

TANTALUM
MOLYBDENUM DISILICIDE
COMMERCIAL
TUNGSTEN

MATERIALS

for structural use

ZIRCONIUM CARBIDE
PURE TUNGSTEN
TITANIUM DIBORIDE
COLUMBIUM ALLOY (B-66)
STEELS
SUPER ALLOYS (NICKEL, IRON, COBALT)
PYROLYTIC GRAPHITE

In the era from 1970 to 1980, manned orbital flights may be quite commonplace. It has been estimated, for example, that the United States alone could have requirements for orbiting up to 1000 passengers each year. Based on disposable rocket systems of the type now employed or under development, it is predicted that even at this level of operation, the cost would remain at the rather extravagant figure of 2.7 million dollars per passenger round trip.¹ It has also been predicted that the cost could be reduced to \$20,000 per passenger with a reusable launch system employing an airbreathing turbo-ramjet to power the first stage.¹ A system that would use the cold hydrogen fuel to accumulate and store liquid oxygen during first-stage flight has been proposed in order to achieve such economy. The liquid oxygen would be used to power second- or third-stage rockets.

Such a scheme involves substantial development risks, but the prospect of such an important economy suggests that some developmental effort should be expended in this direction.

The advantages of airbreathing propulsion have long been recognized at APL, and the Aeronautics Division is currently involved in research that will be of notable importance in the development of hypersonic propulsion systems. The supersonic combustion ramjet (SCRAM) has special advantages that have been investigated under the direction of W. H. Avery and G. L. Dugger of APL.* It has been shown, for example, that it is theoretically possible to develop an airplane based on this type of propulsion that would be capable of achieving orbital velocity with substantially better payload efficiencies than can be gotten with chemical rockets. For missile applications, the supersonic

¹ R. A. Bailey and D. L. Kelley, "The Potential of Recoverable Booster Systems for Orbital Logistics," *Astronautics and Aeronautics*, 2, Jan. 1964, 54-59.

* Dr. W. H. Avery is supervisor of the Aeronautics Division and Dr. G. L. Dugger is supervisor of the Hypersonic Propulsion Group.

ABOVE 3000°F

Hypersonic projects at APL and elsewhere are generating the need for improved materials for use in complex structures that must operate at temperatures up to 5000°F. The present paper discusses the behavior of metallic alloys under stress at temperatures above 3000°F. The usable strength at a given temperature may vary by a factor of ten because of the way in which strength depends on the rate at which the materials are deformed. Estimates of the design allowables are given for currently available alloys, along with predictions of developments for the next decade.

M. L. Hill

ramjet can provide substantial speed and range advantages over conventional rockets, and much of the current research at APL is being conducted with this application in mind.

One of the difficult problems with such hypersonic vehicles is the intense heat that is generated by the friction of the air moving across the structure. At speeds around Mach 10, and at an altitude of about 15 miles, an uncooled or uninsulated structure would rise to temperatures near the 5000°F of the "white hot" filament in an incandescent light bulb. Thus, hypersonic airplanes or missiles will have to employ insulating materials and special cooling techniques to counteract these severe temperatures. In the case of the orbiting airplane, before the very cold liquid hydrogen fuel is burned in the ramjet engines, it would be pumped through passages in the skin to absorb frictional heat. Missile airframes, by virtue of their short-duration missions might be protected by a

passive insulation or an ablative material in much the same way that re-entry vehicles are protected; they are therefore expected to have substantially simpler structures than the regeneratively cooled airplane.

Successful development of such cooling or insulating techniques would permit the use of conventional aircraft materials such as titanium, aluminum, and steel for the major portion of the structures. It is certain, however, that there will be critical regions in which it will be difficult or impossible to hold temperatures to the 500°F to 2000°F range that these materials can tolerate. For this reason the Laboratory is engaged in a program of evaluating metallic alloys of columbium, tantalum, and molybdenum, as well as graphites and refractory oxides, carbides, silicides, and other ceramics for possible use in a hypersonic environment at temperatures in the range of 2000° to 5000°F. At temperatures where ordi-

nary steel melts, some of these have strengths exceeding that of an automobile bumper. However, as temperatures exceeding 3000°F are reached, even these lose strength rapidly, and it is necessary to be intimately familiar with their properties in order to employ them efficiently.

Problems associated with high temperatures are, of course, also encountered in rockets that fly outside the atmosphere. The overall efficiency and, often, the difference between success and failure depend to a great extent on the performance of critical components of rocket propulsion plants that operate at high temperatures. Regardless of the specific modes of propulsion that might be employed, the practical limits of future space and defense programs will be strongly influenced by materials availability and capabilities. Consequently, there is an intense curiosity about what improvements in materials are likely to be achieved in the next decade or so.

The most reasonable basis on which such predictions can be made is an assessment of what has already been accomplished and over what period of time. A brief assessment of this nature is therefore given here; and in the light of it some predictions are made about the probable materials developments during the next decade.

High-Temperature Materials Reviewed

The progress that has been made toward providing high-strength metallic alloys for engineering applications is summarized in Fig. 1 in a general way. As described below, this figure also presents a picture of the current state of affairs, and in another sense it illustrates what some of the problems are in going to higher temperatures.

Shown in this figure are the tensile strengths of a variety of metals and alloys at temperatures up to 5000°F. The upper, heavy boundary line shows the highest strength alloys that have been developed to date (1964), while the dotted extensions of the various segments show the general temperature dependence of the individual alloys. Also shown (lower left) are the strengths of the metallic elements on which the alloys are based. Arrows are drawn to show how much increase in strength has been achieved by application of metallurgical strengthening mechanisms.

DEVELOPMENT OF STEEL—By far the most profound achievement has been in the area of converting iron to steel by the addition of other

elements such as carbon, nickel chromium, and others. However, modern-day metallurgists cannot take much credit for this, for as everyone who watches late TV shows knows, iron-masters in the service of King Louis XIV discovered this strengthening quite by accident when they hurriedly dumped a freshly cast cannon into the castle moat to prevent the enemy from confiscating it. Hollywood researchers are open to metallurgical criticism, however, for it is certain that a cannon of the size shown in their films would have cracked to pieces when quenched in water. Besides, they probably could have made a far more interesting film about Damascus swords, which were hardened centuries earlier by thrusting the red hot blade into the thigh of a choice slave.

