EFFECTS OF REFRACTORY ADDITIONS ON THE STRUCTURE AND MECHANICAL PROPERTIES OF A Hf CONTAINING NICKEL BASE SUPERALLOY

Carl Lund, Consultant
Martin Marietta Corporation
John F. Radavich
Purdue University

The effect of refractory elements Mo+W on the microstructural stability and mechanical properties of a nickel-base superalloy containing Hf was investigated. On an atomic basis, a 1:1 substitution of W for Mo optimizes mechanical properties and serves as a threshold for formation of plate-like phases. Three primary MC phases (with varying amounts of Ti+Ta+Hf) were found. The MC carbides with high Ti+Ta breakdown at high temperatures and relatively stable Hf rich high parameter MCs form. Depending on the W content and the solution temperatures, Mu and/or αW phases were found after exposure at 982°C. Possible effects of high thermal treatments on mechanical properties are discussed.

INTRODUCTION

Early development work on cast nickel-base superalloys stressed "temperature capability" as the basic criterion, often at the expense of other necessary requirements such as castability, microstructural stability, and general ductility. By the end of the 1950's, alloys exhibiting "primary gamma prime" in the as-cast structure signaled the effective end point in volume fraction of gamma prime at roughly 65 per cent. For all practical purposes, the basic limitations had been reached for creep rate and stress rupture at high temperatures.

But these alloys found little commercial use in their original form, and the decade of the 60's was primarily devoted to alloy refinement, maintaining the temperature capabilities developed in the 50's, and providing insights into castability, metallurgical stability, and failure mech-

anisms. Because failure is almost totally a grain boundary phenomenon, a greater appreciation was developed for the powerful effects of small additions of minor elements on mechanical properties, as they produced subtle but important changes in the bulk compositions. The decade of the 70's took the "enlightened empiricism" (re: Chalmers via Decker) of the 60's and applied technologically complex processing techniques such as hot isostatic pressing (HIP), isothermal forging (Gatorizing), and directional solidification (D.S.) to extract the last few degrees of "temperature capability" by means of much improved microstructure. The decade of the 80's will further this scientific inquiry with a return to basic alloy development programs to provide new compositions in direct support of the advanced processing techniques.

The purpose of this study was to take a program done in the 60's and integrate the results into the advanced processing requirements of the 1970's and 80's. These processes require higher temperature exposure, prior to service, than were anticipated during alloy development programs of the 60's. Thermal exposures at 1205°C and above are now commonplace, and could alter microstructural response prior to and during service conditions.

PROCEDURE

The program chosen for illustration was one designed to study the effects of refractory elements Mo and W ranging up to 12% tungsten on a typical nickel-base composition containing 6 Al, 10 Co, 8 Cr, 4 Ta, 1 Ti, and 1.5 Hf. A typical evaluation scheme, as done at Martin Metals, is shown in Figure 1. The tie lines from the 6 per cent point on the Mo ordinate to the intersections on the W abscissa indicate substitutions on an atomic basis of 1/2:1, 1:1, and 1-1/2:1 ratios. The radial lines from the zero point indicate increasing Mo + W contents of constant atomic Mo/W ratios of 5:1, 2:1, 1:1, 1:2, and 1:5. It is useful to remember that for all practical purposes an atomic ratio of 2:1 is approximately equal to a weight ratio of 1:1.

The compositions made and evaluated are defined by the intersectional points, plus an occasional fill-in at an area of interest. The standard evaluation procedure was to machine bars from cast commercial airfoils (MFB) with testing at room temperature, 760°C creep, 982°C stress rupture, and 870°C long time static exposure for stability. These tests were run with two sets of MFB's, one having a commercial heat treatment (1080°C/4 hours + 899°C/10 hours), the other being given a

sensitization treatment of 1095°C/50 hours. The sensitization treatment was the key to the original programs. At that time it was felt that 1095°C/50 hours would adequately represent maximum thermal exposure during production processing of airfoils prior to service exposure. The 1095°C/50 hours sensitization was the basis for stability studies, i.e. formation of unwanted plate-like phases, and the characterization of carbide changes. Thus, alloys chosen for promotion were known to be essentially free of plate-like secondary phases when exposed, for whatever purpose, to thermal exposures up to 1095°C/50 hours during processing. However, the higher thermal exposures of current processing technologies require that the stability studies be re-done with sensitization treatments in excess of 1205°C.

