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A REVIEW OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN ALLOYS

WILLIAM D. KLOPP

NASA Lewis Research Center, Cleveland, Ohio (U.S.A.)

Summary

The mechanical properties of chromium, molybdenum, and tungsten alloys are reviewed, with particular emphasis on high-temperature strength and low-temperature ductility. Precipitate strengthening is highly effective at $0.4 - 0.8\ T_m$ in these metals, with HfC being most effective in tungsten and molybdenum, and Ta(B,C) most effective in chromium. Low-temperature ductility can be improved by alloying to promote rhenium ductilizing or solution softening. The low-temperature mechanical properties of these alloys appear related to electronic interactions rather than to the usual metallurgical considerations.

Introduction

Considerable progress has been made in the development of improved chromium, molybdenum, and tungsten alloys during the last decade, stimulated in large part by the potential usefulness of these materials at high temperatures in advanced airbreathing turbine engines and nuclear space power systems.

The favorable attributes of chromium include a higher melting point, higher modulus of elasticity, and lower density than superalloys. Molybdenum and tungsten also possess high melting points and high moduli of elasticity, inferring good strength at elevated temperatures.

However, these three Group VIa b.c.c. metals also have several limiting characteristics. In particular, they undergo a ductile—brittle transition in common with other b.c.c. elements. For these three metals, the ductile—brittle transitions occur in the vicinity of $0.15\ T_m$, limiting their usefulness in many applications. The Group VIa metals also form volatile oxides at elevated temperatures, thus severely limiting their usefulness in oxidizing environments. In the case of chromium, oxide volatility occurs at a higher homologous temperature than with molybdenum and tungsten, but chromium also suffers from nitrogen embrittlement. Thus, all three metals require protective coatings if they are to be used in air. The densities of molybdenum and tungsten are rather high, but are outweighed by their high moduli of elasticity and melting points, so that their high-temperature strength/density ratios are still favorable.

Emphasis in alloy development during the last decade has been directed, first, toward exploiting their potential for good strength at elevated temperatures and, secondly, toward improving their low-temperature ductilities. Both alloying and substructural control have been emphasized in the improvement of these properties. Because of the similarities in many properties of these three metals from the same Periodic Group, the approaches to property improvement have been similar. Thus, while earlier research emphasized solid-solution alloying for high-temperature strength improvement, most recent studies have shown that precipitate strengthening and thermomechanical processing control offer a more effective approach. Similarly, substitutional alloying to achieve the "rhenium ductilizing effect" and solution softening have improved the low-temperature ductilities of all three metals (though not as much as designers would like).

This paper will review recent research efforts directed toward improvement of the mechanical properties of chromium, molybdenum, and tungsten. Among the major points emphasized here will be the importance of precipitate strengthening at high temperatures and of electronic considerations in controlling low-temperature ductility.

High temperature strength

Solution strengthening

Strengthening by substitutional alloying additions is a widely-employed approach for many metals and, indeed, is quite effective in improving the high-temperature strength properties of the Group Va metals, niobium and tantalum. Early alloy development studies on chromium [1], molybdenum [2], and tungsten [3] also tended to emphasize solution strengthening. Although strength improvements up to 3 to 5 fold are possible by solution strengthening, these alloys become increasingly more difficult to fabricate with increasing solute content. Substitutional alloying also raises the ductile-brittle transition temperature to unacceptably high levels (except for solutes promoting rhenium ductilizing or solution softening). These trends towards decreased fabricability and increased ductile–brittle transition temperature are accentuated by the high moduli of elasticity of chromium, molybdenum, and tungsten. These behaviors, in part, have caused alloy designers to de-emphasize solution strengthening in favor of precipitate strengthening in the development of chromium, molybdenum, and tungsten alloys.

Precipitate strengthening

Chromium

Chromium alloys are of interest primarily for blade and vane applications in advanced air-breathing engines at metal temperatures approaching 2100 °F. Emphasis in the development of high-strength, ductile chromium alloys has shifted during the last few years from alloys strengthened by a combination of substitutional solutes and precipitates to those strengthened
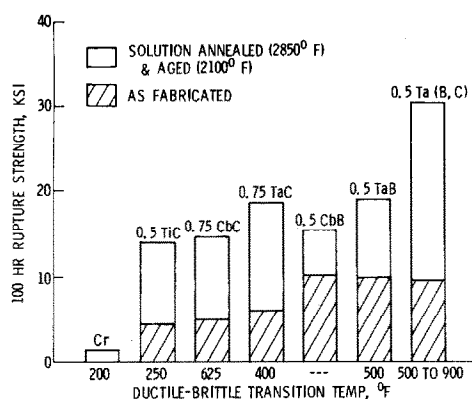
Fig. 1. Rupture strength and ductility of precipitate-strengthened chromium alloys at 2100 °F.
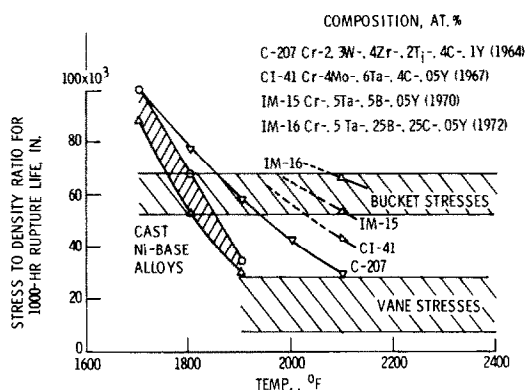

Fig. 2 Stress/density ratios of chromium-base and nickel-base alloys.

