AD-A076 912　ILLINOIS UNIV AT URBANA-CHAMPAIGN DEPT OF METALLURGY --ETC　F/G 20/11
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SEP 79　S GAHR , B J MAKENAS , H K BIRBAUM　N00014-75-C-1012

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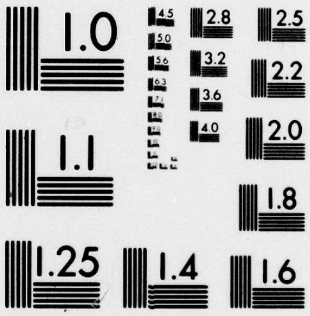
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HYDROGEN EMBRITTLEMENT-HYDRIDE FRACTURE[†]

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Technical Report

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Sept[redacted] 1979

Contract USN00014-75-C-1012

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[†] Work supported by the Office of Naval Research, contract [redacted]N 00014-75-C-1012

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ABSTRACT

Consideration is given to causes for the extreme brittleness observed for most hydrides. Surface energies for cleavage of the β $NbH_{0.82}$ f.c. orthorhombic hydride along the (100) and (110) are obtained using fracture mechanics methods. The values are shown to be about equal to those of b.c.c. niobium. The relative surface energies of niobium and NbH are consistent with measurements of phonon frequencies and elastic constants. None of the data indicates any decrease of atomic bonding due to the incorporation of hydrogen in the metal lattice.

Dislocation mobility is considered on the basis of T.E.M. observations and the crystal structure. It is shown that half of the $\{110\}\langle111\rangle$ slip systems cause hydrogen disordering and therefore experience a high lattice frictional stress. Domain boundaries also are shown to be dislocation barriers. Hydride brittleness is considered to result from the decrease in dislocation mobility and in the slip systems available to cause plastic blunting at elastic discontinuities.

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INTRODUCTION

In a number of recent articles[1-5] it has been shown that hydrogen embrittlement of systems which form stable hydrides occurs by a stress-induced hydride fracture mechanism. In this mechanism, there is a flux of hydrogen solutes to the region of triaxial tension stress at the crack tip as well as a reduction of the hydride free energy relative to that of the solid solution in this region. As the stress is increased, nucleation and growth of the hydride occurs which is then followed by hydride cleavage. Crack propagation occurs by repeated hydride growth and cleavage at a rate which is controlled by the hydrogen flux to the crack tip.[6,7] This mechanism requires : a) a mobile hydrogen species, b) a positive volume of formation of the hydride, and c) a brittle hydride phase. In the metal-hydrogen systems these conditions are generally met. Hydrides form by hydrogen ordering on a subset of interstitial positions accompanied by an elastic distortion of the metal lattice (and in some cases by correlated shears along close-packed planes).[8] The structure of the f.c. orthorhombic β (NbH)hydride and its relation to the b.c.c. α solid solution[9] is shown in Fig. 1. A molal volume increase of about 12% accompanies hydride precipitation and is accompanied by both elastic and plastic accommodation processes.[10,11] The β hydride is extremely brittle and fails by cleavage along {100} and {110} planes.[12] (All crystallographic indices are referred to the bcc axes.) In the present note we will discuss the reasons for this extreme hydride brittleness and its bearing on the general understanding of hydrogen embrittlement.

RESULTS AND DISCUSSION

It has been shown both theoretically[13] and experimentally[14] that the hydrides have a significantly different band structure than the metal from which they are formed. The general result is a lowering of the energies of s-like states by about 3 to 5 eV due to the attractive potentials at the hydrogen sites. Since the bonding states are markedly affected by hydride formation, the hydride brittleness may reflect a marked decrease in atomic bonding and therefore in surface energy. A reduction in atomic bonding for the deuterides is not however indicated by "small strain" measurements such as phonon dispersion[16,17] or elastic constant measurements.[18,19] Increased phonon frequencies and atomic force constants are observed at high hydrogen concentrations in both the α' solid solutions and the β deuterides. These effects are particularly striking in view of the large volume expansions (about 10-20%) which result on deuteride formation and which would be expected to lead to decreases of the phonon frequencies. They are consistent with the increases in elastic constants on forming the hydrides. Neutron scattering and elastic constant measurements probe only the potential energy curve near the equilibrium position. In the present experiments, we have attempted to measure the fracture surface energy directly.

