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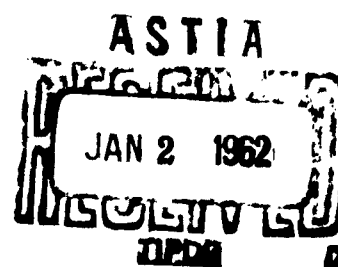
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INTRODUCTION TO METALS FOR ELEVATED-TEMPERATURE USE

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DEFENSE METALS INFORMATION CENTER
Battelle Memorial Institute
Columbus 1, Ohio



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INTRODUCTION TO METALS FOR
ELEVATED-TEMPERATURE USE

by

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to

OFFICE OF THE DIRECTOR OF DEFENSE
RESEARCH AND ENGINEERING

DEFENSE METALS INFORMATION CENTER
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Columbus 1, Ohio

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INTRODUCTION TO METALS FOR ELEVATED-TEMPERATURE USE

SUMMARY

Modern technology, both military and industrial, is increasingly confronted with temperature limitations. There is a never-ending search for materials capable of performing desired functions at both higher and lower temperatures.

This report deals with metals for service at elevated temperatures. Although the technology is relatively well advanced and the metallurgist has a wide background of data on which to base his further developments, there are many people involved in the evaluation of systems and the design and fabrication of structures who have not had an opportunity to obtain this background. This report, therefore, has been prepared primarily for the non-specialist in response to requests for a general review of the field of high-temperature metals in terms understandable to those who have not had extensive metallurgical training.

The general categories of metals suitable for application at temperatures in excess of 800 F are discussed, along with the general advantages and limitations of each. Some generalized mechanical- and physical-property data are included, and the problems of reactions at elevated temperatures are briefly discussed.

CHARACTERISTICS REQUIRED IN MATERIALS FOR HIGH-TEMPERATURE SERVICE

To understand which materials are being considered for "high-temperature" applications, and why, it is necessary to know what characteristics or properties are required.

It is convenient to group the desired properties of high-temperature materials into four categories. The material usually must have certain mechanical properties - strength, ductility, etc. - at the service temperature and also must have certain desirable mechanical properties at room temperature, in order to be fabricated, assembled, and handled successfully. Oxidation and corrosion resistance are important because the material must resist or be protected from chemical attack by air or other service environments at service temperature. It may also have to resist atmospheric corrosion during storage. Physical properties such as density, thermal conductivity, and expansion when heated may also be important. Finally, of course, it is necessary that the material be capable of being formed into useful shapes, so fabricability - that is, ability to be formed, machined, welded, etc. - must be considered.

The above and other characteristics desired in a high-temperature material are discussed in some detail in Appendix A. This appendix should give the reader who is not familiar with such terms as "yield strength", "ultimate strength", "modulus of elasticity", and "thermionic work function" an elementary concept of their meaning. These definitions should help people who are not technical specialists to understand the discussions of various materials later in this report.

THE ROLE OF METALS AMONG HIGH- TEMPERATURE MATERIALS

The properties of those metals which are useful or potentially useful for service above 800 F are discussed in this report. While the report deals in detail only with metals, it is helpful to consider metals in comparison with other materials which are or might be used at such temperatures.

Until a few years ago, the temperature limits for organic materials, plastics, and elastomers (rubberlike materials) have been well below 800 F. Experts in the field believe that in time plastics will be available with useful properties at or above 800 F. Plastics used as ablating materials in rocket nose cones, for example, become hot enough to decompose but serve primarily to dissipate heat instead of supporting structural loads. For present applications, this leaves metals, ceramics, metal-ceramic composites, and

one nonmetallic element, carbon (in the graphite form), for structural components that are subjected to high temperatures. Here the word "ceramics" is used in the broad sense to include not only the usual oxides, silicates, and aluminates, but carbides, borides, nitrides, and intermetallic compounds.

Metals differ from other solids primarily because the type of "atomic bonding" - i. e. , the nature of the forces which hold the atoms of the material together - is different. It is not appropriate here to discuss in detail these differences, which lie in the realm of solid-state physics. It will be sufficient to say that the outward manifestations of "metallic" bonding are the metallic luster, high thermal and electrical conductivity, and ductility usually associated with pure metals.

It is the combination of ductility, toughness, and mechanical strength possessed by many metals and alloys which gives them their usefulness both at room temperature and at temperatures above 800 F. Many metals will deform to a greater or lesser extent instead of breaking under sudden blows or severe stresses. Commercial ceramic materials, on the other hand, are characterized by brittleness and lack of toughness. Therefore, they are used chiefly in components which are not subjected to severe shock loading. Improved ceramics are under development for rocket nozzles, missile nose cones, furnace linings, protective coatings for metal parts, and many other applications which are subjected to high service temperatures. Recently, effort has been devoted, with some encouragement, to developing ceramics with at least some ductility and toughness, but for practical applications these qualities are still associated almost exclusively with metals. (For a more detailed discussion of "ductility" and "toughness" see Appendix A.)

It should be pointed out that continuing research by Government and private industry has resulted in new developments in all categories of materials for elevated-temperature service. Consequently, some of the relatively new alloy developments mentioned in this report will be superseded by others in the near future. For this reason, emphasis will be placed on trends or objectives of alloy-development programs.

HIGH-TEMPERATURE METALS

As implied earlier, the materials which come within the scope of this report must usually meet some elevated-temperature strength requirements. For structural applications, this of course is axiomatic. In nonstructural applications, the material should at least be strong enough not to lose its shape under its own weight. In any case, whether primarily or secondarily, strength must be taken into consideration. Therefore, the matter of strength is emphasized in the discussion that follows.

The maximum temperature to which a metal retains useful strength appears to be roughly related to the melting point. Pure metals usually weaken seriously at about half the melting point on the absolute temperature scale (melting point in degrees F plus 459). By alloying, the limit of strength useful for structural purposes can usually be pushed to about 65 per cent of the melting point on the absolute temperature scale, and in some cases, especially if time under load and temperature is very short, somewhat higher. In nonstructural applications, metals and alloys can frequently be used at temperatures considerably nearer their melting points.

It appears logical, in seeking metals for service at high temperatures, to start with the metals that have the highest melting points. Table 1 lists all the elements that have higher melting points than aluminum, in the order of their melting points (highest first). Aluminum, which melts at 1220 F is about the lowest melting metal which offers any hope for 800 F service, according to the rule of thumb discussed previously. A service temperature of 800 F is 75 per cent of the melting point of unalloyed aluminum on the absolute temperature scale.* Thus, 800 F is a little high for aluminum, but a special type of aluminum-base composition known as SAP (sintered aluminum product) has useful strength for at least short times at this temperature.

Among the elements listed in Table 1, 21 metals and their alloys either are used now or, based on present information regarding their properties and abundance, should be considered seriously for service above 800 F. These metals are listed in Table 2, which also gives some general information about them.

There are 34 other elements (in addition to the 21) with melting points higher than aluminum. These are discussed briefly in Appendix B, together with reasons for omitting them from consideration as high-temperature materials at the present time.

Reserves, Production, and Price

Before discussing the metals individually, it is helpful to provide a brief background on their availability. This factor exercises strong influence on usage.

In Table 3 data are presented on the estimated Free World reserves, production, and price of the 21 metals which with their alloys are now used or appear to have promise for service above 800 F. Additional resource, production, and consumption data on the refractory and platinum-group metals are shown in Figure 1. Aluminum and iron make up about 8 and 5 per cent, respectively, of the earth's crust, while the combined total of the other 19 metals is below 1 per cent. Known reserves of zirconium, titanium, iron,

* $\frac{800 + 459}{1220 + 459} \times 100 = 75.$

TABLE 1. LIST OF ELEMENTS WITH HIGHER MELTING
POINTS THAN ALUMINUM (1220 F)

Those considered as "high-temperature metals"
and discussed in this report are marked*.

Element	Melting Temperature, F	Element	Melting Temperature, F
Carbon	6740	Silicon	2570
*Tungsten	6170	Dysprosium	2565
*Rhenium	5755	Terbium	2472
*Osmium	5432	Gadolinium	2394
*Tantalum	5425	*Beryllium	2332
*Molybdenum	4730	Manganese	2273
*Columbium	4474	Protactinium	2246
*Iridium	4449	Uranium	2070
*Ruthenium	4082	Copper	1981
*Hafnium	4032	Samarium	1962
Boron	3690	Gold	1945
*Rhodium	3571	Actinium	1920
*Vanadium	3450	Promethium	1880
*Chromium	3407	Neodymium	1866
*Zirconium	3366	Silver	1761
*Platinum	3217	Germanium	1719
Thorium	3182	Lanthanum	1688
*Titanium	3035	Praseodymium	1686
Lutetium	3006	Calcium	1540
*Palladium	2826	Europium	1519
Thulium	2813	Ytterbium	1515
Scandium	2802	Arsenic	1503
*Iron	2798	Cerium	1479
Yttrium	2748	Strontium	1414
Erbium	2727	Barium	1317
*Cobalt	2723	Radium	1292
Holmium	2662	*Aluminum	1220
*Nickel	2647		

TABLE 3. RESERVES, PRODUCTION, AND PRICES OF HIGH-TEMPERATURE METALS

Metal	Most Important Minerals	Principal Sources of Ore in World	Estimated Free-World Reserves, short tons contained metal	1960 Domestic Production of Metal, short tons	1960 Free-World Production of Metal, short tons	Price, dollars per pound		
						Powder	Sponge	Ingot Sheet
Tungsten	CaWO_4 (Fe, Mn) WO_4	China, U.S., Korea, Bolivia, Burma, Canada, Brazil, Portugal	293,000	3,005(a)	N.A.	2.90-3.85	--	-- 30-100(b)
Rhenium	ReS_2 (in MoS_2)	U.S., S. America, E. Germany, Finland, U.S.S.R.	1,150	0.1	0.15	600	--	-- 2,000
Osmium	Os (Os, Ir)	S. Africa, Canada, U.S.S.R., Colombia, U.S.	1	<0.05	0.05	--	--	875-1020 --
Tantalum	FeTa_2O_6	Rep. of Congo, Brazil, Mozambique, S. Rhodesia, Australia, others	107,000	150	N.A.	30-58(b)	--	45 50-60(b)
Molybdenum	MoS_2 PbMoO_4	U.S., Chile, Canada, U.S.S.R., China, Japan	2,100,000	1,301	N.A.	3.55	--	8(c) 21-85(b)
Columbium	FeCb_2O_6 and complex columbate of Ce, Ca, Na	Nigeria, Norway, Rep. Congo, Malaya, Brazil, Canada, others	5,970,000	130	N.A.	36(d)	--	55 --
Iridium	Ir (Os, Ir)	S. Africa, Canada, U.S.S.R., Columbia, U.S.	8	<0.1	0.25	--	--	1020-875 --
Ruthenium	Ru RuS_2	S. Africa, Canada, U.S.S.R., Columbia, U.S.	5	<0.1	0.2	--	--	800-1095 --
Hafnium	HfO_2 in Zr minerals	Australia, Nigeria, Senegal, U.S., S. Africa, Brazil, U.S.S.R., Colombia, U.S.	350,000	35	36(e)	--	40	-- --
Rhodium	Rh	U.S.S.R., Colombia, U.S.	27	<0.1	0.9	--	--	2015 --
Vanadium	$\text{K}_2\text{O} \cdot 2\text{VO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ $\text{Pb}_5\text{Cl}(\text{VO}(\text{VO})_3)$ (Fe, Cr) [(Cr, Fe) O_2] $_2$	U.S., S.W. Africa, S. Africa, Finland	840,000	29(f)	N.A.	3.65(g) 35(f)	--	-- --
Chromium		S. Rhodesia, Turkey, S. Africa, Philippines	890,000,000	2,400	5,000(e)	1.15(h)	--	-- --
Zirconium	ZrSiO_4 ZrO_2	Australia, Senegal, U.S., S. Africa, Brazil, Nigeria	17,200,000	1,423	1,600(e)	4(i)	6.50(j) 5.00(i)	-- 16-35(k)
Platinum	Pt PtAs_2 Pt S (Pt, Pd, Ni)S	S. Africa, Canada, U.S.S.R., Colombia, U.S.	405	0.2	17	--	--	1200 --

TABLE 3. (Continued)

Metal	Most Important Minerals	Principal Sources of Ore in World	Estimated Free-World Reserves, short tons contained metal	1960 Domestic Production of Metal, short tons	1960 Free-World Production of Metal, short tons	Price, dollars per pound		
						Powder	Sponge	Ingot Sheet
Titanium	TiO ₂	Australia, U.S., India, S. Africa	3,000,000(l)	5,311	9,200	--	1.60	-- 6.75-15.50(b)
Palladium	Pd	S. Africa, Canada, U.S.S.R., Colombia, U.S.	274	0.2	10	--	--	365 --
Iron	Iron oxides	U.S., U.S.S.R., France, China, Canada, Sweden, W. Germany, U.K., Venezuela, others	100,000,000,000	67,320,000(m)	187,516,000(m)	--	--	0.03(n) --
Cobalt	Sulfides, arsenides, and oxides, often with combined Ni, Cu, Fe, Mn	Rep. of Congo, Canada, N. Rhodesia, U.S., Fr. Morocco	1,860,000(p)	885(o)	16,800(o)	1.50	--	-- --
Nickel	(NiFe)S and Hydrous nickel magnesium silicate	Canada, New Caledonia, Cuba, U.S.	9,400,000(p)	12,530(q)	290,000	0.81	--	-- 1.47(r)
Beryllium	3BeO·Al ₂ O ₃ ·6SiO ₂	Brazil, Mozambique, Argentina, Rep. of Congr. Madagascar, S. Rhodesia, Australia, U.S.	200,000(s)	113	125	54	--	67-71 --
Aluminum	Al ₂ O ₃ ·H ₂ O Al ₂ O ₃ ·H ₂ O	Jamaica, Surinam, Br. Guiana, U.S., Haiti, Dominican Rep., France, Greece, many others	800,000,000	2,014,000	3,967,000	--	--	0.27 0.45-0.62

Footnotes appear on the following page.

Footnotes to Table 3.

N. A. - Information not available.

- (a) Of the 3,005 short tons gross production, 1,624 tons was used as an intermediary in the manufacture of tungsten carbides and the balance of 1,381 tons went into applications for the metal.
- (b) Depends on grade or dimensions.
- (c) Billet form.
- (d) Rondelles.
- (e) Estimate.
- (f) High-purity, 99 + per cent V.
- (g) Commercial grade, approximately 90 per cent V.
- (h) Electrolytic grade, platelets.
- (i) Commercial grade.
- (j) Reactor-grade.
- (k) Reactor-grade cold-rolled strip.
- (l) Rutile reserves only. Does not include ilmenite or titaniferous magnetites.
- (m) Production of pig iron plus ferroalloys.
- (n) Pig iron.
- (o) Cobalt content of all products. Perhaps 75 per cent of Free-World production was in the form of metal.
- (p) Excludes Cuban reserves.
- (q) U.S. production chiefly as ferronickel, but includes some salts.
- (r) Cold-rolled "A" nickel.
- (s) A speculative estimate of Be content of deposits containing 0.1 per cent, or better, of beryl or its equivalent.

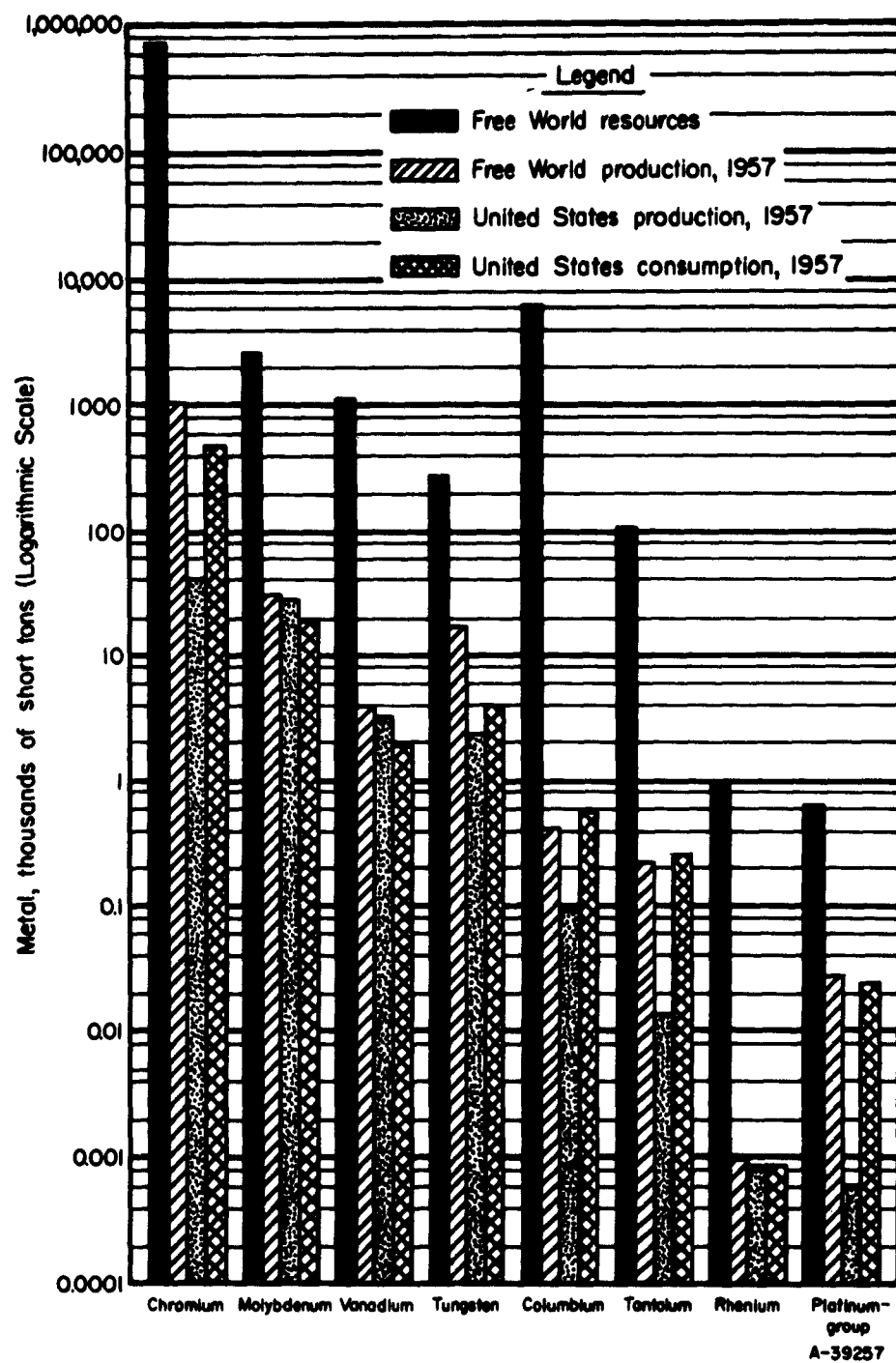


FIGURE 1. FREE WORLD RESOURCES AND PRODUCTION, AND UNITED STATES PRODUCTION AND CONSUMPTION, OF REFRACTORY METALS AND THE PLATINUM-GROUP METALS IN 1957

Rhenium capacity used for U. S. consumption and production. Actual use much less.

Source: Report MAB-154-M, Volume 1, Materials Advisory Board.

cobalt, nickel and aluminum in Free-World ores appear to be adequate for many years, even at increased rates of consumption. Reserves of the high-melting refractory metals, tungsten, tantalum, molybdenum, columbium, vanadium, and chromium range from very large to adequate. Tantalum, hafnium, and rhenium concentrates are normally by-products from concentrating or purifying other metals, and supplies depend on production of the other metals. Rhenium and each of the platinum metals constitute less than 0.01 parts per million of the earth's crust.

While the problem of the availability of metals inevitably demands early consideration of sources and reserves, great caution should be exercised in dealing with figures on reserves. These figures are usually working approximations and change with further mining and exploration. Figures on reserves are strongly influenced also by price-demand relationships and by the attitude of the Government. For example, circumstances may be such that a particular low-grade ore material is not considered in a calculation of reserves; at the market price the working of this ore is impractical. However, should the price rise or should Government support be involved, it may become practical to work the property. Thereupon, it would be taken into account in an estimate of reserves.

Availability depends, then, not only on reserves but also on price, demand, and Government support. In some cases, availability depends on the situation surrounding another metal in the same ore. For example, the availability of tantalum is dominated by the production of columbium, the same ore being the principal source of both metals.

Demand not only influences reserves; it is the dominating factor in the matter of production capacity. The latter, in turn, is important in considerations of availability. Because there have been periods of high demand in recent years, capacity to produce many of the high-temperature metals has increased. To a large extent, the use of some of these metals is related to the National Defense effort, so their production may fluctuate considerably depending on the urgency and the nature of the defense programs in force. On the other hand, some of the high-temperature metals are used in widely diversified applications such as tool bits, electronic components, electrical contacts, thermocouples, heating elements, corrosion-resistant equipment, surgical applications, atomic-reactor components, furnace components, chemical processing equipment and stationary turbines, which are not necessarily related to military or aerospace hardware. Many of these metals are also used as alloying elements in iron-, cobalt-, nickel-, and copper-base alloys. This trend toward diversification has tended to provide increased stability in the so-called rare-metals industries. At the same time, increased production has made it possible to decrease prices of many of the less common metals. The consequence is that considerable production capacity is available for many of the high-temperature metals.

Recovery of the high-temperature metals usually requires difficult and complex processes, a factor also influencing price and hence availability.

Processing of certain of the ores is feasible only because two or more metals can be recovered from the same ore. The chemical symbols of the predominating minerals are given in Table 3. Usually one will find that several different processes may be used in obtaining any one metal from the ore. The particular processes that are used commercially often depend on the characteristics desired in the final product as well as on the economics involved. Certain processes produce powdered products, others produce sponge or crystal bar, while electrolytic methods may yield solid sheets or molten metal at the cathode. Furthermore, certain processes inherently yield purer products than others, and this is often a factor in determining which process is used for a given metal.

Because of the reactive characteristics of many of the metals in Table 2 and the special precautions that are required in producing them, production and processing costs are high. Nevertheless, practical methods for alloying, consolidating, working, casting, heat treating, and welding certain of these metals have been developed as discussed in later sections of this report. In fact, advances in certain areas relative to the processing of these alloys are occurring at a pace that will make some of the information in this report out of date soon after publication. However, considerable research and development work are needed to produce them in larger quantities, at lower prices, and with improved properties. Properties of the metals and alloys that show promise for high-temperature service will be discussed later along with areas for further development.

CATEGORIES OF HIGH-TEMPERATURE METALS

On the basis of expected temperature range of usefulness, availability, and other properties, the 21 metals singled out as materials for service above 800 F may be grouped in the following categories:

Abundant Refractory* Metals

Tungsten, tantalum, molybdenum, columbium, vanadium, and chromium

Rhenium

Platinum-Group Metals

Osmium, iridium, ruthenium, rhodium, platinum, palladium

Hafnium

Zirconium and Titanium (reactive metals)

*Meaning "difficult to melt".