solely by fine precipitates. Results from the recent work of Filippi [4, 5] are summarized in Fig. 1. The carbides and borides of titanium, niobium (columbium, Cb), and tantalum are seen to be effective high-temperature strengtheners in induction-melted, electrolytic chromium. In the as-fabricated condition, 100-h rupture strengths at 2100 °F up to 10 ksi are achievable, compared with 1.5 ksi for recrystallized, unalloyed chromium. However, in order to achieve maximum strengthening, solution-annealing and aging treatments are required. Solution annealing for one hour at 2850 °F converts all of the carbide and boride into massive particles of $Cr_{23}C_6$ and Cr_4B, respectively. Subsequent aging for 3 h at 2100 °F then reconverts these chromium compounds into fine particles of MC (M = solute metal) or M'_3B_2 (M'_3 = 2 at. solute metal/at. Cr) [6]. Tantalum carbide and boride are seen to be more effective strengtheners than those of titanium or niobium in the heat-treated condition.

Best strengthening is obtained in a heat-treated Cr–0.5Ta–0.25B–0.25C–0.1Y alloy. (All compositions are in at.%.) Although the strengthening precipitate in this alloy has not yet been identified, the material exhibits a 20-fold strength improvement over unalloyed, electrolytic chromium.

Unfortunately, the ductile–brittle transition temperatures for all of these materials are rather high, ranging from 25 °F for Cr–TiC to 500 - 900 °F for the Cr–Ta(B,C) alloy (shown in Fig. 1). Ideally, assuming the precipitate components to be absent from the chromium matrix, these alloys should exhibit approximately the same or lower transition temperature as unalloyed chromium. This goal may be approached as our understanding of precipitate-strengthened chromium improves and compositions and processing conditions are optimized.

In Fig. 2 [1, 5], the strengths of representative chromium alloys are compared with advanced, cast, nickel-base alloys on a density-compensated basis. The approximate stress ranges for blade and vane applications in air-breathing turbine engines are also indicated. The early C-207 alloy, which relied primarily on solution strengthening by tungsten, exhibits a 100 - 200 °F potential service-temperature advantage over nickel alloys. The stronger CI-41 alloy was solution strengthened by molybdenum and precipitate strengthened by TaC, while IM-15 was strengthened only by the more effective Ta,B precipitate. The most recent Cr–Ta(B,C) alloy exhibits an approximate 400 °F potential service-temperature advantage over nickel alloys.

In spite of the significant strength improvements which have been made in chromium during the last decade, the outlook for chromium as an engine material remains poor. The major disadvantage of chromium alloys is their unacceptably high ductile–brittle transition temperature which makes careful handling during fabrication and assembly mandatory and also indicates the possibility of catastrophic failure during a cold start-up. This problem has not yet been eliminated; indeed, the recent, stronger chromium alloys also display increased ductile–brittle transition temperatures. Nitrogen embrittlement also remains a serious problem, although recent coatings studies [7, 8] suggest that this problem may be capable of solution. Finally, it should be noted that the potential service-temperature advantages exhibited by chromium alloys are relative to uncooled superalloys. In reality, superalloys can be cooled so that their service temperatures are several hundred degrees above their actual metal temperatures, thus reducing or eliminating the advantage of chromium alloys. The possibility of cooling chromium components does exist, but in view of the brittleness and need for protective coatings, cooling would appear to be more difficult for chromium than for superalloys.

Molybdenum

The technology of molybdenum alloys is fairly well established, especially with regard to those alloys strengthened by TiC and ZrC. However, there have been recent significant developments in the areas of HfC strengthening and thermomechanical processing which indicate that materials with improved
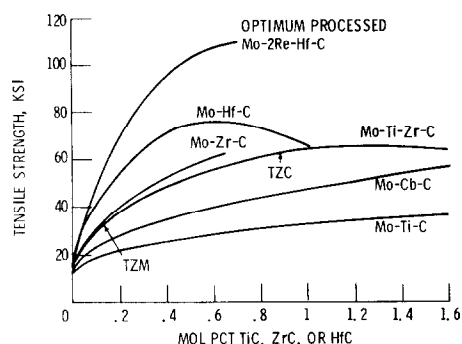
Fig. 3. Tensile strength of swaged, carbide-strengthened molybdenum alloys at 2400 °F.

strength—ductility combinations are possible.

The strengthening effects of various carbides in molybdenum are summarized in Fig. 3 [9 - 18], where it is assumed that strengthening is due to stoichiometric monocarbides, and excesses of the solutes are relatively ineffective strengtheners.

It is seen from Fig. 3 that the order of strengthening in molybdenum is TiC, NbC, ZrC, and HfC. This order is similar to the order of the respective melting points and, for the Group IVa carbides, in order of their respective thermodynamic stabilities.

The synergistic effect obtained by combining TiC and ZrC was recognized in 1962 by Semchyshen and coworkers [15] and is the basis for the commercially important Mo-TZM and Mo-TZC alloys. The compositions of these alloys in terms of mol % carbide are indicated in Fig. 3.

Molybdenum—hafnium—carbon alloys were studied briefly by Semchyshen et al. [9] and by Morgunova [19]. However, the most extensive survey of alloys in this system was conducted by Raffo [13], who determined that alloys strengthened by HfC have a significant strength advantage over those strengthened by TiC, ZrC, or NbC, as indicated in Fig. 3. Additionally, these alloys displayed good low-temperature ductilities, with most having better than 10% tensile elongation and better than 30% reduction in area at room temperature in the worked (as-swaged) condition.

