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CURRENT STATUS AND OPPORTUNITIES FOR IMPROVED HIGH-TEMPERATURE MATERIALS FOR ADVANCED TURBOJET ENGINES

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TECHNICAL PREPRINT prepared for International Meeting on Aircraft Design and Technology sponsored by the American Institute of Aeronautics and Astronautics
Los Angeles, California, November 15-18, 1965

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ABSTRACT

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Improved materials for the hotter components of the turbojet engine are a continuing requirement. The major problem is not merely the achievement of needed high-temperature strength but rather to achieve, simultaneously, resistance to attack by air (both oxygen and nitrogen). Coatings are now required for superalloys for use at advanced temperatures and this need has been accelerated by a trend toward alloying to achieve strength while permitting some sacrifice in oxidation resistance. [The status of the development of conventional superalloys of nickel and cobalt base that are now used in this application will be reviewed.] Future opportunities for improvement in these materials are deemed limited but important. The great need for increased operating temperatures of advanced turbojet engines has stimulated consideration of long-range more novel approaches to material development as an alternative or assistant to cooling. Typical are dispersion-strengthened superalloys, fiber-strengthened superalloys, alloys of the refractory metals tantalum

and columbium, and alloys of chromium. Apparently all will require coatings to provide protection against attack by air.

INTRODUCTION

The requirement for materials that will permit higher operating temperatures in advanced turbine engines has been well advertised in recent years and will not be documented here. Turbine-inlet temperatures have been limited by the survival capability of certain critical engine components. Perhaps the most limiting components are the turbine stator vanes that must withstand direct impingement by the high-velocity gases exiting from the combustion chamber (to redirect these gases against the rotating buckets), and the highly stressed rotating turbine buckets. As the designer has exhausted the capability of the materials available to him, he has turned to the alternative of cooling. Cooling these components must be paid for by increased engine complexity and by some sacrifice in performance, when compared with the same temperatures, if achieved without cooling. It therefore remains an important objective of metallurgical research to find those materials that will survive at higher temperatures thus permitting higher gas temperatures--either without cooling or at least with reduced cooling requirements.

It is the purpose of this presentation to examine where we stand today and to suggest areas of opportunity for research. Finally the scope of the NASA contract program currently underway in pursuit of these opportunities will be outlined.

STRESS AND TEMPERATURE CONSIDERATIONS

To provide proper perspective for our review of these materials, it is desirable to have a knowledge of the required strength levels for each component. Let us first consider the rotating turbine bucket. Several years ago we showed that there was a "critical zone" for failure in uncooled turbine buckets,[1] as illustrated in Fig. 1. In the lower part of the figure are plotted the temperature and stress distribution along the length of a turbine bucket. The stress is highest at the base of the airfoil because the centrifugal loads imposed by total bucket airfoil length must be carried there. The temperature, on the other hand, is purposely designed to be highest near the tip, where the stresses are the lowest. At every point along the airfoil length, there is a specific centrifugal stress and temperature for which an expected stress-rupture life can be calculated, resulting in the top curve. At the base of the airfoil the life is very long as a result of the low temperature, even though the stress is very high. At the tip, the temperature is high but the stress is very low, so again there is a very long life. Somewhere in the vicinity of the middle of the bucket airfoil length there is a combination of stress and temperature that results in the lowest computed life for a turbine bucket. The main point of Fig. 1 is that, from a strength viewpoint, the critical bucket temperature is not necessarily the highest temperature nor is the critical stress the highest stress. We are therefore interested in the typical value of stress at this limiting "critical zone" From a survey of several engines, we find that the stress level in this zone of the first stage buckets is generally between 15,000 and 20,000 psi. These reference values will be used throughout this discussion and materials will be compared on the basis of their stress-rupture capabilities in this stress range. In addition to the stress from centrifugal force, the rotating bucket suffers from exposure to mechanical fatigue, thermal fatigue, and erosion and corrosion. All these factors will tend to reduce the life from that predicted from a consideration of stress-rupture alone,[1] and candidate materials should have good resistance to failure from these causes. Initial comparisons are necessarily and conveniently made on the basis of only stress-rupture, however, this approach will be used herein.

The stationary nozzle vanes are exposed to much lower stresses than the turbine buckets. Usual failure mechanisms are excessive bowing, local distortion and cracking, and erosion or corrosion. The bowing results from inability to withstand the creep-rupture conditions imposed by the bending loads of the high-velocity hot gases as the vanes redirect the flow of these gases toward the rotating buckets. The local distortion and cracking result from conditions of thermal fatigue.

Generally, the initial screening of vane materials may be made on the basis of stress-rupture strength as a measure of ability to withstand the gas loads causing bowing. Thus we will examine candidate vane materials to withstand stresses, typically, in the range of 2500 to 7000 psi. The necessity for good thermal fatigue and corrosion resistance should not be minimized, however.

The general relation of temperature of these components to inlet gas temperature is described in Fig. 2. The temperature of uncooled gas turbine buckets in the critical zone is usually of the order of 150° to 200° less than the turbine-inlet temperature (150°F is shown in the figure). Most of this temperature difference results from the fact that the total temperature of the gas stream relative to the rotor blades is less than the true total temperature of the gas. On the other hand, it is recognized also that there are higher temperatures in the bucket than those associated with the critical temperature and stress. For reasons of oxidation, we must be concerned with the highest temperature.

In the case of the inlet-guide vanes, their temperature, if uncooled, will be somewhat higher than the reported inlet gas temperature. Inlet gas temperature is reported as a mean effective gas temperature, and the actual gas profile will exhibit both higher and lower temperatures than this mean. Whereas the rotating bucket averages out these peaks and valleys, some of the vanes will see the highest temperatures.

Although we have measured vane temperatures 200°F higher than turbine-inlet temperatures,[2] we can expect that gas profiles ~~from the~~ combustor will be improved, and thus it is suggested here that we consider nozzle-vane-material temperatures as being 100°F higher than turbine-inlet temperatures. It is useful, then, to keep in mind that turbine-bucket critical-zone temperatures will be about 150°F less than turbine-inlet temperatures, and nozzle-vane temperatures about 100°F higher. For the same turbine-inlet temperature, vanes will be about 250°F hotter than buckets.