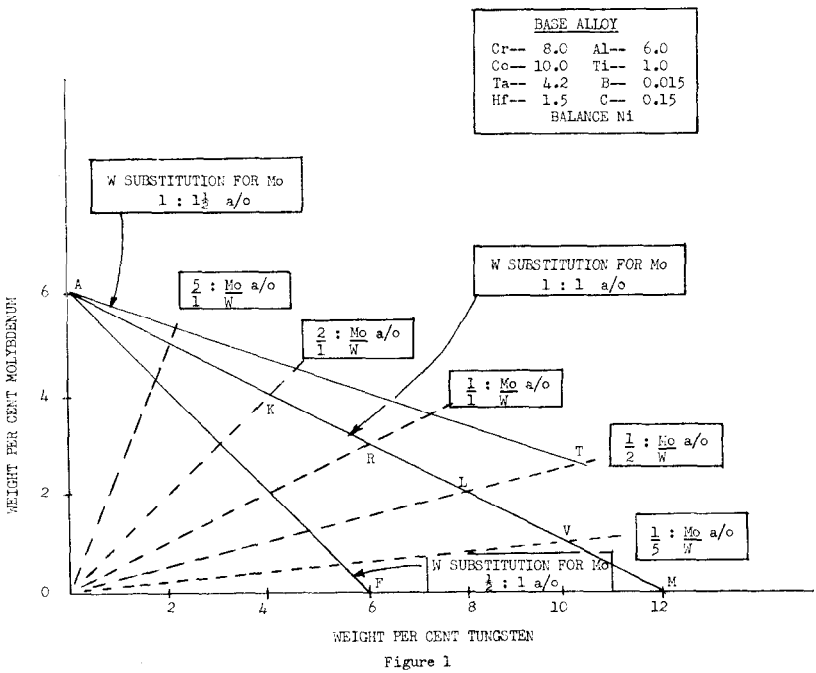

Figure 1

A four hour exposure at 1218°C was chosen as the new appropriate sensitization treatment. A thermal exposure of approximately 100 hours at 982°C was selected as a stability evaluation point. Although 1218°C is not as high as some

current temperatures used for solutioning in D.S. materials, notably the single crystals, it was considered appropriate for the current temperatures used in HIP technology and as a reasonable mean for columnar D.S. After the 100 hour exposure at 982°C, structural and chemical characterizations were carried out and related to those results found earlier with the 1080°C/4 hour and 1095°C/50 hour sensitization treatments.

