Conf-740812--3

METALLOGRAPHIC STUDIES OF HYDROGEN-EMBRITTLED NICKEL

by

M. R. Louthan, Jr.

G. R. Caskey, Jr.

J. A. Donovan

For presentation at the Seventh Annual Technical Meeting of the International Metallographic Society, Gatlinburg, Tennessee, August 4-7, 1974.

This paper was prepared in connection with work under Contract No. AT(07-2)-1 with the U. S. Atomic Energy Commission. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a non-exclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Bay

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

METALLOGRAPHIC STUDIES OF HYDROGEN-EMBRITTLED NICKEL*

by

M. R. Louthan, Jr.

G. R. Caskey, Jr.

J. A. Donovan

E. I. du Pont de Nemours and Company
Savannah River Laboratory
Aiken, South Carolina 29801

ABSTRACT

The reduction in area at fracture and the fracture mode of polycrystalline Marz grade (99.995%) nickel are significantly affected by testing in 69-MPa gaseous hydrogen, even when specimens are prestrained to the limit of uniform elongation before hydrogen exposure. The combined tensile and metallographic observations indicate very rapid hydrogen absorption during plastic deformation. It is postulated that hydrogen is transported to internal boundaries by mobile dislocations thereby causing localized, high hydrogen concentrations. These observations are consistent with an embrittlement mechanism in which hydrogen promotes boundary decohesion, either by enhancing glide (shear) processes, lowering the binding energy, or changing constraint conditions at microcracks.

* This work was supported jointly by USAEC Contract No. AT(07-2)-1 and NASA Purchase Order W-12697.

INTRODUCTION

Hydrogen-induced reductions in the tensile ductility of polycrystalline nickel are well established.¹⁻⁴ The typical fracture mode changes from transgranular ductile rupture to intergranular decohesion in the presence of hydrogen. This change has been attributed to:

- o the transport of hydrogen to grain boundaries by mobile dislocations,³
- o the presence of hydrogen recombination poisons at grain boundaries,² and
- o the formation of an unstable nickel hydride.⁴

Regardless of the cause of the change, grain boundaries appear necessary for the embrittlement processes because single crystals are not embrittled by hydrogen exposures that cause extensive ductility losses in companion, polycrystalline samples.^{1,2} Furthermore, it has been shown that a dispersion of thorium (which is assumed to prevent hydrogen from being concentrated in grain boundaries) inhibits hydrogen embrittlement in polycrystalline

nickel.³ This result is consistent with the conclusion that hydrogen transport by mobile dislocations is involved in the embrittlement process.⁵

Hydrogen-dislocation interactions have been experimentally demonstrated by several techniques. Plastic deformation of samples precharged with tritium enhances tritium offgassing, as would be expected if tritium were bound to and moved with dislocations.⁶ Serrated yielding has also been observed in hydrogen-charged samples deformed in tension at low temperatures.⁷ Hydrogen-induced increases in the rate of work hardening have been reported even for single crystals, which were not embrittled by hydrogen absorption.¹ These experiments demonstrate the importance of the hydrogen-dislocation interaction in the plastic deformation processes in nickel. Recent studies of hydrogen transport in both annealed and cold-worked polycrystalline nickel demonstrate that plastic deformation affects hydrogen absorption and uptake.⁸ With these results in mind, a study of hydrogen embrittlement in samples undergoing simultaneous gas phase charging and plastic deformation was initiated.

EXPERIMENTAL

Smooth bar tensile specimens were machined from as-received, polycrystalline Marz grade (99.995%) nickel. The as-machined specimens were vacuum annealed for one hour at 1025°K and furnace cooled to room temperature.

Several of the specimens were subsequently charged with tritium to saturation by exposure to 30-MPa tritium gas at 473°K. These specimens were subsequently tested at room temperature in tension in an Instron tensile machine* at constant crosshead speeds (initially $\dot{\epsilon} \sim 10^{-2} \text{sec}^{-1}$) to demonstrate tritium-dislocation interactions. Tritium offgassing was monitored by techniques previously described.

