REFRACTORY METALS AS ENGINEERING MATERIALS

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Introduction

The increasing need for materials able to perform at higher and higher temperatures for improved efficiency and for use in new systems has stimulated a great deal of effort directed toward the development of the refractory metals. Aerospace application for propulsion and re-entry, of course, has been the primary driving force. From a scientific standpoint, the body-centered-cubic refractory metals have presented a challenge which the research community has been eager to accept. Their problems and behavior are of such an interesting nature that knowledge gained from studying them is, in itself, stimulus for more work.

Although there are a number of metals that can be considered as refractory metals by nature of their high melting points, the four of primary interest are columbium, molybdenum, tantalum, and tungsten. The high melting platinum group, iridium, osmium, ruthenium, as well as rhenium (Re), have melting points above 4000°F, but have only limited availability. Consequently, the discussion will be limited primarily to the first group, Cb, Mo, Ta, and W.

These metals have certain properties and characteristics that are similar in nature to each other. Some of their physical properties are shown in figure 1. They are all characterized by high melting points, ranging from Cb's 4474°F to W's 6170°F. Also, as their melting point increases, so does their density, from Cb's 8.6 gm/cc (which is a density of little more than iron base alloys) to W's very heavy 19.3.

Not to be overlooked is that utilization of the higher melting points exacts its price—the burden of greater weight. The importance of this fact cannot be overemphasized when considering aerospace applications, since structural weight has become significantly more important than ever before. Because of this fact, higher density metals must be used sparingly and only where their own unique combination of strength at high temperatures, or their high melting points, or other special properties will completely justify paying the penalty.

Applications

Applications of the refractory metals in currently operating systems can be reviewed rapidly, for they are very limited at the present time. They have several uses in a variety of electronic applications, in tubes, condensers, etc., but these will not be discussed in this presentation. Mo and W are being used in propulsion systems even now, particularly in solid fueled rocket nozzle and vector control applications, but the bulk of the applications for these materials is still ahead, some in the rapidly approaching future. The primary uses will be in two major areas, structure and propulsion. A third area of consideration which is just as important, although somewhat farther away in the time cycle, is the generation of power, such as electrical energy, in outer space.

In propulsion applications, summarized in figure 2, refractory metals will be used in all major devices, solid and liquid rockets, nuclear propulsion devices and high performance air breathing devices such as ramjet engines. In solid rocket applications, the most interest as far as refractory metals are concerned is centered about W or possibly suitable W alloys which will be an important part of the materials system comprising the nozzle area and vectoring devices. Whether it will be used in the form of thin wrought sheet to minimize weight, or a plasma sprayed product, or a more massive form which will accomodate a cooling technique by infiltrating with copper or a refractory oxide will depend upon the particular system and upon later developments in this area. The primary advantage of W for these applications is its high melting point. Its resistance to erosion and thermal shock is also very good when compared to other available materials. The drawback is its weight, and designs will undoubtedly incorporate only the amount necessary to do the job. Therefore, developments for this application have been to a great extent in the area of fabrication of W in attempts to obtain a suitable geometry.

There has been recent interest in small, uncooled liquid rockets, primarily for directional control uses. Interest here seems to be in Ta base alloys because of their high melting point and good fabricability. Nuclear propulsion systems such as the nuclear ramjet (Project Pluto) and the nuclear rocket engine (Project Rover) will have a number of requirements for high temperature materials up to 4000°F such as supporting material for fuel elements. In ion-propulsion units, the work function of W in the temperature range 2000° to 2500°F seems to be well suited for the ionizing surface and other refractory metals, such as Cb or Mo which will be used to contain the liquid and gaseous cesium. Ramjets will utilize refractory metals for resistance to aerodynamic heating encountered as a result of their high speed in the atmosphere.

The application which has been instrumental in stimulating effort for refractory metal development is in re-entry vehicle structural requirements, which encompass a variety of problems. Re-entering the earth's atmosphere from orbital or super-orbital flight, requires large quantities of energy to be dissipated in the form of heat. Re-entry in a controlled manner, as opposed to the ballistic re-entry of an ICBM or the semi-ballistic re-entry of the Project Mercury capsule, has precipitated proposals of a number of structural methods for use in constructing lifting vehicles. It is in these structures that many materials challenges exist, and where refractory metals will find use. Examples of two types of proposed radiation cooled re-entry lifting vehicles, a lifting body type and a glider type, are shown in the next two figures. Figure 3, a lifting body, is a refinement of the semi-ballistic type. This type vehicle consists primarily of fuselage, with wing loading of approximately 40 lbs/ft^2 or higher. A second type, figure 4, is a glider which has a higher lift-to-drag ratio, more wing area, and, consequently, lower wing loadings than the first. This type expends much more of its energy at higher altitudes and consequently has lower structural re-entry temperatures than the lifting body type. The equilibrium surface temperatures expected in these types of vehicles are given in figure 5 for both orbital and super-orbital re-entry. Time periods involved are from 25 to 90 minutes. The actual material temperatures will be somewhat lower than these, and will also be dependent upon such factors as sweep angle, wing loading, edge radii, and emissivity, but the requirements for structural materials should be evident. Cb and Mo alloys will find use in the lower temperature range shown, with Mo and perhaps Ta alloys competing in the intermediate range. In the higher range, W and its alloys will have to compete with graphite, ceramics, and other high temperature materials or systems. The requirement for refractory metals in these applications will be in the wrought condition, and primarily in the form of sheet. This is particularly true in radiation cooled structures, where a heat resistant shell is used to protect the load carrying substructure. Consequently the most urgent need for material for these applications is not for high strength sheet material, but for high quality sheet material, with consistent and reproducible properties and, of course, suitable protective coatings.

The third broad area of application is in the generation of power in space. Large quantities of electrical energy will be required to operate low-thrust propulsion devices in space, such as in ion-propulsion and plasma propulsion units, for long periods of time. One approach to generating this electrical energy, the system shown in figure 6, is by use of a nuclear reactor, transferring the heat energy to a turbine-generator combination by use of liquid metals. Refractory alloys, and particularly those of Cb alloys appear to be ideally suited for such an application, for containing liquid metals like sodium and potassium. There will further be a requirement for turbine materials that will not be exposed to oxidizing environments for which refractory alloys should be ideally suited. Boiler and radiator materials are needed in these systems for transferring heat from the liquid metals to the working fluid. In these applications, very long transfer periods, e.g., (10,000 hrs) are required. Unfortunately, data of this nature does not yet exist for the refractory metals.

There are many other uses where refractory metals have potentialities, and it seems very likely that more and more applications will appear as systems are further improved and as the refractory metals themselves are developed.

State of the Art

The important task now, however, is to bring the refractory metals as rapidly as possible to the status of truly engineering materials so that they may be applied with confidence to aerospace projects, whose success is dependent upon them. At an accelerated rate efforts have been expended to appraise and develop the required metallurgical knowledge and production capability to infuse the refractory metals and their alloys in various mill product forms with useful, reliable, and reproducible engineering properties.

The present state of the art for the refractory metals has grown considerably, so that a detailed review of the total effort would far exceed the time available. In fact, a recent DMIC document summarizing only Government sponsored projects related to the refractory metals lists 320 projects active since July 1959. However, a broad review will serve to stimulate discussion concerning the problems surrounding refractory metals and solution of these problems.

In assessing in a qualitative manner the overall stage of development of the refractory metals today, there are some general comments that can be made concerning the kind of work in progress. Needs of the effort have been developmental, in nature, attempting to solve the many practical problems associated with manufacturing useful refractory alloys and fabricating them to the desired shapes. As a result, there has been less emphasis on fundamental research. Recognizing this tendency, the Air Force has devoted a sizeable portion of its refractory metal program to support fundamental research to learn more about the mechanisms of flow and fracture recovery, recrystallization, and, in general, the physical metallurgy of these metals. This will provide the technological basis for the further growth of the refractory metals.

There has been no great problem as yet in the development of alloys that will provide the strength at temperature needed for currently anticipated systems. There is, of course, a constant effort to try to improve these alloys to get a better combination of other properties in addition to strength, such as low temperature ductility. At present, the state of the art seems to be ahead of the applications as far as identifying usefully strong alloys is concerned. However, before these alloys can be translated from the laboratory into useful material for weapons systems, they must be appropriately fabricated. At present there is a shortage of suitable production facilities for providing refractory metals in the wrought forms needed both for evaluation and for use. Because of this limitation much of the production development work and, indeed, some of the thinking, is handicapped because of the tendency to make refractory metals production technology suit the existing equipment, which was designed and built for the production of steel and other less difficult-to-handle metals. While this may be desirable from an economic standpoint, it may not solve the problem. Reproducibility and consistency have not been obtained in the refractory metal mill products that have been produced to date. If the material needs for planned weapons systems are to be met, this problem must be faced and perhaps both the equipment and the thinking changed. More is being learned concerning the importance of processing and processing sequence on the properties of wrought refractory metals. If we are to take advantage of this knowledge, adequate processing facilities will be required.

Several basic problems must be solved to make the refractory metals engineering materials for almost any application, whether it be related to military uses or not, and these are the problems discussed in this paper.

Refractory Metal Properties Problems

There are three general categories which have emerged as the major stumbling blocks to progress: (1) poor oxidation resistance, (2) low temperature brittleness, and (3) consolidation and fabrication difficulties. The third problem is to a certain extent, a result of the combination of the first two mentioned.

The poor oxidation resistance of the refractory metals is well-known. All four of the refractory metals unfortunately have little or no resistance to it in the temperature range where their properties are needed for service applications. Alloy development efforts to alleviate this situation have not been successful. Because of this, a very large share of the effort being expended to make them engineering materials has necessarily been devoted to the development of suitable protective coatings. The degree of success achieved in this endeavor will determine the extent of the applications for which these metals can be utilized. Due to its major importance, this is the subject of another presentation and will not be discussed here, except to emphasize that it is the most difficult problem to be solved, particularly for service above 3000°F.

Related to the oxidation problem is the transition temperature, which is the temperature below which fracture occurs with little or no plastic deformation. The existence of the ductile-brittle transition temperature in the refractory metals has been recognized for some time. The transition temperatures for unalloyed, recrystallized refractory metals are shown in figure 7, as represented by changes in reduction in area in tensile tests as a function of temperature. The temperature or temperature range over which the transition occurs is a function of material and testing conditions, including: microstructure, grain size, grain shape; degree of strain hardening; strain rate; stress condition; and, composition, interstitial content, and substitutional content. The last variable mentioned, composition, deserves further comment.