In common with other carbide-strengthened alloys of molybdenum, these Mo—Hf—C alloys are quite responsive to solution-annealing and aging treatments [14]. Solutioning of the carbides can be accomplished by annealing at 4000 °F, slightly above the Mo—C eutectic temperature, where the carbon solubility is about 1 at.% [20]. Quenching results in precipitation of carbide platelets on the {001} matrix planes, in agreement with the observation of Perkins and Lytton [21] on Mo—Nb—Ti—Zr—C alloys. These solution-annealed Mo—Hf—C alloys are age-hardenable with maximum hardening attainable on aging at 2750 - 2800 °F.

Significant improvements in the high-temperature strength of HfC-strengthened molybdenum were obtained by a new thermomechanical processing schedule involving extrusion at a higher temperature than normally
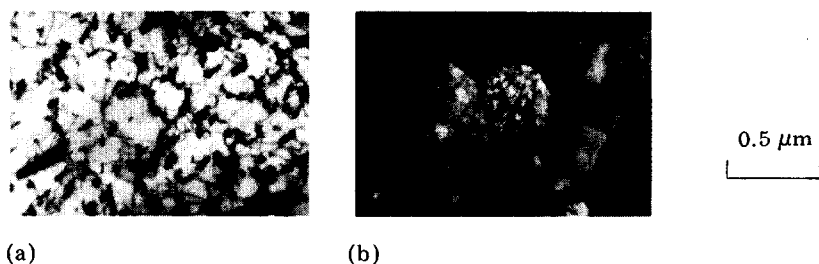
(a)   (b)

Fig. 4. Electron transmission microstructure of Mo–0.60 Hf–0.50 C alloy. (a) Extrude, 4000 °F; age, 2800 °F; swage, 2500 °F. (b) Extrude, 4000 °F; no age; swage, 2500 °F.

employed [14]. Previous thermomechanical processing studies on molybdenum alloys have generally included extrusion at 3400 - 3600 °F, with the prime variables being subsequent swaging and annealing temperatures [22]. Raffo, however, determined that the best high-temperature strength resulted from extrusion at the solution-annealing temperature of 4000 °F followed by swaging at 2500 °F with no intermediate aging treatments. This processing schedule gave an approximate 40% strength improvement for Mo–2Re–Hf–C compared with Mo–Hf–C alloys extruded at 3500 °F (lower Mo–Hf–C curve in Fig. 3) or extruded at 4000 °F and aged at 2800 °F prior to swaging.

Electron-transmission microstructures of a Mo–Hf–C alloy extruded at 4000 °F and swaged with and without a post-extrusion 2800 °F aging treatment are shown in Fig. 4. In the aged and swaged material, carbide precipitates of approximately 400 Å diameter are seen to be interacting with numerous dislocations. This material had a tensile strength of 73 ksi at 2400 °F. However, in the material swaged directly from the extruded condition, the carbide precipitates are too fine to be resolved and the dislocation structure is rather diffuse. This material had a tensile strength of 122 ksi at 2400 °F. The higher strength and finer microstructure of this material are attributed to strain-induced carbide precipitation during swaging, as opposed to the thermally-induced precipitation in the aged material.

The most recently studied Mo–Hf–C alloys have included a quaternary addition of 2 at.% Re to improve the low-temperature ductility through the solution-softening effect. These alloys, examined by Witzke [17], were fabricated by extrusion at 4000 °F and swaging at 2500 °F. The upper curve in Fig. 3 indicates the strength level for these alloys.

An optimum alloying level corresponding to 0.6 - 0.8 mol% HfC appears to exist for HfC-strengthened molybdenum. By contrast, the available data for molybdenum strengthened with TiC, ZrC, and NbC suggest only that the high-temperature strength increases with increasing carbide content.

A minor trend is also detectable relating strength to excess hafnium or carbon for the ternary Mo–Hf–C alloys studied by Raffo [13]. This trend is illustrated in Fig. 5, where optimum high-temperature strength is associated with a near-equiatomic ratio between hafnium and carbon. Excesses of either hafnium or carbon appear to be weakening. Similar trends were observed for Mo–2Re–Hf–C alloys by Witzke [17].
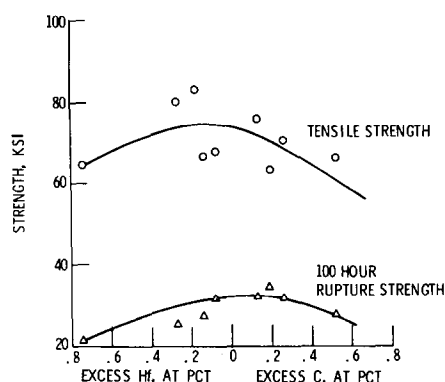
Fig. 5. Effects of excess hafnium and carbon on the strength of swaged Mo- Hf- C alloys at 2400 °F. Alloys contained 0.25 - 1.0 mol % HfC and were extruded at 3500 °F.
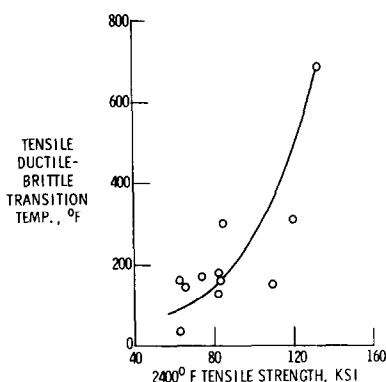
Fig. 6. High-temperature tensile strength and low-temperature ductility of swaged Mo–2Re–Hf–C alloys.