Single crystals of the β hydride (H/Nb = 0.82) were machined to have a rectangular cross section with the {100} or {110} cleavage planes perpendicular to the long axis of the crystal. The specimens were pre-notched along the desired cleavage plane using an electron spark discharge. The depth of the notch was measured with the S.E.M. and they were stressed in three-point bending at 77 K until the cracks propagated. The critical stress intensity, K_{IC}, was determined from the maximum load applied and the corresponding surface energy, γ_{eff}, was calculated using:

$$\gamma_{eff} = \frac{K_{IC}{}^2(1 - \nu^2)}{2E} \qquad (1)$$

where ν and E are the Poisson Ratio and Young's modulus, respectively. The values used are those suitable for the hydride crystals.

In all cases cracks propagated rapidly in a completely brittle fashion after nucleation. No general yielding was noted in the stress-strain data prior to fracture. The fracture surfaces were quite planar, cleavage in nature and oriented along the selected {100} or {110} plane (Fig. 2). Since plastic deformation may accompany the cracking, plastic work can be included in γ_{eff}. A study of strain at the fracture surfaces was carried out using electron channel patterns which were formed using 200 keV electrons. Electron channel patterns have been shown[20] to be present only when the surface strains are less than a few percent. The sharp patterns obtained (Fig. 2) indicated that very little plasticity (probably < 1%) accompanied the cleavage fracture and that γ_{eff} is close to the true surface energy.

Fracture surface energies calculated for the β hydrides are shown in Table I along with selected values of experimental and theoretical b.c.c. surface energies. These have been more completely reviewed by Tyson, Ayres and Stein[21] who also discussed the anisotropy of the surface energies. The measured values generally correspond to high temperatures and should be corrected using the surface entropy of solids, 4×10^{-4} to 1.5×10^{-3} $J/m^2/K$. For Nb this yields a $\gamma \approx 3.23$ to 5.08 J/m^2 at 77 K.

Measured values of the β hydride surface energies are about equal to those determined for niobium and are of the order of those obtained for most b.c.c. metals. They are consistent with the previously discussed neutron scattering and elastic constant measurements since they do not indicate a decrease of cohesion energy in the hydride structure. Models of fracture based on a decrease in atomic bonding due to the presence of hydrogen clearly cannot account for the hydride brittleness.

Lack of crack-tip plasticity, as indicated by the electron channel patterns, despite the high stresses at the crack tip suggest a limited dislocation mobility and generation in the hydride structure. Little is known of the properties of dislocations in hydrides. Based on the lattice geometry, the Burgers vectors are expected to be of the type ⟨111⟩ and the slip planes to be {110}. T.E.M. studies of hydride precipitation from the α solid solution[11] have shown that the β phase remains relatively dislocation free compared to the adjacent α solid solution in which the plastic accommodation which accompanies the precipitate formation occurs. Dislocations are observed in thin hydride crystals and have been observed to move during precipitate reversion (Fig. 3). Their density is always orders of magnitude less than in the adjacent solid solution. Analysis has shown the Burgers vectors to be along the ⟨111⟩.

A high lattice resistance to dislocation motion may be inherent in the hydride structure. As shown in Fig. 1 hydrogen ordering causes half of the a/2 ⟨111⟩ slip vectors to no longer be lattice translation vectors in the β hydride structure. In the hydride domain shown in Fig. 1, the a/2 $[1\bar{1}\bar{1}]$ and a/2 $[\bar{1}\bar{1}1]$ are lattice translation vectors while the a/2 [111] and a/2 $[1\bar{1}1]$ are not. Slip in the latter two directions requires a conservative shear of a [111] or a $[1\bar{1}1]$ respectively. Since about half of the a/2 ⟨111⟩ dislocation Burgers vectors "inherited" from the α solid solution correspond to nonconservative lattice translations, motion of these dislocations would cause a hydrogen order fault.