In general, the effects of interstitial elements on transition temperature are being rather widely investigated. Interstitial content has been shown to have a less significant effect on this parameter in Cb and Ta than in Mo and W. The effect of substitutional additions has also been investigated, although not as extensively as interstitial effects.

Recent data generated by Begley and co-workers on the effect of substitutional addition to Cb are shown in figure 8. Here, the addition of group IVa elements, titanium (Ti), hafnium (Hf), and zirconium (Zr) to this group Va elements, Cb and Ta, have, based upon atomic weight percent additions, less pronounced effect on the transition temperature than do the group VIa elements, Mo, W, and chronium (Cr). Another interesting fact is the sharp increase in transition temperature resulting from the additions of Re. This is in contrast to the results reported by Battelle on the effects of Re additions to Mo and W, where the transition temperature is lowered by sufficient addition. So there are definitely effects from substitutional alloying additives on the transition temperature of refractory alloys, and more investigation of this area may be very helpful in guiding future alloy development efforts.

All four of the refractory metals crystallize in the body-centered-cubic structure and all exhibit a transition from ductile to brittle behavior. This transition temperature decreases from W to Mo to Cb, and although pure Ta is ductile at the lowest temperature tested, its yield strength increases rapidly as the temperature decreases, indicating that at low enough temperatures it will exhibit a transition. Implications as related to our objective of engineering refractory metal alloys are, of course, direct. The higher the temperature, the more severe are the problems that must be encountered—in forming, joining, and handling structures fabricated from these alloys—and the lower their reliability during service.

In contrast to the similarity noted among all four refractory metals, there are also certain characteristics inherent in the group Va metals, Cb and Ta, that differ from the VIa metals, W and Mo. The moduli of elasticity and the thermal conductivities of Cb and Ta are lower than Mo and W. The coefficients of thermal expansion of Cb and Ta are higher than those of Mo and W. Furthermore, the tolerances for interstitial and substitutional alloying additions are much greater in Cb and Ta than in Mo and W. Mo and W strain-harden more than Cb and Ta and, consequently, strengthening by cold working is more pronounced in Mo and W. But, we get back to similarities, when we compare elements of the same group; this is particularly noticeable in those aspects concerning alloying and processing, and was discovered during development of these materials.

Because of the low transition temperature of the base metal of Cb and Ta, it is likely that there will be many useful alloys whose transition temperature, in the recrystallized and as-cast condition encountered in welded structures, will be below room temperature. Some have already been developed. Transition temperatures of recrystallized alloys of Mo and W, however, will be above room temperature, and joining processes such as fusion welding will result in material that has a high transition temperature, a condition in all alloys investigated with the exception of those containing sufficient Re.

Research efforts to investigate various aspects of brittleness include studies of the mechanisms of flow and fracture and the degree to which interstitials are involved. Of particular interest now is the effect that substructure has on the behavior of the refractory metals. Understanding the development of low-angle grain boundary networks, their interaction with interstitial elements, and their effect on recrystallization, yielding, and fracture at all temperatures should throw considerable light on the low temperature brittleness problem. Many problems have not been resolved, such as why varying degrees of cold working in the group VIa elements, Cr, Mo, and W, results in a fiber condition which lowers their transition temperatures. There are also questions concerning fracture itself, such as where it initiates, how it propagates, and what part interstitial elements and twinning have in this process.

Processing Problems

Primary consolidation of the refractory metals has been accomplished principally by one of two methods, by powder metallurgy, or by melting methods, such as arc-melting or electron-beam melting. The powder method is the oldest technique and has been applied primarily to W, Ta, and Mo. The development of melting methods considerably increased the range of alloy compositions and the sizes of ingots that can be prepared, and these methods are now being widely used for consolidation of all refractory metals.

Appreciable purification of the metal can be obtained by vacuum melting by volatilization of impurities, particularly in the case of electron-beam melting of Cb and Ta. Oxygen (O) can further be reduced by adding suitable deoxidizers, such as carbon (C), to the melt.

The breakdown of the generally large-grained ingots resulting from the melting processes is a challenging problem, particularly for the more intractable high strength alloys. The best solution to date has employed the hot extrusion process, particularly since the development of improved glass lubricating and die coating techniques. Forging is also being used, both for primary breakdown of more fabricable alloys and for further working of extruded billets. The general procedure in making sheet product is hot rolling, with suitable intermediate anneals, until the material is sufficiently worked to allow finishing at some lower temperature. If other wrought forms, such as extrusions or forgings are desired, a suitable processing course in that direction is followed. Powder metallurgy techniques are also used for this primary consolidation by pressing, sintering, and further fabricating to mill product forms. The powder process is used as one method of preparing electrodes for arc melting.

Since details of these processes are being discussed by another panel, our comments will be limited to some of the problems associated with the processes.

The problem of oxidation has already been pointed out and, of course, is important in processing because of the high temperatures required for working the refractory metals. Mo and W are traditionally heated in hydrogen atmospheres to prevent oxidation since the solubility of hydrogen (H) in these metals is lower and there is no hydride formation. Although the question has been raised as to whether this is truly an inert atmosphere, there are no apparent reactions to indicate the contrary. Gas fired furnaces with reducing atmospheres are also used. Hydrogen-containing atmospheres cannot be used with Cb and Ta, for large amounts of the interstitials, H, nitrogen (N), and oxygen will dissolve in and embrittle these metals.

Processing of Mo and W is often accomplished in air. The oxides of these metals are volatile, Mo above 1800° and W above 2300°F, and material will vaporize, but the solubility of interstitials is generally low. There is, however, a thin but undesirable surface contamination layer formed which must often be planed by grinding. Cb and Ta cannot be processed in air above about 1000°F. Unalloyed Cb and Ta of commercial purity can be processed at temperatures below this, but many higher strength alloys of Cb and Ta require hot breakdown, and this must be accomplished in inert atmosphere, such as highly purified argon or vacuum. Techniques of canning in Mo, Ti, or stainless steel have also been used, but this is an expensive, not always reliable, and generally undesirable method, particularly for large-scale production. There are some processing coatings that are being used that seem to minimize surface oxidation and contamination, but a certain amount of material must be sacrificed in subsequent scalping or pickling operations.

The value of processing refractory metals in completely inert atmosphere has many interesting possibilities which have not as yet been proved, although the current Infab facility may accomplish some of this. With such an atmosphere, not only can the effects of atmospheric impurities on resulting wrought products be eliminated but, perhaps more important, the opportunity to truly hot work the refractory metals will exist. A facility of this nature may eliminate many of the problems not attributed to processing.

Process Control

One of the most important aspects of any processing procedure used for the refractory metals will be control of the process. There are a number of processing factors that will most certainly affect the behavior of the wrought product. These factors are, for example, the temperature of deformation, the amount of deformation at a given temperature, the sequence of thermal and mechanical processes, and the times at temperatures during processing. The thermally activated mechanisms, such as recrystallization, recovery and polygonization, that will be operative during the warm and hot working operations can definitely affect the properties of wrought products. In addition, it has already been very clearly shown that many alloys will be susceptible to solution heat treating and aging reactions, which also will occur during hot and warm working operations. Some aspects of both of these occurrences have already been investigated. Laboratory data has shown that, in some instances, great variations exist in property data on what is now the closest thing to production sheet available, perhaps as a result of variations in the processing operation from one sheet to another. So it is important to understand such things as the nature of substructure formation, its effect and how to control it, the kinetics of solution treating and aging in various alloys and then control the processing to minimize the deleterious effects and take advantage of the desirable effects.

Since the primary need for refractory metals for aerospace applications is in the wrought form, and particularly in the form of flat rolled sheet, a Materials Advisory Board Refractory Metal Sheet Rolling Panel has been established at the request of the Department of Defense. This panel, in cooperation with the Army, Navy, and Air Force, is reviewing the current efforts to produce refractory metal sheet, making recommendations concerning the programs and the need for further work. The organization of this panel is shown in figure 9. Various subpanels have been established to provide more detailed study and recommendations for certain aspects of the sheet rolling area. There are now four major programs being sponsored by the Air Force and the Navy intended to produce refractory metal sheet which are being followed by the panel. They include projects for the production of Mo alloy sheet, Cb alloy sheet, and two projects for W sheet, one using powder compacts and the other starting with arc cast material. The panel is also kept informed of related projects sponsored by the various military contracting agencies.

In addition to these sheet rolling activities there are also projects on forging of Mo, Cb, and W and extrusion of Mo, Cb, Ta, and W.

In discussing the difficulties facing the refractory metals producers and users, some of the more important aspects were mentioned. There are other problem areas, such as joining, both by thermal and mechanical methods, chemical analysis, machining, and fabrication of components which were not mentioned, but which, nevertheless, are significantly important in their own right and which require adequate developmental effort.

Alloy Development

The most extensive alloy development efforts have been directed toward Mo, dating back to original interest in its potentialities for use in turbine applications. Although never successfully utilized because suitable protective coatings had not been developed for the severe conditions involved, a great deal of valuable data was generated which actually assisted in later developments for all of the refractory metals. Development of W for use in filament applications predates Mo work by many years. However because of the competitive nature of this area, details of much of the work on W were not published and, until recently much of the technology of W processing could be almost classified as an art. Developments in Cb and Ta have been much more recent. The current state of alloy development of each of the four refractory metals will be considered separately.

Columbium Alloys

Of all of the refractory metals, there has been more industry support of alloy development in Cb in recent years than of any of the other three metals. Perhaps the biggest reason for this interest is because of its versatility which makes it competitive for a number of applications. Unalloyed Cb possesses several inherently useful properties. It is ductile, weldable, has excellent fabricability, low density (as compared to other refractory metals) and is not susceptible to low temperature notch sensitivity. By alloying, it can be made resistant to liquid metal corrosion, can be made to have improved oxidation resistance, and can be greatly strengthened for high temperature applications. The problem is that it is not always possible to achieve the desired combination of improvements through alloying without sacrificing some of the other desirable properties of Cb. For example, a high strength, oxidation resistant combination has not yet been found. Neither has anyone as yet achieved the excellent high temperature strength obtainable through alloying without sacrificing something in fabricability and weldability.