SUPERALLOYS

From the birth of the turbojet engine to the introduction of cooling into the turbine bucket, the increases in turbine-inlet temperatures were paced by the improvements in temperature capability of nickel- and cobalt-base superalloys. The present status of nickel-base superalloys is shown in Fig. 3 (More detailed information is given in refs. 3 and 4.) The data are presented in plots of 1000-hour "strength-density" ratio against temperature. Strength is plotted as a ratio of 1000-hour stress-rupture strength to density because this is the important parameter for rotating turbine buckets; stress is a result of centrifugal force, which in turn is a direct function of density. The previously mentioned stress range of 15,000 to 20,000 psi is for typical superalloys now used in engines. If we look to heavier materials, their strengths must be higher because the stress in the bucket will be higher. Thus it is necessary, when considering other materials, to convert bucket stresses of 15,000 and 20,000 psi for nickel-base alloys to a required strength-density ratio of 52,500 and 70,000 inches; a "bucket-stress" band will be shown covering that same strength-density range in subsequent figures. Vanes are stationary parts and stresses are not related to density; the band for vane stresses will always appear in the figures as a range of actual stresses between 2500 to 7000 psi for the material in question, rather than as a constant strength-density requirement.

Comparisons are somewhat arbitrarily made on the basis of 1000-hour life. The spectrum of required lifetimes of advanced engines range from perhaps as low as 50 hours for certain military applications to several thousand hours for commercial supersonic aircraft. Comparison of materials might best be made on the basis of lives several times that of the longest required to provide a factor of safety However, for many of the materials reviewed herein, even the use of 1000-hour strengths required considerable extrapolation, and it was thought undesirable to carry such extrapolations further.

In Fig. 3 the Udimet 700 plot is representative of the best wrought alloys; the remainder of the alloys are cast. (The nominal compositions of all the materials described herein are shown in Table I.) In recent years there has been more acceptance of the use of the higher strength cast alloys with their concomitant lower ductility and fatigue resistance. Recently, a new directional solidification process for cast nickel bucket and vane alloys has been announced[5] that is reported to improve both strength and ductility. The PWA664 shown (Fig. 3) is the MAR-M200 alloy composition processed by directional solidification. The strength advantage is clearly indicated. As a class, these nickel-base cast alloys may be useful for buckets to maximum temperatures near 1750° to 1800°F (turbine-inlet temperatures of 1900° to 1950°F) For stator vanes, use temperatures approximating 2000°F are indicated based on these strength considerations alone, but, in practice, lifetimes would be much less than 1000 hours at this temperature because of oxidation and erosion in the high-velocity gas stream of engines. More will be said about this later.

In considering what future development efforts may achieve in stronger nickel-base bucket alloys, it may be instructive to consider past history. Current alloys have resulted from a relatively slow evolutionary development starting back in World War II with alloys having a capability of surviving, on the basis shown here, at temperatures near 1400°F. Our gains have been about 400°F in, for instance, 20 years. Recently, the increased acceptance of cast alloys has permitted increases in strength that would not have been possible if forgeability were a requirement. In some cases, gains in strength have resulted from a reduction in chromium content (which may, however, compromise corrosion resistance). The TaZ8 alloy[6] in the figure (Fig 3) is a development of personnel at our laboratory it has low chromium. This alloy is workable if working is initiated from small cast slabs rather than from large ingots. The very recent introduction of directional solidification has pointed out another opportunity. It is generally accepted that further improvements in nickel-base alloys will be modest; however, it is suggested that even a 50^{o}F improvement may be useful, and investigation into improved cast alloys should continue.

Because nickel-base alloys are the materials used today, all future figures wherein comparisons are made will contain a curve for a typical cast nickel-base alloy, IN100, for reference purposes.

At the end of World War II, cobalt was in short supply and, by necessity most attention was directed toward development of nickel-base alloys. Since that time, little attention has been redirected toward cobalt alloys. Their status is indicated in Fig. 4. Because they are quite inferior in temperature capability at the stress levels required in buckets, the comparisons are made only for vane conditions Three representative cobalt-base alloys are shown, J1650, MAR-M302, and a recent NASA alloy. It is suggested that the cobalt-base alloys may be of more interest than nickel-base alloys for exploration for vane application for several reasons. The data here suggest that, although the cobalt alloys are weaker at lower temperatures, their strengths may be better at the very high temperatures of interest for vanes--probably because the carbide phases that strengthen cobalt alloys are more stable at these temperatures than are the usual gamma prime intermetallic phases (e.g., $Ni_3(Al, Ti)$) in nickel alloys. Also, materials used at temperatures of 2000^{o}F are only 150^{o} to 250^{o}F below the melting point of minor phases in some of these alloys. It is suggested that our opportunities are better if we pursue materials of the higher melting point. Cobalt has a reported melting point of

2723°F, 76°F higher than that of nickel, and we should capitalize on this advantage.

One advantage of pursuing even modest gains of 50° to 100°F in nickel- and cobalt-base alloys is that alloys amenable to conventional fabrication approaches are being studied, and the resultant alloys may be introduced readily and cheaply into current engine designs.

DISPERSION-STRENGTHENED SUPERALLOYS

It is obvious, however, that if large gains are to be made, other approaches should be pursued. One of the more promising is dispersion-strengthened superalloys. The objective in this approach has been to distribute a very fine, stable, hard particle in a metal matrix, probably by powder-metallurgy methods. The most promising materials of this type reported to date are thoria distributed in nickel shown in Fig. 5. Two materials are shown, nickel plus 3 percent ThO_2 developed at Sheritt-Gordon Company[7] and TD-Ni, which is nickel plus 2 percent ThO_2 developed at Du Pont. The data for the Ni-3 percent ThO_2 material are shown for strip, and the data for TD-Ni are for 1-1/4 inch-diameter bar. Du Pont has reported[8] that their strengths for bar shown here are superior to data for sheet and that this bar further worked to 1/2 inch-diameter bar will result in even better strengths. The Du Pont material is commercially available.

It is immediately obvious that these materials are not competitors with conventional nickel alloys as bucket materials because of low strengths, but they have tremendous potential as vane materials. Indeed, Du Pont's TD nickel is under test for this application by engine manufacturers.[9,10] In addition to this strength advantage, these materials do not have low melting minor phases, but retain the melting point of unalloyed nickel; they do not suffer the damage from momentary over temperatures that might occur in conventional superalloys.

Clearly, if these materials are to find application in the rotating turbine bucket, it is necessary to increase the strength levels. This is the objective of continuing research in dispersion strengthening. The strengths of these dispersion-strengthened materials (such as TD-Ni) are apparently dependent on a combination of factors; particle size and spacing of the dispersed particle (ThO_2), which in turn stabilizes cold-work strengthening in the matrix (and, perhaps, the fine grain size of the matrix).

