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Cleveland, Ohio

HORACE W. GILLETT LECTURE

Presented at the Sixty-Eighth Annual Meeting of the
American Society for Testing Materials
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INTRODUCTION

Horace W. Gillett was one of the eminent men of metallurgy and an early devotee to the cause of promoting metallurgy as a science. His personal contributions and legacies are many, but in reading of him from writings of those who knew him, you will quickly conclude that a major contribution was the indelible mark his insight and character left upon those with whom he associated. He was a teacher to all whom he knew.

Dr. Gillett was the first director of the fine Battelle laboratories and its chief technical advisor for the subsequent years until his death in 1950. He served on many of the committees of ASTM.

The ability to make complex research understandable in written prose is a rare gift that was his. Dr. Gillett founded the magazine, "Metals and Alloys" and through it he promulgated his life interest - "the development, testing, evaluation, and application of metals." In his honor, it is my privilege to discuss these same areas for the refractory metals for structural application. Because progress in recent years has been so dramatic, I have chosen to collect my discussion of these topics under the heading "A Decade of Progress."

In an attempt to provide a somewhat orderly approach, we will first define and review the basic characteristics of these metals.

After defining the character of these metals and the special problems they present in manufacture, evaluation, and application, I think it may then be necessary to justify and defend the expenditure of time and money in the pursuit of such obstinate materials. This will be done very briefly in terms of the need.

The unique facilities that are required and that have been provided for their processing and evaluation will be described, followed by a summary of accomplishments in achieving commercial products and concluding with an indication of where we stand with the most advanced materials in research and development.

FUNDAMENTAL CHARACTERISTICS

Refractory metals and high temperatures are synonymous. Prior to the development of refractory metals, the primary needs for high temperature structural materials were met by special steels and the superalloys based on nickel and cobalt base. It is obvious that if we are to raise use temperatures of metals for structures above 2000° F, we must consider materials of much higher melting points than iron, nickel, and cobalt. The metals available for consideration are tabulated in Fig. 1. For convenience, they are tabulated by their grouping in the periodic table. Shown at the left of group VIII are the reference metals with melting points in the vicinity of 2650° to 2800° F. Seventeen metals have higher melting points. Many of these are very scarce or rare. This fact alone eliminates the metals of group VIII, platinum through osmium. Short supply also eliminates the metals of group VIIA, technicium and rhenium, and thorium and hafnium from group IVA as base metals. Also in group IVA are titanium and zirconium. To date, alloys of these metals have demonstrated very limited high-temperature strengths, much inferior to those of alloys of the lower melting nickel or cobalt. Fortunately, the metals of groups VA and VIA are in sufficient supply to warrant consideration and tungsten (6170° F), molybdenum (4730° F), tantalum (5425° F), and columbium (4475° F) have much higher melting points than nickel and cobalt. Most attention has been concentrated on these four metals and they will be emphasized in this discussion. Vanadium and chromium are also available, but because they offer only modest temperature gains over superalloys and have some special shortcomings, they have received only limited attention during recent years and will be described only briefly herein.

These six metals of groups VA and VIA have many similarities, but there are further distinguishing features more closely relating them by specific groups, VA (Ta, Cb, and V) and VIA (W, Mo, and Cr), and they frequently will be discussed by this periodic grouping.

Of first importance is the strength of these materials at high temperatures (Fig. 2, Refs. 1 to 3). Because cold work is an effective method of strengthening, particularly for the group VIA metals, the data are shown for the metals when in the recrystallized condition to eliminate this variable. It is clear that even the unalloyed refractory metals have useful strengths at temperatures well above the melting points of the superalloys. You may wish to keep two thoughts in mind here. All these metals have a body-centered-cubic crystal structure. Within each group of the body-centered-cubic refractory metals, the strength at any temperature is in the same order as the melting point, for example: tungsten is stronger than molybdenum, and tantalum is stronger than columbium. Also the unalloyed group VIA metals have higher elastic moduli and are generally stronger than group VA metals. The strength comparison is seen most simply by noting that Mo is stronger than Ta although its melting point is 700° F lower.

Another characteristic difference between group VA and VIA metals is indicated in Fig. 3 (Refs. 4 to 7). Here we turn our attention to an unfortunate characteristic almost peculiar to body-centered-cubic metals, namely, a change from ductile behavior to brittle behavior as the temperature is lowered. This has been a problem for many years in body-centered-cubic iron and steels. Figure 3 describes reduction in area in a tensile test against temperature, again for recrystallized material.

The transition from high ductility to essentially zero ductility for columbium occurs at about -200° F, which is then the ductile-brittle transition temperature. Room temperature is shown as a shaded area for emphasis. Fortunately, the group VA metals Ta, V, and Cb have their transition temperatures well below room temperature. In fact, Ta does not exhibit a transition temperature even at liquid helium temperature, and V exhibits a ductility dropoff only in the vicinity of -320° F. The group VIA metals present more of a problem. Tungsten and Cr show a transition temperature near 500° or 600° F, and thus are brittle at room temperature. The transition temperature of molybdenum is near room temperature.

It is generally important to have this transition occur below room temperature for the simple reason that metals are handled and transported at room temperature, and we want them to behave like respectable metals, not like glass. If we drop them, we do not want them to shatter. (It is desired to be able to saw, shear, punch, and form them at room temperature, too, but simple warming with radiant heaters will permit these operations to be performed.) In service, we would like them to be ductile at the minimum exposure temperature, and thus in some cases transition temperatures well below room temperature are sought.

Much of the research in refractory metals has been concerned with the understanding and the control of the transition temperature. As will be pointed out later, transition temperature may be lowered

(1) By an increase in purity, particularly in regard to interstitials,

(2) by cold work

(3) By fine grain size

(4) By a dispersed phase

(5) In the case of group VIA metals by alloying with Re (costing $600 per pound)

Unfortunately, the transition temperature is raised

(1) By contamination

(2) By many alloying additions

(3) By increased strain rate

The data of Fig. 3 are from high quality material in tensile tests at conventional strain rates.

Of particular importance is the effect of interstitial impurities. (An excellent discussion is given in Ref. 8.) An extreme example is shown in Fig. 4. Two conditions for molybdenum are shown; the upper condition showing no transition temperature has been reported by Lawley, et al., (Ref. 9) for electron-beam five-pass zone-refined polycrystalline molybdenum. The lowering of the transition temperature is associated by the authors with the drastic lowering of the interstitial impurities, particularly O and C, (tabulated in the figure). This is an extreme example: in commercial production such extreme purities are never achieved in unalloyed molybdenum. Semchyshen and co-workers, however, have shown other approaches that may provide commercial unalloyed Mo with transition temperatures of below -200° F (Ref. 10). The converse is true too: more impurity raises transition temperature. Systematic data for effects of interstitials in single crystal and polycrystalline W are given in Ref. 11. The need to control and minimize interstitial impurities in refractory metals is obvious.

Let us now turn to another problem in refractory metals, that is, their extremely poor oxidation resistance (Fig. 5, Refs. 12 to 17). Figure 5 is a plot of rate of oxidation in micrograms per square centimeter per hour, for a 1-hour time period, as a function of temperature. Also shown is the rate of oxidation of nichrome on the same scale. At temperatures greater than 1800° F, where we wish to use these materials, molybdenum has an oxidation rate of almost seven orders of magnitude higher than nichrome. Even the most oxidation-resistant metal, chromium, would be satisfactory for only very short-time applications. To obtain a better physical picture of the severity of this problem, we may refer to Figs. 6 and 7 where molybdenum and columbium, respectively, are shown to have oxidation rates at temperatures of interest.

Figure 6 shows a molybdenum strip being heated in air to greater than 3000° F by passing an electric current through the metal. The metal rapidly oxidizes to MoO_3. The oxide is volatile and the metal rapidly loses thickness by conversion to the oxide and sublimation. The oxide of molybdenum is volatile at temperatures above 932° F, and it sublimes as fast as it is formed at temperatures greater than 1415° F. Thus, this behavior is characteristic of molybdenum at all temperatures of interest, and for tungsten at temperatures of about 2500° F and above.

The behavior of columbium in air is somewhat different. On the left (Fig. 7) is unalloyed Cb; on the right is an alloy of Cb with 5 percent Cr, after heating for 3 hours at only 1500° F. Before exposure, the disks were identical in shape - 2 inches in diameter and 1/4 inch thick. Obviously, unalloyed metal is unacceptable.

Alloying helps, but no alloy of Cb or any other refractory metal has been found that combines satisfactory oxidation resistance with needed strength and fabricability. Only coatings offer promise for providing the needed protection; this subject will be discussed later.

Before leaving this discussion of contamination and oxidation, we should emphasize a slightly different characteristic of chromium. It has the best inherent oxidation resistance of the refractory metals, but suffers from severe embrittlement when exposed to air at even moderate temperatures. This is a result of adsorption of N_2 not O_2 as has been shown by the experiments of Wain and co-workers (Ref. 18). They had produced a high-purity, unalloyed, cold-worked chromium that was ductile at room temperature. After the material had been exposed to oxygen for 2 hours at 1200° F, it would remain ductile at room temperature. If it was exposed to nitrogen at the same conditions, however, the material would become brittle when subsequently tested at room temperature. Embrittlement on exposure to air (or nitrogen) remains a major problem with chromium; both alloying and coating are being pursued in an attempt to overcome this deficiency.

This discussion has served to identify the refractory metals of interest. We have indicated their strength potential, the problem of the ductile-brittle transition temperature (and the resultant importance of achieving high purity and avoiding interstitial contamination), and finally the extremely poor resistance to oxidation.

THE NEED FOR REFRACTORY METALS

Let us now consider some typical applications that might justify research and development on such obstinate metals. It is not possible to provide a detailed discussion of systems requiring refractory metals in this paper. Such information may be found in Refs. 19 to 23. A summary of the spectrum of time, temperatures, and environment of applications that require materials with a temperature capability greater than that of superalloys is shown in Fig. 8. The various shadings used are indicative of the aggressiveness of the service environment toward refractory metals. Inert gases or hydrogen (for group VIA metals) are representative of a relatively friendly environment for refractory metals; liquid metals, such as the alkali metals sodium, potassium, and rubidium, are environments of more concern. As shown earlier, air is a particularly antagonistic environment at high temperatures.

Let us consider these requirements briefly. The rocket nozzle presents a need for materials at very high temperature but with lifetimes generally measured in minutes. Fortunately, this atmosphere is frequently nonoxidizing or only slightly oxidizing. In the case of liquid rockets the nozzle may be made of steels or superalloys cooled by the propellant. Solid rockets do not have a coolant available and refractory metals, particularly tungsten, are filling an important need here. Flame temperatures now are being pushed well above the melting point of tungsten, exceeding the capability of even the refractory metals. Cooling in conjunction with refractory metals is one promising avenue being pursued, however.

The nuclear rocket uses a single propellant, hydrogen, heated by passing through a nuclear reactor. Tungsten and molybdenum are unaffected by hydrogen. Minimum reactor temperatures of interest are 3500° F with much higher temperatures desired. Currently, this country is engaged in the development of a graphite reactor, but, in addition, NASA and AEC are studying the feasibility of a tungsten reactor concept where the fuel elements would be tungsten containing uranium dioxide. Considerable promise has been demonstrated by this approach.

Space power systems are almost certain to provide a major opportunity for the application of refractory materials. These systems require materials for reactors, containment of working fluids, and turbine components for operation at very long times - greater than 10 000 hours - in space. The Rankine cycle, presents an environment of corrosive alkali metals, such as sodium or potassium; the Brayton cycle, though requiring higher temperatures, presents a noncorrosive inert gas environment, such as argon. These are areas where refractory metals will surely satisfactorily fulfill a need in the future. To date, the data indicate that tantalum and columbium alloys may be required for the thousands of feet of tubing of such systems, and the ultimate in high-strength alloys of molybdenum, tantalum, or tungsten will be required for the highly stressed turbine components.

In the intermediate time-temperature spectrum are shown several airbreathing propulsion and aerodynamic vehicle requirements wherein the materials must survive in an aggressive, oxidizing environment. If protection of the refractory metals could be achieved through alloying or coating, the future in these systems and the sales market for refractory metals would be bright, indeed. The indicators of optimism are not great here, however, except for very short-time applications, such as reentry.

These, then, are the general needs for refractory metals as structural materials. If we were to detail the specific components, the list would fill several pages.

TEN YEARS AGO

To measure the progress made in the past decade, let us review the status of 10 years ago, in 1955. Figure 9 shows the important refractory metals available at that time. In this figure the tensile strength is plotted as a function of temperature for unalloyed molybdenum and the outstanding molybdenum alloy, Mo-0.5 Ti. A relatively intensive investigation of molybdenum and possible alloys as well as fundamentals of the ductile-brittle transition had been underway for some time under the guidance of a coordinating group led and sponsored by the Office of Naval Research. Major and remarkable advances in melting and alloy development had been achieved by the Climax Molybdenum Company of Michigan. This progress was expertly described by Mr. Alvin Herzig, now President of the company, in the Gillett lecture of 1957 (Ref. 24). Climax had developed vacuum-consumable-electrode arc melting to a semiproduction process. This was a major step toward achieving needed high purity in a commercial product. Molybdenum was deoxidized during melting by the addition of carbon, a process still used for molybdenum. Prior to this contribution, refractory metals had been produced by powder metallurgy, primarily for electronic applications, such as electron tubes and lamps.

The Mo-0.5 Ti alloy was a significant advance over unalloyed molybdenum, but this was the best alloy known. For structural application, there were no columbium alloys, no tungsten alloys, no tantalum alloys, no vanadium alloys. Chromium alloying was under study but with hopelessly discouraging results. The technical literature of 1955 does not mention vanadium, columbium, tantalum, or tungsten as base metals. Earlier (Fig. 2) I presented data for the tensile strength of these unalloyed metals at very high temperatures. Those data did not exist in 1955, and we did not have the material in a form suitable for testing, nor did we have equipment for testing conventional bar stock or sheet at temperatures above 2200° F.

What has been accomplished since that time?

ACHIEVEMENTS

Facilities for Processing

A prerequisite to progress in refractory metals has been the need for facilities to process and evaluate these materials. Processing must be conducted at high temperatures - the difference in the melting point between tungsten and superalloys suggests a need for processing temperatures for ultrastrength alloys as much as 2000° to 3000° F higher than for superalloys (or steels). The processing method must achieve extreme purity and minimize contamination and oxidation at all steps in processing.

Before describing the progress in this area, let us summarize the general characteristics of these metals as we know them today (Fig. 10). This will aid in understanding the equipment needs.

The metals are again listed by their group of the periodic table. Within each group the metals are listed in order of decreasing melting point, which also is the order of decreasing density. Densities shown here are relative to iron or steel. Note that within group VA, tantalum has a density more than twice that of steel, columbium is comparable, and vanadium is about 23 percent less. For group VIA, tungsten is very heavy with a density 2-1/2 times that of steel, molybdenum is 30 percent greater, and chromium about 10 percent lighter.

Of importance are those conditions under which the metals exhibit ductility at room temperature. (Incidentally, the table is set up so that a yes answer indicates a favorable characteristic.)

Consider the question, are the base metals ductile at room temperature when recrystallized? All group VA metals, Ta, Cb, and V are - group VIA metals, W and Cr are not - Mo can be depending on processing and the method of measurement. As mentioned earlier, cold work can lower the ductile-brittle transition temperature and thus group VA metals, of course, retain ductility in this condition. Ductility at room temperature can be achieved by cold rolling in the case of Mo and Cr. Most cold-worked forms of W are not ductile although cold-worked wire and extremely cold-worked sheet may be ductile.