A great number of Cb alloy compositions have been identified within the last few years. In fact, more than thrity alloy compositions have been carried to the point of identification as potentially commercial alloys. Among these are included some alloys with improved oxidation resistance, some that retain Cb's fabricability, and others that have very good high temperature strength. The short time-at-temperature properties of some of what might be considered the first generation of Cb alloys are shown in figure 10. Their compositions are given in table 1. Alloys with better fabricability such as Cb-65, FS-82, and D-31, have lower strength properties at elevated temperatures. Meanwhile, the higher strength alloys, such as Cb-7, F-48, and D-41, are much more difficult to fabricate and their weldability has been reduced. Fabrication difficulties result from the fact that because of their better strength at higher temperatures, the initial breakdown of the large-grained arc-cast ingots must be accomplished at higher temperatures where oxidation and oxygen diffusion to form a hard, brittle layer occur more rapidly.

Emerging from these first generation alloys are two, which for various reasons, will be among the first commercially available Cb base sheet alloys. F-48, because of its higher strength, and D-31, because of its combination of fabrication, fair oxidation resistance, and reasonable strength, are the two alloys included in the current Cb sheet rolling program now in progress. Additional experience with F-48 was obtained as a result of its inclusion in an Air Force program to build a typical hot load carrying structure. These two alloys, along with the Cb-1 Zr alloy, a lower strength alloy which is also promising for liquid metal containment, the FS-82 alloy, and the unalloyed Cb, constitute what are currently the only commercially or semicommercially available Cb alloys in sheet form.

There is now in existence a second generation of Cb base alloys, some of which are shown in figure 11. The alloy selection subpanel of the Materials Advisory Board Refractory Metal Sheet Rolling Panel has recently reviewed the present Cb alloy development efforts of the producers of the country. Of the seven producers that had data to present, a total of 13 alloys were considered as possible candidates for a sheet rolling program to be sponsored by the Bureau of Naval Weapons. Emphasis has now been shifted from the high strength type of alloy to a more fabricable type where ease of fabrication and weldability are the important property considerations. Unfortunately, many of these alloys are in a fairly early stage of development and making a uniform comparison of properties is not entirely possible. There are variations in high temperature strength of these alloys. There are also variations in low temperature ductility and weldability. Considerably more data must still be determined; further work to develop the unique advantage of each is still in progress.

General trends in Cb alloy development indicate that those solid-solution additions which impart the most high temperature strength are the group VIa elements, Mo and W. Also, when added in sufficient quantity to appreciably strengthen, it is these elements that raise the transition temperature and adversely affect fabricability and weldability. Another potent strengthening mechanism characteristic of most of the high strength alloys, is the interaction between one of the reactive metals, Zr or Hf, and the interstitial elements, C, O, or perhaps, N, to form precipitates. These reactions are very effective in high temperature strengthening and are important to ductility after welding.

Tantalum Alloys

For the last year or so, Ta has been the dark horse of the refractory metals. It was bypassed as a base material in early refractory metal developments for three reasons. It is heavy, being only second to W in density. Unalloyed Ta has very low strength, both at ambient and elevated temperatures, and it is expensive because of the comparatively limited supply. Its principle advantages are its high melting point and its excellent low temperature ductility, but its oxidation resistance is no better than that of other refractory metals. Because of its ability to accept a large number of elements in solid solution, it appears to be a very good base for alloy development. Recent developments on Ta alloy study programs have shown that it is possible to greatly improve the high temperature strength of Ta by solid-solution alloying without sacrificing low temperature ductility. The result is that ease of fabricability plus weldability can be achieved while still maintaining good strength at temperature.

The data presented for most of these Ta alloys, unfortunately, are the results of only limited tests of laboratory size quantities of material. Larger size quantities of the more promising alloys are being processed currently, however. High temperature tensile data for some selected alloys are shown in figure 12. Some of the data plotted were determined in the recrystallized condition. Because they are apparently solid-solution strengthened alloys, excellent properties are obtained without strain-hardening, as can be noted by comparing data on recrystallized alloys with stress relieved alloy data.

The Ta-30Cb-7.5V alloy is particularly interesting and is worth discussing further as an indication of what can be achieved in Ta alloys. Its density is much lower than unalloyed Ta because of the 37 weight percent of less-dense alloy addition. Its strength-to-weight ratio is particularly attractive in the 2300° to 2900°F range. But, more than just strength at temperature, it offers the unique property of exhibiting 20 percent elongation in the recrystallized condition in a tensile test at -320°F. To produce this alloy on a commercial basis, it has been consumable-electrode arc melted and further processed to experimental sheet. During the process, it was cold rolled from recrystallized 0.5-inch thick plate to 0.040-inch thickness with no intermediate anneals. After welding, its minimum bend radius at room temperature was approximately 1.5 T, which, by refractory metal standards, is excellent. This alloy must undergo additional testing to further verify its properties. The results to date, however, serve to illustrate the potentialities of alloys of this nature.

There is only one Ta base alloy that can be considered as a semicommercial sheet material at the present time. That is the Ta-10W alloy, which is also shown on figure 12. This material was initially emphasized as nozzle insert material for solid rocket application, but holds promise for structural applications.

It has also been shown qualitatively that the same strengthening effects by precipitation or dispersion of oxides and/or carbides of Ti, Zr, and Hf, that have been identified in Cb alloys can also be achieved in Ta. This data is preliminary and further work is necessary to determine the extent to which it can be used, but the accomplishments already achieved will probably aid in improving the creep and rupture properties of Ta alloys.

Molybdenum Alloys

During the past decade the primary objective of the major research efforts on Mo base alloys has been to increase the high temperature strength of the base metal and to study the effect of thermal and mechanical variables on the properties of these alloys. These programs have advanced the useful temperature range of Mo alloys. Alloys with an increased recrystallization temperature have been developed which are stronger in both short and long time properties, through the addition of elements which have promoted solid-solution strengthening, precipitation strengthening, and/or strain-hardening effects at elevated temperatures.

The most effective strengthening benefits have been derived from increased carbon contents in combination with relatively small amounts of Ti and Zr. A second important advancement in alloy development involves the substitution of W for part of the Mo, which increases the melting point of the alloy. The addition of small amounts of Cb has also been effective in increasing strength. The strength-temperature relationship for certain compositions are shown in figure 13.

Since Mo alloys rely to a great extent upon the increased strength resulting from strain hardening, the effects of alloy addition on recrystallization temperatures are very important, and increased recrystallization temperature has been an important objective of alloy development. To date, the highest recrystallization temperature attained has been in the Mo-1.25 Ti-0.3 Zr-0.15 C alloy, where a 1-hour exposure at 3400°F was required for complete recrystallization.

Currently, the Mo-0.5 Ti alloy is considered commercially available and is the prime candidate for use in construction of heat shields for re-entry glider type vehicles. The Mo-0.5 Ti-0.07 Zr (TZM) alloy is also nearing the stage of commercial availability and will probably replace the Mo-0.5 Ti alloy since it has a higher recrystallization temperature and better high temperature strength.

In addition to these commercial alloys there are a number of more experimental alloys under development that exhibit excellent high temperature strengths. Two of these alloys are also shown in figure 13. The Mo-1.67 Cb-0.49 Ti-0.3 Zr-0.31 C alloy shown has much higher strength at lower temperatures, and although displaced by the Mo-25.1 W-0.11 Zr alloy in actual strength at 2400°F, still appears better when the data is density compensated.

These compositions reportedly present no serious problems in preparation by vacuum-arc casting. They have not yet been produced and tested in sheet form, however. The success that has been attained to date in fabricating these higher strength compositions into the wrought condition for testing is largely attributable to recent progress made in the primary breakdown of arc cast ingots by the hot extrusion process, particularly since coating extrusion dies with refractory oxides were improved and glass lubricants were properly identified.

The relationship that exists between the C, Ti, and Zr contents in Mo base alloys is one of the very challenging areas for alloy research and one that has received a great deal of attention. It is combinations of these three elements that provide the basis for the highest strength Mo alloys through the formation of carbides. Although data has been generated indicating relative additions of these elements necessary to obtain improved strength, and the effects that solution treating and aging have on properties, considerable effort is still needed in this area. It is particularly important to determine carbon's role in the strengthening, since it adversely effects low temperature ductility. Once the quantitative functions of these additions and the kinetics of the heat treating are better understood, it should be possible to determine the extent to which tradeoffs between low temperature ductility and high temperature strength can be made.

Tungsten Alloys

Alloy developments of W have been of two types to date, those made by powder metallurgy techniques and those produced by consumable-electrode arc melting methods.

Included in the powder metallurgy group are unalloyed tungsten and tungsten to which small amounts of various doping agents, such as mixtures of alkaline oxides with silica or alumina, are added. The doping agents are added primarily to retard recrystallization and control the grain structure formed to give interlocking, rather than equiaxed grains. Their effect on strength is probably not significant other than the recrystallization effect. These alloys are commercial, but are available primarily as rod or wire for fabricating filaments. The use of doped powders for production of W sheet material is being investigated on one of the sheet programs mentioned previously.

There are some other additions to powder compacted W which have been investigated that affect high temperature strength. These include Thorium dioxide ($Th0_2$), which also serves as a doping agent, and Tantalum and tetra Boron Carbides (TaC and B_4C).

Arc melting is also being used to prepare alloys and is somewhat more versatile in that there are more alloy systems that can be processed by this method than by powder methods. Limitations are in the volatility of the addition, and in the additions, such as Titanium, Silicon, Cobalt, Iron, Vanadium, and Nickel, which are difficult to retain. Figure 14 presents some data on various alloys of W. Of the alloys shown here, the only one that can be considered as commercially available in sheet form at the present time is unalloyed W. The other data represent results of some very limited tests on laboratory size quantities of material.

Much interest is currently centered on the W-Mo series. Although no significant strengthening effect at temperatures above 4000°F over unalloyed W is noticed for most of the W-Mo alloys, the W-15 Mo, which seems to have maximum strength in the system, shows some superiority up to 4000°F. Mo additions have grain refinement effects that are beneficial in breakdown and machining operations. Small additions of Group Va elements such as Cb and Ta have been shown to improve strength at 3000°F (figure 15). In fact, one of the highest data points recorded for any material at 3000°F, 60,000 psi, is a W alloy containing only 0.57 Cb. Data for other alloys in this composition range prepared by different processing techniques have not yet duplicated this strength, being in the 38,000 to 40,000 psi level. The strengthening mechanism operative has not yet been established, but it seems likely that it is related in part to the processing method used. Tests at higher temperatures were not performed on that particular lot of material, but other data suggest that the tensile strength would start to drop rapidly at higher temperatures.