The magnitude of the frictional stress on the a/2 [111] or a/2 $[1\bar{1}1]$ dislocations can be estimated from the hydrogen ordering energy and the disorder caused by dislocation motion. The hydrogen ordering energy is estimated to be about 1.6×10^{-21} J/H atom from the critical temperature for H ordering.[22] This corresponds to a frictional stress of 90 MPa or $\mu/400$ and must be added to any frictional stress increase caused by changes in atomic bonding on forming the hydride. In addition to the intrinsic lattice resistance, domain boundaries provide dislocation barriers since the subset of conservative $a/2\ \langle 111 \rangle$ Burgers vectors depends on the subset of tetrahedral sites occupied by the hydrogen interstitials in each domain.

The effect of limited dislocation mobility on hydride fracture is expected to be primarily on the amount of plasticity at elastic singularities such as cracks. Since some of the slip systems have high lattice frictional stresses and the domain boundaries act as barriers to the other slip systems, stresses at crack tips, dislocation pileups, etc., can be less easily decreased by plastic blunting once hydrogen ordering occurs. Cleavage fracture can be expected due to this limited plasticity and is observed in the hydrides.

Table I

Fracture Surface Energies of β ($NbH_{0.82}$) Hydride Single Crystals at 77 K

Cleavage Plane	Fracture Surface Energy (J/m^2)
{110}	4.59 ± 0.23
{100}	6.21 ± 0.31

Surface Energies of B.C.C. Metals

Metal	Surface Energy (J/m^2) {100}	{110}	Average	Temperature (K)	Reference
W	3.72	3.48		Theory	21
α-Fe	1.31	1.21		Theory	21
Ta	2.35	2.69		Theory	23
Mo	3.24	3.61		Theory	23
W*			2.83	1770	24
δ-Fe*			2.15	1650	25
Ta*			2.68	1770	24
Mo*			2.05	1770	24
Nb*			2.55	1770	24

*These high temperature values can be used to calculate low temperature values since the surface entropy of solids is 4×10^{-4} to 1.5×10^{-3} $J/m^2/K$.

FIGURE CAPTIONS

Figure	
1a	Unit cell of the f.c. orthorhombic β phase relative to the b.c.c. α phase. Hydrogen atoms are shown to occupy a subset of tetrahedral sites corresponding to a single domain. The Nb atoms are not shown.
1b	Projection of atom positions on the (110) of the domain shown in Fig. 1a. The numbers next to each H position are the fraction of a [110] that the site is located above (+) or below (-) the (110). Large open circles are the Nb sites and filled small circles and X's are the projections of the H sites.
2	Fracture surfaces of $NbH_{0.82}$ single crystals tested at 77 K. The fracture planes are the (a) {110} and the (b) {100}. The arrows indicate the position of the spark eroded pre-crack. Electron channeling patterns made near the notch root are shown in (c) and (d) for the {110} and {100} cleavage planes, respectively.
3a	Transmission electron micrograph of β hydride at room temperature and composition H/Nb = 0.94. The domain boundaries exhibit fringe patterns.

3b Transmission electron micrograph of a large β hydride undergoing dissolution at 60°C. Dislocations are in motion towards the center of the precipitate. The α solid solution adjacent to the hydride has a very high dislocation density while the β hydride has a very low dislocation density.