Iron (as iron-base high-temperature alloys)

Cobalt and Nickel (as high-temperature alloys including
"superalloys" and electrical resistance alloys)

Beryllium

Aluminum (as aluminum alloys)

Refractory Metals

Metals with very high melting points are referred to as "refractory metals". There is no precise definition but, according to the broadest usage, only metals with melting points above that of iron are generally considered as refractory metals. Based on present theoretical concepts and the rule of thumb previously discussed, it appears unlikely that alloys based on iron or lower melting metals can be developed which will have high strength at temperatures above 2000 F. Thus, the term "refractory metals" is also used to refer to metals for service above 2000 F, with the understanding that sufficient strength for structural applications is being implied.

Abundant Refractory Metals

Tungsten, tantalum, molybdenum, columbium, vanadium, and chromium may be classed as relatively abundant refractory metals; that is, Free World reserves of contained metal are over 100,000 tons for each metal. The first four show promise in a considerably higher temperature range than the last two, and sometimes the term "refractory metals" is used narrowly to mean only these four elements and their alloys. At the present time, these four metals are the only metals which are reasonably abundant whose alloys show promise of high strength above 2000 F. It is these elements which are being used or studied for such ultrahigh temperature applications as rocket nozzles, leading edges and "hot structures" of certain re-entry vehicles, special electronic components, advanced gas turbines, and ramjet engines.

Tungsten, molybdenum, vanadium, chromium, and to a lesser extent columbium have been used for years as alloying elements in other metals, especially iron and steel. In addition, tungsten and molybdenum have been used in the lamp and electron-tube industry for more than 50 years. Commercially pure tantalum has been used for many years, in modest quantities, as a structural metal in the chemical industry and elsewhere for its corrosion resistance. It is only since World War II, however, that these metals have been seriously considered for use as elevated-temperature structural metals in their own right. At the present time, a sizable fraction of their total production is for structural uses.

Within the past decade, it has become evident that structural materials having higher service temperatures than nickel- and cobalt-base alloys are desirable to achieve higher power and efficiency for turbojet, ramjet, and rocket engines. Consequently, a number of extensive research and development programs have been initiated to evaluate the abundant refractory metals for critical high-temperature applications.

Development work has been difficult with these metals because of their low-temperature brittleness (except for tantalum and columbium), their tendency to oxidize at elevated temperatures, problems in achieving increased purity, problems in forging and welding, etc. Nevertheless, new techniques for melting, purifying, consolidating, coating, fabricating, and welding have been developed which have overcome many of the original problems. At the present time, several of the abundant refractory metals and alloys are being used as structural materials in a number of high-temperature applications.

Characteristics of the abundant refractory metals and some of their current applications are discussed in the following sections. However, these characteristics are, to a large extent, dependent on the purity, processing variables, section size, etc. As research studies continue on the abundant refractory metals, it will be possible to more accurately define their potential characteristics and properties for high-temperature structural applications.

Tungsten. Tungsten has the second highest melting point of the elements listed in Table 1 and the highest of the metals. This would indicate that it could be used at higher service temperatures than any of the other metals. Consequently, it is being used in high-temperature applications beyond the useful temperature range of the other refractory metals.

Tungsten is one of the most dense metals; its density is exceeded only by rhenium, gold, and some of the platinum-group metals as shown in Table 2. In rocket boosters, for example, that require minimum structural weight, the amount of tungsten used in the nozzles is kept to a minimum because of its high density.

The vapor pressure of tungsten is lower than that of any other metal. This is an advantage in high-vacuum melting and welding. Even impurities having relatively low vapor pressures will vaporize to some extent when tungsten is melted in a high vacuum; thus, partial purification is effected in the operation.

Because of the tendency for tungsten to oxidize in air at elevated temperatures, all sintering, melting, heating, and welding must be done in vacuum, in hydrogen, or in an inert gas. Because of the high vacuum used when melting tungsten by the arc-melting and electron-beam melting methods and the higher temperatures that are possible when using these methods,

ingots formed by these melting techniques are generally purer than those produced by sintering of the metal powders. Commercially, tungsten is forged in air. The oxide formed at the surface tends to serve as a lubricant in the forging operation.

Tungsten metal of commercial purity is relatively hard, brittle, and difficult to form and machine. However, on an experimental scale, tungsten has been produced with sufficient ductility to permit cold rolling at room temperature. Furthermore, it has been reported that electron-beam melted ingots have been made sufficiently pure and with fine enough grains (with a proprietary additive) to permit direct forging of the ingot. Normally, tungsten ingots are extruded to reduce the grain size before forging is attempted.

Tungsten is obtained as powder by any one of several reduction processes. The powder is pressed into bars, presintered in hydrogen, and then resintered by passing high electric currents through it. The current is increased gradually to permit the volatile impurities to escape through the porous structure. The sintered bars may be forged at 2750 to 3100 F and "hot-cold" worked by swaging or rolling. Hot-cold working, which is carried out at elevated temperatures but below the recrystallization temperature, develops a fiber structure in the metal that improves its low-temperature ductility. If the metal is heated above the recrystallization temperature, it is converted to the annealed structure and loses the low-temperature ductility that had been gained by the hot-cold working.

Cast ingots of tungsten may be made by using the sintered bars as electrodes in a consumable-electrode vacuum-arc furnace. The metal is deposited in a water-cooled copper mold to form an ingot. The sintered bars may also be melted in an electron-beam furnace. The ingots then may be hot extruded, using a molten glass lubricant, before forging (except as noted above).

Similar procedures or modifications of these procedures are used in consolidating and fabricating other refractory metals.

In addition to the well established uses for tungsten such as electrical contacts, lamp filaments, and electron-tube components, a relatively large amount of tungsten is being used in solid-propellant-rocket nozzles and other aerospace components that are exposed to high temperatures.

In rocket nozzles, tungsten may be deposited on a refractory base in the nozzle by flame spraying the metal with a special flame-spraying gun. Alternatively, tungsten inserts produced by forging, spinning, or casting may be located in the throats of the nozzles.

Tungsten has been used structurally in applications requiring primarily resistance to high temperatures and secondarily strength at temperature. In such applications, there has appeared to be no advantage in attempting to use

tungsten alloys because the service temperatures were above the recrystallization temperatures of any of the alloys. However, several tungsten-alloy systems have been studied, including those with molybdenum, tantalum, columbium, zirconium, and rhenium, along with the addition of thorium (ThO_2) to tungsten. The following alloys are of interest:

W-7Mo	W-0.88Cb	W- ThO_2
W-15Mo	W-0.1Zr	
W-50Mo	W-30Re	

Mechanical properties of these alloys are discussed in a later section.

Tantalum. Among the metals listed in Table 2, tantalum has the fourth highest melting point. Only tungsten, rhenium, and osmium melt at higher temperatures. In spite of this, tantalum has not been used at elevated temperatures as extensively as have tungsten and molybdenum. However, considerable work is now being done in developing tantalum alloys for service at elevated temperatures. These alloys and their properties will be reviewed later.

Tantalum occurs in columbium ores. As the demand for columbium increases, increasing amounts of tantalum concentrates become available. After a difficult and complex separation and reduction process, both metals are obtained in the form of powder. The powder is pressed in dies to form bars which are vacuum sintered by passing high currents through them in much the same way that tungsten powder is consolidated. Ingots may then be cast in consumable-electrode vacuum-arc furnaces or electron-beam furnaces. The ingots are worked cold because of the reaction of tantalum with air at high temperatures. Heavy cold working is possible because of the high room-temperature ductility of tantalum. Intermediate annealing must be done in vacuum furnaces.

Pure tantalum oxidizes in air at high temperatures even more rapidly than tungsten. Hence, test specimens or structural members of tantalum must be contained in high-vacuum systems if they are to be used at elevated temperatures. Tantalum foil, for example, may be used as a heating element up to temperatures higher than can be obtained with molybdenum foil; however, the vacuum should be about 1×10^{-4} mm Hg or better.

Tantalum has other characteristics which make it attractive for applications which are not related to its high melting point. Pure tantalum and some of its alloys have better ductility and toughness than the other refractory metals and can be rolled and fabricated easily at room temperature. Pure tantalum is one of the metals which retains a high degree of ductility down to -423 F. Furthermore, it does not work harden as rapidly as many other metals, so high reductions by rolling or swaging are possible between anneals.

Tantalum has exceptional resistance to most corrosive media below 300 F. For this reason, tantalum is used in many applications involving exposure to corrosive environments in the chemical industry. Tantalum is resistant to oxidation by air to about 500 F. It has been used as a container for molten sodium, potassium, and other metals and alloys at temperatures as high as 2200 F (in the absence of air) without being attacked.

A surface oxide film with important dielectric properties can be produced on tantalum. This fact has made the metal attractive for electrolytic capacitors. As a consequence, more tantalum has been used for capacitors than for any other purpose. The oxide film on tantalum also permits its use as a rectifier in electrical circuits. Because tantalum is easily formed and welded and has a low vapor pressure, it is also used extensively in electronic tubes.

Objectives of the tantalum-alloy development programs have been to improve the elevated-temperature strength properties and to reduce the rate of oxidation at elevated temperatures. Some progress has been made in meeting these objectives, but alloy development is still in the early stages. Alloys of interest are those with tungsten, molybdenum, columbium, vanadium, hafnium, chromium, zirconium, titanium, and aluminum. Properties of the commercial tantalum alloys are discussed in a later section.

Tantalum has been used successfully as an alloying element in high-temperature alloys based on other metals.

Molybdenum. As shown in Table 2, the melting temperature of molybdenum is 695 degrees below that of tantalum. Because of its high melting point and relative abundance in the United States, it was the first of the refractory metals considered in this country for high-temperature structural applications. The primary use of molybdenum had been as an alloying element in steels and nickel-base alloys. However, several important alloys of molybdenum have now been developed that are among the best for use above 1600 F on the basis of strength-density ratios.

As with the other refractory metals, molybdenum oxidizes rapidly in air at elevated temperatures. Therefore, the use of molybdenum and its alloys for any length of time at elevated temperatures requires protective atmospheres, vacuum systems, or coatings. Considerable work has been done on protective coatings for molybdenum components, as discussed in a later section.

Molybdenum metal is obtained as a powder by a hydrogen-reduction reaction which is the last step in a series of recovery processes. The procedures for hydrogen reduction, sintering, and casting of molybdenum are similar to those used for tungsten. In spite of rapid oxidation in air, molybdenum forgings and other hot-worked products have been made successfully

in air. In hot-cold working of molybdenum, the resulting fiber structure has better strength and ductility than does the annealed recrystallized material. For this reason, the hot-cold worked condition is desired for applications in which the service temperature is below the recrystallization temperature.

The fact that molybdenum may be formed and machined to desired shapes by most fabricating processes adds to its attractiveness for ultra high-temperature structural applications. Many such applications are experimental at the present time. Molybdenum is being considered for ramjet engines, hypersonic vehicles, etc.

Molybdenum has been used for many of the same applications as tungsten where the temperatures involved are not so high as to require the temperature resistance of tungsten. These applications include electrical contacts, electrodes, electronic components, and rocket nozzles.

In applications where resistance to high temperature is of primary concern within the useful temperature range for molybdenum, either pure molybdenum or molybdenum-tungsten alloys may be used. For increased strength and creep resistance over pure molybdenum, the following alloys are of interest:

Mo-0.5Ti	Mo-1.25Ti-0.15Zr
Mo-0.5Ti-0.08Zr	Mo-0.5Zr
Mo-0.5Ti-0.1Zr	Mo-30W

Molybdenum-rhenium alloys containing 40 to 50 per cent rhenium are also available. They have excellent ductility and can be fabricated at room temperature. Furthermore, the molybdenum-rhenium alloys do not become embrittled when heated to above the recrystallization temperature. However, the restricted availability of rhenium precludes the use of molybdenum-rhenium alloys except for small-quantity applications.

Columbium. Columbium has a melting point of 4474 F, which is 256 degrees lower than that of molybdenum. Development of columbium metal and its alloys for elevated-temperature structural applications was started only a few years ago, but considerable progress has been made since then. One factor that has been important in the development of columbium is its low capture cross section for thermal neutrons in nuclear applications. For these applications, its favorable fabrication characteristics and high-temperature mechanical properties also have been an advantage.

In common with the other refractory metals, the tendency for columbium and its alloys to oxidize in air at elevated temperatures has been a serious disadvantage. A number of alloy-development programs have been set up to try to overcome this problem. However, the alloying combinations that have been tried have not achieved the desired oxidation resistance

without increasing the fabrication problems. Coatings are also being developed for columbium and its alloys to prevent oxidation at elevated temperatures.

Pure columbium is very ductile and can be cold worked easily at room temperature. As with tantalum, large reductions are possible between anneals. However, columbium has a tendency to seize and gall in such processes as wire drawing, spinning, and threading, so special techniques are required for these processes. Working and forming are usually done at room temperature to prevent oxidation that would occur at elevated temperatures. However, cast ingots of columbium alloys have been extruded successfully from 1200 to 3000 F and forged at 2300 F. At least one high-strength columbium alloy, which has been so prepared as to contain only very small amounts of contaminating elements, has been extruded successfully at room temperature.

The density of columbium is only slightly greater than that of steel and considerably less than that of other refractory metals with higher melting points. Because of this, and the high-temperature strength and favorable nuclear properties, there has been extensive development of columbium-base alloys for airborne nuclear reactors.

In addition to the use of columbium metal in electron tubes and in other electronic equipment, it is used as an alloying element in certain stainless steels, in special grades of low-alloy steels, and in certain nickel-base superalloys and iron-base electrical alloys.

Columbium alloys that are of interest at the present time for elevated-temperature service are as follows:

FS-80 (Cb-0.75Zr)	Cb-65 (Cb-7Ti-0.8Zr)
FS-82 (Cb-34Ta-0.75Zr)	Cb-74 (Cb-10W-4Zr)
FS-83 (Cb-28Ta-11W-1Zr)	Cb-7 (Cb-28W-7Ti)
F-48 (Cb-15W-5Mo-1Zr-0.05 O-0.05C)	Cb-16 (Cb-20W-10Ti-3V)
F-50 (Cb-15W-5Mo-1Zr-5Ti-0.05 O-0.05C)	15-20 (Cb-15W-20Ta)
D-31 (Cb-10Mo-10Ti)	20-20 (Cb-20W-20Ta)

Vanadium. The melting point of vanadium is about 1000 degrees lower than that of columbium, so there is much less interest in vanadium for high-temperature applications than in the abundant refractory metals discussed previously.

Pure vanadium has only recently become available in quantities large enough for thorough studies of its physical and mechanical properties and for alloy development. Pure vanadium is relatively ductile and does not work harden appreciably. Therefore, it can be worked easily at room temperature. Because the metal oxidizes rapidly at elevated temperatures, it must

be protected during hot working or hot forging. Hot rolling, for example, may be accomplished with the ingot sheathed in a jacket of stainless steel.

Pure vanadium may be extruded, swaged, drawn, stamped, machined, etc., by the usual methods so long as it is not heated to the point where it oxidizes. Components of vanadium can be welded if argon shielding is used or if the welding is done in an enclosed tank containing a protective atmosphere.

Vanadium may have potential use as a structural material for fast reactors because it has low fission-neutron cross section, useful strength at elevated temperatures, and high thermal conductivity. Vanadium foil is used as a bonding material in making titanium-clad steel sheet. At the present time, vanadium metal is not used extensively in any other applications. However, its use as an alloying element in alloy steels, titanium alloys, and in other alloy systems is well known.

Alloys of vanadium that appear to be of interest are the vanadium-columbium and vanadium-columbium-titanium alloys.

Chromium. The melting point of chromium is the lowest of the abundant refractory metals, but it is more than 700 degrees above that of iron. The density of chromium is slightly less than that of iron. At elevated temperatures, it acquires an adherent oxide film on the surface that tends to protect it from further oxidation to about 1700 F. Furthermore, it is available in relatively large quantities. For these reasons, chromium and chromium-base alloys have been studied extensively for high-temperature applications.

Chromium metal may be obtained by a number of different processes, each yielding metal having various levels of purity. Only the purest chromium is considered to be ductile, and the mechanical properties of the various grades of chromium are dependent on such factors as purity, fabricating history, grain size, and surface condition. Specimens containing more than 0.01 per cent carbon, 0.015 per cent sulfur, or 0.02 per cent nitrogen are brittle when fractured at room temperature. Because of the high-purity requirement for chromium-base alloys and the embrittlement caused by many metallic alloying elements in small percentages, development of chromium-base alloys has been rather slow. However, alloys with 1 and 5 per cent tungsten and 1 per cent titanium have been extruded and rolled satisfactorily. Likewise, alloys containing 25 per cent iron, 6 to 9 per cent molybdenum, and small amounts of titanium and aluminum can be hot forged and hot rolled. Alloys of chromium with yttrium and rhenium also are of interest. A recent announcement disclosed the development of a chromium-base alloy containing columbium, molybdenum and tungsten. This alloy is said to be workable hot or cold and capable of being shaped into bars, flats, wire, strip, tubing and forgings. In addition, a cast chromium-nickel alloy has been developed for certain high-temperature applications involving corrosion by flue gases.

Chromium metal is used extensively for chromium plating. This may be a relatively thin decorative plate or a thicker "hard" plate for wear resistance. Large tonnages of chromium are used as various grades of ferrochromium for alloying additions to steels and cast iron. Many of the low-alloy steels contain small percentages of chromium, while the "stainless" steels contain 12 per cent or more chromium. In addition, chromium is an important alloying element in nickel- and cobalt-base alloys.

Rhenium

Rhenium is classified as a scarce refractory metal. It has the second highest melting point of any of the metals and has relatively high density.

Rhenium is produced as a powder from molybdenite (MoS_2), which also contains rhenium sulfide. The powder is consolidated by pressing and resistance sintering in a vacuum or hydrogen atmosphere. Bars produced in this way have excellent ductility at room temperature and can be rolled or cold worked. However, the metal work hardens rapidly and must be annealed after relatively small reductions.

Rhenium has higher tensile strength at high temperatures than any of the other metals. For example, it is reported to have a strength of 49,000 psi at 3000 F. The metal is rapidly oxidized in air at elevated temperatures, so when it is exposed to elevated temperatures it must be contained under vacuum or a protective atmosphere.

Because of the high price and limited supply of rhenium, it is employed in only a few very special applications which make use of its unusual properties. When used in electrical contacts, rhenium has even greater arcing and sparking resistance than tungsten. Under certain conditions, rhenium filaments have less tendency than tungsten filaments to plate out on the cool glass walls of electronic tubes. This is a complex reaction involving traces of water vapor in the evacuated tube and is called the "water cycle" reaction. The addition of 40 to 50 per cent rhenium to molybdenum alloys renders them ductile after heating to temperatures above the recrystallization temperature. Rhenium has a similar effect in several other alloys of the refractory metals.

Rhenium is useful as an alloying element in thermocouple alloys of platinum or platinum-group metals. It is also useful as a thermocouple element with molybdenum or tungsten to measure temperatures above the range of the platinum thermocouples.

Platinum-Group Metals

The platinum-group metals can be described as refractory metals because of their high melting points. This group comprises platinum, osmium,

iridium, ruthenium, rhodium and palladium, i. e., metals which have properties similar to those of platinum. The metals in this group are quite scarce and, hence, can be considered only for very specialized applications even though some of them have exceedingly attractive properties.

The platinum-group metals have been used for years in laboratory apparatus, in the "bushings" (plates with tiny orifices through which molten glass flows to form glass fibers) of the glass-fiber industry, spinnerets for viscose rayon and other fibers, other special chemical equipment, electrical contacts, spark-plug electrodes, catalysts, thermocouples, resistance thermometers, heating elements, dental applications, jewelry, pen nibs, phonograph needles, and cathodic corrosion protection. As little as 0.1 per cent palladium or platinum in titanium increases substantially its resistance to boiling hydrochloric acid and sulfuric acid. Between 0.1 and 1 per cent platinum or palladium in stainless steels increases their resistance to corrosion in sulfuric acid. A little less than 40 per cent of the combined consumption of the precious metals is of platinum itself. About 57 per cent is palladium (in 1958).

Their high melting points and excellent oxidation resistance naturally suggest these metals for high-temperature alloys. Their potential in this direction is being explored, though their scarcity will inevitably limit their use.

One possible application suggested for platinum and rhodium, especially, is as a coating to protect molybdenum from oxidation. Platinum cladding is very effective, but so expensive that attempts have been made to use platinum plating instead, which is not so effective. Rhodium appears to be the most oxidation resistant of the platinum-group metals and also has excellent high-temperature strength. A hazard encountered in working with osmium is that its oxide is extremely toxic.

Special melting and fabricating procedures are used for these metals because of their high cost and the small amounts processed. Melting is often done with torches or by induction heating in lime or zirconia crucibles. Melting may be done in air or in a protective atmosphere or in vacuum.

Platinum and palladium are readily obtained as sheet, foil, wire, and ribbon. Ruthenium and osmium are too hard and brittle to be hot worked.

A large number of alloys of the metals of the platinum group have been prepared for special purposes. For each of the uses mentioned above, there are a number of alloys of these metals that have been found useful*.

The uses mentioned above for the platinum metals are in general not dependent on structural strength but on some other outstanding property.

*For further information, see Rare Metals Handbook, Edited by C. A. Hampel, Second Edition, Reinhold Publishing Corporation (1961), Chapter 16, "The Platinum Metals" (F. E. Beamish, W.A.E. McBride, and R. R. Barefoot).

Therefore, mechanical properties of the metals and alloys of the platinum group will not be reviewed.

Hafnium

Hafnium occurs in zirconium ores. Because this metal must be removed from "reactor grade" zirconium, the production of hafnium is largely dependent on zirconium production, as discussed later. Its melting point is 4032 F. However, it has not been available in sufficiently large quantities to have any extensive elevated-temperature applications other than in control rods for water-cooled nuclear reactors.

The hafnium product from the solvent-extraction step of the zirconium-hafnium separation is treated by the Kroll process to produce a sponge. To obtain the purity needed to make hafnium ductile, the sponge is further refined by the "iodide process" before arc melting in a consumable-electrode furnace. The material is usually processed twice by consumable-electrode arc melting, first with a protective atmosphere and second in a vacuum.

Fabrication techniques for hafnium are much the same as for zirconium and titanium. It can be hot forged and rolled readily at about 1700 F. Intermediate annealing at about 1475 F is required during cold rolling. Hafnium must be welded in a protective atmosphere.

Hafnium is well suited for reactor control rods because of its capability to absorb thermal neutrons, its good corrosion resistance in water, and its good mechanical properties. Hafnium has also been used in various components of X-ray tubes, discharge tubes, radio tubes, television tubes, and in rectifiers. In addition, it has been used as an alloying element in special alloys.

Reactive Metals

Among the remaining metals with melting points above that of iron are zirconium and titanium. These metals are referred to as reactive metals because they combine readily with oxygen, nitrogen, sulfur and other non-metallic elements to form extremely stable compounds. Zirconium and titanium and their alloys are used at moderately elevated temperatures.

Zirconium

When of sufficient purity, zirconium is soft and ductile. It has good corrosion resistance and low absorption capacity for thermal neutrons. These properties are desirable in materials used for certain parts of nuclear reactors. The great increase in production of zirconium since 1945 has been the direct result of construction of nuclear reactors.