Unfortunately, the low-temperature ductilities of the Mo–2Re–Hf–C alloys extruded at 4000 °F and directly swaged are inferior to those of the ternary Mo–Hf–C alloys extruded at 3500 °F. As shown in Fig. 6, the tensile ductile–brittle transition temperatures tend to increase with increasing strength in the as-swaged condition. Thus, there appears to be a trade-off between strength and ductility in these HfC-strengthened alloys as was observed previously for (Ti,Zr)C-strengthened alloys [10].

Coatings for molybdenum have not been sufficiently protective to permit their long-time use in oxidizing environments (such as in air-breathing turbine engines). However, high-strength molybdenum alloys do appear potentially useful for such applications as turbine wheels in advanced dynamic nuclear power systems involving non-oxidizing working fluids.

Tungsten

Hafnium carbide has also emerged as an extremely potent strengthener for tungsten at elevated temperatures.

This alloy system was first observed to have good high-temperature strength potential by Friedman and Dickinson [23] for powder metallurgy W–Re–Hf–C alloys, and by Raffo and Klopp [24] for arc-melted W–Hf–C alloys. Subsequent studies by Semchyshen and Kalns [25] and Rubenstein [26] confirmed and extended these earlier results on arc-melted W–Hf–C alloys.

More recently, Klopp and Witzke [27] have detailed the strength and ductility properties of arc-melted W–4Re–Hf–C alloys. As in molybdenum alloys, the rhenium additions were made to improve the low-temperature ductility through the solution-softening effect. The tensile strengths of arc-melted W–4Re–Hf–C alloys at 3500 °F are shown in Fig. 7 as a function of mol % HfC. The average strength of swaged W–Re–Hf–C varies up to slightly more than 60 ksi, an approximate 7-fold increase over the 9 ksi strength of unalloyed tungsten. The strength maximum occurs at about 0.35 mol % HfC.
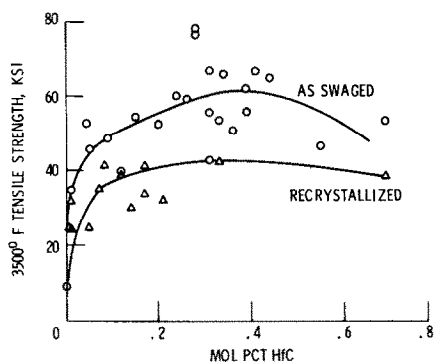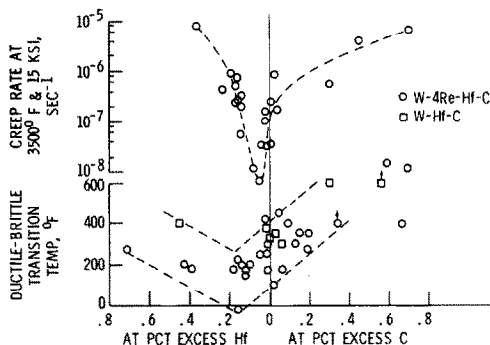
Fig. 7 Tensile strength of W–4Re–Hf–C alloys.

Fig. 8. Effects of excess hafnium and carbon on the creep rate and ductile–brittle transition temperature of swaged W–4Re–Hf–C and W–Hf–C alloys.

The strength of material recrystallized at 3800 °F is substantially lower than that of material in the swaged condition, reflecting the absence of a worked structure and the coarsening of HfC particles, which occurs during annealing.

The effects of minor compositional variations on the strength and ductility of W–4Re–Hf–C and W–Hf–C alloys have been studied by Witzke [28]. As shown in Fig. 8, minima in both creep rate and bend ductile–brittle transition temperature occur at slight hafnium excesses of about 0.05 and 0.15 at.%, respectively. This strength behavior is similar to that observed for Mo–Hf–C alloys to the extent that best high-temperature strength is obtained near an equiatomic ratio between hafnium and carbon.

The improvement in bend ductility with a slight excess of hafnium is probably due to gettering of interstitial impurities from the matrix by hafnium. It is of interest to note that, for these similarly processed materials (extruded at 4000 °F and swaged or rolled at 3200 °F), the addition of 4 at.% Re decreases the bend ductile–brittle transition temperature by up to about 200 °F.

The high-temperature strengths of W–4Re–Hf–C and W–Hf–C alloys are highly dependent on both the morphology and stability of the HfC precipitate. Lattice parameter measurements and spectrographic analyses on extracted carbides from alloys containing up to 0.05 at.% excess Hf and up to 0.45 at.% excess C indicated that the precipitated carbide is actually a solid solution containing up to 18 mol % WC in HfC. The creep rate increases with increasing WC content of the carbide, as shown in Fig. 9. These observations indicate that excess carbon in W–4Re–Hf–C and W–Hf–C alloys promotes increased WC content in the carbide precipitate and further suggest that the increased creep rates may be associated with increased coarsening rates due to the ease of diffusional coarsening of WC. Following similar reasoning, excess Hf may promote coarsening since Hf mobility and concentration in the matrix are rate-controlling for the coarsening of HfC.
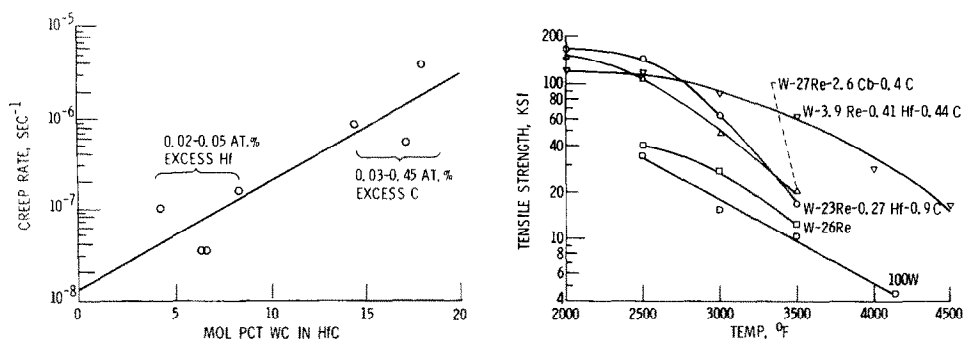
Fig. 9. Effect of precipitate composition on creep rates of swaged W–4Re–Hf–C alloys at 15 ksi and 3500 °F.

