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1 NASA, Washington 3

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I - EMERGING ALLOY TRENDS

Background

I think that as we examine the emerging trends for high strength refractory metal alloys, it is useful to keep some of the background in mind. A portion of this development in the United States was based on guidelines set up by the Materials Advisory Board Refractory Sheet Rolling Panel (1). Combining those guidelines with observations of the current state of the art leads to the following concepts. (Some of these thoughts are described in more detail in reference 2, pages 24 to 33, copy enclosed.)

Group VIA Metal Alloys

Molybdenum and tungsten - Alloys have been sought to have the following:

1. High strength at high temperatures, but the emphasis in early developments was on short-time tensile and rupture strengths.
2. Room temperature ductility in the as-welded condition was not expected for either system and was not achieved.
3. Molybdenum alloys were expected to have a ductile-brittle transition temperature (DBTT) below room temperature in the "as-produced" condition -- and this was achieved.
4. Tungsten alloys of high strength (and high recrystallization temperature) were sought with minimum DBTT, but a DBTT below room temperature was not expected.
5. Tungsten alloys retaining the high melting point of tungsten and modest strength but with DBTT below room temperature were sought.

Chromium alloys - The target here has been to identify compositions with a significant use-temperature advantage over the superalloys of nickel and cobalt base for use in air (or air breathing engines). A DBTT below room temperature is desired and, most important, the DBTT of the alloy must not be raised appreciably when exposed to air (nitrification) at the service temperatures or a coating system must be found to inhibit nitrification.

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Group VA Metals

Tantalum and columbium - Alloys in these systems have been sought that will:

1. For sheet and tubing applications: Be of maximum possible strength at highest temperatures possible yet highly fabricable and with DBTT well below room temperature and ductile when welded at room temperature. (To provide an advantage over molybdenum alloys.) Early developments were for short time applications (e.g., re-entry). For space power systems these alloys are needed in tubing form with good creep resistance at stress levels of near 5000 psi but for lifetimes of greater than 10,000 hours.
2. For forging applications: Be of maximum possible strength compatible with good workability (into bar and forgings) and with a DBTT below room temperature.

Status

The summary of these developments, as I saw it, is again in reference 2, pages 40 to 50, but I have reproduced and updated some of these figures. I have not included all alloys but rather the better alloys in each system. (My apologies to those whose outstanding alloys are not specifically mentioned.)

From a comparison of the properties (Figures 1 to 5 inclusive) and compositions (Figure 3) of the alloys on these figures the following very generalized comments follow:

Group VA

Tantalum and columbium alloys - The strengthening is achieved by the addition of a higher-modulus, higher-melting point VIA metal (W or Mo), plus a Group IVA metal (Hf or Zr) as a carbide former, plus carbon. The "highly fabricable" weld-ductile alloys (represented by Cb-(1) and Ta-T222) are limited to about 10 weight percent W. The higher modulus, higher melting point tantalum alloys have a strength temperature advantage over the columbium alloys of similar alloy content.

The higher-strength forgeable alloys represented by the Cb(2) alloys are achieved by further raising the alloy additions, particularly W, to the 22 to 28 percent level.

Group VIA

Molybdenum and tungsten - The strengthening here is achieved by additions of Group IVA metals plus carbon. High strength molybdenum alloys are ductile at room temperature. High strength tungsten alloys are not.

An outstanding oxide dispersion-strengthened tungsten material has been synthesized by Sell and King (ref. 3). Although weaker than the arc-melted W-Hf-C alloy (containing a dispersed HfC phase) at temperatures of 3500° F (1925° C), it may have an advantage at temperatures near or greater than 4400° F (2425° C) where HfC goes into solution. At temperatures near 0.8 of the melting point of tungsten this W-ThO_2 alloy is reported to have about four times the strength of unalloyed tungsten and appropriate W-ThO_2 alloys may retain useful strength to near the melting point of ThO_2 (5500° F or 3025° C).

Chromium - Here the highest strength (represented by the Cr-Mo-Ta-C alloy) has been achieved by the addition of other refractory metals in solid solution plus Group VA (or IVA) metals and carbon or boron. (Good strengths have been achieved in the Australian alloys with Ti and Si additions and without carbon or boron.) In addition additives are used that will scavenge oxygen and/or nitrogen, e.g., Y. These highest strength alloys have a DBTT in the "as-produced" condition of 300°-500° F. The major problem with all of these chromium alloys, however, is that, although better than unalloyed chromium, they absorb nitrogen from air with the resultant increase in DBTT. This is illustrated for a Cr- alloy in Figure 6. Unless this problem is solved by a coating or by alloying, chromium alloys will not find wide useage. (In inert atmospheres, one would use alloys of Cb or Ta because of increased fabricability and ductility.)

Strength as a Function of Melting Point

Figures 4 and 5 compare the short-time tensile and stress-rupture strengths, respectively, on the basis of homologous temperature (of the base metal). For further comparison, the strength of a wrought superalloy (U700) is shown. These plots indicate that our refractory metal alloys are falling far short of our achievements in superalloys. This might be expected on two grounds: first, higher strength refractory metal alloys may be consolidated, but frequently we are not able to fabricate them because of equipment limitations, and second, the nickel-base alloys have a face-centered-cubic crystal structure, and theory would state that we may never achieve the same strengthening in body-centered-cubic metal systems.

FABRICATION LIMITATIONS

Professor Grant on page 15 (last line) has suggested that higher strengths may yet be achieved but a boundary condition is ability to fabricate (which often is limited by equipment capability). An illustration of what may be required for processing of very high strength alloys is the case of the W-Hf-C alloy shown in Figure 1. This alloy has good strength in the worked condition, a high recrystallization temperature, and its strength is improved by heat treatment. The alloy is extruded at 4000° F (2200° C), swaged to bar stock at 3500° to 3200° F (1925° to 1760° C) and rolled to sheet at 3200° F (1760° C). Its recrystallization temperature is >4200° F (2315° C) (near 4400° F ((2425° C)). The heat treatment involves a solution treatment at >4600° F (2535° C), followed by aging at 2500° F (1370° C). Although unusual temperatures are required in processing, the loads on the equipment are not unusual.

References

1. J. R. Lane and G. M. Ault: Paper presented at Western Metals Congress, Los Angeles, Calif. Feb 26, 1965.
2. G. M. Ault: "A Decade of Progress in Refractory Metals" - 1965 Gillett Memorial Lecture, ASTM.

3. Sell, Heinz G.: Westinghouse Lamp Division, Bloomfield, N. J. Paper presented by G. W. King, Fall Meeting, AIME, Chicago, Ill. 1966.

DISCUSSION SUPPLEMENTS FOR

COMMITTEE 5 REPORT

"ALLOYING PRINCIPLES AND STRENGTHENING MECHANISMS"

G. Mervin Ault

16 July, 1967

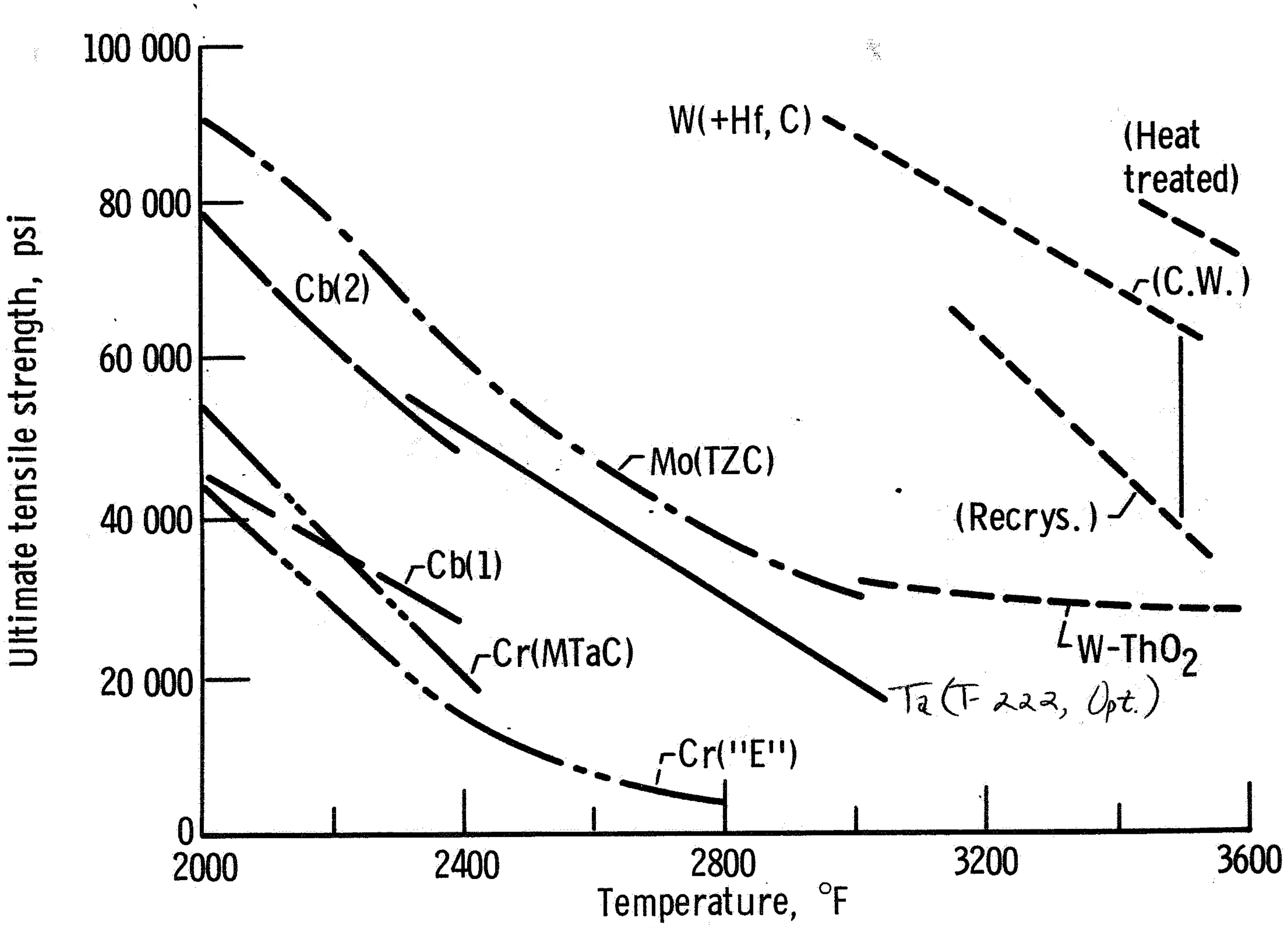

Figure 1. - Strength of best alloys (lab data).

