

UNIQUE METALLURGICAL RESEARCH STUDIES

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UNIQUE METALLIC MATERIALS AND TECHNIQUES

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The aerospace age has ushered in some of the most advanced developments ever to come from human imagination and ingenuity. Each new development has created problems which have severely challenged human engineering capabilities. Every branch of the engineering profession has been presented with problems of varying degrees of difficulty, each problem requiring a solution which substantially contributes to technological development. One of the most important areas today is materials engineering and development.

In the present Air Force metallic materials development programs, we find ourselves confronted with two major barriers—the temperature barrier and the weight barrier. In this first area, we must cope with the problem of developing materials with adequate strength and corrosion resistance for use at temperatures far in excess of 1800°F. The general approach to this problem has been to turn to the refractory metals, such as tungsten, tantalum, molybdenum, and columbium, for use as base materials, and then to rely on alloying or thermo-mechanical processing for increased strength, with simultaneously developed coatings to provide the necessary resistance to oxidation and/or corrosion.

The weight barrier has created the necessity of producing the maximum strength in a structure with a minimum of weight. Aside from the design criteria, we are faced with either making vast improvements in existing alloy systems or developing newer and better alloys. In examining new alloy systems, the Metals and Ceramics Laboratory has investigated the potentials of such metal systems as beryllium, scandium, yttrium, and the rare earth metals. Beryllium has emerged as the most promising of the newer metals investigated. Beryllium has a density comparable to magnesium with a melting temperature twice that of magnesium. However, certain problems, such as the lack of suitable ductility, have detracted greatly from these more desirable properties. In spite of the initial attractiveness of beryllium, we are far from having a suitable alloy which can be readily adapted to modern technology. Therefore, the metallurgist is busily engaged trying to develop some suitable light weight alloy system.

The development of new alloy systems is by nature a slow process; gains tend to be marginal and ultimately the approach is limited by the number of elements in the periodic chart. Realizing the marginal nature of the gain to be realized by sticking with standard or conventional techniques, the Metals and Ceramics Laboratory has initiated programs to investigate unique processes which might result in great strides forward in materials technology. Our efforts in many of these programs in the category of low probability-high payoff. It is this type program that we intend to cover in this presentation.

First, let us examine the state of the art in the field of the rare earth metals as we view them from the standpoint of being unique systems.

The term rare earths has been applied to the series of elements beginning with lanthanum, atomic number 57, and ending with lutecium, atomic number 71. Scandium

($Z = 21$) and yttrium ($Z = 39$) behave very similarly to the rare earths chemically and are, therefore, often included in considerations of the rare earth elements. These elements are often sub-divided into two groups--the "light" rare earths, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, and europium ($Z = 57-63$); and the "heavy" rare earths, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium ($Z = 64-71$). Scandium and yttrium are also generally included in the "heavy" rare earth group. The term "misch metal" refers to the alloy of the rare earths in the proportion in which they occur in the ore from which they are extracted. "Didymium" refers to an alloy of the "light" rare earths from which the cerium has been removed.

Rare earths have been used for some time as minor additions to engineering alloys. In various steels, rare earth additions increase melt fluidity, decrease tendency toward hot shortness, improve corrosion resistance, and improve impact properties. Cerium and misch metal can be used to produce nodular iron, with or without magnesium additions. Generally, rare earth additions to magnesium alloys impart better elevated temperature properties. Cerium additions are sometimes used in aluminum alloys for use in pistons for internal combustion engines. Small amounts of cerium increase the service life of nichrome resistance elements. In summary, additions of rare earths, such as cerium, lanthanum, or misch metal, are known to improve certain metallurgical properties of alloys. However, many reports are conflicting, and the question often arises, what are the metallurgical characteristics of the individual rare earths? Since individual rare earth metals have recently become available in sufficient quantity for metallurgical evaluation, a program has been undertaken to determine the mechanical properties, oxidation resistance, alloying characteristics, and other important metallurgical properties of the individual rare earth metals. The mechanical properties and oxidation resistance of the individual rare earth metals thus determined are shown in figures 1 and 2, respectively.

There is a considerable difference in the properties of the individual rare earths, but none of the rare earths have sufficient strength or oxidation resistance to warrant further intensive research effort on rare earth rich systems for structural purposes. Phase relationships have been determined and all available phase diagrams have recently been compiled by Love. There are many areas in which the rare earths warrant future effort, including the electrical, magnetic, and nuclear fields, but current Air Force interest in the rare earths in structural alloys is limited to their use as minor additions, particularly to the refractory metals. Two effects of minor additions of the rare earths are of immediate interest in refractory metal alloys: their effect on oxidation resistance; and, their effectiveness as scavenging elements and grain refiners.

Interest in the first effect stems from known effects of rare earth additions in improving the high temperature oxidation resistance of iron, nickel, and chromium-base alloys. Since columbium-base alloys have been developed which have a somewhat adherent and protective scale at elevated temperatures, the effect of rare earth additions upon these alloys and upon modifications of these alloys is being evaluated. The ultimate goal of this work is to develop columbium-base alloys which have adequate oxidation resistance with acceptable engineering strength and ductility.

Use of the rare earth metals as scavengers depends upon the strong affinity of the rare earths for oxygen. The addition of too much rare earth to a given refractory alloy results in rapid deterioration of strength and oxidation resistance. This deterioration stems from the extremely low solubility of the rare earths in the refractory metals, any excess rare earth being present has a deleterious second phase. Therefore, a program is cur-

rently being sponsored for the determination of the solubility limits of yttrium and scandium in chromium, molybdenum, tungsten, columbium, and tantalum.

Following this brief discussion of current interest in the metallurgical properties of the rare earth metals, it seems appropriate to discuss three unique techniques which are being explored by the Air Force in the search for advancement in materials technology. The first of these techniques, which warrants considerable discussion, is the application of high static pressure to materials. It should be emphasized that studies of this nature not only may contribute to materials technology through the production of new materials by the application of high pressure, but may significantly advance our understanding of important phenomena which occur at atmospheric pressure.

Since the synthesis of diamond and "borazon" (cubic boron nitride) by the General Electric Company, the possibility of using high pressure techniques to synthesize other new phases or produce materials with unique properties has been investigated. Several questions arise as to what effects might be anticipated from the use of high pressures in treatment of materials. Can new compounds or new phases be formed? Can equilibrium be shifted? Can structures be made more "perfect"? Can the kinetics of important transformations be changed?

Since the initiation of the Air Force program on high pressure metallurgy, many of these questions have been partially answered. However, before considering the above questions in detail, it seems appropriate to define terms used and to discuss the apparatus used to generate the high pressures simultaneously with temperature. The generally accepted unit of pressure is the kilobar; one kilobar is approximately equal to 14,700 psi. Most of the work which has been sponsored by the Air Force has been done at pressures between 30 kilobars and 100 kilobars, or 450,000 to 1,500,000 psi. It is obvious from the magnitude of these pressures that very few materials have strengths sufficient to withstand the lower pressure limit, let alone the higher pressure limit. Therefore, design tricks are employed to make the structural materials "think" they are operating at lower stress levels than they really are. A schematic of a high pressure device is shown in figure 3.

In principle, all that must be done is to exert a large force on a small area. In practice, this is achieved by employing tapered tungsten carbide pistons for the compressive components of the device and by using tungsten carbide cylinders held in compression by interference fitted tool steel rings for the tensile components of the device. Pressures of 100 kilobars are attained using proper gasketing to seal the pressure chamber and to provide lateral support for the relatively unsupported areas of the pistons. Heating is achieved by electrical resistance, using a cylindrical heating element within the pressure chamber, the heating current being introduced through the pistons. Thermocouples for temperature measurement are normally brought out through the gaskets between the piston and the cylinder. A typical cell is shown in figure 4. The dimensions of the cell are of particular interest; the diameter is only 0.35 inch and the length 0.45 inch.

It seems appropriate to mention that many precautions must be taken in the interpretation of results from high pressure experiments, but one of the most important of these is to separate the effects of hydrostatic pressure from those of the non-hydrostatic component which exists within most solid media cells, particularly upon application and release of pressure. The plastic deformation which may result from the application and release of pressure can markedly change the interpretation of results of high pressure experiments. Precautions must be taken to prevent sample contamination and to reproduce pressure and temperature accurately during a series of experimental runs. Inves-

tigators are forced to use small samples, in comparison to overall cell size, to minimize the effects of pressure gradients, temperature gradients, and contamination. For example, in the cell shown, the useful specimen size is approximately 0.15 inch diameter by 0.10 inch length. This small specimen size severely limits the type of evaluation tests that can be made on pressure treated samples. From this short discussion, the advantage of larger chamber volumes becomes apparent. However, increasing the chamber size is difficult and costly, particularly for cells to be used above 40 kilobars. Much apparatus development is necessary before high pressure will become an important materials development tool. An apparatus has recently been developed which will allow high pressure heat treatment of $\frac{1}{8}$ -inch diameter by 2-inch slugs up to 40 kilobars. This apparatus will allow much more complete evaluation of products than has been possible previously. We hope that even larger high pressure-high temperature apparatus will be available in the near future.