Other specimens without prior exposure to hydrogen isotopes were strained to fracture in hydrogen or helium gas at pressures of 69 MPa. Several of these specimens were prestained in a helium environment before being fractured in hydrogen.

Specimen fracture surfaces were examined using an AMR-900 scanning electron microscope.

* Product of Instron Corporation, Canton, Mass.

RESULTS

The grain structure following the 1025°K anneal was, as expected, typical of relatively equiaxed large grain nickel (Figure 1). Plastic deformation distorted the grains and, if hydrogen was present during deformation, caused intergranular cracking (Figure 2). Plastic deformation also caused dislocation transport of hydrogen from the tritium-charged specimens. The stress strain curves for both control and tritium-charged specimens showed yielding, work hardening, necking, and, finally, fracture.

The tritium release rate as a function of strain is compared with the stress-strain curve in Figure 3. At strains up to yielding, the release rate decreased slightly as expected from diffusion-controlled off-gassing. At yielding, the tritium release rate increased and then passed through a maximum with additional strain. The release rate increased slightly when the specimen began to neck and continued to increase until fracture. Fracture was accompanied by a large burst of tritium due to the release of tritium that was accumulated in microvoids during deformation.

Similar results have been previously reported⁶ and ascribed to hydrogen transport by mobile dislocations. These earlier studies also showed that the temperature and strain rate effects on deformation-enhanced release are consistent with the dislocation-hydrogen interaction thesis.⁶ No embrittlement was noted in the tritium-charged specimens.

Fracture of uncharged specimens both in air and high-pressure helium occurred primarily by ductile rupture processes (Figure 4). As is typical of ductile (cup-cone) rupture of relatively pure metals, the failure apparently began internally by the initiation and coalescence of microvoids during necking to form new internal surfaces. This sequence reduces the specimen cross section; final fracture to form the cone surface is probably by shear. An extreme example of this shear is shown in Figure 5.

The stress-strain curves for uncharged specimens tested in high-pressure hydrogen were almost identical to those for specimens tested in helium or air (Figure 6); however, the fracture modes

and reduction in area to fracture are radically different (Figure 7).

Although the fracture path is not obviously intergranular, fracture apparently followed some form of boundary (e.g. twin boundaries).

This is in contrast to the obvious intergranular path reported

for specimens tested in air after exposure to low-pressure (~ 0.1

MPa) hydrogen and for specimens tested while being cathodically

charged.¹⁻² However, mechanical polishing to reveal the secondary

cracks remote from the main fracture surface indicated intergranular

crack initiation. The fine scale topography of the fracture

surface was similar to the areas of shear-type fracture seen on

the specimens tested in helium and thus may be indicative of large-

scale plastic deformation (Figure 8a). Alternatively, the fracture

features could represent delamination along grain and twin boundaries.

For convenience, this feature will be termed delamination throughout

the remainder of this paper. These observations suggest that

intergranular microcrack initiation accompanied plastic deformation

in hydrogen and that delamination was promoted by the accumulation

of hydrogen in the microcracks. Slip lines on the fracture surfaces support the hypothesis that plastic deformation accompanied final fracture (Figure 8b).

The fracture surfaces of specimens prestrained to necking in helium and then fractured in hydrogen were similar to those of specimens strained only in hydrogen (Figure 9a). The major difference between the hydrogen and helium-hydrogen fractures was the numerous microvoid-like sites where delamination apparently initiated (Figure 9b). This observation suggests that during the final stages of deformation hydrogen is rapidly transported, either by mobile dislocations or short circuit diffusion, to microvoids, which were formed during deformation in helium. The final fracture was then promoted by the accumulation of hydrogen in the microvoids.

DISCUSSION

Interpretation of the fracture features of these hydrogen-embrittled nickel specimens in terms of most of the proposed embrittlement mechanisms is difficult. The observation of

delamination across the entire fracture surface in helium-hydrogen test specimens required that hydrogen accumulation precede final fracture. The result is interpreted as support for the hypothesis that hydrogen transport by mobile dislocations is involved in the embrittlement process.⁵ Although dislocation cell structure has been shown to provide a short-circuit path for hydrogen in nickel,⁸ the <10-fold higher permeability along such paths could not account for hydrogen transport across the entire surface.