This facetious discussion is made only to point out that much of the development of high-strength steels from iron took place over several centuries and in the absence of scientific understanding of the process. Basic understanding of the transformation—hardening of steels—was obtained about 50 years ago, and as a result of this understanding usable strengths have been extended from about 150,000 psi to the 350,000 psi now obtainable. Newer knowledge of dislocation behavior, phase transformations, and fracture mechanisms has resulted in achievement of 450,000 psi in recent experimental steels,² and a half-a-million-psi tensile strength steel may be an engineering reality within the next decade.

RECENT ALLOY DEVELOPMENT—In contrast to the centuries of steel development, the large increase in strength of titanium alloys has been achieved almost entirely within the last decade.³ When recovery of this metal from ores became economically feasible, no time was lost in applying previously accumulated metallurgical knowledge of phase changes, precipitation-hardening, cold-working, and other strengthening mechanisms. Because of their relatively low density and high strength, titanium alloys are currently used in many aircraft applications. Total world production in 1950 was only a few thousand pounds, while in 1963, U.S. production alone amounted to about 7000 tons. Higher strength alloys are still under development, and some of the current research on titanium alloys is aimed at increasing their temperature capability. It is reasonable to expect the knee of

² C. W. Marshall, "Hot-Cold Working of Steel to Improve Strength," Battelle Memorial Institute DMIC Report 192, Oct. 1963.

³ "The Current Status and 1970 Potential of Selected Defense Materials," Battelle Memorial Institute DMIC Memo 183, Oct. 1963.

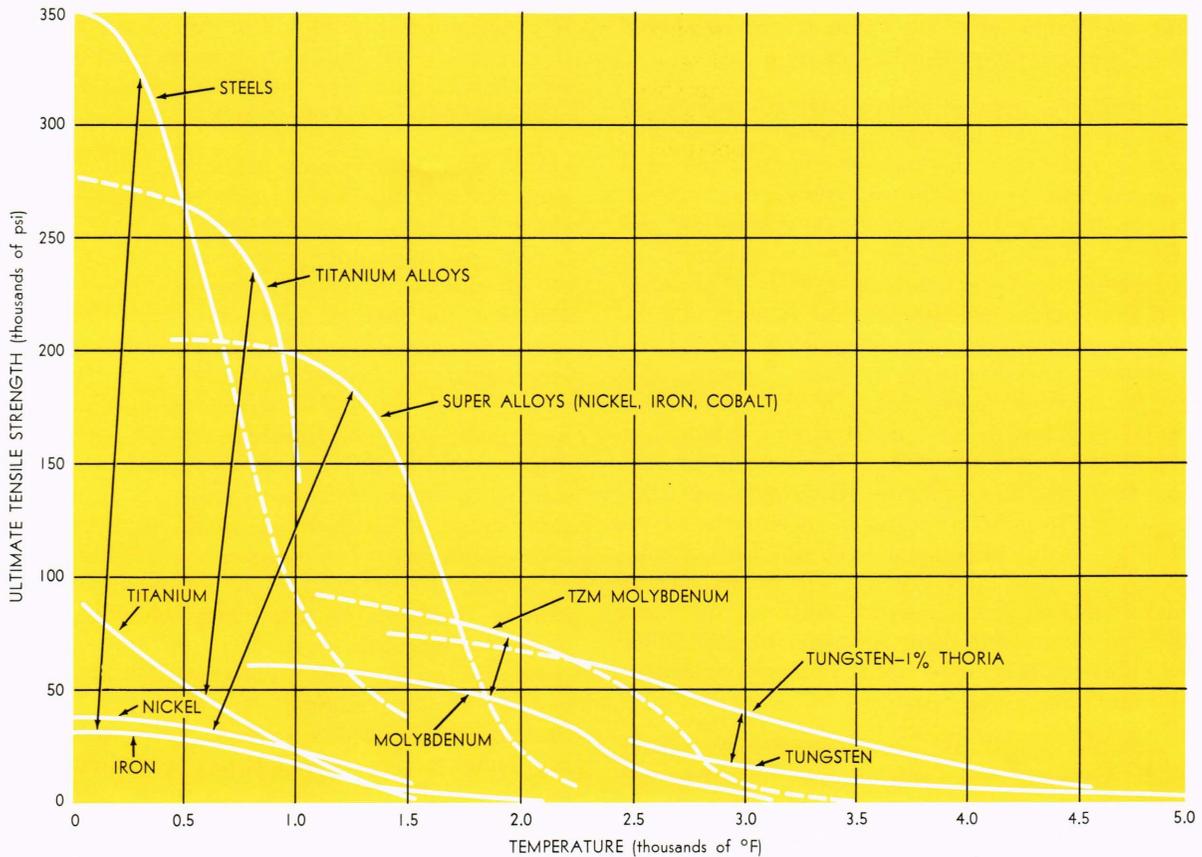


Fig. 1—Summary of tensile strengths of a variety of metals and metal alloys at temperatures to 5000°F.

this curve to be shifted out to perhaps 1300°F during the next decade.

Much of the credit for improvements in super alloys belongs to those who have been involved in the theoretical aspects of metal physics. A number of methods of increasing strength and decreasing creep rate were suggested by modern theories about imperfections and dislocations in metallic crystals. Many of these ideas have been converted into practical usage and remarkable engineering gains. For example, during the past two decades the aircraft turbine has evolved from a risky, inefficient propulsion plant of practical interest to only a few military planners into a reliable and unsurpassed system for commercial transport. The role of metallurgy in this development was not minor.

Some gains in strength of these nickel, cobalt, and iron-base "super alloys" are still forthcoming, but it is unlikely that the knee of this curve can be shifted much above 1700° to 1800°F.³ Major improvements in fabricability are being made, particularly with respect to welding. Alloys similar

to TD nickel³ (a dispersion of thoria powder in nickel) will probably be more common. These will have substantially less strength than shown here for super alloys at 1600°F, but will retain usable strength to 2400°F.

In the area in which we are currently most interested (2000°F and up) it is seen that relatively small improvements in strength have been accomplished. Unfortunately this is not the result of mere lack of understanding or inadequate effort; it is a reflection of basic properties that frustrate most attempts to add strength. Conventional strengthening mechanisms such as phase-transformation, precipitation-hardening, and cold-working, which are widely employed in aluminum, steels, and titanium, are usually ineffective above the recrystallization temperature of the base metal. In a simplified sense this is the temperature at which thermal activation is sufficiently intense to permit easy diffusion of atoms within the crystal lattice. In pure metals it usually occurs at about one half the melting point. It is an inherent property, but

like the boiling point of water, it can be altered by a "pinch of the proper kind of salt."