Recent experimental data on the W-Ta-Mo-Cb alloy series has outlined a number of very interesting solid-solution alloys. One of these alloys W + 5.7 Mo + 5.7 Cb tested at 3000°F resulted in an ultimate strength of 62,000 psi. Other alloys in this series, which were essentially W and W-Ta base, gave strength levels above 50,000 psi. These alloys are being explored further, both from a fabricability standpoint and also for strength above 3000°F.

In general, alloy developments in W have been very limited. Many problems have been encountered in preparing W alloys, and testing capabilities at temperatures above 3000°F are limited. With the exception of the addition of the refractory metals to W, most alloys are dilute in nature and permit the advantage of strain hardening. At temperatures above 3000°F, where W will be competitive as a structural material, strain hardening will not be effective because of recrystallization, solid-solution strengthening will become less effective and, to get higher strengths, the addition of inert dispersed particles will probably be the most important strengthening method.

Fundamental Work

The importance of strong efforts in what can be considered fundamental work cannot be over emphasized. Problems to be overcome in the time available are such that empirical solutions will not be adequate.

A more thorough understanding of the mechanisms of flow and fracture at both low temperatures and high temperatures must be obtained for use in both processing and application. Although considerable effort is now underway concerning the effects of interstitials in the refractory metals on strain aging and other behavior, more work is needed, particularly on problems of interactions between interstitial elements and substitutional elements and their effect on strength and ductility. For coating applications and applications where dissimilar metals will come in contact, diffusion data are needed. A variety of physical properties must be determined at elevated temperatures such as thermal conductivity, heat capacity, thermal expansion, etc., particularly as new alloys emerge that seem to be suitable for particular applications.

Other Needs

Alloy development must necessarily be emphasized probably as long as refractory metals will be used. The efforts should be to achieve optimum combinations of strength at temperature combined with other properties for specific applications. The quest for alloy additions to Mo and W that will improve low temperature ductility must continue, for the obvious desirability of a weldable W or Mo alloy, which will only be achieved by this method. Related to alloy development is what appears to be one of the most interesting and perhaps fruitful areas for work and one which has not yet been very deeply explored— combining suitable alloy composition with proper heat treatment to give improved properties. Of particular importance are the formation of carbides and oxides, and learning to control their shape and location in the matrix to combine strength with maximum ductility. It is also very important that much additional data be generated on alloys that have already been identified. Needed are data at elevated temperatures, particularly above 3000°F. There has been practically no compilation of fatigue data, including sonic fatigue. The same kind of data are needed for material systems, that is, refractory metal alloys with suitable protective coatings. Long time creep and rupture data up to 10,000 hours are needed. Much of this data on alloys can only be determined when processing procedures have been properly developed and suitable quantities of material produced. In fact, it does not seem unlikely that far more material will be consumed in testing in the near future than will be used in applications thereafter.

So far, many promising refractory metal alloys have emerged from the laboratory research efforts, although developments in Cb and Mo base alloys to date far exceed those in Ta and W. While the discussion has been centered upon comparisons of high temperature strength and particularly short time strength, we obviously do not intend to imply that alloy development efforts are or need to be based on this one criterion. Just as important to specific application will be the alloy's ability to be drawn into tubing or complex shape, or to be rolled to very thin sheet or foil, or its ability to be welded or brazed, or to withstand stresses for very long periods. This diversity requires that development of alloys of all four refractory metals be pursued rather than a concentrated effort on only one or two of them. Only in this way can suitable material be available to the designer to satisfy specific jobs.

There is apparently no aspect of refractory metals technology that can be neglected or where progress has been sufficient to date that more effort would not be justified. The problem is in assigning the correct priority to individual tasks and areas so that achievement of the goals of providing suitable high temperature materials can be attained in the shortest possible time.

The importance of processing the refractory metals has already been emphasized. The problem of getting wrought products of uniform and consistent properties, thickness, and flatness is currently second only to the coating problem as far as application of the refractory metals is concerned. It, therefore, must rank high as an area requiring continued effort. A better understanding of processing as related to microstructure properties, and effects of thermal treatments is needed, which should then be followed by the development of improved methods of controlled processing. To achieve this, new processing facilities may be needed, particularly those housing production size equipment where vacuum or controlled inert atmosphere is available.

Although not mentioned in any detail, the development of coatings and the testing of the resulting systems ranks as the number one problem to be solved and must seemingly be given high priority in any recommendations for refractory metal development.

Conclusion

In summary, we again remind you that there are difficult problems ahead. The future of many important space endeavors depends in some degree upon the extent to which the problems are solved and upon the time necessary to achieve solutions. The primary uses for the refractory metals now are generated by government requirements and the resulting markets that will be introduced will probably not be sufficient, at least initially, to stimulate widespread investment by industry in the research and development aspects of the refractory metals. Research in this area is expensive because of the high cost of materials and equipment required. The government has and will have to continue supporting a large portion of the effort. However, there is at the present time an industry supported effort for research both for nonmilitary and military uses and it seems very likely that this effort will expand as availability of material and processing equipment increases and additional nonmilitary applications come forward to take advantage of these new materials. Expansion of research support by industry, in refractory metals, to solve mutual problems faced by both government and industry will aid greatly in overcoming the tremendous obstacles. Government and industry working together can provide the necessary effort so that the refractory metals can take their place as engineering materials.

TABLE I

COLUMBIUM ALLOYS

DESIGNATION	PRODUCER	Ti	Zr	Hf	V	Ta	Mo	W
F-48	General Electric		1				5	15
AS-55	" "			PROPRIETARY				
Cb-7	Union Carbide	7						28
Cb-16	" "	10			3			20
Cb-65	" "	7	0.8					
Cb-74	" "		5					10
D-31	Du Pont	10					10	
D-41	" "	10					8	20
82	Fansteel		0.75			32.5		
80	"		0.75					
CT2WZ	"		1			24		10
B-22	Westinghouse	1	1	5				
B-77	"		1		5			10
C-103	Wah Chang	1	0.5	10				
SCb-41	Stauffer Metals			PROPRIETARY				

THE REFRACTORY METALS

	MELTING POINT °F	DENSITY GM/CC	MODULUS psi × 10^6 Cal./CM. /CM./SEC./°C	THERMAL CONDUCTIVITY	COEFF. of EXPANSION Micro./in./°F
Cb	4474	8.6	15.1	0.125	4.06
Mo	4730	10.2	47	0.34	2.7
Ta	5425	16.6	27	0.130	3.6
W	6170	19.3	50	0.397	2.55

Figure 1.

PROPULSION SYSTEM REQUIREMENT FOR REFRACTORY METALS

- SOLID ROCKET
  - Nozzle Area
  - Vector Controls

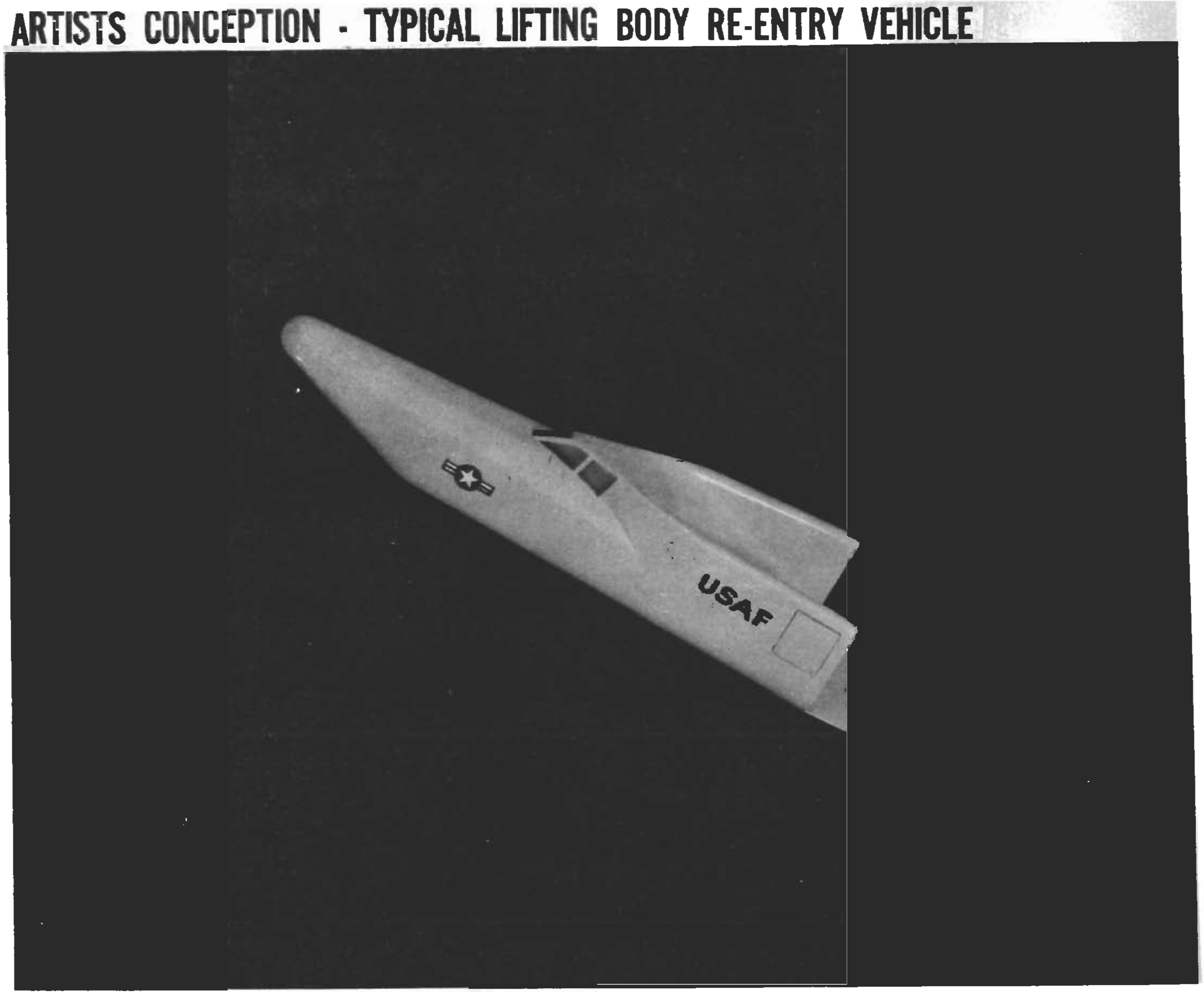
- LIQUID ROCKETS
  - Thrust Chamber
  - Uncooled Nozzles