Further development will optimize these parameters and in addition introduce solid-solution strengthening and perhaps conventional precipitate strengthening in combination with dispersion strengthening. Du Pont researchers have recently investigated solid-solution strengthening by adding molybdenum to the nickel matrix of TD-Ni. The pro duct is called TD-NiM.[8] The results (Fig. 6) indicate that the strength level of TD-Ni has been increased markedly at low temperatures, but strengths at 1900°F and above are comparable to TD-Ni. A sought after goal of a general elevation of the properties at all temperatures has not been achieved. These data indicate that TD-NiM does not have sufficient strength to replace nickel-base alloys in buckets.

In the opinion of the author, dispersion strengthening is the most promising approach to realizing an increase of 200°F in permissible metal temperatures in turbine buckets and vanes. As mentioned before, an important factor in the strengthening of these materials is the retention of cold work by the proper dispersion of the stable, hard particle. As the dispersion is optimized for maximum strength, experience with these materials suggests that ductility may be compromised. Increased emphasis on dispersion strengthening of solid-solution matrices is deemed the route of greatest opportunity. It is suggested that a cobalt superalloy matrix may have advantages over a nickel matrix. Historically, cobalt superalloys have been more "forgiving" in processing; for example, vacuum melting of these alloys has not been necessary as contrasted to nickel-base alloys. Studies are now underway at several laboratories, as will be described later.

CHROMIUM ALLOYS

Other candidate materials for vanes and buckets are alloys of chromium. The potential advantages of chromium have long been recognized; a melting point of 3407°F, 684°F higher than cobalt, a density of 0.260 pound per cubic inch, nearly 20 percent less than nickel and cobalt, some inherent oxidation resistance, and it is available in quantity. Unfortunately, these advantages have been overwhelmed by the disadvantages. Chromium experiences a change from ductile to brittle behavior as temperature is lowered, and, for unalloyed chromium, this ductile-brittle transition is above room temperature except when the material is produced in very high purity. Some alloying additions lower the ductile-brittle transition temperature but those particular additions do not, simultaneously, provide needed increases in strength. Also, when exposed to air at high temperatures, chromium rapidly absorbes nitrogen with a rapid increase of the ductile-brittle transition temperature to temperatures above the desired use temperature. Because of discouraging progress in extensive studies conducted about 15 years ago, little research on the alloying of chromium to increase strength has been conducted recently. Research was continued in Australia until recently, and General Electric's Materials Development Laboratory at Cincinnati has had studies underway in the past few years. Advanced alloys of these programs are summarized in Fig. 7. Alloy E is the alloy reported by Wain and Johnstone[11] of Australia and contains 2Ta-0.1Ti-0.5Si. C207 and the alloy labeled "Advanced Cr Alloy" are from the G. E. program and the compositions are proprietary. These alloys have resulted from continuation of other studies described in reference 12. All are wrought alloys that could be forged into a bucket or vane. Clearly from a strength consideration, as plotted here, chromium alloys have potential for increased operating temperatures in both buckets and vanes; for example, at a 1000-hour stress-density of 70,000 inches, C207 alloy offers 100°F increase and the "Advanced Cr Alloy", 200°F over the nickel alloy shown. The problems have not all been solved, however. Alloy E has good strength in combination with ductile-brittle transition temperature below room temperature. C207 and the advanced alloy are of higher strength but have a ductile-brittle transition temperature somewhat above room temperature but well below the normal operating temperature of these parts. This experience suggests that improved strength alloys can be produced with a ductile-brittle transition temperature below room temperature; but further strengthening may raise the ductile-brittle transition temperature above room temperature. Also, because of nitrogen embrittlement, all three alloys experienced an increase in ductile-brittle transition temperature on continued high-temperature exposure to air Because of composition differences, these alloys vary in nitrification susceptibility, however.

Future studies in chromium might pursue several paths, and guidelines are available to us. Many characteristics of chromium are similar to the other group VI A refractory metals, tungsten and molybdenum. All experience the problem of a high ductile-brittle transition temperature (unalloyed Mo near room temperature and W at well above room temperature) and require extremely careful consolidation and processing in protective atmospheres. Both Mo and W require coatings for protection against oxidation if used in air at high temperatures. Intensive research on W and Mo has been conducted in recent years utilizing advanced facilities for processing and evaluation, facilities that purify the metals during consolidation, and avoid contamination during processing. The progress in these areas has been dramatic.[13] Some of the coatings that resist oxidation of Mo may minimize nitrification in chromium. It seems timely to direct some of these facilities and talents toward the similar important problems of chromium.

Alloying objectives are to seek strengths comparable to or better than those of the "Advanced Cr Alloy" of Fig. 7, but with ductility at room temperature. Another objective of alloying is to minimize sensitivity to nitrogen embrittlement (some progress has been made in this area). Coatings should be pursued to stop nitrification as well as to improve oxidation resistance.

Another approach to improving ductility in high-strength alloys may be via the dispersion-strengthening route. It has been found[14] that 6 percent MgO additions to chromium react with chromium oxides to form a dispersed spinel phase resulting in good room-temperature ductility and low notch sensitivity. The spinel is dispersed as large particles, and only modest strengthening results. Very fine dispersions warrant study. Researchers at Battelle have found[15] that a dispersed ThO_2 phase lowers the ductile-brittle transition temperature of tungsten, and additional investigations have shown advantages for a combination of a dispersed phase and rhenium additions in low percentages to W.[16,17] The same approaches may benefit chromium. Surely there is opportunity in the application of new knowledge and techniques in pursuit of chromium alloys

REFRACTORY METALS

Whenever materials are required for applications at temperatures above 1800°F, it is obvious that we should consider the refractory metals W, Ta, Mo, and Cb having melting points of 6170°, 5425°, 4730° and 4475°F, respectively. Of these, Ta and Cb are the more likely candidates because of combined strength, fabricability, and better potential for protection from oxidation. Tungsten is brittle at room temperature and, although the oxidation resistance of all refractory materials is poor, molybdenum has the disadvantage of forming a volatile oxide that sublines as fast as it is formed at temperatures above 1415°F. Coated molybdenum alloys have proved unsatisfactory because pin holes caused by coating defects or foreign-object damage in engines cause local catastrophic failure. The strength of alloys of tantalum and columbium are shown in Fig. 8. The columbium alloys are those currently under study by Begley, et al.[18] and contain approximately 22W-2Hf-0.1C. The tantalum alloy is T222 (Ta-10W-2.5Hf-0.01C) Ammon, et al.[19] These strength data indicate that both could be used at bucket temperatures of 2200° to 2350°F (turbine-inlet temperatures of 2350° to 2500°F). Because the tantalum alloy has better rupture strength at higher temperatures, the band for vane stresses is plotted for this material and suggests possible vane temperatures to at least $2500^{\circ}F$. These alloys are fabricable and can readily be made into bucket shapes by forging, and are ductile at room temperature. The tantalum alloy has been produced in high quality sheet and tubing.