In general, solid-solution alloying (addition of metallic elements having slightly larger or smaller atomic radii than the base element) is the most effective way to raise the recrystallization temperature. Shifting this temperature upward by this means usually permits the use of precipitation hardening up to higher temperatures. The latter is a more potent strengthening mechanism, and the two mechanisms are often combined to yield appreciable improvements in both strength and temperature resistance. Many of the alloy studies in the refractory metals—molybdenum, columbium, tantalum and tungsten—have been aimed at finding additions that raise the recrystallization temperature. In general, however, increases to above 60% of the melting point have not been accomplished in these alloy systems.⁴ In others such as nickel, recrystallization temperatures up to about 80% of the melting point have been accomplished, and this appears to be about as far as it can be shifted in any useful system.

Metallic alloys can, of course, be used above their recrystallization temperatures, but then one finds that they behave somewhat like highly viscous fluids. Their ability to carry loads depends strongly on the velocity at which they are deformed and on the temperature. Parameters used to characterize the flow of metals^{5,6} are distantly analogous to

Reynolds number of fluid flow. Insofar as is known, this behavior has not been critically reviewed by specialists in fluid flow, but it does show promise of being a fertile field of research.

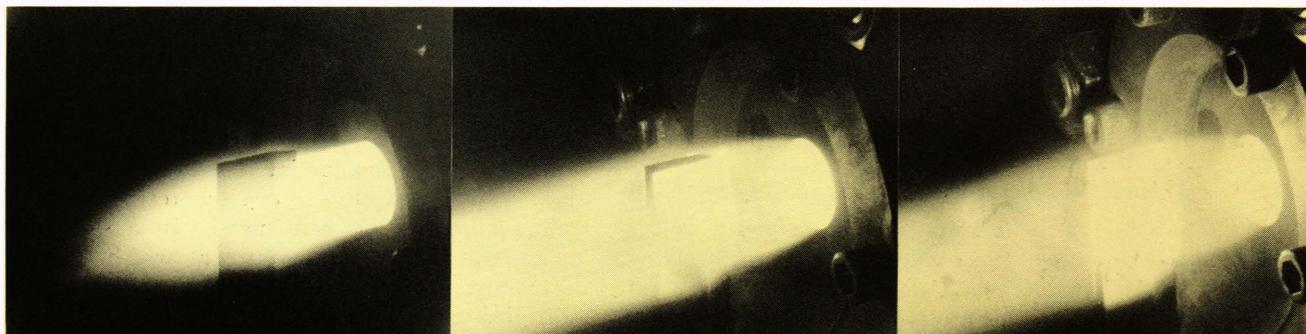
DISPERSION HARDENING—At temperatures much above recrystallization, the only effective strengthening mechanism that has been employed is one known as dispersion hardening. This consists of introducing an insoluble phase into the alloy matrix in the form of a fine dispersion. To some extent the presence of this phase can raise the recrystallization temperature, but it usually contributes some measure of strength even above the recrystallization temperature. The foreign phase can be produced by heat treatments that are similar to aging treatments used to strengthen super alloys, it can be mixed with metal powders before sintering (TD nickel is an example), or, as in the case of most refractory metal alloys, it can be produced by traversing solubility limits during solidification or cooling from forging temperatures (TZC, a relatively new alloy of molybdenum, is an example of the latter, where titanium and zirconium carbides are formed during cooling). Some attempts to mix powders with molten metals have also been partially successful.

The dispersion hardening principle is somewhat analogous to the process of blending sugar with butter. Many male readers of this text are possibly familiar with this process because it is essential to baking a good cake, and many wives become fatigued by it as a result of the stiffness of the mixture. In dispersion-hardened alloys, phases of hard particles of oxide or carbides are generally used in the ductile matrix of the base metal to strengthen the composite alloy. Dislocation theory has dealt with the detailed atomic mechanisms of plastic flow in the presence of such particles, but in a simplified view the particles can be interpreted

⁴ J. E. Campbell, H. B. Goodwin, H. S. Wagner, R. W. Douglas, and B. C. Allen, "Introduction to Metals for Elevated Temperature Use," Battelle Memorial Institute DMIC Report 160, Oct. 1961.

⁵ F. R. Larson and J. Miller, "A Time Temperature Relationship for Rupture and Creep Stresses," *Trans. Am. Soc. Mech. Engrs.*, 74, 1952, 765-771.

⁶ S. S. Manson and A. M. Haferd, "A Relation for Extrapolation of Creep and Stress Rupture Data," NACA Report TN 2890, 1953.



Plasma arc test, in the Propulsion Research Laboratory, of a pyrolytic graphite wing-leading

as increasing the viscosity of an already very viscous fluid.

Unfortunately, some of the other characteristics of the sugar-butter analogy are also present in dispersion-hardened alloys. In the case of the sugar-butter mixture, a homogeneous caramel-like fluid is formed as the temperature is raised. In dispersion alloys the particles usually dissolve at some temperature well below the melting point, and become ineffective. In general the analogy goes one step further. Cooling of the melted sugar-butter mixture results in the binder used for making peanut-brittle candy. Likewise, cooling of an overheated dispersion-hardened alloy often results in a brittle material; this occurs in practically all refractory metal alloys, and it severely limits the welding and general fabricating of such alloys.

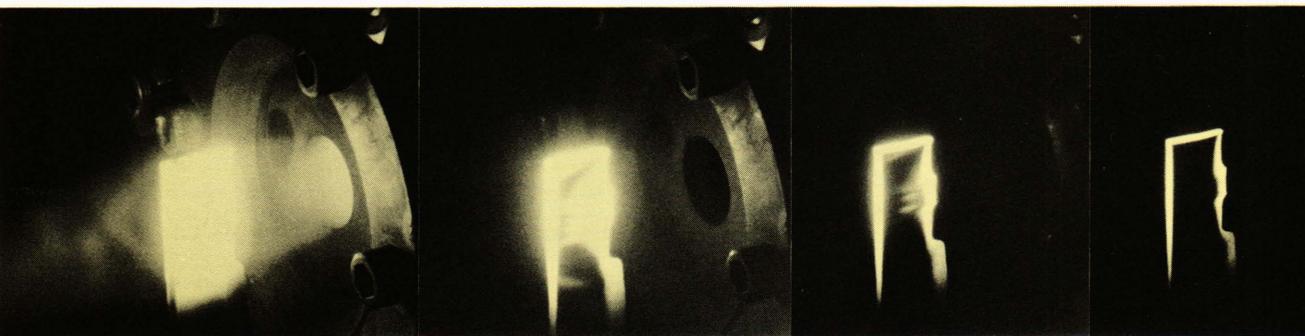
Assessment of the Future

With this simplified analogy in mind, the directions of research that may lead to stronger alloys for service above 2500°F are reasonably obvious. The first is, of course, that of raising the recrystallization temperature by means of adding soluble elements to the matrix; the second is to find dispersed phases with increased resistance to dissolving in the matrix. Major research projects in the first area have been underway for the past decade. Binary and ternary systems for raising the recrystallization temperature of molybdenum, tantalum, columbium, and tungsten have been reasonably well surveyed. The TZM now available has a recrystallization temperature around 2700°F, this being 60% of the melting point. Several columbium alloys having recrystallization temperatures at 60% of their melting points are also available commercially. A few tantalum-tungsten alloys with this characteristic are also available. This 60% level may be close to the practical limit in