Welding is important in fabrication of components and it is obviously desirable that welded components be ductile at room temperature. Uncontaminated welds in group VA metals are ductile; welds in group VIA metals are generally brittle as would be expected because the metals are brittle whenever recrystallized.

Because these metals pick up contaminants from the atmosphere when at high temperatures, it is desirable that they have characteristics which permit them to be finish worked near room temperature. For example, if we can roll sheet at low temperatures, contamination would not occur because oxidation and diffusion are negligible. Group VA metals in sheet and tubing can be worked near room temperature by using intermediate stress-relief anneals. The group VIA metals generally must be worked hot, out of protective atmosphere furnaces, and surfaces must be cleaned by pickling or machining (although both tungsten and molybdenum <u>can</u> be rolled near room temperature subsequent to receiving large amounts of cold work at high temperatures).

One liability for group VA metals is that they are not ductile after hydrogen atmosphere exposure at moderately-high temperature: group VIA metals are ductile after such exposure and thus hydrogen furnaces can be used for hot working. Inert atmospheres or vacuum furnaces must be used for group VA anneals. (Because of rapid attack by hydrogen, group VA metals are not of interest for nuclear rockets where the propellant is hydrogen. Group VIA metals, W or Mo, are possible.)

Let us now examine the nature of processing facilities.

Earlier it was pointed out that the commercial development of the vacuum-consumable-electrode process by the Climax Molybdenum Company of Michigan was a pioneering step. This is still the most common method for melting of refractory metals. Refinements, primarily in improved vacuum control, have been achieved. Since that time, the electron-beam melting process has been developed to commercial status by Charles Hunt and associates, of the Temescal Metallurgical Corporation.

Figure 11 is a schematic drawing for description of the process. A tungsten filament is heated to a white heat causing electrons to be emitted. The electrons are focused and directed toward the material to be melted, for example, a partially sintered tungsten bar, as shown. When the electrons strike the bar, they give up their great kinetic energy as heat causing the bar to melt into a molten pool. The melt is contained in a water-cooled copper mold. As the melt solidifies, the ingot is slowly retracted as bar stock is fed into the top. The melting must be conducted in high vacuum to maintain the electron beam (unless a remote separately-chambered gun is used), but exposure of the melt to this high vacuum is an important method of purification. In the electron-beam furnace, melting is conducted in vacuum between 10^{-4} to 10^{-5} mm Hg. The molten pool is always exposed to the vacuum of the chamber (as contrasted with the usual conditions in consumable-electrode arc-melting where melting is conducted deep inside a copper mold). If metal is to be purified by exposure to a vacuum, the electron-beam melting process may be superior to the arc process because the melt sees a better vacuum and the melting rate can be slower. On the other hand, alloying may be difficult because elements of high vapor pressure will be lost. It may be desirable to use both systems, purifying in the electron-beam furnace and remelting to add alloying additions in the arc furnace where melting rates may be more rapid and vaporization less. A comparison of the melting methods for tungsten is described in Ref. 25.

With proper care, very high purities can be achieved in electron-beam melting, as shown in Fig. 12, for data obtained at Lewis with 2-1/4-inch-diameter ingots. The analysis of the starting material, after first melt, and second melt or remelt is given for columbium. Oxygen has dropped from perhaps 1500 to 20 ppm, nitrogen from 550 to 55 ppm, carbon from 390 to 40 ppm, then back to 65. Because of some carbon-oxygen interaction, oxygen and carbon drop together until oxygen reaches a low value and then carbon begins to climb, apparently as a result of backstreaming from the oil diffusion pump. Hardness is as low as 60 Vickers. In tungsten, oxygen as low as 1 to 3 ppm, nitrogen as low as 5 to 10 ppm, carbon as low as 5 ppm, and total metallics as low as 3.5 ppm have been measured. This columbium has about 99.98 percent purity and the tungsten after several remelts close to 99.998 percent purity. Purities near this can be realized in commercial melts if care is taken. Not too many years ago, such purities were achieved only in laboratory research specimens of low melting metals.

Facilities for arc melting and/or electron-beam melting of refractory metals are now available in at least seven companies. Molybdenum ingots to 12 inches in diameter have been arc-melted. An electron-beam furnace with a power of 1.3 MW is available.

Although I have emphasized consolidation by melting, the powder-metallurgy route continues to progress, and most tungsten commercially produced today is consolidated by the powder-metallurgy process. Industry has made great strides in scaling-up pressing and sintering facilities.

When the melting route is used, the ingot is a casting, and it is desirable to break down this ingot by some working method. The preferred method for primary breakdown has been extrusion. The major requirement for successful extrusion of refractory metals is high temperature, as would be expected when processing alloys with a melting point as much as 3500° F above that of steel. Although some of the alloys are successfully extruded at only 2500° F, many require much higher temperatures. DuPont has a production-type extrusion facility operating with a furnace that permits temperatures to 3500° F. In the laboratory we are extruding at temperatures to 5000° F. The high temperatures bring additional problems; one is a requirement for speed. We find that the center of a 2-1/4-inch-diameter billet heated to 4000° F will lose 40° F per second when exposed to room-temperature air. In 10 seconds, the billet center may lose 400° F of heat, and the surface would lose much more. Also, the extrusion chamber and other tooling are made of steels melting near 2600° F. We may not leave 4000° F metal in contact with tooling for very long. Speed also minimizes oxidation and contamination. Lubrication is a serious problem at high temperatures.

Figure 13 shows a typical tungsten billet 2 inches in diameter, a ceramic-coated steel die, and a finished extrusion. Coated dies are an important innovation of the AF Materials Laboratory; the ceramic coating provides die protection and, at some temperatures, lubrication. Figure 14 shows the 1000-ton vertical extrusion press at the Lewis Research Center. To achieve short billet transfer time, the furnace has been placed directly over a metal track. The furnace may use either an inert gas or hydrogen atmosphere, and the billet is inductively heated. The furnace has been used to 5000° F. The hot billet drops into the track, is pushed quickly along the track where, at the end, it drops into the container. As the ram descends, a cable attached from the ram to the chute pulls the chute out of the way. Normal time from opening of the furnace to completion of extrusion is 5 seconds. This facility and the procedures used for extrusion at very high temperatures are described in Ref. 26. Even at these high temperatures we are unable to extrude some materials. The component limiting extrusion pressure is usually the strength of the ram stem. Another important problem is the lack of well-developed lubricants for use at extremely high temperatures. Two innovations have been of major help here: the use of ceramic-coated dies described above, and the use of heavy wall refractory metal claddings around the material to be extruded. This cladding is a material of greater ductility and lower strength than the material to be extruded at the extrusion temperature.

I should hasten to remind you that this is a laboratory or pilot operation that explores new alloys and new methods. Commercial equipment is limited to about 3500° F and, with much bigger billets, moves at slower speeds. With larger billets center temperature loss is less rapid, of course.

Having discussed the facilities for consolidation and breakdown of ingots, let us turn our attention to the problem of primary fabrication and rolling. Again we must be concerned with problems of high temperature and protection during working. Generally, it has been found that commercial tungsten and molybdenum alloys (group VIA metals) after initial ingot breakdown at very high temperatures must be worked at high temperatures; for example, commercial sheet alloys may be rolled at temperatures of 1600° to 1800° F. Ultra-high-strength alloys are worked in the laboratory at much higher temperatures. These temperatures, though high, are in the cold-working range for these alloys, and the metals occasionally may require recrystallization and/or stress-relief anneals at even higher temperatures during processing. Generally, these tungsten and molybdenum alloys must be protected during heating, usually in hydrogen furnaces. Time in air is minimized, and contaminated surfaces are pickled. Several mills have suitable furnaces in conjunction with their rolling mills, for example, Universal Cyclops, Union Carbide Stellite, Climax Molybdenum Company, Wah Chang, and General Electric, Cleveland. In the case of G. E., they have hydrogen furnaces at both sides of a hot mill so that sheet may pass from the hydrogen furnace through the mill and into another hydrogen furnace.

Processing of the final sheet products of tantalum and columbium alloys (group VA metals) is somewhat different. These metals after initial breakdown usually may be rolled cold, from room temperature to less than 800° F. At this temperature, interstitial contamination from the atmosphere is not a problem. The metal must be annealed at intervals between rolling passes. These anneals must be performed in inert gas or vacuum furnaces because hydrogen is destructive to group VA metals. Typical mills producing this product are DuPont Metals Center, Union Carbide Stellite, Fansteel, Wah Chang, and Universal Cyclops.

A truly unique facility for the processing of refractory metals at very high temperatures while in a protective atomsphere has been developed by the Universal Cyclops Company under the direction and sponsorship of the Bureau of Naval Weapons and with recent support from the Air Force. The unique features are that it permits true hot working to temperatures of 4000° F with the metals completely protected in an inert gas argon atmosphere. The facility has been called "Infab" - coined from the words "inert fabrication." Metal processing equipment is contained in a room about 100 feet by 40 feet with a height somewhat over 20 feet, completely filled and maintained with a high-purity argon atmosphere. The total impurities of the gas are less than 5 ppm.

Among the pieces of equipment in the room are a hot impactor for forging-type breakdown of ingots, a rolling mill for hot rolling of bar (with capability for sheet to 18 in. wide) and TIG welding equipment. The control of most of this equipment is from outside the room, but men are required inside the room to move material between pieces of equipment, to feed the material into the rolling mill, and to operate the welder. Figure 15 shows the men clad in space suits while working on the bar mill. Surely this can be called "space-age" fabrication of metals!

While metals are being worked in In-Fab, they are, of course, completely surrounded by an inert atmosphere and the smoking of the metal (Fig. 6) is completely eliminated, and contamination of all refractory metals during processing has been proved to be negligible. The product comes out bright and clean, and pickling or surface machining to remove interstitial contaminates is unnecessary. In the case of the molybdenum alloy, TZM, advantages have been shown for true hot working in the impactor prior to the rolling of sheet. (The usual practice is to warm cold-work.)

As mentioned earlier, the industry generally has found alternate methods for protection of the refractory metals during processing or has been able to remove contamination at the end of processing. Methods for protection include the use of atmosphere furnaces, previously described, coupled with the use of metal claddings or in-process coatings that were later removed. Unfortunately, at this point in time, neither economics nor the need to avoid contamination, nor the development of truly unique properties have been sufficient to justify the continued operation of "Infab," at a cost of about $1000 per day.

Equipment for Evaluation and Contamination Problems

The preceding discussion should give the impression that in this country, we have developed facilities generally suitable for consolidation and processing of these very reactive refractory metals. The final problem area is the evaluation of these materials. Here, particularly when measuring long-time creep or rupture properties, we become much more concerned with the problems of contamination. For space power systems, it is necessary to know the creep rates of these materials out to a minimum of 10 000 hours.

All testing of unprotected refractory metals must be conducted in vacuum or inert atmosphere, such as argon. For short-time tensile tests, modest vacuums, modest in today's standards, of 10^{-4} or 10^{-5} mm Hg, are suitable. The refractory metals of group VA are strong "getters" for oxygen, however, and when hot they will scavenge oxygen from such vacuum environments. Contamination with oxygen may strengthen the metal during the test. (Also, it will embrittle and the transition temperature will be raised.) Space is, for practical purposes, a near perfect vacuum, and contamination can be expected to be nil. It is imperative that the properties measured in the laboratory are those that the designer can expect in his vehicle in space. The question is how good a vacuum must be achieved in the laboratory test chamber to avoid unwanted contamination and incorrect property measurements? Some data to indicate the severity of this problem are given in Fig. 16, (Ref. 27), which shows the contamination by oxygen of columbium-0.75 percent zirconium alloy at 2000° F. We have plotted the relations of oxygen pressure and time that will cause contamination of this alloy to either 100 or 1000 ppm oxygen. These are reasonable contamination limits for tantalum or columbium alloys. The data presented are for a typical tube that has a 20-mil-thick wall with the oxygen penetrating from one side. For example, if we wished to limit contamination of this tube to 1000 ppm in 10,000 hours, it would be necessary to conduct our tests in an atmosphere with a partial pressure of oxygen of almost 10^{-8} mm Hg. From another viewpoint, for a system operating at about 10^{-8} mm Hg, our contamination would reach 100 ppm in about 2000 hours. These data suggest that extremely good vacuum environments are required for the conduct of creep tests for long times. An alternative, of course, is to use an inert gas, such as argon. The horizontal dashed line is the oxygen pressure corresponding to a very high-purity argon gas containing only 0.1 ppm oxygen. This is a maximum theoretical contamination from continuously supplied argon. In practice contamination may not be this rapid, but, clearly, the use of neutral gases is not a simple solution.

Figure 17 describes a high-temperature creep apparatus developed at Lewis Research Center to permit evaluation at ultrahigh vacuum (Ref. 28). The method of heating is that of passing an electric current through a tungsten or tantalum tube that has a longitudinal slit, this heating element then radiates to the test specimen. This test method of heating is used also in short-time tensile equipment to 5000° F. Heat transfer to the vacuum chamber shell is minimized by a series of refractory metal heat shields. The chamber is pumped by a fac-ion pump. An extremely low leak rate is achieved by the use of metal seals at all removable openings and the complete absence of any entry into the furnace during the lifetime of the test. For example, even the application of stress to the specimen is achieved by weights that are contained within the vacuum chamber. This apparatus has operated continuously at pressures down to 5×10^{-9} mm Hg. Currently we have six such creep units for evaluation of very long-time properties and another 18 having a somewhat lesser vacuum capability for shorter time tests. Another 14 ultra-high-vacuum units are being constructed at TRW laboratories under contract to NASA, and Westinghouse laboratories has four such units. Currently NASA in-house and contract facilities are conducting screening tests of the creep properties of 13 commercial tantalum and columbium alloys and several high-strength molybdenum and tungsten alloys for possible use in space power systems.

Even in these test facilities, however, some pickup of oxygen occurs as would be predicted from Fig. 16. The magnitude of this contamination along with other effects of vacuum environment are summarized in Fig. 18(a). Here it is shown that group VA metals, columbium, tantalum and their alloys, will contaminate with oxygen even in high vacuum, thus their transition temperature will be raised and their strength altered. Specific data are shown for an increase in oxygen during a creep test. For the columbium alloy FS-85 (Cb-28Ta-10W-1Zr) tested for 1522 hours at an average pressure of approximately 6×10^{-9} mm Hg, the increase in oxygen was 62 ppm (or 30 percent)(Ref. 28).

Another example shows data for the previously stated fact that poor vacuum may lower creep rate (raise strength). Begley (Ref. 29) has conducted comparative tests with the tantalum alloy T-111 (Ta-8W-2Hf) at the same temperature of 2400° F and stress of 9000 psi. As shown, two vacuum conditions were used, and creep was measured in both after 172 hours. In the poor vacuum of 10^{-6} mm Hg, the creep was only one-tenth of the value in higher vacuum. The metal has been strengthened by exposure to "poor" vacuum. I should reemphasize that this is primarily a problem in evaluation of these materials. In their intended application of space, the vacuum is far superior even to these values, and contamination is not expected to be a problem. Because poor vacuum conditions in the measurement of strength in the laboratory results in overly optimistic data, it is particluarly important to avoid contamination during evaluation. Although our new equipment may limit contamination to reasonable levels, actual data beyond 5000 hours are not yet available.