Now it seems wise to present some data which partially supplies answers to the questions previously raised regarding the potential of high pressure techniques in effecting new phase formation and changing equilibrium, crystal perfection, and transformation kinetics.

The synthesis of diamond, borazon (cubic boron nitride), coesite (a dense form of silica), and several minerals had illustrated the potential of high pressure techniques in producing new compounds before the Air Force program was initiated. Continued effort on compound synthesis has resulted in the production of a face-centered-cubic form of molybdenum monocarbide and the production of vitreous silica with a density almost as great as that of quartz, the most dense naturally occurring form of crystalline SiO_2 . An interesting plot of density vs. refractive index is shown in figure 5.

The vitreous phases of high density were produced by various combinations of pressure and temperature. We find that the vitreous materials of varying refractive indices may be produced from the same starting material by the application of pressure.

As might be expected, pressure has a profound effect upon phase equilibria in several metallurgically important systems. Since iron-based alloys have been extensively studied, they will be discussed here in detail. The transformation of ferrite (α -iron) to austenite (γ -iron) is of utmost importance to the ferrous metallurgist. Therefore, this transformation is a logical one to consider in this discussion on high pressure technology. Figure 6 shows that the effect of increasing pressure is to lower the transformation temperature. Thus, pressure tends to stabilize austenite, as might be expected from the decrease in volume observed when ferrite transforms to austenite. This stabilizing influence is further shown in the iron-chromium system and the iron-carbon system. Some of the metallurgical importance of these diagrams can be stated as follows: Iron-chromium binary alloys, which contain over 12 percent Cr, normally do not respond to heat treatment, since no phase transformation takes place upon heating (figure 7). However, by applying pressure during heat treatment, the α - γ phase transformation may be induced in alloys of chromium content in excess of 12 percent, making these alloys, with their inherently good corrosion resistance, respond to heat treatment. Pressure has a similar effect on the Fe-Si and Fe-Al systems.

The iron-carbon system is familiar to materials engineers, and the changes such as shown in the diagram need very little interpretation (figure 8).

In essence, the effect of pressure upon the iron-carbon system is to decrease the solubility of carbon in austenite, decrease the eutectoid composition, and lower the eutectoid temperature. Thus, although the phases present after a high pressure heat treatment are

identical to the phases present after a one atmosphere heat treatment, the composition and distribution of these phases may be widely different. An interesting phenomena to note is the difference in the morphology of carbides precipitated by lowering the temperature and those precipitated by increasing the pressure. Figure 9 illustrates that carbides precipitated upon cooling tend to form as grain boundary aggregates, whereas those precipitated by an increase in pressure form as discrete particles within the grain. This phenomenon, if it extends to other systems, may be of considerable importance in cases where the formation of a brittle intergranular phase is undesirable. Iron-base alloys have been chosen as an example, since they are well known to most materials engineers; however, similar effects of pressure upon phase equilibria are noted in many other metallic, nonmetallic, and organic systems.

One of the most interesting areas of high pressure research in metallurgy is the effect of pressure upon transformation kinetics. In this area, the data obtained not only contribute to a better understanding of rate controlling mechanisms, but also may lead to superior materials for advanced systems. Again, it seems natural to use the iron-base alloys for purposes of comparison, since the one atmosphere kinetics are reasonably well known, and the transformation rates at high pressure have been quite thoroughly studied.

Of utmost importance in the heat treatment of steel is a knowledge of the hardenability of the specific alloy to be heat treated. Hardenability may be defined as "the property which determines the depth and distribution of hardness induced by quenching." In general, the higher the alloy content of a steel, the higher the hardenability. This increase in hardenability is reflected by a shift to the right in the isothermal transformation diagram. Pressure has an effect on the isothermal transformation diagram similar to the effect of increasing alloy content (figure 10). This diagram is for an iron-.75 percent C alloy, not for a plain carbon steel. An idea of the effect of pressure upon transformation kinetics in 1080 steel can be obtained from the isolated points on the diagram. Pressure is very effective in increasing hardenability when substitutional elements, such as the Mn found in 1080 steel, are present in addition to the interstitial carbon. The importance of this effect on hardenability is dramatically illustrated by the increase in hardness obtained in pressure treated plain carbon steels (table 1). The high hardness of the low carbon steel, is of particular interest. If such hardnesses can be consistently reproduced in larger specimens, steels with exceptional hardness plus the toughness normally associated with lower carbon steels may be produced.

Another pressure effect of importance to steel metallurgy is the retarding of tempering by the application of pressure. This is graphically shown in figures 11 and 12 as the difference in hardness between iron-carbon alloys tempered at various temperatures at one atmosphere and at 42 kilobars.

From isothermal studies made on several systems, including Fe-C, Al-Cu, Cu-Be, Pb-Sn, and Au-Ni, we found that one pressure effect was common to all. In every case, the application of pressure retarded the rate of isothermal transformation; however, the changes in rate vary from a factor of 4 to a factor of over 400. The decrease in rate depends on many factors, including whether or not nucleation, interstitial diffusion, substitutional diffusion, bulk diffusion, or grain boundary diffusion is the rate controlling factor.

The last factor to consider is crystalline perfection. Is it possible, by heating a solid under pressure, to drive out dislocations, giving a structure of theoretical strength? Data obtained thus far indicate that although the application of pressure may energetically favor the annihilation of dislocations, the mobility of these defects is so reduced by the

pressure that no overall reduction in dislocation concentration is observed. This effect is shown in figure 13. No conclusive evidence has been produced which would indicate that a material solidified under pressure has fewer dislocations. The marked reduction in the rate of substitutional diffusion at high pressures does, however, indicate a reduction in vacancy concentration as a result of pressure treatment. Therefore, the application of high pressure to solids results in a reduction of the number of point defects but has very little effect on the number of line defects.

From the discussion of static high pressure apparatus, we find that the ultimate size of parts to be treated will always be limited. Such is not the case if the pressures are generated dynamically by explosive, spark discharge, or other techniques. Explosive forming is well known and is being widely exploited, but the hardening produced in metals by the passage of a strong shock wave is relatively unknown. This hardening can be realized even though the sample is not deformed. Commonly, the curve of hardness vs. shock pressure shows a continuous increase in hardness with pressure such as the curve for columbium in figure 14. However, the same curve for iron shows a sharp change in slope at 130 kilobars. This change in slope corresponds with the transformation observed by Bancroft, as indicated above in figure 6. The exact nature of this transformation is not known, but the volume change observed is very similar to the volume change involved in the transformation. A marked discrepancy exists between the pressure at which the shock induced transformation takes place at room temperature and the pressure at which the $\alpha \rightarrow \gamma$ transformation should take place according to thermodynamic calculations which have been applied successfully to static measurements of the $\alpha \rightarrow \gamma$ transformation up to 80 kilobars. Much work remains to be done on the mechanism of this transformation of iron, but the possibilities of utilizing the transformation for hardening purposes should be investigated immediately. It is the purpose of two Air Force sponsored programs to investigate this possibility, and to utilize shock as a means of imparting energy into "metastable" phases prior to final heat treatment.

One more unique technique which warrants mention here is the ultra rapid cooling ("splat" cooling) technique developed by Duwez and co-workers. Extremely rapid cooling rates are achieved by impinging a small droplet of the alloy on the inside wall of a rapidly rotating copper drum. The alloy is deposited as a thin film which is held tightly against the drum by centrifugal force. As a result of the rapid cooling achieved, Duwez et. al. have observed completely new structures in binary and pseudo binary systems. The type of result obtained is shown schematically in figure 15. Here, the silver-copper system is shown as a simple eutectic. When a complete series of Ag-Cu alloys is "splat" cooled, a series of solid solutions is formed. The lattice parameters obtained from these alloys, fall on a smooth curve connecting the two previously known segments which lie within the solubility limits at both ends of the equilibrium diagram. Similar behavior is observed in the germanium-gallium antimonide pseudo binary system. In other systems, for example Ag-Ge, compounds are formed in regions where only terminal solid solutions previously existed.

Presently, the Air Force is attempting to use "splat" cooling techniques to study certain selected beryllium rich binary systems in an effort to gain a more complete understanding of the alloying characteristics of beryllium. This program may also produce new materials with unique properties, for use in advanced systems, although with the present state of the art of ultra rapid quenching, such materials could be formed only as small, ultra thin foils.

In summary, the Air Force is investigating unique materials and techniques with the hope that such investigations may lead to quickening strides in materials technology. The

materials investigated have included beryllium, scandium, yttrium, and the rare earths. The techniques employed have included application of high static and dynamic pressures and ultra rapid quenching. Admittedly, the probability of success in some of these programs is low; however, the necessity for rapid gains in materials technology makes some effort in these areas highly desirable.

