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INTERNAL NITRIDING OF Mo-Hf ALLOYS

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INTERNAL NITRIDING OF Mo-Hf ALLOYS*

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ABSTRACT

This report summarizes the work of several experimenters at the Lawrence Radiation Laboratory who investigated the strengthening of a molybdenum-base alloy by internal nitriding. The material tested was a 0.050-in.-thick Mo-1 at.% Hf alloy, nitrided by the inward diffusion of nitrogen. The alloy was tested at 1100 to 1500°C for both short and long time mechanical properties; in addition the microstructure was examined extensively.

The high-temperature mechanical properties of the nitrided alloy were found to be greatly superior to the properties of commercial, thermomechanically processed alloys. The strength is due to the precipitated HfN, whose morphology is well suited for imparting strength through coherency strain. In general, the strength is improved by small precipitate size and close spacing. These properties can be controlled by a correct choice of Hf concentration, temperature of nitriding, and nitrogen pressure. The alloys described in this work were not optimized.

In addition to having excellent strength, the nitrided alloy was found to maintain this strength for long times at high temperatures. This is in contrast to carbide-strengthened commercial alloys. The stability is thought to be due to

the slow kinetics of the processes leading to coalescence of the precipitate. It should be possible to extend the lifetime of such alloys even further by operating them in a high pressure of nitrogen.

INTRODUCTION

Although metallurgists have traditionally emphasized the use of carbides for dispersion-strengthening bcc refractory alloys, there are situations where the nitrides may prove to be preferable. This is especially true for alloys whose primary constituents are metals such as Mo, W, and Re with unstable nitrides. For these metals, it is often possible to form the strengthening dispersed phase by direct precipitation from solution, with nitrogen as the precipitant. This technique, known as internal nitriding, is analogous to the more familiar and better-studied internal oxidation process.

It is surprising that internal nitriding has received so little attention. Mukherjee and Martin,¹ in their pioneering papers, found that molybdenum-based alloys strengthened with TiN or ZrN had very good high-temperature mechanical properties. Iden and Himmel² did a careful study of the internal nitriding process in W-Hf alloys and were able to demonstrate hardening that persisted for long times at extremely high temperatures. Their kinetic data showed that the nitrid-

*This work was performed under the auspices of the U. S. Atomic Energy Commission.

ing was predictable and reproducible, and that the process could be completely described by the diffusion-controlled model first proposed for internal oxidation by Wagner,³ and subsequently extended by Bohm and Kahlweit.⁴

More recently, Himmel and Mitchell,⁵ and Mitchell, Himmel and Kane⁶ have published their results on the properties of internally nitrified Mo-1 at.% Hf. This alloy was shown to have outstanding high-temperature, short-time tensile properties. These properties resulted from a very stable, finely divided dispersion of HfN, which was found to impart a large amount of coherency strain to the matrix lattice.

In the preparation of an internally nitrified alloy, the starting material consists of a matrix metal containing a small (usually 1 to 3 at.%) fraction of the nitride former in solution. Nitrogen is then diffused in by exposing the alloy to N_2 or NH_3 at a pressure and temperature sufficiently high so that the permeation of nitrogen results in complete precipitation of the nitride in a reasonable time. The nitriding thus proceeds by the diffusion-controlled advance of a nitriding front that remains essentially parallel to the external surface. At the nitriding front, the inward diffusion of the nitrogen and the outward diffusion of the Hf continuously provide concentrations in excess of those corresponding to the solubility product of HfN in the Mo matrix. A repeated nucleation accompanied by some growth of the HfN particle results. The growth occurs by Ostwald ripening during the time precipitation is occurring; as soon as precipitation is complete, the high nitrogen activity suppresses further growth. Thus the size—and spacing—of the particles depends upon the rate of advance of the nitriding front. In

principle, this process can be controlled to give a desired volume fraction of precipitate of a specified size.