Molybdenum and tungsten alloys may purify in high vacuums at very high temperatures with removal of oxygen, carbon, and hydrogen (Fig. 18(b)). This change can lower transition temperature. The example (after Harwood, Ref. 30) shows that molybdenum exposed to 3800° F for 12 hours in a vacuum of 5×10^{-5} mm Hg decreased in oxygen content from 18 to 3 ppm, and the ductile-brittle transition temperature decreased from -130° to -200° F.

Carbide-phase-strengthened refractory metal alloys lose carbon and lose strength at high vacuum. Examples are shown for both molybdenum and columbium alloys. The molybdenum example is a typical occurrence during heat treatment at very high temperatures (Ref. 31). Carbon can be lost at temperatures as low as 2400° F. Two explanations are possible: carbide decomposition and evaporation or, more likely, reaction of carbon with traces of oxygen of the atmosphere.

For the columbium alloy D-43 (Cb-10W-1Zr-0.1C) in a creep test, a decrease in carbon occurred at the same time that oxygen was increasing (Ref. 32), as described previously. This loss in carbon represents about a 10-percent decrease from the initial value: the increase in oxygen is about 25 percent. Studies are currently underway to find methods to avoid this loss of carbon during high-temperature vacuum exposures.

I think it is clear that we have made great strides in the processing and testing of these materials. The methods of protection and avoidance of contamination of the final product during refractory metal processing are well known and in use. For testing to very long times, the data indicate that contamination is being minimized, but it has yet to be proved that the new apparatus is good enough for ensuring acceptably correct creep measurements to 10 000 hours and beyond. Because carbon is such an important strengthener in many refractory alloy systems, we can anticipate that solutions to the problem of decarburization in long-time tests in high vacuum may be required.

This discussion has highlighted the character of facilities that have been made available for consolidation, processing, and testing of refractory metals and their alloys. The development of these facilities is, alone, a significant achievement.

Refractory Metal Sheet Rolling Program

Let us now turn to a discussion of progress in refractory metals in an area I will call commercial development. It was our purpose to discuss the progress of the past decade, but let us go back to only 1958 and describe the situation at that time. In 1958, very few refractory metal alloys were available, surface and dimensional control was poor, and worst of all, product quality was extremely variable. This was the era when unalloyed molybdenum was beginning to be replaced by the molybdenum alloy containing 1/2 percent titanium, columbium plus 1 percent zirconium was the columbium alloy, there were no tantalum alloys, and no sizable tungsten sheet.

A major quality problem was lack of uniformity. Variable formability and tendency to delaminate or crack during shearing and forming (Fig. 19) were persistent problems in attempted applications. These problems were most pronounced with molybdenum and tungsten materials. As mentioned earlier, all the refractory metals considered for commercial development (tungsten, tantalum, molybdenum and columbium) are body-centered-cubic metals and at least tungsten, molybdenum and columbium exhibit a transition from ductile to brittle behavior as temperature is lowered. It is desired that this transition temperature be below room temperature to facilitate handling and forming. Commercially available molybdenum sheet was found to have an extremely variable transition (Fig. 20) usually above room temperature (Ref. 33). This does not provide the consumer with a reliable material.

Approach

An agreement was reached among the Department of Defense, the Navy, and the Air Force that the National Academy of Science should be asked to form a panel under the materials Advisory Board to coordinate development activities aimed at providing high-quality sheet of the needed alloys of the refractory metals. (The nature and current status of this activity is described in Ref. 34. The intent here is to outline briefly the accomplishments to date.)

The panel decided that the program should be divided into three phases for each alloy:

Phase I - Development of a production process followed by production of a quantity of sheet to establish quality and uniformity

Phase II - Measurement of preliminary design data for the "pedigreed" sheet from Phase I

Phase III - Establishment of limits of formability and definition of forming and joining procedures for sheet, followed by tests of fabricated structural elements

Of major importance was the decision as to which refractory metals or alloys should be supported in the program. This portion of the activity was the responsibility of the subpanel on Alloy Requirements and Selection headed by Dr. R. I. Jaffee of Battelle. At the initiation of the program, they conducted a survey to learn the status of refractory metal alloy development in this country and to identify the requirements for such alloys. Based on these surveys, they decided it was desirable to set target properties for six specific classes of alloys:

(1) Fabricable molybdenum

(2) High-strength molybdenum

(3) Fabricable high-strength columbium

(4) Tantalum alloy

(5) Unalloyed or dilute tungsten

(6) High-strength tungsten

Figure 21 shows typical targets for three classes. The specific targets were prepared keeping in mind the general characteristics of the base metals.

An example of the philosophy in creating the targets can be seen by comparing "fabricable" and "high-strength" molybdenum classes. The significant difference appears in high-temperature-strength and room-temperature-ductility requirements. The high-strength alloy was to have a comparable strength but at a 400° F higher temperature. This strength was to be obtained at a sacrifice in room-temperature ductility.

Another point of philosophy can be illustrated for columbium alloys. It was decided and stated (by the targets) that, to be of interest, columbium alloys must retain a major attractive characteristic of columbium - good ductility in the welded condition at room temperature. Molybdenum alloys with high strength but lacking weld ductility were already available.

These targets provided the industry with specific objectives permitting them to focus their efforts for alloy development and also listing specific test data that should be obtained to permit valid comparisons to be made. The stimulus for the industry was the opportunity for government support for further development (Phases I, II, and III) for the selected alloys. Government support was important because the market was limited and uncertain, and cost of the finished product in 0.040-inch sheet is between $30 and $280 per square foot.

The targets were submitted to the industry, and candidate alloys were screened. Following selection of candidates, the government agencies could fund development through the three phases as deemed necessary.

Alloy selection was an intensive process spanning several years. Those of us involved in the program were particularly impressed with the manner in which industry responded to the challenge. Once clear objectives had been established, producers, whether under contract or not, made rapid progress. Within a few years, several alloys in each class were available for selection. It is significant to note that, at this date, the target properties have been achieved for all classes except high-strength molybdenum.

Progress

To highlight the progress, we may compare the status of the alloys of the program when the program began in November 1959 with current status (Fig. 22). This table shows that several alloys, which have advanced to a point where sheet can be produced in large sizes with good quality and uniformity, were unknown at the start of the program.

Another point of interest is to compare the properties of the selected materials that have been investigated in the "scale-up" program with the more significant targets of strength, ductility, and weldability (Fig. 23). For each of four classes, the bar graphs compare the high-temperature tensile strengths of the selected alloys to the targets (shaded bars). The tabular data at the top of the figure compare the ductile-brittle transition temperatures with targets and also compare the ductility at room temperature after welding with the target.

For the fabricable molybdenum class, the selected alloy, TZM, exceeded the strength targets at 2000° and 2400° F, but of more significance is the ductile-brittle transition-temperature comparison. Earlier problems in molybdenum were described with emphasis on the problems of delamination, and the fact that the only consistent feature of the ductile-brittle transition-temperature was that it was almost always above room temperature (Fig. 20). As a result of the program, attention was focused on an alloy, TZM, that had much better strength, which now consistently demonstrates a ductile-brittle transition temperature below a -60° F. Room temperature weld ductility was, of course, not sought in molybdenum and was not achieved. (An excellent general discussion of the problem of delamination may be found in Ref. 35).

Unalloyed tungsten was pursued for use at very high temperatures and met the targets for tensile strength at 3000° and 3500° F. Capability of producing large sheet with good quality and uniformity in flatness and in gage control was sought and generally achieved. Ductility at room temperature was not expected.

Columbium alloys were desired with good strength but with major emphasis on the requirement that they should be ductile when welded. (Otherwise they would have little advantage over molybdenum alloys.) The resultant alloys described here have high strength, a ductile-brittle transition temperature lower than -250° F, and after being welded will survive a bend over a radius equal to the sheet thickness (1T) at room temperature. They are ductile when welded.

Tantalum alloys were sought with a higher use temperature than columbium alloys and with even better ductility. These have been achieved.

It was thought desirable to describe the strengths of the alloys selected or identified in this program. This comparison should provide a perspective of strengths for the materials, but, of course, is not the only basis for selection of an alloy for any application. Many other factors must be considered. Figure 24 shows this comparison on the basis of only ultimate tensile strength. The several columbium alloys are shown as a band. The order of increasing strength generally is Cb alloys, Ta alloy, T-222, Mo alloy TZM, and unalloyed W.

The density of these materials varies widely as follows:

Alloy	Density, lb/in^3
Cb alloys, FS-85 and D-43	0.39 and 0.33, respectively
TZM	0.37
T-222 and GE-473	0.60
Tungsten	0.69

The tantalum and tungsten alloys have very high density.

Although for some applications, even some of those in aerospace, density is not an important factor, it surely is in most such applications and thus often must be taken into account when comparing strengths. These materials are compared on the basis of strength-to-density ratio in Fig. 25. On this basis, the tantalum alloys are only slightly superior to columbium alloys, and the advantage of the molybdenum alloy is clearly indicated. Unalloyed tungsten is of interest at temperatures above about 3100° F.

Another indication of progress is to note the formability of the sheet product of the Phase I programs in contrast to the status presented earlier. The determination of formability and formability limits has been the responsibility of Phase III contractors. These studies are underway for the molybdenum alloy TZM at McDonnell Corporation (e.g., Ref. 36) and for tungsten at Solar (e.g., Ref. 37) and at Super-Temp Corporation (e.g., Ref. 38) under sponsorship of the Bureau of Naval Weapons.

Formed parts of TZM are shown in three figures: a curved channel (Fig. 26), corrugations formed at room temperature (Fig. 27, Ref. 6), and formed, corrugated panels from powder-metallurgy tungsten (Fig. 28). Deep drawn cups that were formed at about 1650° F are shown in Fig. 29. These figures are from the contract of Ref. 37. Clearly it has been shown that proper procedures can produce quality parts of these alloys. The summary reports of Phase III contractors of the sheet rolling program will provide guidelines for the forming of these materials. Summaries of all the contractor activities of the sheet rolling program are prepared by DMIC (Ref. 39 is typical).

Forging Development

The refractory-metal-sheet rolling program just described, has, of course, concentrated on sheet materials. Another particularly important accomplishment in refractory metals has been the development of good quality forged tungsten for nozzles of the solid propellant rocket. To this date, the solid rocket nozzle has been responsible for perhaps 80 percent of the consumption of refractory metals in finished hardware. Here the need has been to provide a material that will resist the erosive effects of impinging gases at gas temperatures greater than 5000° F. Thin sheet material has not been successful because it tends to deform or buckle under the pressures. The need was for heavy wall forgings.

Forged nozzles resulting from this development program are shown in Fig. 30 (Ref. 40). The nozzles are produced from initial powder-metallurgy billets 6 inches in diameter, 11 inches high, and weighing about 250 pounds. These large billets are upset to a flat pancake and then formed into the shape of a cup. The bottom of the cup is then removed, and the resulting cylinder is ring-rolled to the final product shown. These are the largest tungsten nozzles ever produced and have a diameter of about 16 inches. The tensile properties of this material are also shown in the figure. The controlled working has produced comparable properties in both the axial and circumferential directions. The strength levels are fully equivalent to high quality sheet, and the transition temperature is remarkably low for this product, apparently less than 200° F, as indicated by the high ductility at 200° F.

An equally important development for rocket nozzles is that of porous tungsten infiltrated with silver. The microstructure of the cross section of a nozzle after firing is shown in Fig. 31. An important feature of these nozzles is that some cooling is achieved as a result of evaporation of silver from the hot surface. From the microstructures and the numbers on the cross section of the nozzle, you can see the magnitude of the evaporation of the silver. The processing variables of these composite nozzles have been systematically investigated and reported by the Aerojet Company (Ref. 41). Although the advantage of this nozzle over the solid nozzle from the standpoint of evaporative cooling is obvious, it is not the most important advantage in the opinion of the consumer. Surprisingly, when compared with unalloyed tungsten, lower cost, better machineability, and better toughness at room temperature are more important advantages.

Atmosphere Protection

Refractory metals have fulfilled an important need for the nozzle of the solid propellant rocket, in part because the components of the exhaust gases of the particular rocket engines are not highly reactive with these metals. Unfortunately, as we saw earlier, most applications that require the high-temperature strength of refractory metals also require resistance to highly oxidizing atmospheres. Important examples are the components of air-breathing engines, such as the turbojet or the ramjet. The need to increase operating temperatures in such applications is great. Refractory metal alloys with the required strength, ductility, and fabricability to permit increased operating temperatures are now available. Oxidation-resistant alloys or suitable coatings are not available, except for short-time reentry applications.

The state of development of coatings for refractory metals is indicated in Fig. 32 where we have shown the protective life as a function of service temperature for the best coatings on the four primary refractory metals (Refs. 42 and 43). The data are for exposure in still air at atmospheric pressure. Most research and development to date has been directed toward coatings for columbium and molybdenum. Much less experience has been gained with tantalum and with tungsten.

Although the relations shown by these curves are reasonably correct, the difficulties in the application and use of coatings are such that consultation with an expert is required before one attempts to apply coated refractory metals to a particular component or use. For example, if we take a temperature of 2200° F, these data would state that the coated molybdenum would have a greater lifetime than coated columbium. This would be true in a laboratory furnace in still air; however, in a turbine bucket operating in a jet engine, where foreign objects may strike the surface, the opposite would probably be true. As noted earlier (Figs. 6 and 7), the oxidation of the base metals, molybdenum and columbium, are completely different in this temperature range. The oxide of molybdenum vaporizes as rapidly as it is formed. A pinhole through the diffused coating may result in complete loss of the underlying molybdenum by its conversion to molybdenum oxide and evaporation through the hole. The oxide of columbium, on the other hand, is a porous, flaky material, and thus it tends to oxidize more slowly near an imperfection. Thus columbium would certainly be the better choice for this application. On the other hand, considering a lifetime of 1 hour, the data give a clear picture. Coated columbium would be limited to a temperature of about 2700° F, and molybdenum would permit operation to higher temperatures. Such has been the philosophy in the construction of reentry structures. Coated columbium because of its superior ductility and fabricability is used to the maximum temperature possible, with hotter areas using coated molybdenum.

Another important factor in the use of coatings is the fact that coatings affect the properties of the base metal as indicated in Fig. 33 (Ref. 44). As one of my colleagues has said to emphasize this point, "It ain't paint." This figure describes the effect of six different commercial coatings on the transition temperature of one columbium sheet alloy, D-31. The lower dashed line indicates that the transition temperature of the uncoated sheet was below -100° F. In every case, the application of the coating has raised the transition temperature, and three coatings have raised this temperature to above room temperature.

It is recognized that we should consider coated refractory metals as new composite materials and measure the properties of these new composites. In many cases the effects can be more damaging than shown here. In most cases, the coatings are diffused coatings that may alter the chemistry of the surface to a depth of 2 or 3 mils. If we were to coat a sheet of 5-mil thickness for honeycomb, it is obvious that the composition through the entire thickness could be changed and we would have a totally new material. It is a continuing objective of researchers in coatings to identify those coatings and process conditions that will minimize the changes to the properties of the base metals while providing a maximum of protection. To date, coatings that will permit the application of refractory metals to the more important long-time environments have not been achieved. The needs are great.

Application

Another corrosive environment for refractory metals is the containment of boiling alkali metals for Rankine space power systems and liquid metals for heat-transfer systems. Here we may report that the future looks bright.