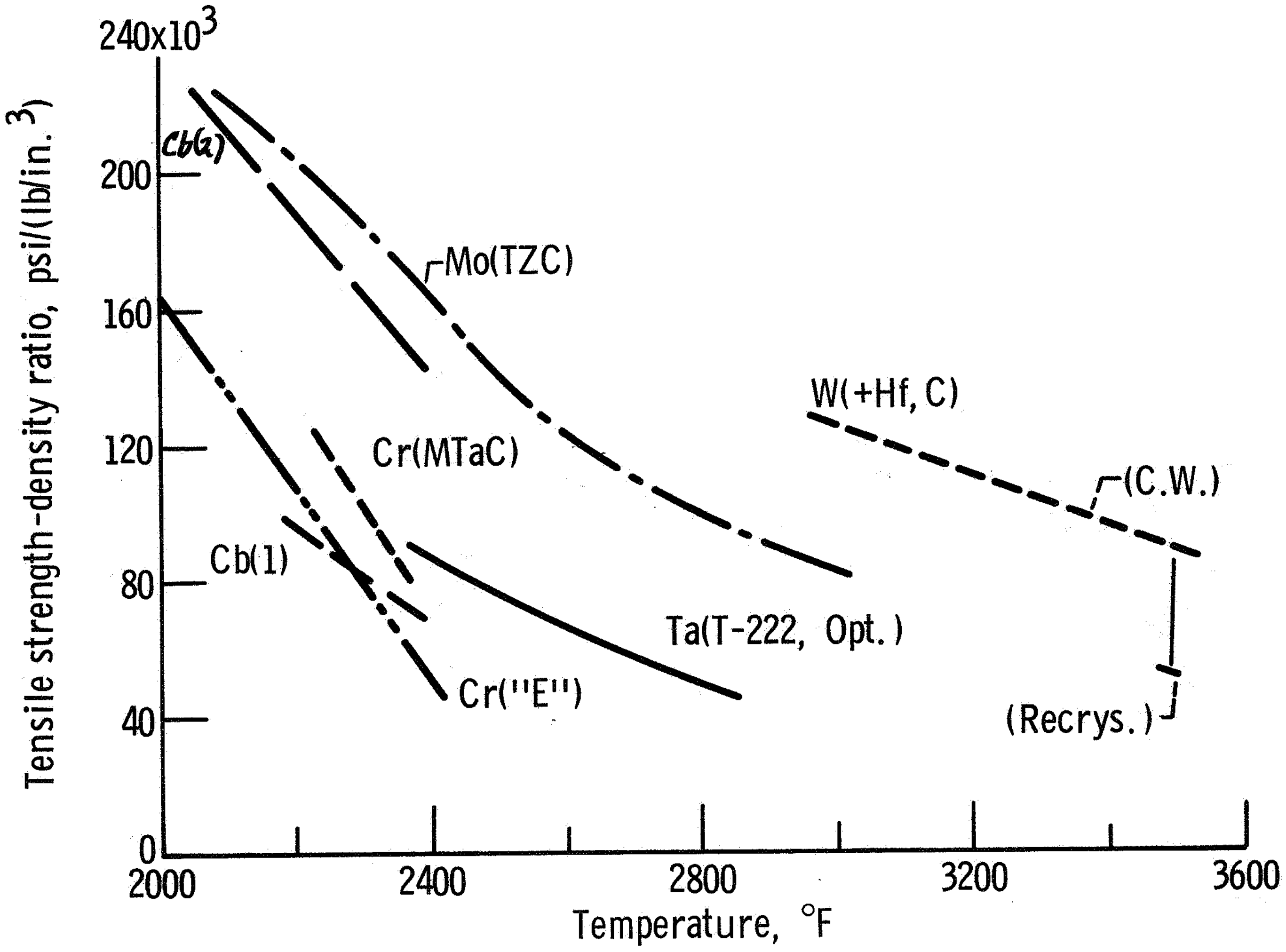

Figure 2. - Strength-density ratio of best alloys (lab data).

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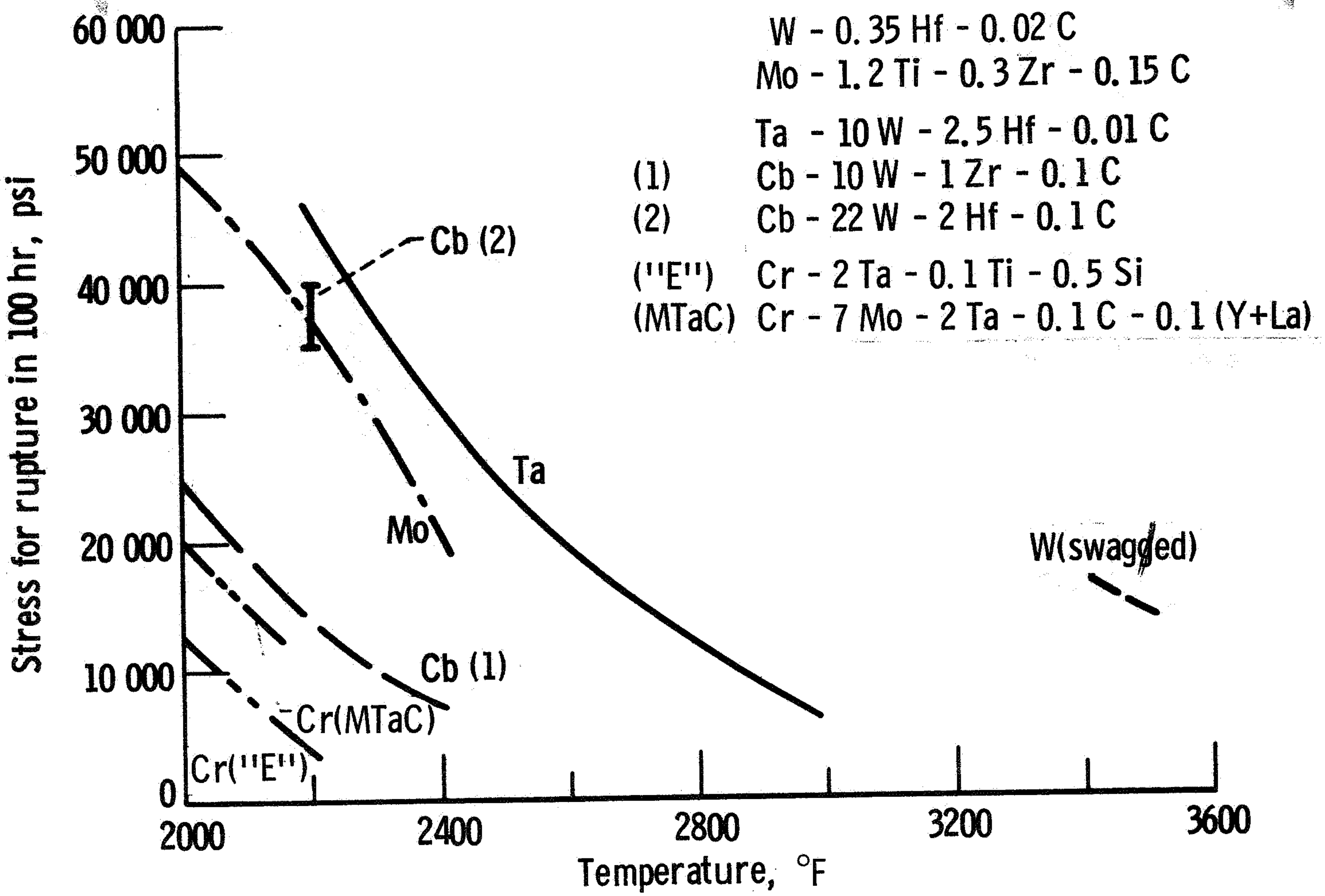

Figure 3. - Stress rupture strength of best alloys (includes lab data).

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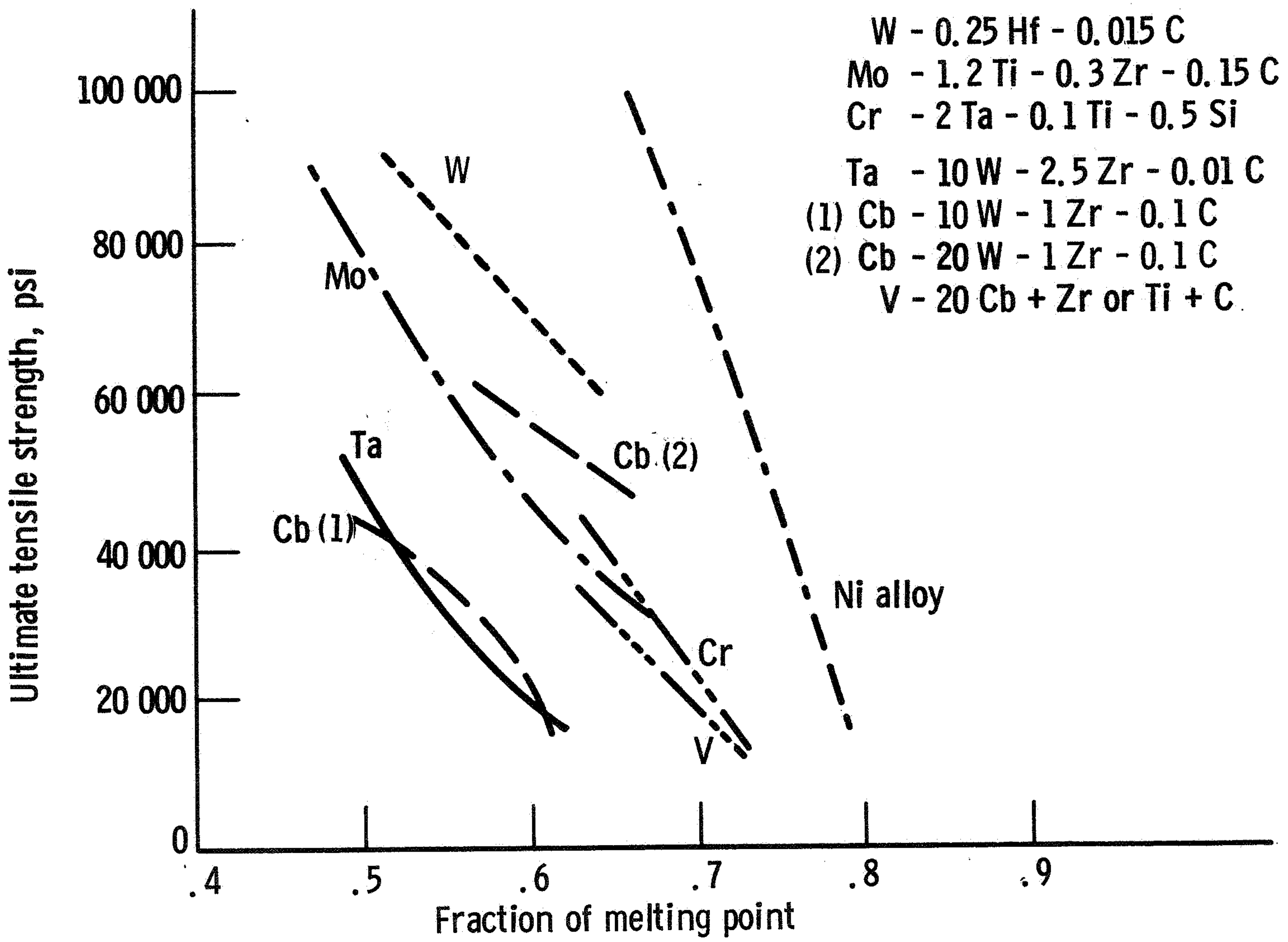


Figure 4. - Strength as function of homologous temperature.