While this simplified description gives a general picture of the internal nitriding process, there are several variables that influence the exact nature of the alloy obtained and certain conditions must be met for internal precipitation to take place. The following comments illustrate this point. For simplicity, Mo is assumed to be the matrix metal and HfN the precipitate.

- The technique is feasible only when the chemical stability of the solute metal nitride greatly exceeds that of the matrix metal nitride. This supports the choice of Hf, whose nitride is among the most stable. In contrast, Mo nitride is far less stable, thus, the nitriding process can be carried out at relatively high pressures of nitrogen without Mo nitrides forming.

- Suitable dispersions are obtained only when the rate of transport of nitrogen in the Mo matrix is much greater than that of Hf. If this is not true, a surface scale rather than a homogeneously distributed precipitate will result. The results of Mukherjee and Martin,¹ Iden and Himmel,² and Himmel and Mitchell⁵ have shown that the diffusivity of nitrogen is much greater than that of Hf in Mo, W, and W-Re alloys and that internal nitriding is observed for these matrix metals. Nitrogen permeates rapidly by an interstitial mechanism, whereas the Hf moves slowly by substitutional vacancy migration. In the temperature range covered by our Mo-HfN experiments, the diffusivity of nitrogen is approximately three orders of magnitude greater than that of Hf.

● The size and spacing of the dispersant particles increase with increasing depth from the surface (when nitrided at constant T and gas pressure), since both properties are a function of the rate of advance of the nitriding zone.* In practice, it may be possible to nitride thick specimens by varying conditions so that the rate of advance of the front, and, hence, particle size and spacing are constant throughout the specimen. There are, however, definite limits to the thickness that it is feasible to nitride.

● The strength of the alloy depends primarily on the concentration of the precipitate and on its particle size and spacing. As discussed in detail by Mitchell,⁷ the HfN structure is extremely well suited to impart maximum coherency strain to the Mo matrix; it is a highly effective strengthener.

The material in this report is based on work done at the Lawrence Radiation Laboratory during the period 1966-70. The contributions of several scientists are included

* The depth of the nitride precipitation front, ξ , increases as a parabolic function of time. Thus

$$\xi = 2\gamma (D_N t)^{1/2}$$

where γ is a constant and D_N is the diffusivity of nitrogen in Mo. The rate of advance of the nitriding front is given by

$$\frac{d\xi}{dt} = \gamma \left(\frac{D_N}{t} \right)^{1/2}$$

Thus at a given nitrogen pressure, the rate of advance of the nitriding front decreases with time or depth and increases with increasing temperature.

in abbreviated form; a more complete treatment of each aspect of the work is given in the references. The overall intent of the research was to develop a creep-resistant structural alloy that was compatible with a nitrogen environment, specifically for use in a UN-fueled, high-temperature nuclear reactor.⁸ An internally nitrided alloy of Mo was selected for study. The reactor project has been terminated and, unfortunately, no further research on these extraordinary alloys is being performed.

EXPERIMENTAL

All of the work reported in this paper used a Mo-1 at.% Hf alloy (1.83 wt% Hf). This material, fabricated to order by American Metal Climax Co.,* was prepared by vacuum arc casting, hot extruding, and rolling at ~1300°C to a final thickness of 0.055 in. Only the single Hf concentration was studied; no attempt was made to optimize this variable.

The material was supplied in two different work-hardened conditions. Sheet "A" received a final rolling reduction corresponding to 55% hot-cold work. Sheet "B" was given a 70% reduction in the final rolling. Both sheets were stress-relieved 1 hr in vacuum at 1230°C.

Nitriding Kinetics and General Observations

The nitriding experiments were all done on the 0.055-in. material. Tensile specimens with 1-in. gage

* Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

sections were machined from the sheet stock, ground and lapped to a thickness of 0.050 in., and diamond polished. These specimens, with several small coupons to be used for metallurgical examination, were then nitrided to completion under 1 atm N_2 for 290 hr at 1260°C, 186 hr at 1310°C, and 72 hr at 1410°C. These times were chosen on the basis of data from earlier studies which had established the nitriding kinetics.⁹ The process was found to obey the diffusion-controlled model described earlier.