Figure 34, from work at the Lewis Research Center (Ref. 45), indicates that columbium and tantalum alloys containing minor alloying additions of Zr and Hf appear excellent in corrosion resistance to boiling potassium at 2200° F. Shown on the left in the figure is the corrosion that occurs in a commercial Cb-10W-10Ta alloy in 1000 hours. The intergranular attack is obvious. On the right is shown a Cb-10W-28Ta alloy with 1 percent Zr. Although the Ta has been increased, it is known that the dramatic improvement shown here is a result of the presence of Zr. After 4000 hours exposure, no corrosion has occurred. For this particular kind of space power application, refractory metals in the form of high quality tubing with ductility when welded are required. Many of the Ta and Cb sheet alloys of the sheet rolling programs appear suitable. The better ones have either Hf or Zr added for strength. As we see here, these same additions may have provided the needed resistance to corrosion. Certainly more data are needed under conditions that more nearly duplicate the service environment and with exposure for long times, but we have every reason to be optimistic.

A particularly fine example of the fabrication of hardware from refractory metals is demonstrated by the ASSET vehicle shown as an exploded view in Fig. 35. ASSET was a research reentry vehicle developed by the McDonnell Corporation and the Air Force (Ref. 46). On reentry, the structural materials would be subjected to a range of temperatures from 4000° F for the nose cap to 1000° F for the aft bulkhead. A ceramic nose cap was used to withstand the 4000° F temperature. The philosophy of application of the metals was to use coated molybdenum at temperatures of near 3000° F, and at lower temperatures down to where coated columbium might survive, approximately 2600° F. Coated columbium was used because of its greater fabricability and ductility. As would be expected, superalloys were used at temperatures of 2000° F and below.

An assembly of fabricated coated refractory metal panels from the lower structure of this vehicle is shown in Fig. 36. The two different colors are the result of the use of different types of coatings on the structure. I think you can see that this is a very sophisticated metal structure.

The final figure (Fig. 37) of this series shows the completed ASSET vehicle. Its total length is about 6 feet. Six ballistic reentry trajectories have been flown by these vehicles, but only one vehicle has been recovered from the ocean. I was privileged to see the recovered vehicle and can vouch for the fact that there was little visible evidence of its having been flown. In fact, the vehicle was subjected to a second reentry flight with apparent good performance although the vehicle was not recovered for examination.

EMERGING ALLOY TRENDS

The final area I wish to summarize is the strengths of the best alloys discovered to date. Laboratory developments are, of course, ahead of commercial developments, and examination of the laboratory data will indicate the trend of future commercial alloys. Whereas 10 years ago there were only a few molybdenum alloys identified, today there are at least 16 columbium alloys, seven tantalum alloys, seven tungsten alloys, and five molybdenum alloys. Many of these, however, are not high-strength alloys.

Tensile Properties

The short-time tensile strength as a function of temperature of the best alloys reported to date is shown in Fig. 38. Only one material here (T-222: Ta-10W-2.5Hf-0.01C) was in the previous comparisons, but this time it is called "optimum" because, as a result of systematic study, slightly higher strengths have been achieved (Ref. 47). Whereas Cb alloys were shown as weaker than the Ta alloys before, the alloy (AS-30: Cb-20W-1Zr-0.1C, Ref. 48) shown here is appreciably stronger. This high-strength alloy is a forging alloy and could not be produced readily in high quality sheet. It could be of interest for high-strength parts such as turbine buckets, however. TZC (Mo-1.25Ti-0.3ZR-0.15C) is the molybdenum alloy, having somewhat higher alloying additions than the previously described TZM. Shown also is a tungsten alloy (W-0.2Hf-0.017C). This is the best of many arc-melted compositions recently explored at our laboratory by Raffo and Klopp (Ref. 49). The remarkable high-temperature tensile strength of this alloy is, in part, due to retained cold work. The magnitude of this cold-work strengthening is indicated by the almost 40-percent drop in strength when recrystallized. The retention of cold work at 3500° F is extremely interesting. (Remarkably, this alloy has a recrystallization temperature of approximately 4200° F, about 0.7 of the melting point). A powder-metallurgy alloy of similar composition (W-0.5Hf-0.02C) and with a strength somewhat less than this value was developed earlier by Sylvania Corporation. They call this alloy "Sylvania A."

In the lower portion of the figure are shown properties of chromium and vanadium alloys (Refs. 50 and 51, respectively). These particular alloys would be of interest only at temperatures near 2000° F in almost direct competition with superalloys. Vanadium alloys have been studied extensively by IITRI. Better chromium alloys that can be produced in high quality forgings are known, but they are proprietary. They still have the disadvantages of having a ductile-brittle transition temperature of greater than room temperature and of embrittling severely due to nitrification upon exposure to air at the desired use temperatures.

For comparison, the best wrought superalloys have an ultimate strength of 40,000 psi at 1850° F. Thus, on the basis of the short-time strengths, these V and Cr alloys are about 150° F better and Cb, Mo, and Ta about 850° F better. Superalloys have an ultimate strength of 80,000 psi at about 1700° F. The tungsten alloys are about 1300° F better.

In many applications the strength-density ratio must be considered. Thus it is appropriate to examine this property. Before viewing such a comparison let me remind you that the Cb and Mo alloys in this figure have about the same density because of large amounts of W added to the Cb. The Ta, and particularly the tungsten alloys are much heavier, thus their strengths will shift downward in relation to Cb and Mo. Cr and V are lighter, and thus will shift upward.

Figure 39 makes a comparison on the basis of the stress-density ratio. It is suggested that the Cr or V alloys are competitive to about 2200° F. Mo and Cb alloys demonstrate a considerable advantage over Ta, and the W alloys stand alone at very high temperatures.

Stress-Rupture Properties

Most applications of material for use at high temperatures are designed on the basis of creep or rupture strength. Thus, such comparisons are of more interest than those discussed. Stress-rupture strengths for rupture in 100 hours of the best alloys are shown on Fig. 40.

These data are expensive and difficult to obtain. Equipment is required to operate at very high temperatures and with high quality vacuums. Because only limited data are available, it has been necessary to extrapolate some short-time data to obtain the plots shown here. Tungsten is, of course, the strongest material at the highest temperatures. (The data for the W alloy shown here are for the previously mentioned Sylvania alloy. Data are not available for the higher strength "cold-worked" arc-melted W alloy of Fig. 38). Notice that here, contrary to the situation shown for short-time strength, Ta alloys are indicated to be superior to those of Cb and Mo. Two strength levels are shown for Cb alloys. The lower level represents the ductile materials that can be made into high quality sheet or tubing. The upper level indicated by the vertical bar is for high-strength forging alloys.

I think it is particularly instructive to examine the compositions of these materials. Although these data are for specific alloys, they are remarkably typical of the general trend of alloying development. These compositions are the result of many screening studies by many laboratories, and in many cases represent compromises of strength for ductility. First note that the group VIA metals, tungsten and molybdenum, are alloyed differently than the group VA metals, Ta and Cb. Consider first the high strength W alloys, and note that the total alloying addition is only 1/2 of 1 percent: Hf plus C (to form an extremely fine dispersed carbide phase). In Mo, additions are somewhat similar - small amounts of carbide formers, Ti and Zr, plus C.

In the group VA metals, Cb and Ta, small amounts of carbide formers, Hf and Zr plus C are again used, but in this case group VIA metals, usually W, are also added in solid solution. The Ta alloys and the Cb-1 alloys both contain 10 W. Both are ductile alloys with low transition temperatures and are easily fabricated into high quality sheet. To give a large increase in strength to Cb, much more W has been added. (These are forging alloys currently under study by Begley, et al., Ref. 52.) Increased tungsten provides appreciable strengthening but with a sacrifice in ductility and fabricability.

The alloying of Cr is a little different. Here additional improvements are sought by alloying: improvements in ductility and resistance to nitrification. The alloy at the strength level plotted here has ductility at room temperature. Alloys of much better strength but with a transition temperature above room temperature have been identified. They are proprietary, however.

Once again we should compare the materials on the basis of strength-density ratio. Before examining the figure (Fig. 41), let us recall that both tungsten and tantalum are very heavy metals, and we would expect them to be shifted downward to the columbium and molybdenum alloys. You will note that this is essentially what has happened. The tantalum alloy has not fallen below the molybdenum, but is still appreciably better than the ductile columbium alloy (1) in spite of its high density. This figure would suggest that the tungsten alloy is superior at temperatures as low as 2700° or 2800° F, but data are not available in that temperature range. A serious limitation of the tungsten is its brittleness at room temperature. We will discuss this subject in more detail subsequently.

A contributing factor to the rather orderly trend just described is that most of the alloys have followed a similar pattern of development and are now at a somewhat similar state. These compositions are the result of systematic solid-solution alloying additions made to the base metal followed by additions of second phases such as carbide, nitride, or oxide formers to a selected solid-solution alloy matrix. One boundary conditions is that the composition must be fabricable. Many of the alloys gain appreciable additional strengthening from cold work (particularly the VIA metals) or from dispersion of the second phase; in some cases properly dispersed second phases will permit greater retention of cold work or retention to higher temperatures. Thus, it has been obvious that studies of the control of processing along with control of morphology of dispersed phases should give appreciable gains in strength for some alloys over the strengths shown here. Early significant research in precipitate morphology was contributed by Chang and Perlmutter (Ref. 53). Recently Perkins and Lytton (Ref. 54) have combined the benefits of processing and heat treatment of a Cb-modified TZC alloy (Mo-1.5Cb-0.5Ti-0.3Zr-0.07C) and achieved strengths $1\frac{1}{2}$ times that of the molybdenum alloy shown on the stress-rupture plot (Fig. 40). The data are almost identical to those for T-222. On a strength-to-density basis, the alloy in the "optimum" condition is superior to any material in the temperature range of 2000° to 2800° F. It is reported to be extremely notch sensitive, however.

Strength as a Function of Melting Point

Final comparisons of strength in the refractory-metal alloy systems are made as a function of homologous temperature. Plots of this type permit us to eliminate the differences in melting point and measure directly the effect of alloying or other variables. The first, Fig. 42, is on the basis of tensile strength. Examining first the group VA metals, tantalum and columbium, it would seem that the degree of strengthening achieved by alloying is very similar. This is not surprising, of course, if we examine the similarity of the alloying additions. You will note that both alloys generally have about 10 percent tungsten plus small amounts of zirconium and carbon. If we examine the group VIA metals, tungsten and molybdenum, we find that their strengths are well above the group VA metals with tungsten superior to molybdenum. If you recall from the earlier slides, however, it was pointed out that this tungsten alloy retains a very large amount of cold work in a short-time tensile test, at least to 60 percent of the melting point of W, whereas this molybdenum alloy does not. If we were to recrystallize the tungsten alloy, thus removing the cold work, we would find that the strengths are similar. (The strength at a homologous temperature of 0.60 would be 35,600 psi.) On the other hand, the ability of these tungsten alloys to retain cold work is of considerable interest and may be put to use in many applications. The third group VIA metal in the figure, chromium, is apparently behaving very similar to molybdenum and tungsten.

The group VA metal, vanadium, seems to fall well above the tantalum and columbium, but this may be associated with the large addition (20 percent) of the higher melting columbium. You will note that the columbium 2 percent alloy is a close competitor with the group VIA metals. This high-strength level has been achieved largely because of the addition of large amounts of the VIA metal, tungsten. As mentioned earlier, the behavior of this alloy moves toward that of the group VIA metals in that we have sacrificed some of the characteristic ductility and weldability to achieve a high-strength forging alloy.

It is difficult to predict how much additional strengthening might yet be achieved in these refractory-metal systems. For comparison, we have included the strength of an outstanding wrought nickel-base alloy. It is highly unlikely that we can ever achieve this magnitude of high-temperature strengthening, as will be discussed later.

Figure 43 again makes a comparison on the basis of homologous temperature (again for the melting point of the unalloyed base metal), but this time the data are for stress-rupture strength rather than short-time tensile strength. The strength of the group VA metals, tantalum and columbium, are almost identical. The VIA metals, molybdenum, tungsten, and chromium, are less similar and generally above the group VA metals.

Sherby (Ref. 55) has pointed out that, at temperatures above about half the melting point, creep strength is diffusion controlled. He relates five factors that are important in slowing diffusion and thus increasing creep (or rupture) strength.

The first three of these are: crystal structure with the relatively open body-centered-cubic structure being poorest, melting point with higher melting points of course desirable, and modulus - the higher the modulus, the higher the creep strength. He placed a lesser emphasis on the desirability of a higher valence state and argued that benefits of dispersion strengthening in materials, such as sintered-aluminum powder (alumina in aluminum) and TD nickel (thoria in nickel), related to achieving and maintaining a fine and perhaps optimum grain size.

Earlier in discussing Fig. 2 it was pointed out that the strengths within each group were in the same order as the melting point but that the group VI metals were stronger than those of group V. In this figure (Fig. 43) by comparing strengths of the materials on the basis of homologous temperature, we have eliminated the effect of melting point except perhaps for the comparison of Cb (1) and (2). Cb (2) apparently has much higher strength in part because it contains twice as much tungsten, the highest melting metal (and a material of much higher modulus).

In regard to modulus, the strength superiority of the group VIA metals, Mo, W, and perhaps Cr over the group VA metals, Ta and Cb, may be associated with the fact that the modulus of these group VIA metals is almost twice that of the VA metals.

The influence of crystal structure cannot be measured for the refractory metals because all are body-centered cubic; however, the strength of an outstanding wrought nickel-base superalloy U-700 is shown in Fig. 43. This plot would suggest that our refractory metal alloys are falling far short of our achievements in superalloys. This would be expected on two bases: First, higher strength refractory metal alloys may be consolidated, but frequently we are not able to fabricate them because of equipment limitations; second, the nickel-base alloys have a face-centered-cubic crystal structure, and theory would state that we may never achieve the same strengthening in body-centered-cubic metal systems. Let us not say that we will not do better in the refractory-metal alloys, however. You may be sure that better alloys are just around the next corner.

Ductility Improvements in Tungsten

We have examined the strength of the refractory metals with particular emphasis on alloys of Cb, Ta, Mo, and W. In addition to strength, we must always be concerned with transition temperature with the initial goal of providing high-strength alloys with a ductile-to-brittle transition temperature below room temperature. This goal has been achieved for commercial alloys of all these metals, except perhaps tungsten.

An important research area of the past 2 or 3 years has been to seek methods of achieving similar improvements in tungsten. It has been known for several years that single crystals of tungsten are very ductile at room temperature, but the same material converted to polycrystalline form is not. The Linde Division of Union Carbide has been successful (Ref. 56) in producing single crystal tungsten sheet that retains the ductility and single crystal form even after rolling and welding. Certainly this is a remarkable achievement but to date it has been limited to laboratory studies on small samples. Studies to achieve ultra-high-purity polycrystalline tungsten as a route to ductility at room temperature have not been successful.

Some years ago it was reported by Geach and Hughes (Ref. 57) that an alloy of tungsten with 25 percent rhenium did have a transition temperature well below room temperature. This alloy is ductile in the cold-worked form and may be ductile in the recrystallized condition if not heated much above the recrystallization temperature. Rhenium, however, is more expensive than gold, and although the tungsten 25 percent rhenium alloy may be purchased commercially, the cost is $600 to $1000 per pound.

In recent months, it has been found that other approaches are feasible Several of these are tabulated in Fig. 44. Pugh, et al., of the General Electric Company (Ref. 58) showed that doped lamp filament tungsten when alloyed with 3 percent rhenium by the powder-metallurgy process would be ductile in either the cold-worked or recrystallized form, but only when drawn into small diameter wire. When applied to sheet, the process did not result in ductility. At the Lewis Research Center (Refs. 59 and 60) we have recently found that an alloy of tungsten with 3 percent rhenium prepared by electron-beam melting is ductile at room temperature in the cold-worked condition. This achievement appears dependent on the high-purity tungsten achieved by the electron-beam-melting process because sheet prepared in the same way but arc melted is brittle at room temperature. Maykuth, et al., of Battelle (Refs. 61 and 62) have prepared, by powder metallurgy, an alloy of doped tungsten plus 5 percent rhenium plus 2.2 percent of dispersed phase, thoria. Early data reported here suggests that this alloy in sheet form may be ductile in both the cold-worked and recrystallized condition in tensile tests at room temperature but with restricted ductility in bend tests.