REFERENCES

1. S. Gahr, M. L. Grossbeck and H. K. Birnbaum, Acta Met., 25, 125 (1977).
2. M. L. Grossbeck and H. K. Birnbaum, Acta Met., 25, 135 (1977).
3. S. Gahr and H. K. Birnbaum, Acta Met., 26, 1981 (1978).
4. D. G. Westlake, Trans. ASM, 62, 1000 (1969).
5. S. Takano and T. Suzuki, Acta Met., 22, 265 (1974).
6. S. Gahr and H. K. Birnbaum, Scripta Met.,
7. B. Hindin and H. K. Birnbaum, to be published.
8. V. A. Somenkov, A. V. Gurskaya, M. G. Zemlyanov, M. E. Kost, N. A. Chernoplekov, and A. A. Chertkov, Sov. Phys. Sol. State, 10, 1076 (1968).
9. V. A. Somenkov, Ber. der Bensenges. fur Phys. Chemie, 76, 733 (1972).
10. T. Schober, Scripta Met., 7, 1119 (1973).
11. B. J. Makenas and H. K. Birnbaum, to be published.
12. H. K. Birnbaum, M. L. Grossbeck and M. Amano, J. Less Comm. Met., 49, 357 (1976).
13. A. C. Switendick, Ber. der Bensengess. fur Phys. Chemie, 76, 535 (1972).
14. A. C. Switendick, Hydrogen in Metals I (Springer Verlag, Berlin, 1979) ed. by G. Alefeld and J. Völkl, p. 101.
15. E. Gilberg, Phys. Stat. Sol. (b), 69, 477 (1975).
16. T. Springer, Hydrogen in Metals I (Springer Verlag, Berlin, 1979) ed. by G. Alefeld and J. Völkl, p. 75.
17. V. Lottner, A. Kollmar, T. Springer, W. Kress, H. Bilz, and W. D. Teuchert, Lattice Dynamics (Flammarion Sciences, Paris, 1978) ed. by M. Balkanski, p. 247.
18. M. Amano and H. K. Birnbaum, Proc. of Sixth Int. Conf. on Internal Frict. and Ultrasonic Attenuation in Solids (University of Tokyo Press, Tokyo, 1977) ed. by H. Hasiguiti, p. 323.

19. A. Magerl, B. Berre and G. Alefeld, Phys. Stat. Sol. (a), 36, 161 (1976).

20. D. L. Davidson and F. F. Lyle, Corrosion NACE, 31, 135 (1975).

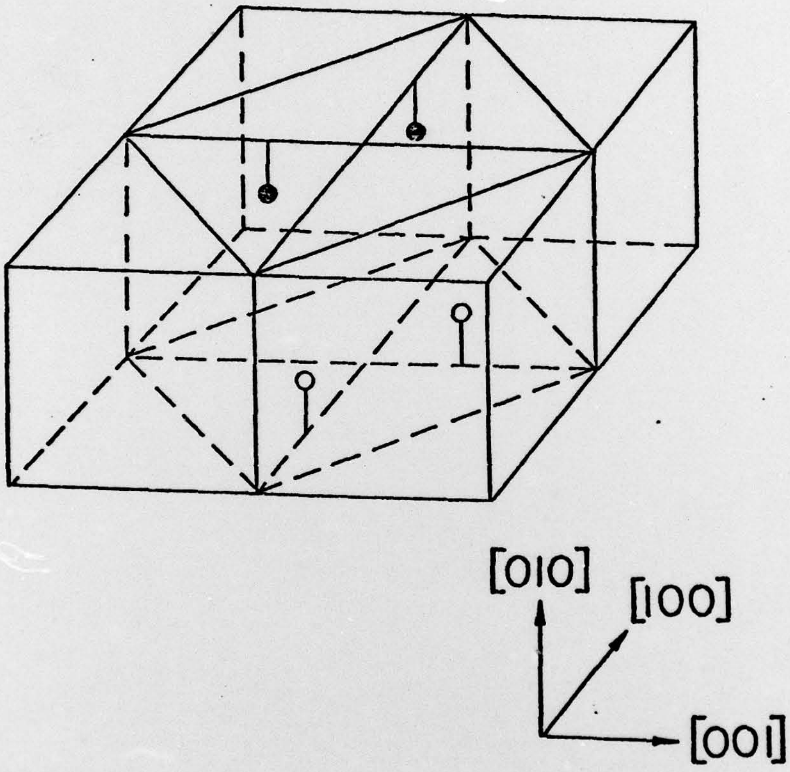
21. W. R. Tyson, R. A. Ayres and D. F. Stein, Acta Met., 21, 621 (1973).