DISCUSSION OF RESULTS

A. Strength and Stability

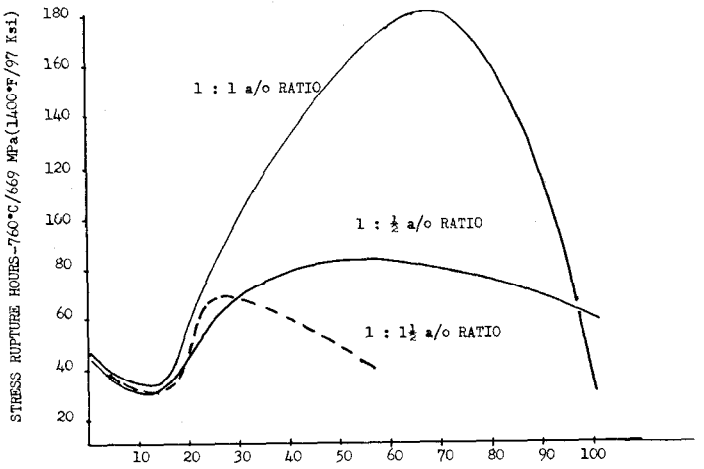

Figure 2a

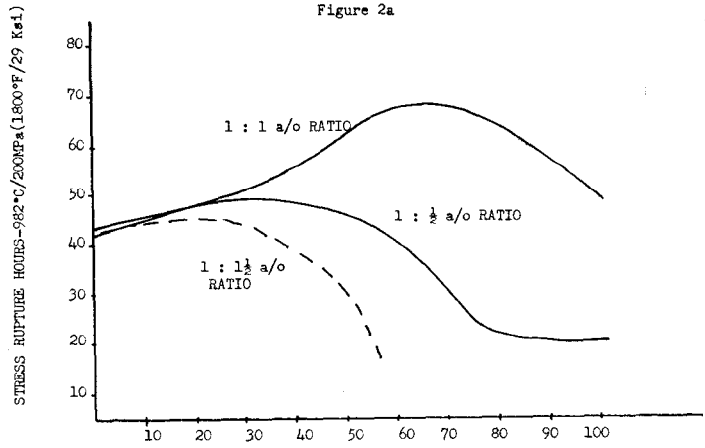

Figure 2b

Because of publishing space limitations, the bulk of detailed mechanical property and phase stability data for the original study are not presented here, but Figures 2 and 3 summarize the pertinent values. Figures 2a and 2b are plots of the stress rupture data on the basis of life (hours) versus the per cent replacement of Mo by W on an atomic basis. These data show that replacement in excess of 60 atomic per cent to be the most attractive. Figure 3 shows the threshhold for the formation of plate-like phases on the basis of thermal exposures of 870°C/1500 hours and 1095°C/50 hours; the threshhold meaning that plates are observed to form in compositions to the right and above the lines indicated. It is interesting to note that the maximum stress rupture strength and the threshhold of plate-like phases follow a common line with the 1:1 atomic substitution of Mo by W, particularly in the most attractive strength area of at least 8 per cent (weight) tungsten.

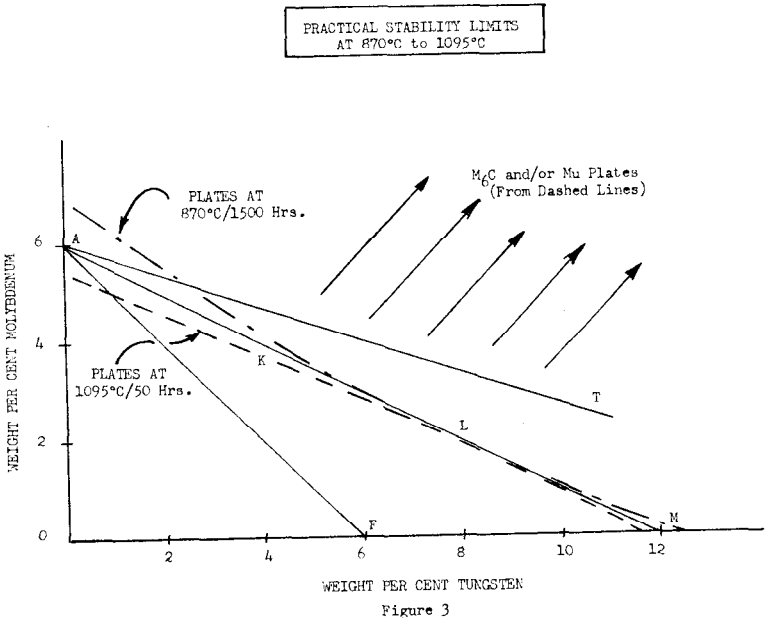

Figure 3

B. X-Ray Diffraction Studies

In all samples which had a 1080°C/4 hour thermal treatment prior to exposure at 982°C, the X-ray diffraction studies confirm that, other than some M_6C and boride phase in the base sample A, only MCs of at least three lattice parameters are present. These three MCs are designated as MC-1, MC-2, and MC-3 with lattice parameters of approximately 4.39 Å, 4.50 Å and 4.59 Å, respectively. Previous work has shown that the MC-1 phase contains large amounts of Ti+Ta with small amounts of Mo+Hf. The MC-2 phase contains varying amounts of Ti+Ta with increased Hf, while the MC-3 phase contains large amounts of Hf+Ta with small amounts of Zr+Ti (1)(2).