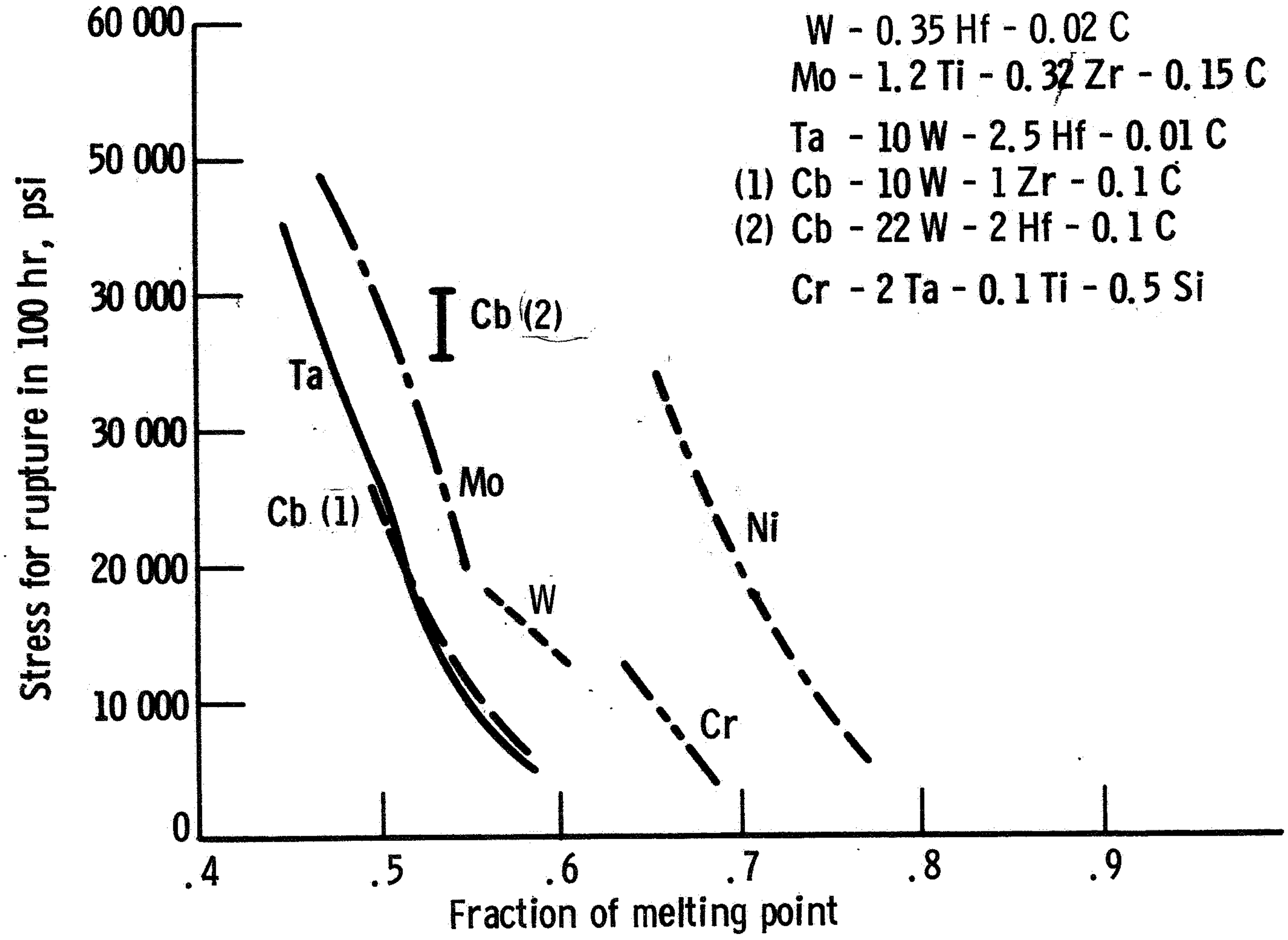


Figure 5. - Stress-rupture strengths as function of homologous temperature.

-3597 96

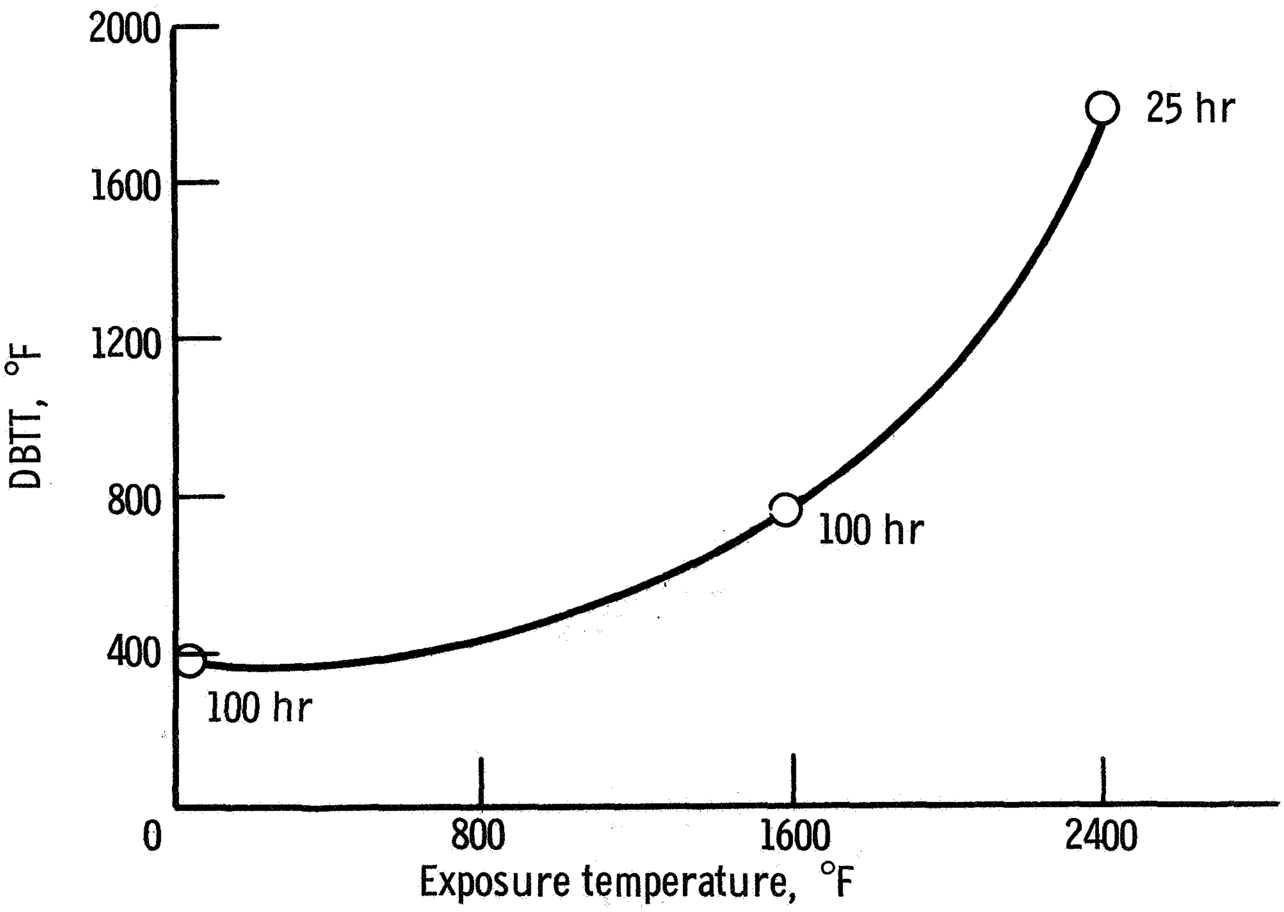


Figure 6. - The rapid embrittlement of chromium alloy (C-207) upon exposure to air at high temperatures.

E-3937

II - ALLOYING AND THE DUCTILE-BRITTLE TRANSITION TEMPERATURES

The Group VA and VIA refractory metals have a BCC crystal structure and exhibit the characteristic transition from ductile to brittle behavior as the testing temperature is lowered. This transition temperature for the unalloyed VA metals is well below room temperature but, unfortunately, for the unalloyed recrystallized VIA metals it is near room temperature (Mo) or well above (Cr and W). Much of the research in refractory metals has been concerned with the understanding and the control of the transition temperature. In general, the transition temperature may be lowered

(a) by an increase in purity, particularly in regard to interstitials
(b) by cold work
(c) by fine grain size
(d) by a dispersed phase
(e) in the case of Group VIA metals, by alloying with Re.

Unfortunately the transition temperature is raised by

(a) contamination with interstitials during processing and use
(b) many alloying additions that improve strength
(c) increased strain rate.

(Of major importance has been the role of interstitials. An excellent discussion was presented by Hahn, Gilbert and Jaffee (ref. 1).)

In recent years we have understood the importance of the interstitials, contamination, and processing to the point that alloys with good strength and with DBTT well below room temperature have been developed for Ta, Cb and Mo. In W and Cr, however, progress has not been equally satisfactory.

Tungsten

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

Stephens (ref. 3) has studied the effect of oxygen and carbon, the usual interstitial impurities, on the DBTT of both single crystal and polycrystalline tungsten. Additions of either to high purity polycrystalline tungsten produced a marked increase in the DBTT but a much smaller increase to single crystal tungsten. Addition of oxygen to polycrystalline tungsten lowered both the ultimate tensile strength and the yield strength, but had no measurable effect on the strength properties of single crystal specimens. Carbon additions to both polycrystalline and single-crystal specimens did not affect the ultimate tensile strength; however, a large increase in the yield strength resulted. The results suggest that oxygen embrittlement in tungsten is caused by grain-boundary segregation, while carbon embrittlement results from an interaction between carbon atoms and dislocations within the tungsten lattice.

Some years ago it was reported by Geach and Hughes (ref. 4) that an alloy of tungsten with 25 percent rhenium did have a transition temperature well below room temperature. This alloy is ductile in the cold-worked form and may be ductile in the recrystallized condition if not heated much above the recrystallization temperature. Rhenium, however, is more expensive than gold, and although the tungsten 25 percent rhenium alloy may be purchased commercially, the cost is $600 to $1000/lb.

It has been found that other approaches are feasible. Pugh et al, of the General Electric Co. (ref. 5) showed that doped lamp filament tungsten when alloyed with 3 percent rhenium by the powder-metallurgy process would be ductile in either the cold-worked or "recrystallized" form but only when drawn into small diameter wire. When applied to sheet, the process did not result in ductility. Klopp et al (ref. 6) found that an alloy of tungsten with 2-9 percent rhenium in bar and sheet form prepared by electron-beam melting is ductile at room temperature in the cold-worked condition. They reported DBTT's as low as -100° F. This achievement appears dependent on the high-purity tungsten achieved by the electron-beam-melting process because sheet prepared in the same way but arc-melted is brittle at room temperature.

Studies of the mechanism acting in these cold-worked dilute W-Re alloys have noted that in <100> oriented single crystals (ref. 7), Re additions up to 9 percent increased the proportional limit stress, decreased the flow stress and the rate of work hardening, and changed, somewhat, the planes of favored deformation. From a study of dislocation structures in polycrystalline W-Re alloys, Stephens (ref. 8) suggests that the primary effect of low rhenium concentrations (2 to 9 percent) in tungsten is to increase dislocation multiplication after macroyielding by reducing the Peierls-Nabarro force (lattice resistance to dislocation motion).

Particularly important is the achievement of room temperature ductility in alloys of tungsten that have much higher strength and recrystallization temperature than unalloyed tungsten.

Maykuth et al (refs. 9, 10) have prepared, by powder metallurgy, an alloy of doped tungsten plus 5 percent rhenium plus 2.2 percent of dispersed phase, thoria. Their data suggest that this alloy in sheet form may be ductile in both the cold-worked and recrystallized condition in tension tests at room temperature but with restricted ductility in bend tests.