Zirconium is obtained from zircon sand, which also contains a small percentage of hafnium oxide. In making reactor-grade zirconium, the hafnium must be removed so that the concentration of hafnium in the zirconium will be no more than 0.01 per cent. The production of hafnium is largely dependent on the production of reactor-grade zirconium. Zirconium and hafnium react much the same way in the usual refining processes, so separation is difficult. Nevertheless, several processes have been developed for accomplishing the desired separation.

Cast ingots of zirconium and the group of alloys known as the Zircalloys are produced by arc melting or by powder-metallurgical processes. The resulting ingots or compacts may be hot forged and rolled without protective atmospheres. Forging temperature is about 1550 F for the unalloyed metal and 1800 F for the Zircalloys. Vacuum annealing is used in the finishing stages of fabrication to provide improved surface characteristics.

Zirconium may be hot extruded at about 1800 F, but some means must be used to protect the surface during heating. This may be done in a salt bath. The metal may also be cold worked. Welding may be done in a suitable protective atmosphere.

Several alloys of zirconium have been developed to provide improved room-temperature and elevated-temperature strength and corrosion resistance without sacrificing other favorable properties. Zircaloy-2 contains about 1.5 per cent tin and Zircaloy-3 contains about 0.25 per cent tin. Both alloys also contain small amounts of iron, chromium, and nickel and traces of other elements.

In addition to nuclear-reactor components, zirconium is used for special corrosion-resistant equipment for the chemical industry, in photoflash bulbs, and for surgical applications.

Titanium

Titanium has a melting point of 3035 F, which is 200 to 300 F above those of the group comprising iron, nickel and cobalt. In addition, its density is only about 57 per cent that of iron. From the position of its melting temperature, it would be expected that titanium alloys could be developed which would outperform the so-called superalloys, i. e., high-temperature alloys based on iron, nickel, and cobalt. Moreover, because of their low density, titanium alloy components should weigh considerably less than the equivalent superalloy component.

These prospects prompted an intensive and comprehensive research and development program by the United States Government, which was directed toward titanium production and alloy development. It was extremely desirable to have a superior light-weight metallic material that could be

used in aircraft structures exposed to temperatures far above those which the current aluminum alloys could withstand. Suitable ores were identified, extraction and refining processes were developed, and much of the metallurgy of titanium and its alloys was worked out, all with remarkable rapidity. Production rose rapidly through the period from 1950 to 1957.

A host of titanium alloys was developed. Many have superior mechanical properties and offer substantial weight savings at intermediate temperatures up to about 1000 F. Thus, the titanium alloys are more competitive with the high-strength low-alloy steels than with the superalloys. Titanium metallurgy has continued to advance. On its strength-density advantage, titanium has won important applications in military and civilian aircraft and in missiles and advanced aerospace vehicles. In addition, its superior corrosion resistance up to moderate temperatures is opening up many industrial uses. This market will grow as the price of the metal declines.

An important reason for interest in titanium is the large supply of ore, essentially TiO_2 , which exists in North America. In the most widely used refining process, the TiO_2 is converted to TiCl_4 by chlorination. In the Kroll process, the TiCl_4 is reacted with molten magnesium, which leaves titanium sponge and magnesium chloride. Other processes have also been used to obtain ductile titanium, and work is continuing on new processes that are intended to decrease the costs of titanium metal. Whatever the process, it is highly desirable to limit such contaminants as carbon, oxygen, and nitrogen to low levels for maximum ductility and toughness. Contamination by hydrogen must also be avoided.

Titanium sponge must be melted to consolidate it into ingots before it can be fabricated into mill products. This is done in consumable-electrode arc-melting furnaces in a vacuum. Water-cooled copper molds are used, and the ingots may be as large as 25 inches in diameter. Titanium for casting also is being melted in consumable-electrode arc-melting furnaces. The molten titanium is poured from the melting crucible into a graphite mold in the vacuum chamber.

Titanium ingots may be hot forged or rolled in air. The maximum fabrication temperature depends on the alloy content. In general, the fabrication temperatures should be kept as low as possible consistent with the good fabricability characteristics of a particular alloy. This practice minimizes the contamination problem. Forming and bending operations on titanium and titanium alloys also are often done at elevated temperatures to minimize spring back and cracking. Pure titanium and several titanium alloys may be welded satisfactorily if a protective atmosphere is used.

The large number of titanium alloys which have been produced on an experimental scale, or which have reached commercial production, may be classified in three categories based on their crystalline structure at room temperature: (1) alpha alloys, (2) alpha-beta alloys, and (3) beta alloys.

The several grades of titanium of commercial purity are of the alpha type. The alpha-beta and beta alloys may be heat treated to improve their strength.

The best known and most widely used alloys of each type are as follows:

Alpha - Ti-5Al-2.5Sn
Alpha-beta - Ti-6Al-4V
Beta - Ti-13V-11Cr-3Al .

The alpha alloys are normally used in the annealed condition, while the alpha-beta and beta alloys may be used as annealed or heat treated, depending on the desired properties. Heat treating includes heating to a specified solution temperature, quenching in water, and then aging at some lower temperature depending on the alloy. The heat-treated beta alloy has higher strength than the other two types. This type of alloy is solution treated before the final working or forming operations. After working and forming, it may be aged at 800 to 900 F. Properties of these alloys will be discussed later. For elevated-temperature service, the annealed alpha alloys or the heat-treated alpha-beta alloys show the most promise. However, service temperatures should not exceed aging temperatures, if service loads and temperatures are of long duration, because overaging and consequent loss of strength will occur.

Titanium is used in other than aircraft and aerospace vehicles principally because of its good corrosion resistance and high strength at very low temperatures. For example, titanium is used for special chemical equipment and in marine applications and also for cryogenic equipment, where it is exposed to temperatures as low as -423 F.

Iron-Base Alloys

Commercially pure iron has relatively low strength. In consequence, it finds major use as a nonstructural or a low-strength structural material. On the other hand, iron-base alloys, i. e. steels, comprise the world's principal metallic structural material. An enormous number of different kinds of steel are available. Many are used at elevated temperatures, some at temperatures as high as 2300 F. Because of the abundance of iron ore, the production capacity for iron-base alloys, and the availability of the alloying elements, even highly alloyed steels are relatively low in cost.

The types of iron-base alloys for elevated-temperature service are discussed in the following paragraphs, which are arranged according to increasing alloy content. Details of their mechanical properties are discussed in a later section.

Low Alloy Heat-Treatable Steels

Examples of these steels are those standard low-alloy AISI-SAE* types that are hardenable by heat treatment. These steels usually contain small amounts of such elements as manganese, silicon, chromium, nickel, and molybdenum in addition to carbon. Representative types are AISI 4130 and 4340. They are hardened by heating to 1500 to 1600 F and quenching, and are tempered from 400 to 1100 F. These steels may be used for short periods of time above their tempering temperatures because tempering is a time-dependent process. If heat-treated steel components of AISI 4130 steel, for example, are heated and loaded rapidly in short-time service applications as in some rocket components, launchers, etc., they may serve adequately to about 1200 F. Such steels may be used for longer periods of time at 900 to 1000 F in either the hardened or normalized conditions. However, they are subject to corrosion in corrosive atmospheres and develop oxide coatings at elevated temperatures.

Low-Alloy Normalized Steels

A series of low-alloy steels containing 1.0 to 9.0 per cent chromium, 0.5 to 1.0 per cent molybdenum, sometimes up to 2.0 per cent silicon, and 0.10 to 0.20 per cent carbon are available for extended service at temperatures up to about 1000 F. These steels are used in the normalized condition (heated to about 1700 F and cooled in air). They are frequently employed in the form of pipe and tubing and, as such, are used in boilers, heat exchangers, high-pressure steam lines, etc. This type of steel cannot be considered as more than modestly corrosion resistant. However, those with higher chromium and silicon contents have somewhat improved resistance to oxidation and attack by other gaseous environments.

5 Per Cent Chromium-Molybdenum-Vanadium Steels

These steels, which are more generally known as the 5 per cent chromium hot-work die steels, were developed many years ago for shear blades, dies, and other tools to form metal at high temperatures. More recently, attention has been focused on them for high-strength structural applications, particularly in air frames. These steels retain relatively high strength in short-time tests up to about 1200 F. They are normally hardened by heating to 1850 F, air quenching, and tempering at about 1000 F. For prolonged service at elevated temperatures, the maximum temperature should be about 50 degrees below the tempering temperature.

The chromium hot-work die steels were originally available only in the form of forgings, bar stock, and flats. Today, through research and

*AISI = American Iron and Steel Institute.
SAE = Society of Automotive Engineers.

development efforts by the producers, these steels are obtainable in many forms including sheet and strip. A typical composition for such a steel is Fe-0.35C-5.0Cr-1.50Mo-0.40V (AISI-SAE Type H-11). However, several modifications of this steel, having increased strength at elevated temperatures, have been developed. One composition, illustrative of the trend toward modifications, is Fe-0.40C-7.0Cr-6.0Mo-5.0Co-1V.

Wrought Stainless Steels

A simplified classification of the wrought stainless steels is shown in Table 4.

TABLE 4. CLASSES OF WROUGHT STAINLESS STEELS

Type	Principal Alloying Elements	Principal Characteristics
Martensitic	Major : Cr, C Minor : Ni, Mo, V, Cu, B, W	High hardness and strength; moderately corrosion resistant; service temper- atures to 1000 F
Ferritic	Major : Cr Minor : C, N	Corrosion resistant; ser- vice temperatures to 800 F and from 1000 to 1100 F; oxidation resistant to 1550 F
Austenitic	Major : Cr, Ni Minor : Mo, C, N, Cu, Mn, Ti, Cb	Corrosion resistant; ductile; medium strength; hardenable by cold rolling; service temperatures to 1200 F
Precipitation hardenable	Major : Cr, Ni Minor : Al, Mo, Cu, C, N, Cb	High strength; ductile before heat treating; corrosion resistant, service temper- atures to 1000 F

The martensitic stainless steels contain 11 to 14 per cent chromium and sufficient carbon to permit hardening by a heating and quenching treatment. After quenching, they are tempered for stress relief and to achieve the desired combination of strength and toughness. They are considered moderately corrosion resistant. This type of stainless steel is used for steam valves, bolts, steam-turbine blades, etc., where strength and

corrosion resistance are required as well as capability to withstand exposure to elevated temperatures. Of course, they have a wide variety of room-temperature applications.

The ferritic stainless steels contain 16 to 27 per cent chromium and are not hardened by a heating and quenching treatment. The higher chromium content of the ferritic steels provides improved oxidation resistance at elevated temperatures. When these steels are heated for prolonged periods from 800 to 1000 F they become embrittled, so service temperatures in this range are to be avoided. They can be used at higher or lower temperatures. Among high-temperature applications of the ferritic stainless steels are heat exchangers, furnace parts, and glass molds.

The austenitic stainless steels, including the well-known 18-8 stainless steel, contain over 17 per cent chromium, which provides excellent corrosion and oxidation resistance, and over 7 per cent nickel, which enhances corrosion resistance and causes retention of the ductile austenitic structure at room temperature following the annealing treatment. In annealing, the austenitic stainless steels are heated to about 1900 F and quenched in water. These steels are not usually considered hardenable by heat treatment. However, they may be hardened by cold rolling. In fact, some grades may be hardened to an exceedingly high strength by cold rolling.

The cold-rolled grades retain high strength up to 800 F. All grades of austenitic stainless steel may be used to 1200 F, depending on the circumstances. The more highly alloyed stainless steels may have useful properties at temperatures up to 2000 F.

The austenitic stainless steels may be fabricated by most of the methods used for low-alloy steels. However, because of their work-hardening characteristics, cold working and forming the austenitic steels require higher working pressures and more frequent anneals. These austenitic steels may be welded by any of the common methods. However, if corrosion is involved, the extra-low-carbon grades or stabilized grades are preferred to minimize corrosive attack in the heated area of the weld. This problem also may be avoided by annealing after welding.

High-temperature applications of the austenitic stainless steels include furnace parts, aircraft cabin heaters, jet-engine parts, engine exhaust systems, steam-turbine blades, and equipment for the chemical industry.

A number of different types of precipitation-hardenable stainless steels have been developed in recent years. Parts made from these steels are formed to final shape with the steel in the relatively soft solution-treated condition. Then they are aged to increase hardness and strength. The precipitation-hardenable stainless steels contain such elements as aluminum, molybdenum, copper, nitrogen, and/or columbium in addition to chromium and nickel to achieve the age-hardening effect. The heat treatments for these steels are rather complicated and depend on the composition or type of steel

involved. However, such steels are preferred for many aircraft components that are subjected to elevated temperatures, high stresses, and corrosion. Service temperatures may be as high as 800 to 1000 F, depending on allowable time at temperature, stresses, and other factors.

The precipitation-hardening stainless steels may be fabricated and welded in much the same way as the austenitic stainless steels. However, fusion welds in the precipitation-hardening types will have best properties if the weldments are given the complete solution treating and aging treatments after welding.

The precipitation-hardening grades are used for landing-gear hooks, poppet valves, hydraulic lines, compressor casings, gas-turbine compression blades, honeycomb structures, etc., for aircraft.

Compositions of the high-temperature wrought iron-base superalloys are reviewed in a later section.

Cast Steels and Irons

Cast alloys to withstand service temperatures of 1200 F and higher contain substantial amounts of chromium or both chromium and nickel. As these alloys have been developed primarily for furnace components (for heat treating and processing furnaces), selections of alloys are based on tendency to carburize, thermal-shock resistance, thermal-fatigue resistance, oxidation resistance, etc.

One of the more common types (HH) contains 26 per cent chromium and 12 per cent nickel. It has good strength and oxidation resistance to 2000 F. With the proper balance in composition, the alloy will be entirely austenitic, which is desired for best properties at elevated temperatures. A high-carbon modification of another type (HK) can be used to 2200 F.

Castings of the heat-resistant alloys can be made in a wide variety of sizes and shapes for furnaces and processing equipment. They can be used in air or special atmospheres.

Cobalt- and Nickel-Base Alloys

Cobalt and nickel have melting points slightly below that of iron but, in the temperature range of 1200 F to perhaps 2000 F, many cobalt-base and nickel-base alloys have higher strength than the best iron-base alloy available at the present time.

Cobalt

Cobalt is obtained from ores that normally contain nickel, copper, silver, and gold in various proportions along with the cobalt. Ores from different locations vary chemically and mineralogically and, hence, require different processing procedures. Separating the minerals and recovering the metals from these ores involve complex refining methods. Nonetheless, practical high-production processes have been developed. In fact, consumption of metallic cobalt in the United States was nearly 7,000,000 pounds in 1960.

Cobalt metal is obtained as a powder or as granules. The powder can be consolidated and alloyed by powder-metallurgical techniques. Cobalt-base alloys are usually melted in air-atmosphere furnaces. Some of the alloys can be used only in the cast form. Certain of the alloys used for turbojet-engine turbine blades are in this category. Other alloys are formable. These are cast into the form of ingots which may be hot forged and rolled. When such alloys are cold worked, frequent intermediate anneals are required.

The primary use of pure cobalt, as such, is as cobalt-60, a radioactive isotope prepared by irradiation of the pure metal in a nuclear reactor. Cobalt-60 is used in equipment for radiographic inspection, for certain types of therapy, for thickness measurement, and other specialized applications.

Cobalt, iron, and nickel are the three ferromagnetic elements. When these elements are alloyed together in certain proportions, with or without the addition of other elements, exceptional magnetic properties are obtained. These alloys may contain as much as 50 per cent cobalt.

Cobalt has also been used as an alloying element in high-speed steels and as a binder in tungsten carbide cutting tools. Both of these applications require retention of high hardness at elevated temperatures.

With the advent of the gas turbine, development of alloys having oxidation and corrosion resistance together with high strength at high temperatures was accelerated. The effort to develop such so-called superalloys got into full swing during World War II. Among the numerous metallic materials investigated, were those containing cobalt as an alloying element and those with cobalt as the base metal. Early in the program it was discovered that the cast cobalt-base dental alloy, Vitallium, had superior high-temperature strength and oxidation resistance. This material became a superalloy for gas-turbine blades; it is now more commonly called HS-21. Since then, several other cast cobalt-base alloys and a number of wrought cobalt-base alloys have been developed with exceptionally good elevated-temperature properties. A generalized classification of cobalt-base high-temperature alloys is given in Table 5. Strengthening is accomplished by the solution of alloying elements in the matrix and through a heat treatment by which a

TABLE 5. HOW COBALT-BASE AND NICKEL-BASE HIGH-TEMPERATURE ALLOYS ARE STRENGTHENED

Type	Principal Alloying Elements	Uses
<u>Cobalt Base</u>		
Elements participating in solid-solution strengthening	Major : Cr, W, Mo Minor : Ni	Jet-engine turbine buckets, combustion chambers, and afterburners
Elements participating in precipitation hardening	Major : Cr, Ni, W, C, Ti Minor : Cb, Ta	
<u>Nickel Base</u>		
Elements participating in solid-solution strengthening	Major : Mo, Cr, Fe Minor : Co	Chemical equipment, heat treating fixtures
Elements participating in precipitation hardening	Major : Al, Ti Minor : B	Jet-engine rotor blades and wheels, skin of aerospace vehicles

second phase is caused to precipitate in the matrix. Some of the cobalt-base superalloys have useful strength up to 1650 to 2000 F.

Important among alloys to which cobalt is added as an alloying element are several nickel-base superalloys. Details of the mechanical properties of these alloys are discussed in a later section.

New developments under way in the cobalt-base field include alloys with improved strength in the range of 1800-2000 F, development of new precipitation-hardenable alloys, improvement in casting techniques, and development of powder-metallurgical methods of consolidating and compacting alloys.

Nickel

Nickel ores usually contain metals such as copper and iron, and sometimes chromium, which must be separated in the extraction and refining process. Because there are differences in the ores, in the refining processes, and in the requirements of the consumers, nickel is available in a considerable number of forms and degrees of purity. The forms include sheared cathodes, rondelles, ingots, and several types of powder.

Equipment for melting, forging, rolling, and drawing nickel and nickel-base alloys is somewhat similar to that used for alloy steel. Melting may be done in electric-arc, induction, or gas-fired furnaces. Slags are often used on the melts, and materials are added for degasifying and deoxidizing. The molten metal may then be poured into ingot molds or cast to shape. Surface defects are removed from the ingots and they are reheated for forging and hot rolling, which may be done in the range of 1750 to 2300 F, depending on the particular alloy. Lower temperatures are used for finish rolling. Extrusion of nickel and its alloys is more difficult than for some other metals, but extrusion of even the higher-strength alloys may be done readily with molten glass as the lubricant.

Nickel and nickel-base alloys may be cold worked by all of the methods commonly used for steel. Welding is by oxyacetylene torch, inert-gas-shielded arc, resistance, and spot-welding methods. Machining operations are somewhat similar to those used for stainless steel.

Uses of nickel for nickel plating and as an alloying element in low-alloy heat-treatable steels are well known. The importance of nickel in various grades of stainless steels and high-temperature iron-base alloys has been discussed in a previous section. Use of nickel in magnetic alloys with cobalt has also been discussed. In addition, nickel is used with iron and other metals in alloys having specific thermal expansion and thermoelastic characteristics.

A considerable amount of nickel is used in the nickel-copper alloys called Monels. These alloys are noted for their resistance to corrosion in structural applications. An age-hardenable grade known as "K" Monel contains small amounts of aluminum and titanium which enter into the age-hardening reaction. A number of copper-nickel alloys containing up to 30 per cent nickel are known as cupro-nickels. These also have excellent corrosion resistance and good mechanical properties. The cupro-nickels are used extensively in heat-exchanger equipment.

A major use of nickel is in nickel-base alloys designed for high-temperature service. A large number of such alloys have been developed, many to meet rather specific sets of requirements. These alloys generally retain high strength and good oxidation and corrosion resistance at temperatures that are relatively close to the melting point of the alloys. Table 5 shows the principal alloying agents used for strengthening these materials.

An alloy of 80Ni-20Cr has been used for many years in electric heating elements. Another alloy called Inconel (77Ni-15Cr-7Fe) is highly oxidation resistant and has good corrosion resistance in many environments. Modifications of the Inconel composition have been developed which contain such additional elements as molybdenum, manganese, columbium, cobalt, titanium, and aluminum to provide increased high-temperature strength and oxidation resistance. Some of these alloys have useful strengths at 1800 F or higher.

The Nimonic alloys constitute another series of superalloys. These alloys are 80Ni-20Cr alloy with additions of cobalt, titanium, and aluminum.

Another series of nickel-base high-temperature alloys is the Hastelloys. They are based on the initial composition 59Ni-20Mo-20Fe. Modifications of this series of alloys contain chromium, cobalt, tungsten, titanium, and aluminum.

Other proprietary nickel-base alloys have also been developed containing the same alloying additions mentioned above. These other alloys may contain small amounts of vanadium, zirconium, and boron. It is evident that most of the high-temperature metals including the abundant refractory metals have been used in nickel-base alloys in attempting to improve their high-temperature properties. Vacuum melting and casting of the nickel-base superalloys normally results in higher creep properties than air melting. Some of these alloys are best suited for use in the as-cast condition. Others may be hot and cold worked to develop the desired shapes. The wrought alloys are usually heat treated to develop optimum high-temperature properties. These heat treatments result in precipitation hardening, which involves rather complex structural changes within the material.

Another category of superalloys contains high percentages of nickel, chromium, and cobalt. These are complex alloys with not more than about 43 per cent of the major element. Minor alloying additions include the same

elements mentioned above. Some of these alloys also have useful strength to 1800 F and higher.

Superalloy development is continuing, but evaluation of alloys for high-temperature service requires considerable time. Costs of testing programs involving high-temperature equipment are high. In spite of these factors, improvements have been made steadily in the high-temperatures performance of the superalloys. Recent developments indicate that new alloys may have useful strength to 2000 F.

Nickel-base alloys based on powder-metallurgical techniques are being investigated. In current studies, nickel-base materials dispersion hardened with alumina and magnesia particles are being evaluated. The best dispersion-hardened alloys compare favorably with some of the better superalloys.

Beryllium

Beryllium has a melting point of 2332 F, which is 466 degrees lower than that of iron. However, beryllium has an unusual combination of properties which makes it extremely effective in a number of important applications involving high temperature. Its density is nearly as low as that of magnesium, while its elastic modulus is 44×10^6 , about 1.5 times the elastic modulus of iron. Therefore, the modulus-to-density ratio of beryllium is far higher than that of other metals. At the same time, beryllium has good thermal conductivity and high specific heat compared with that of other structural metals. Consequently, this metal is an outstanding "heat sink" material, i. e., it has the capacity to absorb large quantities of heat without melting. Heat shields for Mercury capsules have been forged of beryllium to absorb re-entry heat with minimum structural weight. Though this application has been the most publicized, the metal is being considered for other aerospace applications where its unusual combination of properties can be applied advantageously for structural components.

For such applications, there are problems in fabricating beryllium as discussed later. Beryllium also has a tendency to be brittle at room temperature, particularly under multiaxial loading conditions. Furthermore, beryllium compounds are toxic under certain conditions. Soluble compounds of beryllium may cause skin irritation, and inhalation of mists, dusts, or fumes of these compounds may cause acute pneumonitis.