The density of the columbium alloy is only 35 to 40 percent higher than conventional superalloys, but the density of the tantalum alloy is about 2.2 times that of superalloys. For buckets, if all other factors were equal, the choice would be columbium alloys to minimize stresses in the turbine disk and engine weight. (A high density bucket raises turbine disk loading, thus requiring a heavier disk, which in turn requires heavier shafts, bearings, bearing supports, etc.) For vanes, the high density of the tantalum alloys is of lesser importance because only vane weight is a consideration. The higher temperature potential is an advantage. The characteristic inhibiting use of these materials is their poor oxidation resistance. Alloying helps, but no alloy has been identified that combines oxidation resistance with needed strength and fabricability. Coatings are the only hope at present.

Coatings for columbium have been intensively studied in recent years, primarily for very short-time application in reentry vehicles. Some of these have shown considerable promise in this application to temperatures as high as $2600^{\circ}F$. Much less attention has been directed toward coatings for tantalum. It may be possible (though unlikely in the author's opinion) that satisfactory coatings will be developed for these alloys for turbine buckets for very short-time engine lives, for example, less than 50 hours. Development of reliable coatings for very long lives in rotating buckets is highly improbable. Local coating defects will lead to bucket failure, and failure of a rotating bucket can cause severe damage to other buckets or engine components. The greater opportunity is for the low-stress stationary vanes where local failures occurring in service may be found on inspection and the vane repaired or replaced before catastrophic failure occurs The Air Force is continuing to support needed coating research for columbium alloys. It is suggested that additional studies to develop coatings for tantalum alloys for use in the temperature range of interest here (rather than at the very high temperatures now under study for the reentry requirement) may be profitable. The fact that the oxide of tantalum melts at 3434°F contrasted to 2660°F for the oxide of columbium indicates a possible opportunity in tantalum.

The refractory metals clearly have outstanding strength, but their extremely poor oxidation resistance offers little assurance of their application to engines in the near future. Perhaps there is a way to utilize the advantage while minimizing the disadvantage through the concept of composite materials

FIBER-REINFORCED SUPERALLOYS

The refractory metal alloys might be converted to wire and embedded in a superalloy matrix that has a superior oxidation resistance.

Figure 9 is illustrative of this concept and uses a model system. A composite material of tungsten wires is shown embedded in a copper matrix; the tungsten wires have a strength much greater than copper and serve to strengthen copper. Figure 10[20] illustrates the strengths achieved as a function of volume percent of tungsten wire added to the copper. This is for continuous fibers all oriented parallel to the load axis. Clearly, the strength of the composite increases directly with the volume percent of tungsten added in accord with the law of mixtures.

If, for lack of several temperatures, we were to substitute the 1000-hour strength density of our reference superalloy IN100 at the left side of the figure and the 1000-hour strength-density of representative high-strength refractory metals for the fiber point (at 100 percent) on the right side, we may then draw a line between them and have an indication of the strength of the composite as a function of volume percent of refractory metal fiber added to the superalloy matrix. Crossplotting for several temperatures provides a set of parameter curves from which we can assess the potential for improvement of temperature capability of superalloys by strengthening with refractory metal fibers. In the fabrication of composites, the goal is to incorporate as much reinforcing fiber as possible, consistent with adequate matrix content, to provide a protective oxidation-resistant film around each fiber. Very high volume percentages of fibers (>80 percent) present fabrication problems that also restrict fiber content. (At low fiber contents, on the other hand, necessary constraints on the matrix may not be present.) Figure 11 shows the improvement over the allowable use temperature for IN100 at two volume percentages of fiber, 30 and 70. The "allowable" temperature here is defined as the temperature at which the material would have a 1000-hour stress-rupture to density ratio of 52,500 inches, which for IN100 is about 1800°F. A representative high-strength alloy for each of the refractory metal systems except tungsten (where unalloyed material is shown) is used as the fiber in this plot. At 30 volume percent fiber, improvements of 120° to 290°F might be achieved; at 70 volume percent fiber, improvements of 250°F to 480°F might be achieved. At a 1000-hour stress-density ratio of 70,000 psi, not shown here, similar calculations would suggest that, as compared with improvements of 120°F to 480°F here, the range would be 75° to 435°F.

More dramatic improvements in strengthening could be expected by the introduction of ultrahigh-strength ceramic whiskers into superalloys. For example, Sutton[21] has calculated a predicted 1000-hour rupture strength of a composite of unalloyed nickel containing 50 volume percent of alumina whiskers near 80,000 psi at 2200°F

It should be remembered that these are calculated values, not experimental, and it is a long, tortuous path from here to successful composites of superalloys reinforced with refractory metals. A most serious problem will be the reaction of the refractory metal fiber with the superalloy matrix both during fabrication and in service at high temperature. An example is shown in Fig. 12. In Fig. 10, the strengths of W-Cu composites are shown. These are ideal materials for study because there is no reaction between the tungsten fiber and the copper matrix. Further studies have been conducted[22] where the copper matrix has been alloyed with other metals that will react or are mutually soluble with tungsten. The two photomicrographs clearly show the effect of an addition of 10 percent Ni to the copper matrix, and the strength data show that the tensile strength was reduced from 250,000 to 100,000 psi. In the same reference, other matrix additives damaged strength as little as 10 percent, and some information was provided which indicated that for the case where the damage to the fibers was severe, it might be minimized by the use of an additional additive.

From the known reactions and solubilities of nickel and cobalt alloy with the refractory metals, compatibility problems will be formidible and will almost certainly result in lower strength than predicted in Fig. 11. There may be some counteracting factors, however. Figure 13 shows that, from recent data,[23] the stress-rupture strengths of wires are better than comparable bar or sheet. For example, in this figure the 100-hour rupture strength at 2200°F of 5-mil wire is 33 percent better than 50-mil sheet; the temperature advantage in this range is 135°F

To date, few data have been available from studies of reinforcement of superalloys with refractory metals or fibers. Figure 14 shows data of Baskey, et al.[24] who conducted studies to reinforce cobalt and a cobalt alloy, L605. These short-time tensile data at 2000°F show a dramatic improvement in unalloyed cobalt and about a 250 percent improvement in tensile and yield strength of L605. The ductility decrease from 34 to 4 percent should not be overlooked, however. Also these are short-time tensile data. Long-time high-temperature exposure may cause severe interactions and damage.