The cross section of a specimen partially internally nitrided at 1360°C and 1 atm N_2 pressure for 4 hr is shown in Fig. 1. The nitriding front has advanced approximately 0.006 in. below the external surface during this exposure. The microhardness profile shows a substantial hardening of the alloy; the hardness decreases with increasing depth. At the nitriding front, the hardness falls abruptly to that of the solid solution.

In Fig. 2, a representative example is shown of the microstructure and microhardness profile of a 0.050-in.-thick sample (Sheet A) nitrided to completion at 1360°C. In addition, data are given for the same material nitrided at 1260°, 1310° and 1410°C. The HfN particle size, grain structure, and the microhardness show the expected variation with depth below the surface; the maximum hardness is observed ~0.003 in. below the surface. With increasing depth the hardness decreases, the particle size increases, and the grain structure shows an increasing degree of recovery of work hardening.

Comparisons of samples nitrided at different temperatures show that the lower nitriding temperatures produce smaller precipitates and less recovery of the work hardened structure. Thus,

it is not surprising that the lower nitriding temperatures resulted in higher average hardness.

All of these observations are in accord with the predictions of the diffusion-controlled model of Wagner.

Observations on Microstructure

Thin foils for transmission electron microscopy were spark machined from various depths in the specimen cross section. An extensive investigation of the microstructural aspects of this alloy was made by Mitchell.⁷ Only a few of the observations are reported here.

Figures 3 and 4 are transmission electron micrographs of the internal structure ~0.005 in. below the surface of a sample of Sheet A nitrided at 1310°C. These micrographs show matrix strain and displacement fringe contrast resulting from peripheral coherency at the small, plate-like HfN particles. The platelets are less than 20 Å thick, and 100 to 500 Å in diameter. These small precipitates, formed early in the nitriding process, have withstood a temperature of 1310°C for ~170 hr without significant coarsening or loss of coherency. Thus, as predicted, the high nitrogen activity in the alloy behind the nitriding front effectively inhibits dissociation and growth of the precipitates by Ostwald ripening.

Short-Time Tensile Tests

Short-time tensile measurements were made on the nitrided alloy at test temperatures from 1100 to 1500°C in vacuum ($<5 \times 10^{-6}$ Torr). The strain rate was 0.01/min. For comparison, tests were made under similar conditions on 0.060-in.-thick specimens of the commercial alloys TZM and TZC, supplied by American Metal Climax Co. These alloys were both of the standard

Fig. 1. Cross section of Mo-1 at.% Hf alloy partially internally nitrided at 1360°C, showing nitriding front and microhardness profile.

Fig. 2. Cross section, microstructure, and microhardness profiles of fully nitrated Mo-1 at.% Hf alloy.

composition and had been subjected to the standard thermomechanical processing.

Tensile stress-strain curves at 1100°C for the Mo-1 at.% Hf alloy in the recovered solid-solution condition and after internal nitriding at 1260°C are shown in Fig. 5. Data for TZM are also shown.

In Fig. 6, the ultimate tensile strengths are shown for TZM, TZC, and the nitrated Mo-1 at.% Hf alloy.

From the results of these tests, the following conclusions can be drawn.

- Remarkable strengthening effects are produced by internal nitriding. Nitriding in-

Fig. 3. Transmission micrograph showing strain contrast near coherent HfN precipitates at a depth of 0.005 in. after nitriding at 1310°C.

Fig. 4. Transmission micrograph showing displacement fringe contrast on HfN precipitates at a depth of 0.005 in. after nitriding at 1310°C.

Fig. 5. Tensile stress-strain curves for Mo-1 at.% Hf and TzM at 1100°C.

creased the 1100°C strength of the recovered Mo-1 at.% Hf from about 40 to 135 ksi.