In earlier figures it was indicated that the highest strength tungsten alloy contained small amounts of carbide formers and carbon, for example, 0.5 percent hafnium plus 0.02 percent carbon. Friedman and Dickinson of Sylvania have recently found (Ref. 63) that an addition of 3 to 5 percent rhenium in their powder-metallurgy-produced version of this alloy will result in room-temperature ductility in the cold-worked condition. Although the preliminary data indicate that this alloy may be brittle when recrystallized, the alloy has a relatively high recrystallization temperature of 3300° F. Only limited data are available in these new materials and undoubtedly other shortcomings will be revealed; nevertheless, the data should permit cautious optimism in our achieving tungsten alloys with ductility at room temperature. These data suggest that either the route of high purity plus rhenium or a combination of rhenium and a dispersed phase will achieve this goal.

SUMMARY

Surely it can be said that the past decade has resulted in dramatic progress in refractory materials for structural applications, undoubtedly a greater rate of progress than ever before achieved for any one class of structural materials. This progress has required the development of unique processing and evaluation facilities incorporating high temperatures and protective or vacuum environments. Through a coordinated government-industry program, high quality sheet alloys of high strength are now available commercially. Laboratory research demonstrates that further improvements in properties will be realized.

Important research areas will relate to contamination and stability in long-time testing and service, improved alloys, both conventional and dispersion strengthened, and heat treatment coupled with process control to improve and tailor properties. The great need in refractory metals is to combine the alloys of today with suitable coatings to permit operation at long times in an air environment. This is the most difficult task before us. I am hesitant to predict success but the search must continue.

Thank you for permitting me to speak in honor of Horace W. Gillett.

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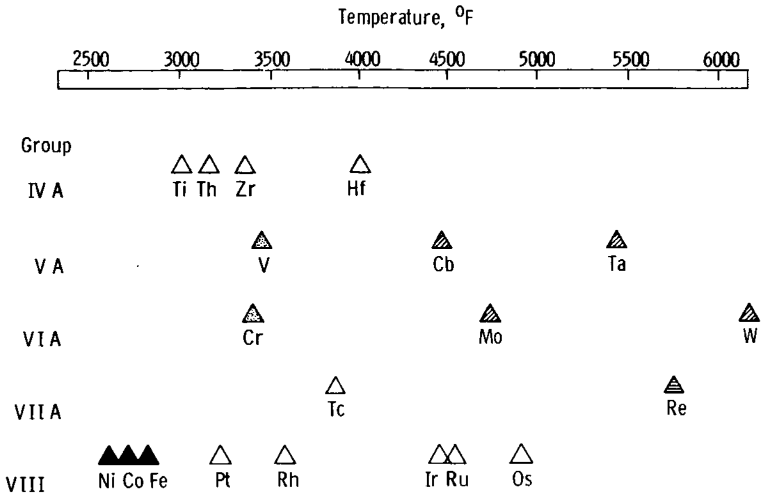


Figure 1. - High-melting-point metals.

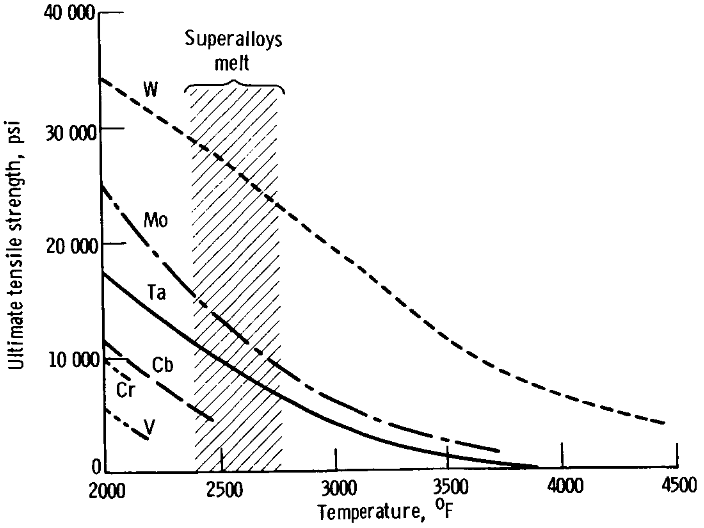


Figure 2. - Tensile strength of unalloyed recrystallized refractory metals.

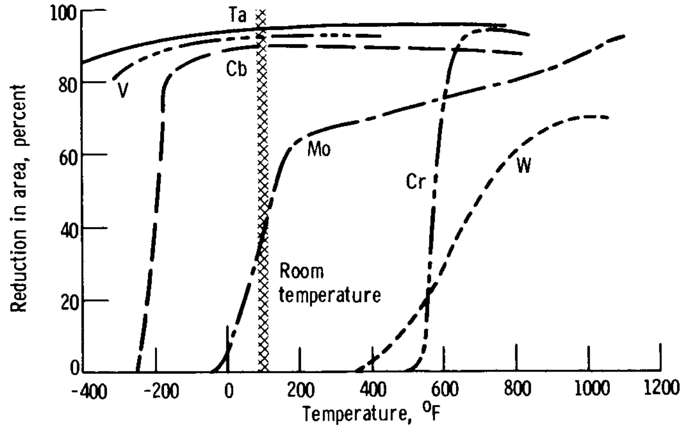
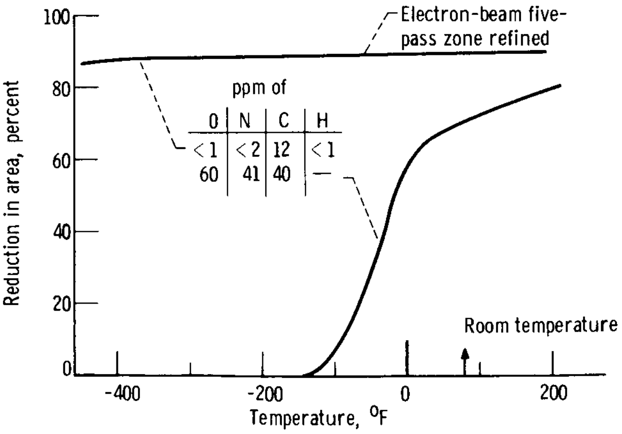


Figure 3. - Ductile-brittle transition temperature of recrystallized metal.



ppm of

O	N	C	H
<1	<2	12	<1
60	41	40	—

Figure 4. - Effect of purity on transition temperature of recrystallized molybdenum.

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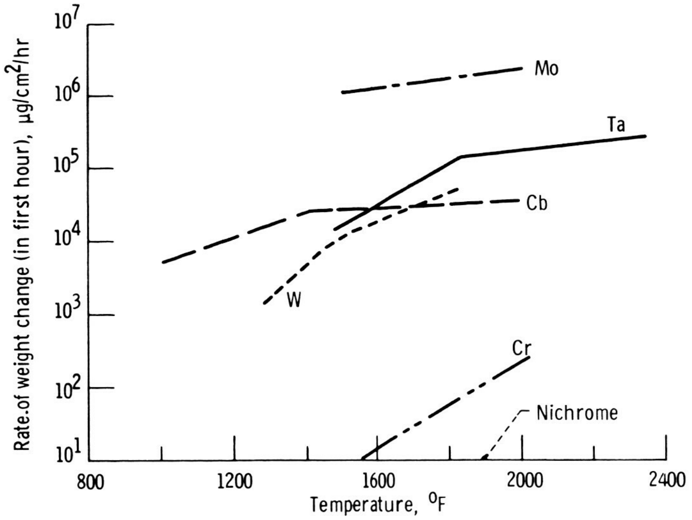

Figure 5. - Oxidation of refractory metals.

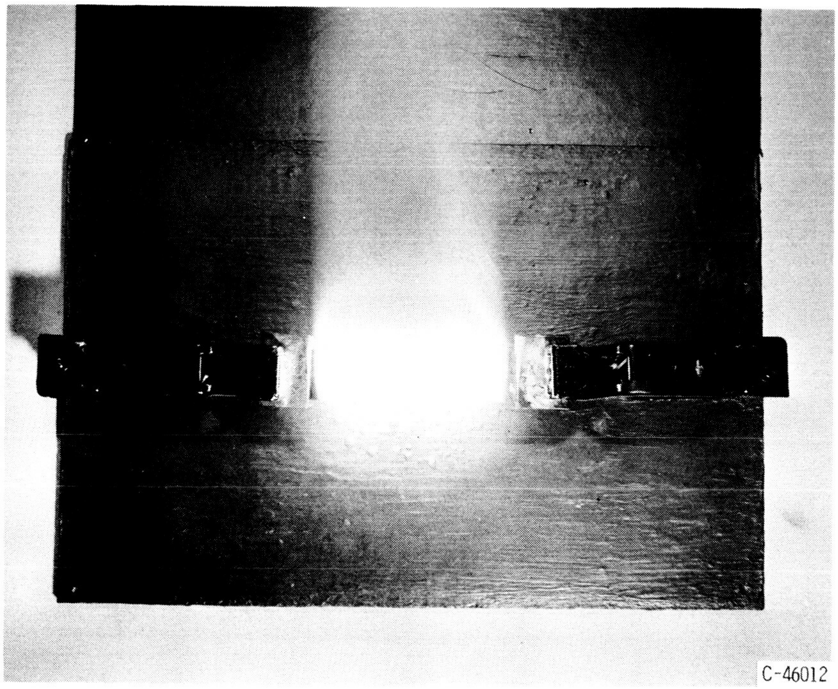

Figure 6. - Molybdenum heated to 3500° F in air.

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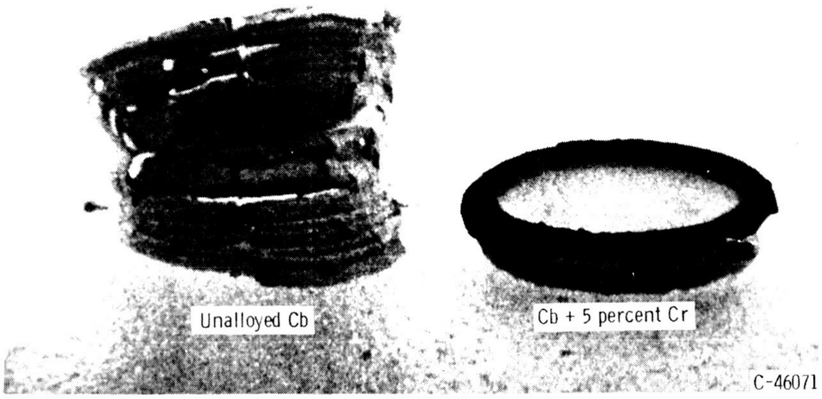

Figure 7. - Comparison of columbium oxidation at 1500° F in air after 3 hours exposure.

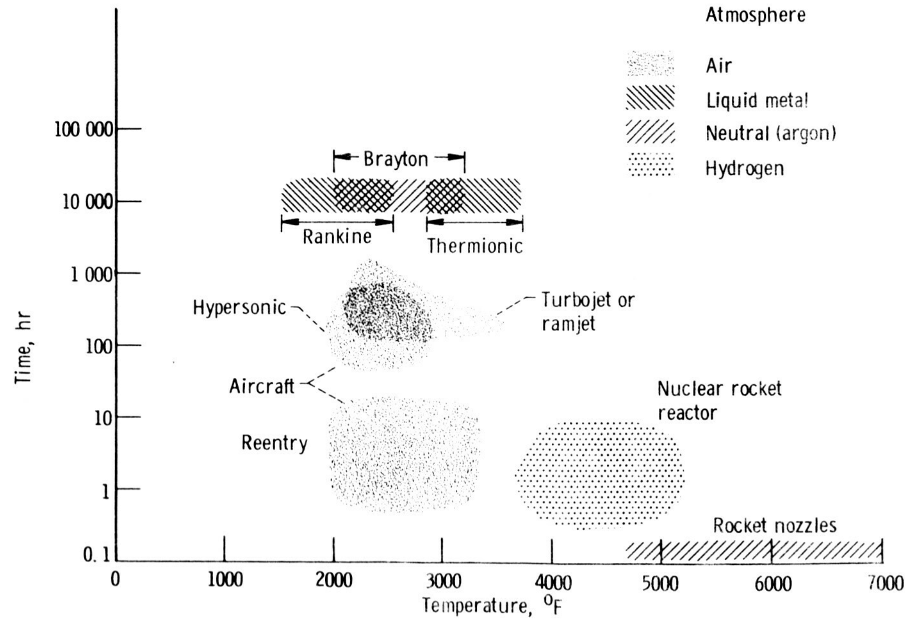

Figure 8. - Requirements for refractory metals.

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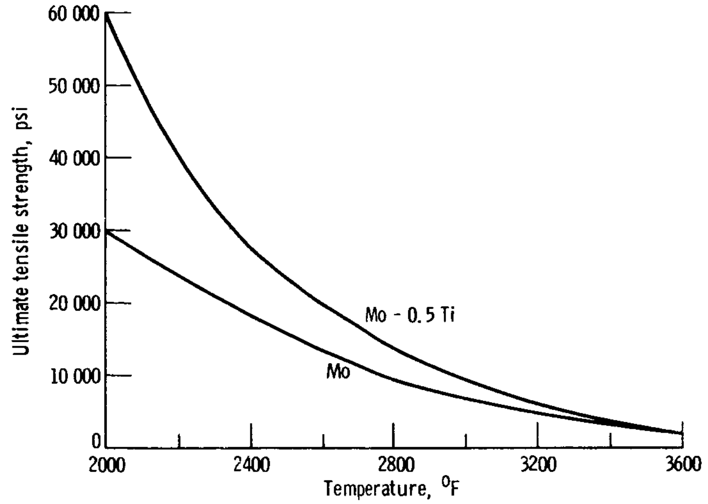

Figure 9. - Strengths of refractory metal alloys in 1955.

Group	Base metal	Density, relative to iron	Ductile at room temperature when -			May be finished near room temperature	Ductile in hydrogen
			Recrystallized	Cold worked	Welded		
VA	Ta	2.1	Yes	Yes	Yes	Yes	No
	Cb	1.1	Yes	Yes	Yes	Yes	No
	V	.77	Yes	Yes	Yes	?	No
VIA	W	2.5	No	No	No	No	Yes
	Mo	1.3	No	Yes	No	No	Yes
	Cr	.91	No	Yes	No	No	Yes

Figure 10. - Characteristics of base metals.

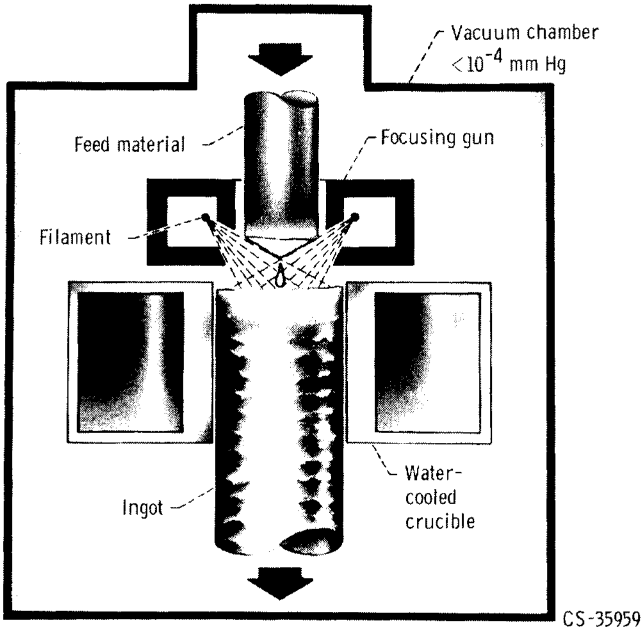

Figure 11. - Electron beam melting.