22. T. Schober and H. Wenzl, Hydrogen in Metals II (Springer Verlag, Berlin, 1979) ed. by G. Alefeld and J. Völkl, p. 11.

23. M. H. Richman, Trans. A.S.M., 60, 719 (1967).

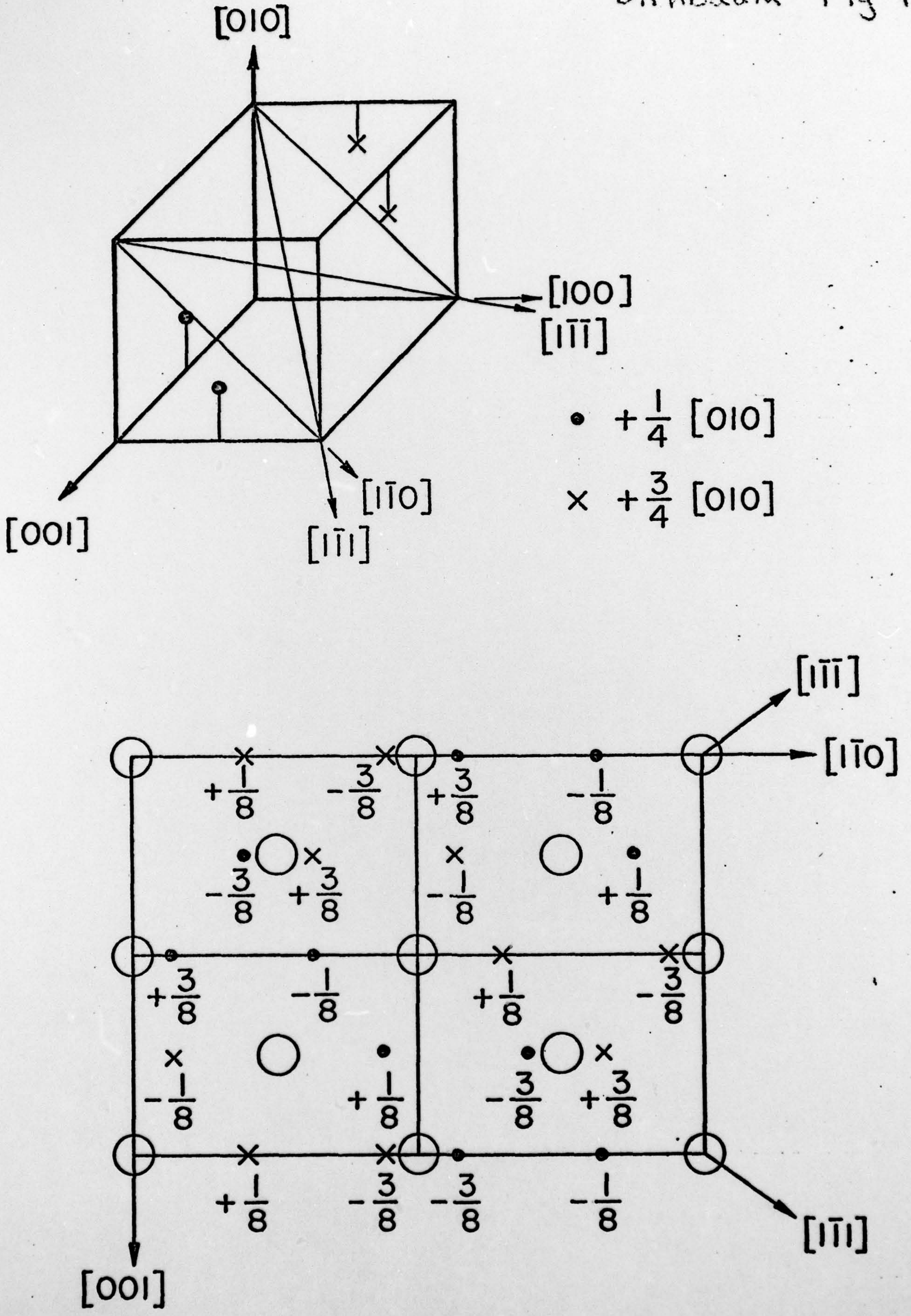
24. E. N. Hodkin, M. G. Nicholas and D. M. Poole, J. Less Common Met., 20, 93 (1970).