- Some strengthening arises from the retention of strain hardening originally introduced during rolling. Sheet A specimens, which retained more of their cold work during nitriding, were stronger than specimens from Sheet B.
- Tensile strength of the alloy nitrided at 1260°C is approximately twice that of TzM at 1100°C; at 1500°C it is four times as great.
- Nitrided alloys are more stable at high temperatures than TzM. When TzM was annealed for 2 hr in vacuum at 1300°C, its strength at 1100°C decreased from 65 to 48 ksi. The nitrided alloys, already exposed to temperatures of ~1300°C for as long as 290 hr, showed virtually

Fig. 6. Ultimate tensile strength vs temperature for internally nitrided Mo-1 at.% Hf, TzM, and TzC.

no loss of strength under the same conditions.

- Lower nitriding temperatures produce higher tensile strength. This behavior is in accord with the increase in hardness seen at lower nitriding temperatures.
- Variation in precipitate size and microhardness over the cross section of the internally nitrided specimens indicates that the tensile properties would be even greater if precipitate size and spacing were constant throughout. This could be done by holding the rate of advance of the nitriding front constant by varying either temperature or nitrogen pressure, or both.
- Even higher strength can be achieved in thinner sections where the average rate of advance of the nitriding front is faster and, hence, the particle size is smaller. A 0.018-in.-thick specimen nitrided for 24 hr at 1260°C showed remarkably greater strength. (See point Ⓞ, Fig. 6.)

Creep Tests

Creep measurements were made to observe the long-time, high-temperature performance of the alloy and to measure the effect of an external pressure of nitrogen on the stability of the precipitate.

The samples tested had been nitrided for 290 hr at 1260°C, and had been shown to be the strongest in short-time tests. The creep measurements were made in an all-tungsten, deadweight loaded creep machine that could be operated in nitrogen at 1 atm or vacuum (<10⁻⁶ Torr). The gage length of the creep specimen was measured at appropriate intervals with a precision cathetometer.

Two specimens of the nitrided Hf-Mo alloy were tested at 31.5 ksi

stress and 1250°C. One was tested in vacuum (<10⁻⁶ Torr); the other in 1 atm N₂. In addition, a specimen of TZM was measured at the same conditions in vacuum.

Unfortunately, the data on the sample tested in nitrogen were not available in time for this paper. The measured deformation vs temperature for TZM and the Mo-1 at.% Hf alloy is shown in Fig. 7. From the data, it is obvious that in vacuum the internally nitrided alloy is far superior to TZM. The properties in nitrogen can be expected to be even better.

DISCUSSION

All of the data obtained on the Mo-1 at.% Hf alloy show that the nitride dispersion-strengthened alloys are very strong and that the strength-giving structure persists for long times at high temperatures. The strength is derived from the superior ability of the dispersed phase to strengthen the matrix; the stability results from the great resistance of the particles toward coarsening.

In his paper on the microstructural aspects of this alloy, Mitchell⁷ has described the properties of HfN

Fig. 7. Creep of internally nitrided Mo-1 at.% Hf and TZM in vacuum at 1250°C.

that make it so well suited for strengthening Mo. As a complement to Mitchells' work, the emphasis of this paper is on what are believed to be the reasons for the extraordinary high-temperature stability of the nitride dispersion toward coalescence.

The data show that, in contrast with the behavior of the nitrided alloy, TZM does not maintain its strength for long times at high temperatures. The creep-resistant properties of TZM are thought to be derived from the presence of a fine dispersion of ZrC and TiC, both thermodynamically more stable than the carbide of Mo. It is instructive to speculate as to why the strength of this alloy is lost so rapidly compared with the stability of the nitride strengthened alloy.

In general, a precipitate consisting of a distribution of different particle sizes is not thermodynamically stable. In the approach to equilibrium, smaller particles coalesce into larger ones, hence the average size increases and so does the average spacing between particles. This process of growth of the precipitate by solution of smaller particles and growth of larger ones is usually termed "Ostwald ripening," and, of course, leads to degraded strength.