Recent studies have shown that hydrogen reduces the friction stress in iron⁹ and thus increases the ability of dislocations to move through the lattice. This result is support for the hypothesis that hydrogen-assisted cracking occurs because "the presence of sufficiently concentrated hydrogen dissolved in the lattice just ahead of the crack tip aids whatever deformation process the lattice will allow."¹⁰

If the role of hydrogen in embrittlement is assumed to promote dislocation motion, the delaminated surfaces could be explained by large-scale shear (probably along boundaries) producing the

topographic similarities to shear portion of the helium fracture.

However, formation, fracture, and decomposition of a nickel hydride could also produce the delaminated fracture, although the existence of such a process is rather difficult to prove because of the disappearance of the brittle phase. The pressure theory of embrittlement could also explain the fracture features if the high hydrogen pressures generated by dislocation pumping changed the constraint conditions at the microvoid (or microcracks) and thereby changed the fracture modes. Finally, if hydrogen in solution lowered the energy required to cause decohesion in regions of high hydrogen concentration (created by hydrogen motion with dislocations), the observed fracture features could be developed.

In summary, plastic deformation of pure nickel in high-pressure hydrogen causes significant changes in the rupture processes. The fact that the fracture mode under these conditions differs from the mode typically reported for hydrogen embrittlement of cathodically

charged or gas-phase precharged nickel indicates that several embrittlement processes may be operative. Experiments designed to elucidate the fractographic observations and the embrittlement processes are in progress at Savannah River Laboratory.

REFERENCES

1. B. A. Wilcox and G. C. Smith, *Acta Met.* 13, 331 (1965).
2. R. M. Latanision and H. Oppenheimer, Jr., *Met. Trans.* 5, 483 (1974).
3. A. W. Thompson and B. A. Wilcox, *Scripta Met.* 6, 689 (1972).
4. G. C. Smith, "Effect of Hydrogen on Nickel and Nickel-Base Superalloys," paper presented at *Hydrogen in Metals - Effects on Properties, Selection and Design*. Seven Springs, Pennsylvania, September 1973.
5. M. R. Louthan, Jr., G. R. Caskey, Jr., J. A. Donovan and D. E. Rawl, Jr., *Mater. Sci. Eng.* 10, 357 (1972).
6. J. A. Donovan, "Accelerated Evolution of Hydrogen from Metals During Plastic Deformation," paper presented at Spring Meeting of the AIME, Philadelphia, Pennsylvania, May 1973.

7. J. S. Blakemore, *Met. Trans.* 1, 145 (1970).
8. M. R. Louthan, Jr., J. A. Donovan and G. R. Caskey, Jr.,
"Hydrogen Diffusion and Trapping in Nickel," to be published.
9. I. M. Bernstein, *Scripta Met.* 8, 343 (1974).
10. C. D. Beacher, *Met. Trans.* 3, 437 (1972).

Figure 1. Grain Structure of Annealed Samples

Figure 2. Grain Structure Near Fracture of Specimen Tested in 69-MPa Hydrogen. Note intergranular cracks at arrows.

Figure 3. Comparison of Tritium Release Rate with Stress-Strain Curve

Figure 4. Fracture Tip of Specimen Ruptured in High-Pressure Helium

Figure 5. Fine-Scale Topography of Shear Fracture in 69-MPa Helium

Figure 6. Stress-Strain Curves for Unchanged Specimens Tested in 69-MPa Hydrogen and 0.1-MPa Air

Figure 7. Fracture Tip of Specimen Failed in 69-MPa Hydrogen

a. Delamination

b. Apparent slip lines on fracture surface

Figure 8. Fine-Scale Topography of Fracture Surface Formed in 69-MPa Hydrogen

a. Fracture Tip

b. Delamination and microvoid-like initiation areas

Figure 9. Fracture Surface of Specimen Strained to Necking in Helium then Fractured in 69-MPa Hydrogen