Quantitatively, the Ti rich MC-1 phase is the predominant phase while the amounts of MC-2 and MC-3 phases are weak and vary from sample to sample. The MC-1 is found most commonly as script morphology in high Mo samples, but changes to blocky or discrete form as the W increases. The MC-3 is most generally found as small discrete particles surrounded by gamma phase in the eutectic γ' areas, and its amount is related to the number of primary γ' islands in the sample as well as time and temperature of the solution heat treatment.

After 100 hours of exposure at 982°C following the 1080°C/4 hours, very few changes occur in the matrix or in carbide particles with varying Mo+W contents until a W level near 12% is reached. At this high W level, the 982°C exposure produces a Widmanstatten array of Mu phase plates.

However, after 4 hours at 1218°C, the same group of samples show extensive rearrangement of the MC phases. The high parameter MC-3 phase becomes the predominant phase, the MC-2 phase is next strongest, and the low parameter MC-1 phase is weakest. The lattice parameters of the MC-3 and MC-2 phases decrease about .04 Å while the MC-1 parameter remains the same. Such lattice parameter and carbide volume changes would indicate that the MC-1 phase is breaking down and releasing Ti+Ta. A portion of the Ti must partake in the MC-2 and the rest in formation of additional γ'. The Ta forms more MC-2 and also partakes in the MC-3 formation. Once formed, the MC-3 phase carbides are extremely stable and do not readily react or break down.

With the extensive rearrangement of carbides in the 12% W sample and resultant release of Ti, Ta, etc., the matrix solubility for W is radically changed and αW is rejected in

the form of needles or plates.

The 100 hour exposure at 982°C after the 1218°C solutioning did not show any changes in the tendency of any of the samples to form plate phases. The 12% W sample still showed αW and no Mu phase was formed as was previously noted after the 1080°C treatment.

C. Chemical Analysis Study

Qualitative chemical analyses were carried out using the nondispersive analyzer on the SEM on particles in situ and on extracted residues. The low parameter script carbides contain large amounts of Ti+Ta and small amounts of Mo+Hf. As the parameter of the carbides increased, the amounts of Ta+Hf increased with a decrease in the amount of Ti+Mo. In the samples containing only W, the tungsten, if present, is in very small amounts and is difficult to detect in the carbides. Other work has shown the tungsten to be primarily in the gamma and gamma prime (3).

The results of the present study show that the discrete particles in the primary γ' islands are Hf rich and also contain Zr which would account for the very high parameter of this MC-3 phase. Hf rich MC-3 carbides formed as a result of high temperature solutioning do not show the same Zr levels and the lattice parameter of these carbides accordingly dropped to about 4.55 Å.

Selective probing of the various microstructures showed that the Hf is concentrated in the primary γ' islands and in areas near the grain boundaries. In addition to some borides at the grain boundaries, a number of discrete particles show high Hf contents.

A stick-like phase commonly found in Hf modified Ni base superalloys near the primary γ' islands contains Hf, Zr, and S primarily. This phase previously has been reported and identified as a Ti_2S,C type phase (2)(4).

Chemical analyses of various discrete carbides having duplex morphologies show the interiors of many of the carbides to be rich in Ti+Ta while the outer shell or layers to be enriched in Hf. In the case of elongated or blocky particles, the ends of the particles are higher in Hf compared to the elongated section.

Chemical analysis of the αW plate phase shows that only tungsten is present. On the other hand, the Mu phase found in this study shows high W+Cr with somewhat lesser amounts of Co+Ni. When a Mu phase forms in samples containing Mo, the Mo is found in small amounts compared to the above elements.

D. Microstructural Study.

The microstructural study focused primarily on the effects of W on the nature and types of carbides, the primary γ', and the structural stability of the matrix after 1080°C and 1218°C solution treatments. While some of the variations in microstructures may be due to slight variations in casting, the structures found in the MFB test bars should be more representative of the effects of compositional changes.

In the base sample A, small and well distributed primary γ' islands are found. As the tungsten content increases, the primary γ' islands tend to become larger and more plentiful, Figures 4a and 4b. Associated with the primary γ' islands are a number of small discrete high parameter MC-3 carbides and some stick-like particles.