It has been indicated that the highest strength tungsten alloys contain small amounts of carbide formers and carbon, for example, 0.5 percent hafnium plus 0.02 percent carbon. Friedman and Dickinson of Sylvania, Corp. have recently found (ref. 11) that an addition of 3 to 5 percent rhenium in their powder-metallurgy-produced version of this alloy will result in room-temperature ductility in the cold-worked condition. Although the preliminary data indicate that this alloy may be brittle when recrystallized, the alloy has a relatively high recrystallization temperature of 3300° F.

Chromium

Large additions (65 w/o) of rhenium to chromium lowers the DBTT (ref. 12) but the benefits of 2 to 9 percent Re noted in the case of tungsten have not been observed for chromium. The importance of "tying up" nitrogen and carbon by alloying has been demonstrated (ref. 13, 14, 15). Solid solution alloying additions to improve strength generally raise the DBTT of high purity chromium and amounts of these alloying additions that provide a significant advantage over superalloys seem to result in a DBTT greater than room temperature.

Research directed toward improved strength in chromium, comparable to Cr-MTC (see Emerging Trends), but with a DBTT below room temperature should continue. Perhaps more emphasis should be placed on strengthening by dispersed particles.

The desire to use chromium alloys in air, as improvements to superalloys, imposes the most important problem with chromium. Exposure of all known alloys to air at the intended service temperatures raises the DBTT at a very rapid rate and, with time, the DBTT will approach the use temperature. Solutions to this problem through alloying or coating are needed.

Improved Ductility with Dispersions

It is accepted that properly distributed particles may retain strength to higher temperatures. Some evidence can be presented to suggest the intriguing possibility that particles, if properly distributed, can improve ductility. Rosenfield and Hahn(14) have conducted an analysis of the effect of second-phase particles on ductility and present arguments that suggest that under some conditions ductility can be improved, and DBTT lowered, by second-phase particles. To experimentally verify their predictions, they have conducted tensile tests at 77° K on iron and iron with dispersed Al_2O_3. They showed that the iron with dispersed Al_2O_3 was ductile whereas the iron without Al_2O_3 was brittle. In addition, the iron with Al_2O_3 supported almost twice the stress. Sell and co-workers in their work on tungsten - 3.8 V/o ThO_2 alloys report that the DBTT of their material after annealing at 2400° C was 190° C and thus was much lower than unalloyed tungsten (though still well above room temperature). Earlier, Maykuth and co-workers (ref. 9) reported that ThO_2 as well as other oxide additions reduced the tensile DBTT of tungsten and when ThO_2 was added to a tungsten alloy of 5 percent Re, they found tensile ductility at room temperature. Ryan and Johnstone (ref. 15) suggest that similar effects may also be achieved by particles in chromium.

This potential for lowering DBTT while improving high temperature strength warrants further study, particularly in tungsten, chromium, and recrystallized molybdenum.

References

1. G. T. Hahn, A. Gilbert and R. I. Jaffee: Refractory Metals and Alloys, II, Metallurgical Society Conferences, AIME, vol. 17, M. Semchyschen and I. Perlmutter, editors, Interscience Publishers, Inc., New York, 1963, pp 23-63.
2. L. Raymond: Final Report, Aeronutronic Div., Philco Corp., Subcontract to Union Carbide Corp., May 14, 1965.
3. J. R. Stephens, NASA TN D-2287, NASA Cleveland, Ohio, June 1964
4. G. A. Geach and J. E. Hughes, Proceedings, Second Plansee Seminar, 1955, Pergamon Press Ltd., London 1956, pp 245-253. F. Benesovsky, editor.
5. J. W. Pugh, L. H. Amra, and D. T. Hurd, Transactions, Am. Soc. Metals, vol. 55, No. 3, Sept. 1962, pp 451-461.
6. W. D. Klopp, W. R. Witzke, and P. L. Raffo: NASA TN D-3483, NASA Cleveland, Ohio, Sept. 1966.

7. M. Garfinkle: NASA TN D-3190, NASA, January 1966.

8. J. R. Stephens: Paper presented at AIME Fall Meeting, Chicago, Ill., February 1966.

9. D. J. Maykuth, H. R. Ogden, and R. I. Jaffee: Paper presented at AIME Refractory Metals Symposium, French Lick, Ind., Oct. 3-5, 1965.

10. J. L. Ratliff, D. J. Maykuth, H. R. Ogden, and R. I. Jaffee: Summary Report, Contract N600(19)-5928 (Bureau of Naval Weapons) Battelle Memorial Inst., April 30, 1964.

11. S. Friedman and C. D. Dickinson: Paper presented at AIME Refractory Metals Symposium, French Lick, Ind., Oct. 3-5, 1965.

12. Allen, B. C., Reid, C. N., and Jaffee, R. I.: Unpublished report under NASA Contract NASw-101, Battelle Memorial Institute, March 1962.

13. Ryan, N. E.: Jr. Less Common Metals, 6, pp 21-35 (1964)

14. Rosenfield, A. R. and Hahn, G. T.: Battelle Memorial Institute, To be published.

15. Ryan, N. E. and Johnstone, S. T. M.: Jr. of Less Common Metals, Vol 8, No. 3, pp 159-164, March 1965.

III - STRENGTHENING OF REFRACTORY METALS

In agreement with the view expressed by Professor Grant, experimental data on the strengthening of the refractory metals have been somewhat limited. A summary paper on the "Mechanisms of Alloy Strengthening in Refractory Metals" was presented by Armstrong, Bechtold and Begley in 1962 (ref. 1) and they noted that "the research necessary to provide an over-all quantitative theory of the strengthening of refractory metal alloys has barely begun." The various investigations related to the dispersion hardening of Mo- and Cb-base alloys were reviewed by Chang in 1960 (ref. 2). The nature of carbide dispersion in representative Mo-base alloys has been discussed by Chang and Perlmutter who investigated the solution and aging reactions in these alloys on the basis of hardness, microstructural and phase changes (ref. 3). The latter investigation correlated carbide dispersion to the precipitation-hardening process in the Mo-TZC alloy (analyzed 1% Ti, 0.1% Zr and 0.14% C) which typifies current high-strength Mo-base alloys. As depicted in Figure 1, the alloy contained three carbide phases, Mo_2C, TiC and ZrC. The Mo_2C phase alone was stable above about 3750° F (2065° C) and coexisted with ZrC in the temperature range of 3750° to 3500° F (2065° to 1925° C). These two carbides in turn coexisted with TiC between 3500° and 3000°F (1925° and 1450° C). Below the latter temperature, TiC became increasingly more stable and appeared to be the only thermodynamically stable carbide below approximately 2800° F (1550° C). The hardening reaction was thus based on the extensive TiC precipitation, accompanied by simultaneous dissolution of the pre-existing Mo_2C phase. In addition to the aging reaction, there was evidence to indicate that the 1% Ti may also have played the reversed role of increasing the C solubility at high temperatures.

In reference 4 Chang reported further studies of the Mo-TZC class of alloys and the effect of composition variations on properties. He noted the following in regard to these alloys:

1. The strength of Mo-TZC was greatly increased by high-temperature annealing with or without subsequent working. The strength increase resulted from strain-induced TiC precipitation, either during working or upon loading of the as-annealed condition. By virtue of this mechanism, it was possible to develop high strength in the annealed condition, comparable to that of the worked condition. In contrast to annealing, an aging treatment which produced extensive but coarse TiC dispersion resulted in inferior strength at elevated temperatures. When followed by extensive working, however, such an aging treatment was found to endow the worked condition with high strength.

2. Although the low-C, MoTZ alloy was not age-hardenable, the strength of this alloy was also enhanced by high-temperature annealing. Prior aging, however, always led to low strength due to deficiency in carbide dispersion.

3. In contrast to Mo-TZ and Mo-TZC, the strength properties of the Mo-0.5Ti-0.035C alloy were relatively insensitive to heat treatment as a result of the low Ti/C ratio which restricted both carbide dissolution and its precipitation.

4. Finally, the present results suggest that the optimization of strength properties of complex refractory alloys must be based on an understanding of the pertinent solution and aging reactions and their dependence on temperature, time and plastic deformation. As a general rule, a desirable combination of strength and ductility may be achieved by utilizing either a reasonably high primary processing temperature to maintain an adequate degree of super-saturation, or an extensively aged condition to provide a large volume fraction of dispersion. In either case, a reasonably low final processing temperature should be used to maximize the interplay of dispersion hardening and strain hardening.

Chang clearly pointed out the importance of the interplay between heat treatment and processing (popularly knows as "thermal-mechanical" processing) for refractory metals.

Additional important studies have been conducted on thermal-mechanical processing of molybdenum alloys by Perkins and Lytton (ref. 5).

¶ Recently, systematic studies of the solid solution and dispersed phase strengthening of tungsten have been conducted. Here the carbide strengthening of the final alloy system that resulted (W-Hf-C) appears much simpler than the systems that have been studied in most detail in molybdenum, namely Mo-TZC or Mo-Cb-TZC. The following discussion is from papers by Raffo and Klopp (ref. 6), copy enclosed, and Rubenstein (ref. 7).

The ultimate tensile strength of their binary tungsten alloys at 2500° to 3500° F (1370° to 1925° C) is plotted as a function of composition in figure 2. At 2500° to 3500° F (1370° to 1925° C) hafnium has the greatest strengthening effect in tungsten. Columbium, tantalum, and rhenium are progressively less effective. At 2500° (1370° C), the columbium and rhenium points fall on the same curve, and at 3500° F (1925° C), the data for tantalum and columbium also scatter about one curve. The tantalum data were not shown at 3500° F (1925° C) for clarity. Data at 4000° F (2200° C) (not shown) were available only for hafnium and rhenium additions and the same order of effectiveness prevailed.

The creep strengths for these binary systems at 3500° F (1925° C) are plotted against solute content in Figure 3. The creep strengths are the stresses at a minimum creep rate of 10^{-6} per second. The same order of effectiveness is apparent in the creep data as was observed in the tensile data.

The tensile data for the binary alloys can also be utilized to predict the strength of the ternary alloys. It is a common conclusion that the solid-solution-alloying elements contribute the same increment of strength to a ternary as they do to a binary alloy (ref. 8). To test this for tungsten alloys, the increments of strengthening from the binary alloy data in Figure 2 were calculated for each of the solutes in the W-Cb-Hf, W-Ta-Hf, W-Ta-Re, and W-Re-Hf ternary alloys. These increments were then added to the average strength for unalloyed W at the temperature of interest. Figure 4 compares the calculated and experimental strengths for alloys annealed at 3600° F (1985° C). The agreement with the assumption of additive strengthening was good especially when considering that no corrections were made for variations in grain size or interstitial contents among the alloys.

In order to understand the mechanisms by which the various solutes strengthen, the deformation mechanisms at elevated temperatures should be considered. Strain hardening in body-centered-cubic metals is thought to be related to the formation of jogs on screw dislocations by the interaction of dislocations on two intersecting slip planes (ref. 9). As the jogs move, they produce vacancies that act as a drag on the motion of the screw dislocations. However, the excess number of mechanically produced vacancies may promote climb of the edge segments of the dislocation networks. Such processes constitute "dynamic recovery" and as such reduce the rate of work hardening and consequently the elevated-temperature strength.