these alloy systems since it has been found that alloy additions that are effective in pushing the recrystallization temperature above this point usually result in brittleness of the alloys at room temperature. In this sense these alloy systems are far more limited than nickel alloys in which the pure element is very ductile and tolerant to many alloy additions.

The few programs in progress that are aimed at studying the solubility of promising dispersed phases in refractory metals are generally side-line efforts in specific alloy development programs. A more fundamental approach to this problem would probably yield more useful results. This is also true of the role that diffusion of dissolved species away from the reaction region may play in obtaining maximum possible strength. Some advantages may be gained in this area, particularly in materials for the missile structures that may be designed to perform their entire function within a few seconds. The time required for solution and diffusion of dispersed phases above 3000°F is of the same order of magnitude. A challenging complication in this part of the problem is the fact that both the solubility and the subsequent diffusion rates are often significantly changed by the minor alloy additions used to raise the recrystallization temperature. Substantial confusion can result if the fundamental factors are not understood separately.

Considering all aspects of the problems of developing strength and maintaining fabricability, it appears likely that the next decade will not see a lot of improvement in strength of metallic materials beyond the values that are shown in Fig. 1 for the tungsten-thoria alloy above 3000°F. Instead, the major progress will probably deal with improvements in the fabricability and quality of alloys whose strengths fall below that of this material.



edge section, showing representative variations of the heating rate on different areas of the sample.

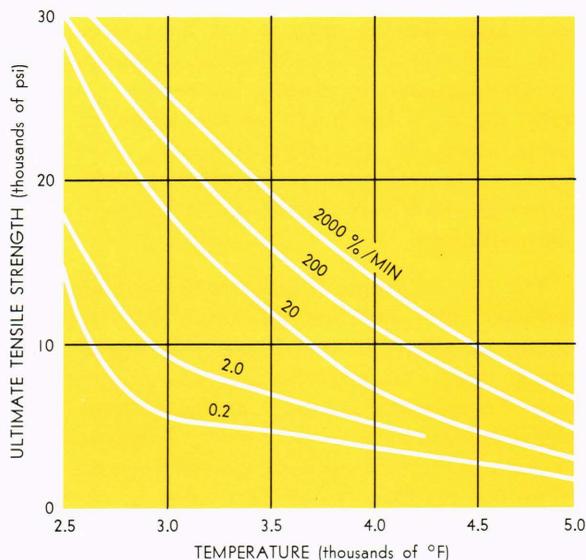


Fig. 2—Tensile strength of tungsten as a function of strain rate and temperature.

BEHAVIOR ABOVE RECRYSTALLIZATION TEMPERATURE—The basic pattern of behavior at temperatures above the recrystallization temperature is described by data in Fig. 2. Here we see the ultimate tensile strength of commercially pure tungsten at temperatures from 2500° to 5000°F.⁷ The family of curves demonstrates the high dependence of strength on the rate at which the material is elongated. For example, the bottom curve was obtained in tests in which the strain rate was held constant at 0.2%/min, while in the top curve the strain rate was 2000%/min. At temperatures around 3000°F, we see that the material is about five times as strong at the fast strain rate as it is at the slow rate. The higher strength at fast strain rates persists at all temperatures up to 5000°F, but the magnitude of the effect changes with temperature. The lower two curves show a steepening at lower temperatures, caused primarily by a variable degree of recrystallization that occurs during such tests.

Recrystallization is both time- and temperature-dependent, and in very rapid tests, or in slow tests at low temperatures, the rate of recrystallization can lag behind the rate at which the structure is deformed. Whenever recrystallization lags behind the deformation rate, extra strength is obtained. In a simplified sense this is the reason for the higher strength at fast strain rates. Atomically scaled processes known as “recovery” or “relaxation” are also involved, but it is generally easier to

think in terms of recrystallization since this is something that can be readily observed in optical microscopes. Large variations in the yield strength of materials also result from changes in the rate of strain. The effect can be even larger than the five-fold increase in the ultimate tensile strength shown in Fig. 2. A ten-fold variation in yield strength occurred in similar tests.

DESIGN FACTORS—In the midst of these variations in strength it is not a straightforward matter to specify *stress allowables* in terms of a certain percentage of yield or ultimate tensile strength as is often done in engineering design. In order to build a reliable and efficient structure, it will be necessary to take this behavior into account and develop strength data with the specific requirements in mind. One way would be to decide first what degree of deformation can be tolerated by a given component and then evaluate the material in terms of the stress it can withstand without exceeding this deformation during a temperature-time simulation of the missile flight. *Design allowables* determined in this way will permit the use of *minimum* safety factors, so essential because of the inordinately heavy structures that can result from overdesign with these relatively dense materials.

There is currently very little creep information on refractory metals above 3000°F that is amenable to this kind of an approach. Even standard tensile tests are quite expensive and tedious to perform, and as a result only a sketchy description of ordinary tensile properties is available for many of the alloys that are now being publicized.

In Fig. 3 a comparison is made between steady-state creep properties^{8, 9, 10} and the short-time, tensile, ultimate strength of tantalum,¹⁰ molybdenum,¹¹ and tungsten.¹² The data shown as broken lines indicate the tensile stress that results in 1% creep elongation during a 1-min exposure at steady temperature (this does not include thermal or elastic expansion). The tensile data are all from tests conducted at a strain rate of

⁷ P. F. Sikora and R. W. Hall, “Effect of Strain Rate on the Tensile Properties of Tungsten,” NASA Report TN-d 1094, 1962.

⁸ W. V. Green, M. C. Smith, and D. M. Olson, “Short Time Creep Behavior of Molybdenum at High Temperatures,” *Trans. Am. Inst. Mining Met. Engrs.*, 215, Dec. 1959, 1061-1066.