A larger portion of the MC carbides in high Mo alloys tend to be more script-like as compared to discrete shapes. As the W is increased to about 4%, the script-like nature gives way to blocky or discrete form, Figures 5a and 5b. Alloys containing only W still show some script-like matrix carbides. Some Hf discrete MC precipitates are found in the grain boundaries in all samples.

The addition of Hf to nickel-base alloys produces carbides with many duplex morphologies, i.e. the centers or ends of particles appear very different from the rest of the carbide. One such typical morphology shows the ends of the elongated particle to have a sharp point similar to an arrowhead. The arrowhead type MC is common near primary γ' islands and chemical analysis of such points indicate high Hf contents. It is also interesting to note that many of the arrowhead MCs point towards the primary γ' islands where the Hf content is highest. Another common discrete matrix carbide shows a "nut" shape morphology with the center containing high Ti+Ta and the exterior or shell high in Hf. Figures 6a, 6b, and 7a illustrate these morphologies. Similar observations of the nut-shaped MC particles have been previously reported (1).

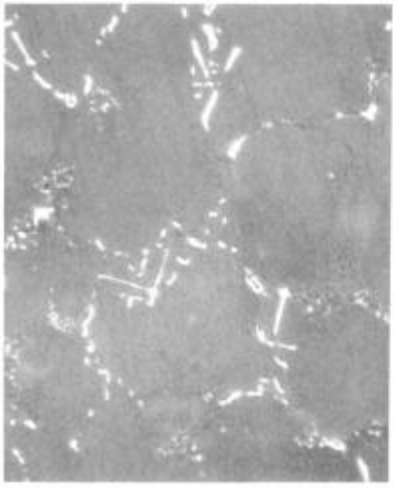

Figure 4a Base Alloy 300X
Script + Discrete MCs

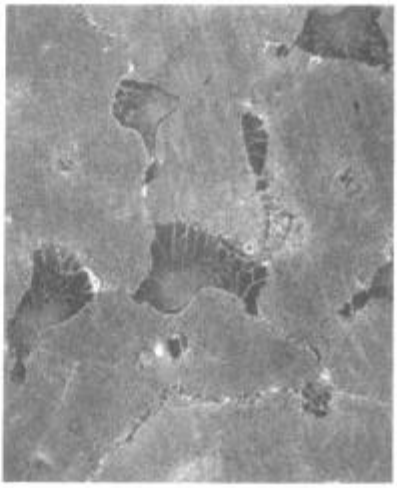

Figure 4b 12% W Sample 300X
Primary γ' Islands

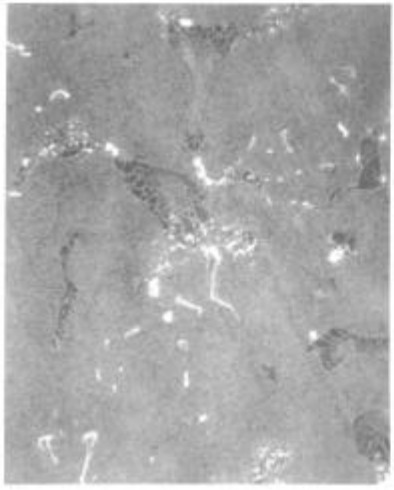

Figure 5 4% W Sample 300X
Blocky Type Carbides

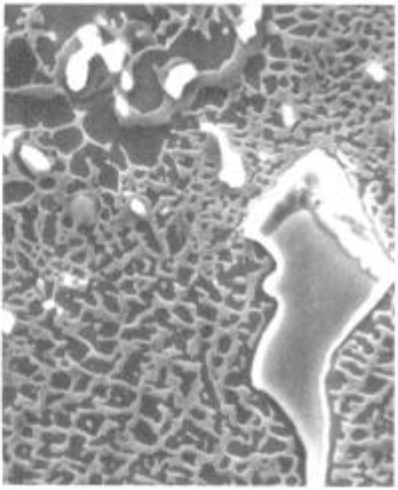

Figure 6a 4% Sample 300X
Arrow Shape MC + Discrete MC-3

Figure 6b 4% W Sample 3000X
Duplex Shape MC

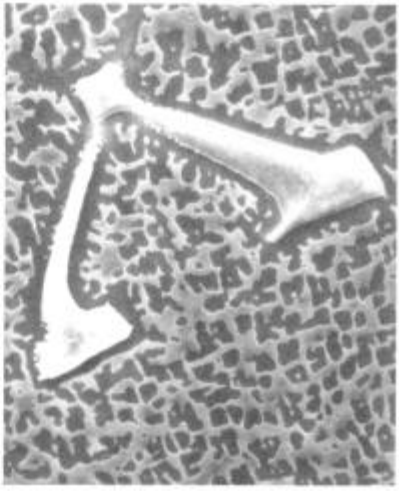

Figure 7a Base Alloy 2000X
MC-1 Breakdown after 1080°C/4 hr.

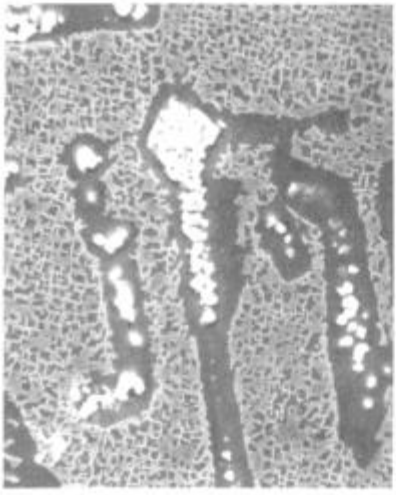

Figure 7b Base Alloy 2000X
MC-1 Breakdown after 1218°C/4 hr.

Figure 8a 12% W Sample 1000X
MC-1 Breakdown + αW Plates +
Discrete MC-3 after 1219°C/4 hr.

