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August 19, 1970

DISPERSION HARDENING OF A Mo-1 at.% Hf ALLOY
BY INTERNAL NITRIDING[*]

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Introduction

Several years ago, Mukherjee and Martin (1) established that dilute Mo-base alloys containing Ti or Zr in solid solution could be internally nitrided and that the resulting nitride dispersions significantly enhance the high temperature strength of molybdenum. It has since been demonstrated that W-Hf alloys also can be hardened appreciably by internal nitriding even when the nitriding is performed at temperatures as high as 2000°C (2). Ryan and Martin (3) recently used the nitrides and carbides of Group IVa elements to precipitation-harden Mo by conventional quench-aging procedures. They showed that the nitrides of Ti, Zr, and Hf all precipitate initially as coherent plate-like particles on {100} habit planes of the Mo matrix. Consistent with the greater thermodynamic stability of HfN compared to ZrN or TiN, they also found that the greatest hardening increments and most uniform particle distributions were obtained with the Mo-Hf-N system.

These results suggested that HfN dispersions produced in Mo by internal nitriding might give rise to some truly outstanding hardening effects. The present study of the structure and high temperature mechanical behavior of an internally nitrided Mo-1 at.% Hf alloy was undertaken to explore this possibility. As will be seen, the strength levels we achieved, though by no means optimum, are far superior to those of the best commercial high strength Mo-base alloys, i.e., TZM and TZC.

Experimental Procedure

The Mo-1 at.% Hf alloy (1.83 vt.%) was vacuum arc-cast, hot extruded, and rolled at about 1200°C to a final thickness of 0.055 in. This material was supplied by the Climax Molybdenum Co. 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 pass. Both sheets were stress-relieved for 1 hr in vacuum at 1230°C. For comparison, tests were also carried out on Mo-TZM and Mo-TZC, supplied by Climax as 0.060-in. thick sheets stress-relieved 1 hr in vacuum at 1100°C. These materials were both of standard composition; both were subjected to standard thermomechanical processing.

Tensile specimens with 1-in. gauge sections were machined from the sheets, ground and lapped to a thickness of 0.050 in., and diamond polished. To prevent excessive re-crystallization during nitriding, the Mo-Hf specimens were arbitrarily given an additional 2-hr recovery anneal in vacuum (<10⁻⁷ torr) at 1325°C prior to nitriding. The specimens were then nitrided to completion under 1 atm N_2 at 1260°, 1310°, and 1410°C, the required times having been established during preliminary studies of the diffusion-controlled nitriding kinetics. Several small test coupons were nitrided with the tensile specimens; these were used for metallographic examination, microhardness measurements, and electron microscopy. Tensile tests were carried out on all specimens at temperatures from 1100° to 1500°C in a vacuum to <5 × 10⁻⁵ torr at a strain rate of 0.01/min.

Results and Discussion

High-Temperature Tensile Properties. The 0.2% offset yield strengths and ultimate tensile strengths of nitrided alloys at elevated temperatures are shown in Fig. 1, with corresponding data for TZM and TZC. The main conclusions from the results are these:

● Some remarkable strengthening effects are produced by internal nitriding, the strength generally increasing with lower nitriding temperatures. For example, the tensile strength of the recovered Mo-1 at.% Hf solid solution alloy is increased from about 40 to 134 kpsi by nitriding for 286 hr at 1260°C.

● Although this strengthening is largely due to the presence of dispersed HfN particles, some strengthening also arises from retention of the strain hardening originally introduced during rolling. Thus, the differences in strength between nitrided specimens of Sheet A and Sheet B can be attributed to the fact that less recovery of the cold-work structure occurs during nitriding of Sheet A than Sheet B.

● The tensile strength of Mo-1 at.% Hf nitrided at 1260°C is approximately twice that of TZM at 1100°C and six times as great at 1500°C. The strengths produced by nitriding also compare favorable with those recently obtained with Mo-Hf-C alloys by optimum thermomechanical processing treatments (4).

● The longterm structural stability of the nitrided alloys at high temperatures also is vastly superior to that of TZM. When TZM is annealed for 2 hr in vacuum at 1300°C, its yield strength at 1100°C decreases from 58 to 42 kpsi; the nitrided alloys, having already been exposed to temperatures ~1300°C for as long as 280 hr, exhibit virtually no loss in strength under these same conditions.