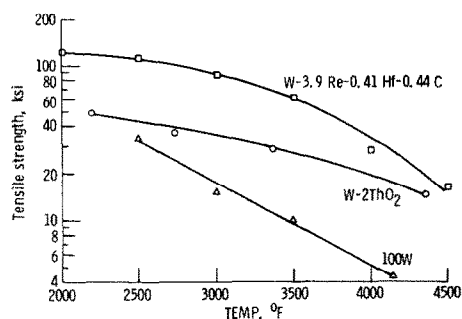Fig. 10. High-temperature tensile strength of carbide-strengthened W–Re alloys.

Fig. 11. High-temperature tensile strength of W–2ThO$_2$.

These results further indicate that the properties of W–4Re–Hf–C and W–Hf–C alloys are very sensitive to minor compositional variations, and precise compositional control is necessary to achieve optimum properties.

Carbide strengthening of the ductile W–26Re alloy has also been studied by Chang [12] using NbC and more recently by Klopp and Witzke [29] using HfC. The high-temperature tensile strengths of these two alloys are compared with those for unalloyed tungsten, W–26Re, and W–4Re–Hf–C alloys in Fig. 10. The carbide-strengthened W–26Re alloys have good tensile strength to 2500 °F, but become progressively weaker above this temperature as compared with the W–4Re–Hf–C alloy. This weakening may be due to a higher solubility of carbon in W–26Re than in tungsten and W–4Re alloy, as postulated recently by Savitskii *et al.* [30] for a Mo–30Re–0.5Zr–0.6C alloy.

Figure 11 illustrates the high-temperature tensile strength of a novel-processed W–2ThO$_2$ alloy developed by King [31] as compared with unalloyed tungsten and W–4Re–Hf–C alloy. The strength of the W–2ThO$_2$ alloy has a lower temperature-dependence than either of the other two materials and is probably superior strengthwise to W–4Re–Hf–C at temperatures above 4500 °F. This crossover in strength is probably due to the greater stability of ThO$_2$ towards coarsening and dissolution as compared with HfC.

High-strength tungsten alloys are potentially suitable for certain specialized applications in high-temperature, nuclear power systems, such as fuel claddings which must resist fuel swelling.

Low temperature ductility

The poor, low-temperature ductility of the Group VIa metals is a major deterrent to their more widespread use. The approaches towards improving low-temperature ductility have included improvement of purity (particularly with respect to interstitials), maintenance of a fine-grained or worked structure, incorporation of inert dispersoids such as ThO_2, and alloying to promote the rhenium ductilizing effect or solution softening. Progress has been made during the last few years in improving the ductility through the incorporation of inert dispersoids [32] and in characterizing and understanding the rhenium ductilizing effect and solution softening [33].

Rhenium ductilizing effect

The rhenium ductilizing effect was first observed in 1955 by Geach and Hughes [34], who found that alloys of W–25Re and Mo–35Re possessed considerably improved fabricability and low-temperature ductility as compared with unalloyed tungsten and molybdenum. It was later shown by Klopp *et al.* [35] that Cr–35Re also exhibited improved fabricability and ductility in a manner similar to W–25Re and Mo–35Re. This rhenium ductilizing effect is thus common to all three Group VIa elements.

Numerous suggestions have been put forward to explain the mechanism(s) by which rhenium effects this remarkable improvement in the cold ductility of chromium, molybdenum, and tungsten, most of which concern the solubilities and distributions of oxygen, oxides, and other interstitials [36 - 38]. The validity of these suggestions remains unsubstantiated, however, and, further, they have not been useful in identifying other ductilizing solutes which may be more effective or less costly than rhenium.

Several non-rhenium systems appear to be rhenium analogs in that they exhibit the improved ductility and twinning associated with the rhenium ductilizing effect. Wukusick has observed improved low-temperature ductility in concentrated, single-phase Cr–Ru alloys [39] and improved fabricability in chill-cast Cr–50Fe and Cr–35Co alloys [37]. Baird *et al.* [40] and Klopp *et al.* [41] have also observed improved fabricability and twinning in Mo–120s. These observations suggest that the promotion of ductility in concentrated alloys is not unique to rhenium.