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Table 1

STEEL	VICKERS HARDNESS	(100 gm Load)
	PRESSURE HEAT TREATMENT 3 9 Kb	ONE ATMOSPHERE HEAT TREAT
0.4 C	1050	625
0.8 C	925	700
1.1C	940	675

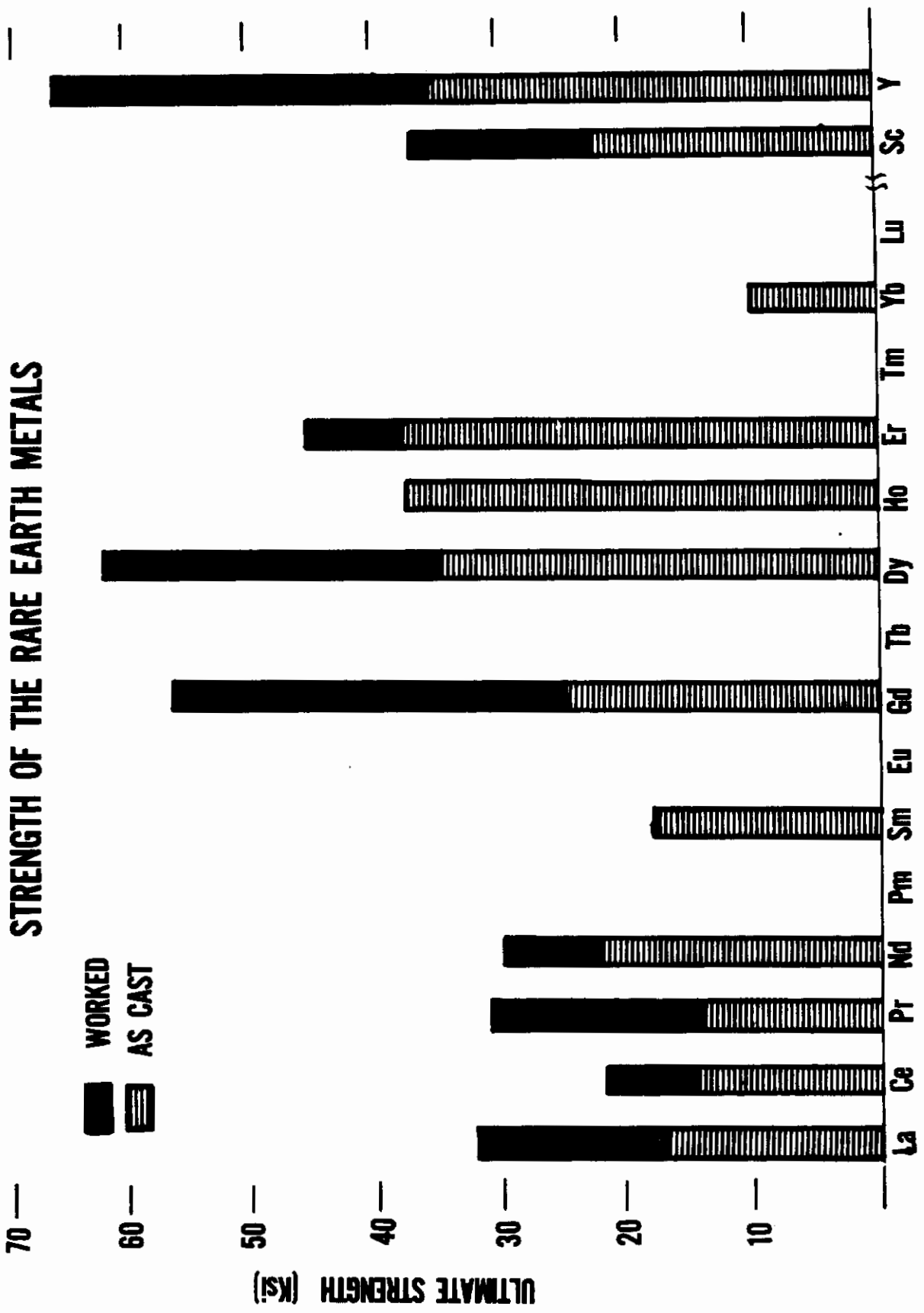


Figure 1.

**ATMOSPHERIC CORROSION OF THE RARE EARTH METALS
IN DRY AIR AT 750°F**

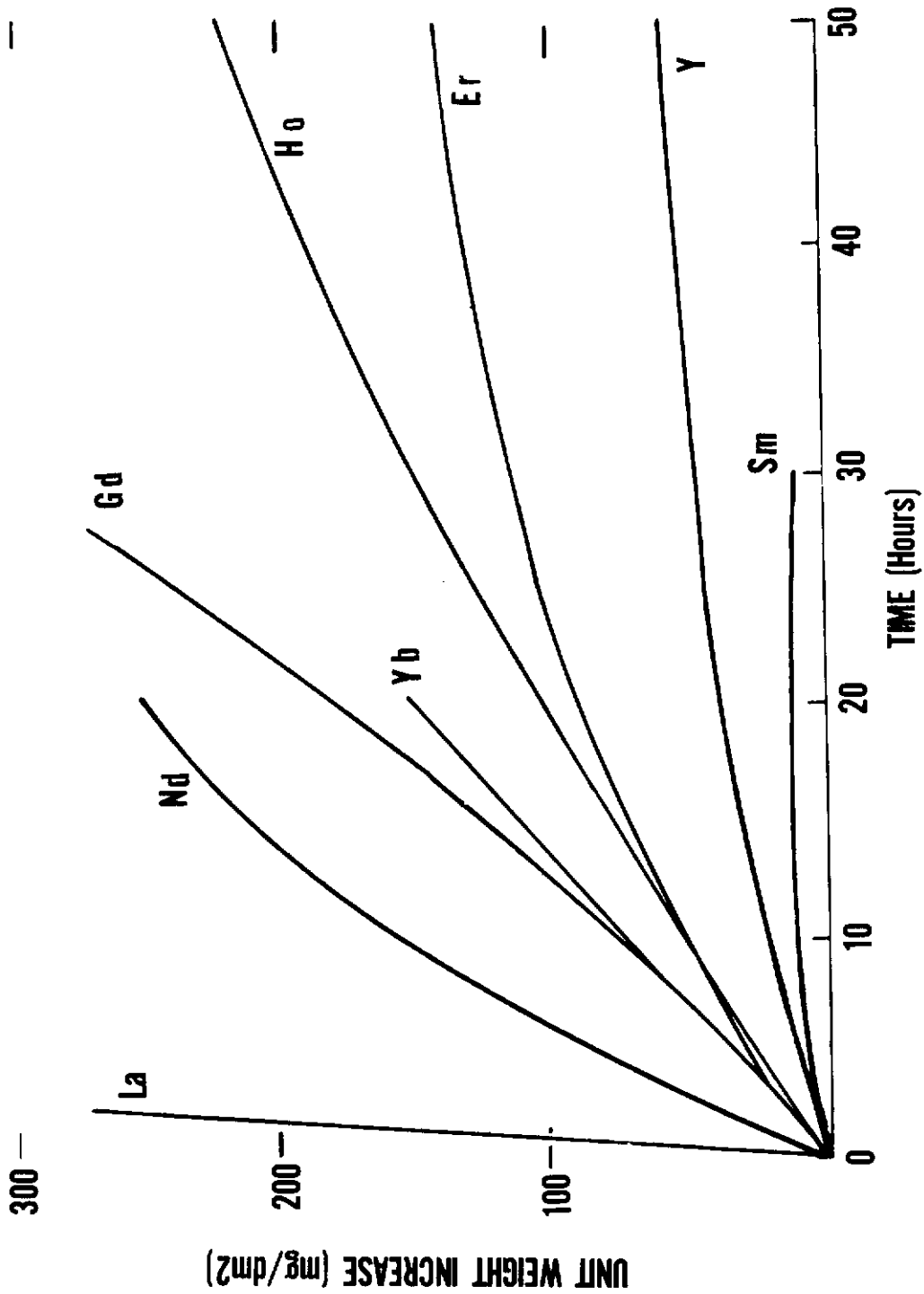


Figure 2.