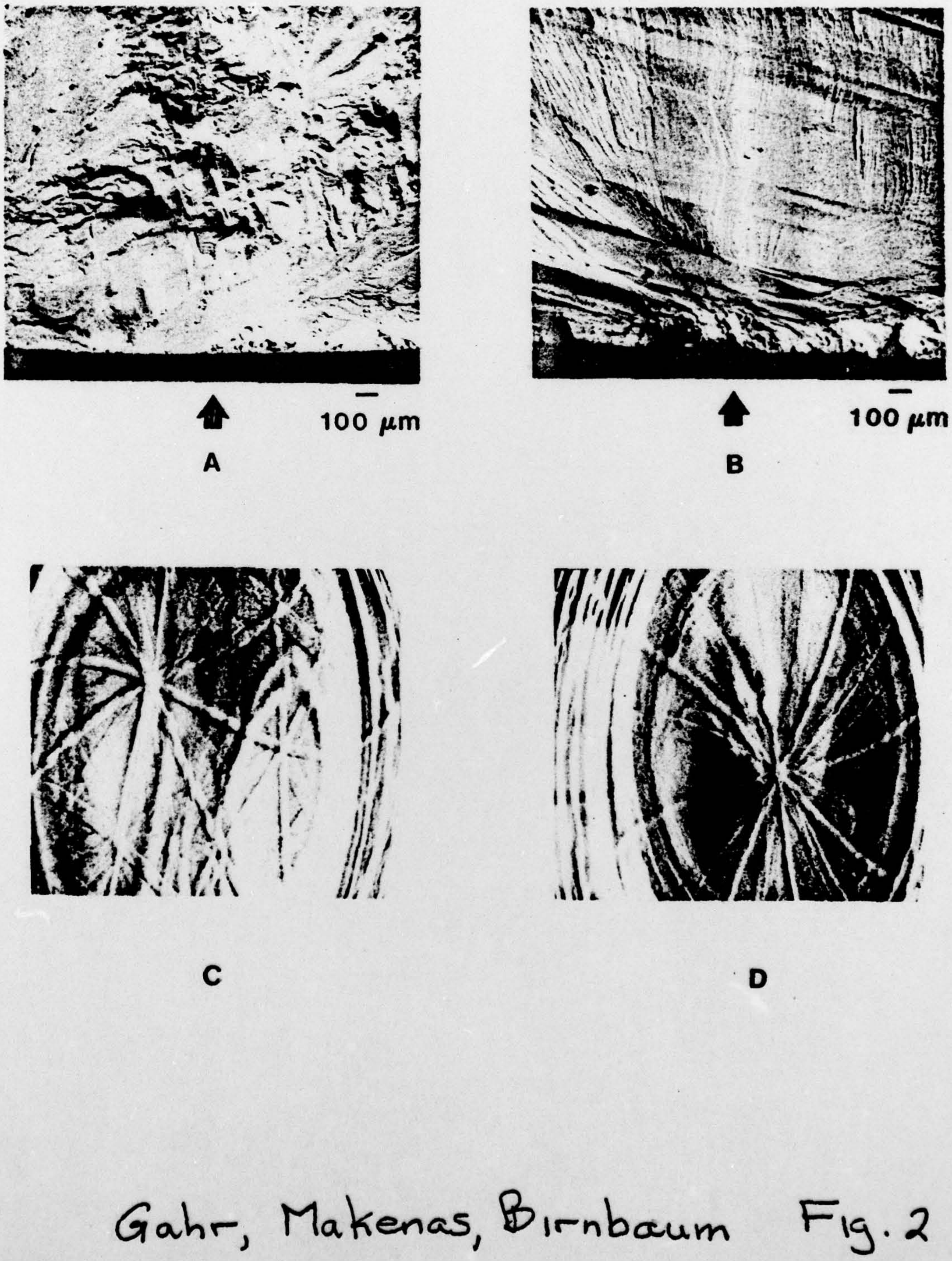
25. A. J. Price, M. A. Hall and P. Greenough, Acta Met., 12, 49 (1964).