It would seem that studies to reinforce superalloys with refractory metal or ceramic fibers or whiskers should be expanded Whisker reinforcement of nickel is underway;[25] neither high-strength-ceramic nor refractory-metal-alloy fibers are available, however (Only unalloyed tungsten wires from the lamp industry are now produced.) In addition to studies of compatibility and methods of fabrication to select suitable composite component combinations efforts are needed to provide suitable fibers.

INTERMETALLIC COMPOUNDS

This survey would be incomplete without at least a cursory examination of intermetallics. Studies were conducted at Lewis Research Center of $MoSi_2$ (e.g., ref. 26), TiC cermets (e.g., ref. 27 and 28), NiAl, and Ni_3Al (refs. 29 and 30, respectively) some 10 to 15 years ago. The conclusion at that time was that the $MoSi_2$ and carbide cermets generally had an impact strength too low for use in turbine buckets. Methods of fastening such brittle materials to turbine disks was also a problem, but here ideas were proposed that looked favorable.[27,28] Ni_3Al, although apparently having more ductility (and perhaps impact strength) at high temperatures, did not have sufficient strength. Many studies have been conducted by several laboratories since that time.

Among the new materials synthesized, the beryllides of tantalum and columbium[31] have stimulated some interest, primarily because of their outstanding oxidation resistance at high temperature (as will be shown later). Some limited data on strengths of these materials are shown in Fig. 15.[32] In contrast to all other figures of this type previously shown, these data are for 100 hours rather than 1000 hours. Extrapolation to 1000 hours did not seem justified. The low stress-rupture strength of these materials is compensated by their low density of only 40 to 65 percent of IN100; when compared on a stress-density basis, an allowable temperature increase of 375°F is indicated. This plot alone does not place the strength of these materials in proper perspective, however. Figure 16 (ref. 31) shows short-time bend-strength data for these materials as a function of temperature. Although these data cannot be converted to long-time conventional stress-rupture properties, the trend is probably indicative and suggests that useful strength at lower temperatures is less than that at high temperatures--in fact, the previous stress-rupture data were measured at about the optimum temperature range.

Referring again to Fig. 1, we are reminded that the stress band for buckets in Fig. 15 is at a critical zone near the middle of the airfoil length and stresses toward the base of the airfoil are higher.

In the usual case of metal alloys, allowable stresses increase rapidly with decreasing temperature. If the strength of a material is constant or decreases with decreasing temperature the maximum allowable engine operating temperature may be controlled by the more highly stressed base of the airfoil or even the fastener zone, rather than by the much lower stressed midspan. Allowable temperatures thus would be much lower. To clarify this problem, stress-rupture data are needed over a wide spectrum of temperatures.

The intermetallics also suffer from brittleness and resultant low resistance to foreign-object damage at low temperatures, and these properties may not be satisfactory even at maximum use temperatures (although many are superior in this respect to the oxides and carbides). More information is needed in this area. Their major attractive feature is outstanding oxidation resistance. It has been suggested that this feature could be utilized by forming a composite part where the leading edge that is subjected to the most severe oxidation and erosion would be made from a protective intermetallic. This may be possible but has yet to be fully demonstrated.

OXIDATION RESISTANCE

A review of the candidate materials would not be complete without a consideration of what may be the most difficult problem of all: poor oxidation resistance of many of the candidates. Directly comparable data are not available for all the materials discussed, but Fig. 17 is illustrative of the present status. Most oxidation data are collected in terms of weight gain or loss per unit area per unit time, and these data are useful in mechanistic studies but usually difficult to interpret in practical terms. A measure of depth of surface recession or oxide-scale penetration is preferred, though limited in availability, and is shown in the figure. The data are for 100-hour exposure because 1000-hour data again are not available. The allowable limit of about 1 mil penetration shown in the figure is arbitrary and merely a reference point. For engines that are to have a 100-hour life this is probably conservative; but if we seek to use an engine for 5000 hours, this allowable limit may be much too high.

Three superalloys are shown, IN100, L605, and 713-C. These data suggest that superalloys may be limited to use temperatures of 1700° or 1800°F because of poor oxidation resistance unless satisfactory coatings are applied. Coatings are being applied to engine parts of superalloys of flight engines at this time. The oxidation rate of TD-Ni is not appreciably higher than the superalloys (which has been surprising in view of the fact that it contains neither Cr or Al conventionally added to superalloys for oxidation protection). TD-Ni requires a coating at high temperatures, and studies of Al and Cr coatings are underway that show promise to perhaps 2150°F. Du Pont[8] has reported a new material (TD-NiC) in which the nickel has been alloyed with chromium. This material shows remarkable oxidation resistance (Fig. 17). It is greatly superior to Nichrome. Data are not available for its oxidation rate at higher temperatures. TD-NiC has a strength comparable to TD-Ni sheet (lower than that for 1-1/4-in.-diam. bar in Fig. 5) and is logically of great interest for nozzle vanes. If the oxidation resistance of TD-Ni and TD-NiC can be a guide, dispersion-strengthened superalloys being sought for strength improvements over superalloys may include a bonus of improved oxidation resistance.

Comparable data were not available for chromium. The alloys do not have sufficient oxidation resistance for long-time application and, more seriously, suffer from the nitrification problem described earlier. Improved alloys or coatings are required.

The unprotected refractory metals are not shown because they are so poor that they cannot fit on this scale. Although coatings are available and have been engine tested, none is deemed suitable for application. Further research and development studies are deemed desirable as described previously.

Ta_2Be_{17} also stands out in oxidation resistance, but Cb_2Be_{17} has not been shown on Fig. 17 because, although good at 2300°F, it suffers from a "pest phenomenon" (catastrophic oxidation near 1800°F). Although the beryllides have good oxidation resistance, they suffer from other shortcomings, as described earlier.

As we examine the situation in regard to oxidation resistance, it is indicated that none of the materials that have the necessary strengths for turbine buckets have the required resistance to attack by air. Even the characteristically oxidation-resistant superalloys are at the limit of their capability and will need coatings to extend their use to higher temperatures. The only material reviewed here that may combine oxidation resistance with other desirable properties is TD-NiC, a candidate for immediate application to nozzle vanes. Obviously research on protective coatings for all these materials is needed.

SUMMARY OF OPPORTUNITIES

This survey has indicated that potential exists to achieve improved materials that as an alternate or complement to cooling will permit operation at higher turbine-inlet temperatures. In general, we can see methods of achieving strengths of interest; the major difficulty is in achieving, simultaneously, satisfactory resistance to attack by air (oxygen and nitrogen). More specifically:

1. There is opportunity for continued, though modest, improvements in conventional superalloys. It is suggested that more attention be directed toward cobalt as a base material for stator vanes.