⁹ W. V. Green, “Short Time Creep Rupture Behavior of Tungsten at 2250 to 2800°C,” *Trans. Am. Inst. Mining Met. Engrs.*, 215, Dec. 1959, 1067-1072.

¹⁰ J. B. Preston, W. P. Roe, and J. R. Kattus, “Determination of Mechanical Properties of Aircraft Structural Materials at High Temperature After Rapid Heating,” Southern Research Institute Report WA DE TR 57-649, Jan. 1958.

¹¹ R. W. Hall and P. F. Sikora, “Tensile Properties of Molybdenum and Tungsten from 2500 to 3700°F,” NASA Memo 3-9-59E, Feb. 1959.

¹² P. F. Sikora and R. W. Hall, “Tensile Properties of Wrought and Sintered Tungsten,” NASA Technical Note D-79, Sept. 1959.

0.05 in./in./min. The tantalum and molybdenum creep data are seen to correspond quite closely to these particular ultimate strength curves, each of which must be recognized as one of a family similar to that in Fig. 2. For tungsten the correlation is not as good, but this could well be caused by variations in purity and/or by experimental errors in different laboratories. However, it is apparent that for all three materials, design allowables derived from these particular ultimate strength data would be of the correct magnitude for a structure limited to 1% deformation during one minute. This is a case of practical interest in missile application. Other correlations for smaller deformations, shorter or longer times, or varying temperature and load can also be derived. Eventually design with such materials will be done best by using computers to estimate design allowables for transient loads and temperatures. These, however, will require specific creep data that are as yet unavailable for most alloys.

The behavior of alloy systems (above recrystallization temperatures) follows that of the base metals reasonably well. Therefore, until such time as creep data become available, it is reasonable to use the ultimate strength (determined in tensile tests at strain rates of about 0.05 in./in./min) for preliminary estimates of the weight and size of components that are permitted 1% deformation. Because strain rates in the vicinity of 0.05 in./in./min are usually employed in preliminary evaluation of alloys, much of the tensile data are applicable. However, we should point out that unusually high strengths are sometimes reported without an accompanying reference to the fact that abnormally high strain rates were used.

TENSILE STRENGTHS OF REFRACTORY ALLOYS—The ultimate tensile strength of the highest-strength refractory alloys that have thus far been made available commercially are shown in Fig. 4. All of these were obtained in tests at strain rate of 0.05 in./in./min. They therefore represent the best estimates that can be made currently of design allowables that might be used for preliminary planning and evaluation of structure weights for hypersonic missiles. Data for pure tungsten are shown for comparison.

The columbium alloy B-66 is not very useful above 3000°F. Most columbium alloys are highly fabricable, have good impact resistance and have ductile weld characteristics. Such advantages compensate somewhat for relatively high cost, and these alloys are usually the preferred choice for service from 2000° to 2700°F. The density of B-66 is 0.32 lb/in.³, and current cost is about \$120.00/lb.

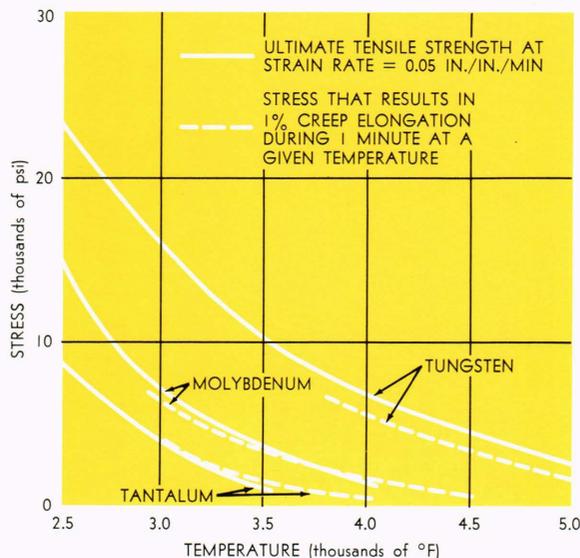


Fig. 3—Comparison of ultimate tensile strength with steady-state creep strength for tungsten, molybdenum, and tantalum.

A molybdenum-base alloy, TZM, was also developed, primarily for service below 3000°F. This alloy is reasonably fabricable and it can be formed in dies or spun into shapes. It is ductile at room temperature except when subjected to impact loads. While it can be joined by fusion welding, the welds are very brittle at temperatures below about 500°F. This imposes severe restrictions on the structural use of TZM. The material has a density of 0.36 lb/in.³, and the current price is about \$25.00/lb.

A tantalum-base (Ta-10W-2.5Hf) alloy, which is ductile at room temperature and can be joined by welding, is T-222. Because it is relatively easy to fabricate into complex shapes, T-222 is probably the best candidate for complex structures under high-temperature conditions. No strength data are available above 3500°F; strength will probably be found to drop below that of tungsten at temperatures above ≈ 4000°F, but should remain at about 80% of the strength shown here for tungsten up to 4500°F. The alloy has a density of about 0.61 lb/in.³; the current cost is about \$150.00/lb.

The tungsten-1% thoria alloy is used primarily in wire form as filaments in incandescent lights and electronic tubes¹³ but is available in limited sizes of strip and rod. A drawing operation is a necessary part of the process for developing strength.

¹³ R. W. Hall, P. F. Sikora, and G. M. Ault, "Mechanical Properties of Refractory Metals and Alloys Above 2000°F," *Proc., Am. Inst. Mining Met. Engrs., Technical Conference on Refractory Metals and Alloys*, Detroit, 1960 (Interscience Publishers, London, 1961), 483-503.