Beryllium metal is obtained from beryl ore by a series of complex processes in which the beryllium in the ore is converted to a water-soluble salt, to beryllium hydroxide, and then to beryllium fluoride. The latter compound is reduced with magnesium at elevated temperatures. The resulting beryllium pebbles are melted in a beryllium oxide crucible in a vacuum furnace and cast in a graphite mold. The ingots obtained are

converted to chips by machining, and the chips are ground to powder. The powder is then vacuum hot pressed in steel dies at about 2000 F to produce large blocks often called QMV beryllium. The vacuum hot-pressed beryllium usually contains 0.6 to 2.0 per cent beryllium oxide which inhibits grain growth at elevated temperatures.

Components may be machined from blocks of hot-pressed powder. Hot-pressed material may be extruded if it is encased in steel. The steel case prevents oxidation of the beryllium at the extrusion temperatures of 1750 to 1950 F. The hot-pressed beryllium can also be forged if encased in a steel jacket. Heat shields for the Mercury capsules were forged by this technique. Recent studies have shown that certain types of beryllium forgings may be made without steel jackets if the forging temperature is about 1400 F. This is below the temperature at which rapid oxidation occurs.

Sheet and strip may also be hot rolled from hot-pressed beryllium if it is jacketed in steel. After rolling to about 1/8-inch thickness, the jacket is removed before further rolling. Properties of the material will vary considerably, depending on the degree of working and the direction of testing. Extrusion, forging, and rolling may also be used to work cast ingots if encased in steel jackets, but the properties are not so good as those obtained when the starting material is vacuum hot-pressed block.

Formability of beryllium sheet is poor at room temperature but improves at temperatures to 1400 F. It can be deep drawn at 1000 to 1400 F using generous radii and slow deformation speeds. It can be sheared and punched at 800 F. Cold riveting can be performed by using aluminum rivets. The success of these operations is largely dependent on the prior history of the material. Grain size, degree of hot and warm working, and extent of cross rolling affect the properties. Studies to improve the room-temperature ductility and toughness of beryllium are under way with both single crystals and polycrystalline material. Warm working at 1400 F and cross rolling of sheet are advantageous. Effects of impurities are also being studied.

Beryllium has other unusual properties which make it useful for X-ray and nuclear-reactor components. Since X-rays penetrate beryllium better than other metals, it is used for windows in X-ray tubes. Beryllium has a small capture cross section for thermal neutrons and low affinity for slow neutrons in nuclear applications. Consequently, moderators and reflectors have been machined from nuclear-grade hot-pressed beryllium.

In addition to the above-mentioned applications, beryllium metal is being used for instrument components that require light weight and stiffness (high elastic modulus). These include inertial-guidance instruments, gyroscopes, and accelerometers.

No beryllium-base alloys have been developed for commercial production (except the beryllium-beryllium oxide combination). However, beryllium is well known as an alloying element in beryllium-copper alloys, which

contain up to 3 per cent beryllium. Beryllium is also used in several nickel-base and iron-base alloys.

Aluminum and Magnesium

Alloys of aluminum and magnesium are not normally considered for use at temperatures as high as 800 F. However, certain alloys of these metals have capabilities which justify considering them for use at comparatively high temperatures.

Aluminum alloys have been the primary materials of construction in the commercial airframe industry. The light weight, good strength, ease of fabrication, and corrosion resistance of these alloys have made them ideal for subsonic aircraft. Wrought alloys are usually used in the airframe, while cast aluminum alloys were used in many aircraft piston-engine components.

Magnesium alloys have also been used in both the wrought and cast conditions for applications requiring minimum weight.

At room temperature, the higher-strength aluminum alloys are stronger than the magnesium alloys. However, at elevated temperatures, the strength-weight ratios of the higher-strength commercial aluminum alloys and the higher-strength commercial magnesium alloys are in the same range.

Because of a need for high strength with light weight and corrosion resistance at temperatures of 800 F and higher, some rather unusual techniques have been evolved to prepare high-temperature alloys. One class of alloys, the result of an unusual method of preparation, is known as SAP (sintered aluminum product) and is a mixture of aluminum and various amounts of aluminum oxide. The dispersion of aluminum oxide in the aluminum matrix provides improved strength at elevated temperatures. This development has not reached full commercial scale, but is indicative of a trend in methods that are being tried to improve elevated-temperature properties. As a result of the development of SAP, similar techniques are being tried for other powder-metal systems.

It should be pointed out that when service loads are applied rapidly and for short periods of time, materials such as commercial aluminum and magnesium alloys will withstand higher loads than they would normally withstand under conditions of slow loading. This effect is more pronounced at elevated temperatures than at room temperature. Studies of the effects of rapid loading and rapid straining have received considerable attention in recent years in evaluating the elevated-temperature properties of materials. Certain missile components, such as fins, are subjected to rapid loading and aerodynamic heating. In fact, magnesium-alloy castings have been used successfully for fins in some rockets.

DATA ON MECHANICAL AND PHYSICAL PROPERTIES

Mechanical Properties

As has been mentioned in an earlier section, metallic materials for use at elevated temperatures must usually meet certain mechanical-property requirements. This, of course, is axiomatic for structural components. As has also been indicated previously, those room-temperature properties which relate to forming capability, handling, and storage are important.

Among high-temperature mechanical properties of interest are tensile strength and ductility. For structures designed to withstand loads for short times, tensile strength is important. The corresponding ductility value gives an indication of the ability of the material to yield or deform without breaking. When minimum weight is required in the structure, it is usual to consider the strength-density ratio in selecting the material. On this basis the materials may assume an order of merit different than that obtained when only strength is considered.

When stiffness is of primary importance as well as weight, the various materials may be evaluated on the basis of elastic modulus-density ratios. On this basis, beryllium for example has a much higher ratio than other materials because of its high modulus and low density.

Under certain conditions, some of the high-temperature metals and alloys are so brittle at room temperature, and even at moderately higher temperatures that they cannot be fabricated readily. Such factors as the presence of contaminants in the material, the grain size, and the prior fabrication and heat-treating history influence the degree of brittleness. In most cases, the degree of brittleness diminishes with increasing temperature. In fact, for most metals which display brittleness at or near room temperatures, there is a fairly distinct temperature range in which the behavior changes from brittle to ductile as discussed in Appendix A, page A-4. The midpoint of this temperature range is frequently chosen as the ductility transition temperature. Though knowledge of brittle-ductile behavior cannot be used directly in design, such information is often important in determining the limitations on the use of a material.

Often of utmost importance in considering materials for structural applications at high temperatures is their creep and stress-rupture properties. Considerable data on these properties are available for most high-temperature metals and alloys. Another property which may be of equal importance in many applications is high-temperature fatigue resistance. Unfortunately, information on this subject is rather meager.

Mechanical Properties of Unalloyed Metals

In reviewing the properties of unalloyed metals, it should be understood that there are many factors which affect the values obtained. Such factors as degree of purity, the condition of the material (whether as cast, hot worked, hot-cold worked, cold worked or annealed), the grain size, the surface finish, and the rate of testing must be considered. The inertness of the material to the test environment must also be considered; reactions between the metal and the environment may improve or detract from properties, depending on circumstances. In addition, interactions of properties must be taken into account. For example, a very brittle material may break prematurely in test, thus yielding a spurious value for strength. Again, internal changes may occur in the material at particular temperatures and affect the properties.

Values for the ultimate tensile strength and elongation of annealed "pure" metals at elevated temperatures are listed in Table 6 and plotted in Figure 2. It is seen that tensile strength tends to decrease as temperature increases and that the metals with the higher melting temperatures generally tend to have the higher strength. For the metals reported, the curve of strength versus temperature is expected to be smooth. The anomalous curves in Figure 2 are thought to reflect reactions with the environment. Furthermore, strength values for materials showing little or no ductility are suspect. An example is the strength value at room temperature reported for chromium.

The tensile strength-density ratios of the "pure" metals in the annealed condition are given in Table 7 and plotted in Figure 3. Comparison of these data with those for tensile strength shows how the order of merit of the metals may change when the density factor is introduced.

Values of stress for rupture in 10 and 100 hours at various temperatures are listed in Table 8. The data again reflect the tendency of the metals with the higher melting points to have the superior properties.

Mechanical Properties of Alloys

The need for materials with better elevated-temperature mechanical properties than those of the pure metals has caused the initiation of a large number of programs to develop high-temperature alloys during the past 20 years. As a result of these alloy-development programs, commercial alloys of aluminum, beryllium, titanium, iron, nickel, cobalt, columbium, molybdenum, tantalum, and tungsten base are now available for use in structural applications that involve exposure to elevated temperatures and stresses which exceed the limits of the pure metals. Alloys of zirconium and the platinum metals also have been developed for special elevated-temperature applications.

TABLE 6. TENSILE STRENGTH AND ELONGATION OF ANNEALED PURE METALS AT ELEVATED TEMPERATURES

Metal	Property Values at Indicated Temperature, F												
	75	800	900	1000	1200	1400	1600	1800	2000	2500	3000	3500	Other
Tungsten^(a)													
Tensile Strength, 1000 psi	215	85	--	81	77	78	66	62	59	45	20	10	6.8
Elongation, per cent	0.2	3.5	--	18	16	14	14	16	15	26	47	25	2.0
													4100 F
Rhenium													
Tensile Strength, 1000 psi	164	--	114	--	--	--	--	85	--	--	--	--	7.7
Elongation, per cent	28	--	9	--	--	--	--	2	--	--	--	--	2
													4200 F
Tantalum													
Tensile Strength, 1000 psi	67	65	--	60	45	30	22	22	17	--	--	--	3.7
Elongation, per cent	25	24	--	16	17	23	33	33	43	--	--	--	44
													4000 F
Molybdenum^(a)													
Tensile Strength, 1000 psi	97	--	--	--	65	--	52	52	44	15	7	3	
Elongation, per cent	42	--	--	--	22	--	24	23	19	5	6	72	
Columbium													
Tensile Strength, 1000 psi	35	--	--	32	--	--	--	--	9.2				
Elongation, per cent	20	--	--	38	--	--	--	--	84				
Hafnium													
Tensile Strength, 1000 psi	65	--	26	21	1100 F								
Elongation, per cent	23	--	63	56									
Rhodium													
Tensile Strength, 1000 psi	61	--	49	--	--	49	--	17	--	8.9	2300 F		
Elongation, per cent	--	--	32	--	--	29	--	61	--	100 RA ^(b)			
Vanadium^(c)													
Tensile Strength, 1000 psi	91	99	750 F	40	1110 F	23	1470 F	7.1	1830 F				
Elongation, per cent	22	19		3		36		50					
Chromium													
Tensile Strength, 1000 psi	41	41	40	38	--	26	17	--	9				
Elongation, per cent	0	19	20	18	--	50	66	--	104				
Zirconium													
Tensile Strength, 1000 psi	49	16	13										
Elongation, per cent	34	60	>100										
Platinum													
Tensile Strength, 1000 psi	20-24	13 (750 F)	--	--	8 (1470 F)		4 (1830 F)						
Elongation, per cent	35-40												
Titanium													
Tensile Strength, 1000 psi	90	31	27	23									
Elongation, per cent	25	27	33	60									
Palladium													
Tensile Strength, 1000 psi	21	18 (750 F)	--	--	8.3 (1470 F)		3.8 (1830 F)						
Elongation, per cent	24												
Iron^(d)													
Tensile Strength, 1000 psi	35												
Elongation, per cent	31												

TABLE 6. (Continued)

Metal	Property Values at Indicated Temperature, F												
	75	800	900	1000	1200	1400	1600	1800	2000	2500	3000	3500	Other
Cobalt													
Tensile Strength, 1000 psi	37												
Elongation, per cent	--												
Nickel													
Tensile Strength, 1000 psi	46	32	--	25	--	10							
Elongation, per cent	55	64	--	75	--	70							
Beryllium^(e)													
Tensile Strength, 1000 psi	44	31	--	22	12	4	2						
Elongation, per cent	<1	8	--	4	3	1	<1						
Aluminum													
Tensile Strength, 1000 psi	10	--	0.44	} 932 F									
Elongation, per cent	50	--	15										

(a) Stress relieved (not recrystallized).

(b) RA = reduction of area.

(c) Hot rolled.

(d) Vacuum melted.

(e) QMV Beryllium with about 1 per cent BeO.

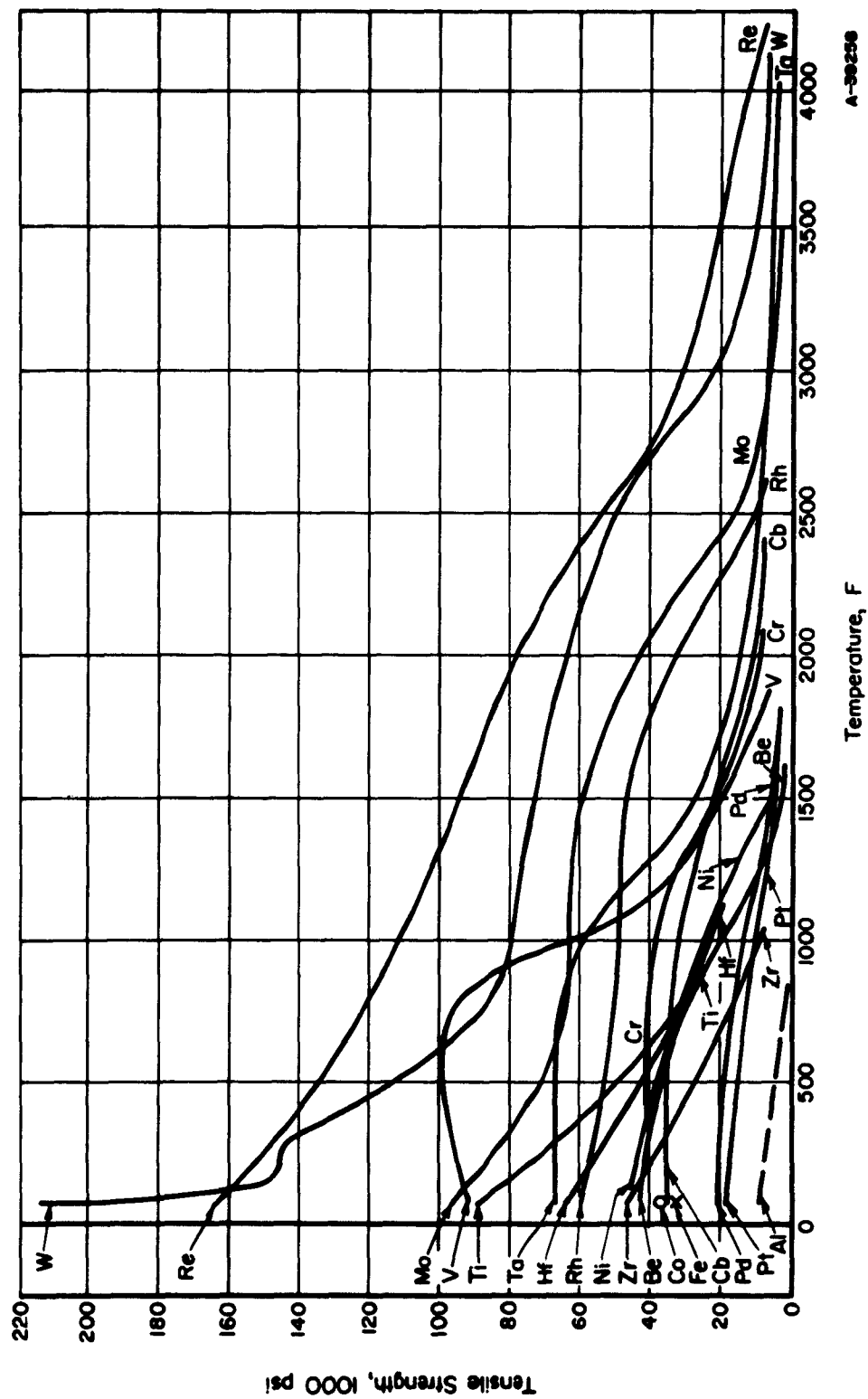


FIGURE 2. TENSILE STRENGTH OF PURE METALS AT ELEVATED TEMPERATURES

Data from Table 6.

TABLE 7. TENSILE STRENGTH-DENSITY RATIOS FOR PURE METALS AT ELEVATED TEMPERATURES^(a)

Metal	Density, lb/in. ³	Ratios of Tensile Strength, 1000 psi, to Density, lb/cu in., at Indicated Temperature, F												
		75	800	900	1000	1200	1400	1600	1800	2000	2500	3000	3500	Other
Tungsten	0.697	309	122	--	116	110	112	95	89	85	65	29	14	10 (4100 F)
Rhenium	0.756	217	--	151	--	--	--	--	112	--	--	--	--	10 (4200 F)
Tantalum	0.600	112	108	--	100	75	50	37	37	28	--	--	--	6 (4000 F)
Molybdenum	0.369	263	--	--	--	176	--	140	140	119	41	19	8	
Columbium	0.310	113	--	--	103	--	--	--	--	30				
Hafnium	0.473	137	--	55	44 (1100 F)									
Rhodium	0.447	131	--	110	--	--	110	--	38	--	20			
Vanadium	0.220	414	450 (750 F)		182 (1110 F)		105 (1470 F)		32 (1830 F)					
Chromium	0.260	157	157	154	146	--	100	65	--	35				
Zirconium	0.234	210	68	55										
Platinum	0.775	26	17 (750 F)		--	--	10 (1470 F)		5 (1830 F)					
Titanium	0.163	552	190	166	141									
Palladium	0.434	48	42 (750 F)		--	--	19 (1470 F)		9 (1830 F)					
Iron	0.284	123												
Cobalt	0.322	115												
Nickel	0.322	142	99	--	78	--	31							
Beryllium	0.067	657	463	--	328	180	60	30						
Aluminum	0.0975	103	--		4 (932 F)									

(a) Based on tensile strengths in Table 6.

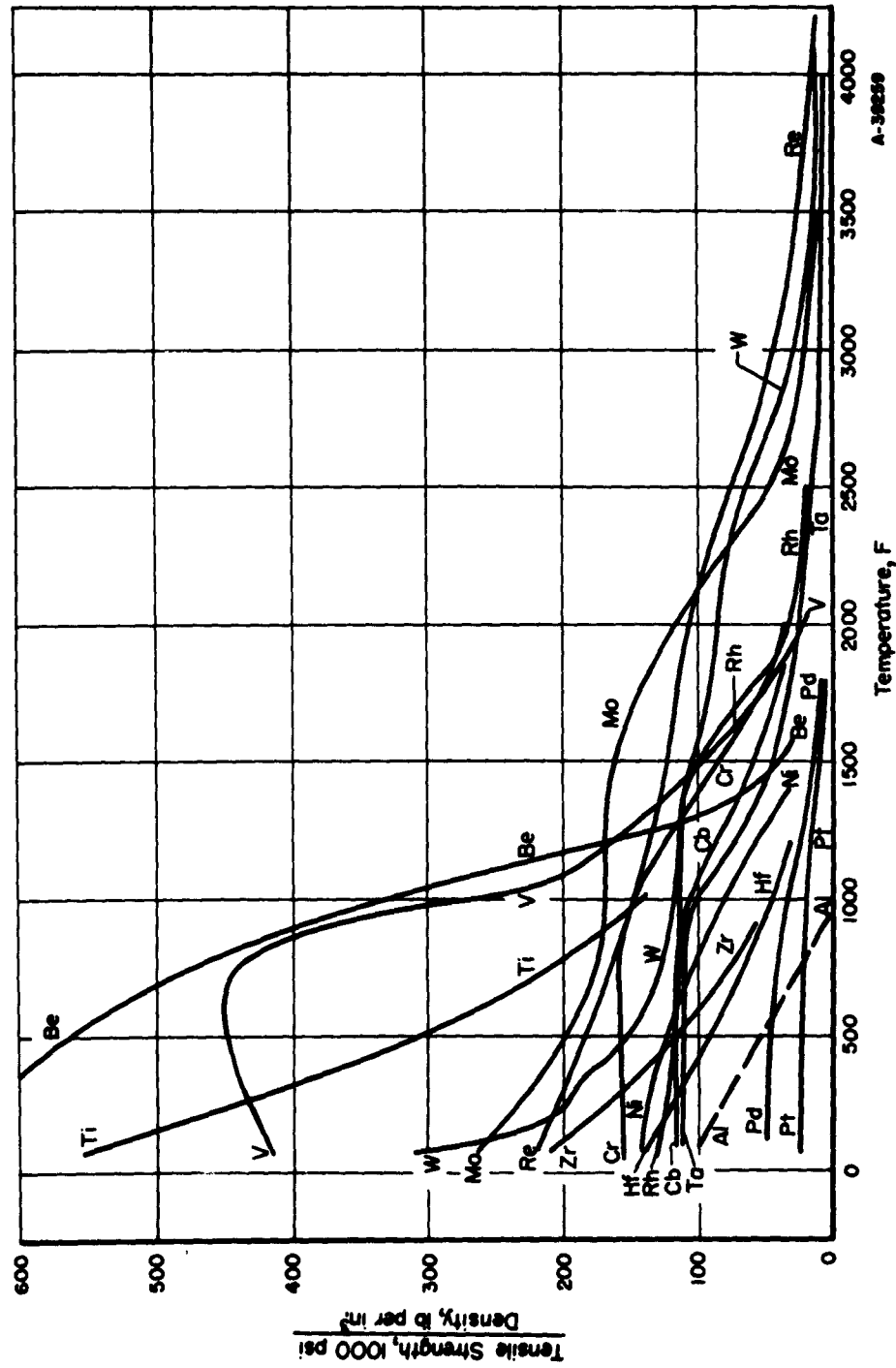


FIGURE 3. TENSILE STRENGTH-DENSITY RATIOS FOR PURE METALS
AT ELEVATED TEMPERATURES

Based on data in Table 7.

TABLE 8. STRESS TO PRODUCE RUPTURE OF PURE METALS

Metal	Stress, 1000 psi, at Indicated																	
	800		900		1000		1100		1200		1300		1400		1500		1600	
	10	100	10	100	10	100	10	100	10	100	10	100	10	100	10	100	10	100
	Hr	Hr	Hr	Hr	Hr	Hr	Hr	Hr	Hr	Hr	Hr	Hr	Hr	Hr	Hr	Hr	Hr	Hr
Tungsten	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	35	33
Rhenium	No rupture data available																	
Tantalum	--	--	--	--	--	--	--	--	--	--	--	15	8	--	--	--	--	--
Molybdenum	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	35	32
Columbium	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Iridium	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Ruthenium	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Hafnium	No rupture data available																	
Rhodium	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Vanadium	No rupture data available																	
Chromium	--	--	--	--	--	--	--	--	--	--	--	17	11.6	--	--	--	12.5	11
Zirconium	No rupture data available																	
Platinum	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Titanium	27	20	--	--	10	8	--	--	--	--	--	--	--	--	--	--	--	--
Palladium	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Iron	No rupture data available																	
Cobalt	--	--	--	--	--	--	--	--	12.5	--	--	--	--	--	3	--	--	--
Nickel	--	--	--	--	25	18	19	14	18	11	--	--	--	--	--	--	--	--
Beryllium	21	17	--	--	6	5	--	--	3.4	2.8	--	--	--	0.35	0.28	--	--	--

IN 10 AND 100 HOURS AT ELEVATED TEMPERATURES

[illegible]

In the compounding of alloys for high-temperature structural applications, the primary reasons for alloy additions are to increase the strength at elevated temperatures and to increase the oxidation and corrosion resistance. The increased strength at high temperatures may result from increased resistance to recrystallization or by solution, precipitation, or dispersion hardening. Alloy additions that provide increased resistance to recrystallization (i. e. , to softening by annealing) essentially promote retention of the high strength associated with wrought structures. The improvement may be manifested either by retention of strength for an increased length of time at a given temperature or by retention of useful strength at increased temperatures. In solution hardening, the alloying element dissolves in the base metal producing a solid solution of greater hardness than the pure metal. Optimum effects of precipitation hardening are achieved by a heat treatment which develops a precipitate in the metal structure that causes increased hardness and strength. In dispersion hardening, an insoluble phase which may be a metallic or a refractory material is finely dispersed throughout the structure. The dispersed phase tends to retard plastic deformation of the alloy structure under load and thereby increases the hardness and strength.