2. Both dispersion-strengthened superalloys and composites of fiber-reinforced superalloys are deemed capable of providing materials of strength levels of interest that may be more readily protected from attack by air than are the refractory metals. In the case of fiber-superalloy composites, considerable effort may be required to synthesize material combinations that are compatible and thus able to achieve the indicated potential. Both the dispersion-strengthened superalloys and the fiber composites will require coatings although the need may be a minimum in dispersion-strengthened materials.

3. Chromium-base alloys have potential, but they also have the problem of low ductility at room temperature and are further embrittled by exposure to air at high temperature. Improved alloys and suitable coatings should be sought. The concept of dispersion strengthening, if properly applied to chromium, may provide a route to combined high-temperature strength and low-temperature ductility.

4. Refractory metal alloys are available now that have sufficient strength for operation uncooled at greatly increased turbine-inlet temperatures and that could be fabricated into the required shape. They oxidize catastrophically in air, however. and coatings are not now available that have the quality and reliability that would permit utilizing these in long-life engines. With additional research it may be possible to provide coatings that would permit the refractory metals to be used for static engine components. It seems unlikely that coatings of a quality suitable for rotating components will be achieved in the foreseeable future.

5. Intermetallic compounds generally suffer from low ductility and impact resistance and perhaps low strength at low temperatures, making their application to conventionally designed engines unlikely. The outstanding oxidation resistance of some make it desirable to study further such materials with a view toward finding a better combination of properties. A more immediate approach may be to seek methods of utilizing the outstanding oxidation resistance in a composite structure or composite material.

CONTRACT PROGRAM

In response to the viewpoints expressed here, a contract program (augmenting a long-standing in-house program) has been initiated This program is outlined in Table II and augments previous Air Force and Navy programs.

The first area is superalloys. The first contract seeks improved bucket alloys through further alloying studies in nickel; the second seeks improved vane alloys through studies of cobalt alloys as described earlier.

Transpiration cooling involves the use of structures with very small holes through which air is passed. The temperature of these structures may be limited by the rate at which oxide scale builds up on the metal and plugs the holes, rather than by the strength of the materials. Contract IC seeks to determine the oxidation rate of superalloys in terms of scale growth and to identify superior commercial superalloys from this viewpoint.

Because of the potential of the dispersion-strengthening route in superalloys, six contracts have been placed. Six somewhat different processes are being studied with various superalloy matrices of both cobalt and nickel. An important point of philosophy here is that these contracts require proof of attainment of very fine dispersed particle size and spacing, high billet purity, and high structural stability before the programs will be extended to the measurement of strength.

For the area of fiber strengthening, contracts have been placed to develop fibers of both ceramics and refractory metal alloys for later addition to superalloy matrices.

For chromium, the program consists of conventional alloying utilizing vacuum-arc melting, three routes to dispersion strengthening (all having microstructural targets similar to those for dispersion-strengthened superalloys), and three routes to coatings.

In the case of refractory metals. the program is limited to two approaches to the coating of tantalum for stator vanes. Extension development of coatings for columbium is underway under Air Force sponsorship.

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Table I. - Composition of Alloys Described

Nickel Alloys

U700	:	Ni-18.5Co-15Cr-5.2Mo-4.2Al-3.5Ti-0.15C
INC. 713C	:	Ni-12.5Cr-4.2Mo-2.0Cb-6.1Al-0.8Ti-0.1Zr-0.012B-0.12C
IN100	:	Ni-15Co-10Cr-3Mo-1V-5.5Al-4.7Ti-0.01Zr-0.015B-0.15C
TaZ8	:	Ni-6.0Cr-4Mo-4W-8Ta-2.5V-6Al-1Zr-0.12C
MAR-M200	:	Ni-10Co-9Cr-12.5W-1Cb-5Al-2Ti-0.5Zr-0.015B-0.15C
PWA664	:	Ni-10Co-9Cr-12W-1Cb-5Al-2Ti-0.5Zr-0.015B-0.13C

Space Dispersion Strengthened Materials

TD-Ni	:	Ni-2 v/o ThO_2
Ni-3ThO_2	:	Ni-3 v/o ThO_2
TD-NiM	:	Proprietary
TD-NiC	:	Proprietary

Cobalt Alloys

J1650	:	Co-27Ni-19Cr-12W-2Ta-3.8Ti-0.02B-0.2C
MAR-M302	:	Co-21.5Cr-10W-9Ta-0.2Zr-0.005B-0.85C
NASA Co	:	Co-3Cr-25W-2Re-1Zr-1Ti-0.4C
L605	:	Co-10Ni-20Cr-15W-1.5Mn-0.1C

Chromium Alloys

Alloy E	:	Cr-2Ta-0.1Ti-0.5Si
C207	:	Proprietary
Adv. Cr	:	Proprietary

Refractory Metal Alloys

Ta Alloy (T222)	:	Ta-10W-2.5Hf-0.01C
Cb Alloy	:	Cb-22W-2Hf-0.1C
AS3C	:	Cb-20W-0.9Zr-0.1C
TZM	:	Mo-0.5Ti-0.08Zr

Table II. - NASA Contract Program to Seek Improved Bucket and Vane Materials

	Contract number	Contractor
I. Superalloys (Ni- and Co-Base)		
A. Nickel (buckets)*	3-7267	TRW
B. Cobalt (vanes)*	3-7600	TRW
C. Oxid. Resist. for Transpiration Cooling	3-7269	Bendix
D. Dispersion Strengthened*		
1. Arc Process	3-7275	Vitro
2. Vapor Deposition	3-7271	Melpar
3. Stabil. Precip. Plus Oxide	3-7297	Ilikon Corp.
4. Salt Precip. and Selective Reduct. to Form Prealloyed Powder	3-7272	Curtiss-Wright
5. Selective Reduct. Plus Mech. Mixing	3-7265	NEM Lab
6. Salt Precip. and Selective Reduction	3-7611	Sylvania
E. Fiber Metallurgy*		
1. Refractory Metal Alloy Fibers	3-7906	G.E., Cleveland
2. Stable Refractory Oxide Fibers	3-7903	Monsanto
II. Chromium Alloys		
A. Forgeable Alloy	3-7260	G.E., Evendale
B. Dispersion Strengthened*		
1. Vapor Plate	3-7608	Melpar
2. Ball Mill	3-7607	G.E., Evendale
3. Electrodeposition	3-7606	Gen. Tech. Corp.

* Also in-house program at Lewis Research Center.