Although the precipitates observed in the nitrided alloy were all platelike, their behavior can be qualitatively represented by the simpler model in which spherical particles of differing radii coalesce. If one considers two particles of radii $r_1 > r_2$, separated by distance δx , the transport of matter between them will be governed by the equation,

$$J = -\bar{C}B \frac{\delta\mu}{\delta x},$$

where J is the matter flux, $\bar{C}$ and B the average concentration and

mobility of the diffusing species, respectively, and $\delta\mu$ the difference in chemical potential of the diffusing species in the vicinity of the two surfaces. The chemical activity at the surface of the smaller particle is greater than the activity at the surface of the larger particle by a factor related to the ratio of the two radii. For this reason there will always be a gradient in the chemical potential between particles of differing size. This gradient is the driving force for coalescence, and it cannot be eliminated in a population of differing radii.

It should be noted, however, that if the average concentration of the diffusing species is reduced, there is a corresponding reduction in the interparticle flux. If an alloy is intended for use at high temperatures for long times, the concentration of the diffusing species that bring about coarsening of the dispersion should be made as low as possible.

The process by which a small particle of a binary compound, such as TiC or HfN, can coalesce onto a larger particle is likely first, dissociation into atoms, second, a random walk process that eventually leads the atoms to the surface of lower chemical potential, and finally, recombination on the surface of the larger particle. It has been assumed in this discussion that the rate limiting process is the transport step, i.e., the diffusion of the atoms through the matrix. Both N and C are known to diffuse interstitially in bcc metals, and therefore it seems reasonable that the rate determining step in the coalescence process is the substitutional diffusion of Hf (or Ti or Zr) in Mo.

If this model is correct, to minimize the coalescence flux between particles one should mini-

mize the concentration (or more correctly the chemical activity) of the metallic constituent of the precipitate, i.e., Ti, Zr, or Hf. This point is usually ignored in thermomechanically prepared commercial alloys, where there often is an excess of the metallic constituent of the precipitate. Thus, in TZM and TZC there is greater than 0.5 at.% unreacted Ti and Zr that remains dissolved in the Mo lattice. Their presence in such relatively high concentrations may be a reason that these alloys rapidly lose their strength at high temperatures.

In contrast, the internally nitrided alloys inherently possess a very low activity of the metallic constituent of the precipitate. After passage of the nitriding front, nitrogen is always in excess. Because HfN is so stable, this high activity of nitrogen leads to a correspondingly low concentration of Hf.

If the alloy is used at high temperature in a vacuum, or an atmosphere containing no nitrogen, loss of nitrogen can lead to a lowered stability of the dispersion. The nitrogen will volatilize and, as a result, the HfN will dissociate and the Hf activity will rise, leading to solution of the precipitate as well as coalescence.

It should be possible to suppress the rate of coalescence transport even further than that of the as-nitrided alloy. It was previously pointed out by Kane¹⁰ that by increasing the nitrogen pressure in which the alloy operates, the activity of the Hf will be reduced according to the mass action law. This is analogous to "salting out" a precipitate by adding an excess of a common ion.

If the model assumed for the coalescence process is valid, the dispersion will be most stable

against coarsening when the alloy is operated in the highest possible pressure of nitrogen that can be tolerated without forming the Mo₂N phase.

It is not meant to imply that these kinetic processes are the only ones that make HfN so stable toward coarsening. But, it seems most reasonable that coarsening must be slowed as the Hf activity is reduced.

The internally nitrided Hf-Mo alloys are thus seen to have advantages in two respects: (1) the structure, morphology, and chemical stability of HfN are especially well suited for maximum strengthening, and (2) these alloys are inherently very stable toward coalescence, which brings about an inevitable loss of strength.

FURTHER IMPROVEMENTS

It is important to realize that the properties of the alloys described in this work were in no sense optimized for maximum strength. The two variables that could be expected to most affect the strength are the concentration of HfN and the size of the precipitated particles. Because our experiments were limited to the one batch of Mo-Hf, the HfN concentration was constant in all specimens. Also, we did not try to control the particle size.