In addition to strengthening by alloying alone, the properties of those alloys that are ductile enough to be worked by swaging, forging, and rolling are usually improved up to the temperature at which recrystallization occurs by the working processes. Such processes break down the coarse as-cast structures which are often brittle at room temperature. On the other hand, when service temperatures are above the recrystallization temperature range of the wrought alloys, some of the cast alloys have better creep resistance. The factors involved are discussed in more detail in subsequent paragraphs which deal with specific alloy systems.

As alloy-development studies are continued, alloys suitable for service at higher temperatures and higher stresses will become available. At the present time, the greatest need is for alloys with increased oxidation resistance at high service temperatures and increased ductility at room temperature (lower ductility-transition temperature). Current work to achieve these objectives will also be discussed.

Tensile-strength capabilities of various alloy systems, as indicated by the present state of the art, are shown in Figure 4. The curves are based on the performance of the important commercial alloys in each system. Some of the curves are illustrative of the tensile strength of a particular alloy. In some instances, current experimental alloys have higher strengths than those represented by the curves in the figure. New titanium alloys for use above 1000 F are an example. Properties of the alloys of each of the important base metals are discussed in the following paragraphs.

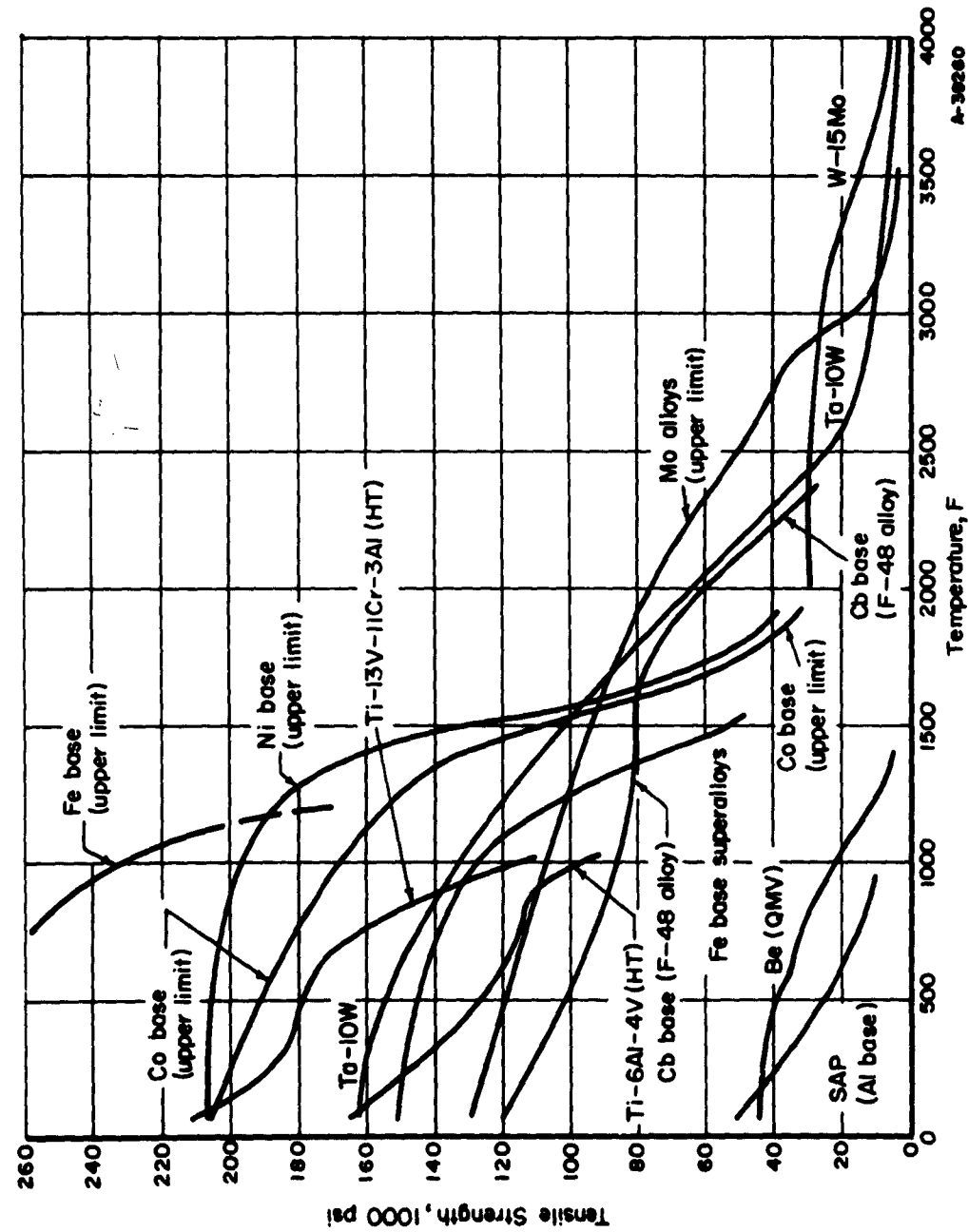


FIGURE 4. ELEVATED-TEMPERATURE TENSILE STRENGTH
ACCORDING TO ALLOY SYSTEM

Alloys of Refractory Metals. Of the six abundant refractory metals discussed previously, there are commercial alloys of tungsten, tantalum, molybdenum, and columbium. These alloys are listed in Table 9. Mechanical properties of some of them are shown in Table 10. The alloys listed are not necessarily commercial in the sense that they are available "off the shelf". However, most of the forging alloys, for example, have been produced on a commercial scale.

The primary uses of tungsten and tungsten alloys are for applications in which the service temperatures are extremely high. Rocket-nozzle inserts are examples that have been mentioned previously. Improved performance of rocket engines is dependent on increased reaction temperatures, and these temperatures are limited by the properties of the materials used in the throats of the nozzles. Therefore, alloy development of tungsten-base alloys has been directed toward improved strength at even higher temperatures, beyond the range of other metals. At the same time, for many applications these alloys must be workable. The tungsten-base alloy with which most experience has been gained is the one containing 15 per cent molybdenum. The tensile strength of this alloy at elevated temperatures is shown in Figure 4.

Because of the high cost of rhenium, the W-30Re alloy is too expensive for most structural applications. However, the ductile-brittle transition range of this alloy is relatively low for tungsten-base alloys. Furthermore, the strength of this alloy remains remarkably high up to the recrystallization-temperature range.

Additions of up to 3 per cent ThO_2 improve the tensile strength of tungsten by dispersion hardening. Other insoluble compounds, such as MgO and Al_2O_3 , also have been added to tungsten for dispersion hardening. An addition of ZrH_2 was found to have a substantial effect in delaying recrystallization.

Because tantalum and many of the alloys of tantalum are very ductile at room temperature, in contrast to tungsten, tantalum alloys have a definite advantage in ease of fabrication over the tungsten-base alloys. However, contaminating elements, such as oxygen, tend to reduce the ductility. Considerable progress has been made in developing tantalum-base alloys that are more resistant than pure tantalum to oxidation, but these alloys are only experimental. They contain various amounts of titanium, zirconium, and hafnium.

The main commercial alloy of tantalum is the Ta-10W alloy which is of the solid-solution type. The tensile strength of this alloy also is plotted in Figure 4. Two other alloys which have high strength at temperatures above 2300 F are Ta-10Hf-5W and Ta-30Cb-7.5V, which are in the advanced experimental development stage. The Ta-30Cb-7.5V alloy has excellent toughness at cryogenic temperatures and maintains strength to 3000 F.

TABLE 9. COMMERCIAL ALLOYS OF THE ABUNDANT REFRACTORY METALS

Base Metal	Alloying Elements, per cent	Type
Tungsten	7Mo	Binary solid solution
	15Mo	Ditto
	50Mo	"
	0.88Cb	"
	0.1Zr	--
	30Re	Two-phase solid solution
	0.5-2ThO ₂	For dispersion hardening
Tantalum	10W	Solid-solution alloys; low ductile-to-brittle transition temperature
	30Cb-7.5V	
	10Hf-5W	
Molybdenum	0.5Ti	Solid-solution alloy
	0.5Ti-0.08Zr (TZM)	Ditto
	0.5Ti-0.10Zr	"
	1.25Ti-0.15Zr	"
	1.0Ti-0.1Zr-0.005C (TZC)	Precipitation hardenable
	0.5Zr	Solid-solution alloy
	30W	Has higher melting point than pure Mo
Columbium	FS-80: 0.75Zr	
	FS-82: 34Ta-0.75Zr	
	F-48 : 15W-5Mo-1Zr-0.05 O-0.05C	
	F-50 : 15W-5Mo-1Zr-5Ti-0.05 O-0.05C	
	D-31 : 10Mo-10Ti	
	Cb-65: 7Ti-0.8Zr	
	Cb-74: 10W-5Zr	
	Cb-7 : 28W-7Ti	
	Cb-16: 20W-10Ti-3V	
	15-20: 15W-20Ta	
	20-20: 20W-20Ta	

TABLE 10. MECHANICAL PROPERTIES OF COMMERCIAL ALLOYS OF REFRACTORY METALS

Alloy and Condition	Property Value at Indicated Temperature, F					
	75	1800	2000	2200	2400	3000
W-15Mo, arc cast						
Tensile Strength, 1000 psi	41		30			25
Elongation, per cent	0		14			17
Ta-10W, recrystallized						
Tensile Strength, 1000 psi	180	94		67		21
Elongation, per cent	4	4		4		17
Mo-0.5Ti, stress relieved						
Tensile Strength, 1000 psi	97	63			20	
Elongation, per cent	1	6			30	
100-Hr Rupture Stress, 1000 psi		50	35	18	10	
Mo-0.5Ti-0.07Zr (TZM), stress relieved						
Tensile Strength, 1000 psi	124	80			40	
Elongation, per cent	14	4			9	
100-Hr Rupture Stress, 1000 psi		70	50			
Mo-1.25Ti-0.15Zr (TZC), stress relieved						
Tensile Strength, 1000 psi	130		102	63		
Elongation, per cent	0		15	6		
10-Hr Rupture Stress, 1000 psi				35		
100-Hr Rupture Stress, 1000 psi				28		
Cb-32.5Ta-0.75Zr (FS-82), worked						
Tensile Strength, 1000 psi	80		30		12	
Elongation, per cent	3		2		--	
10-Hr Rupture Stress, 1000 psi			25			
100-Hr Rupture Stress, 1000 psi			18			
Cb-15W-5Mo-1Zr (F-48), hot worked						
Tensile Strength, 1000 psi	125		65	48	31	
Elongation, per cent	25		19	21	--	
10-Hr Rupture Stress, 1000 psi			44	25		
100-Hr Rupture Stress, 1000 psi			35	16		
Cb-10Mo-10Ti (D-31), worked						
Tensile Strength, 1000 psi	100		35	25	20	
Elongation, per cent	22		12	14	8	

Many molybdenum-base alloys have been studied on an experimental scale. Those shown in Table 9 have reached commercial production. The Mo-0.5Ti alloy has been used more than the others. Most of the present commercial molybdenum alloys are of the solid-solution type. The mechanical properties of these alloys depend mainly on the mechanical working and subsequent annealing treatments. Therefore, one of the principal objectives of alloying molybdenum is to increase the recrystallization-temperature range so that the properties obtained by mechanical working can be retained for high-temperature service. Small amounts of zirconium, hafnium, and titanium are effective in retarding recrystallization.

Molybdenum-base alloys may be prepared by powder-metallurgical methods, or by arc casting, followed by extruding and mechanical working. At temperatures below the recrystallization temperature, the wrought alloys have the best mechanical properties. The ductility-transition temperatures of the wrought commercial molybdenum-base alloys are usually below room temperature as determined by tensile tests (see Appendix A).

A number of columbium-base alloys have been developed for service at elevated temperatures. The most promising are listed in Table 9. The tensile properties of F-48 alloy are shown in Figure 4 and Table 10. The elemental additions in these alloys produce solid-solution or dispersion hardening. The most common elements for solid-solution strengthening in columbium-base alloys are tungsten, molybdenum, and vanadium. Tantalum and titanium also produce solid-solution strengthening but to a lesser extent. Zirconium provides dispersion hardening in columbium. A small addition of carbon with the zirconium induces strengthening by means of a carbide dispersion. These dispersion-hardened alloys may be further strengthened by solution treating at over 3000 F and aging at 1500-2500 F.

For increased strength, the usual approach is to alloy to the limit of fabricability with the solid-solution strengthening elements. However, the commercial alloys are readily fabricated at room temperature.

No commercial alloys of vanadium are available, although alloy development programs are under way on this metal. Additions of columbium, yttrium, rare-earth metals, etc., have been made to vanadium in studies of vanadium-base alloys.

A few chromium-base alloys have been developed, but so far as is known little or no commercial use has yet been made of them. A wrought chromium alloy containing columbium, molybdenum, and tungsten has recently become available, while a cast chromium-nickel alloy has been developed. A chromium-base alloy containing 10 per cent tungsten appears to have creep properties at 1800 F that are superior to most of the nickel- and cobalt-base superalloys.

Alloys of Reactive Metals. The commercial zirconium-base alloys are limited to the Zircalloys, which are used primarily in certain atomic-reactor applications. These solid-solution alloys have been discussed in a previous section. No commercial high-temperature alloys of zirconium are available, but zirconium is used as an alloying element in many of the high-temperature alloys.

Several titanium-base alloys are of interest for service from 800 to 1000 or 1100 F. The tensile strength at elevated temperatures for the heat-treated alloy, Ti-6Al-4V, is shown in Figure 4 and in Table 11. This alloy has good ductility and is readily fabricated at room temperature. However, for certain severe forming operations, the spring back in sheet is less if it is worked warm with warm dies.

The Ti-6Al-4V alloy is described as an alpha-beta alloy because of the presence of the alpha and beta phases in the alloy at room temperature. The types of alloying elements and their amounts determine the phases that will be present in annealed titanium alloys at room temperature. Additions of aluminum, tin, and zirconium, for example, tend to retain the alpha phase, which is the same as in pure titanium at room temperature. On the other hand, additions of vanadium, chromium, and molybdenum tend to cause some of the high-temperature phase (beta) to be retained at room temperature. Whether an alloy is composed of alpha, alpha plus beta, or beta, depends on the balance that is achieved in the alloy composition between the alpha-forming elements and the beta-forming elements. Ti-5Al-2.5Sn and Ti-8Al-1Mo-1V are examples of alpha alloys, which are always used in the annealed condition. The alpha-beta alloys may be solution heat treated by heating to between 1400 and 1700 F, depending on the alloy, followed by cooling in air or quenching in water. The aging of solution-treated metal at 800 to 1100 F results in precipitation of the alpha phase, which causes an improvement in strength. Other examples of alpha-beta alloys are Ti-4Al-3Mo-1V, Ti-4Al-4Mn, and Ti-16V-2.5Al. These alloys may be used in either the annealed or heat-treated (solution treated and aged) conditions, but heat treatment provides higher strengths at room and at elevated temperatures.

One of the highest strength titanium-base alloys is Ti-13V-11Cr-3Al which is referred to as a beta alloy. This alloy may be heat treated to develop tensile strengths of 210,000 psi or higher at room temperature, depending on the section size and the degree of cold working prior to aging. The heat treatment for this alloy involves solution annealing at 1400 F for 1/2 hour and air cooling. The material may then be formed, machined, or cold worked, after which it may be strengthened by aging at 800 to 900 F for 12 hours or more. The temperature limit for this alloy in long-time creep applications is 500 F. However, the material may be used at higher temperatures for short times.

New high-strength titanium alloys are being studied for elevated-temperature service. Some of these experimental alloys have useful strengths for short times to 1600 F. These alloys contain substantial amounts of aluminum and columbium.

TABLE 11. MECHANICAL PROPERTIES OF COMMERCIAL ALLOYS OF REACTIVE METALS AND OF SAP

Alloy and Condition	Temperature, F				
	75	800	900	1000	1100
Zircaloy-2, annealed					
Tensile Strength, 1000 psi	78.8	26	25		
Elongation, per cent	20	39	40		
10-Hr Rupture Stress, 1000 psi		18			
100-Hr Rupture Stress, 1000 psi		16			
Ti (commercially pure), annealed					
Tensile Strength, 1000-psi	85	29		23	20
Elongation, per cent	22	27		51	136
10-Hr Rupture Stress, 1000 psi	75	27		10	
100-Hr Rupture Stress, 1000 psi	72	20		8	
Ti-8Al-1Mo-1V (alpha alloy), duplex annealed					
Tensile Strength, 1000 psi	152	111		92	
Elongation, per cent	18	19		29	
10-Hr Rupture Stress, 1000 psi				67	
100-Hr Rupture Stress, 1000 psi				55	
Ti-6Al-4V (alpha-beta alloy), solution treated and aged					
Tensile Strength, 1000 psi	152	105		81	
Elongation, per cent	15	18		30	
10-Hr Rupture Stress, 1000 psi		96	79		
100-Hr Rupture Stress, 1000 psi		83	58		
Ti-13V-11Cr-5Al (beta alloy), solution treated and aged					
Tensile Strength, 1000 psi	198	167	145		
Elongation, per cent	5	5	5		
SAP (sintered aluminum product)					
Tensile Strength, 1000 psi	50		10		
Elongation, per cent	10		<1		
10-Hr Rupture Stress, 1000 psi			9		
100-Hr Rupture Stress, 1000 psi			8.4		

Iron-Base Alloys. As mentioned in one of the previous sections, a large number of iron-base alloys are available. Depending on the composition and the application, they may be used at various temperatures. Some are used at temperatures as high as 2300 F. Typical elevated-temperature tensile strengths for some iron-base alloys are plotted in Figure 5.

Elevated-temperature strength of 5Cr-Mo-V steel is shown in the figure. This steel is normally used in the quenched-and-tempered condition. The strengths shown were obtained on specimens tempered at 1000 F. The service temperatures for this type of steel should be lower than the tempering temperature by 50 to 100 degrees.

Elevated-temperature tensile strengths for a modified grade of 12Cr stainless steel are shown in Figure 5. This steel also is used in the quenched and tempered condition. Typical strengths of Type 301 stainless steel cold rolled 65 per cent, PH15-7 Mo stainless steel (precipitation hardened), and annealed Type 304 austenitic stainless steel are also shown in the figure. Some of the more highly alloyed austenitic stainless steels (wrought) have somewhat higher strengths than Type 304. Tensile data for one of the normalized alloy steels and one of the high-temperature iron-base casting alloys (HH) are also shown.

Compositions of some of the iron-base high-temperature alloys are given in Table 12. The upper limit of the tensile strengths of these alloys at elevated temperatures is shown in Figure 4, and the temperatures for rupture in 100 hours at 15,000 psi stress are shown for some of them in Figure 6. These alloys contain relatively large amounts of nickel, chromium, and molybdenum for strengthening purposes. Their oxidation resistance at elevated temperatures is enhanced by the nickel and chromium. They also contain titanium and/or aluminum, which make possible precipitation hardening. The latter involves solution treating at about 1800 F and aging at about 1300 F. All steps in processing these alloys must be controlled carefully to obtain the desired properties.

Several new grades of iron-base alloys containing 18 to 27 per cent nickel have been developed recently that show promise for service at high strength levels and at elevated temperatures. The 20 to 27 per cent nickel grades contain small amounts of titanium, aluminum, and columbium, while the 18 per cent nickel grade contains 7 per cent cobalt and 5 per cent molybdenum and less than 0.5 per cent titanium. These steels are solution treated by heating to 1500 F and cooling in air. After fabricating, they are aged at about 900 F to develop yield strengths over 250,000 psi. Ductility and toughness of these steels are very good. Elevated-temperature properties have not been established, but they will doubtless have excellent strengths around 800 F.