Table II. (Concluded) NASA Contract Program to Seek Improved Bucket and Vane Materials

	Contract number	Contractor
C. Coatings to Resist O_2 and N_2*		
1. Aluminides	3-7273	Chromalloy Corp
2. Silicides	3-7266	Solar Aircraft
3. Metallic Claddings	3-7612	Battelle
III. Coatings for Tantalum Alloys		
A. Silicides	3-7276	Solar Aircraft
B. Intermetallics on Diffusion Barriers	3-7613	Vitro

* Also in-house program at Lewis Research Center.

CRITICAL ZONE OF TURBINE BUCKETS

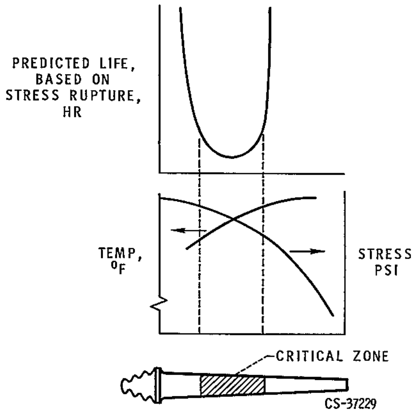


Figure 1.

GENERAL RELATION OF TEMPERATURE OF BUCKETS AND VANES TO TURBINE INLET GAS

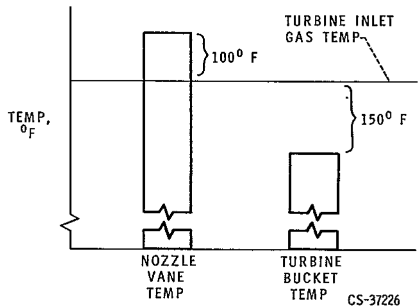


Figure 2.

E-3195

COMPARISON OF SEVERAL NICKEL ALLOYS

RATIO OF 1000-HR STRENGTH TO DENSITY

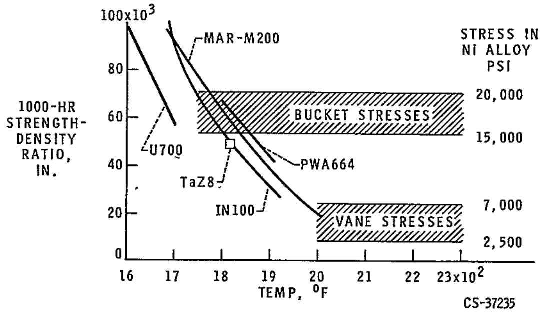


Figure 3.

COMPARISON OF COBALT- AND NICKEL-BASE ALLOYS

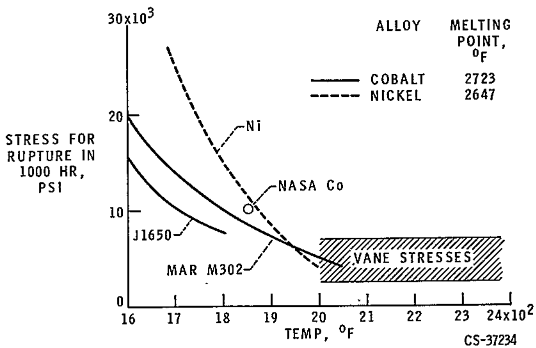


Figure 4.

STRENGTH OF DISPERSION–STRENGTHENED SUPERALLOY

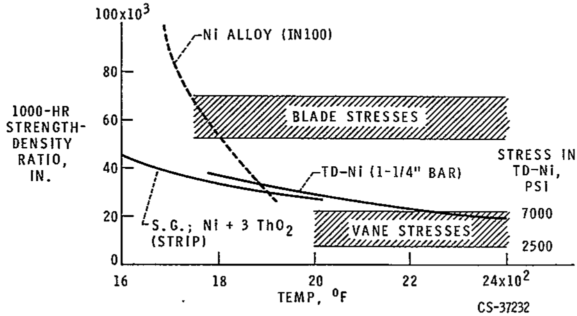


Figure 5.

EFFECT OF ALLOYING MATRIX ON STRENGTH OF DISPERSION–STRENGTHENED NICKEL

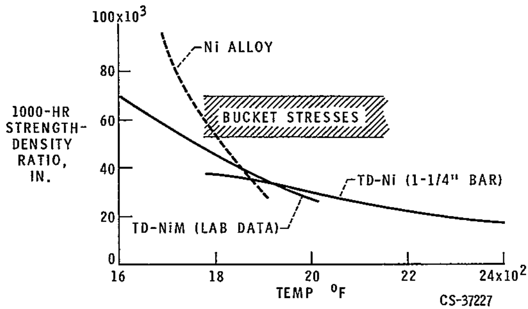


Figure 6.

STRENGTH OF CHROMIUM ALLOYS

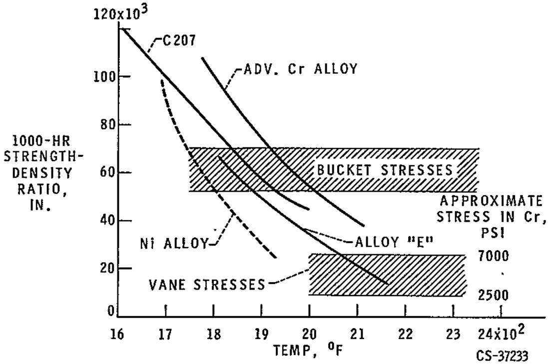


Figure 7.

STRENGTH OF REFRACTORY METAL ALLOYS OF Cb AND Ta

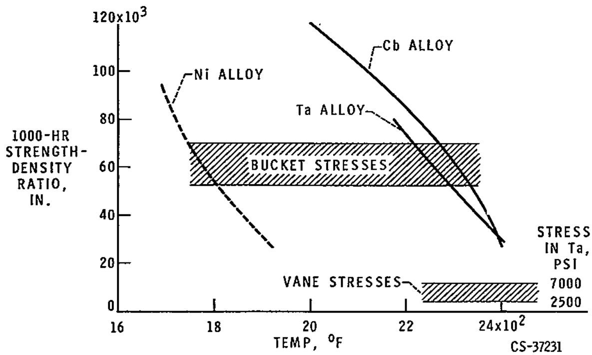


Figure 8.

COMPOSITE MATERIALS FROM METAL FIBERS

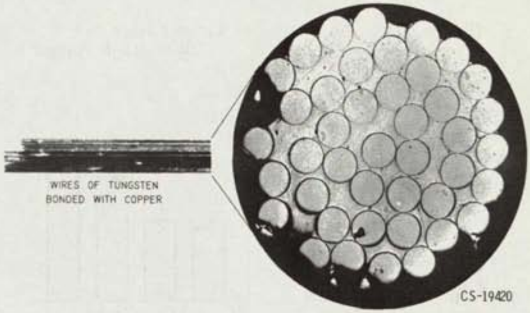


Figure 9.