Stephens and Klopp [42] have recently studied the low-temperature ductility behavior of several chromium-based alloys in order better to characterize possible rhenium analogs and to identify their common characteristics. The major results from this study are shown in Fig. 12. These results confirm the earlier data on Cr–Re and Cr–Ru alloys and also indicate that cobalt and iron are also true analogs to rhenium in improving the low-temperature ductility. However, in the cases of cobalt and iron, the alloys must
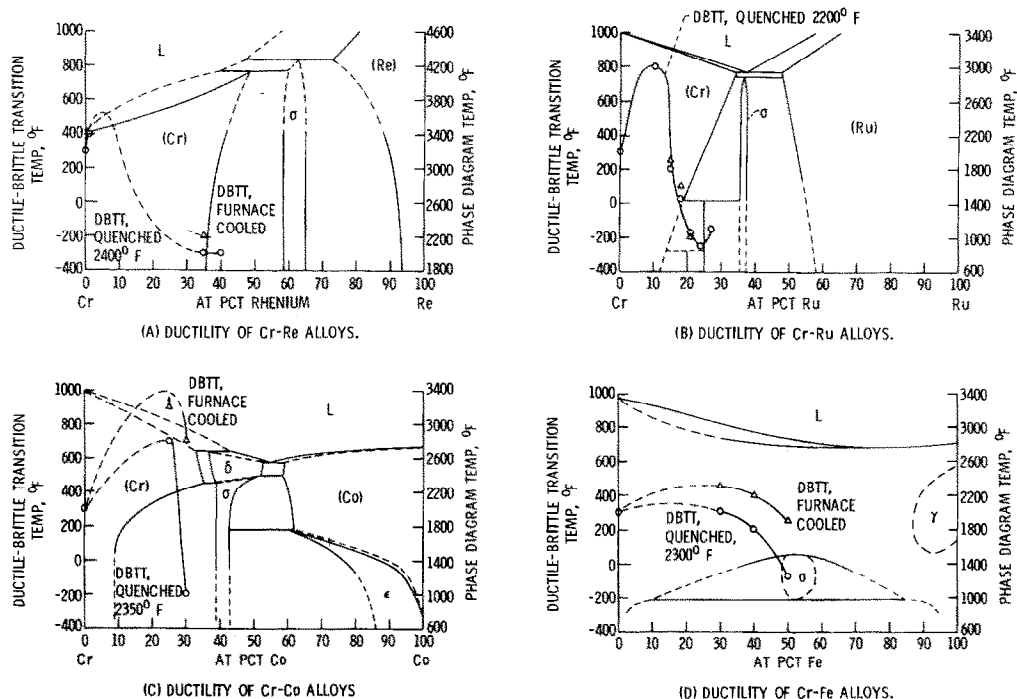
Fig. 12. Ductile–brittle transition temperatures and phase diagrams for chromium–base alloys. (a) Cr–Re, (b) Cr–Ru, (c) Cr–Co, (d) Cr–Fe.

be quenched from the single-phase region before they exhibit the twinning and improved cold ductility associated with the rhenium ductilizing effect. In contrast, both slow-cooled, and quenched Cr–Re and Cr–Ru alloys exhibit good, low-temperature ductility because of the lesser temperature-dependence of the solvus lines bordering the chromium solid solution. Good, hot fabricability was observed in Cr–12 and –150s, but these alloys had higher transition temperatures than unalloyed chromium. Cr–10Ir and Cr–55 and –65Mn exhibited fair fabricability, while alloys of Cr–15 to –45V, Cr–20Ni, and Cr–20Ti were unfabricable.

From these observations, several common characteristics of solutes promoting the rhenium ductilizing effect can be tentatively identified. These common characteristics are:

(1) The ductilizing solutes are from Groups VIIa and VIIIa of the Periodic Table.

(2) The ductilizing solutes form intermediate sigma phases with chromium.

(3) The ductilizing solutes have relatively high solubilities in chromium, at least 20 at.%.

(4) Maximum cold ductility occurs in saturated or supersaturated single-phase, solid-solution alloys.

Although these observations do not indicate the mechanism(s) of the rhenium ductilizing effect, they do provide a means for identifying other

possible rhenium analogs. Based on the characteristics listed above, possible ductilizers for chromium, molybdenum, and tungsten are listed as follows:

Solvent	Known ductilizers	Possible ductilizers
Cr	Re, Ru, Fe, Co	Mn, Tc, Os
Mo	Re	Ru, Tc, (Mn), (Fe), (Os), (Ir)
W	Re	Tc, Os, Ru

The most probable ductilizing solutes are underlined, while the possible but least probable ductilizing solutes are parenthesized. Those solutes not underlined or parenthesized are fairly probable ductilizers.

The correlation of ductilizing ability with phase-diagram considerations implies a further correlation with electronic properties (such as number of $s + d$ electrons), since phase relations among these transition elements are known to be related to electronic characteristics [43]. If the ductilizing effect is related to $s + d$ electrons in the solute, it may be possible to combine appropriate amounts of several ductilizing solutes to design a ductile material with other desireable properties, such as an improved strength/density ratio at high temperatures.

Solution softening

In addition to the rhenium ductilizing effect, the cold ductility of chromium, molybdenum, and tungsten can be improved by alloying to promote solution softening.

This phenomenon was first observed as hardness minima in dilute W−Re and Mo−Re alloys [35]. It was later determined that the decreased hardness of these alloys was accompanied by reductions in the ductile−brittle transition temperatures, as shown in Fig. 13 [44, 45]. A minimum ductile−brittle transition temperature occurs in recrystallized W−Re at about 2 at.% Re and is probable in recrystallized Mo−Re alloys. No minima are observed in worked W−Re or Mo−Re alloys to at least 8 - 9 at.% Re. Chromium−rhenium alloys do not display ductility improvements at low rhenium contents and normal strain rates, as shown previously in Fig. 12(a), but improvements have been noted at much lower strain rates [46].

The low-temperature hardness behaviors of Cr−Re, Mo−Re, and W−Re alloys have been studied by Stephens and Witzke [47]. Representative hardness curves for Mo−Re alloys are shown in Fig. 14. Solution softening here becomes evident at 80 °F (0.104 T_m) and increases in magnitude with decreasing temperature. The rhenium content at the hardness minimum also increases with decreasing temperature.