THE BELT APPARATUS

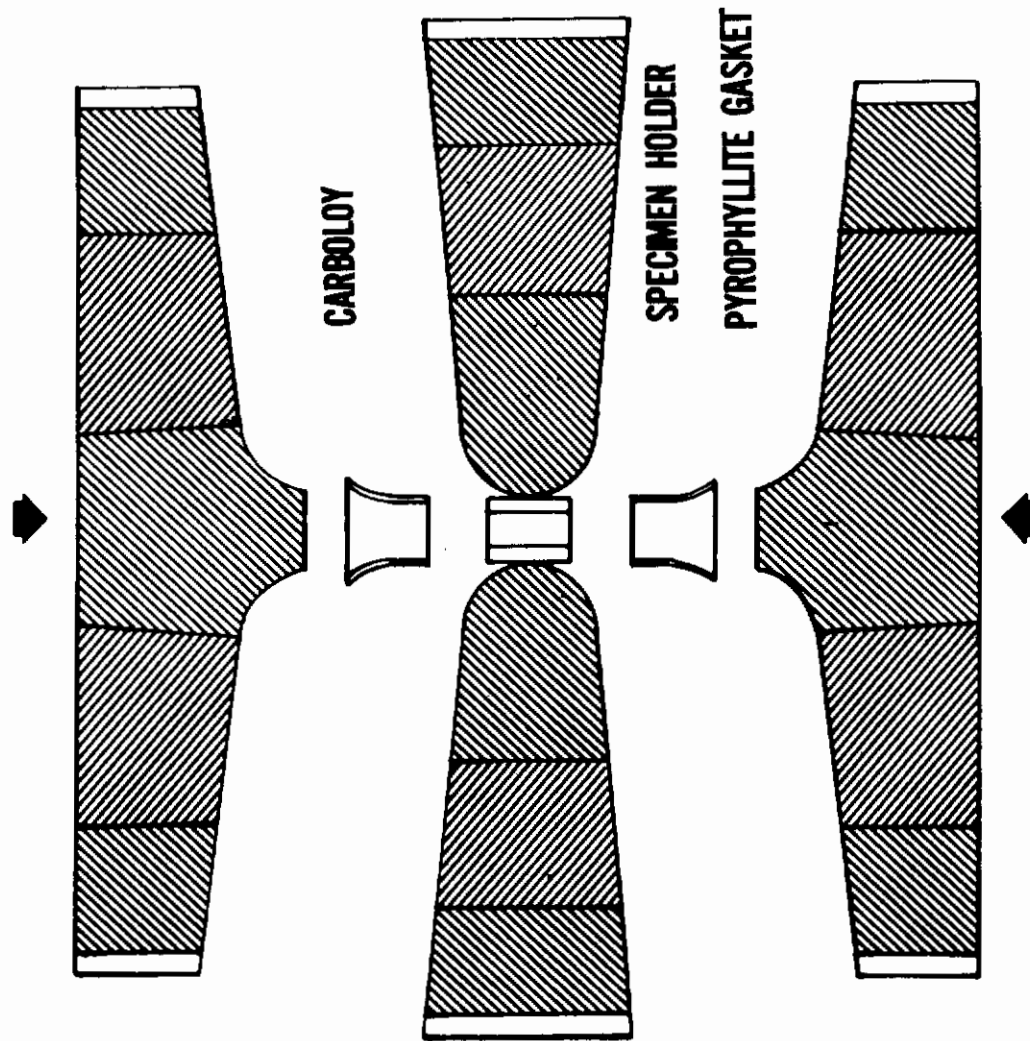


Figure 3.

A TYPICAL HIGH PRESSURE CELL

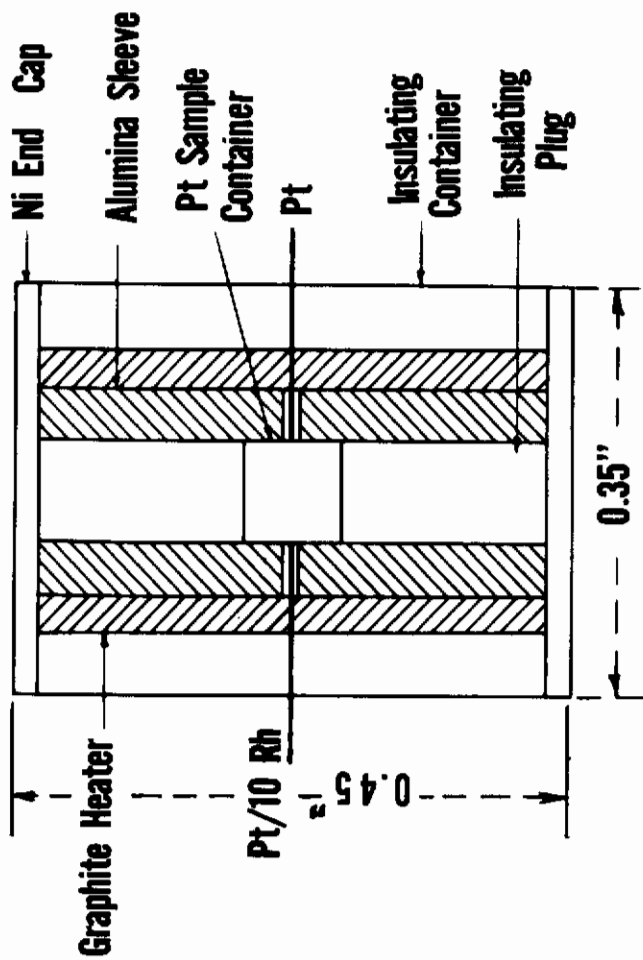


Figure 4.

REFRACTIVE INDEX—DENSITY RELATIONSHIP FOR SiO₂

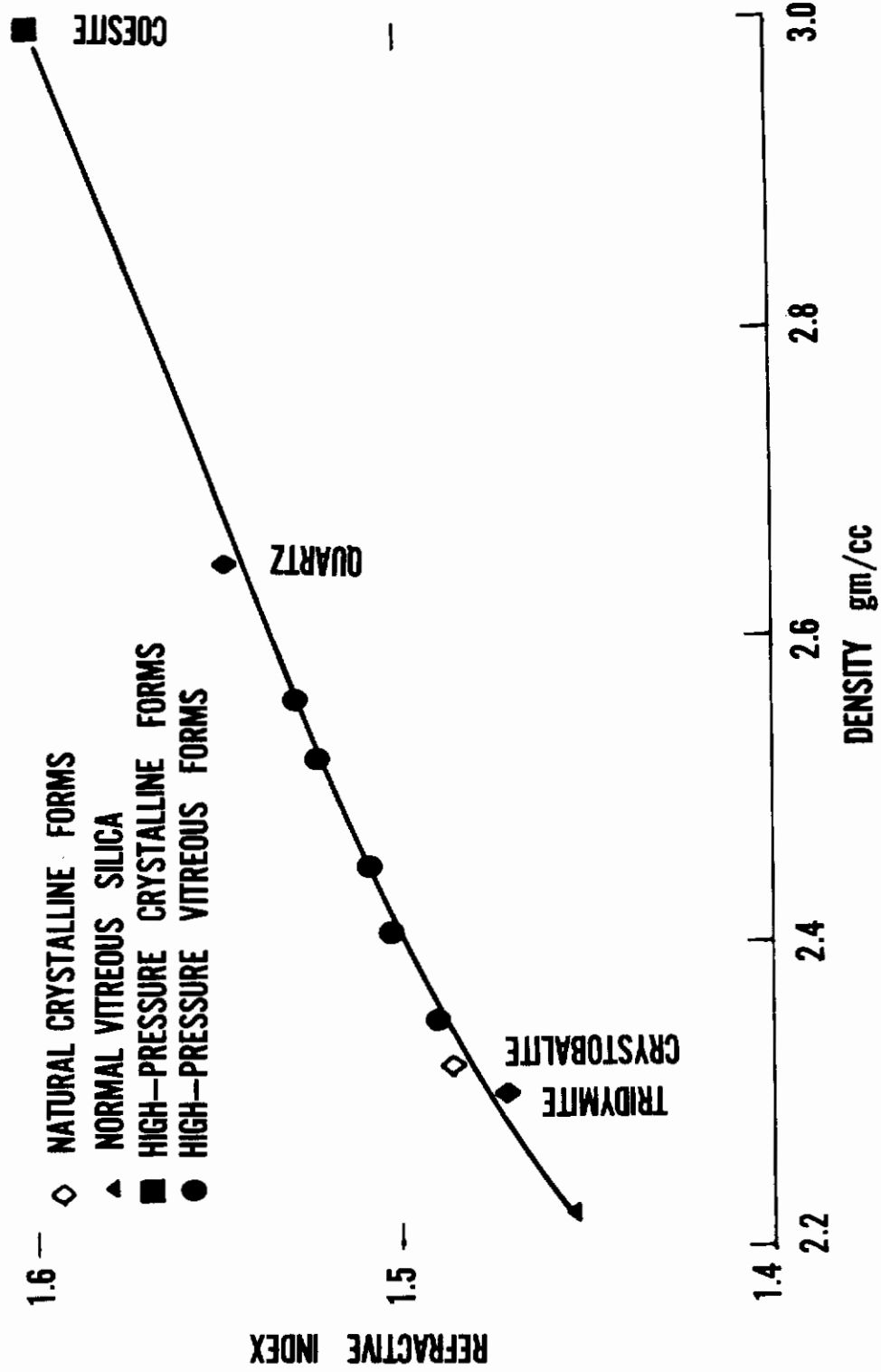


Figure 5.