The MCs in all the samples are fairly stable and show little breakdown after the 1080°C treatment; however, the 1218°C high temperature treatment produces drastic breakdown of primary MC carbides, especially the Ti+Ta rich MC-1 carbide. In many cases the breakdown is so complete that only islands of γ' remain where the carbide was previously. Figures 7a and 7b show the effects of the 1080°C versus the 1218°C treatments on the MC-1 carbides in the base sample A. The 12% W sample not only experienced primary carbide breakdown, but also formed large amounts of αW in the breakdown area. Figure 8a shows the broken-down MC-1 carbide, the precipitated αW plates, and the small discrete MC-3 carbides in the primary γ' islands. Figure 8b shows the typical shape of the extracted broken-down arrowhead type MC, while Figure 8c shows an extracted plate of αW.

Further exposure of the samples at 982°C for 100 hours after 1080°C and/or 1218°C produced only a Mu phase in the 12% W sample which had the 1080°C treatment. Figure 9 shows the arrays of Mu phase plates in the 12% W sample. The αW found at 1218°C was still present after the 982°C exposure.

The 12% W sample containing the Mu phase which formed at 982°C was reheated at 1218°C for four hours and re-examined. The Widmanstatten pattern originally showing the Mu phase was still present but the precipitate in the pattern had reverted to discrete or globular αW, Figure 10.

After further exposure for 100 hours at 982°C, no additional Mu phase precipitated, probably due to the reduction of W by the αW formation.

Thus, it appears that the temperature of thermal exposure during airfoil production processing will have a definitive bearing on future microstructures. It appeared that all hafnium-bearing alloys will demonstrate the progressive transition of carbides from largely MC-1 (as cast) to largely MC-2 and/or MC-3 with increasing quantitative content of the higher parameter carbides. These carbides presumably are very stable both thermodynamically and with relation to their surrounding matrix and must be considered as permanent.

In those alloys prone to plate formation of whatever type, i.e. generally those above the 1:1 atomic substitution line, the thermal exposure largely determines whether M_6C forms at the 1095°C/50 hour range or Mu phase at temperatures in excess of 1205°C. A special case exists for tungsten contents near 12% where Mu forms at the lower 1080°C-1095°C temperature range and α tungsten at the higher temperatures.