The similarity in the low-temperature hardness behaviors of Cr−Re, Mo−Re, and W−Re alloys is emphasized in Fig. 15, which shows the rhenium contents at the hardness minima as a function of homologous temperature for all three systems. The minima are seen to be similar at similar homologous temperatures. This behavior strongly suggests that solution softening in these alloys is an intrinsic phenomenon related to basic properties of the solvents
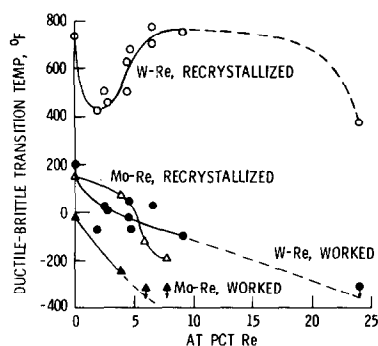
Fig. 13. Bend ductile–brittle transition temperatures for Mo—Re and W—Re alloys.
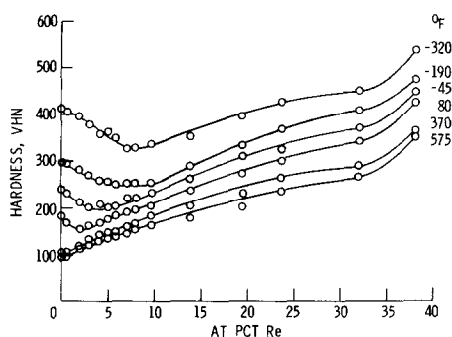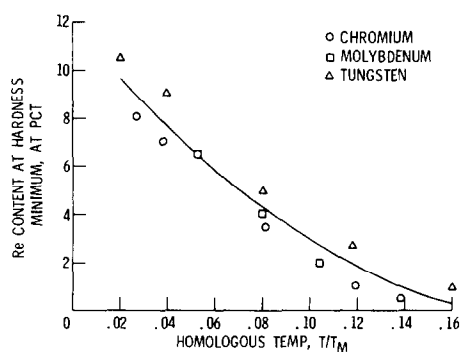
Fig. 14. Low-temperature hardness of Mo–Re alloys.

Fig. 15. Solute contents at hardness minima for Group VIa–Re alloys.

and solutes, as opposed to an extrinsic phenomenon related to interstitials such as is apparently responsible for solution softening in niobium and tantalum [48]. Solution softening is also seen to be exclusively a low-temperature phenomenon, disappearing above an homologous temperature of about $0.16\ T_m$.

Stephens and Witzke [49] also examined the hardness behavior of molybdenum alloyed with hafnium, tantalum, tungsten, rhenium, osmium, iridium, and platinum at -320 to $+280\ ^\circ$F (0.027 to 0.143 T_m). Hardness curves for these alloys at $-320\ ^\circ$F are shown in Fig. 16(a) and (b).

Alloying of molybdenum with hafnium, tantalum, or tungsten produced only alloy hardening, with no indications of solution softening. The rates of hardening at $-320\ ^\circ$F appear related to the differences in atomic radii, indicated on the curves in Fig. 16(a).

Solution softening, however, was observed in alloys of molybdenum with rhenium, osmium, iridium, and platinum, as shown in Fig. 16(b). Moreover, it is evident that the solute contents at the hardness minima decreased and the subsequent hardening rates increased with increasing number of $s + d$ electrons in the solutes, indicated on the various curves. These relationships are shown in Fig. 17. There appears to be a power relationship between
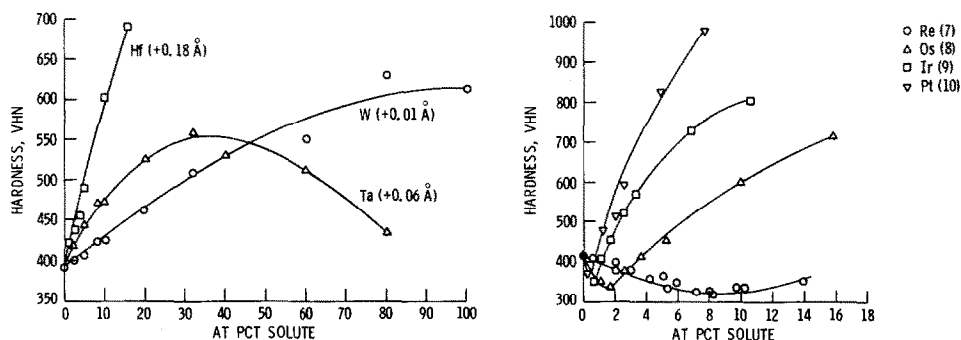
Fig. 16. Hardness of molybdenum-base alloys at −320 °F. (a) Mo–Hf, Mo–Ta, and Mo–W, (b) Mo–Re, Mo–Os, Mo–Ir, and Mo–Pt.

these quantities, with a power factor of slightly greater than 2. No correlation between softening and hardening was evident with atomic size.

This correlation between hardness behavior and number of $s + d$ electrons is further illustrated in Fig. 18, which shows the hardness of molybdenum alloys with rhenium, osmium, iridium and platinum from Fig. 16(b) replotted as a function of the parameter, $c(\Delta V)^2$. Here, c is at.% solute and ΔV is the difference in the number of $s + d$ electrons between solute and solvent. This correlation fairly describes the hardness behavior of these four systems at −320 °F. The hardness behavior of ternary molybdenum alloys with these solutes also follows the relationship shown in Fig. 18 [50], indicating that softening and hardening in these alloys is additive, based on the number of $s + d$ electrons supplied by the solutes.