Impurities, ppm	Columbium			Tungsten
	Starting material	After first melt	After second melt	After melting
O	[a]≈1500	55	20	1 to 3
N	550	70	55	5 to 10
C	390	40	65	5
H	----	1	2	------
Total metallics	----	--	--	3.5 to 50
Hardness, VHN	----	89	60	345

[a]Not measured; typical value.

Figure 12. - Purification achieved by electron-beam melting in high vacuum. (Chamber pressure, 10^{-4} to 10^{-6} mm Hg; ingot diameter, $2\frac{1}{4}$ in.)

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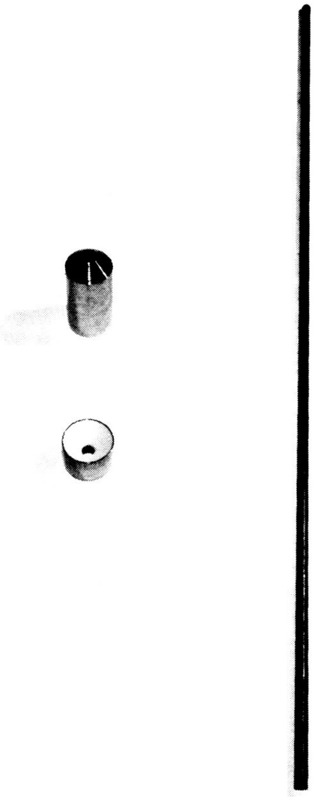

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Figure 13. - Tungsten billet, coated die, and finished extrusion.

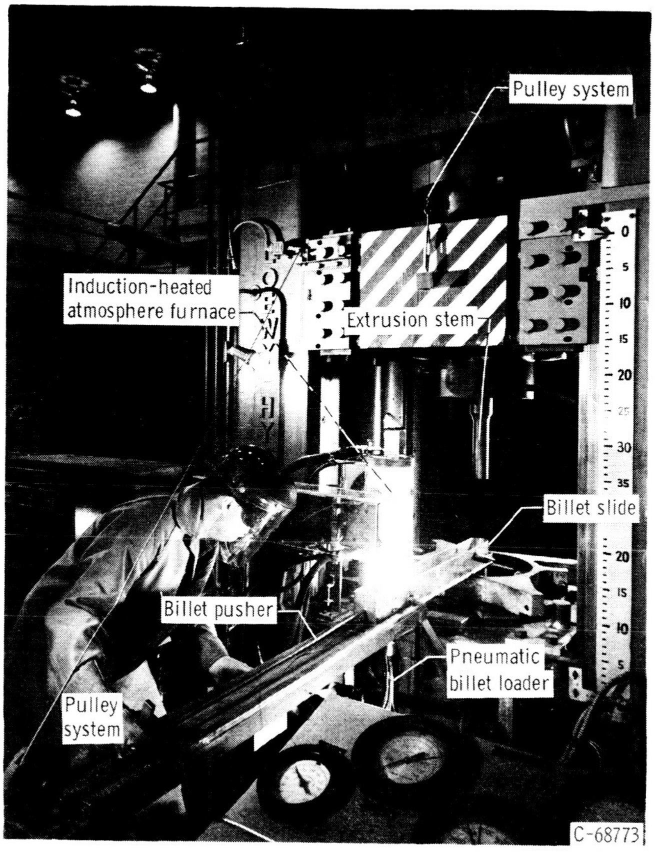

Figure 14. - Lowering of billet from furnace into rapid billet loader device.

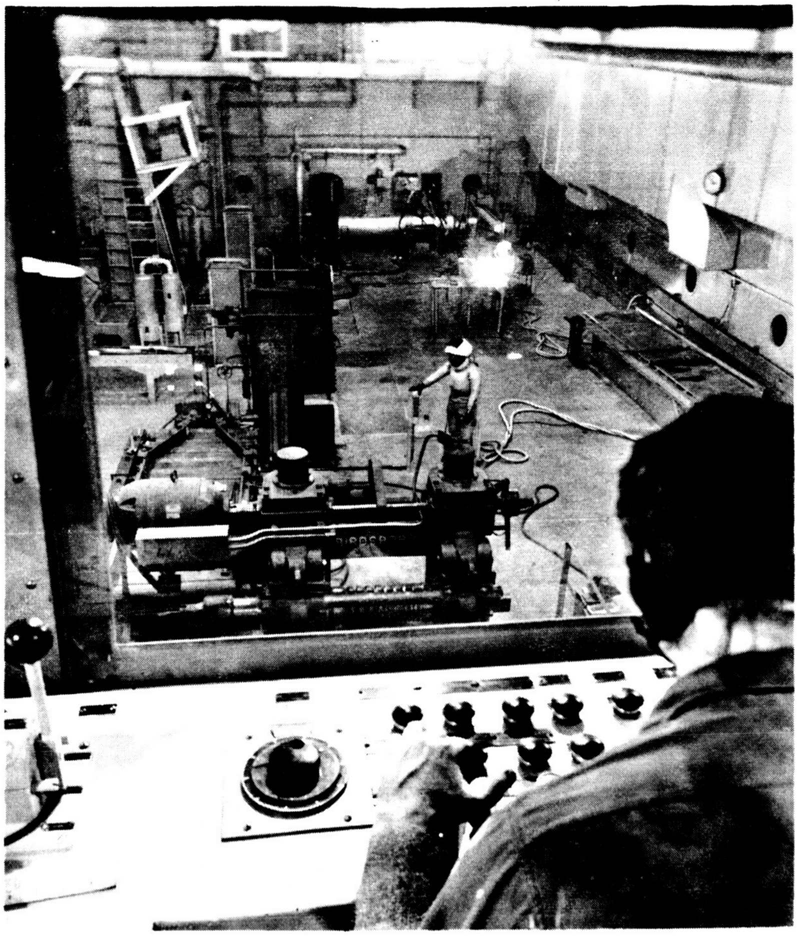

Figure 15. - Space-suited men working within the argon filled room of In-Fab.

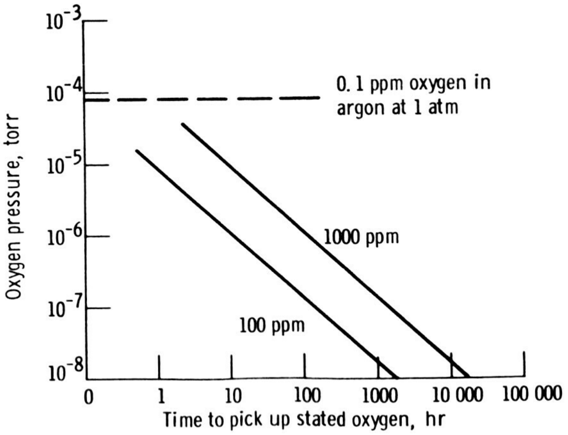

Figure 16. - Contamination at low pressures and 2000^{0} F of columbium-1 percent zirconium. 20-Mil wall tube exposed on one side.

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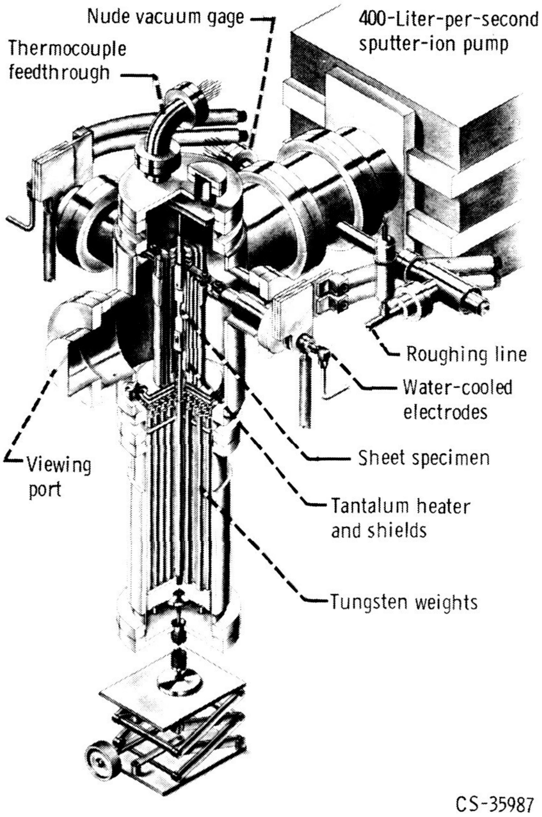

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Figure 17. - Creep units for high temperature and high vacuum (5×10^{-8} to 4×10^{-9} mm Hg).

Columbium, tantalum, and their alloys may contaminate with oxygen even in high vacuum; raising ductile-brittle transition temperature and altering strength

Increase in oxygen during creep test:

Example:

FS-85; 1522 hours; 2×10^{-7} to 4×10^{-9} mm Hg; 2000° F; increase in oxygen, 62 ppm

Poor vacuum may lower creep (raise strength)

Example:

T-111; 2400° F; 9000 psi

Vacuum	5×10^{-9} mm Hg	1×10^{-6} mm Hg
Creep in 172 hr, percent	3.0	0.26

(a) Group VA metals.

Figure 18. - Effects of vacuum environment.

Molybdenum and tungsten tend to purify in high vacuums; oxygen, nitrogen, carbon, hydrogen are removed; ductile-brittle transition temperature is lowered

Example:

Molybdenum exposed to 3800^{0} F at 5x10^{-5} mm Hg for 12 hours

	Oxygen, ppm	Ductile-brittle transition temperature, ^{0}F
Initial	18	-130
Final	3	-202

Carbide-phase-strengthened refractory-metal alloys lose carbon at high vacuums and lose strength

Example:

Molybdenum alloy (TZC) exposed to 3685^{0} F at 10^{-5} mm Hg for 60 hours

	Carbon, ppm	Hardness, R_B
Initial	680	96
Final	100	86.6

Columbium alloy (D-43) exposed to 2000^{0} F at 5x10^{-9} mm Hg for 1000 hours

Carbon change, ppm	Oxygen change, ppm
-87	+29

(b) Group VIA metals.

Figure 18. - Concluded.

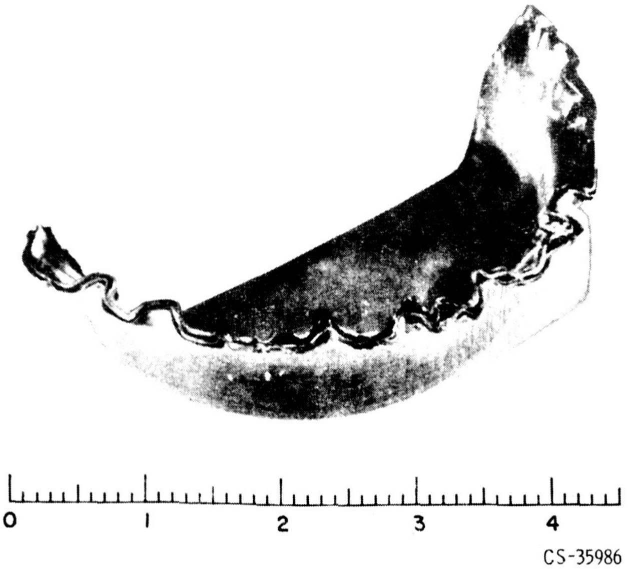

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Figure 19. - Delamination of molybdenum sheet during spinning.

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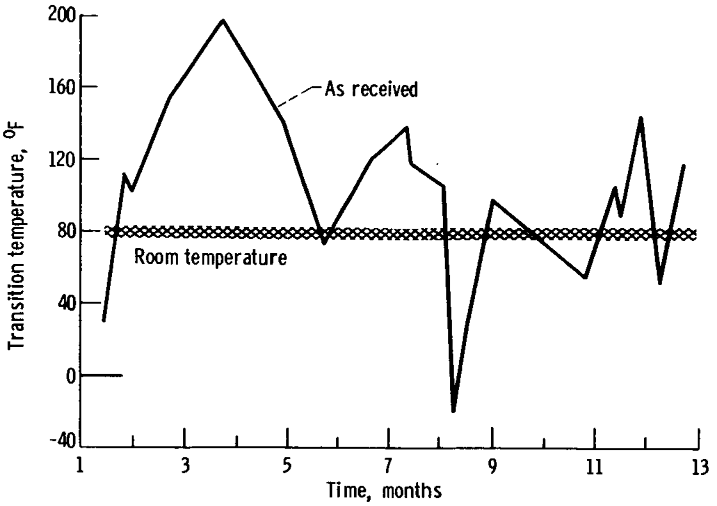

Figure 20. - Bend-transition temperatures for Mo - 0.5 Ti alloy sheet for 1958.

Requirements	Fabricable molybdenum		High-strength molybdenum		Fabricable columbium	
	In optimum condition	Complete recrystallization	In optimum condition	Complete recrystallization	In optimum condition	Complete recrystallization
Room temperature tensile						
Ultimate tensile strength, ksi	*	*	*	*	*	*
Yield strength, 0.2 percent offset, ksi	*	*	*	*	*	*
Elongation, percent	10	10	2	2	15	15
Elevated temperature tensile	In optimum condition		In optimum condition		In optimum condition	
Temperature, °F	2000	2400	2400	3000	2000	2400
Ultimate tensile strength, ksi	75	50	75	25	50	20
Yield strength, 0.2 percent offset, ksi	60	35	60	15	40	15
Elongation, percent	*	*	*	*	*	*
Creep-rupture (state stress and elongation at -						
Temperature, °F	2000	2400	2400	3000	2000	2400
Rupture time, hr	1 10	1 10	1 10	1 10	1 10	1 10
Recrystallization (in optimum condition) 50 percent by metallurgial observation						
Time	1 hr		1 hr		1 hr	
Temperature, °F	2600		3200		2400	
Notch sensitivity - Ratio	1.0 (room temperature)		1.0 (200° F)		1.1 (room temperature)	
Transition temperature (in optimum condition)						
In bending 4T	-40		Room temperature		-100	
Tensile: Notched	State		State		State	
Smooth	State		State		State	
Impact, Charpy	State		State		State	
Bend ductility (room temperature)						
Base metal	1T		4T		1T	
Welded (weld transverse to bend axis)	4T		State		2T	

*No target specified.

Figure 21. - Targets for alloy selection.

Alloy class	Status	
	November 1959	1965
Fabricable molybdenum:		
Mo - 0.5 Ti	Large sheet: poor quality	Completed production program (24- by 72-in. sheet)
TZM (Mo - 0.5 Ti - 0.1 Zr - 0.03 C)	Small sheet	Completed production program (24- by 72-in. sheet)
Tungsten:		
Unalloyed	Laboratory size sheet	Completed production program (18- by 48-in. sheet)
Fabricable and weldable columbium:		
D-43 (Cb - 10 W - 1 Zr - 0.1 C)	Unknown	Completed production program (24 in. wide)
Cb-752 (Cb - 10 W - 2.5 Zr)	Unknown	Completed production program (24 in. wide)
FS-85 (Cb - 28 Ta - 10 W - 1 Zr)	Unknown	Completed pilot production (18 in. wide)
Tantalum:		
T-222 (Ta - 10 W - 2.5 Zr - 0.01 C)	Unknown	Completed pilot production (18 in. wide)
GE-473 (Ta - 7 W - 3 Re)	Unknown	Completed pilot production (18 in. wide)

Figure 22. - History of alloys identified for production development by sheet rolling panel.