- NUCLEAR PROPULSION
  - Nuclear Ramjet
  - Nuclear Rocket

- ION PROPULSION
  - Cesium Container
  - Ionizing Surface

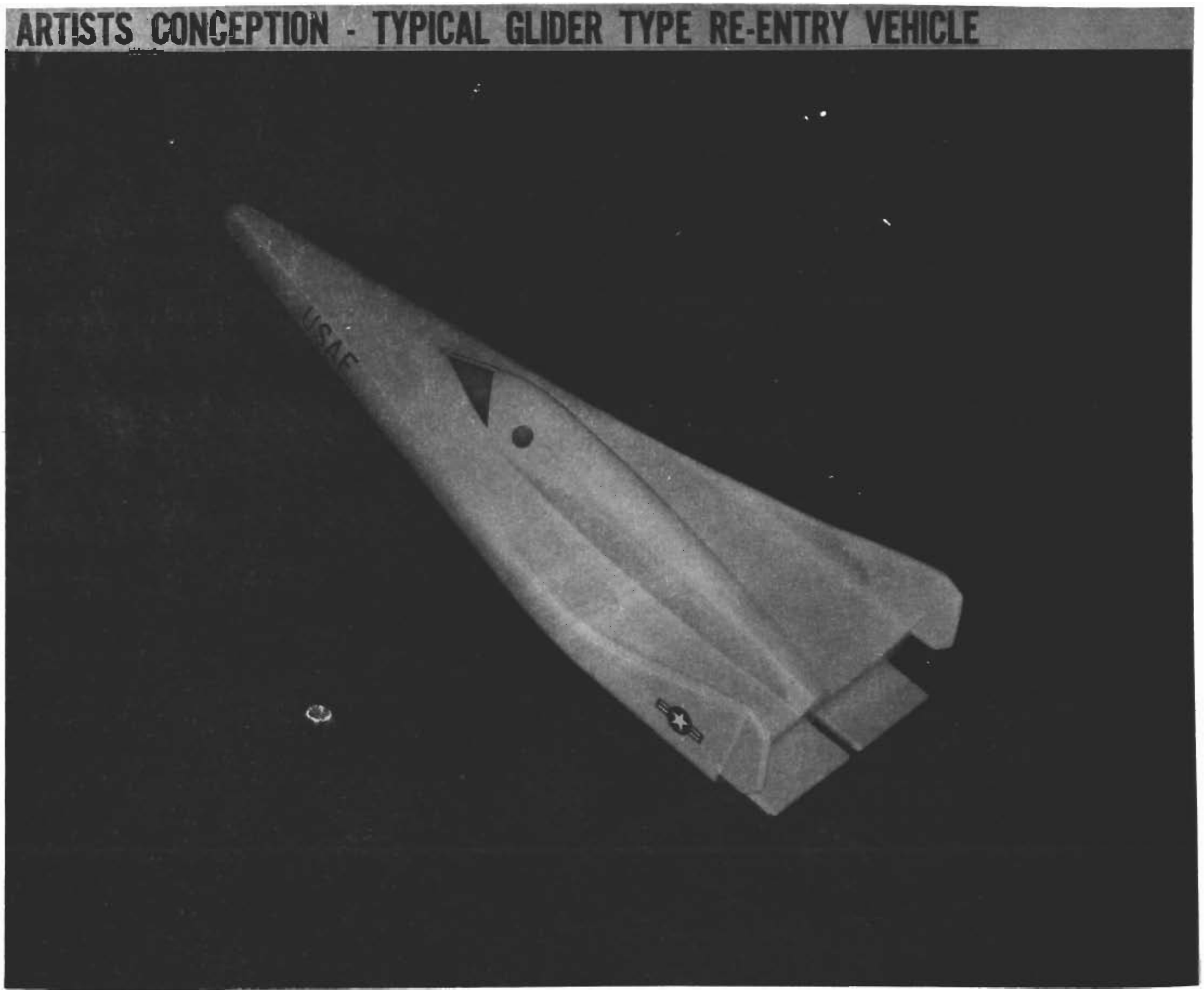
- AIR BREATHING RAMJET

Figure 2.



ARTISTS CONCEPTION - TYPICAL LIFTING BODY RE-ENTRY VEHICLE

Figure 3.



ARTISTS CONCEPTION - TYPICAL GLIDER TYPE RE-ENTRY VEHICLE

Figure 4.

EXPECTED EQUILIBRIUM TEMPERATURES DURING RE-ENTRY

	ORBITAL 26,000 Ft./Sec.	SUPER-ORBITAL 36,000 Ft./Sec.
LIFTING BODY		
Nose	4000°F	7000-8500°F
Lower Surface	2300-2700°F	4000-4500°F
Upper Surface	2000-2500°F	3400-4000°F
GLIDER		
Nose	3600-4000°F	6800-8300°F
Leading Edge	2700-3000°F	4500-5200°F
Lower Surface	1700-2400°F	2700-3750°F
Upper Surface	1500-2000°F	1800-3000°F

Figure 5.

SCHEMATIC OF SPACE POWER GENERATION SYSTEM

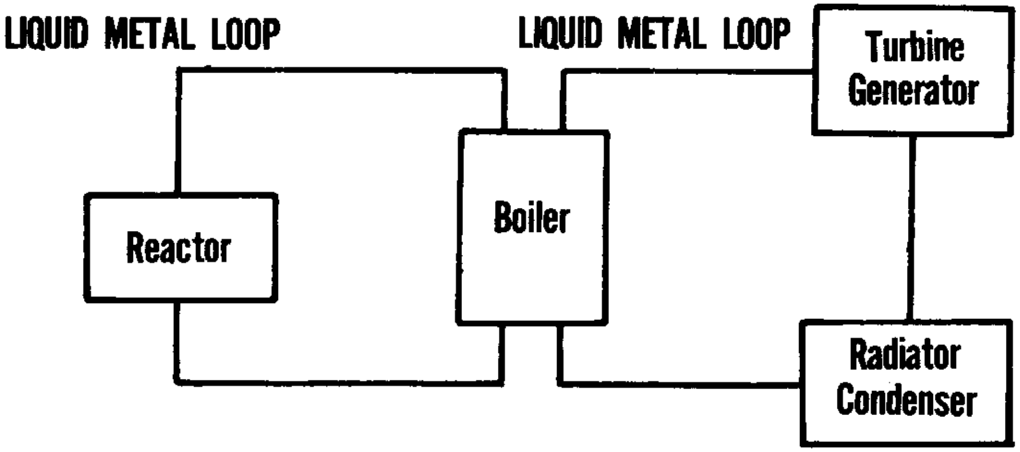


Figure 6.

TRANSITION TEMPERATURE FOR REFRACTORY METALS (RECRYSTALLIZED CONDITION)

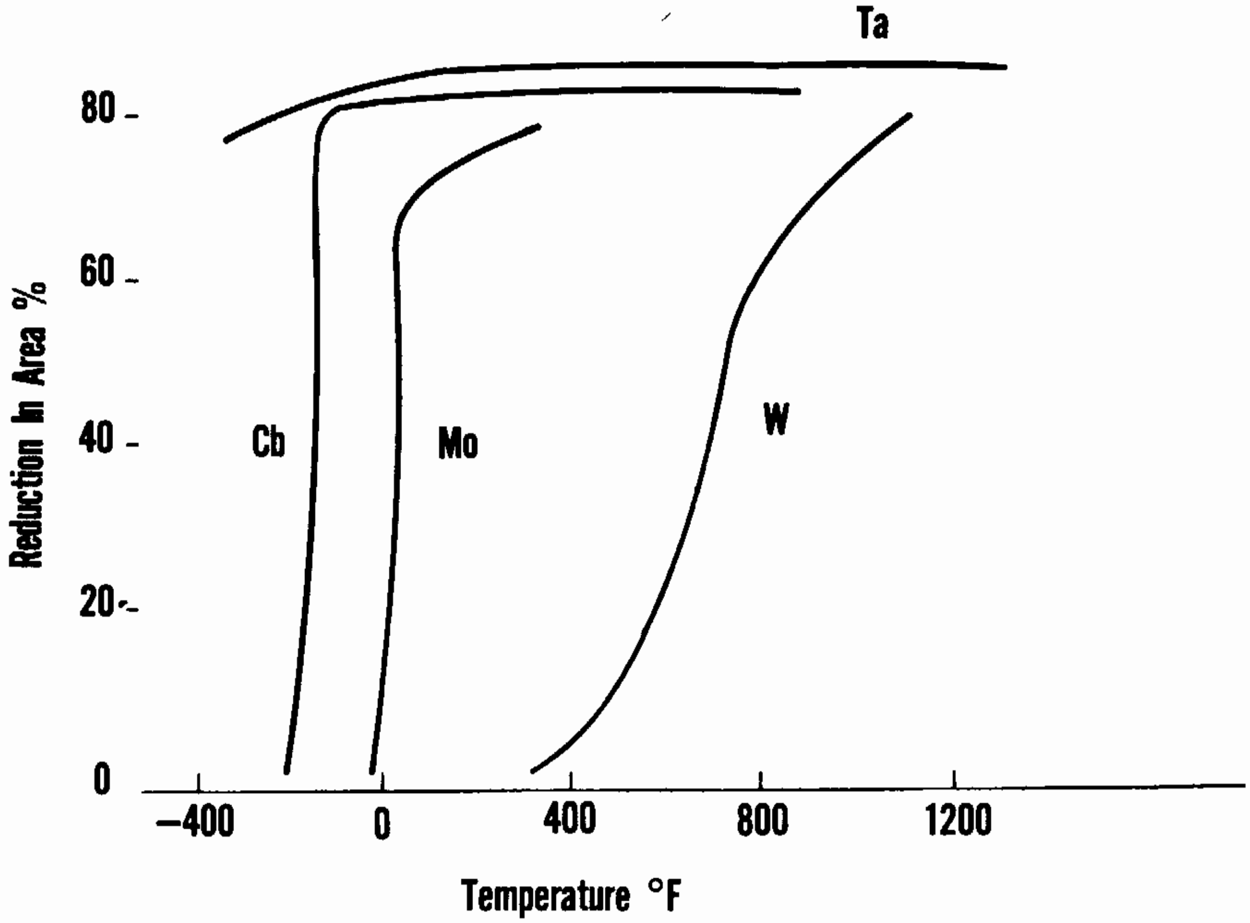


Figure 7.