Previous softening and hardening data on chromium, molybdenum, and tungsten alloys with solutes from Groups VIIa and VIIIa can also be correlated with the number of $s + d$ electrons in a similar fashion [33], indicating that this behavior is common to all three Group VIa metals.

The most significant aspect of these observations is the correlation of a mechanical property, in this case low-temperature hardness, with the electronic structure of the solvent and solute elements. This behavior strongly emphasizes the previously-known electronic dependence of many properties of the transition metals in general, and of Group VIa metals in particular. Previous observations include the correlation between the ductility of chromium alloys and the electronic configuration of solute elements observed by Abrahamson and Grant [51] and the correlation between phase diagrams and electronic configurations for the transition metals described by Hume-Rothery [43]. Solution softening can now be added to this list of properties dependent on electronic configuration.

It should, however, be noted that the observation of solution softening may not be a reliable indication of improved ductility. Such improved ductility has, to date, only been observed in dilute Mo–Re and W–Re alloys.
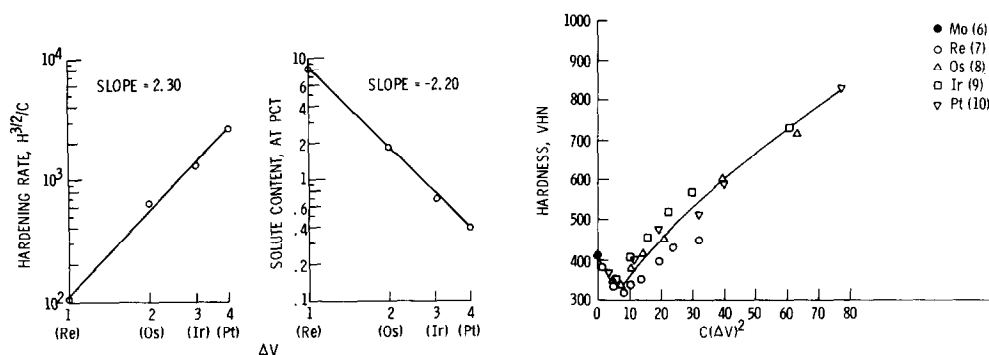
Fig. 17. Hardening rates and solute contents at hardness minima for molybdenum-base alloys at $-320\,^{\circ}$F.

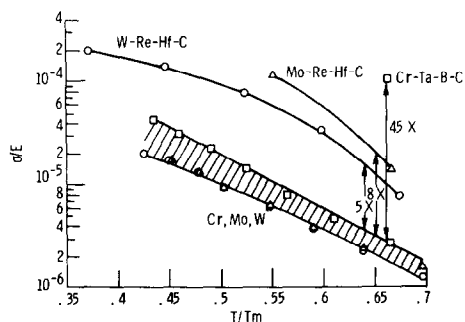Fig. 18. Softening and hardening in molybdenum-base alloys at $-320\,^{\circ}$F

Fig. 19. Modulus-compensated 100-h rupture strengths of Group VIa alloys.

Discussion

It is appropriate here to consider how far we have come and where future opportunities lie in the development of improved chromium, molybdenum, and tungsten alloys.

The high-temperature strengths of the strongest chromium, molybdenum, and tungsten alloys, compensated for elastic modulus and melting point, are compared in Fig. 19 with the average strengths of the unalloyed metals. We have obviously done best in improving the high-temperature strength of chromium, the strongest alloy being approximately 45 times stronger than the average strength of high-purity unalloyed chromium, molybdenum, and tungsten at 0.65 T_m. Conversely, least improvement has been achieved in tungsten-based alloys. This disparity reflects, at least in part, the higher hardness of the strengthening compounds at 0.65 T_m of chromium, compared with that at 0.65 T_m of tungsten.

There do, however, appear to be means for further improving the high-temperature strengths of these metals. These include:

(1) Composition optimization, particularly for chromium alloys.

(2) Complexing of the metallic component of the precipitate to obtain synergistic effects as shown for Mo–Ti–Zr–C alloys.

(3) Complexing of the non-metallic component of the precipitate, such as in the Cr–Ta–B–C alloy.

(4) Optimization of thermomechanical processing schedules to further refine and stabilize precipitate particle sizes.

Considerable progress has also been made during the last few years in understanding the rhenium ductilizing effect and solution softening in chromium, molybdenum, and tungsten. We now know, for example, which solutes are most likely to promote these effects, and that the solution softening phenomenon at least is largely controlled by electronic interactions between solvent and solute. There are areas in need of further definition, such as:

(1) Ductility characterizations of new solutes which appear probable in promoting the rhenium ductilizing effect and solution softening.

(2) Ductility characterizations of complex alloys combining two or more ductilizing solutes or two or more solution-softening solutes.

(3) The basis for the correlation between solution-softening effects and the number of $s + d$ electrons should be further explored.

Conclusions

The major conclusions from this review of chromium, molybdenum, and tungsten alloys are:

(1) Precipitate strengthening is the most effective mechanism for improving high-temperature strength. Hafnium carbide is the best precipitate for strengthening molybdenum and tungsten, while Ta(B, C) is best for chromium.

(2) Rhenium, ruthenium, cobalt, and iron promote the rhenium ductilizing effect in chromium. Other solutes appear as possible rhenium analogs, based on their locations in the Periodic Table and their phase relations with chromium, molybdenum, and tungsten.

(3) Solutes from Groups VIIa and VIIIa promote solution softening in chromium, molybdenum, and tungsten, based on hardness measurements. The hardening and softening characteristics are related to the number of $s + d$ electrons in the solutes.

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