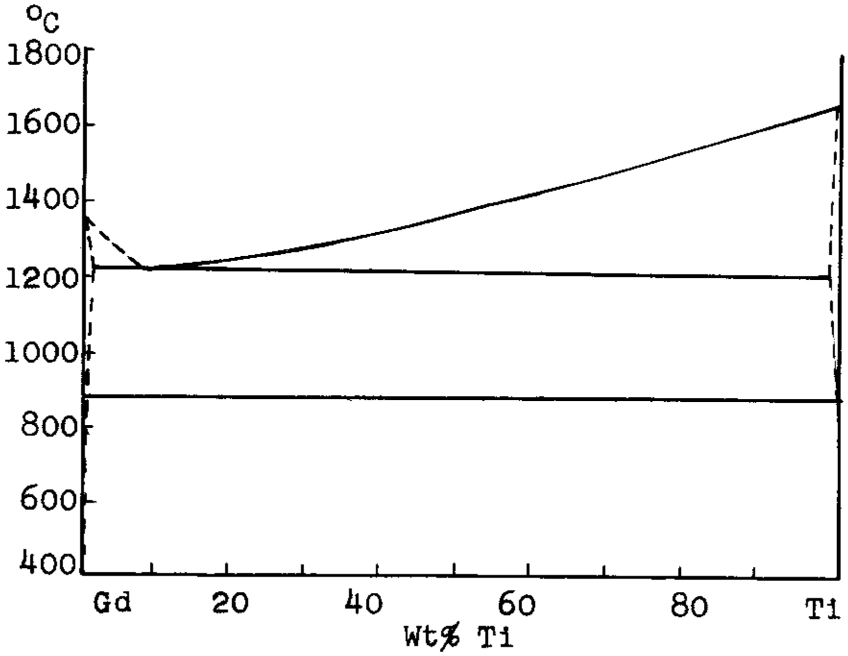

Figure 113. Gadolinium-Titanium Constitutional Diagram. Armantrout (852).

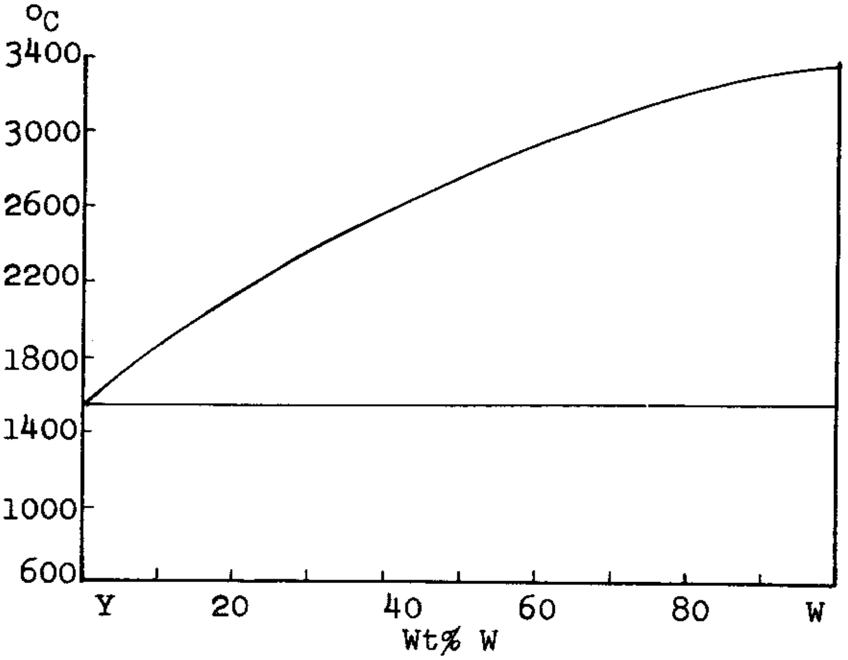

Figure 114. Yttrium-Tungsten Constitutional Diagram. Lundin and Klodt (471).