EFFECT OF ALLOY ADDITION ON TRANSITION TEMPERATURE OF COLUMBIUM

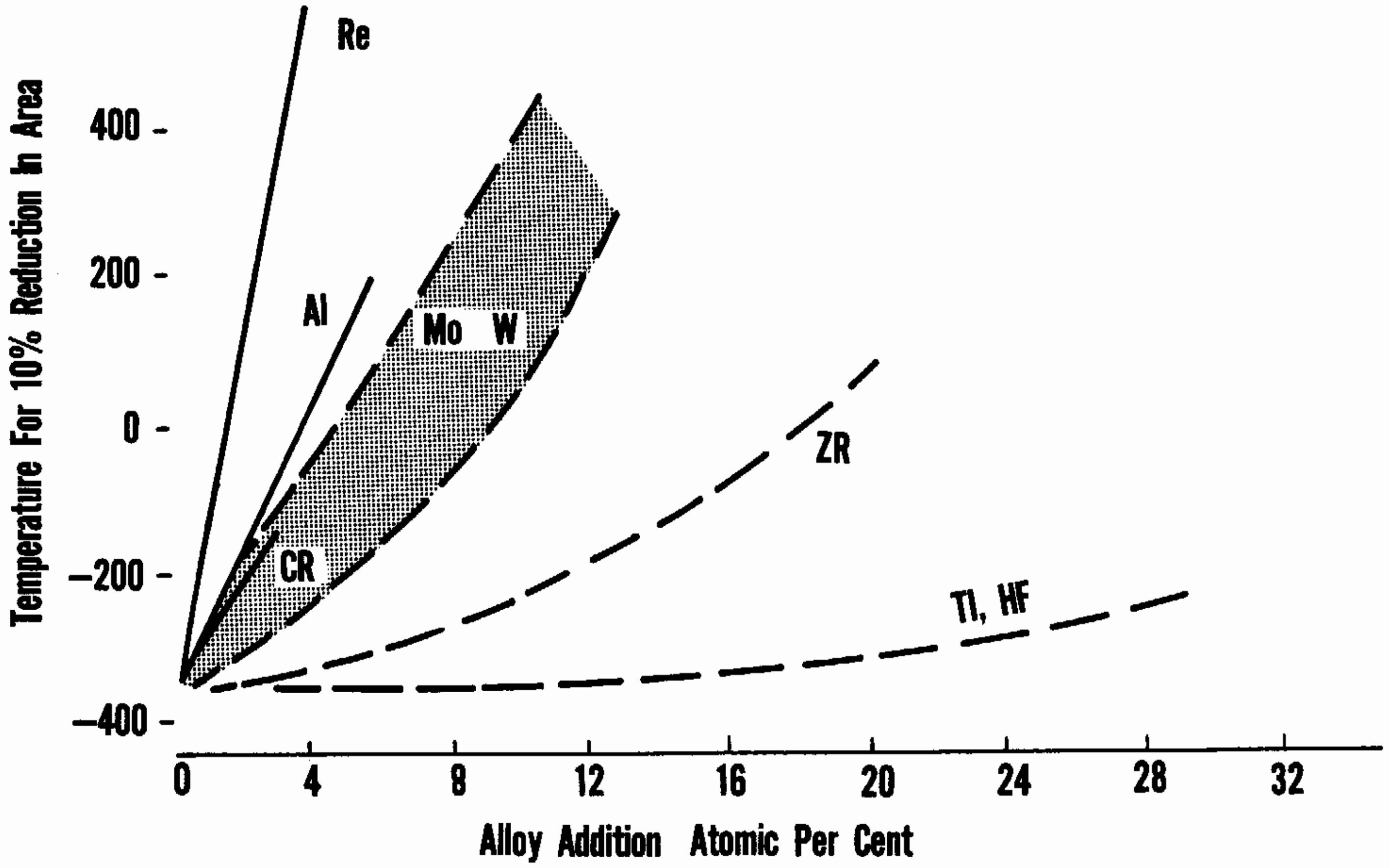
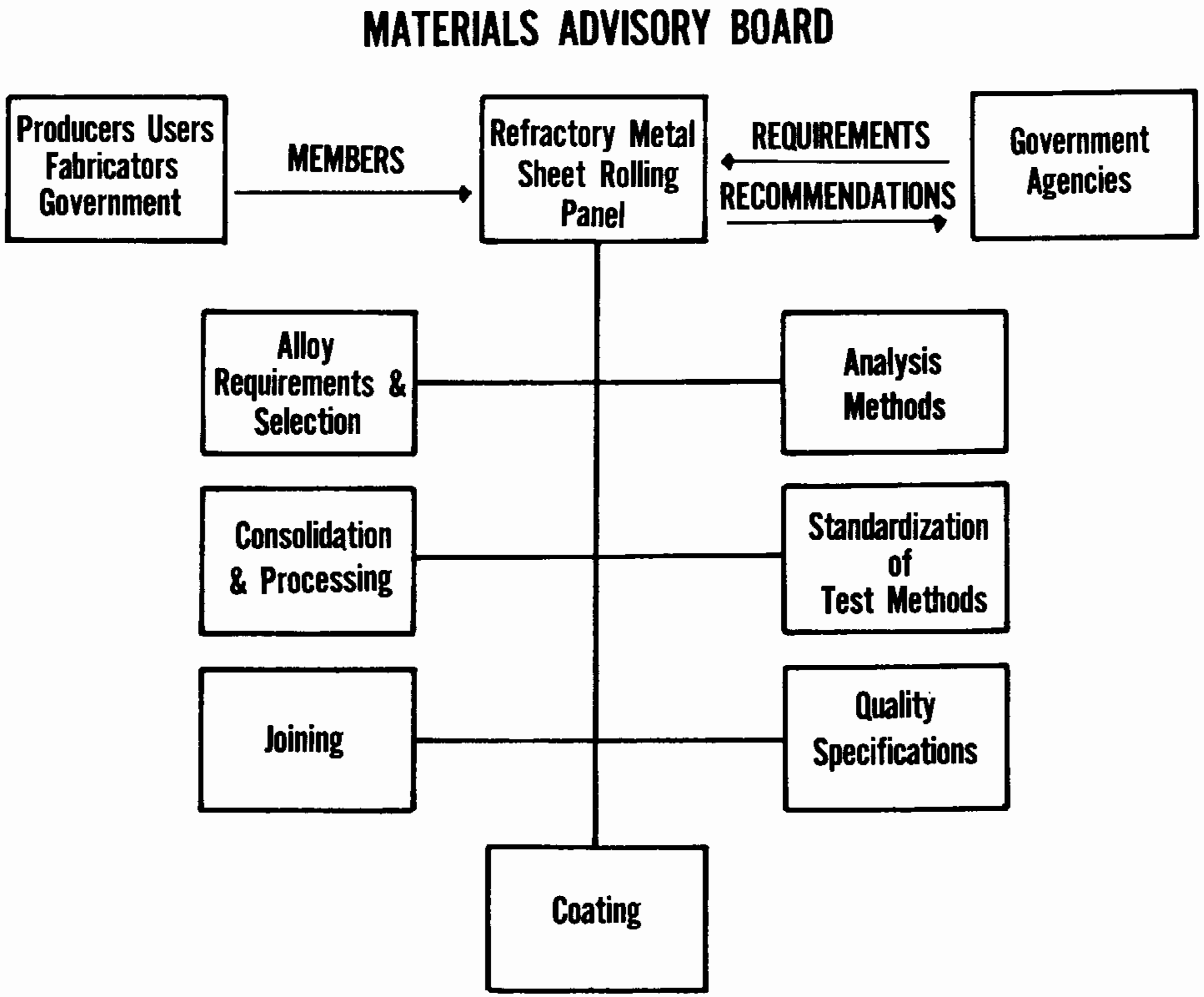


Figure 8.



MATERIALS ADVISORY BOARD

Figure 9.

ULTIMATE TENSILE STRENGTH OF COLUMBIUM ALLOYS

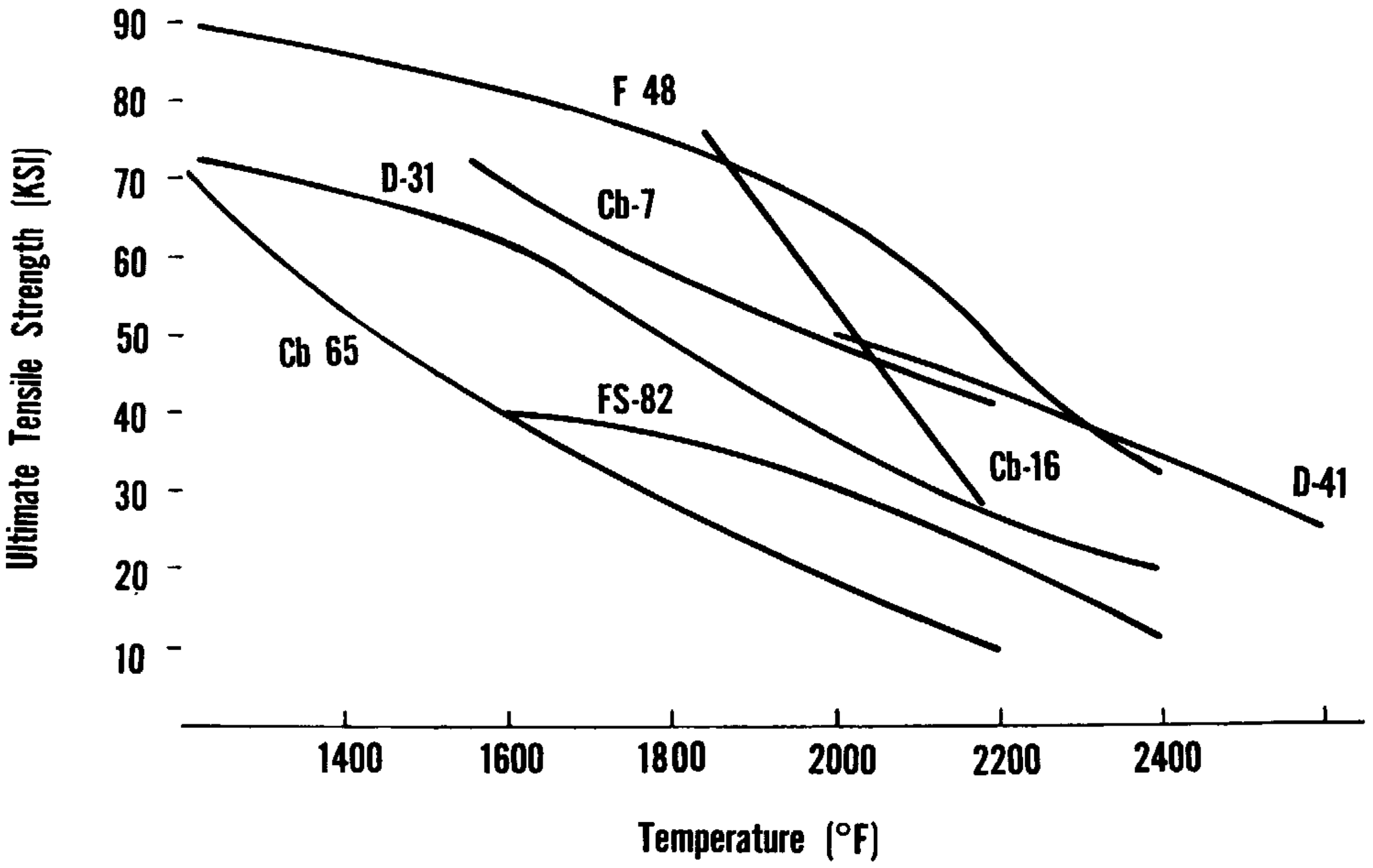


Figure 10.