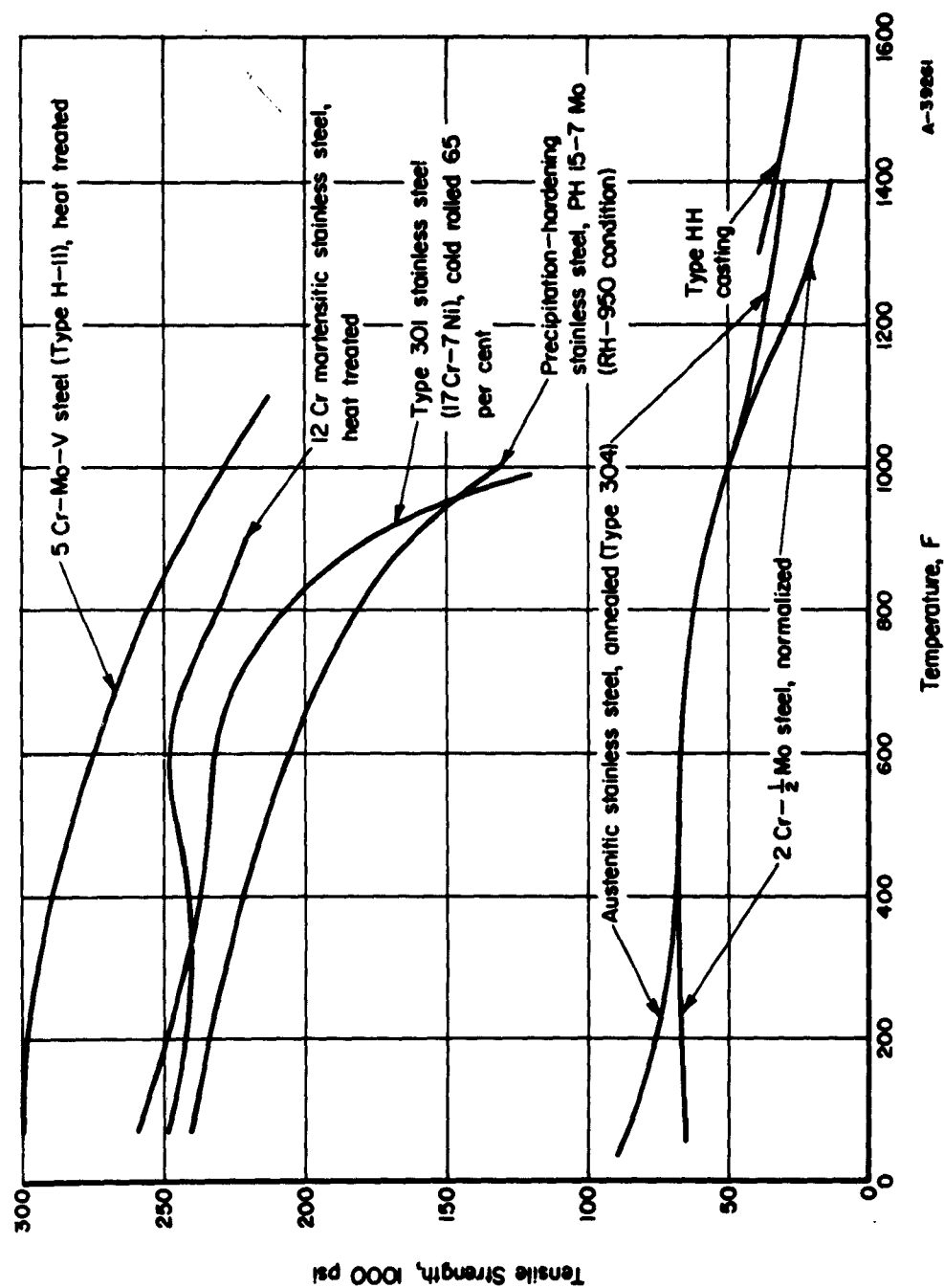


FIGURE 5. ELEVATED-TEMPERATURE TENSILE STRENGTH OF SEVERAL TYPES OF IRON-BASE ALLOYS

TABLE 12. SOME HIGH-TEMPERATURE ALLOYS OF IRON, COBALT, AND NICKEL

Name	Form ^(a)	Composition, per cent												
		C	Mn	Si	Cr	Ni	Co	Mo	W	Cb	Ti	Al	Fe	Other
<u>Iron Base</u>														
A-286	Wrought	0.05	1.35	0.50	15	26	--	1.25	--	--	2.0	--	Bal.	0.3V, 0.005B
M-813	Wrought	0.08	--	--	18	35	--	4.0	--	--	2.25	1.4	Bal.	--
Incoloy 901	Wrought	0.05	0.5	0.35	13	40	--	6.0	--	--	2.5	0.2	Bal.	--
HS-88	Wrought	0.07	1.5	0.50	12.5	15	--	2.0	0.6	--	0.6	--	Bal.	0.15B
<u>Chromium, Nickel, Cobalt, Iron Alloys</u>														
S-590	Wrought	0.43	1.25	0.40	20.5	20	20	4.0	4.0	4.0	--	--	Bal.	--
Haynes No. 99	Wrought	0.10	1.50	0.70	21	18	12	4.0	2.5	--	--	--	Bal.	0.05B
N-155	Wrought	0.15	1.50	0.50	21	20	20	3.0	2.5	1.0	--	--	Bal.	0.15N
Refractaloy 70	Wrought	0.05	2.00	0.20	20	20	30	8.0	4.0	--	--	--	15	--
<u>Cobalt Base</u>														
S-816	Wrought	0.38	1.20	0.40	20	20	Bal.	4.0	4.0	4.0	--	--	4	--
S-816 + B	Castings	0.40	1.00	0.40	20	20	Bal.	4.0	4.0	4.0	--	--	3	1.0B
HS-25	Wrought	0.15	1.50	0.50	20	10	Bal.	--	15	--	--	--	--	--
J-1570	Wrought	0.20	--	--	20	28	38	--	7	--	4.0	--	2	--
J-1650	Wrought	0.20	--	--	19	27	Bal.	--	12	--	3.8	--	--	2.0Ta ^(b) , 0.02B
HS-31	Castings	0.50	1.00	1.00	25.5	10.5	Bal.	--	7.5	--	--	--	2	--
Haynes No. 151	Castings	0.55	--	--	20	--	Bal.	--	12.5	--	--	--	--	--
WI-52	Castings	0.45	0.50	0.50	21	1	Bal.	--	11	--	--	--	2	1.75Ta ^(b)
<u>Nickel Base</u>														
M-252	Wrought	0.15	0.50	0.50	19	55	10	10	--	--	2.5	1.0	2.0	--
Astraloy	Wrought	0.10	--	--	15.4	Bal.	15.4	5.8	--	--	4.0	4.2	0.2	0.03B
René 41	Wrought	0.09	--	--	19	Bal.	11.0	10	--	--	3.0	1.5	--	--
Udimet 700	Wrought	0.15	--	--	15	Bal.	18.5	5	--	--	3.5	4.0	1	0.1B
Unitemp 1753	Wrought	0.25	--	--	12	Bal.	10.0	--	8	--	4.0	4.0	9.5	0.008B, 0.05Zr
IN-100	Castings	0.17	--	--	10	Bal.	15.5	3	--	--	5.0	5.5	--	1.0V, 0.01B, 0.05Zr
Inconel "713C"	Castings	0.20	--	--	12.5	Bal.	--	4.2	--	--	0.75	6.0	5	--
Inco "717C"	Castings	0.20	--	--	12	Bal.	8.0	4.2	--	--	1.0	7.5	2	0.1B, 0.1Zr
Nicrotung	Castings	0.10	--	--	12	Bal.	10.0	--	8	--	4.0	4.0	--	0.05B, 0.05Zr

(a) All wrought alloys are heat treated.

(b) Ta + Cb.

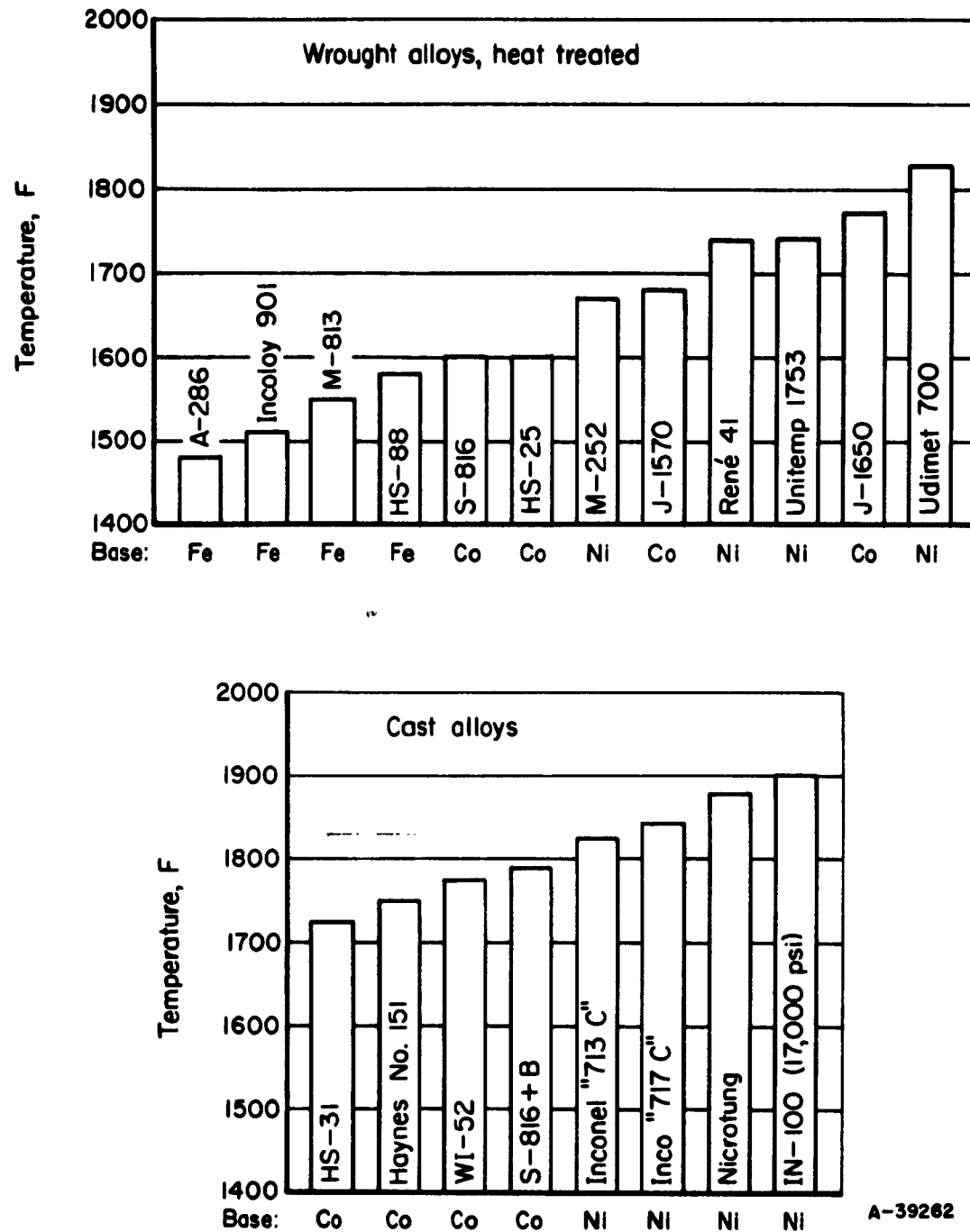


FIGURE 6. TEMPERATURES FOR 100-HOUR RUPTURE TIME AND 15,000-PSI STRESS FOR VARIOUS SUPERALLOYS

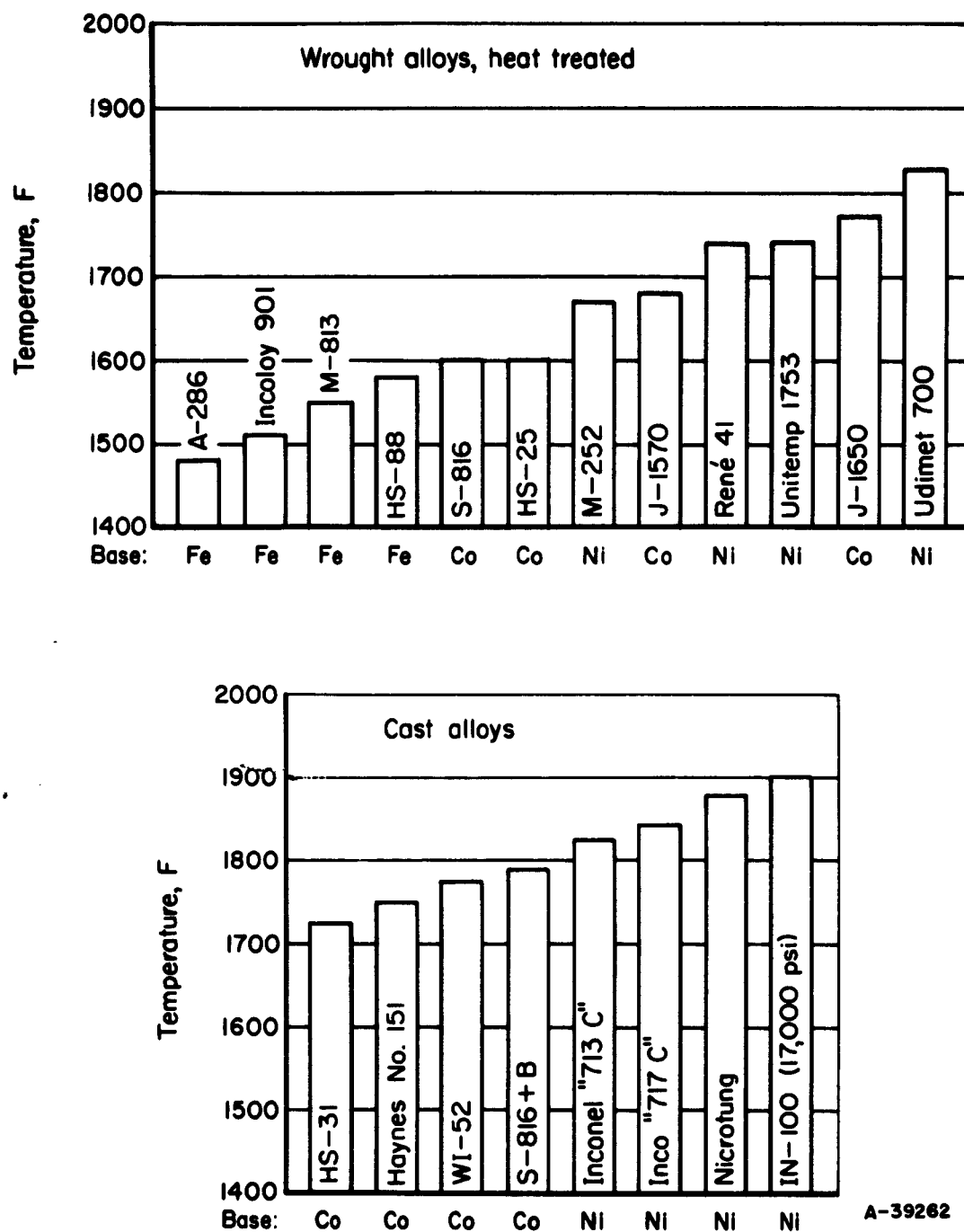


FIGURE 6. TEMPERATURES FOR 100-HOUR RUPTURE TIME AND 15,000-PSI STRESS FOR VARIOUS SUPERALLOYS

Cobalt and Nickel Alloys. Development of cobalt-base alloys has been directed toward achieving alloys with high strength at temperatures above the upper limits of the iron-base alloys. The current cobalt-base superalloys contain 19 to 25 per cent chromium, which together with the carbon yields a high-strength material hardened by a carbide-precipitation mechanism. Nickel is usually included in the alloys, and at least one of the high-melting carbide-forming elements such as tungsten, molybdenum, tantalum and columbium is present in various amounts. Boron additions to the S-816 alloy have yielded improved high-temperature mechanical properties. Titanium is an important addition to the two wrought alloys, J-1570 and J-1650. Table 12 shows the nominal compositions of some of the cobalt-base superalloys. The upper limit of their elevated-temperature tensile strengths is shown in Figure 4, and typical stress-rupture data are shown in Figure 6. The cast alloys have better stress-rupture properties than the wrought-and-heat-treated alloys. Other properties are shown in Table 13.

With respect to composition, the current nickel-base superalloys have much in common (Table 12). They all consist of a nickel-chromium solid solution to which have been added various amounts of tungsten (8 per cent) or molybdenum (4 to 10 per cent) to strengthen the matrix solid solution. Except for Inconel "713C", all of the newer nickel-base superalloys contain appreciable amounts of cobalt, which increases the creep strength of precipitation-hardenable nickel-base alloys. Precipitation hardening, which contributes to the high-temperature strength, is brought about by the presence of aluminum (1.5 to 7.5 per cent) and titanium (0.75 to 4 per cent). Boron and zirconium are present in some of these alloys and appear to have a beneficial effect on the high-temperature strength and ductility. In order for the alloys to be workable, limitations must be put on the amounts of titanium, aluminum, zirconium, and boron present. Vacuum melting these alloys permits better control of composition and improved creep properties.

The cast nickel-base alloys also have better stress-rupture properties than the wrought-and-heat-treated alloys, as shown in Figure 6.

Beryllium Alloys. Development of beryllium alloys is limited, and no "true" alloys are available commercially. However, the BeO content (to 2 per cent) in vacuum-hot-pressed beryllium has a definite effect in inhibiting grain growth of the beryllium at elevated temperatures. Typical elevated-temperature strengths of this material are shown in Figure 4.

Aluminum Alloys. Sintered aluminum product material (SAP) is being developed for its elevated-temperature properties. It is made by powder-metallurgical techniques from aluminum powder partially oxidized, giving a finely divided aluminum-aluminum oxide mixture. It is somewhat like the Be-BeO mixture mentioned in the above paragraph. Typical tensile properties at elevated temperatures are also shown in Figure 4 and Table 11 for SAP material. It has properties at 800 F that may warrant its use. The

TABLE 13. MECHANICAL PROPERTIES OF SOME SUPER-ALLOYS

Alloy and Condition	Property Value at Indicated Temperature, F						
	75	800	1000	1200	1400	1600	1800
<u>Iron Base</u>							
A-286, wrought and heat treated							
Tensile Strength, 1000 psi	150	138	131	104	64	37 (1500 F)	
Elongation, per cent	18	18	18	13	18	68 (1500 F)	
100-Hr Rupture Stress, 1000 psi			100	63	30	13 (1500 F)	
<u>Nickel Base</u>							
René 41, wrought and heat treated							
Tensile Strength, 1000 psi	208	206	204	193	161	92	40
Elongation, per cent	14	14	14	13	11	18	37
10-Hr Rupture Stress, 1000 psi					92	45	18
100-Hr Rupture Stress, 1000 psi					68	28	10
Nicrotung, as cast							
Tensile Strength, 1000 psi	130	123	121	120	116	88	66
Elongation, per cent	5	9	11	11	7	4	6
10-Hr Rupture Stress, 1000 psi						65	36
100-Hr Rupture Stress, 1000 psi						48	22
<u>Cobalt Base</u>							
J-1650, wrought and heat treated							
Tensile Strength, 1000 psi	208	178	168	155	130	90	40
Elongation, per cent	27	14	11	7	4	3	14
10-Hr Rupture Stress, 1000 psi					80	47	22
100-Hr Rupture Stress, 1000 psi					65	33	13
No. 151, as cast							
Tensile Strength, 1000 psi	103			85		62 (1500 F)	
Elongation, per cent	8			13		9 (1500 F)	
10-Hr Rupture Stress, 1000 psi						42 (1500 F)	16
100-Hr Rupture Stress, 1000 psi				72		37 (1500 F)	14

TABLE 14. REPRESENTATIVE PHYSICAL PROPERTIES OF

Element	Melting Temperature, F	Crystal Structure (68 F to mp)	Density lb/in. ³ at 68 F	Thermal Conductivity Near 68 F Btu/(hr)(ft ²)(F/in.)	Electrical Resistivity Near 68 F, microhm-cm
Tungsten	6170	Bcc	0.697	1150	5.65
Rhenium	5755	Hcp	0.756	495	19.3
Osmium	5432	Hcp	0.815	--	9.5
Tantalum	5425	Bcc	0.600	375	12.45
Molybdenum	4730	Bcc	0.369	990	5.2
Columbium	4474	Bcc	0.310	360	12.5
Iridium	4449	Fcc	0.813	405	5.3
Ruthenium	4082	Hcp	0.441	--	7.6
Hafnium	4032	Hcp (bcc, 3200 F-mp)	0.473	155	35.1
Rhodium	3571	Fcc	0.449	610	4.51
Vanadium	3450	Bcc	0.220	215	25
Chromium	3407	Bcc	0.260	465	12.9
Zirconium	3366	Hcp (bcc, 1584 F-mp)	0.234	145	40
Platinum	3217	Fcc	0.775	495	10.6
Titanium	3035	Hcp (bcc, 1620 F-mp)	0.163	140	42
Palladium	2826	Fcc	0.434	495	10.8
Iron	2798	Bcc (fcc, 1670-2534 F)	0.284	520	9.71
Cobalt	2723	Hcp (fcc, 785 F-mp)	0.322	480	6.24
Nickel	2647	Fcc	0.322	640	6.84
Beryllium	2332	Hcp	0.067	1000	4
Aluminum	1220	Fcc	0.0975	1540	2.66

Note: Melting temperatures are from Metals Handbook 8th Edition, American Society for Metals (1961), except for osmium and ruthenium. Their melting points have been more recently determined at Battelle Memorial Institute. This work by R. W. Douglass and E. E. Adkins has been submitted to AIME for publication.

METALS WITH USEFUL STRENGTH ABOVE 800 F

Coefficient of Linear Thermal Expansion Near 68 F, in./in.(F)	Tensile Elastic Modulus Near 68 F, 10 ⁶ psi	Specific Heat Near 68 F, Btu/(lb)(F)	Heat of Fusion, Btu/lb	Spectral Emittance at 0.65 Micron on Unoxidized Solid Surface	Thermionic Work Function, electron volts
2.55	50	0.033	70	0.43	4.52
3.7	67	0.033	--	0.42	5.1
2.6	81	0.031	--	--	--
3.6	27	0.034	68	0.49	4.19
2.7	47	0.066	126	0.37	4.20
4.1	15	0.065	124	0.37	4.01
3.8	76	0.031	--	0.30	--
5.1	60	0.057	--	--	--
3.3	17	0.035	--	--	3.53
4.6	42	0.059	--	0.24	4.80
4.6	19	0.119	--	0.35	--
3.4	41	0.11	173	0.34	4.60
3.2	14	0.067	110	0.32	4.12
4.9	21	0.031	48	0.30	5.32
4.67	17	0.124	188	0.63	--
6.53	16	0.058	62	0.33	4.99
6.5	28.5	0.11	118	0.35	4.04
7.66	30	0.099	105	0.36	4.40
7.4	30	0.105	133	0.36	5.03
6.4	42	0.45	470	0.61	--
13.1	9	0.215	170	--	--

common alloys of aluminum are usually limited to temperatures lower than 800 F except for rapid-loading applications. The same is true for magnesium alloys.

General Comment. From this review of the mechanical properties of alloys, it is evident that tungsten- and tantalum-base alloys are useful in the temperature range from 3000 to about 4000 F (or higher for tungsten). Present molybdenum alloys are useful to about 3000 F and columbium-base alloys to about 2500 F. Certain cobalt- and nickel-base alloys can be used to 2000 F, while the best iron-base alloys are limited to about 1600 F (except for the high-temperature casting alloys). Some current titanium-base alloys may be used to 1000 or 1100 F, while the SAP material is probably limited to 800 F. Oxidation resistance and ease of fabrication must also be considered in all applications for these alloys. These factors are considered in later sections.

Physical Properties

Representative physical properties of the 21 metals considered for use above 800 F are given in Table 14. The metals have melting points which range from 1220 F for aluminum to 6170 F for tungsten. Vapor pressures at the melting point generally are below 0.1 mm Hg except for chromium, which has a vapor pressure of about 10 mm. Crystal structures are cubic or close-packed hexagonal, with iron, cobalt, titanium, zirconium, and hafnium having allotropic transformations above 700 F. Typical values of density, thermal conductivity, electrical resistivity, expansion coefficient, elastic modulus, specific heat, heat of fusion, emittance, and work function are listed.*

The values listed for pure metals do not necessarily hold for alloys, even if a linear mixture rule is applied. For example, the austenitic Type 302 stainless steel - Fe-18Cr-8Ni-<0.15C-<2Mn-<1Si - has properties quite different than those of iron, even though chromium and nickel have many physical properties similar to those of iron. Alloying the iron causes:

- (1) Melting temperature to fall from 2802 to about 2570 F
- (2) Crystal structure to change from body-centered cubic to face-centered cubic
- (3) Reduction in the thermal conductivity at 68 F by a factor of 4/5
- (4) Sevenfold increase in electrical resistivity

* These terms are defined in Appendix A.

- (5) Fifty per cent increase in the thermal expansion at 68 F
- (6) Little change in density, elastic modulus, heat of fusion, specific heat, emittance, and work function.

The physical properties of a specific alloy may be found in handbook tables if it is a common alloy composition. If not, the desired physical properties may have to be determined experimentally. Physical properties are important considerations in melting and purifying operations, as well as in fabrication and use. They become increasingly important when applications in space environments are under consideration.