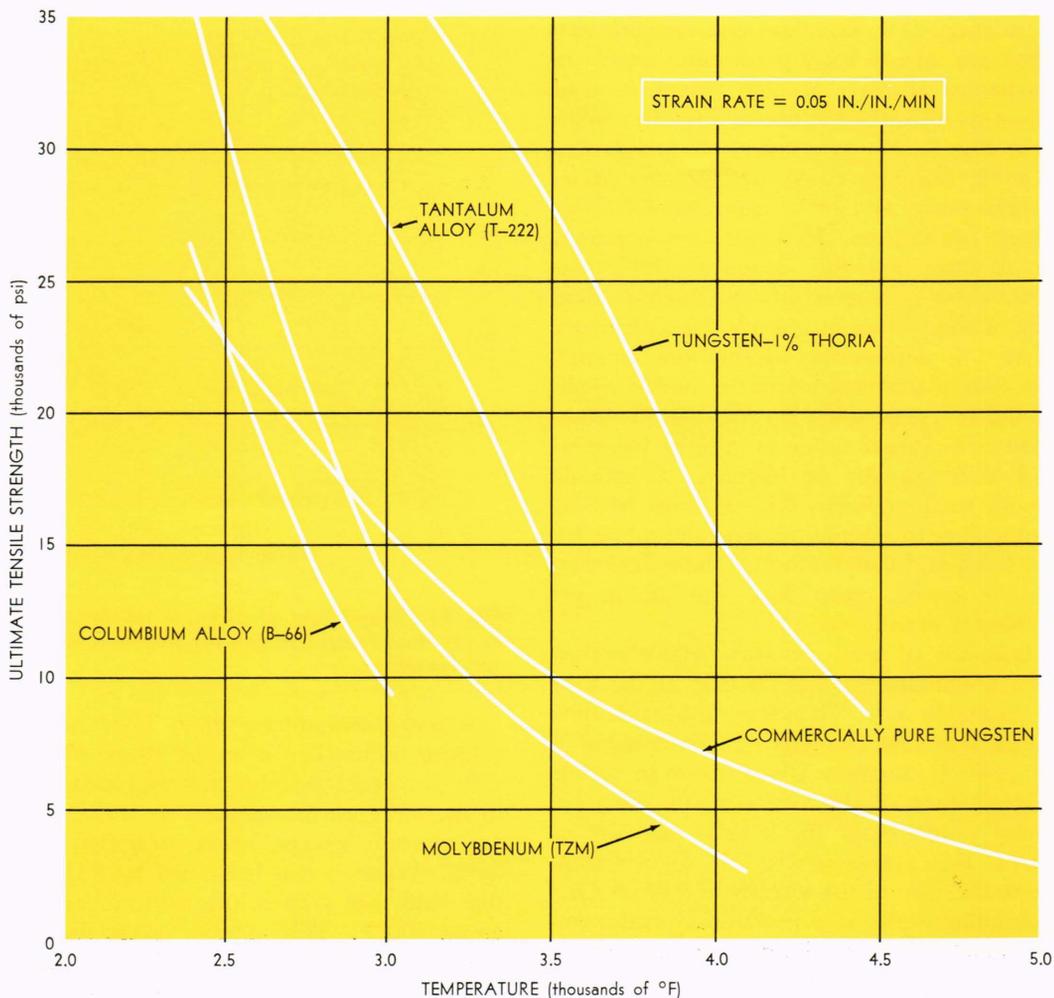


Fig. 4—Ultimate strengths of the five best refractory metal alloys available in 1964.

Both tungsten and tungsten-1% thoria are very brittle at temperatures below about 300°F, therefore have limited fabricability, and are usable in welded forms. The density of tungsten is 0.70 lb/in.³, and current cost is about \$30.00/lb.

The tungsten-1% thoria alloy is essentially a dispersion-hardened alloy. As we have mentioned, this is the only effective strengthening mechanism at temperatures above about 3000°F. Some improvement in strength may be possible by altering the size and distribution of the dispersion in such alloys, but the curve shown here is probably close to the upper limit of strength that can be achieved in any metallic alloy system. Major emphasis of alloy-development effort during the remainder of this decade will probably be on raising the strength of fabricable alloys up to this limit rather than attempting to push tungsten alloys beyond it. For

purposes of planning for 1970, therefore, it seems unreasonable to assume a design allowable in excess of the tensile strength of this material.

Comparison of Ceramic and Metallic Materials

The term *ceramics* is derived from the Greek word for earthenware, and its common meaning still applies only to pottery, tiles, or other articles made by baking clay, oxides, silicates, titanates, etc., found in the earth's crust. In the technical sense today, the term includes a host of other compounds such as carbides, borides, silicides, nitrides, beryllides, and other intermetallic compounds having high melting points.

Use of ceramics in engineering applications has been limited because they are inherently brittle and their strength varies widely as a result of minor

changes in processing or composition.¹⁴ In spite of this the severe requirements of missiles and rockets have stimulated interest in them, and some promising research programs aimed at understanding the behavior and use of brittle materials are underway. The result of these efforts will very likely be that they will permit the development of oxidation-resistant materials with modest but reproducible strength properties, rather than an unusually high strength at extreme temperatures.

Ceramic materials exhibit the same general tendency as metals to lose strength rather drastically at temperatures above about half the melting point. This is due primarily to a change in the fracture mechanism, in which fracture usually occurs along grain boundaries at high temperature but passes through grains at low temperature.¹⁴ Some plasticity sets in at temperatures of about two-thirds of the melting point, and the brittle fracture problems then become less severe. However, ductility seldom reaches the amount characteristic of metals (often 100% elongation) and fracture typically occurs at less than 5% elongation. Creep under stress is also observed in such materials, and, characteristically, the creep strengths fall below those of refractory metals.

The tensile strengths of several oxides at elevated temperatures are shown in Fig. 5. The steep decrease in strength at temperatures from 2000° to 3000°F is quite evident, and at temperatures above 3000°F the strengths fall in a range not exceeding ≈ 500 psi.

These tensile tests were made on material of the highest density that could be produced in the laboratory (probably < 1% porosity).¹⁴ Generally, most commercial ceramics—and particularly pure oxides—contain fine pores equal to about 10% of the total volume. This porosity results in substantially less strength than that of the fully dense materials. Figure 6 shows how the room-temperature strength of alumina decreases with porosity.¹⁵ This porosity effect persists at all temperatures of practical interest and causes comparable losses in the creep strength when tested above one-half the melting point. Porosity is the factor that is probably most responsible for the variability of properties of commercially available materials. To some extent the strength values normally published in current handbooks do not represent the true strength that might be available with better quality control during manufacture.

¹⁴ W. D. Kingery, "Oxides for High Temperature Applications," *Proc., International Symposium on High Temperature Technology*, Stanford Research Institute, Oct. 1959 (McGraw-Hill Book Co., New York, 1960), 108-133.

¹⁵ R. L. Coble and W. D. Kingery, "Effect of Porosity on Strength of Aluminum Oxide," *J. Am. Ceram. Soc.*, 39, 1956, p. 377.