EFFECT OF PRESSURE ON THE $\alpha \rightarrow \gamma$ TRANSFORMATION IN IRON

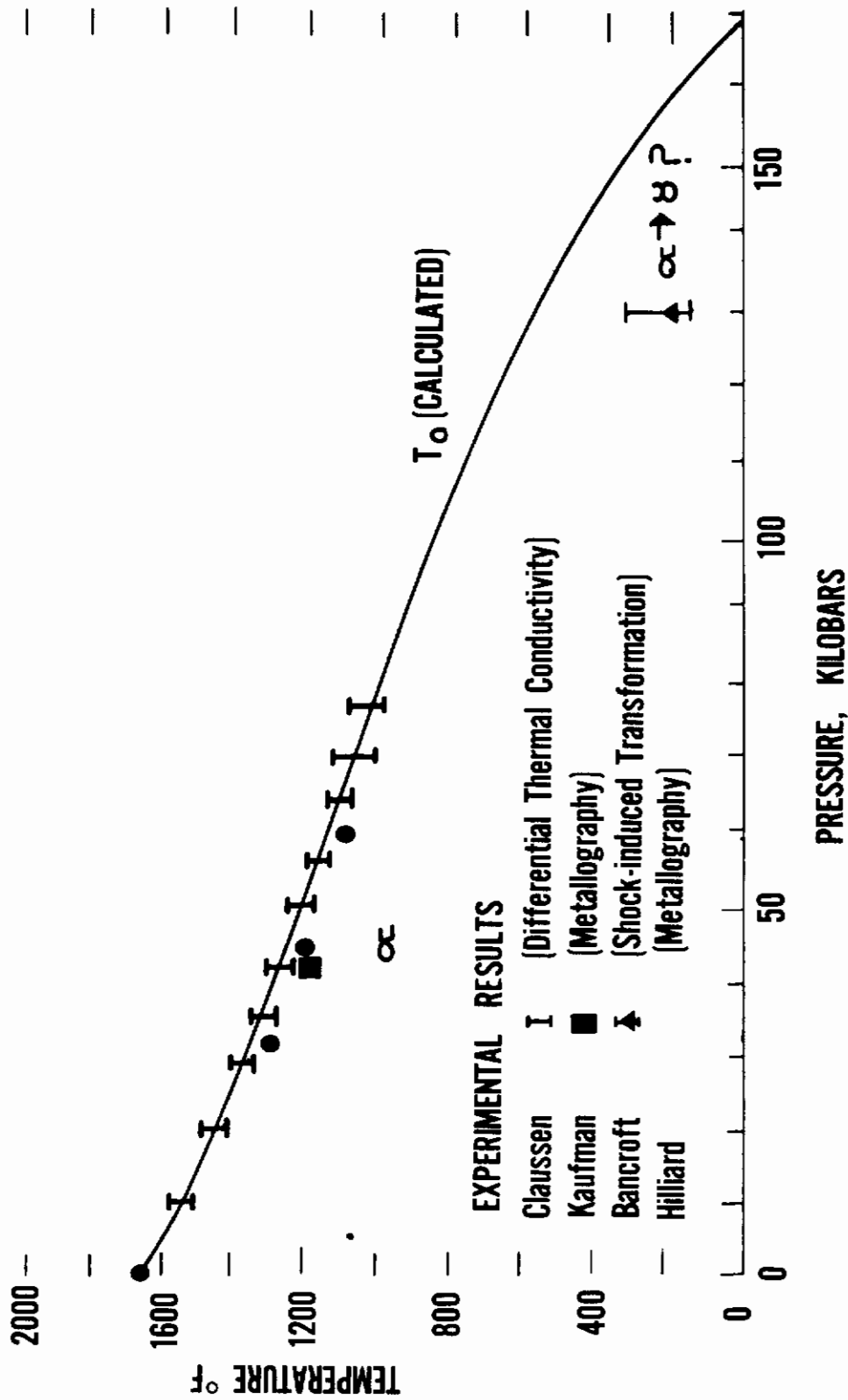


Figure 6.

THE IRON—CHROMIUM SYSTEM

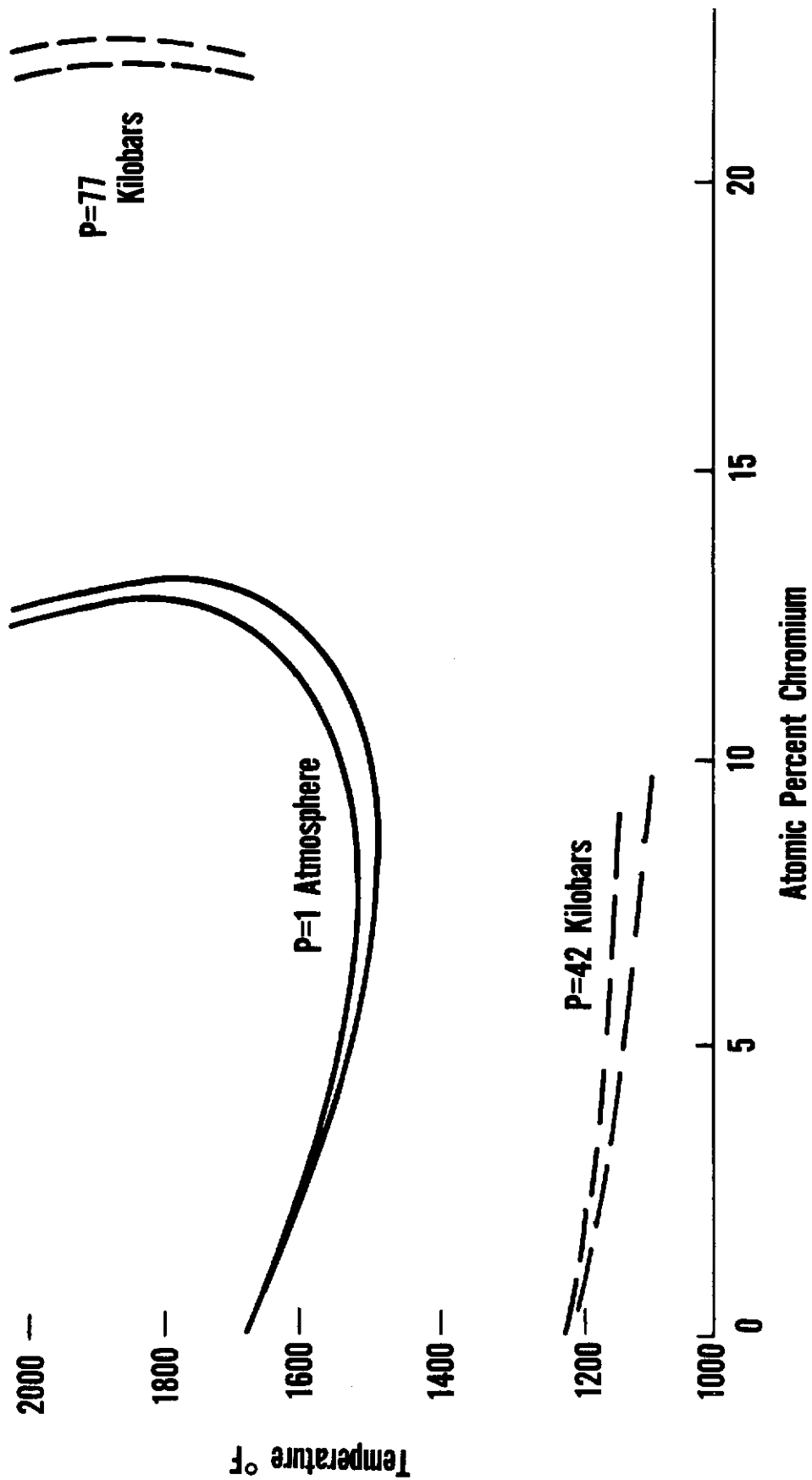


Figure 7.