	Molybdenum	Tungsten	Columbium	Tantalum
	Transition temperature			
Target	-40° F	300° F	-100° F	-320° F
Achieved	-60° F	200° F	-250° F	<-320° F
	Weld bend at 70° F			
Target	None	None	2 T	2 T
Achieved	Brittle	Brittle	<1 T	<1 T

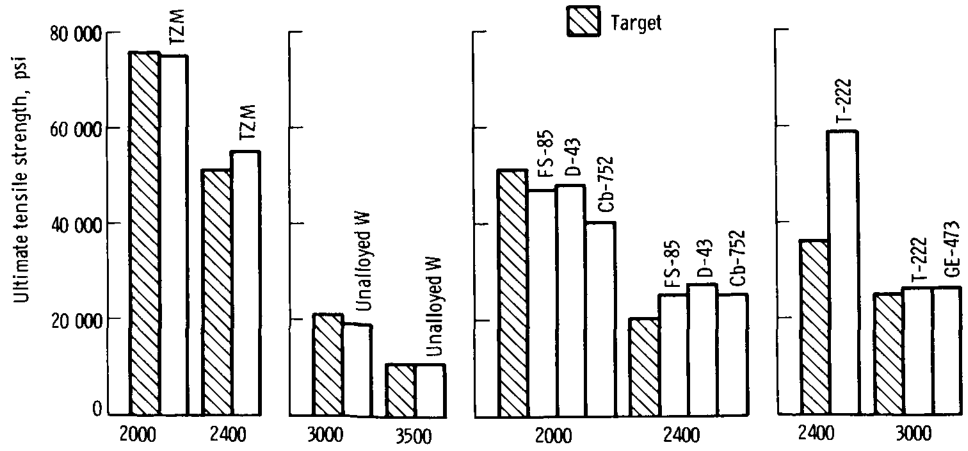

Figure 23. - Comparison of properties achieved with targets.

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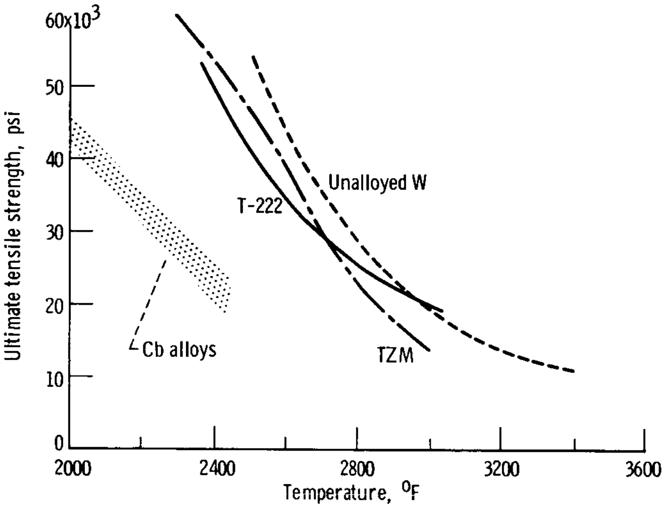


Figure 24. - Strength of selected commercial alloys.

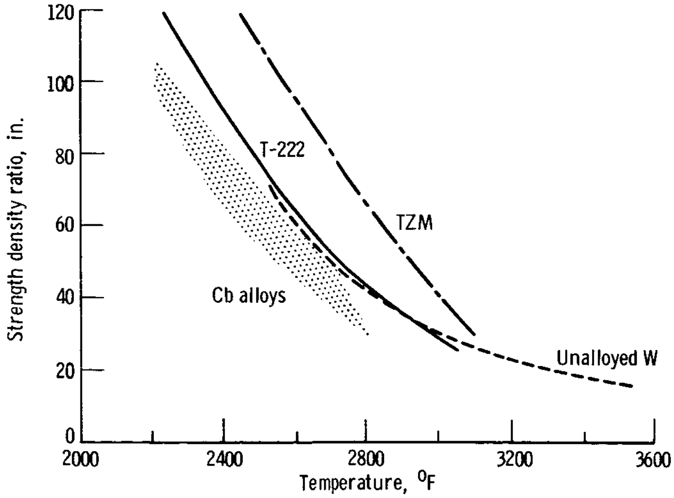
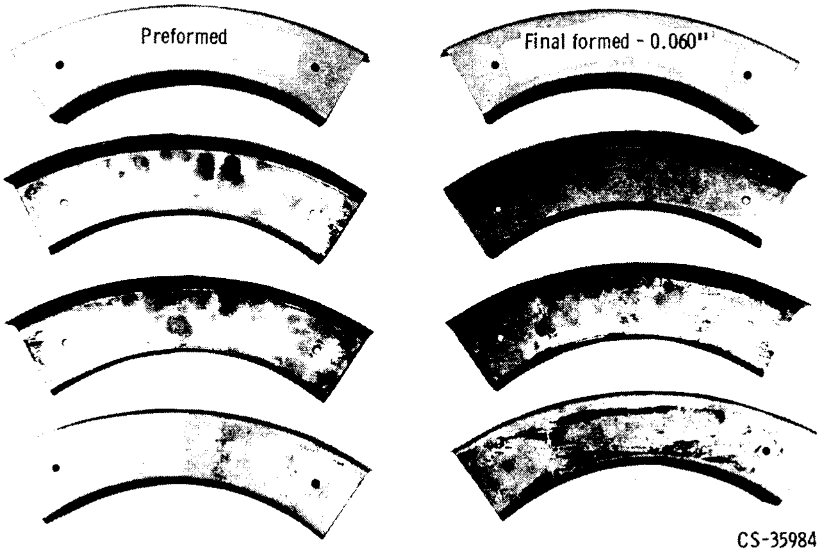
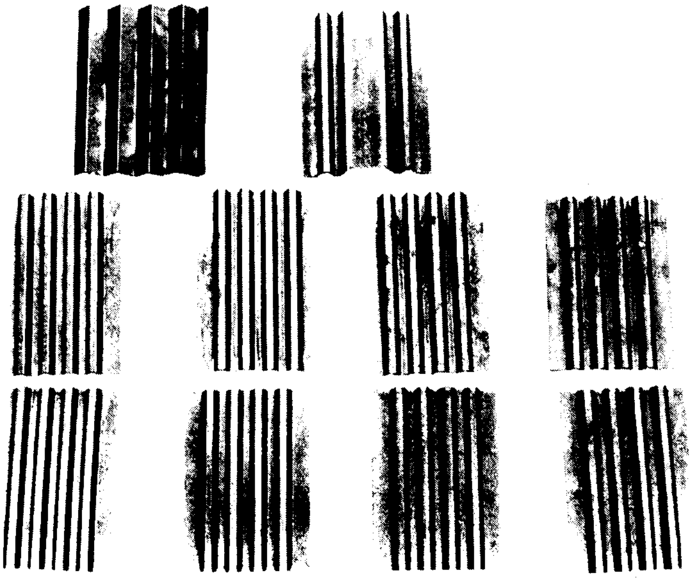


Figure 25. - Strength-density ratios of selected commercial alloys.



CS-35984

Figure 26. - Curved channel. 0.060-inch TZM molybdenum after finish. Formed at 300° F in double-acting, hot sizing press.



CS-35985

Figure 27. - Corrugation - 0.016-inch TZM molybdenum formed at room temperature.

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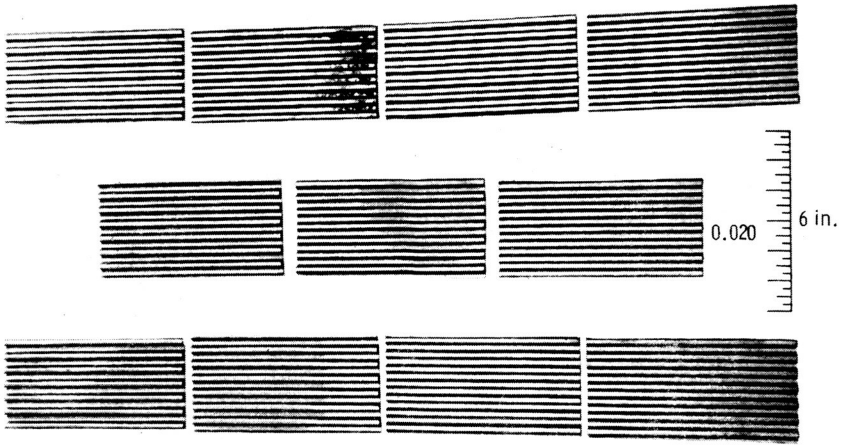
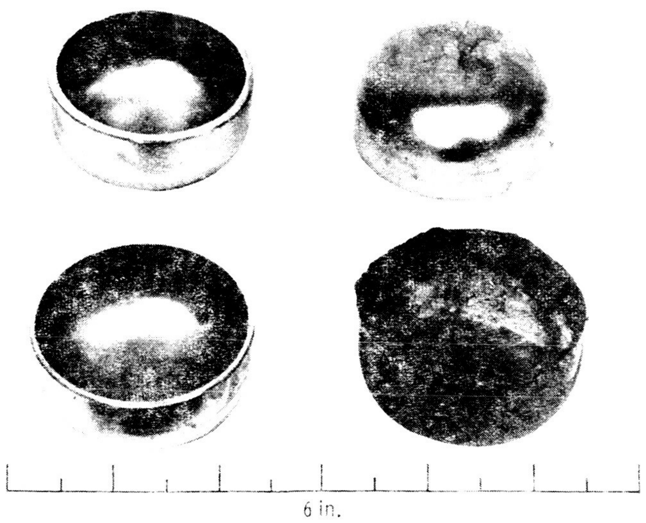


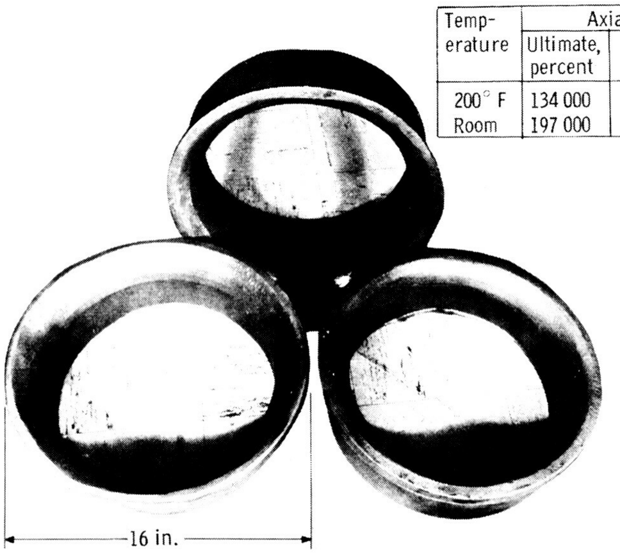
CS-35983

Figure 28. - Corrugated test panels from 0.020-inch tungsten sheet formed at ≈ 500° F.



CS-35982

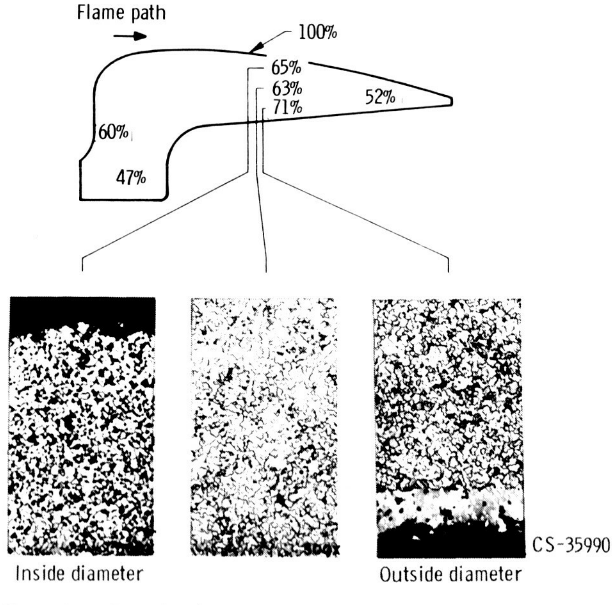
Figure 29. - Deep drawn cups made from 0.06- and 0.100-inch RMSRP tungsten sheet formed at 1650° F.



Temp-erature	Axial		Tangential	
	Ultimate, percent	R/A, percent	Ultimate, percent	R/A, percent
200° F	134 000	25	135 000	29
Room	197 000	0	216 000	0

CS-35980

Figure 30. - Forged, ring rolled throat inserts of tungsten.



CS-35990

Figure 31. - Tungsten infiltrated with silver for rocket nozzle. Silver loss during firing.

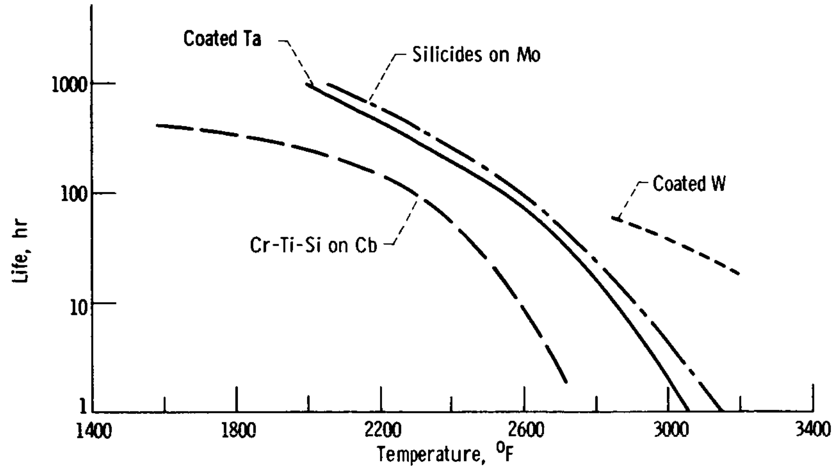


Figure 32. - Protective life of coatings.

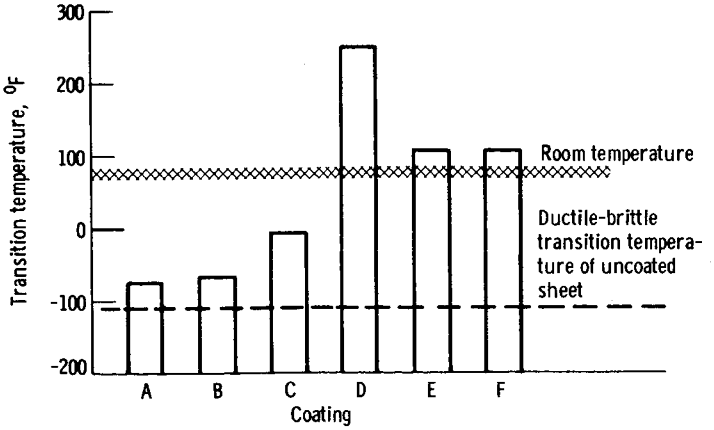
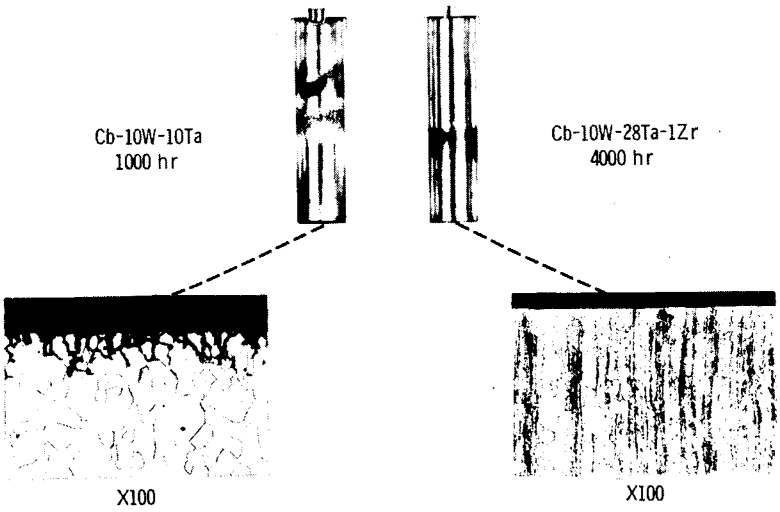


Figure 33. - Effect of coating on transition temperature of columbium sheet (D-31). "It ain't paint."