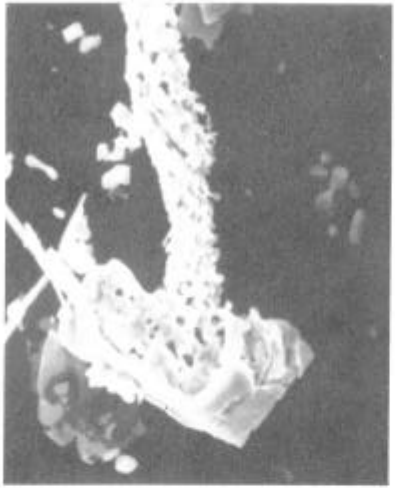

Figure 8b 12% W Sample 3000X
Extracted Arrow Shape MC-1
after 1218°C/4 hr.

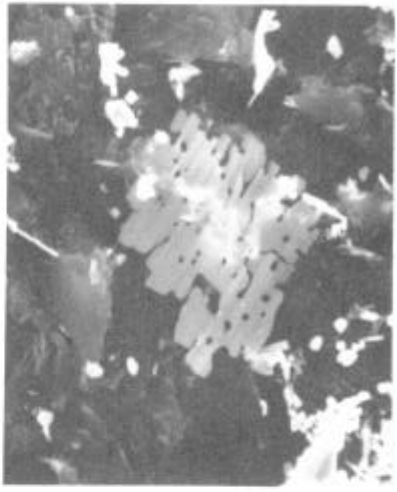

Figure 8c 12% W Sample 2000X
Extracted αW Plate after 1218°C/4hr

Figure 9 12% W Sample 300X
Widmanstatten Mu Phase
after 1080°C/4 hr. + 982°C/100 hr.

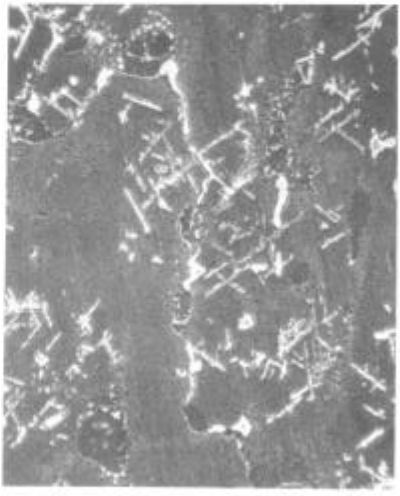

Figure 10 12% W Sample 300X
Widmanstatten αW Pattern
after Mu Phase + 1218°C/4 hr.

CONCLUSIONS

All the following conclusions apply only to the system studied:

1. Substitution of molybdenum by tungsten on a 1:1 atomic basis not only optimizes mechanical properties but also serves as a threshold for formation of plate-like (TCP) phases.

2. The above replacement results in an increase in blocky carbides and also larger and more primary γ' islands. Hafnium is found concentrated in the primary γ' islands.

3. Three MC carbides (MC-1, MC-2, and MC-3) with increasing lattice parameters are formed during soldification. The predominant low parameter MC-1 contains mostly titanium and tantalum while the highest parameter MC-3 contains mostly hafnium with some tantalum. Elevated thermal exposures accelerate the breakdown of the lower parameter carbides with increased formation of those of higher parameter, i.e. higher hafnium content, with the release of tantalum and titanium to the solid solution.

4. At temperatures of 1095°C or under, breakdown of primary MC carbides leads to precipitation of plate-like secondary M_6C carbides for tungsten contents up to about 11% and Mu phase precipitation at higher tungsten contents.

5. At temperatures of 1205°C or higher, the breakdown results in the formation of Mu phase up to about 11% tungsten and alpha tungsten precipitation at higher tungsten levels. This precipitation is determined by the change in the solid solubility of tungsten in the basic gamma solid solution due to the added Ta+Ti from the breakdown of primary MC carbides. Alpha tungsten reportedly can dissolve about 3-4% chromium but very little nickel or titanium (5).

6. For equi-axed castings of good quality, it is suggested that any elevated temperature exposure (above 1205°C) will accomplish little beneficial homogenization but will initiate the MC-1 to MC-3 permanent transition with possible drop in mechanical properties.

7. For D.S. castings, the initial heat treatment or HIP plus heat treatment can increase mechanical properties due to at least partial solution of large primary gamma prime particles and subsequent re-precipitation of optimized structures.

Additional treatments of this type will parallel the equi-axed findings, i.e. the possible reduction in mechanical properties.

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