HYDROGEN EMBRITTLEMENT OF MOLYBDENUM

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The effect of hydrogen (present as an interstitial solute or as a gas atmosphere) on the mechanical properties of a wide variety of metals has been extensively investigated. In the b.c.c. metals such as the Group Va (Nb, Ta, V) or the ferrous base alloys, or the f.c.c. nickel base alloys, or the h.c.p. alloys based on Ti or Zr, the deleterious effects of hydrogen on the fracture behavior have been amply documented. The Group VIA b.c.c. alloys (based on Mo or W) have generally been considered to be unaffected by hydrogen. These latter systems have no stable hydrides, a very low hydrogen solubility and a positive heat of solution in equilibrium with the gas phase (1).

Increases in the yield strength and the development of a yield point in Mo after quenching in a hydrogen atmosphere have been reported, but significant embrittlement was not observed (2). While the effects observed were ascribed to interaction of quenched-in hydrogen with dislocations, it is equally likely that they were caused by the quenching of N impurities and the subsequent precipitation of a nitride (3). In view of the interest in using refractory metals, the question of hydrogen effects on the Group VIA metals requires further investigation. Studies of hydrogen embrittlement in the Group Va metals (4) have shown that the hydrogen related fracture requires (a) that hydrogen have sufficient mobility to move to stress concentrations such as crack tips, (b) that a hydride be induced by the stress at the crack tip, and (c) that the hydride be a brittle phase which undergoes cleavage. The existence of a hydride has not been established in the Mo-H system. In addition the hydrogen mobility in Mo
is significantly less than in the Group Va metals (5). Nonetheless it will be seen that significant hydrogen embrittlement of Mo does occur.

Tension tests were carried out at 297°K on fine grained polycrystalline Mo sheet specimens having gauge dimensions of 15 x 3 x 0.5 mm. The specimens were prepared from Climax Molybdenum sheet which was given a recrystallization and carburization anneal for one hour at 1800°C in a vacuum of 10⁻⁶ torr. The furnace had been previously carburized and under these conditions about 450 ppm (atomic) of C were introduced. The grain size was about 35 microns. The introduction of carbon results in intergranular carbide films and intragranular carbides associated with high dislocation densities (6). The presence of these carbides increases the room temperature ductility of the Mo sheet. Under these conditions the strain to failure was 10-15% uniform elongation. The fracture was transgranular in nature.

Specimens were tested under various environments and electrolytic charging conditions. Cathodic charging was carried out just prior to tension testing in a 0.1N H₂SO₄ solution at about 5 volts at 25°C for various periods of time. Quite significant variations in the amounts of hydrogen introduced in the specimens were noted on hydrogen analysis by vacuum extraction. The concentrations were in the range of 40-125 ppm (atomic) H. Cathodic charging was also carried out at about 300°C in a fused salt bath of KHSO₄ at 5 volts to attempt to obtain a more uniform distribution of hydrogen. Charging times of up to several days were used and resulted in hydrogen concentrations of 40-80 ppm (atomic).

The results of these tests are shown in Table I. The values shown for εₚ are generally the average of several repeated tests. Testing in a low pressure hydrogen atmosphere did not result in any significant reduction in εₚ. Cathodically charging prior to the tension tests, either in an aqueous or fused salt environment, also did not lead to any decrease in εₚ despite the fact that the specimens did contain significant amounts of hydrogen.

The lack of hydrogen embrittlement in pre-charged specimens may be associated with the limited mobility of hydrogen in molybdenum at room temperature. In order to be effective, the hydrogen must concentrate at the crack tip either by diffusion in the solid solution (4) or by entering the solid at the crack tip (7). The latter situation might be expected to occur on testing in a hydrogen gas atmosphere. The lack of embrittlement in 5 psi H₂ gas could result from insufficiently clean surfaces or impurities in the gas which "poison" the surface or to a hydrogen fugacity which is too low to cause embrittlement.
A significant decrease in $\epsilon_f$ was observed on testing during simultaneous cathodic charging (Table I). The specimen was made the cathode in a cell having a molybdenum anode and using 0.1M H$_2$SO$_4$ electrolyte. Using a cell voltage of 3 volts resulted in a large amount of hydrogen evolution at the cathode (specimen). The cathode potential relative to a calomel reference electrode was measured using a potentiostat. Under the cell conditions, the cathode potential relative to the standard hydrogen potential was -1.3 volts. The $\epsilon_f$ values were reduced to an average of 3.3% (Table I) by this cathodic charging during tension testing.

The cathodic polarization of the specimen should be sufficient to prevent dissolution and stress corrosion of the molybdenum (8). In the acid solution, dissolution is not expected at cathodic potentials below about -0.3 volts (8). The magnitude of the cathode potential used in the present experiments is large enough to be expected to maintain even the bottom of a crack (9) at a potential sufficient to evolve hydrogen. As a further check, tests were carried out in the 0.1M H$_2$SO$_4$ without any cathodic polarization and no embrittlement was observed (Table I). The embrittlement therefore requires hydrogen evolution.

Under conditions of simultaneous tension testing and cathodic charging, the hydrogen is present at high fugacity at the tip of a crack or other stress concentrations. Thus hydrogen entry into the lattice in relatively high concentrations is possible at the point where it is most effective in causing fracture, the crack tip. Under these conditions, significant hydrogen embrittlement of molybdenum occurs.

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References

6. A. Kumar, private communication (1975) to be published.

<table>
<thead>
<tr>
<th>Strain Rate (sec⁻¹)</th>
<th>Temperature (°C)</th>
<th>Condition</th>
<th>Strain to failure (εₚ) (%)</th>
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<td>10⁻⁴ torr Air</td>
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