TENSILE STRENGTH OF COMPOSITES OF CONTINUOUS TUNGSTEN FIBERS IN COPPER

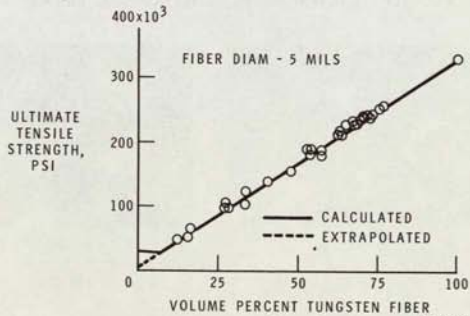
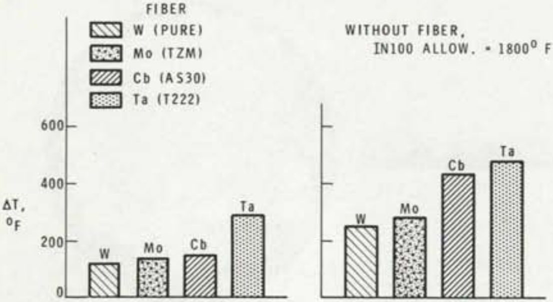


Figure 10.

CS-25502

INCREASE IN ALLOWABLE TEMPERATURE BY ADDITION OF REFRACTORY FIBERS TO SUPERALLOY (IN100) (CALCULATED)

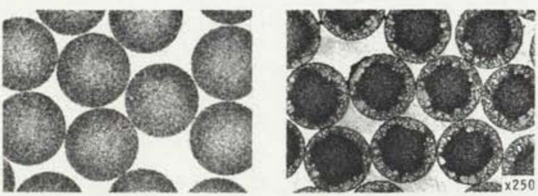
(AT STRENGTH/DENSITY OF 52,500 IN. FOR 1000 HR)



CS-37228

Figure 11.

EFFECT OF REACTION BETWEEN MATRIX AND FIBERS



	W IN Cu	W IN Cu - 10% Ni ALLOY
TENSILE STRENGTH, PSI	250,000	100,000

CS-37241

Figure 12.

E-3195

STRENGTH ADVANTAGE OF TUNGSTEN WIRE

100-HR STRESS RUPTURE

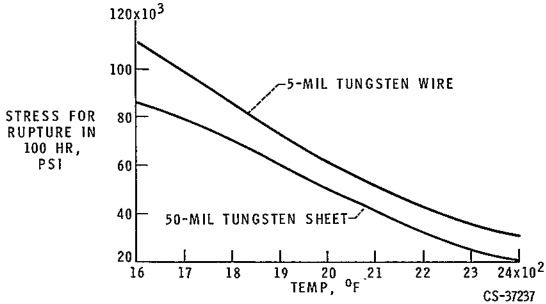


Figure 13.

TENSILE STRENGTH IMPROVEMENTS RESULTING FROM COMPOSITES WITH TUNGSTEN WIRE AT 2000° F

(REF. R. H. BASKEY)

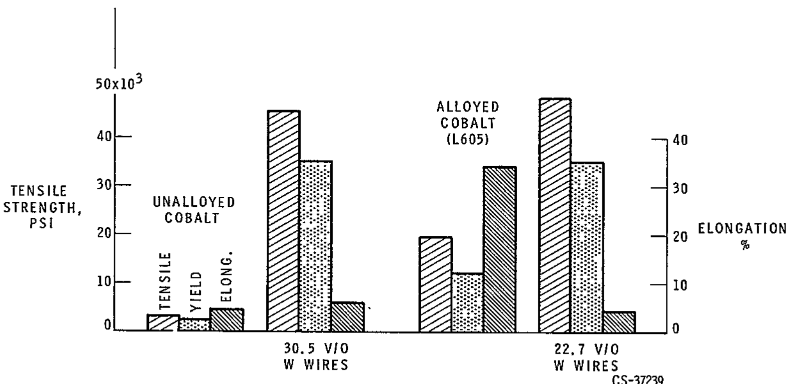


Figure 14.

STRENGTH OF INTERMETALLICS

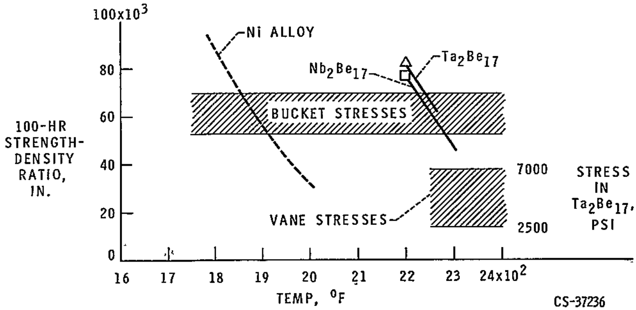


Figure 15.

SHORT-TIME STRENGTH OF Nb_2Be_{17} AND Ta_2Be_{17} OVER RANGE OF TEMPERATURES

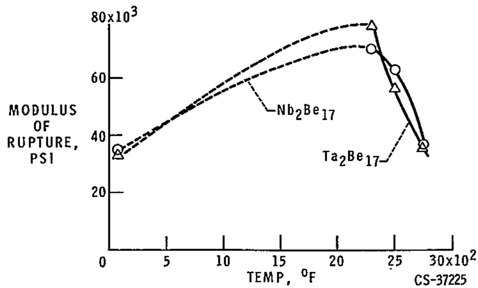


Figure 16.

E-3195

E-3195

OXIDATION RESISTANCE OF SEVERAL MATERIALS

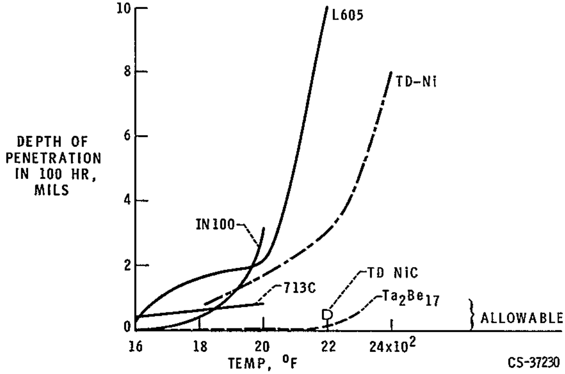


Figure 17