There is another, more important variable that was not controlled in our work: the variation in precipitate size across the thickness of the specimen. As previously mentioned, the particle size is controlled by the rate of advance of the precipitation front. After this front has passed, further growth is negligible during our times of nitriding. In our work, the temperature and nitrogen pressure were held constant during nitriding and,

thus, the rate of advance decreased parabolically with time as nitriding proceeded toward the center of the specimen. It was found that the precipitate diameter increased ~100 fold over a 25-mil depth of penetration. The hardness, and almost certainly the strength, are, therefore, quite different at different depths in the material.

Mitchell⁷ also found that if the precipitate size was too small, there was a subsequent rapid coalescence to very large, serricoherent particles, accompanied by a dramatic decrease in hardness. He showed that the coarsening took place when the alloy contained a high density of extremely small, fully coherent particles. The very large amount of matrix strain energy caused the grain boundaries to migrate, sweeping up the small particles, the components of which feed large, semicoherent particles growing behind the moving boundary. It seems that either very large or very small precipitates can lead to decreased strength. Very fine precipitates lead to superior short-time strength but may have short high-temperature lifetime. Larger particles may result in lower strength, but have a greater stability toward coalescence. The alloy must, therefore, be optimized to give the best combination of strength and lifetime for the intended application.

Within limits, the dispersion size can be controlled by varying the nitrogen pressure and the temperature during the nitriding process. One could choose the rate of advance of the precipitation front to give an optimum precipitate size, and then keep the rate of advance and, hence, the particle size constant across the thickness of the specimen by increasing the nitrogen pressure as nitriding progressed. In practice, thick

parts might require pressures of nitrogen so high that Mo nitrides would form. Increasing the temperature increases the rate of advance of the nitriding front, but it also results in an even more rapid increase in precipitate size, since the activation energy for Hf diffusion in Mo is larger than that for N. It is the diffusion of Hf that controls the precipitate size.

Mitchell et al.,⁶ showed that by using a thin (0.018 in.) specimen and by increasing the nitrogen pressure in steps as the nitriding front advanced, he was able to obtain a much more uniform particle size throughout the cross section of his specimen. He started the nitriding process at 50 Torr, increasing to 760 Torr in 24 hr. The low starting pressure prevented the subsurface coarsening due to the very small precipitates, and the thin specimen allowed a fairly rapid advance of the nitriding front even at the center of the specimen.

The results of this experiment are shown in Fig. 8; the micrograph is taken at the center, i.e., 0.009 in. from the surface. As shown in Fig. 6, this sample had the highest strength of any tested. Similar strengthening could have been achieved in a 0.050-in. specimen, but Mitchells' furnace was limited to 1 atm N₂ pressure. It is quite likely that the "engineering" properties of the alloy can be greatly improved over those attained in our sharply limited exploration.

TECHNOLOGICAL APPLICATIONS

It is quite probable that the inherent limitations of the internal nitriding process will restrict its use to relatively thin structural members. Even with this limitation, it still should be useful for many engineering applications. For many specimens, it may be necessary to

Fig. 8. Transmission electron micrograph of precipitates and substructure at the center of 0.018-in.-thick specimen after nitriding at 1260°C.

go to two-phase vapor deposition processes, as developed by Landingham.¹¹⁻¹³ Although the vapor deposition process is more complex than internal nitriding, there is, in principle, no limitation to the thickness that can be achieved.

There are several technological problem areas where the unique features of the internal nitriding process might be advantageous.

- It could alleviate the joining problem, which plagues most applications of precipitation strengthened alloys that require fusion welding. The entire mechanism or assembly could be fusion welded prior to nitriding and subsequently the whole structure, including welds, uniformly strengthened.
- It may be possible to achieve some room temperature toughness in the part by nitriding only a "case," leaving a weaker but tougher core.
- It should be possible to extend the time-temperature lifetime by operating the stressed part in an environment of high nitrogen activities. For example, the material could be used on turbine elements in either Brayton or Rankine conversion cycles, provided the remainder of the system could be designed to be nitrogen tolerant.

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