ULTIMATE TENSILE STRENGTH OF COLUMBIUM ALLOYS

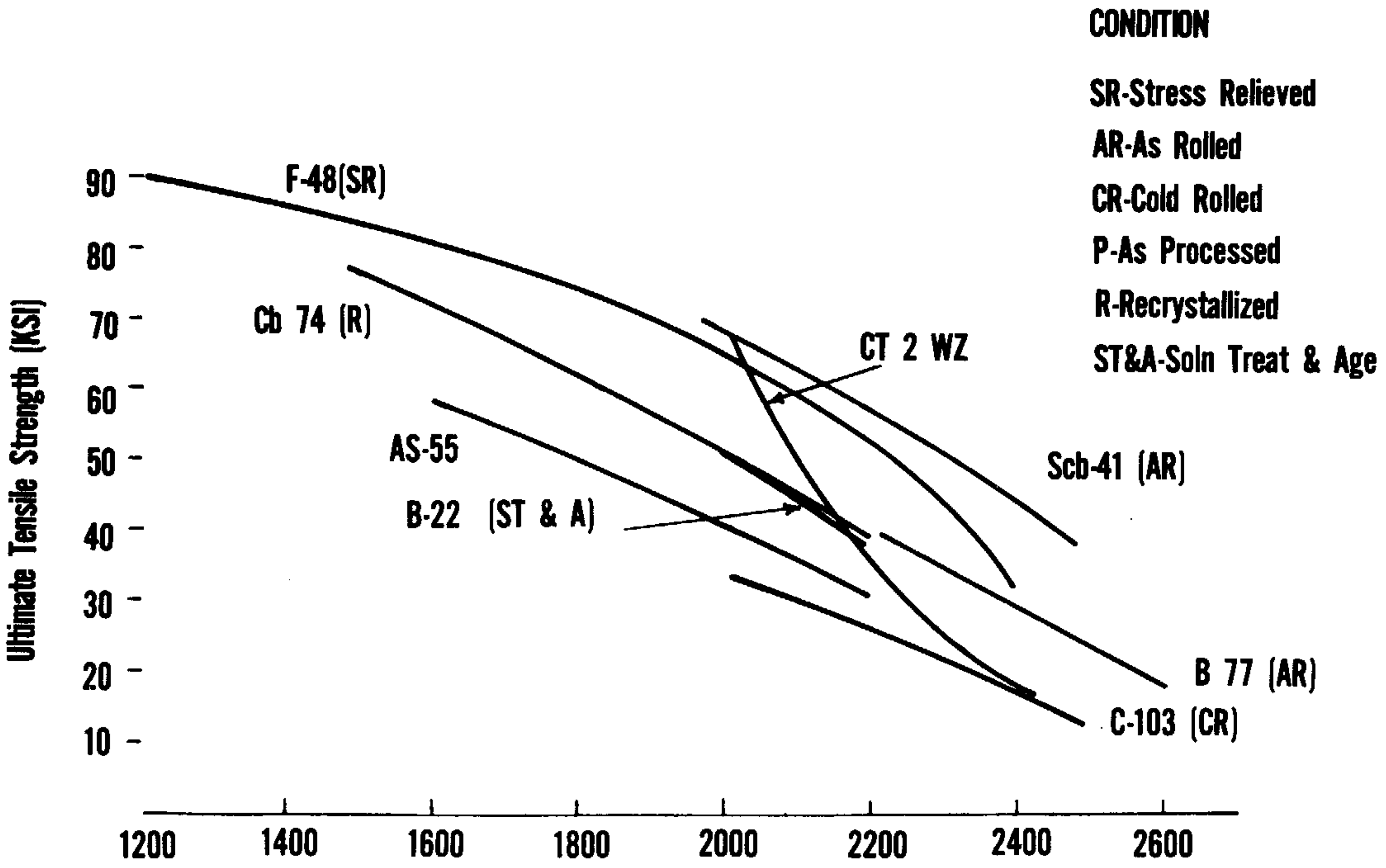


Figure 11.

ULTIMATE TENSILE STRENGTH OF TANTALUM ALLOYS

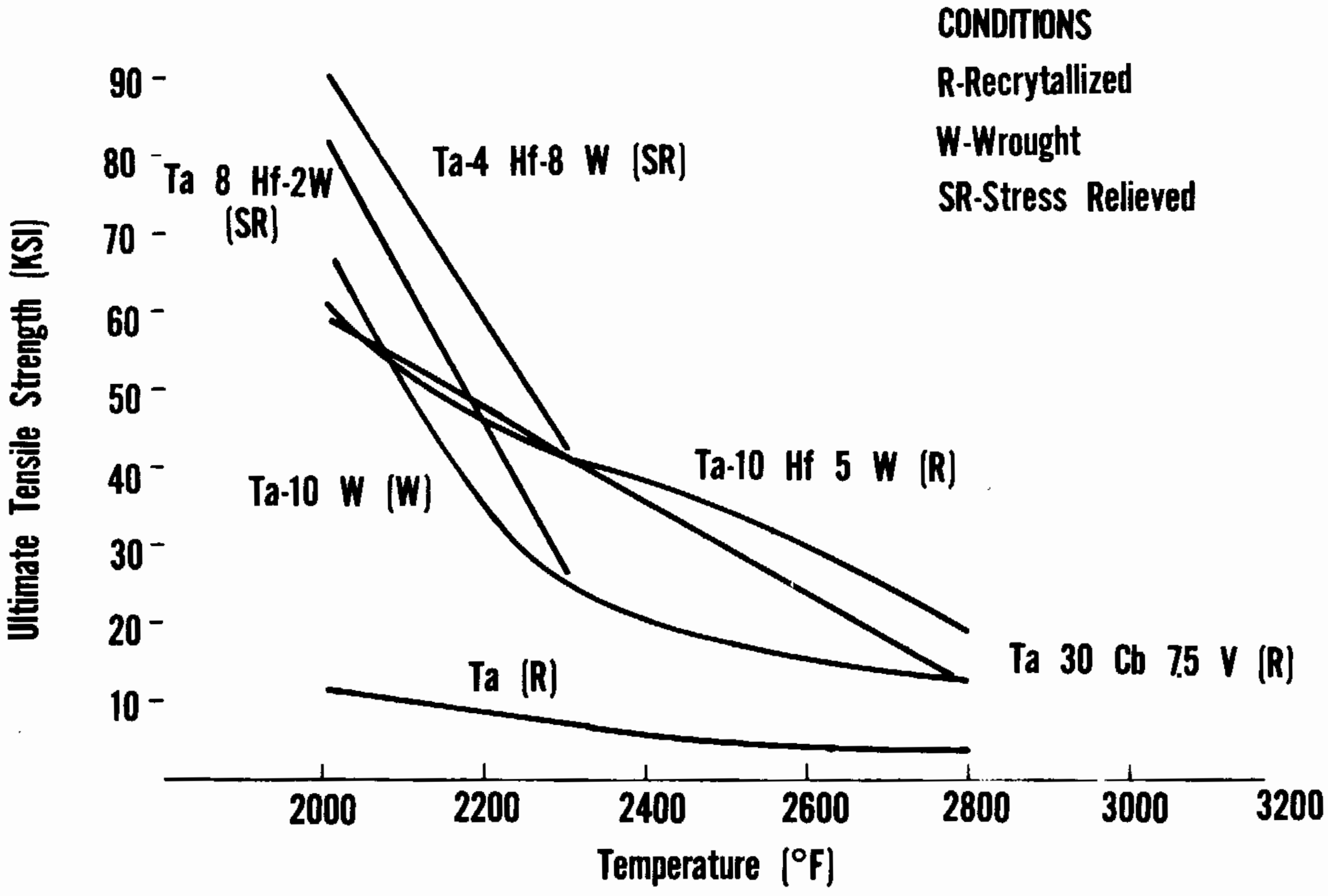


Figure 12.