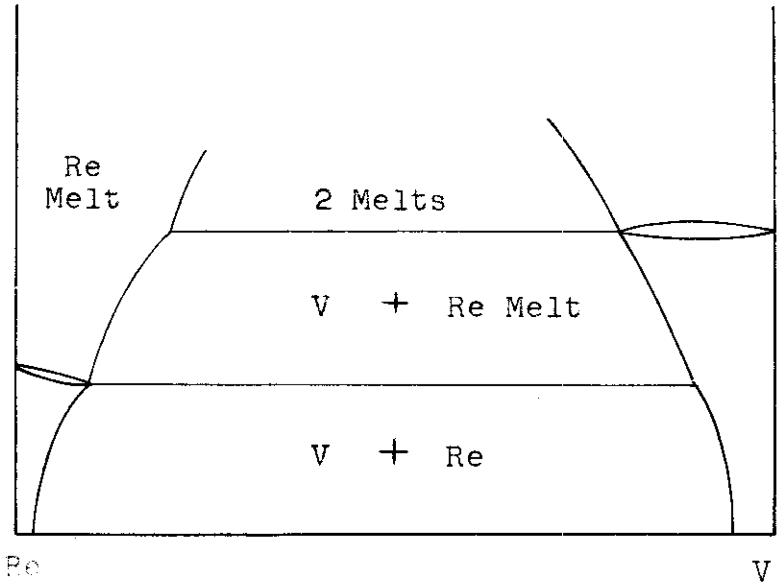

Figure 115. Rare Earth-Vanadium Generalized Constitutional Diagram. Komjathy, Read, and Rostoker (401).

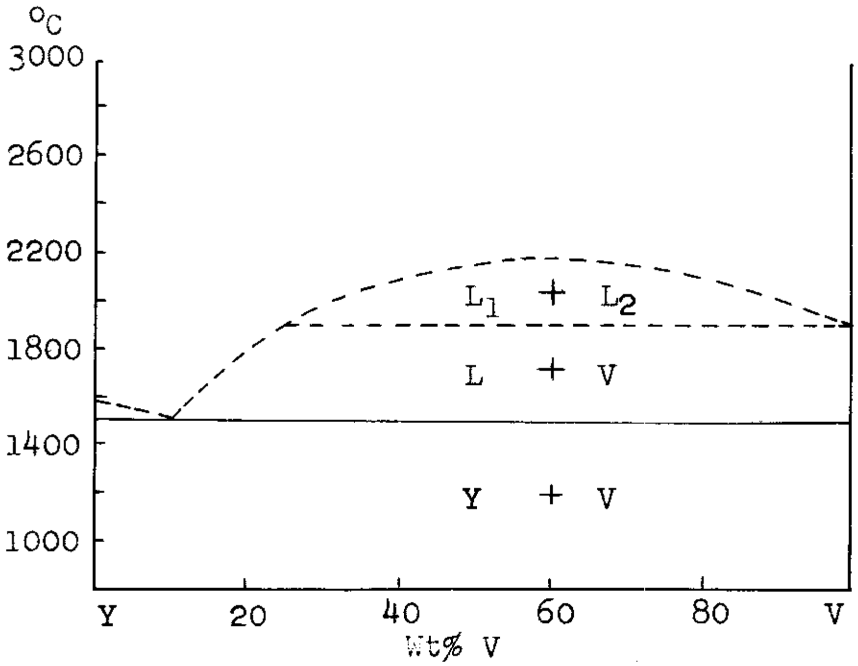

Figure 116. Yttrium-Vanadium Constitutional Diagram. Love (463).