Alloying may increase the strength by decreasing either the jog or vacancy mobility. The motion of jogs may be impeded by solute atoms segregating to their stress field (ref. 10). Solute atoms and vacancies may also be strongly bound to one another (ref. 11). As a consequence, vacancies may tend to exchange places more often with solute than solvent atoms, which results in a lower self-diffusion rate since the vacancies are bound to the solute atoms and do not aid in solvent self-diffusion.

The strength of the binding between solute atoms and jogs or vacancies would be expected to depend on the difference in atom size between the solvent and solute (refs. 10 and 11). A quantitative correlation was attempted by plotting the slopes of the strength-composition curves in Figure 2 against the percent difference in atomic radius. Figure 5 illustrates this correlation. The log-log plot shown does indicate a definite atom size effect and provides support for the mechanisms outlined previously, although no estimation of the relative importance of solute-jog or solute-vacancy interactions can be deduced.

Strengthening of Carbon and Boron in Tungsten

Elevated-temperature tensile data were obtained by Raffo and Klopp on both the W-C and W-B systems (ref. 12). Carbon has been shown to exist as an interstitial in tungsten (ref. 13), while it has been proposed that boron may exist simultaneously as a substitutional and interstitial (ref. 14). A comparison of the strength data for both systems was made to examine whether or not the difference in the type of solid solution formed could have any influence on the elevated-temperature strength.

Figure 6 shows the effect of both carbon and boron on the ultimate tensile strength of tungsten at 2500° and 3500° F (1370° to 1925° C). Carbon additions up to at least 0.3 atom percent decreased the strength, while in contrast, boron produced a rapid initial increase in strength followed by a leveling off at higher boron contents. The same trends were observed at 3000° and 4000° F (1450° and 2200° C). It was thought that these differences between the W-C and W-B alloys reflected the previously mentioned differences in the type of solid solution formed. The initial strengthening by boron additions was examined previously by these authors and they concluded that the magnitude of the initial slope of the strength-composition curve fit well with the concept of a simultaneous interstitial-substitutional solid solution with the balance tending toward substitutional (ref. 12). In contrast, carbon additions apparently weaken by promoting an increase in the self-diffusion rate of tungsten. This behavior has been previously noted for carbon additions to gamma iron (refs. 15 and 16). The increase in the self-diffusion rate has been suggested to result from the carbon atoms increasing the vacancy mobility due to the lattice distortions associated with the interstitial solid solution (ref. 21).

Carbide-Strengthened Alloys

The increase in strength conferred by carbon additions to W-Hf, W-Cb, W-Ta, and W-Ta-Re alloys were also considered (ref. 6). Carbon additions to W-Hf alloys produced the greatest increases in both the strength of recrystallized alloys and in the retention of cold work at elevated temperatures.

The relative strengthening effects of carbon on these alloys may be compared in the following manner. First, the strength of the alloy without the carbon addition was interpolated from the curves in Figure 2. This value was then subtracted from the strength of the alloy under consideration to give an increment in strength due to the carbon addition. Figure 7 is a plot of this strengthening increment as a function of carbon content for alloys tested at 3500° F (1925° C). The data may be seen to fall into three groups. First, carbon additions to unalloyed tungsten result in an initial decrease in strength (which was discussed previously) followed by an increase in strength and a subsequent leveling off at higher carbon contents. In contrast, carbon additions to W-Hf alloys produced a rapid increase in strength, while the data for W-Cb, W-Ta, and W-Ta-Re alloys showed a less rapid increase. The data for the latter alloys showed a great deal of scatter and are represented by a broad band.

These relative strengthening effects may be correlated qualitatively with the carbide particle size. The finest particle sizes were observed in the W-Hf-C alloys. The swaged alloys contained some large precipitates on the order of 0.1 to 0.2 microns in size and many small precipitates about 0.02 micron (200A°) in size. The volume percent for optimum strength was near 0.5. In contrast, the carbides in the other systems were coarse and usually oriented in the swaging direction. The fine particles in the W-Hf-C alloys apparently are most effective in stabilizing the dislocation substructure formed during deformation. This is also evident in the high resistance to recrystallization exhibited by these alloys.

The coarse precipitates, however, apparently contribute equally well to the strength at 3000° F (1925° C) and lower, as the fine precipitates. For example, the strengths of three carbide-strengthened alloys are compared in the swaged condition in Figure 8. The strengths at 3000° F (1450° C) for all the alloys are nearly equal while at 3500° F (1925° C), the strengths vary from 16,600 to 62,500 psi. This reflects largely the stability of the cold-worked structure. The first two alloys recrystallized during testing at 3500° F (1925° C), while the W-Hf-C alloy retained its cold-worked structure.

In creep, the fine particle sizes in the W-Hf-C alloys did not appear to produce as high strengths as found in some of the solid-solution-strengthened alloys. For example, the creep strength of recrystallized HC-3, W-0.2 atom percent Hf-0.26 atom percent C was 8000 psi at 3500° F (1925° C), while alloys HF-3, W-1.7 atom percent Hf, and TH-2, W-1.56 atom percent, Ta-0.40 atom percent Hf had strengths of 10,000 and 8300 psi, respectively, in spite of the W-Hf-C alloy having a higher tensile strength at this temperature.

Recently the arc-melted W-Hf-C alloys have been studied in more detail by Rubenstein at the NASA Lewis Research Center (ref. 7). He investigated the effects of composition ranges for both Hf and C, and the effects of heat treatment and substructure on the strength and ductility. The strongest alloys contained equiatomic amounts of carbon and hafnium and strengths increased with increasing HfC contents up to approximately 0.5 v/o, after which further additions caused a slight decrease in strength. The 3500° F (1925° C) tensile strength for swaged material was linearly related to the inverse square root of the cell size.

Limited tensile and microstructural studies indicated that the W-Hf-C alloys are heat treatable. The minimum solution temperature of hafnium carbide in tungsten is approximately 4600° F (2535° C), and one hour at 2500° F (1370° C) is an effective aging temperature. A tensile specimen heat treated in this manner displayed a tensile strength of 69,000 psi at 3500° F (1925° C) compared to approximately 9000 psi for unalloyed tungsten. The hafnium carbide precipitation-strengthened alloys exhibited one hour recrystallization temperatures in excess of 4200° F (2300° C). In the heat-treated alloys it is difficult to determine the specific nature of the particle-dislocation interactions but the absence of dislocation cells or networks leads to the conclusion that the HfC particles were directly responsible in controlling the tensile strength.

The stress for a 3500° F (1925° C), 100-hour rupture life was approximately 14,000 psi in the swaged condition. A solution annealed and aged specimen tested at 3500° F (1925° C) in a step-load creep test required a stress of approximately 20,000 psi for a minimum creep rate of 6×10^{-7} sec^{-1} (corresponding perhaps to an approximate 100-hour rupture life).

References

1. Armstrong, R. W., Bechtold, S. H. and Begley, R. T.: "Mechanisms of Alloy Strengthening in Refractory Metals" - Refractory Metals and Alloys II, Metallurgical Society Conferences, vol. 17, 1962, Interscience Publishers, New York
2. W. H. Chang, "Strengthening of Refractory Metals," Refractory Metals and Alloys, 1961, p 83. Interscience Publishers, New York.
3. W. H. Chang and I. Perlmutter, "Solutioning and Aging Reactions in Molybdenum-Base Alloys" Proceedings of High-Temperature Materials Conference held in Detroit, Mich, April, 1961.
4. Chang, W. H.: "The Effect of Heat Treatment on Strength Properties of Molybdenum-Base Alloys," ASM Transactions Quarterly, vol. 56, No. 1, March 1963, pp 107-124.
5. Perkins, R. A. and Lytton, S. L.: "Ultra-high Strength Molybdenum Alloy for High Temperature Service," AIAA 6th Structures and Materials Conference, Palm Springs, Calif., AIAA, April 5-7, 1965, pp 443-446.
6. Raffo, P. L., and Klopp, W. B.: "Mechanical Properties of Solid-Solution and Carbide-Strengthened Arc-Melted Tungsten Alloy" - NASA TN D-3248, Feb. 1966.

7. Rubenstein, L. S.: "The Effect of Composition, Heat Treatments, and Substructure on the High Temperature Tensile and Creep Strengths of Arc-Melted W-Hf-C Alloys." NASA TN to be published.

8. Parker, E. R.; and Hazlett, T. H.: "Principles of Solution Hardening. Relation of Properties to Microstructure," ASM, 1954, pp 30-70.

9. Gregory, D. P.; Rowe, G. H.; and Stroh, A. N.: "Work Hardening Mechanisms in Body-Centered Cubic Metals." Rept. No. ASD-TDR 62-354, Pratt & Whitney Aircraft, Sept. 1962.

10. McLean, D.: "Mechanical Properties of Metals." John Wiley & Sons, Inc., 1962.

11. Eikum, A.; and Thomas, G.: "Effect of Solute Atoms Upon Vacancy Climb of Prismatic Dislocations in Al-5% Mg Alloy." Phys. Soc. Japan J., vol 18, suppl. III, 1963, pp 98-104.

12. Raffo, P. L.; and Klopp, W. D.: "Influence of Boron Additions on Phy;ical and Mechanical Properties of Arc-Melted Tungsten and Tungsten-1 percent Tantalum Alloy." NASA TN D-3247, 1966.

13. Goldschmidt, H. J.; and Brand, J. A.: "Investigation into the Tungsten-Rich Regions of the Binary Systems Tungsten-Carbon Tungsten-Boron and Tungsten-Beryllium." Rept. No. ASD-TDR-62-25, pt. 1, Birmingham Small Arms Res. Centre, Mar. 1962.

14. Goldschmidt, H. J.; Catherall, E. A.; Ham, W. M.; and Oliver, D. A.: "Inves. into the Tungste-Rich Regions of the Binary Systems Tungsten-Carbon, Tungsten-Boron and Tungsten-Beryllium" Rept. No. ASD-TDR-62-25, pt. II, Birmingham Small Arms Res. Centre, July 1963.

15. Sherby, O. D.: "Factors Affecting the High Temperature Strength of Polycrystalline Solids." Acta Met., vol. 10, No. 2, Feb. 1962, pp 135-147.

16. Mead, H. W.; and Birchenall, C. E.: "Self-Diffusion of Iron in Austenite." Trans. AIME, vol. 206, Oct. 1956, pp 1336-1339.