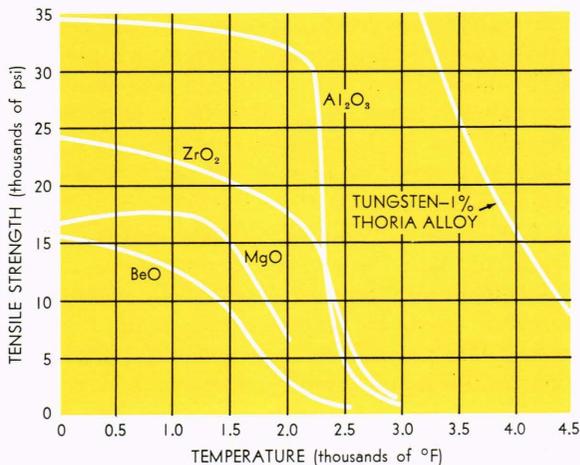


Fig. 5—Tensile strengths of a variety of ceramic oxides at elevated temperatures.

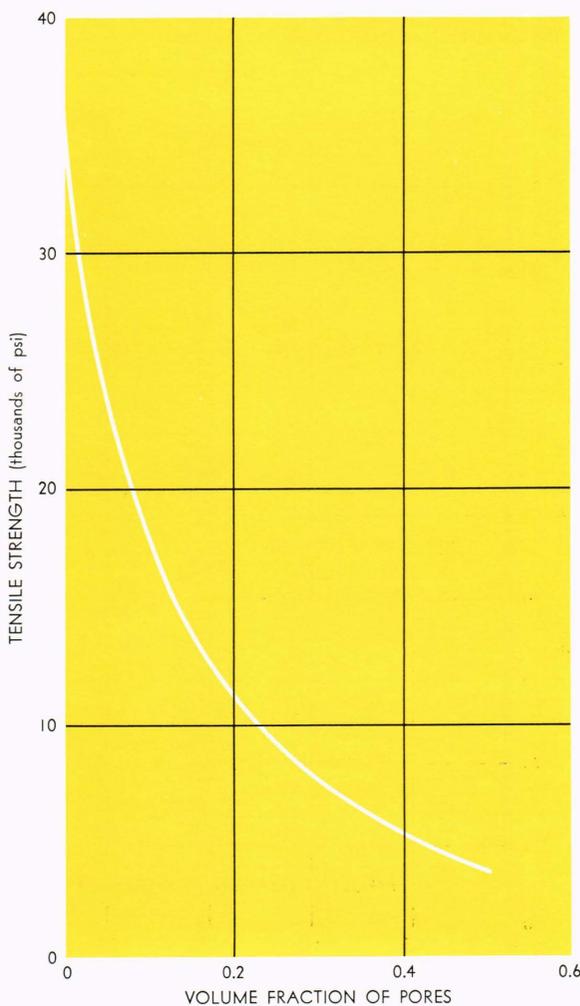


Fig. 6—Effect of porosity on the relative strength of alumina at ambient temperature.

Essentially no creep data exist for the ceramic oxides, and it is not possible to ascertain a probable design allowable as was attempted here previously for metals. Some data have been obtained on zirconia (one of the stronger ceramic oxides available) at a very low stress of 50 psi.¹⁴ The creep rate varied from 0.003%/sec at 3450°F to 0.36% at 4200°F. From this we estimate that this stress would produce 1% elongation during one minute at temperatures around 3700°F. In comparison tungsten would be expected to sustain loads of about 7000 psi without exceeding the 1% elongation; in this light, ceramic oxides appear very poor candidates for true structural applications above 3500°F.

In Fig. 7 the tensile strengths of a variety of materials are shown in order to compare nonoxide ceramics, oxide ceramics, graphite, and metals.¹⁶

These show the strongest of each breed. Zirconium carbide has a strength about equal to the oxide. It is not known at what temperature the strength of this material will drop off sharply, but it is likely to occur below 3500°F. Molybdenum disilicide shows a gradual increase in strength up to about 2200°F and then a sudden drop. The rise in strength probably is associated with the onset of ductile behavior (or less susceptibility to the nucleation of brittle fracture mechanisms). The same is probably true of titanium boride,¹⁷ and of pyrolytic graphite,¹⁸ which appears in this figure as the highest-strength material at temperatures above 3200°F.

Pyrolytic graphite is a special form of carbon that is obtained by a high-temperature process in

¹⁶ R. I. Jaffee and D. M. Maykuth, "Refractory Materials," Battelle Memorial Institute DMIC Memo 44, Feb. 1960.

¹⁷ V. Mandorf, J. Hartung, and E. J. Seldin, "High Temperature Properties of Titanium Diboride," *Proc., Am. Inst. Mining Met. Engrs., Technical Conference on Refractory Metals and Alloys*, Detroit, 1960 (Interscience Publishers, London, 1961), 455-467.

¹⁸ "Pyrolytic Graphite Engineering Handbook," General Electric Company Form PG-63-1, Detroit, Michigan, 1963.