● Even higher strength levels can be achieved in thinner sections. A specimen 0.015 in. thick, nitrided for 14 hr at 1260°C, exhibited a tensile strength at 1370°C of 128 kpsi, compared to 93 kpsi for a 0.050-in. specimen nitrided at the same temperature.
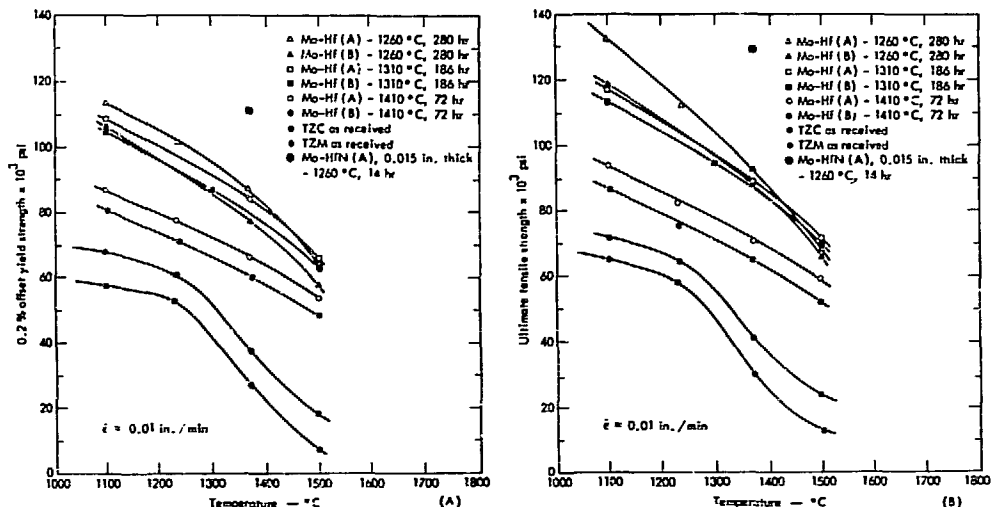

FIG. 1
Elevated temperature strength properties of internally nitrided Mo-Hf, TZM, and TZC:
(A) 0.2% offset yield strength; (B) ultimate tensile strength.

Microstructure and Precipitate Morphology. As shown in Fig. 2, significant varia-
tions exist in the grain and substructure, HfN particle size and morphology, and micro-
hardness over the cross sections of the completely nitrided sheet specimens. In general,
a uniform particle distribution is seen across the entire section but, as expected, the
average particle size increases rapidly with increasing depth. The increase in particle
size correlates, at least qualitatively, with the observed decrease in microhardness.
Smaller particles are produced at a given depth as the nitriding temperature is reduced,
thus accounting for the progressive increase in strength when the nitriding temperature is
lowered from 1410° to 1260°C. Because of an unusual softening reaction at the surface
(described more fully below), maximum hardness is not observed at the surface of the sheet
but at a depth of 0.002 to 0.004 in., depending on the nitriding temperature.
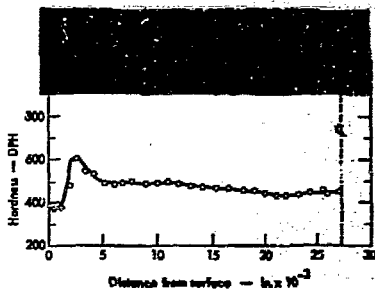

FIG. 2

Variation in microstructure and
hardness across a section of Mo-1
at.% Hf alloy 0.050 in. thick, ni-
trided to completion at 1360°C in
1 atm N_2.

The variation in substructure across the thickness of the nitrided specimens is the
result of two competing factors: the rate of dislocation annealing, and the rate of
advance of the nitriding front. Once the HfN particles are nucleated behind the front,
they effectively lock in (stabilize) the existing substructure; however, recovery can and
does occur ahead of the advancing front. Thus, dislocation annealing becomes progressively
more extensive at greater depths as well as higher nitriding temperatures. Since the
driving force for recovery (and recrystallization) is greater for Sheet B (70% hot-cold
work) than for Sheet A (55% hot-cold work), recovery and recrystallization proceed rela-
tively more rapidly in Sheet B under all nitriding conditions. The resulting differences
in substructure are reflected in the mechanical behavior, as previously noted.

At all nitriding temperatures, the HfN particles precipitate homogeneously in the
form of disc-shaped platelets on {001} planes of the Mo matrix, confirming the observations
of Ryan and Martin (3). Transmission electron micrographs of the precipitate structure at
depths of 5, 15, and 25 mils in a specimen nitrided for 186 hr at 1310°C are shown in
Figs. 3A-C. At a depth of 5 mils, the HfN particles are about 200 Å in diam, 10 Å thick,
and fully coherent. The displacement fringe contrast arising from the peripheral coherency
strain associated with these particles is clearly evident in Fig. 3A. This region is also
characterized by narrow precipitate-denuded zones adjacent to grain and subgrain boundaries;
the boundaries themselves contain a relatively high density of particles. It should be noted
that the HfN particles in Fig. 3A were nucleated within the first 10 hr of nitriding, yet,
despite having been held at 1310°C for an additional 175 hr, they remain small and fully co-
herent. By contrast, the particles formed last, in the center of the sheet, are at least an