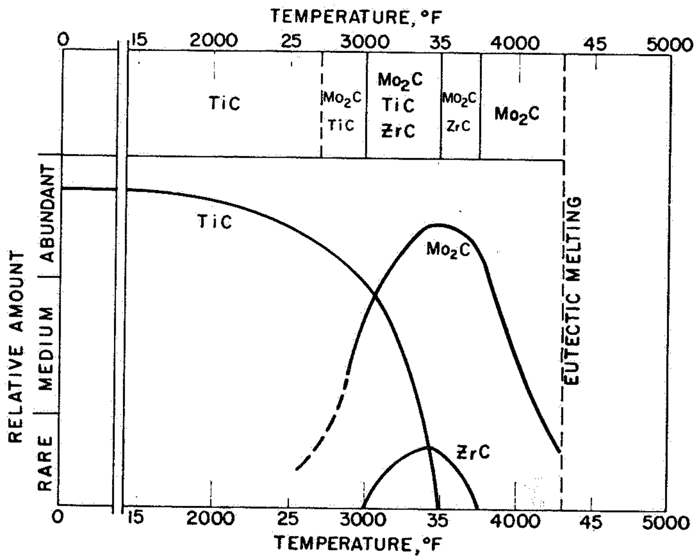
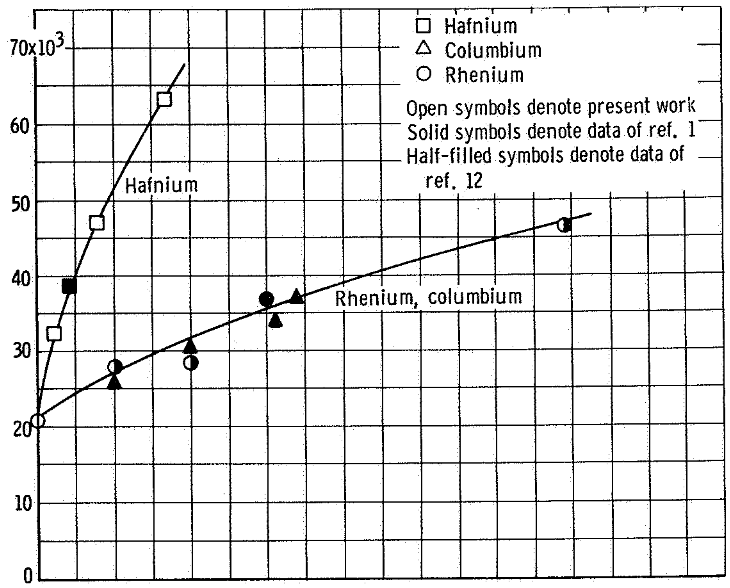
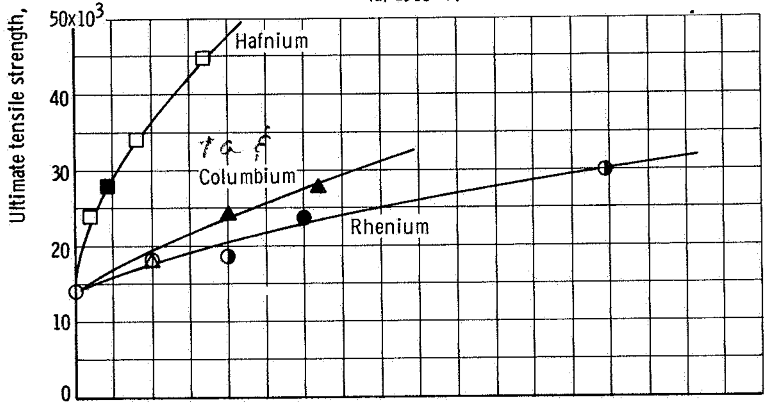


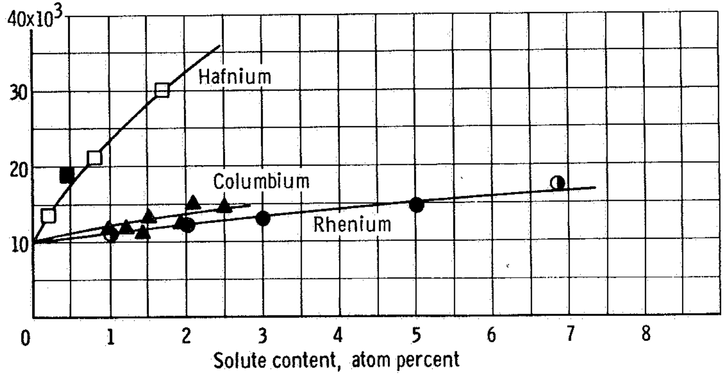
Fig. 1. Approximate carbide stability ranges in Mo-TZC alloy.



(a) 2500° F.



(b) 3000° F.



(c) 3500° F.

Figure 2 - Effect of alloying on strength of arc-melted tungsten at 2500° to 3500° F.

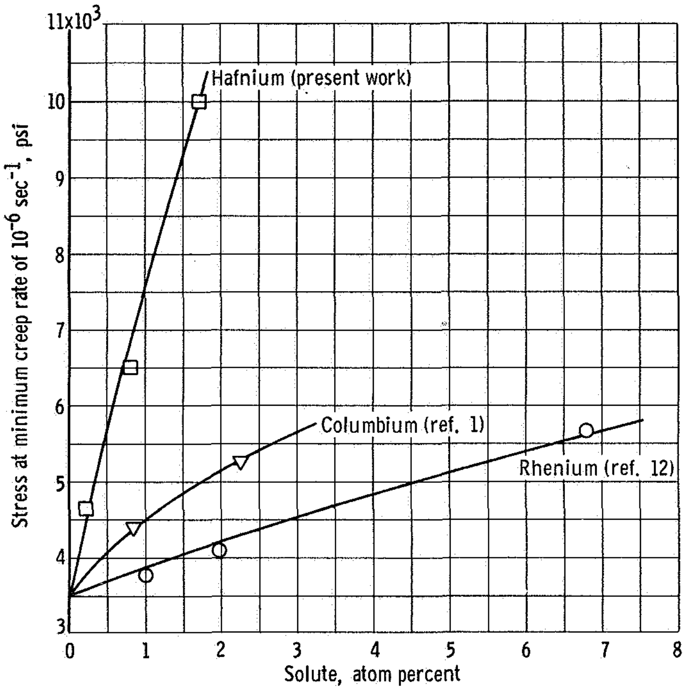


Figure 3 - Influence of alloying on 3500° F creep strength.

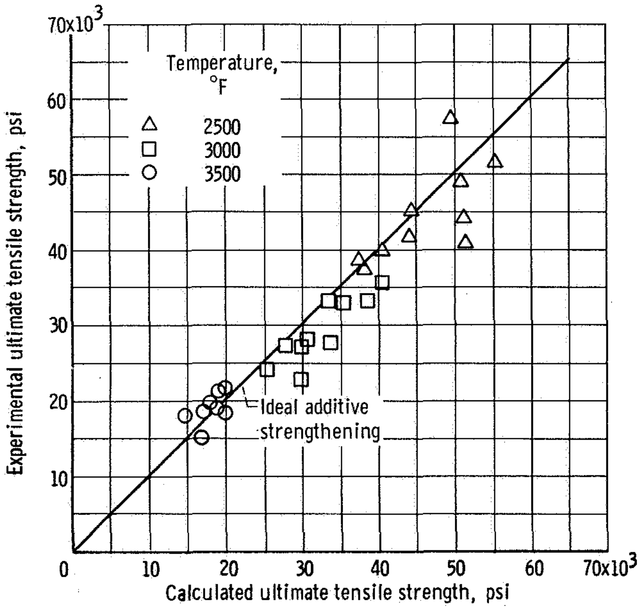


Figure 4 - Comparison of experimental tensile strengths with values calculated assuming additive strengthening effects. (Alloy systems include W-Ta-Re, W-Re-Hf, W-Ta-Hf, and W-Cb-Hf.)

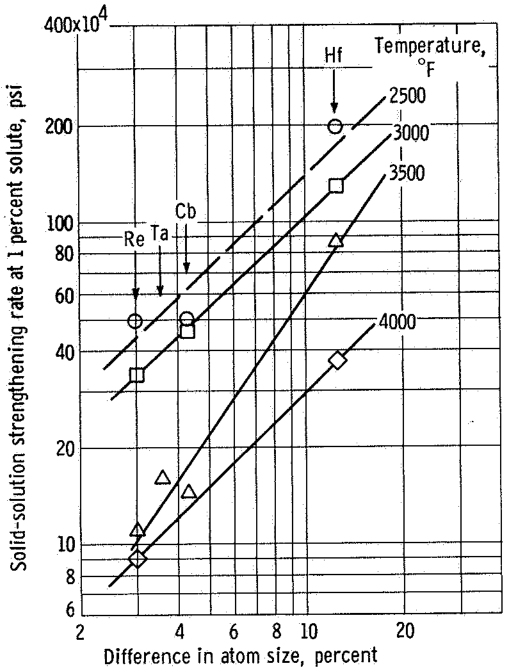


Figure 5 - Variation of solid-solution strengthening rate with difference in atom size between tungsten and solute.

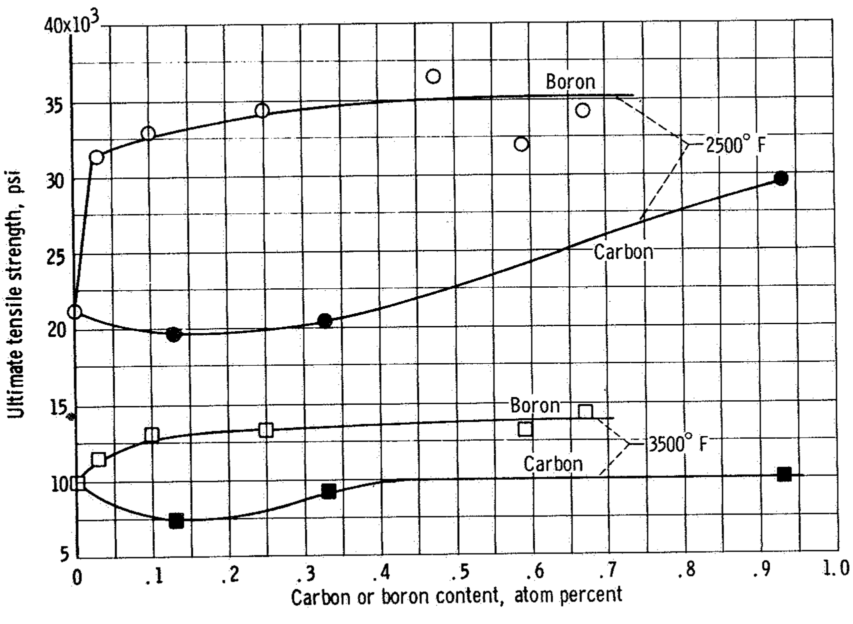


Figure 6 - Effects of carbon and boron on ultimate tensile strength of arc-melted tungsten at 2500° and 3500° F (W-B data from ref. 7).

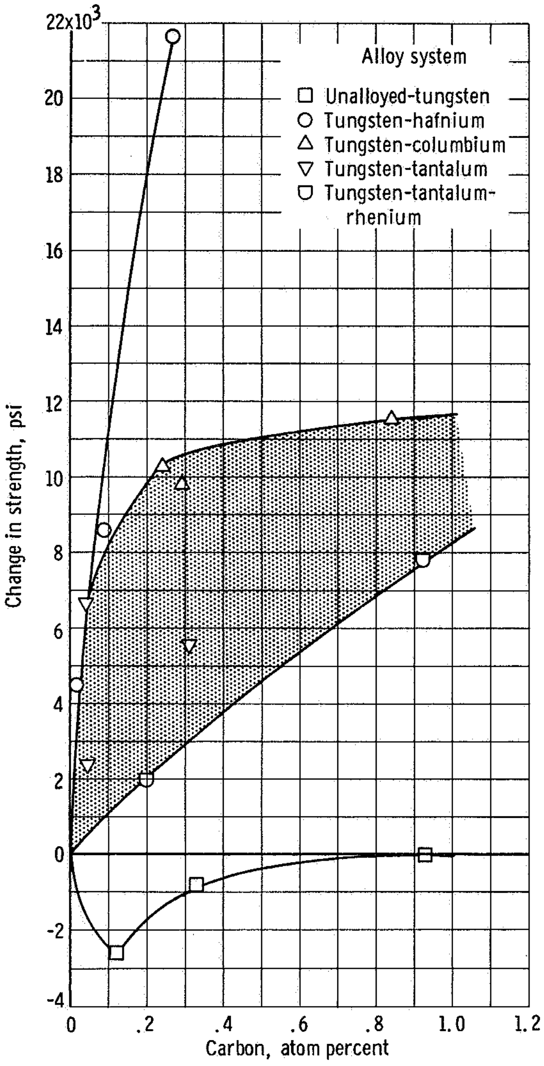


Figure 7 - Change in strength due to carbon additions to unalloyed tungsten and several tungsten alloy systems at 3500° F.