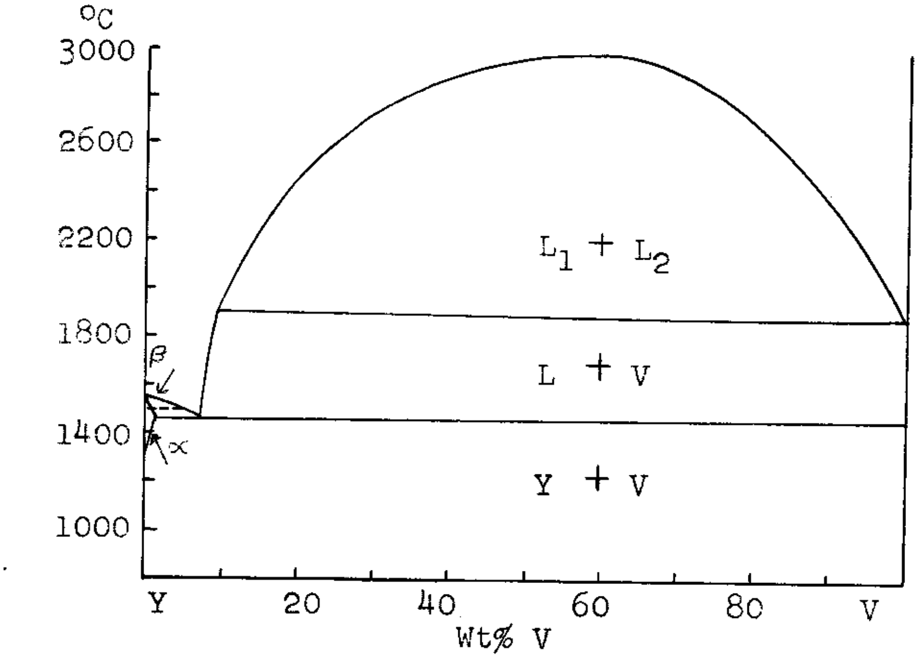

Figure 117. Yttrium-Vanadium Constitutional Diagram. Lundin and Klodt (471).

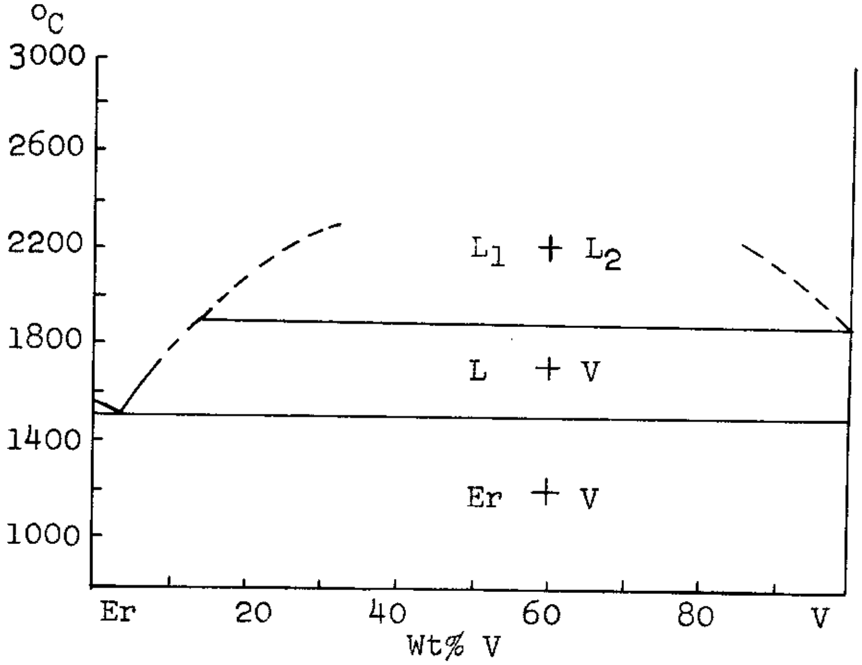

Figure 118. Erbium-Vanadium Constitutional Diagram. Love (463).