REACTIONS WITH GASES

Oxidation of Unalloyed Metals

The usefulness of many of the high-melting-point metals is restricted by their poor oxidation resistance. The oxidation behavior of some of these metals is indicated in Figure 7. In some cases oxidation results in a weight loss because the oxide melts or volatilizes and in other cases an oxide scale builds up. Above 2200 F tungsten oxide volatilizes appreciably. Vanadium forms a molten oxide at 1220 F and is not considered oxidation resistant. Nickel oxidizes at about the same rate as chromium, while iron oxidizes considerably more rapidly. Generally the metals tungsten, rhenium, tantalum, molybdenum, and columbium, which show the highest strengths and creep properties at elevated temperatures, have poor oxidation resistance. For example, tungsten oxidizes in air about 1000 times too rapidly for satisfactory service at 1800 F. The adherent oxide film on chromium inhibits further oxidation to about 1700 F, but exposure to nitrogen above 1300 F causes embrittlement of chromium. Use of aluminum, platinum, rhodium, zirconium, and hafnium is limited more by strength than by oxidation resistance at elevated temperatures.

Effect of Alloying on Oxidation Behavior

Alloying can improve the oxidation resistance of pure metals. With 10 to 30 per cent chromium in iron, nickel, or cobalt, the resulting oxidation resistance is sufficient at temperatures of use (up to about 2000 F). An addition of 15 per cent aluminum to iron also improves its oxidation resistance. Additions of molybdenum, tungsten, vanadium, hafnium, zirconium, titanium, and silicon have significantly improved the oxidation resistance of columbium by inducing more stable complex oxides to form. Tantalum is expected to be improved similarly. Additions of under 1 per cent yttrium to chromium reduce nitrogen penetration.

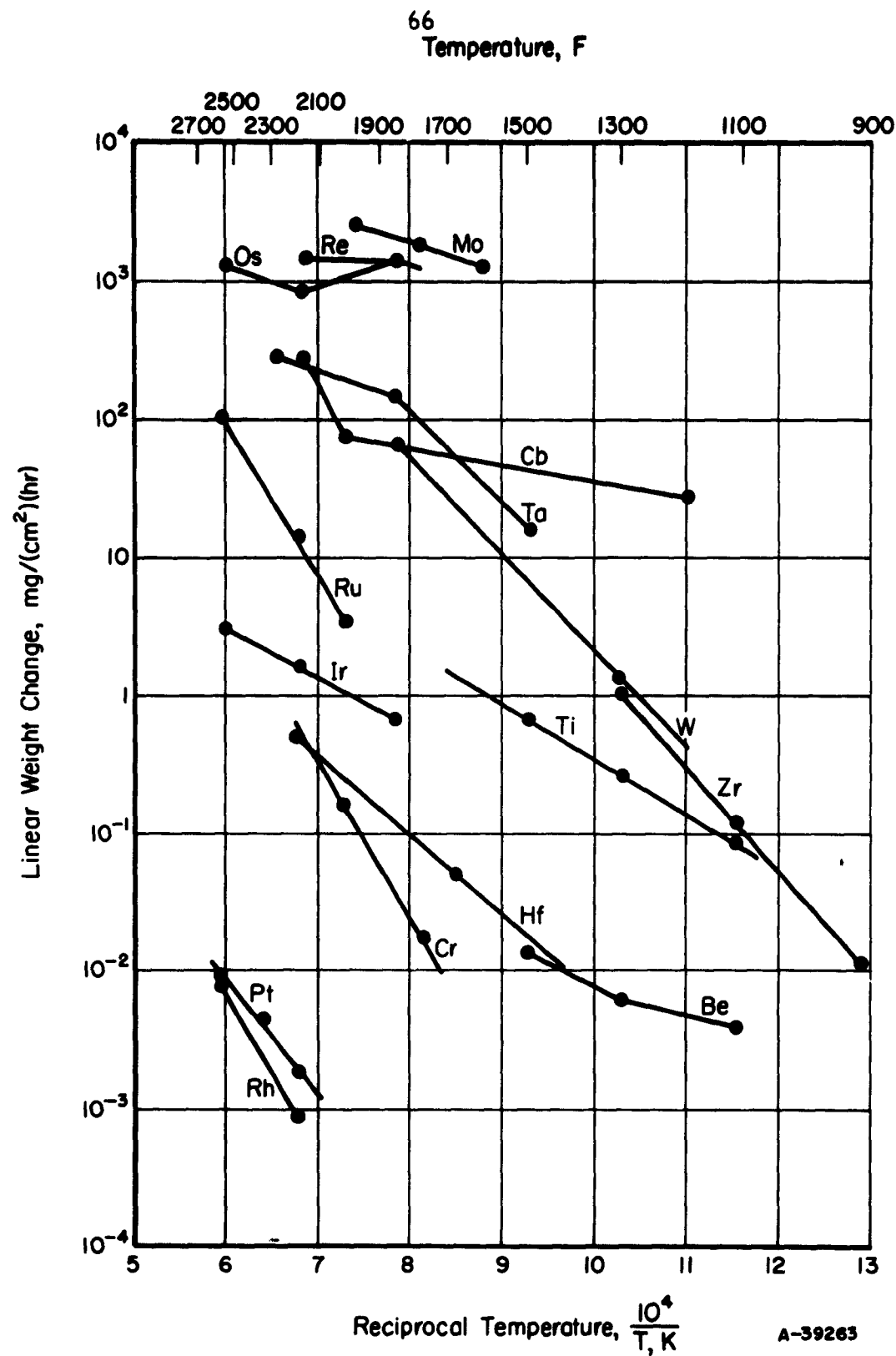


FIGURE 7. OXIDATION OF SOME METALS

Data for Mo, Re, Os, Ru, Ir, and Rh are weight-loss rates.

Alloying can increase the oxidation resistance of metals which develop low-melting volatile oxides (molybdenum, tungsten, rhenium, and vanadium). Generally, if the refractory metal base is retained, the alloys still do not have sufficient oxidation resistance at high temperatures. Furthermore, such additions as 20 to 30 per cent tantalum or columbium to molybdenum or tungsten increase the solubility of oxygen in the material and thereby promote embrittlement.

At temperatures over 800 F, steels, superalloys, and refractory metals can be corroded by such gases as H_2S , SO_2 , CO , CO_2 , HCl , NO , N_2 , and H_2 , which are contained in rocket exhausts. Corrosion rates generally increase with increasing temperature, gas concentration, gas velocity, and moisture content. Stainless steels and superalloys are quite resistant to oxygen-containing gases, but less so to sulfur-containing gases, moist HCl , or $N_2 + H_2$ mixtures. Tungsten, tantalum, columbium, and molybdenum resist sulfur-containing but not oxygen-containing gases.

Abrasion resistance tends to increase as the hardness of the alloy increases. Abrasion resistance is important in resisting wear or penetration by abrasive particles in primary air (for compressor blades), in high-temperature high-velocity exhaust gases, in space (micrometeorites), etc.

Protective Coatings

A logical method of increasing the oxidation resistance of refractory metal alloys and superalloys is to coat them with some protective material. Coating materials can be weaker but more resistant to oxidation than the metal to be coated. Little work has been done on coating superalloys since they already have good oxidation resistance. However, proprietary diffusion coatings of nickel and aluminum or iron-aluminum reduce intergranular attack and raise useful operating temperatures to as high as 2300 F for Alloy No. "713C", for example. No promising coatings have been developed for chromium and vanadium alloys.

Considerable research has been done and is in progress on the problem of protecting tungsten, tantalum, molybdenum, and columbium alloys from oxidation at high temperatures. Molybdenum as the metal or alloy-base substrate has received the most attention. Additional research will be required on oxidation-resistant coatings for these refractory metals before reliable coating systems will be available for service at high temperatures in air. However, coated molybdenum-alloy jet-engine buckets have been satisfactory on an experimental basis.

The status of coatings development should be viewed from the standpoint of three different temperature-time applications as follows:

Coating Class	Temperature, F	Time
I	2000-2500	50 to 100 hours
II	2500-3000	Up to several hours
III	Over 3000	Up to several hours

In addition to the diffusion coatings discussed above for superalloys, a number of other processes have been used for applying protective coatings. These processes include electrodeposition, flame spraying, vapor and pack deposition, cladding, and enameling. More recently, flame spraying with a plasma torch has been used for applying coatings. Progress has been made in overcoming many of the original problems, such as matching thermal expansion of the coating to the base metal and compatibility of the coating and base metal. However, many of the coatings are brittle, or require firing at temperatures above the recrystallization temperature of the base metal, or offer protection only to 2000 F, or are porous.

No satisfactory protective coatings for tungsten or tantalum for service over 3000 F are available. A sprayed coating of 50Al-50Sn protects tantalum and Ta-10W for 10 hours at 2500 to 3000 F.

For molybdenum and molybdenum alloys, nickel-chromium-boron, nickel-silicon-boron, aluminum-chromium-silicon, and molybdenum disilicide modifications have been applied by flame spraying with considerable success. Siliconized and chromized coatings are the foremost among coatings that can be applied by vapor deposition. Excellent coverage, uniformity of coating, and control of thickness are characteristics of vapor-deposited coatings. Modification of the chromized coating has resulted in a reliable coating for use up to about 2700 F. Inconel and Ni-20Cr claddings have been applied to molybdenum with good results.

These coatings and combinations of them have been tried on components used in gas turbines, ramjet engines, and other applications with marked improvement in service performance. However, further improvements in coatings are needed for molybdenum alloys to achieve the high-temperature service that is indicated by the mechanical properties.

For columbium and columbium alloys, coatings of (Cr-Ti)-Si have been used successfully. The optimum coating consists of a Cr-50Ti layer about 0.001 inch thick (applied by vacuum distillation at 2350 F) overlaid with silicon about 0.001 inch thick (applied by vacuum distillation at 2200 F). The coating life decreases with increasing temperature. Columbium, D-31, and F-48 alloys are protected in cyclic oxidation at 2500 F for 12, 24, and 20 hours, respectively. At 2800 F, this coating protected D-31 alloy for 1 hour.

APPENDIX A

CHARACTERISTICS DESIRED IN A METAL
FOR HIGH-TEMPERATURE SERVICE

APPENDIX A

CHARACTERISTICS DESIRED IN A METAL FOR HIGH-TEMPERATURE SERVICE

GENERAL

In reviewing high-temperature materials, it is desirable to define what these materials are. A tentative definition is presented in this section.

To understand which metals are most suitable for various high-temperature applications and why, it is necessary to know what characteristics or properties are required for these applications and the properties of the available metals and alloys at room temperature and at the service temperature. It is convenient to classify the desired properties of high-temperature materials into four categories: mechanical properties, oxidation and corrosion resistance, physical properties, and fabricability. These terms are also discussed in this section.

TENTATIVE DEFINITION OF HIGH-TEMPERATURE MATERIALS

"High-temperature materials" will be defined as all materials which are solid at the temperature of intended application and which are to be used at temperatures above the following:

- 800 F for metals
- 800 F for ceramics and metal-ceramics composite materials
- 300 F for plastics, metal plastic composites, elastomers and other materials

This definition will include materials intended for both structural (load bearing) and nonstructural applications. It will specifically include coatings and coating materials intended to protect the base material against oxidation, corrosion, erosion, ablation or other attack or intended to change the emissivity, work function, or other surface properties of the base material at service temperatures exceeding those given above. (It will not, however, include reflective or flame-retardant paints intended for temporary protection of inflammable materials). This definition will also specifically include

solid sealants and gasketing materials intended for use at temperatures above those indicated. It will also specifically include adhesives, brazing compositions, and weld filler metals. It will include materials intended to dispose of heat through ablation (this is a specific exception to the stipulation that all materials included in the definition are solid at the service temperatures) and solid materials used as "heat sinks" at service temperatures exceeding those specified.

This definition will specifically exclude materials intended for use as fuels. It will also exclude semiconductor materials and materials for solid-state amplifying, rectifying, or power-generation devices. Solid lubricants are also excluded.

Since only solid materials are included in this definition, materials intended for use as hydraulic fluids, heat transfer fluids, or coolants are excluded.

Fire retardant materials for treating wood, fabrics, etc., are specifically excluded.

MECHANICAL PROPERTIES

Strength

For structural (load bearing) applications, one of the important mechanical properties is strength at service temperature. The strength of metals decreases markedly as the temperature is increased, but the change is different for each metal, so the strongest material at one temperature may not be the strongest at a different temperature. Many of the applications for materials at high temperature are in aircraft or missiles where weight is important; in these cases, strength-to-weight ratio is more important than strength alone. For example, a piece of high-strength steel may be nearly three times as heavy as the same size piece of a certain aluminum alloy. But if the steel is four times as strong, a steel structure of a given strength will be lighter than the aluminum structure with the same strength.

Two strength values are commonly reported, yield strength and ultimate strength. Yield strength is the stress necessary to deform the metal beyond the point where it will "spring back" when the stress is removed. This is important because a metal part need not break to "fail" - it may become just as useless if bent or stretched too far. Yield strength is usually reported as the stress necessary to cause 0.2% permanent elongation (offset) in a test bar, although other elongations may be specified. Not all

materials have a definite yield strength. Some yield a little even at very low stresses (the amount of yielding increases with stress after yielding starts) and some break without any plastic yielding. Ultimate strength is the maximum stress reached before the metal breaks and is based on the original cross-sectional area.

Creep Resistance

Closely allied to strength is "creep resistance". A continued stress too small to cause immediate yielding (deforming beyond the point of spring back) can nevertheless cause gradual deformation of a piece of metal over a period of time. This is referred to as "creep". The rate at which metals creep under a given load increases greatly with increasing temperature. Thus, the time required for a metal part to deform too much to be of further use may vary from hundreds of years at room temperature to a few minutes at a temperature near the melting point. At room temperature, creep is a practical problem for only a few of the low melting metals like lead and zinc. At high temperatures, it is a problem with all materials.

In practice, one designs for creep by noting the maximum deformation permissible in the part and noting the desired service life (which may range from seconds for some missile parts to many years for boilers). After the stress necessary to cause this amount of deformation in the specified length of time at the service temperature has been determined experimentally*, the structure is designed so that stresses do not exceed this level. It is somewhat easier to determine the stress necessary to cause rupture (to actually break the specimen) than to determine the stress necessary to cause some small precise amount of deformation in a given length of time. Therefore "stress rupture" data are widely used as a measure of the relative creep resistance of materials. For comparing high-temperature materials, it is a common practice to determine the stress necessary to cause rupture in 10 hours and the stress necessary to cause rupture in 100 hours.

Notch Sensitivity

There is one other aspect of strength that it is necessary to consider in some detail. This is the effect of small defects or "notches" on the strength of a material. Materials differ greatly in their ability to tolerate such defects without being seriously weakened, that is, they vary in their "notch sensitivity" or "fracture toughness". Various tests have been devised in which notched or deliberately cracked test specimens are used to

*Fortunately there are ways of predicting long-time behavior from relatively short-time tests so it is not necessary to run 30-year creep tests.

evaluate sensitivity to defects and "crack-stopping ability", which is closely related. Thus, the "notched bar strength", the ratio of "notched-to-unnotched" strength, or fracture toughness criteria are often used to characterize materials in this respect.

Ductility

Another very important mechanical property in high-temperature materials is ductility. Roughly speaking, ductility is the ability of a metal to deform plastically without fracturing.

In a ductile material, if the stress in some localized region exceeds the material's yield strength, the material simply deforms a little in this area and thus lowers the localized stress and redistributes the stresses in the part. In practice, even with the most careful design, it is very difficult to avoid localized stress concentrations in highly-stressed components.

The standard tensile test also gives information on ductility. Both the amount the bar stretches before breaking (per cent total elongation) and the amount by which it "necks down" to a smaller diameter before breaking (per cent reduction in cross-sectional area) are indicative of ductility.

It should be made clear that although we speak of ductile and brittle materials, these are only relative terms. Actually, the measured ductility of the same material varies greatly with the conditions under which it is measured. The most important things which affect ductility are the stress system, the speed at which one attempts to deform the metal (strain rate), and the temperature.

Under the proper stress system (high hydrostatic pressure) even marble and granite will behave as if ductile. On the other hand, when we pull a test bar of a ductile metal, it can become longer only because it narrows down in diameter. If the metal is restrained so it cannot narrow down, it will tend to behave as if brittle.

By far the most important factor which affects ductility is temperature. Aside from a few metals (silicon and boron, for example*) which are completely brittle at all temperatures, all the rest are ductile at some elevated temperature. They fall into two classes, however, with respect to ductility at lower temperatures. In one broad class of metals (nickel and copper are examples) ductility gradually decreases with decreasing temperature, but some, or even considerable, ductility is retained at the lowest attainable (subzero) temperatures. In the other broad class of materials, ductility

*One could perhaps argue whether these are really metals at all.

suddenly practically disappears, below a critical temperature which is called the "ductility-transition temperature". Carbon steels, molybdenum, and tungsten are examples. Above the transition temperature, these metals are ductile - below it, brittle. Since strain rate (speed of deformation) and the stress system also affect ductility as noted, the exact transition temperature depends on these factors and, therefore, different testing procedures give different values for transition temperature. In reporting transition temperatures, it is therefore necessary to specify the test used. The same test must be used in comparing materials. Transition temperature has become an important criterion in the selection of materials, particularly refractory metals.

Ductile/brittle transition can be shown by several different types of tests. In the tensile test, specimens will break with little or no elongation or necking below the transition temperature and with considerable elongation and necking above the transition temperature. The temperature range depends on the speed of testing and the geometry of the specimen. In bending, a bar will bend considerably before it breaks above the transition temperature but will break without plastic deformation below it. Numerous special tests have been devised to correlate with various types of service. Tests in which notched bars are struck an impact blow (Charpy test and Izod test) have been especially useful because the rapid deformation and multidirectional stress system around the notch make test conditions particularly severe. In these tests, the energy* required to break the specimen is what is usually measured. It may require ten or twenty times as much energy to fracture the specimen above the transition temperature as it does below it.

The amount of energy required is a measure of the "toughness" of the material. Materials which absorb considerable energy before fracturing are said to be "tough".

It happens that many of the metals used for high-temperature applications exhibit this ductile-brittle transition. These metals, however, are usually ductile at service (elevated) temperatures. The problem is that components must be handled and assembled at room temperature. Some materials with very attractive high-temperature properties are relatively brittle at room temperature. They tend to fracture when subjected to assembly stresses, either deliberate (tightening of bolts, etc.) or accidental (for example from forcing slightly misaligned parts into alignment). Also, in startup, parts may encounter high loads before they are heated to full service temperature. Ideally, of course, it is desirable that materials have a transition temperature below room temperature under the severest stress system and strain rate likely to be encountered during fabrication, assembly, or startup.

*It is entirely possible to measure the energy used in other tests too, such as bend test or tensile test, but in practice this is seldom done. Usually, only the load and deformation are measured.

Brittleness of a material may be accommodated to some extent by proper design (primarily a matter of avoiding an unfavorable stress system), but it is better to select a ductile material if one is available.

Fatigue Strength

Another property which can be important is fatigue strength. Any metal part that is vibrated severely or repeatedly stressed may eventually fail by fatigue even though the highest stress was well below the tensile strength of the material. Fatigue can occur at any normal service temperature. If fatigue is a problem, the stress on the part must be limited to a level which will not cause failure in the number of loading cycles anticipated during the service life of the part. Materials are often characterized by specifying one or more of the following: (Definitions from Metals Handbook, Volume 1, Eighth Edition, American Society for Metals).

Fatigue life: the number of cycles of stress that can be sustained prior to failure for a stated test condition.

Fatigue limit: the maximum stress below which a material can presumably endure an infinite number of stress cycles. If the stress is not completely reversed, the value of the mean stress, the minimum stress, or the stress ratio should be stated.

Fatigue ratio: the ratio of the fatigue limit (for cycles of reversed flexural stress) to the tensile strength.

Fatigue strength: the maximum stress that can be sustained for a specified number of cycles without failure, the stress being completely reversed within each cycle unless otherwise stated.

Fatigue tests are made on notched and unnotched specimens. The values obtained for fatigue properties depend on specimen geometry as well as stress, temperature, and other factors.

Thermal Fatigue

Repeated temperature cycling with accompanying alternate expansion and contraction can produce a similar kind of failure by what is known as "thermal fatigue". This is often a serious problem for high-temperature materials.

Modulus of Elasticity

The modulus of elasticity of a material is a measure of its stiffness. The higher the modulus the stiffer the material. This refers to elastic deformation only; that is, deformation small enough that the piece "springs back" to its original size and shape when the stress is removed. Mathematically, modulus of elasticity is:

$$\frac{\text{Stress (pounds per square inch)}}{\text{Fractional increase* in length caused by this stress (inches elongation* per inch of length)}}$$

The units are pounds per square inch.

Modulus is important because certain parts of structures are designed on a stiffness rather than a strength basis. A notable example is the B52 wing, which is made considerably stronger than necessary in order to be sufficiently stiff. If made just strong enough to carry the expected loads, it would be too flexible for flying stability.

For all metals, modulus of elasticity decreases with increasing temperature. Thus, it is important to know the modulus at service temperatures for high-temperature materials.

For applications in which design is based on stiffness and where minimum weight is important, the designer wants to know the ratio of modulus of elasticity to density at service temperature.

Directionality

All the properties discussed may depend on direction of test specimen in relation to direction of rolling, i. e., the properties may be "directional". One may get quite different results in testing specimens cut from the metal in different directions. Thus, rolled sheet may be more ductile when pulled in the direction of rolling than transverse to the direction of rolling. It is sometimes necessary to specify strength and ductility in both the longitudinal (with respect to rolling) and transverse directions.

*In the case of compression test change these words to "decrease" and "shortening".

Effect of Prior Treatment

Also, of course, the properties of a metal may be considerably altered by heat treatment, or by cold working (swaging, rolling, etc., at room temperature for example). Therefore, in reporting test results, it is necessary to specify the condition of the material, with respect to prior treatment, when tested.

Recrystallization Behavior

For best mechanical strength and ductility, refractory metals such as molybdenum are worked to develop grains that are elongated (fiber structure) as compared with grains of uniform dimensions in annealed or recrystallized material. When the worked metal is heated to above the recrystallization temperature range, the elongated grains recrystallize to form grains of generally uniform dimensions. However, when worked metal is worked to thinner sections and at lower temperatures, the recrystallization temperature becomes lower. The degree of recrystallization is dependent on the temperature and the time at temperature. In general, for refractory metals the recrystallized metal has lower strength and ductility than the worked metal in room-temperature tests.

Additions of alloying elements and insoluble dispersion agents tend to increase the recrystallization-temperature range.

OXIDATION AND CORROSION RESISTANCE

All chemical reactions are speeded up by increasing temperature. Metals which show little tendency for reaction with the atmosphere at room temperature tend to react rapidly at high temperatures. Many metals spontaneously form protective oxide films on their surfaces which are tightly adherent and prevent further oxidation at room and moderately elevated temperatures. These coatings may melt, volatilize, or crack at very high temperatures.

One of the most important properties of any material for high-temperature service is its resistance to chemical attack in the service environment and at the service temperature. Exhaust gases, in jet and

rocket engines and air are typical of the environments encountered. It is common to express oxidation behavior in terms of penetration (depth to which surface is oxidized) rate, in mils per year for example, or in terms of weight loss or weight gain per unit time. If the oxide melts, volatilizes, or spalls off, there may be a weight loss. Otherwise, the metal gains weight by combining with oxygen.

It is an unfortunate fact that the metals with the highest melting points are also most susceptible to oxidation. Some metals, notably chromium, react with the nitrogen in the air at high temperatures.