Figure 8 - TENSILE STRENGTHS OF AS-SWAGED CARBIDE-STRENGTHENED ALLOYS AT 3000° AND 3500° F

Alloy, atom percent	Test temperature, °F	
	3000	3500
	As-swaged strength, psi	
W - 0.97 Ta - 2.62 Re - 0.92 C	85 300	25 700
W - 0.43 Ta - 0.31 C	84 100	16 600
W - 0.20 Hf - 0.26 C	88 200	62 500

IV - GRAIN SIZE AND STRENGTH

(See page 10 of Prof. Grant's draft)

Although in superalloys it has been generally accepted that a coarse grain size is stronger at high temperatures than a fine grain size, this is not necessarily true in refractory metals. It is suggested that, at least in pure metals and solid solution alloys, greater tensile and creep strengths may be associated with finer grain sizes. Some illustrative data follow:

Klopp, Witzke, and Raffo (ref. 1) studied the relation of grain size to both short-time tensile and creep strengths of unalloyed tungsten. (All of the following is from their paper.) A plot of ultimate strength and yield strength for the arc-melted specimens and ultimate strength for the EB-melted specimens against average grain diameter, presented in Figure 1, shows that the strengths decrease with increasing grain size. The grain-size dependencies, which appear to be unaffected by temperature over the range 2500° to 3500° F, were expressed as

$$\sigma_u = AL^{-0.12} \tag{1}$$

$$\sigma_y = BL^{-0.25} \tag{2}$$

where

σ_u = ultimate tensile strength (at 0.05 min^{-1}), psi,
σ_y = 0.2 pct offset yield strength (at 0.005 min^{-1}), psi,
A,B = temperature-dependent constants,
L = average grain diameter, cm.

Thus, decreasing the grain size from 0.1 cm, typical for arc-melted tungsten annealed above 4000° F, to 0.005 cm, typical for just-recrystallized arc-melted tungsten, increased the ultimate strength by 40 pct and the yield strength by 80 pct.

(It is also apparent from Figure 1 that the ultimate strengths of the EB-melted materials were only about 85 pct as high as the ultimate strengths of arc-melted tungsten at the same grain sizes. It was suggested that this difference reflected the differences in purity between the two types of materials.)

The authors pointed out that variations in tensile strength with grain size at high temperatures have been observed previously (ref. 2, 3), although a complete picture of the mechanism has not yet emerged. A mechanism based on strain hardening has been described by McLean (ref. 2) who suggests that the increased strength with decreasing grain size results from the increased complexity of slip within the individual grains. During deformation of a polycrystalline material, the individual grains are partially constrained by their neighbors so that slip on a given plane can proceed only to the extent that the neighboring grains can deform to accommodate the changing grain shape. As the limit of deformation in a given direction is approached, the resolved stresses within the grain increase and slip begins on other planes more favorably oriented with respect to the neighboring grains. Decreasing grain size reduces the total strain that can be accommodated on the most favorably oriented slip planes, and the stress increases more rapidly with total strain in order to activate slip on less favorably oriented planes, giving rise to the observed increasing strength and strain-hardening rate with decreasing grain size.

A second possible explanation is concerned with the effect of grain boundaries on dislocation density. It has been shown (ref. 4) that the average dislocation density ρ is approximately proportional to the first power of strain ϵ :

$$\rho = D\epsilon^{c} \tag{3}$$

where c is approximately equal to 1.

The flow stress σ to produce plastic strain is proportional to the square root of the dislocation density

$$\sigma = \sigma_o + a\sqrt{\rho} \tag{4}$$

where

σ_o = stress to initiate dislocation motion, psi,
a = proportionality constant.

By substituting Eq. (3) into Eq. (4), a parabolic relation between σ and ε is obtained:

$$\sigma = \sigma_o + \alpha\sqrt{D\varepsilon^c} \qquad (5)$$

It is further seen that increasing the dislocation density for a given strain, i.e., increasing the proportionality factor D between ρ and ε, increases the required flow stress for a given strain. Since grain boundaries can act as sources for dislocations, an increase in the grain boundary area per unit volume (reduction in grain size) increases the dislocation density and thus the strength.

For creep, Klopp, et al, analyzed their data to determine the best values for a and b in a relation of the type proposed by Sherby (ref. 5):

$$\dot{e} = K\sigma_c^a L^b \qquad (6)$$

where

K = temperature-dependent constant,

a,b = temperature-independent constants,

σ_c = engineering creep stress.

Average values of 5.8 were determined for a, the stress factor, and 0.43 for b, the grain size factor. The stress factor decreased slightly with increasing temperature, but no temperature dependency was apparent for the grain-size factor b. The average stress factor of 5.8 is close to the value of 6.3 observed by Green (ref. 6) for powder-metallurgy tungsten at higher temperatures.

The grain-size factor of 0.43 is less than the value of 2 proposed in the review by Sherby (ref. 5) and observed by Feltham and Meakin in copper (ref. 7) and Sutherland and Klopp in powder-metallurgy tungsten (ref. 8). The increase in creep rate (decrease in creep strength) with increasing grain size, however, is in qualitative agreement with these and other recent observations on lead (ref. 9), and on brass and copper (ref. 8). In contrast, studies on aluminum (ref. 2) and a recent study on copper (ref. 9) showed the opposite effect; that is, the coarse-grained materials were stronger. Studies on Monel (ref. 12) and an austenitic iron-base alloy (ref.

13) have indicated that the creep rate exhibits a minimum at an intermediate grain size, where the grain size for this minimum creep rate increases with increasing temperature. This relation has been interpreted (ref. 13) to result from mobile dislocations being formed at intragranular sources at low temperatures and/or high stresses, while at high temperatures and/or low stresses mobile dislocations are generated at grain boundaries. Although the shift in grain size for minimum creep rate from fine to coarse has been reported to occur over the range 0.4 to 0.6 T_m (ref. 13), no minimum in a plot of creep rate vs grain size was observed in the study by Klopp et al, which covered the temperature range 0.4 to 0.7 T_m.

The calculated stress necessary to give a creep rate of 10^{-6} sec^{-1} at 3000°, 3500°, and 4000° F was plotted against grain size in Figure 2. The stress during creep was proportional to the -0.074 power of grain size, as calculated from Eq. (6). This value is measurably less than the factor of -0.12 observed for the dependency of the short-time ultimate tensile strength on grain size (shown in Figure 1), reflecting the probability that there is a change or modification in the rate-controlling reaction. The strength at elevated temperatures is considered to be determined from competition between strain-hardening and recovery reactions. During tensile testing, where the total time is short, strain-hardening may exert the predominant influence on strength. During creep testing, however, the test times are considerably longer and recovery reactions are considered rate controlling. The mechanisms by which decreasing grain size is postulated to increase strength are increasing the complexity of slip and/or increasing the dislocation density. Since these are both associated with strain hardening rather than recovery, the decrease in grain-size dependence may reflect the increasing importance of recovery as the rate-controlling reaction at low strain rates.

It is also apparent from Figure 2 that the creep strengths of both arc-melted and EB-melted tungsten are similar when compensated for grain size; in contrast, EB-melted tungsten was weaker than arc-melted tungsten of similar grain size in short-time tensile tests. This behavior suggests that impurities, perhaps as widely dispersed precipitates, can moderately strengthen tungsten during tensile testing by interfering with slip and increasing the rate of strain hardening. These impurities, however, are relatively ineffective as strengtheners during creep, where recovery processes such as cross slip and climb allow the dislocations to bypass these obstacles.

References

1. Klopp, W. D., Witzke, W. R., and Raffo, P. L.: Trans. Met Soc. of AIME, Vol. 233, p. 1860, Oct. 1965.
2. D. McLean: Mechanical Properties of Metals, pp. 122-24, 285-334, John Wiley and Sone, New York, 1962.
3. M. Gensamer: Relation of Properties to Microstructure, pp. 16-29, Am. Soc. Metals, Cleveland, 1954.
4. A. S. Keh and S. Weissmann: Electron Microscopy and Strength of Crystals, pp. 231-300, Interscience, New York, 1962.
5. O. D. Sherby: Acta Met., 1962, vol. 10, pp 135-47.
6. W. V. Green: Trans. Met. Soc. AIME, 1959, vol. 215, pp 1057-60.
7. P. Feltham and J. D. Meakin: Acta Met., 1959, vol. 7, pp 614-27.
8. E. C. Sutherland and W. D. Klopp: NASA TN D-1310, NASA, Cleveland, Ohio, 1963.
9. P. Feltham: Proc. Phys. Soc. (London), 1956, vol. B69, pp 1173-88.
10. E. R. Parker: Trans. Am, Soc. Metals, 1958, vol. 50, pp 52-104.
11. C. R. Barrett and O. D. Sherby: Trans. Met. Soc. AIME, 1964, vol. 230, pp 1322-27.
12. P. Shahinian and J. R. Lane: Trans. Am. Soc. Metals, 1953, vol. 45, pp 177-99.
13. F. Garofalo, W. F. Domis, and F. von Gemmingen: Trans. Met. Soc. AIME, 1965, vol. 230, pp 1460-67.

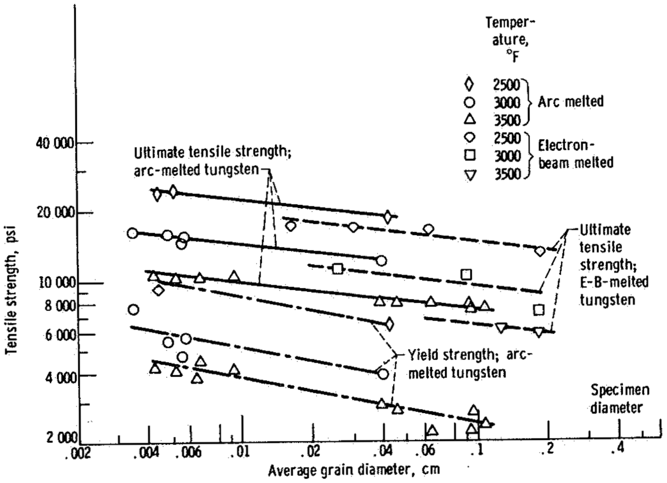


Fig. 1 -Yield and ultimate tensile strengths of arc-melted tungsten and ultimate tensile strength of electron-beam-melted tungsten as a function of grain size. Crosshead speed, 0.005 in. per min for yield strength and 0.05 in. per min for ultimate strength.