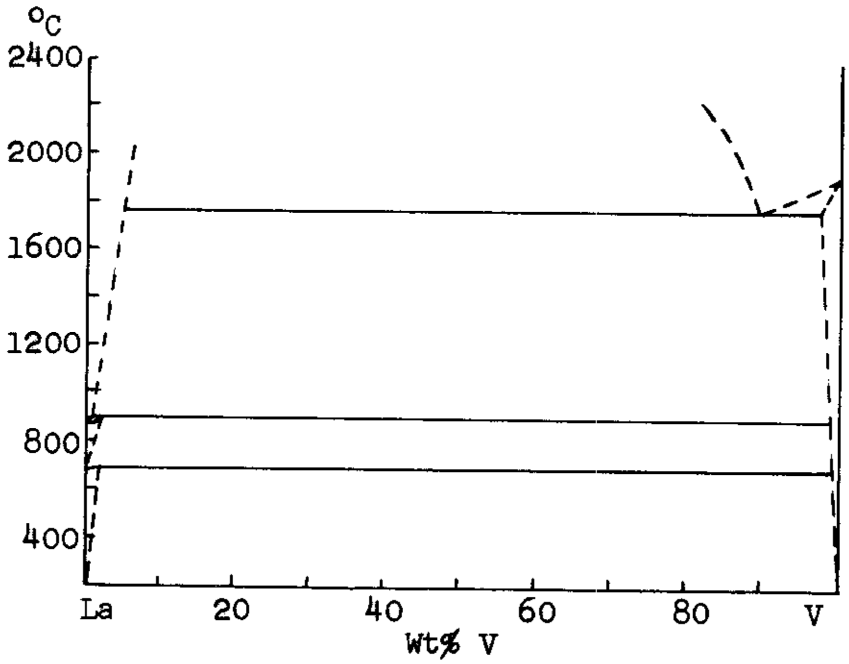

Figure 119. Lanthanum-Vanadium Constitutional Diagram. Savitskii (709).

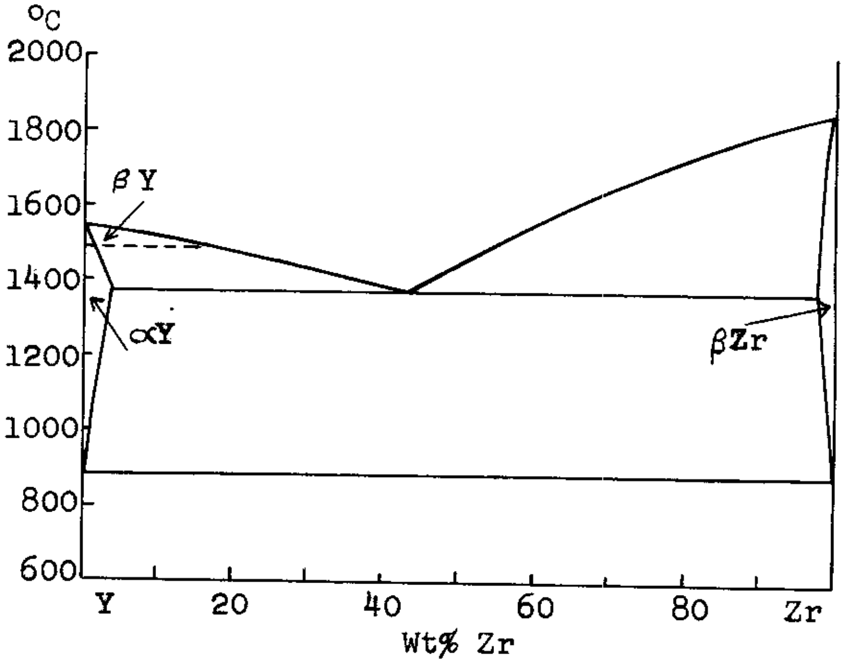

Figure 120. Yttrium-Zirconium Constitutional Diagram. Lundin and Klodt (471).

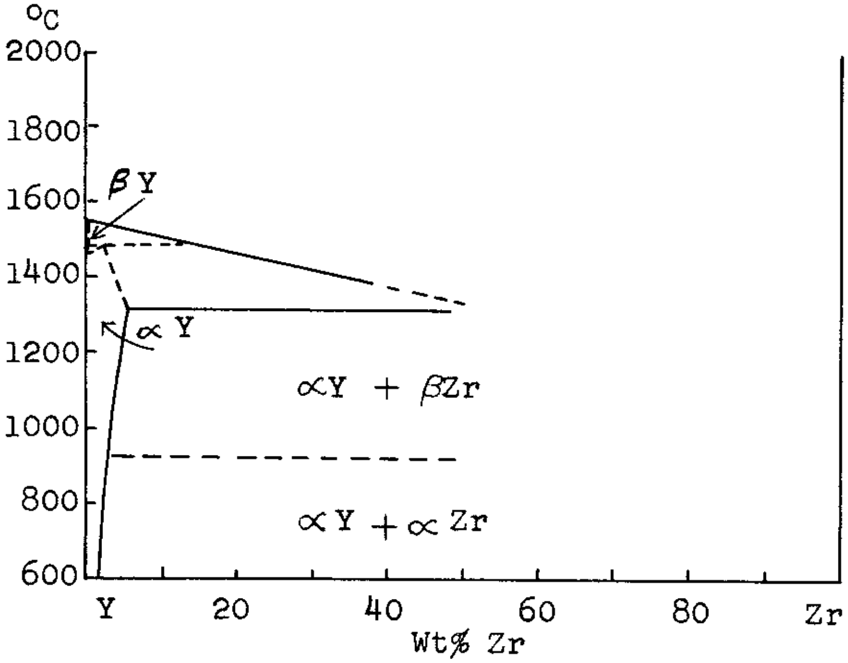

Figure 121. Yttrium-Zirconium Partial Constitutional Diagram. Love (463).