While it may be possible to use protective coatings on high-temperature materials, it would be advantageous to develop materials with sufficient oxidation and corrosion resistance that they would not require coatings.

PHYSICAL PROPERTIES

In certain applications, physical properties are as important as mechanical properties. Some of the important physical properties are discussed in the following paragraphs.

Crystal Structure

A crystal consists of atoms arranged in an orderly three-dimensional array. The smallest unit from which a particular crystal can be built is called the unit cell. One can say that, almost without exception, the kind of crystal structure determines whether an element behaves as a metal or as a nonmetal.

The crystal structure of a metallic element is of great importance since it is intimately related to the physical, chemical, and mechanical properties of that element either alone or alloyed with other elements. Of immediate concern to the metallurgist is the effect of crystal structure on such things as plastic deformation, strength, alloying behavior, and elevated-temperature properties.

Density

As pointed out in the discussion on strength, a high ratio of strength to weight may be important in certain applications. Metals are often

compared on the basis of their yield strength-to-density (weight per unit volume, e.g., lb/cu in.) ratio. Generally, for aircraft and missile applications, a high strength-to-density ratio is desirable for both elevated- and low-temperature use. The densest metal, osmium, at 0.815 lb/cu in. is more than 40 times as dense as the lightest metal, lithium, at 0.019 lb/cu in.

Thermal Properties

General

Because of aerodynamic heating (air friction and compression) and/or the very high temperatures and enormous amounts of heat generated by rocket motors and other propulsion systems, the thermal properties of metals used in the construction of rockets, missiles, and high-speed aircraft are extremely important. In these applications, the demands made upon metals involve a great many thermal properties which heretofore have not been of great concern. The material problem is especially complex because of the desire for certain combinations of properties. Often the requirements are contrary to normal known behavior of metals such as good high-temperature strength coupled with low density. For high-temperature service, the ideal material would be an impossible metal with the density and availability of magnesium, coupled with the high-temperature strength of tungsten or molybdenum and with added oxidation resistance.

Thermal Conductivity, Melting Point, and Specific Heat

Thermal properties such as conductivity, melting point, heat of fusion, specific heat, and coefficient of expansion are assuming more and more importance as man contemplates flight through the atmosphere into space and back into the atmosphere. The control of heat is the biggest problem and this involves knowledge of thermal properties. As an example, the beryllium metal shield at the base of the Mercury capsule acts as a "heat sink" or heat absorber during re-entry to the atmosphere. This part requires optimum strength with low density. To act as a heat sink, the desirable thermal properties of a metal are good conductivity (ability to conduct heat*), high melting temperature, and high heat capacity (specific heat). Conductivity is important because heat must be conducted away from the leading face of the material as rapidly as possible without the face reaching

*A good conductor is the opposite of an insulating material. If one end of a short bar is heated, the rapidity with which the other end gets hot is a rough measure of its conductivity.

the melting temperature. The amount of heat which can ultimately be absorbed is determined by the specific heat or the thermal capacity per unit mass.*

Heat of Fusion

Heat of fusion is the quantity of heat (measured in British thermal units in the English system of measures) required to change a unit mass of material from the solid to liquid state without any change in temperature.

Heat of Vaporization

Heat of vaporization is the quantity of heat required to change a unit mass of material from the liquid to the gaseous or vapor state at the same temperature. It is conceivable that much heat could be dissipated from a missile or other vehicle (for a short time) by permitting part of the outer skin to melt or to melt and vaporize. In this case, a high heat of fusion and high heat of vaporization would be desirable.

Coefficient of Expansion

Coefficient of expansion is defined as the change in unit dimensions of a body when its temperature is changed by one degree. Most metals increase in length or volume as their temperature is increased. This may become important when dimensional stability is necessary under conditions of heating or cooling. For example, in a metal-to-glass seal, the metal is tailored to have a coefficient of expansion practically equivalent to that of the glass. In a large structure, there can be considerable change in shape or size due to a large temperature change.

Emittance

Any hot surface "radiates" heat; that is, the heat waves are transmitted through space in the same way as rays of light. Not all materials radiate heat from their surfaces equally well. The measure of a material's

*When a material body absorbs heat, its temperature rises. For a given weight of material, the amount of heat required to cause a given rise in temperature varies considerably among materials. Thus, it takes about 15 times as much heat to heat up a pound of water one degree as to heat a pound of aluminum one degree. In other words, water can absorb more heat than aluminum (for a given temperature rise). The ability to absorb heat is referred to as the "specific heat" of a material. It is usually given as the ratio of amount of heat required to heat one pound of the material one degree to the amount of heat required to heat one pound of water one degree. The amount of heat required to heat a pound of water 1 degree Fahrenheit is a British thermal unit (Btu).

ability to radiate heat is its emittance (sometimes referred to as emissivity, which is the theoretical limiting value). A material which readily radiates heat has high emittance. The hemispherical total emittance of a substance relates to the rate at which its surface at any given temperature emits energy of all wavelengths and in all directions per unit area of radiating surface. Spectral emittance is the rate at which the surface emits energy of one wavelength. The rate at which heat radiates from a surface depends not only on its emittance but also on its temperature; the higher the temperature, the more heat is radiated. This property has become important in designing thermal protective systems for re-entry flight vehicles. Radiation systems and materials are effective when the material can reach a sufficiently high surface equilibrium temperature that it can reradiate the heat as fast as it is received. The maximum surface temperature, and hence, the maximum heat input that can be handled is governed by the upper temperature limit of the material. In general, for a given state of equilibrium heat input to the surface, the surface temperature is lowest when the emittance is highest. The use of metals for radiation cooling during re-entry of certain types of vehicles is a possibility now being seriously considered. There are, however, limitations to the use of metals for radiators. As the heat input increases, the radiation equilibrium temperature increases, and the higher the temperature, the more difficult it is to find a suitable metal to meet the conditions.

Thermionic Work Function

When a metal (or metallic oxide) is heated, electrons or ions (electrically charged atoms) may break away from the surface. The rate at which the electrons or ions are given off increases rapidly with increase in temperature. The rate is also sensitive to the state of the "emitter" surface, which is defined to a large extent by the thermionic work function. A low thermionic work function means that electrons are easily removed from the surface. This emission of electrons makes the electronic tube function and also makes possible the melting and welding of refractory metals by the electron-beam method. The thermionic work function of the alkali metals such as sodium and potassium is low, while for metals such as platinum it is high.

The work function is of importance not only in materials for electron-tube filaments but also may be important in materials for proposed electrical space-propulsion systems. In these systems, the vehicle is propelled by a stream of ions, which has a reactive force similar to that of the gas stream from a gas turbine.

Electrical Conductivity

The electrical conductivity of a material is a measure of the ease with which an electrical current flows in the material. A material with poor conductivity has high electrical resistance, which may be likened to friction. In materials for electrical heating wire, it is important to have just the right amount of conductivity or of resistivity which is the reciprocal of conductivity. The amount by which conductivity or resistivity change with temperature (temperature coefficient of resistivity) is also important.

In metals, the properties of thermal conductivity (as described earlier) and electrical conductivity are proportional to one another. A metal such as silver with a high thermal conductivity also has a high electrical conductivity. Conversely, metals with low thermal conductivity have low electrical conductivity. Thus, it is often possible to calculate thermal conductivity from electrical conductivity measurements, which are easier to make.

Thermoelectric Effects

If two dissimilar metallic conductors are joined at both ends forming a closed circuit, electric current will flow in the circuit if one of the junctions is at a different temperature than the other. This is known as the Seebeck effect. By measuring the thermal electromotive force producing this current, we can determine the temperature at the junction of the two wires. This is the principle of the thermocouple. Different combinations of wires are available for measuring various temperature ranges from extremely low temperatures to temperatures as high as 5000 F.

Conversely, if a current is made to flow across the junction of two metals, it gives rise to an absorption or a liberation of heat depending on the direction of current flow. This is the Peltier effect.

It has been suggested that thermoelectricity could be used to control heat by absorbing it and converting it to electricity which could be put to use as a power source elsewhere in the system. Some of the power obtained with the Seebeck effect could be fed back into a Peltier junction to provide cooling.

Nuclear Cross Section

In nuclear reactors, the tendency of a material to absorb neutrons (thermal-neutron-capture cross section) is important. Materials with a

high cross section* cannot be used in the construction of reactors since they would absorb too many neutrons to permit the sustaining of a chain reaction. However, a material with a high cross section is desired in control rods, which are inserted in the reactor to slow down or stop the reactor by soaking up neutrons. These control rods are also required to have adequate strength at the operating temperature of the reactor.

Damping Capacity

When a metal is stressed repeatedly within the elastic range, it will dissipate energy into heat because of the internal friction. This property is also known as "damping capacity" and can be expressed as the amount of work dissipated into heat by a unit volume of the material during a completely reversed cycle of stress. It is important that the damping properties of metals used in such applications as turbine buckets be known. Low damping capacity, for example, could lead to early fatigue failure.

Coefficient of Friction and Seizing and Galling Tendency

In the construction of a piece of equipment or machinery, there must be interaction between the part and the tool. Also, the use of the machine will require movement of one part in relation to another. Due to friction, there is a tendency for these moving parts to be impeded in their movement. Should the friction become sufficiently great, the mating parts will tend to seize. This seizing is caused by galling of the mating surfaces, which is a tendency of the parts to weld to each other. Normally, lubrication eliminates or controls the seizing and galling between metal surfaces. However, different combinations of metals have different seizing and galling tendencies. Furthermore, under unusual conditions involving higher speeds and pressures, higher (or very low) temperatures, and unusual atmospheres or the vacuum of space, the prevention of seizing and galling becomes increasingly difficult. This problem is always present where metals are in moving contact, especially in bearings, wire-drawing dies, cutting tools, drill bits, fasteners, extrusion and drawing presses and the like.

*For strict accuracy, this statement needs some qualification since it applies only to "thermal" reactors and not to "fast" reactors.

FABRICATION PROPERTIES

Machinability

Machinability is the relative ease of machining or of forming a piece of metal by selective removal of material in the form of chips. Some metals are easy to machine and some are difficult to machine. Generally, the higher strength metals, and especially those needed in very high-temperature applications, are the most difficult to machine. Some metals, especially those newly developed, are nearly impossible to machine by known tools and techniques, and new methods must be devised.

Weldability

The suitability of metals for joining by welding is called weldability. Some metals are not suited to welding, and others can be welded only under extreme difficulty. Large sections, intricate shapes, dissimilar metal parts, hardened pieces, and highly reactive metals, among others, require special and constantly changing approaches to the problem of welding. Lack of weldability may severely limit the applications for which a metal is suitable.

Formability

Another method of forming a part is to shape it plastically as by forging, stamping, etc. This process is sometimes performed at room temperature but usually involves elevated temperatures and high stresses. The relative ease with which a metal can be formed or shaped through plastic deformation is termed formability. New high-strength, high-temperature metals used in much of today's hardware require extremely high pressures and temperatures to form to the desired shapes.

Ease or Difficulty of Rolling Thin Sheet

In recent years, there has been an increasing need for relatively thin sheets of many different kinds of metals. Ease of rolling is an important property of these metals from a cost standpoint. Moreover, the new requirements call for sheets that are wider, longer, and more uniform in thickness

than any sheets heretofore available. Unfortunately, many of the metals and alloys that are wanted in sheet form are difficult to roll into thin sheets of large size. "Exotic" elements such as tungsten, molybdenum, columbium, and zirconium, along with high-strength alloys and special high-temperature superalloys, present certain problems during rolling into thin sheets. Many of these metals are extremely stiff and springy, and the wider the sheet the more difficult it becomes to maintain exacting thickness tolerances throughout any one sheet or from sheet to sheet.

It may not be possible to utilize the full strength of a metal if the thinnest sheet which can be rolled is thicker than is required for a given application. Also, in designing a light structure thickness variation is important. Suppose a sheet of 0.018 inch minimum thickness is desired, but it is impossible to control its thickness any closer than ± 0.002 inch. It will be necessary to specify 0.020-inch sheet since the most uniform sheet that can be obtained will vary between 0.018 and 0.022 inch in thickness. The average will be 0.020 inch. Since the average of all the sheet in the structure is 0.020 inch, the whole structure will be about 10 per cent heavier than necessary.

Castability

A cast material is one that is shaped into approximately the desired final form directly from the molten state. Most wrought materials are first cast into molds from the molten state prior to being processed further.

The ease with which a metal can be cast, that is, made to assume the shape of the mold, is termed castability. This term generally refers to metal that will be used in the cast condition. Castability is an inherent characteristic of a metal. There are, of course, optimum conditions under which a metal will cast easily. It still remains a problem to determine what these conditions are for many of the newer metals. However, techniques have been developed recently for casting tungsten, molybdenum, titanium, and other high-temperature metals. Castability or fluidity is often measured by pouring the molten metal at a known temperature into a spiral mold. The length of the spiral that is filled with metal is a relative indication of its ability to flow in a mold. This usually increases with increased pouring temperature. Use of alloying elements that reduce the melting temperature also increase the castability. Shrinkage problems, gas evolution during solidification, and reaction with the mold material must be considered in producing castings of the refractory metals. Graphite, which is often used as a mold material, tends to react with many metals when they are cast.

APPENDIX B

HIGH-MELTING POINT ELEMENTS EXCLUDED FROM
CONSIDERATION AS HIGH-TEMPERATURE METALS

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HIGH-MELTING POINT ELEMENTS EXCLUDED FROM
CONSIDERATION AS HIGH-TEMPERATURE METALS

As previously explained, all elements with melting points below aluminum have been excluded from consideration for service above 800 F. However, there are 34 elements with melting points higher than that of aluminum which are not included in the list of 21 metals (Table 2) discussed in detail in this report. A brief discussion of the reasons for exclusion of some of these materials will help convey a better picture of the whole field. The excluded elements are discussed in order of melting points (highest first) although some are grouped together.

Carbon (Graphite)

Carbon is in a class by itself, having the highest melting point of all the elements and being quite abundant (in coal, etc.). It is hence very interesting as a high-temperature material, but being nonmetallic is outside the scope of this report. Nevertheless, there is considerable research being done on carbon and graphite to improve its properties for high-temperature service.

Boron

Boron has a melting point of approximately 4200 F, which places it between columbium and ruthenium.

Boron may be considered a sort of semimetal which does not possess toughness, although there are some metallurgists who feel the development of metallic properties in boron-base materials is possible. We cannot now consider it a potential structural material, although its very low density, high melting point, and thermal properties make it of possible interest for certain nonstructural applications. If it is ever developed to the point where it can be used for structural purposes, its high modulus of elasticity will be of interest.

Thorium

Thorium has a melting point of about 3100 F. It may be a principal nuclear fuel if breeder* reactors are developed, but it has been found to be weak at elevated temperatures and unsuitable for structural applications.

Scandium

Scandium has a melting point of 2802 F. It has been produced in small quantities as a pure metal and as such has good fabricating properties. However, because of its scarcity and because no unusual uses have been found for it, it is not produced commercially.

Yttrium

This metal always occurs with the rare-earth elements and is very similar to them. Yttrium has low neutron-absorption cross section and for this reason is of interest as an alloying element in reactor alloys. It has been produced in sufficient quantities for extensive studies regarding its alloying characteristics. When yttrium is added to iron-base alloys, it improves workability, causes grain refinement, promotes resistance to high-temperature recrystallization, and improves the oxidation resistance. It has similar beneficial effects in chromium- and vanadium-base alloys.

Rare-Earth Metals

The rare-earth metals are a group of 15 elements that have properties much as the same as yttrium's. These elements are lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. A number of these elements occur together in the ores and, because of their similar properties, have been difficult to separate. However, they have been separated in recent years. An alloy of the metals that are produced together from the ore is called misch metal. It is composed of approximately 45 to 50 per cent cerium, 18 per cent neodymium, 5 per cent promethium, 1 per cent samarium, and 22 to 25 per cent lanthanum along with small amounts of other rare-earth metals.

*A nuclear reactor that converts thorium-232 into uranium-233, which is a fissionable isotope suitable for nuclear-reactor fuel.

The common lighter flint is about 30 per cent iron with the balance composed of misch metal. When misch metal is added to some steels, it has a desulfurizing effect and improves the hot workability. Misch metal is also used with beneficial effects in some alloys of magnesium, aluminum, nickel, and copper.

Pure cerium and some of the other pure rare-earth metals also have been used as alloying elements. However, these metals have not been used as structural materials. Fission products from atomic reactors are the only sources of promethium.

Silicon

About 28 per cent of the earth's crust is silicon, which is always combined with oxygen as silica or silicates. It is produced in pure form for semiconductors and other electronic devices and as alloys for alloying additions such as ferrosilicon. All commercial steels and irons contain silicon. It is extremely brittle and has no value as a structural material.

Manganese

Manganese also is used in all commercial steels and irons as a deoxidizer and alloying element (and for sulfur control). It is used in many commercial aluminum and magnesium alloys and in manganese bronze. There are no commercial manganese-base alloys primarily because of extreme brittleness and lack of any unique properties.

Uranium

The primary use of uranium is as a nuclear fuel. Until it was needed for this purpose, there was very little information on its metallurgy. However, the properties and alloys of uranium have been studied extensively in the past 15 years in order to improve its corrosion resistance and its strength at elevated temperatures for atomic-energy applications. Uranium or uranium alloys are not used as structural materials. There is a growing stockpile of depleted uranium which may be used for alloying or other purposes, pigments for example, but these other uses are limited at the present time.

Copper

Copper was not included with the metals for use above 800 F because copper or copper alloys are not generally used above this temperature. However, copper-nickel alloys are used in condensers, heat exchangers, and other elevated-temperature equipment. For such uses, the copper-nickel alloys have good strength, corrosion resistance, and thermal conductivity. Brass and bronze castings are also used at elevated temperatures.

Gold and Silver

The primary use for gold and silver alloys at elevated temperatures is in brazing alloys; a number of alloys have been developed for brazing various materials. Brazing of honeycomb sandwich structures for aircraft has been the most notable application for high-temperature brazing alloys.

Germanium

Interest in production of germanium resulted from the development of germanium rectifiers and transistors. At the present time, it is recovered from zinc ore and from flue dusts from coal-fired boilers, as some coals contain small amounts of germanium. It is usually classed as a metalloid because it has properties intermediate between those characteristic of metals and nonmetals. It may be cast into ingots but so far has not been fabricated.

Although germanium has not been used as a structural material, new uses for it in electronics and instrumentation are being developed.

Other Elements

Calcium, strontium, and barium are known as the alkaline earth metals. Calcium is the fifth element in abundance in the earth's crust. It will form a precipitation-hardening alloy when small amounts are added to lead. It is used as a reducing agent for such metals as thorium, zirconium, uranium, chromium, vanadium, and the rare earths. In various ferrous and nonferrous alloys, it tends to deoxidize, decarburize, or desulfurize the alloys. It is also used in certain aluminum, copper, and magnesium alloys and beryllium.

Strontium and barium metals are very seldom used in metallurgy.

Arsenic metal has not been mentioned previously, but it is used in small amounts in lead shot. The arsenic addition tends to make the shot more spherical as the liquid droplets fall through the air in the shot towers. Arsenic has been added to copper to increase its corrosion resistance and to raise its recrystallization temperature. It has also been used in lead-base solder and babbitt alloys.

Radium is a radioactive metal and is used only where its radioactivity is important. These uses are in treatment of cancer and in self-luminous paints.

APPENDIX C

COMPOSITE MATERIALS

APPENDIX C

COMPOSITE MATERIALS

The use of coatings to inhibit oxidation of the refractory metals at high temperatures has been discussed previously. However, in addition to coatings, many different composite structures have been investigated in order to achieve the benefits of more than one material in a given structure. The use of stainless steel cladding on a carbon-steel core provides the corrosion protection of the stainless steel but at a lower cost. Mill practice for cladding of this type has been well established.

More recently, experimental composite materials have been investigated for high-temperature applications. Porous tungsten powder compacts have been impregnated with copper to increase the thermal conductivity and to improve the ductility. Composites of beryllium powder with 20 per cent silver have been cold rolled 83 per cent. The silver provides a ductile matrix. Under these conditions the beryllium powder particles elongate in the direction of rolling.

Honeycomb metals have been used to reinforce ceramics to improve the resistance to heat shock. Composites of this type have been used for nose cones. Wire mesh has been used to reinforce plastics for unusual service conditions.

In another type of composite, metal or ceramic whiskers (filamentary crystals) have been combined with metals. Examples of this type of composite are as follows:

Reinforcing aluminum with sapphire whiskers to provide a high-strength, high-temperature composite

A combination of half columbium metal and half sapphire whiskers for improved high-temperature strength

Chromium with an addition of a ceramic material has been developed for use at 2600 F. Electrolytic chromium was used, and the composite had a tensile strength at 3000 F comparable to that of René 41 at 2200 F. This material was cold worked, hot formed, and machined. It had a tensile strength of 1800 psi at 3100 F and reduction in area of 10 per cent. The composite is not seriously oxidized below 3800 F.

Titanium diboride is representative of the refractory compounds that are being developed. Shapes of this material have good strength to about 3500 F. Composites of this material may also be of interest.

Compounds of the refractory metals often have lower melting points than do the corresponding metals. However, hafnium carbide and tantalum carbide have melting points over 7000 F. Other compounds may also have melting points above 7000 F. It is conceivable that such compounds could be incorporated in a composite structure that would have a better combination of high-temperature properties than available at the present time.

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46E	Department of Defense Titanium Sheet-Rolling Program - Thermal Stability of the Titanium Sheet-Rolling-Program Alloys, November 25, 1958 (PB 151061 \$1.25)
46F	Department of Defense Titanium Sheet-Rolling Program Status Report No. 4, March 20, 1959 (PB 151065 \$2.25)
46G	Department of Defense Titanium Sheet-Rolling Program - Time-Temperature-Transformation Diagrams of the Titanium Sheet-Rolling Program Alloys, October 19, 1959 (PB 151075 \$2.25)
46H	Department of Defense Titanium Sheet-Rolling Program, Status Report No. 5, June 1, 1960 (PB 151087 \$2.00)
46I	Statistical Analysis of Tensile Properties of Heat-Treated Ti-4Al-3Mo-1V Sheet, September 16, 1960 (PB 151095 \$1.25)
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159	Gas-Pressure Bonding, September 25, 1961

Battelle Memorial Institute, Defense Metals Information Center, Columbus, Ohio. INTRODUCTION TO METALS FOR ELEVATED-TEMPERATURE USE, by J. E. Campbell, H. B. Goodwin, H. J. Wagner, R. W. Douglass, and B. C. Allen. October 27, 1961. [92] pp incl. illus., tables. (DMIC Report 160) [AF 33(616)-7747] Unclassified report The general categories of metals suitable for application at temperatures in excess of 800 F are discussed along with the general advantages	UNCLASSIFIED 1. Metals 2. Heat-resistant alloys I. Campbell, J. E. II. Goodwin, H. B. III. Wagner, H. J. IV. Defense Metals Information Center V. Contract AF 33(616)-7747 UNCLASSIFIED
(over) and limitations of each. Some generalized mechanical and physical property data are included. The report, while not compromising with technical accuracy, has been prepared primarily for the nonspecialist and is in terms understandable to readers without extensive metallurgical training.	UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED UNCLASSIFIED
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