THE IRON-CARBON DIAGRAM

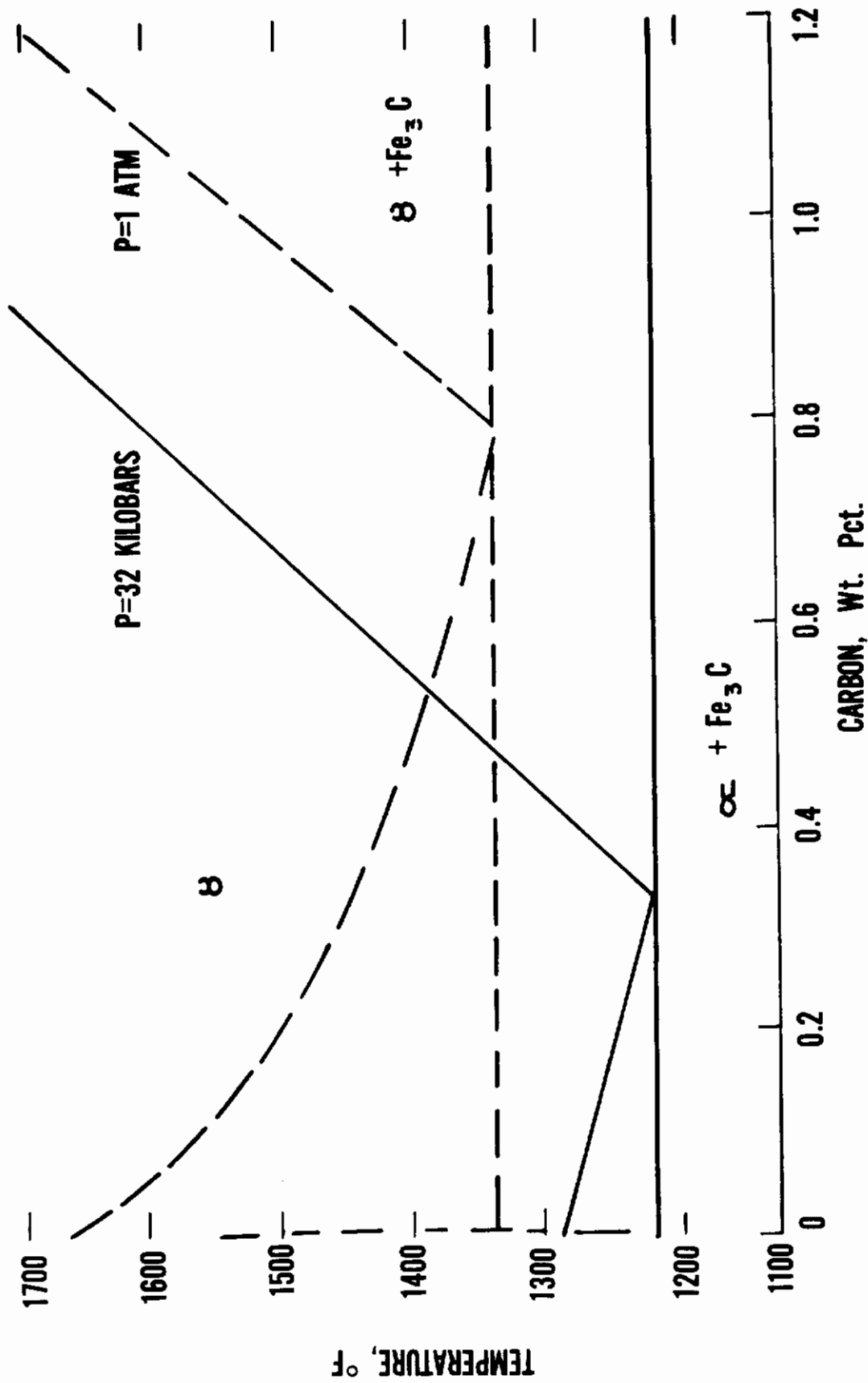
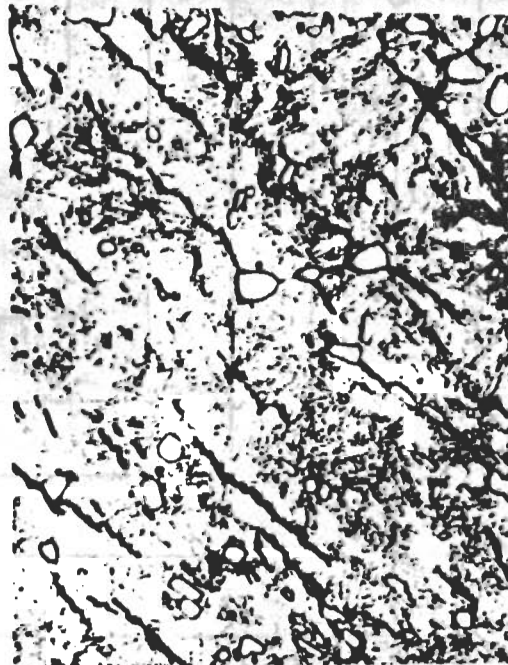
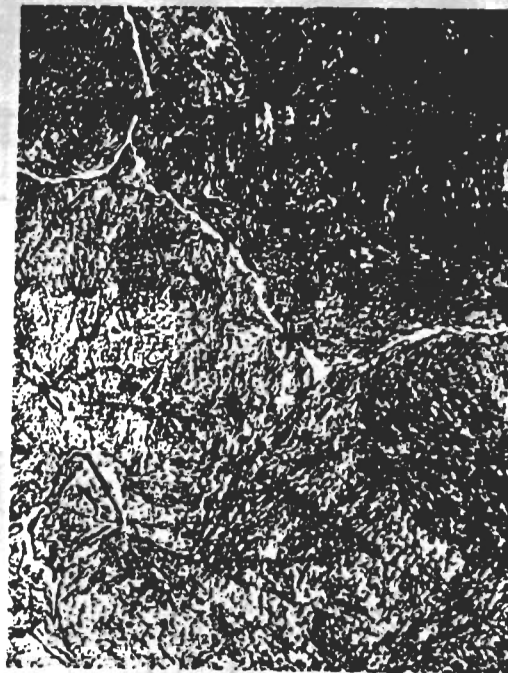


Figure 8.

CHANGES IN CARBIDE MORPHOLOGY



**CARBIDES PRECIPITATED BY
INCREASING PRESSURE**



**CARBIDES PRECIPITATED BY
DECREASING TEMPERATURE**

Figure 9.

ISOTHERMAL TRANSFORMATION DIAGRAM FOR AN IRON-0.75% CARBON ALLOY

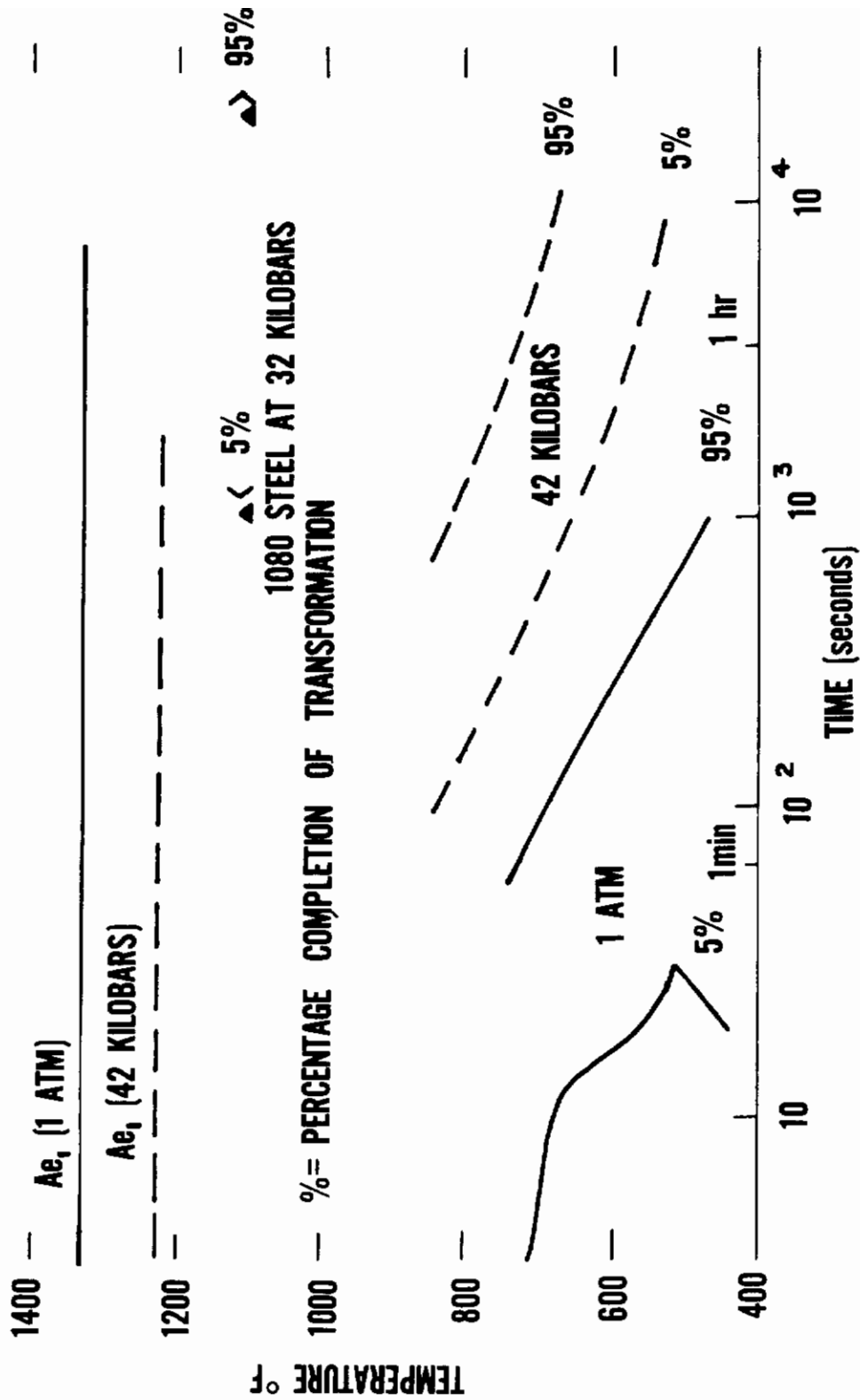


Figure 10.