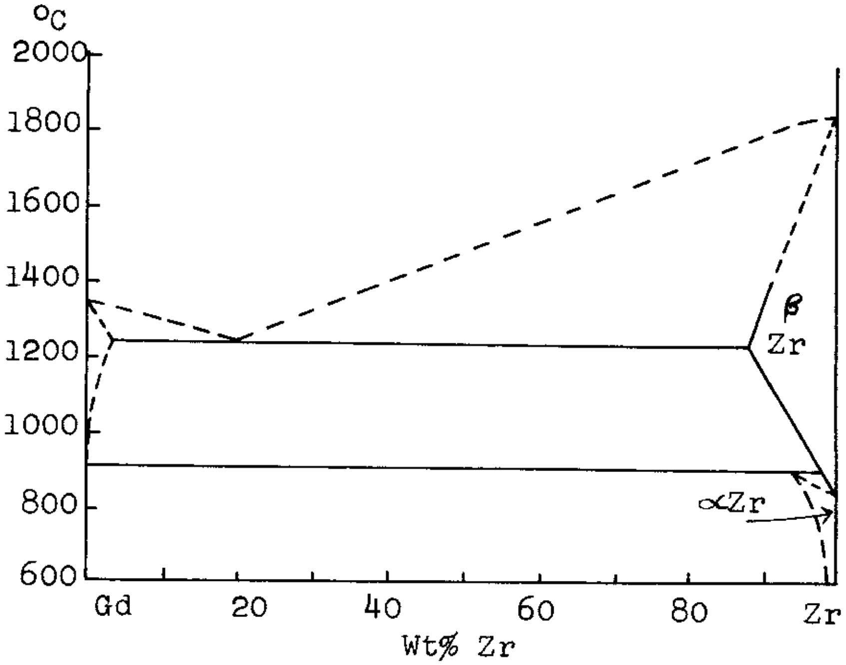

Figure 122. Gadolinium-Zirconium Tentative Constitutional Diagram. Armantrout (851).

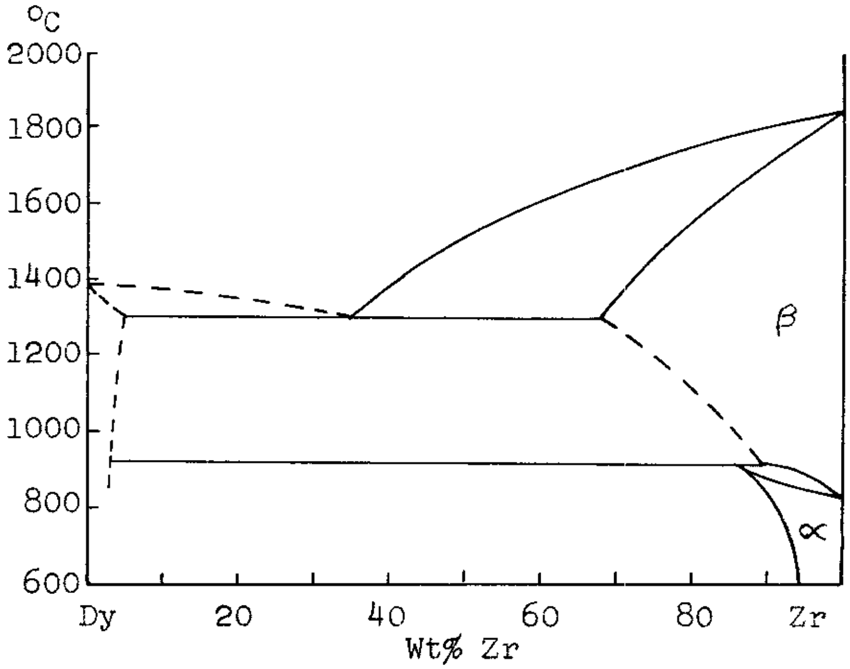

Figure 123. Dysprosium-Zirconium Tentative Constitutional Diagram. Armantrout (850).