ULTIMATE TENSILE STRENGTH OF MOLYBDENUM ALLOYS

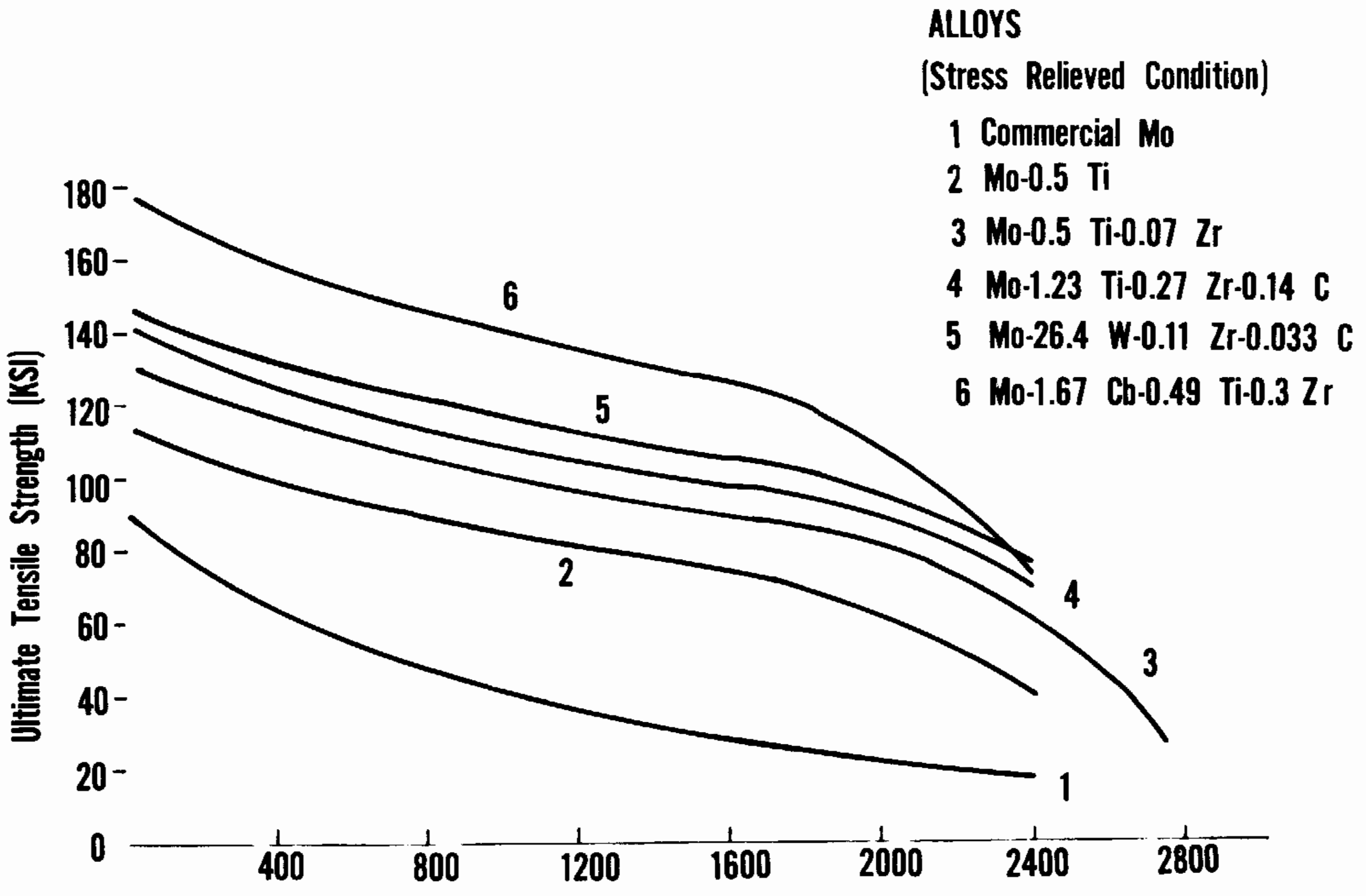


Figure 13.

ULTIMATE TENSILE STRENGTH OF TUNGSTEN ALLOYS

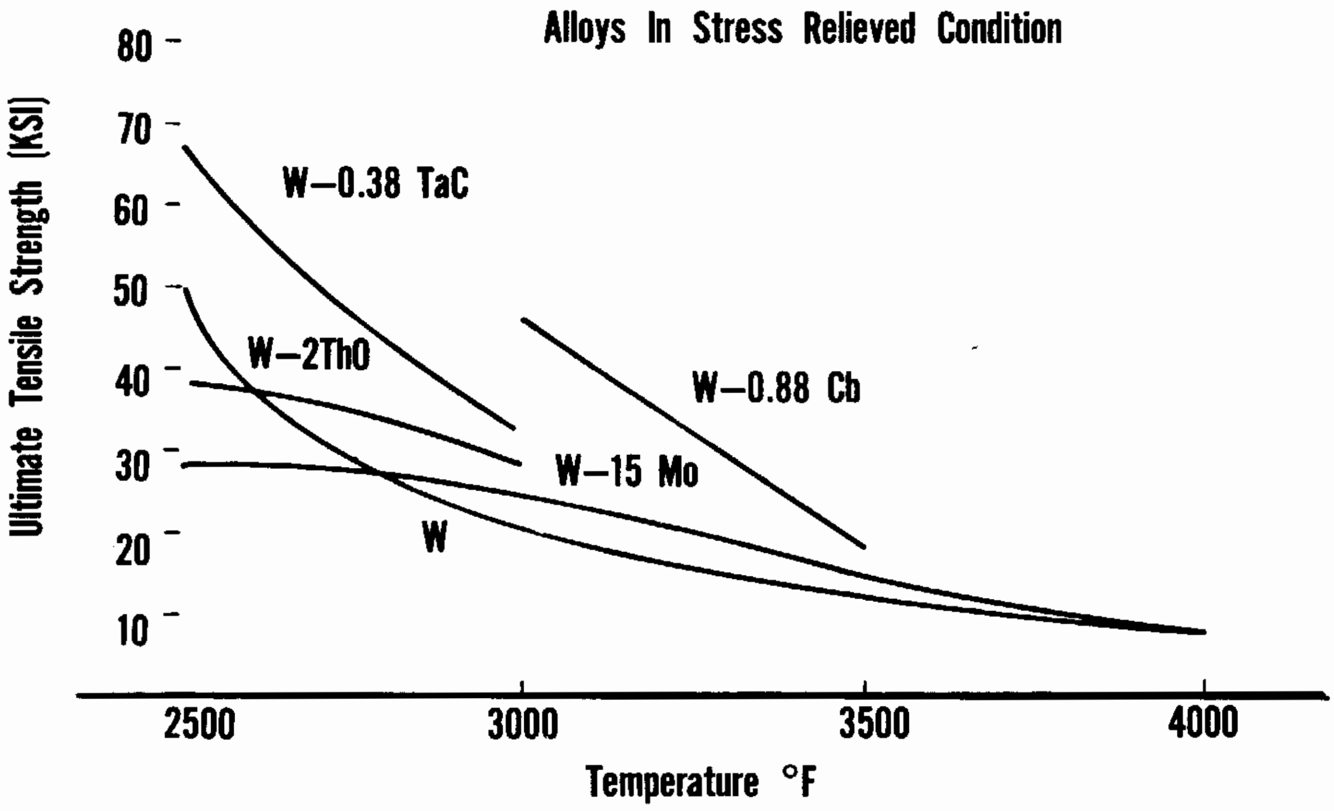
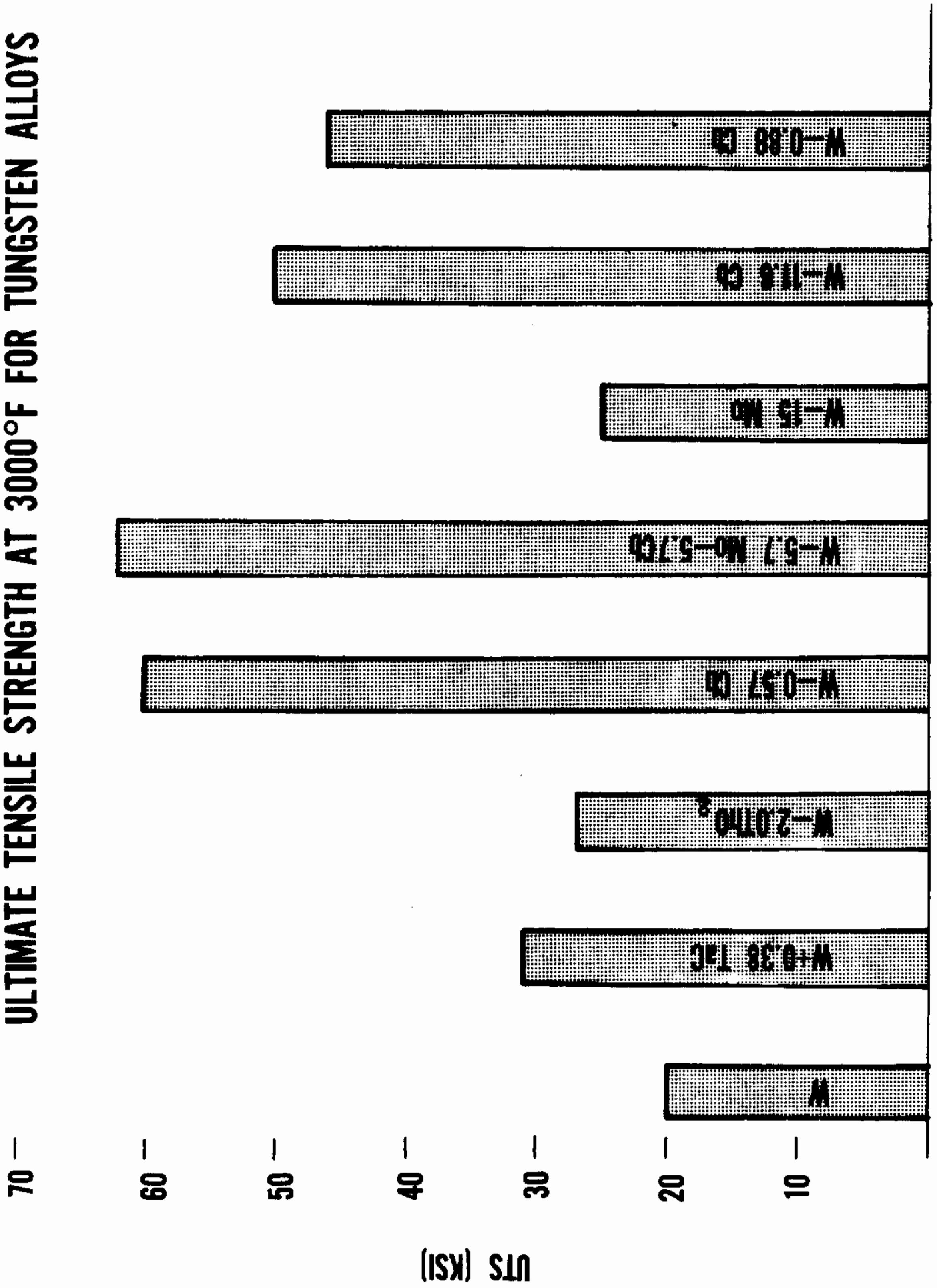


Figure 14.



ULTIMATE TENSILE STRENGTH AT 3000°F FOR TUNGSTEN ALLOYS

Figure 15.