HARDNESS DIFFERENCE BETWEEN IRON-CARBON ALLOYS, TEMPERED AT 1 ATM AND 42 KILOBARS

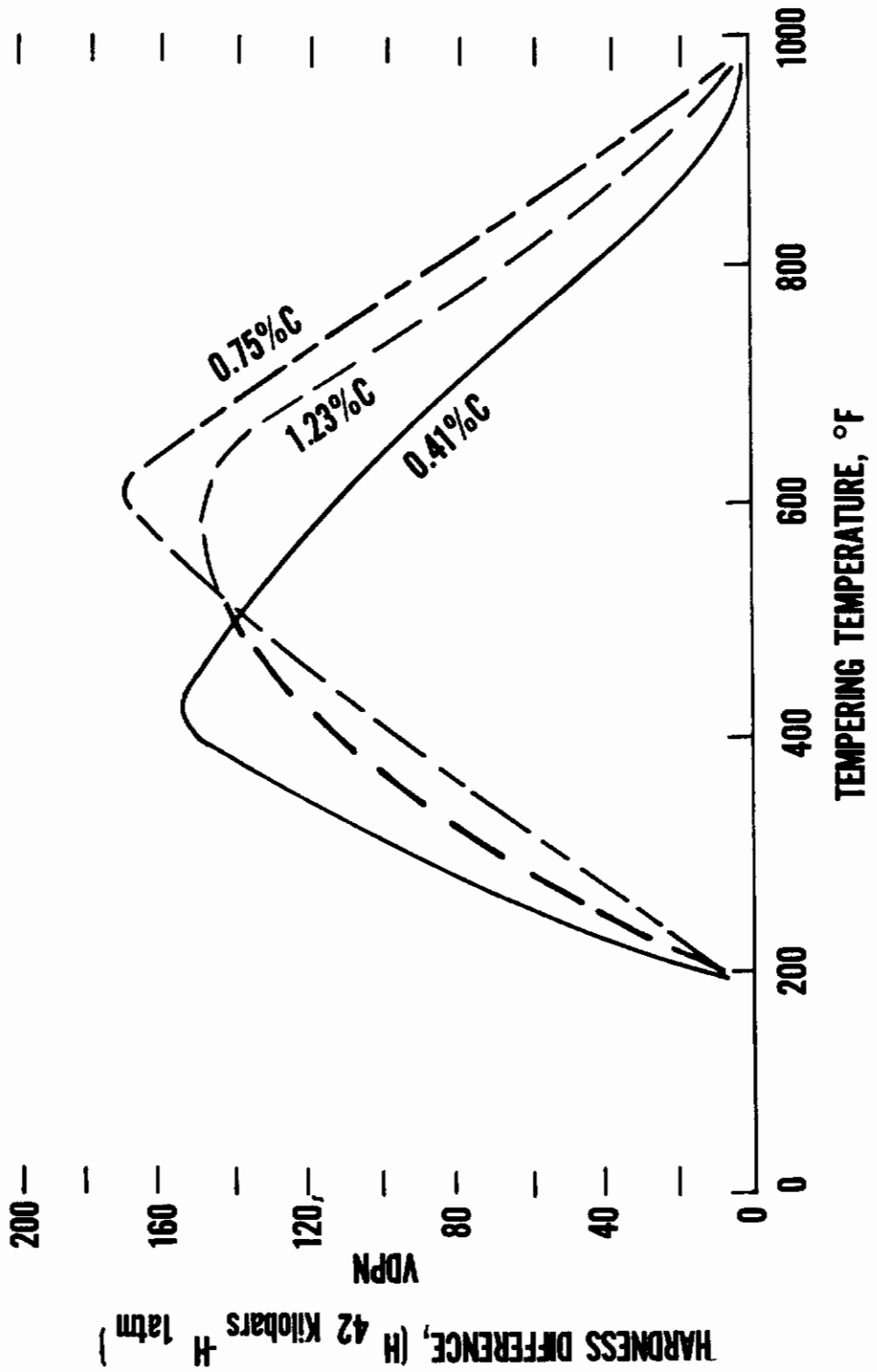


Figure 11.

AS-TEMPERED HARDNESS, OF AN IRON-0.41 WT % CARBON ALLOY

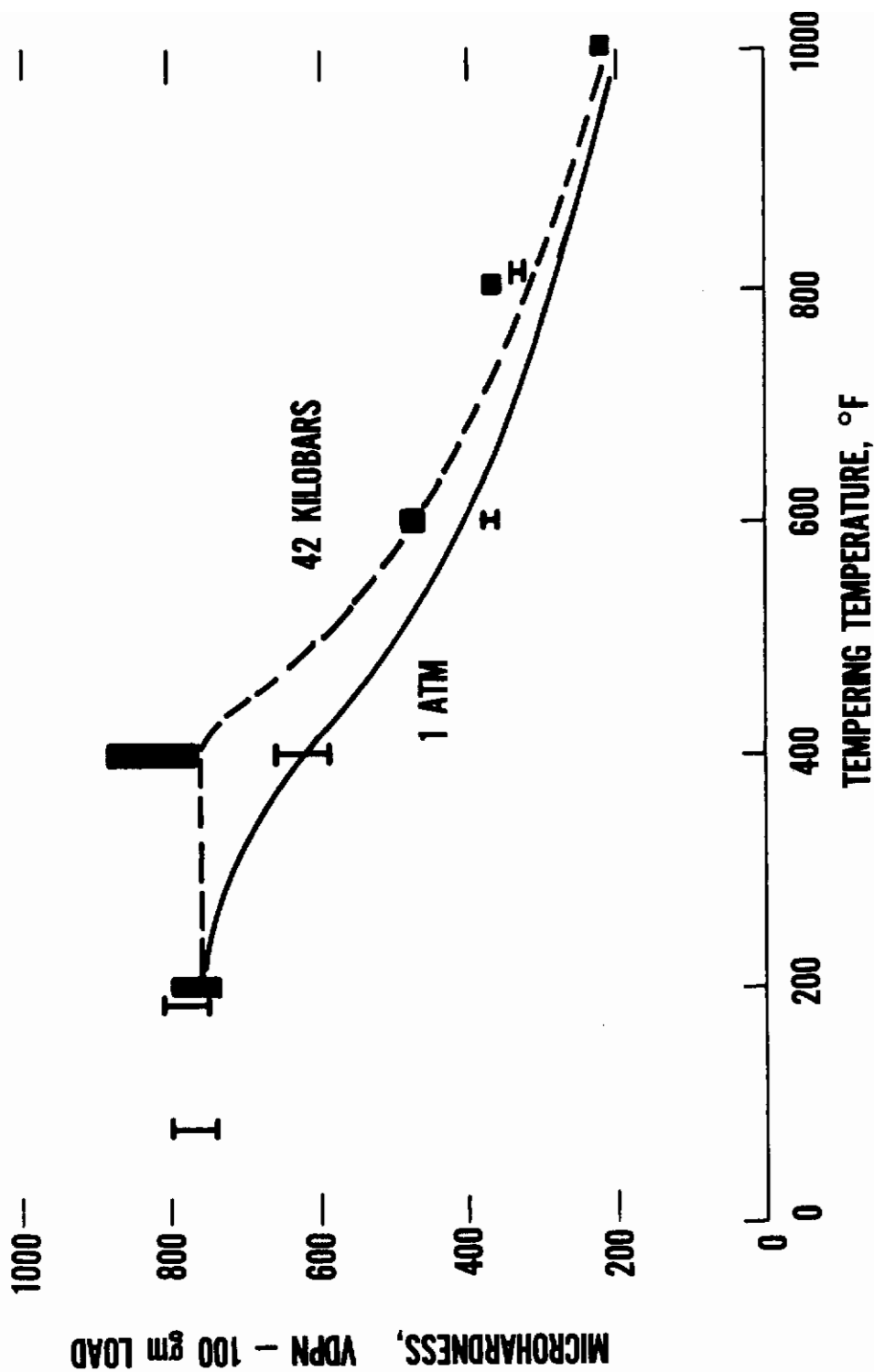
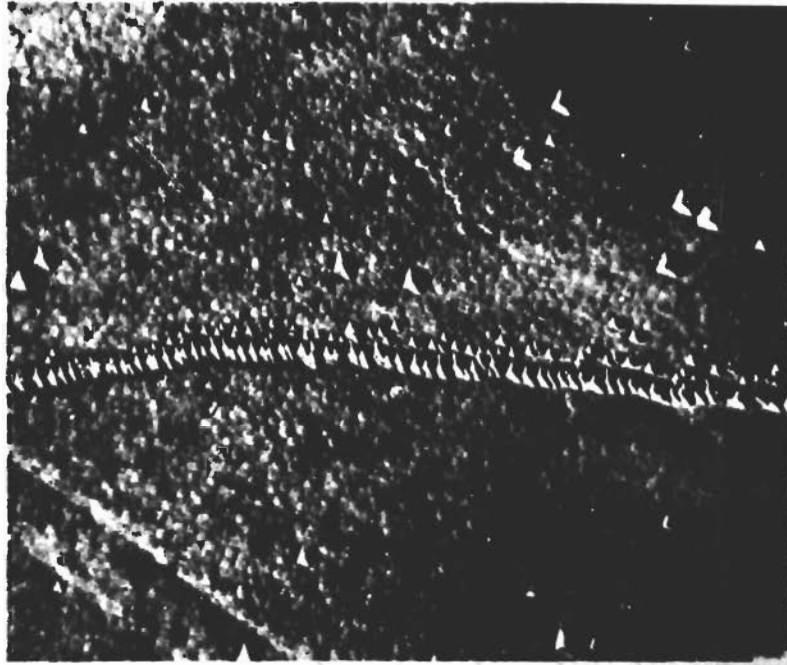


Figure 12.