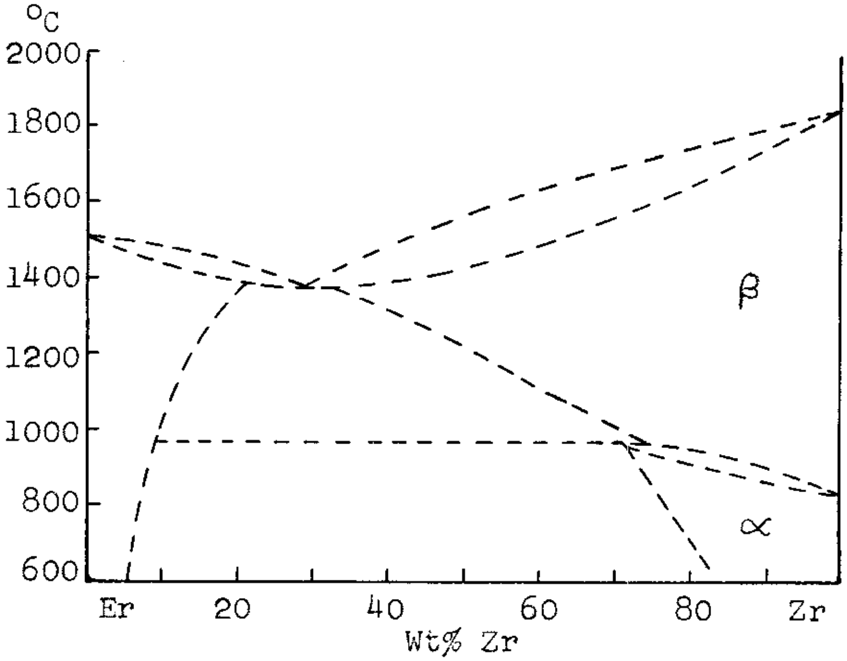

Figure 124. Erbium-Zirconium Tentative Constitutional Diagram. Armantrout (850).

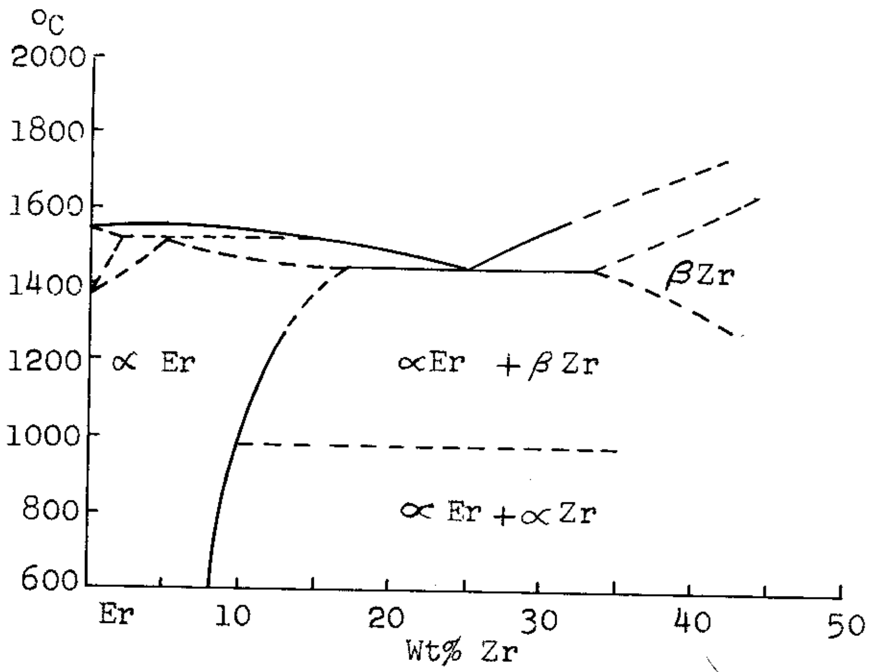

Figure 125. Erbium-Zirconium Partial Constitutional Diagram. Love (463).