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order of magnitude larger (Fig. 3C). This indicates that the particles grow at a rapid rate only in the presence of macroscopic concentration gradients which exist at the advancing nitriding front, their size being determined by the time available for diffusion during passage of the front. After the front moves through a given region, particle coarsening behind the front by Ostwald ripening takes place at a much reduced rate.
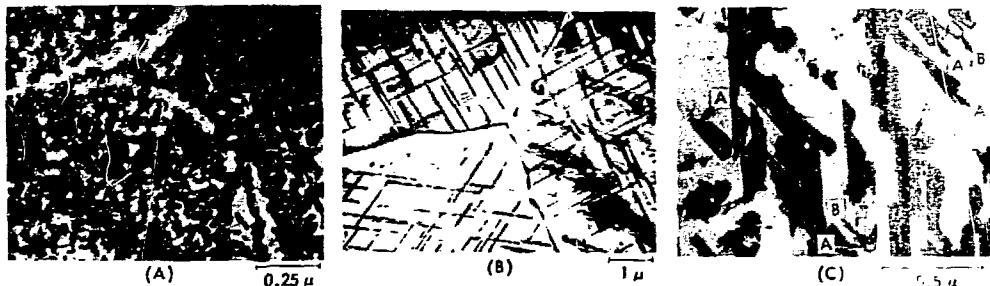

FIG. 3

Precipitate morphology at various depths in a Mo-1 at.% Hf alloy nitrided for 160 hr at 1310°C: (A) fully coherent HfN particles at depth of 0.005 in.; (B) 0.015 in. below surface; (C) 0.025 in. below surface.

The relatively large nitride particles shown in Figs. 3B and 3C were formed at greater depths, where the nitriding front advances more slowly. Analysis of the diffraction patterns from such precipitates, together with dark field experiments, yields the precipitate-matrix orientation relationship shown in Fig. 4, which is identical to that inferred by Ryan and Martin (3). The lattice mismatch between the fully coherent precipitate and the matrix gives rise to a large positive misfit normal to the habit plane of the nitride plates and to a small positive misfit in this plane. Although these particles have grown to a diameter of roughly 5000 Å, coherency is maintained across the large faces of the plates. Thickening has also occurred but to a relatively lesser extent. It appears that thickening proceeds by the nucleation and propagation of small climb ledges along the planar surfaces of the particles; these ledges appear as extrinsic dislocation loops on the particles (A in Fig. 3B). The increased peripheral compressive strain resulting from the thickening process is partially relaxed through the formation and growth of intrinsic edge dislocation loops within the particles (B in Fig. 3B) via coalescence of vacancies. Since the peripheral coherency strain around the particles is mainly responsible for the observed hardening and a substantial degree of peripheral coherency is maintained during growth, even the larger particles contribute to strengthening.

The structure seen near the external surface of one of the nitrided specimens is shown in Fig. 5. The softening reaction occurring in this region obviously leads to the development of extremely large HfN particles. Apparently, some time after passage of the nitriding front, certain grain boundaries at or near the surface begin to migrate into the interior, sweeping up or absorbing the small coherent precipitates, the component of which then feed the large semicoherent particles growing behind the moving boundary. The reduction in the matrix strain energy associated with the small fully-coherent particles provides the driving force for this reaction, which also occurs even in specimens that have been completely recrystallized prior to nitriding. This explains why softening extends to increasingly greater depths as the nitriding temperatures are lowered.
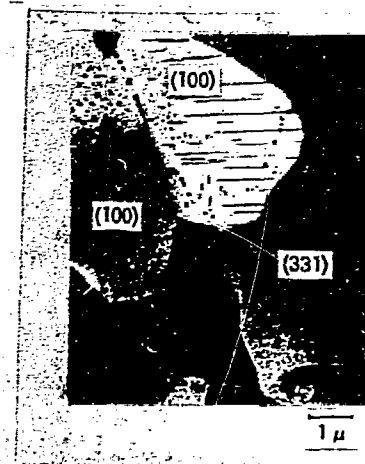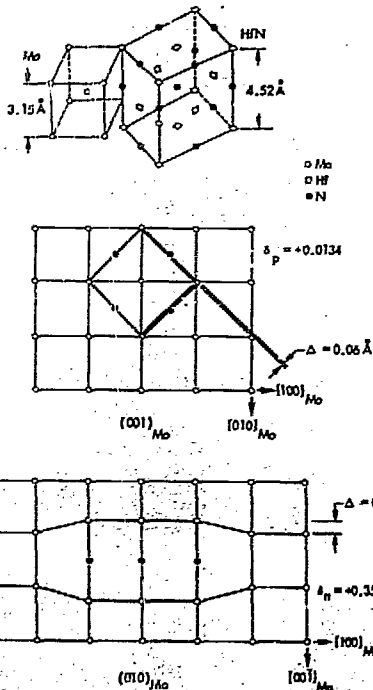
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FIG. 4
Orientation relationship between HfN precipitates and Mo matrix.

FIG. 5
Particle coarsening near the external surface of a nitrided Mo-1 at.% Hf specimen.

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