MATCHING CLEAVED SURFACES OF A LIF CRYSTAL



Annealed 1 hr at 932° F and 40 Kilobars



**Annealed 1 hr at 932° F
at atmospheric pressure**

Figure 13.

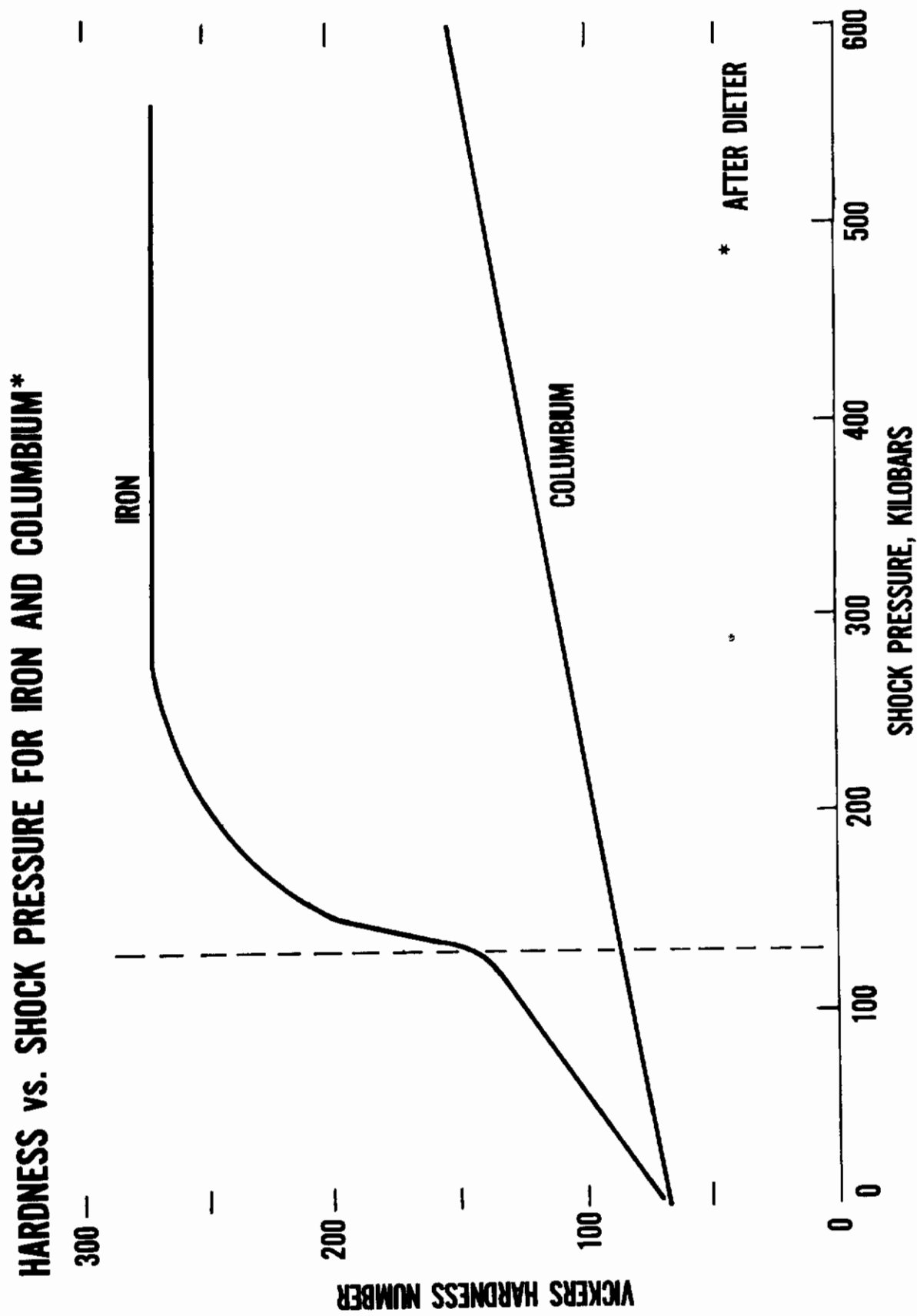


Figure 14.

SCHEMATIC REPRESENTATION OF THE Ag-Cu SYSTEM

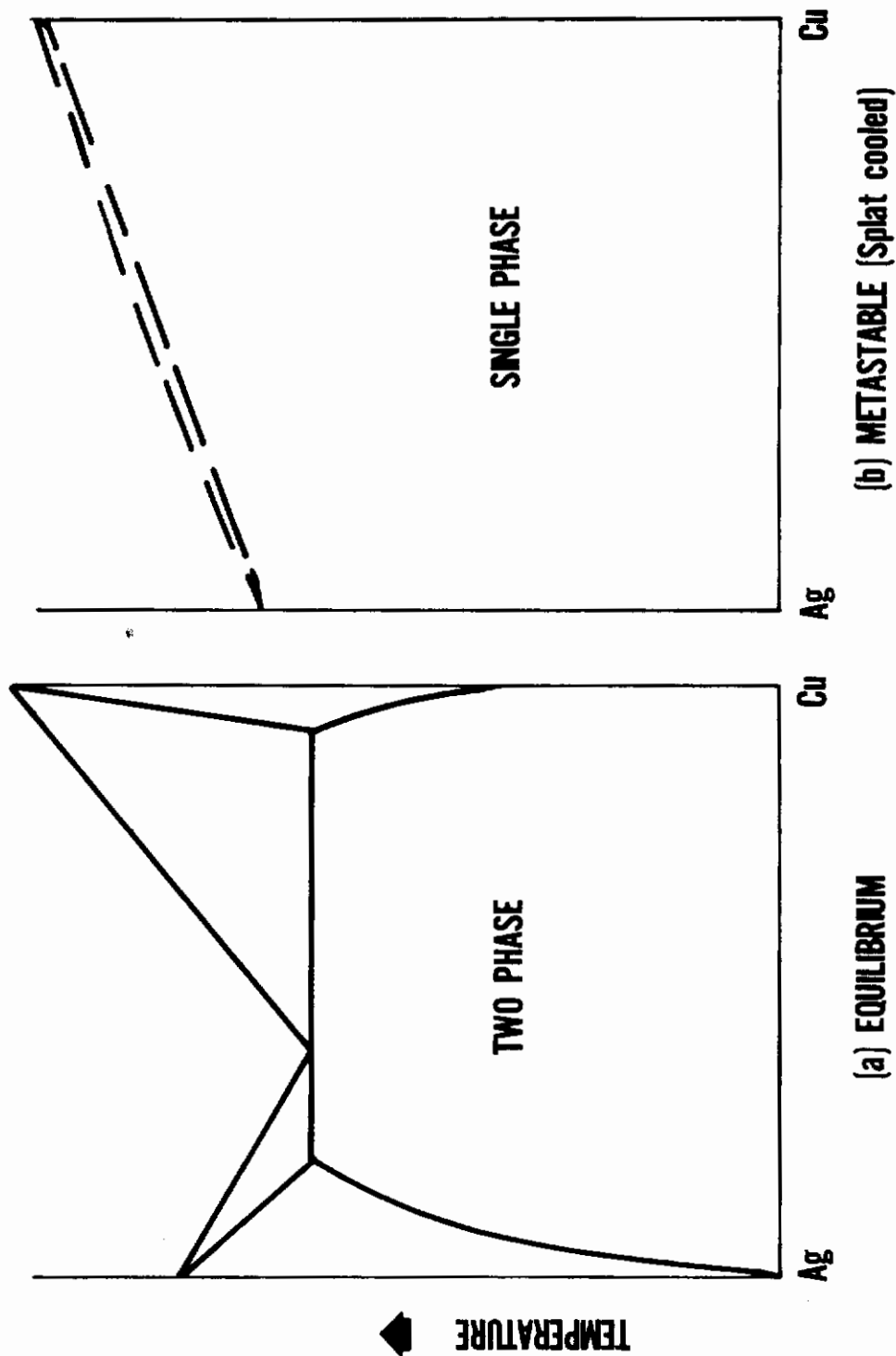


Figure 15.

Contrails