CS-35981

Figure 34. - Columbium and tantalum alloys with zirconium or hafnium are excellent in corrosion resistance to boiling potassium at 2200° F.

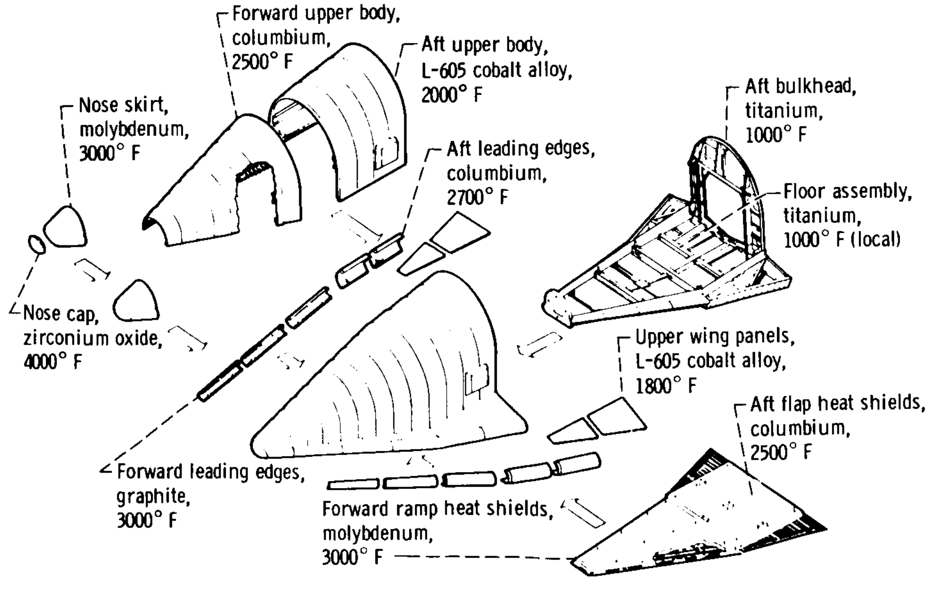


Figure 35. - ASSET manufacturing breakdown.

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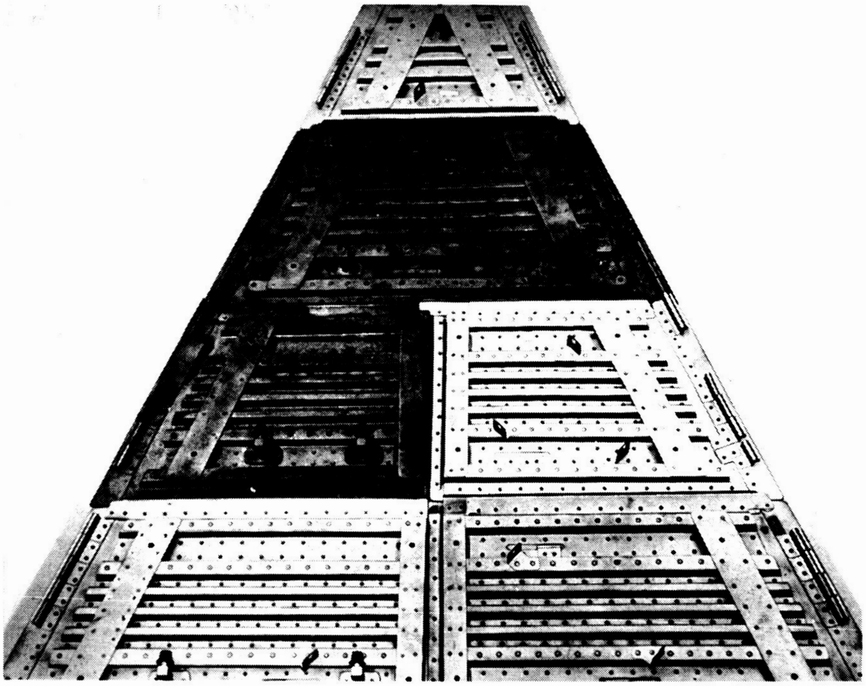

Figure 36. - Assembly of fabricated coated refractory metal panels from lower structure of ASSET research reentry vehicle.

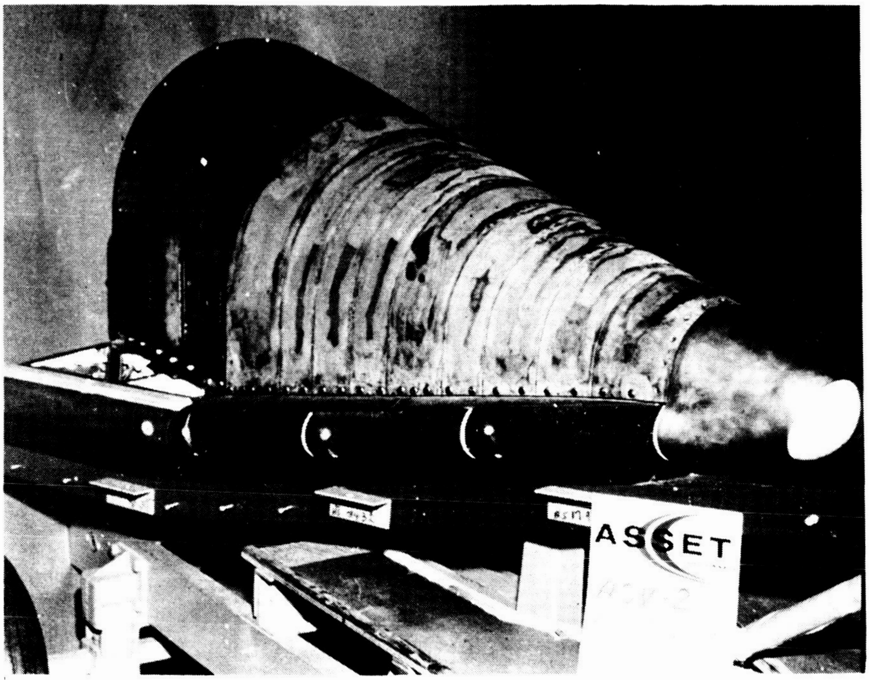

Figure 37. - Completed ASSET vehicle prior to flight.

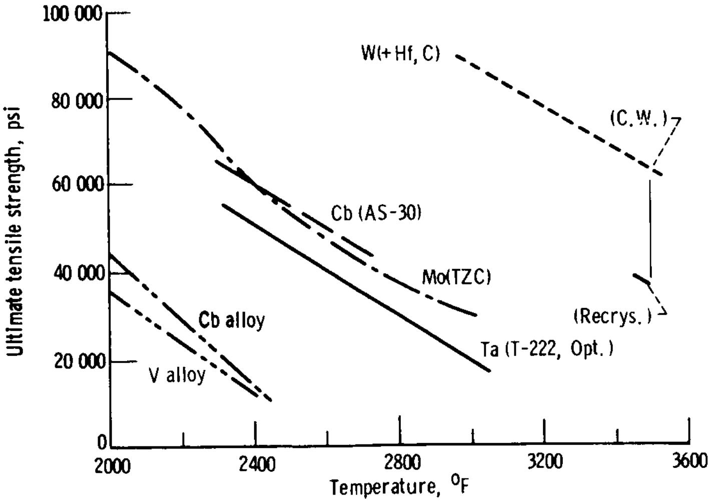

Figure 38. - Strength of best alloys (lab data).

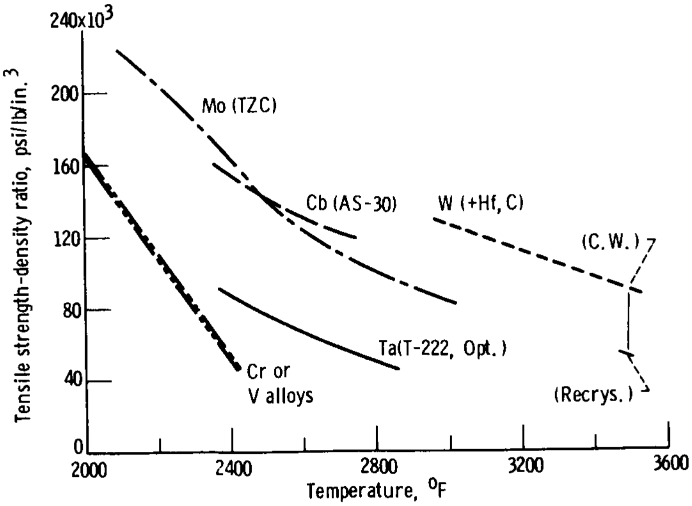

Figure 39. - Strength-density ratio of best alloys (lab data).

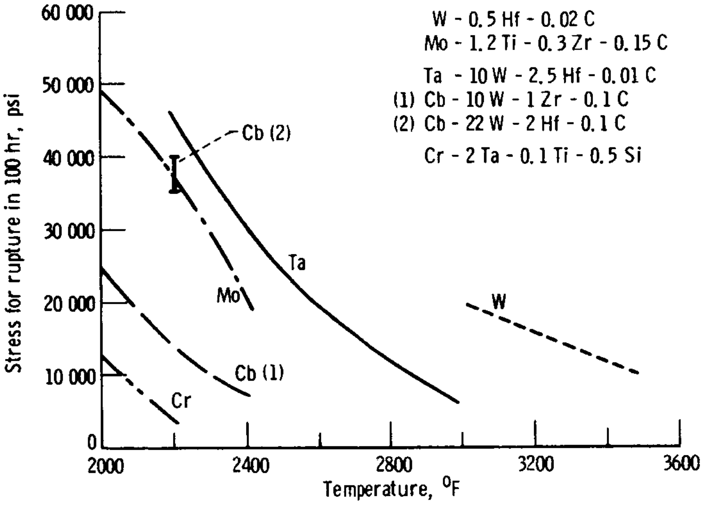

Figure 40. - Stress rupture strength of best alloys (includes lab data).

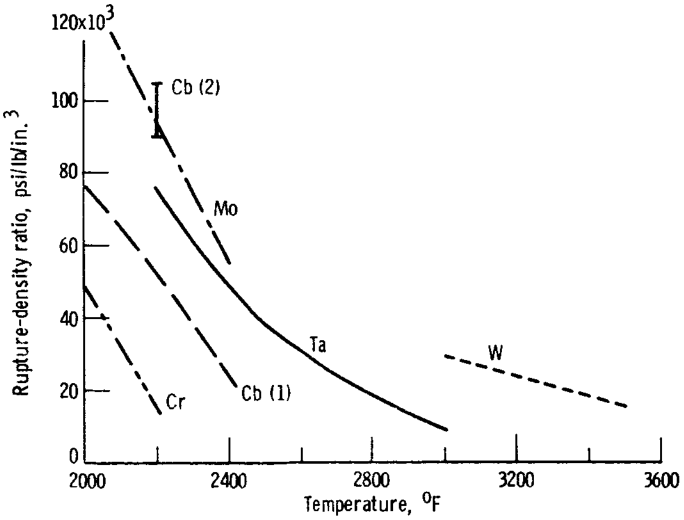

Figure 41. - 100-Hour stress-rupture to density ratio of best alloys (includes lab data).

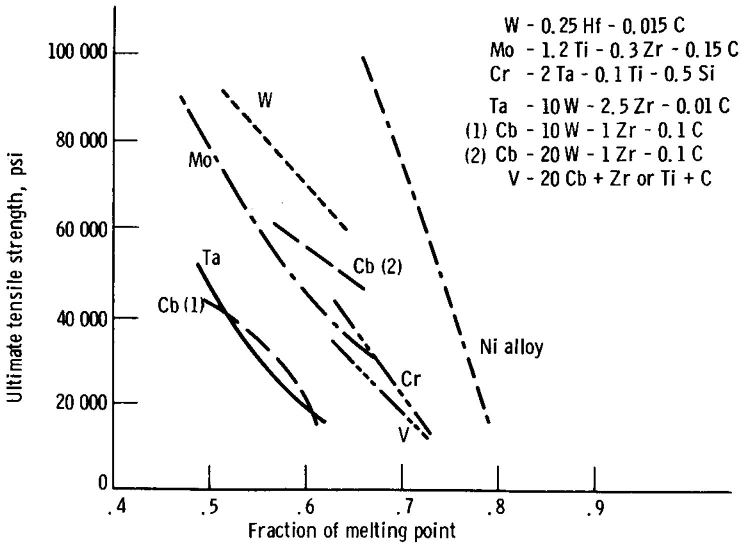

Figure 42. - Strength as function of homologous temperature.

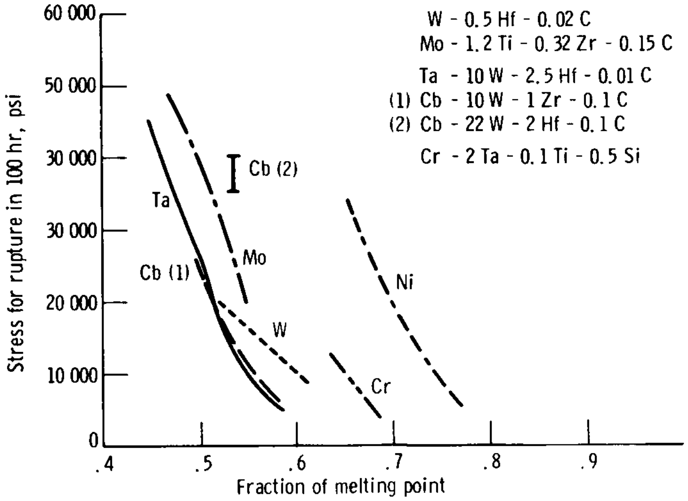

Figure 43. - Stress-rupture strengths as function of homologous temperature.

Composition	Material condition
1. Tungsten - 25 percent rhenium	Cold worked or recrystallized
2. Doped tungsten - 3 percent rhenium (powder-metallurgy wire)	Cold work or recrystallized (but in wire form only)
3. Electron-beam-melted tungsten - 3 percent rhenium	Cold worked only
4. Powder-metallurgy doped tungsten - 5 percent rhenium + 2.2 percent thoria	Cold worked or recrystallized (in tension-limited ductility in bend test)
5. Powder-metallurgy tungsten - 3 to 5 percent rhenium + carbide formers and carbon	Cold worked (but having recrystallization temperature of 3300° F)

Figure 44. - Tungsten materials indicated to have transition temperature below room temperature.