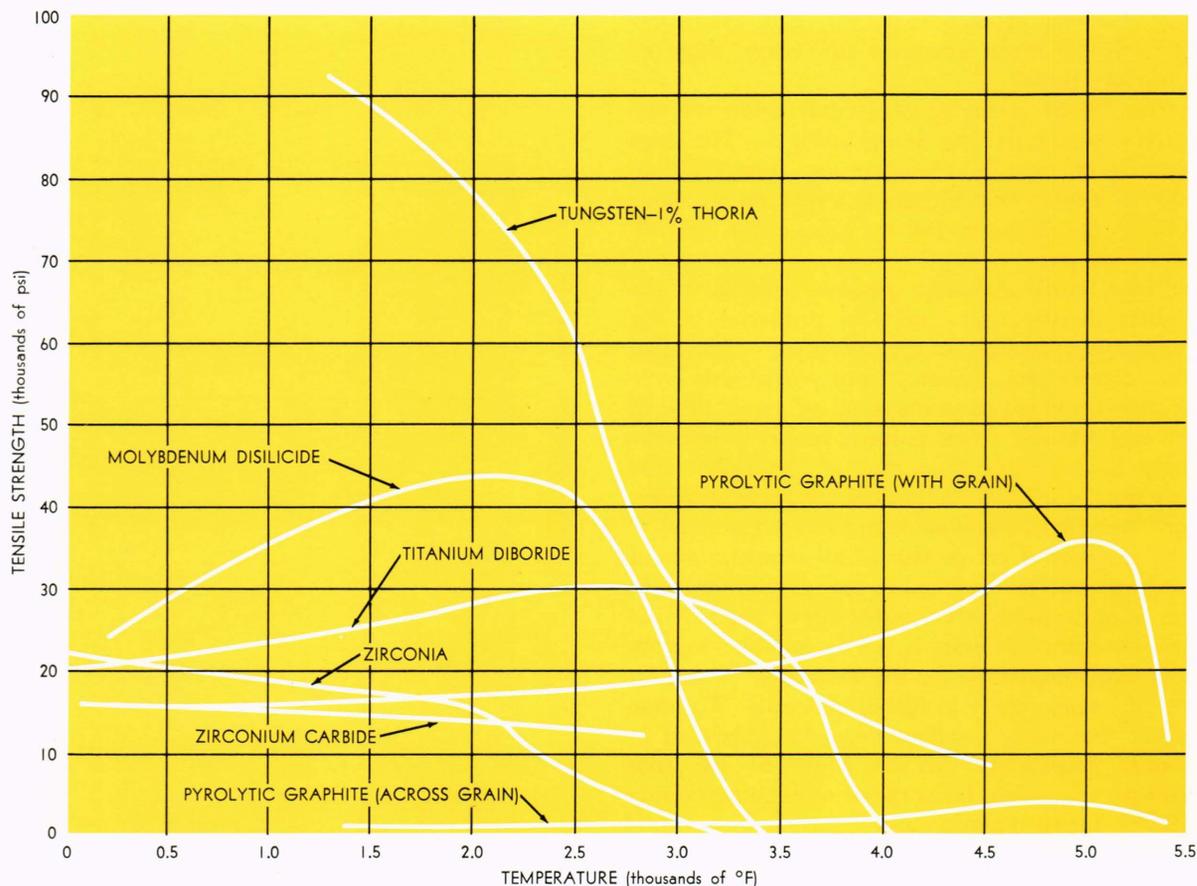


Fig. 7—Summary comparison of the strengths of various metals, metal alloys, and ceramics at elevated temperatures.

TABLE I
CRITICAL PROPERTIES OF SOME HIGH-TEMPERATURE MATERIALS

| Material | Melting Point, °F | Density, lb/in. ³ | Heat Capacity, BTU/lb °F | | Thermal Conductivity, BTU ft /ft ² °F hr | | Thermal Expansion Coefficient 78°F (10 ⁻⁶ in./in. °F) | Modulus of Elasticity, 10 ⁶ psi | | Maximum Temperature For Use In Oxidizing Atmosphere, °F |
|-----------------------|-------------------|------------------------------|--------------------------|--------|---|--------|--|--|--------|---|
| | | | 78°F | 3000°F | 78°F | 3000°F | | 78°F | 3000°F | |
| Tungsten | 6170 | 0.70 | 0.033 | 0.040 | 97 | 74 | 2.5 | 60 | 17 | 3500† |
| Tantalum | 5425 | 0.60 | 0.033 | 0.041 | 32 | 42 | 3.7 | 27 | 8 | 3000† |
| Molybdenum | 4730 | 0.37 | 0.061 | 0.098 | 85 | 69 | 3.0 | 48 | 9 | 3150† |
| Columbium | 4379 | 0.31 | 0.065 | 0.083 | 30 | ≈40 | 3.9 | 18 | 4 | 2900† |
| Zirconia* | 4620 | 0.20 | 0.10 | 0.15 | 1.0 | 1.4 | 3.7 | 22 | ≈0 | 4620 |
| Alumina | 3690 | 0.14 | 0.16 | 0.33 | 7.0 | 0.5 | 4.5 | 53 | ≈0 | 3690 |
| Magnesia | 5072 | 0.13 | 0.23 | 0.40 | 24 | 3.0 | 7.5 | 31 | ≈8 | ≈4800 |
| Beryllia | 4660 | 0.11 | 0.24 | 0.50 | 121 | 9.0 | 4.3 | 45 | ≈0 | 4660 |
| Zirconium carbide | 6390 | 0.24 | — | — | 12 | — | 3.7 | — | — | 3000 |
| Titanium diboride | 5000 | 0.16 | — | — | — | 24 | 5.5 | 63 | 54 | ≈3000 |
| Molybdenum disilicide | 3400 | 0.23 | — | — | 19 | — | — | — | — | 3150 |

* Stabilized with 4% CaO and 4% HfO₂.

† Coated.

which methane is decomposed and the resultant graphite deposited with a highly oriented hexagonal crystal structure. The process was discovered late in the last century, and the material was of interest to Edison, among others, for filaments in incandescent bulbs. New interest has been stimulated by the severe requirements of rocket propulsion systems, and much progress in understanding the material has been made in the past five years. Owing to its highly anisotropic structure, it exhibits wide variations in strength, thermal and electrical conductivity, and other properties when tested in different directions with respect to the crystal orientation. The material is brittle at room temperature, but like some ceramics it becomes ductile at elevated temperatures. Owing to the grain of its structure, it is relatively weak in one direction and has a tendency to split like wood. As a result, fabrication techniques similar to the "hole and peg" methods used in early American furniture have been used in some quite modern structures. Pyrolytic graphite is not very resistant to oxidation at extreme temperatures, and it has an unfavorable tendency to shrink in some directions and expand in others when heated above about 4000°F. In spite of all these problems, the material has been used successfully in operational rockets.

Pyrolytic materials with two or three times the strength shown here will probably be available within the next decade, and many of the problems that have been encountered due to directionality will be better understood and used to good advantage. Apart from purely structural applications, the material is of great interest because of its unique ability to conduct heat along its grain as rapidly as does copper, and yet insulate as well as asbestos across the grain. This attractive character-

istic will stimulate continued progress in this class of materials.

Apart from pyrolytic graphite, it appears that the strengths of nonmetallic materials at temperatures much greater than half their melting points may also be limited, by some inherent characteristics, to values ranging in the hundreds of pounds per square inch at temperatures above 3000°F. However, ceramic materials have not been explored as much as metals, and it is possible that the predominant trend for low strength at these temperatures could be altered by better scientific understanding. Unfortunately the current level of effort on this problem in this country is meager compared with what it should be, and improvements during the next decade are not likely to be very numerous.

A comment should be made here on the use of ordinary tensile strength as a basis for comparison of materials, rather than the ratio of ultimate tensile strength to density that is generally more significant in airframe uses. In many applications of these materials in hypersonic vehicles, the geometry of a component is limited by aerodynamic factors such as drag and shock deflection. It is often not possible to use thicker sections of lower density material; thus maximum strength within the fixed volume must be achieved. The ultimate strength/density ratio is, of course, more appropriate in cases where such limitations do not exist. Likewise, there are areas where such thermal properties as conductivity, heat capacity, oxidation rate, etc., are more important than strength, and where final selection of material will be based on combinations of all such properties. For a general comparison, Table I has been assembled to show the properties of some of the materials discussed in this paper.