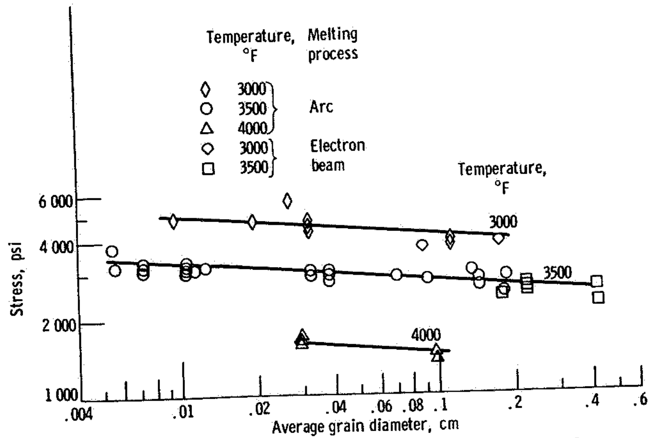


Fig. 2 -Grain-size dependency of stress for a steady-creep rate of 10^{-6} per sec.

V - REFRACTORY METAL 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 1 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 2 (ref. 1) 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 each of several temperatures, we were to substitute the 1000-hour strength density of a 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 3 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

(1980° C). 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 (65° to 160° C) might be achieved; at 70 volume percent fiber, improvements of 250° F to 480° F (140° to 270° C) 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 (65° to 270° C) here, the range would be 75° to 435° F (40° to 240° C).

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 Figure 4. In Figure 2, 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 (ref. 2) 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 Figure 3. There may be some counteracting factors, however. Figure 13 shows that, from recent data (ref. 3), 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 (1200° C) of 5-mil wire is 33 percent better than 50-mil sheet; the temperature advantage in this range is 135° F (75° C)!

To date, few data have been available from studies of reinforcement of superalloys with refractory metals or fibers. Figure 5 shows data for tungsten wire reinforcement of Hastalloy X from Davies of Clevite and for tungsten wire reinforcement of another nickel-base alloy from Glenny (ref. 4).

Additional studies along these lines should prove profitable.

References

1. McDanels, D. L., Jech, R. W., and Weeton, J. W.: NASA TN D-1881, NASA, Cleveland, Ohio, 1963
2. Petrasek, Donald W., and Weeton, John W.: NASA TN D-1568, NASA Cleveland, Ohio 1963.
3. McDanels, D. L., and Signorelli, R. A.: NASA TN D-3467, NASA Cleveland, Ohio, 1966.
4. Glenny, R. J. G., Beeton, A. B. P. and Barnes, J. F. AIAA Paper 65-743, presented at Royal Aeronautical Society and Japan Society for Aeronautical and Space Sciences, Aircraft Design and Technical Meeting, Los Angeles, November 15-18, 1965.

COMPOSITE MATERIALS FROM METAL FIBERS

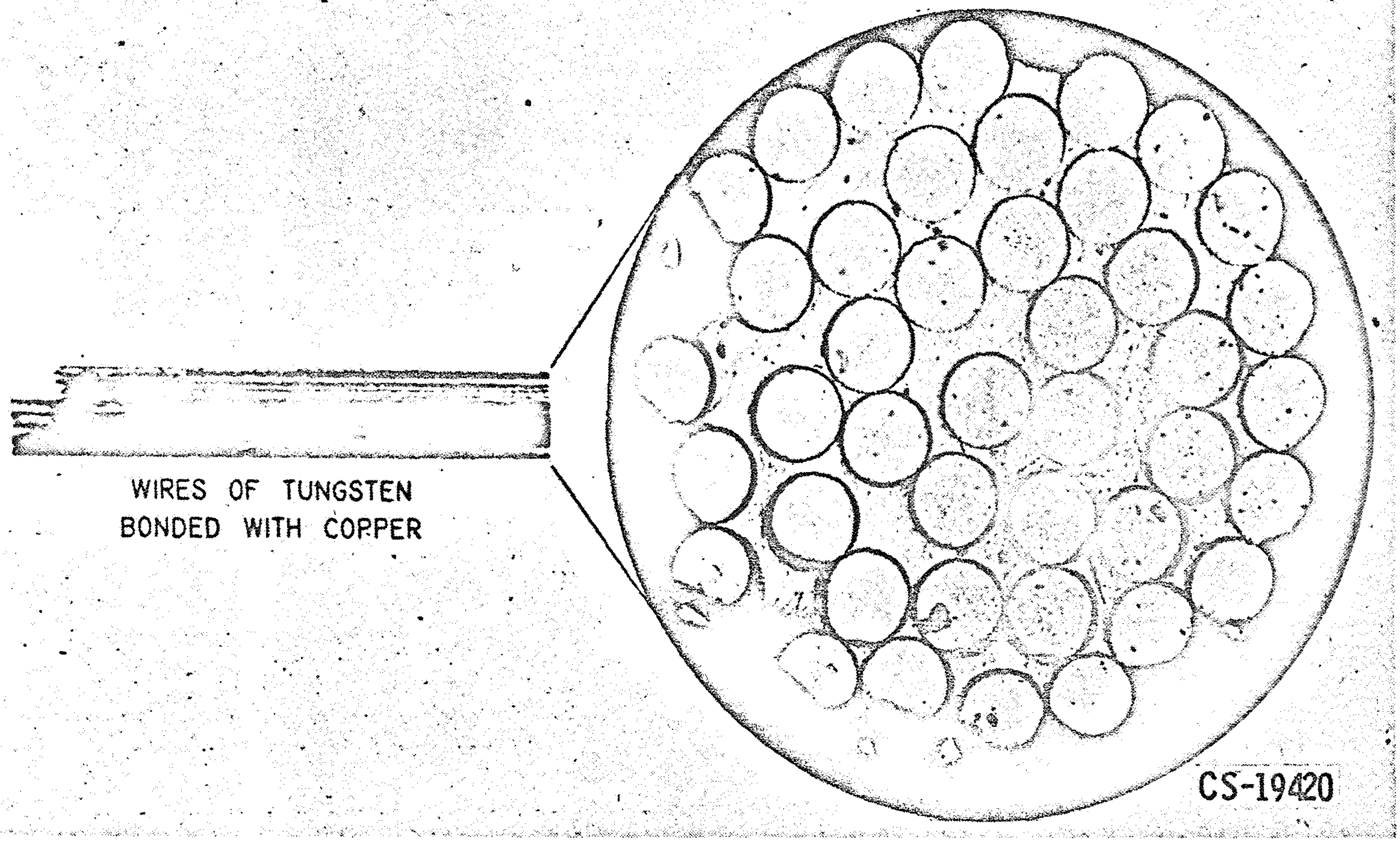


Figure 1.

TENSILE STRENGTH OF COMPOSITES OF CONTINUOUS TUNGSTEN FIBERS IN COPPER

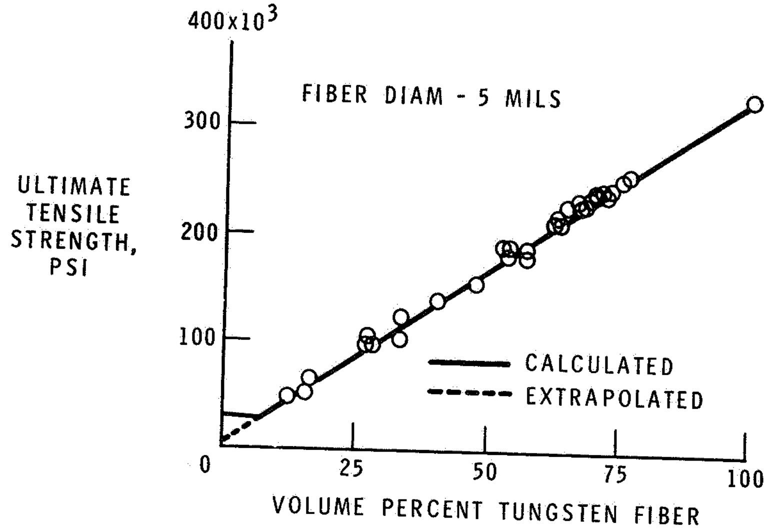


Figure 2.

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

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

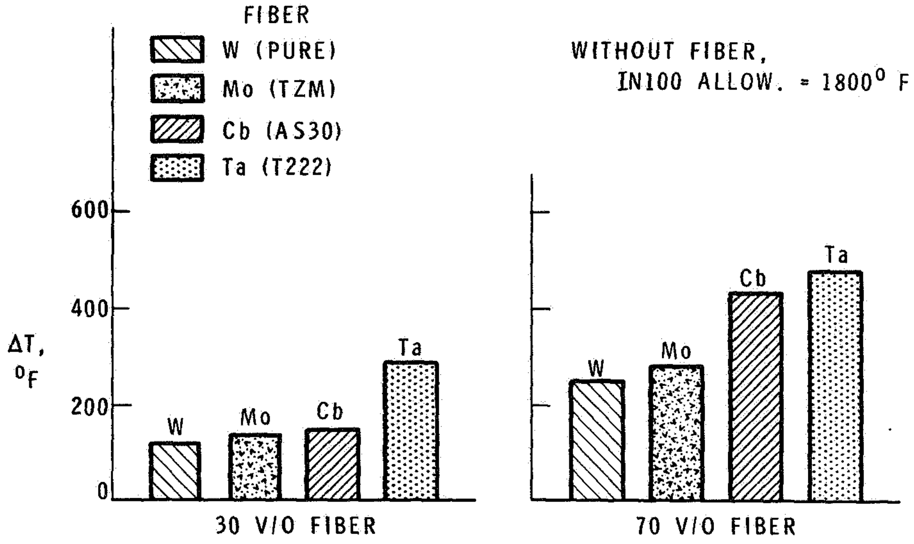
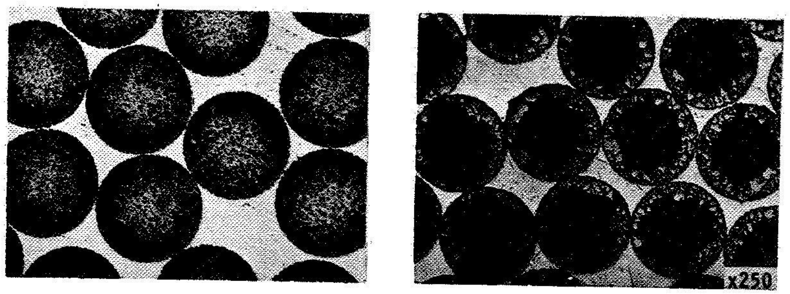


Figure 3.

EFFECT OF REACTION BETWEEN MATRIX AND FIBERS



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

Figure 4.

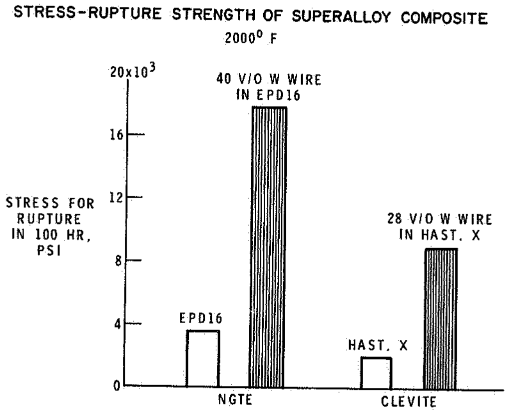

STRESS-RUPTURE STRENGTH OF SUPERALLOY COMPOSITE
2000° F
STRESS FOR RUPTURE IN 100 HR, PSI
20x10³
16
12
8
4
0
40 V/O W WIRE IN EPD16
EPD16
28 V/O W WIRE IN HAST. X
HAST. X
NGTE
CLEVITE

Fig. 5