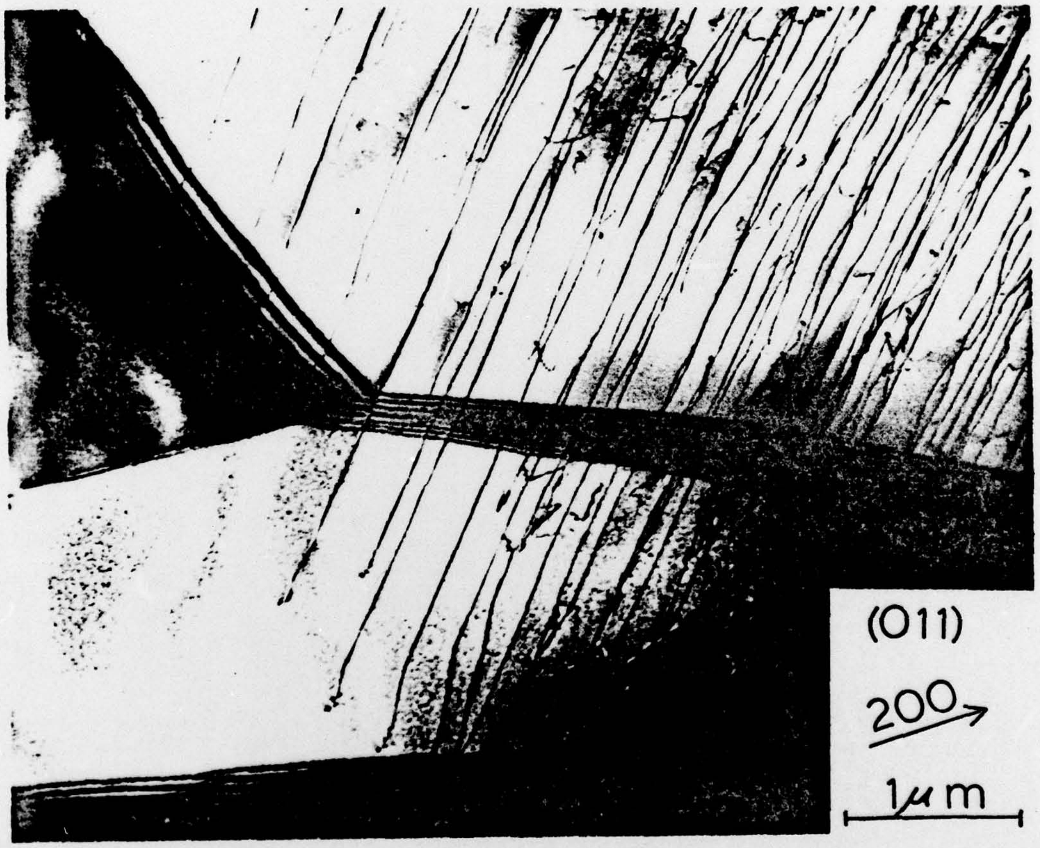
Gahr, Makenas, Birnbaum Fig. 1a

Gahr, Makenas,
Birnbaum Fig 1b

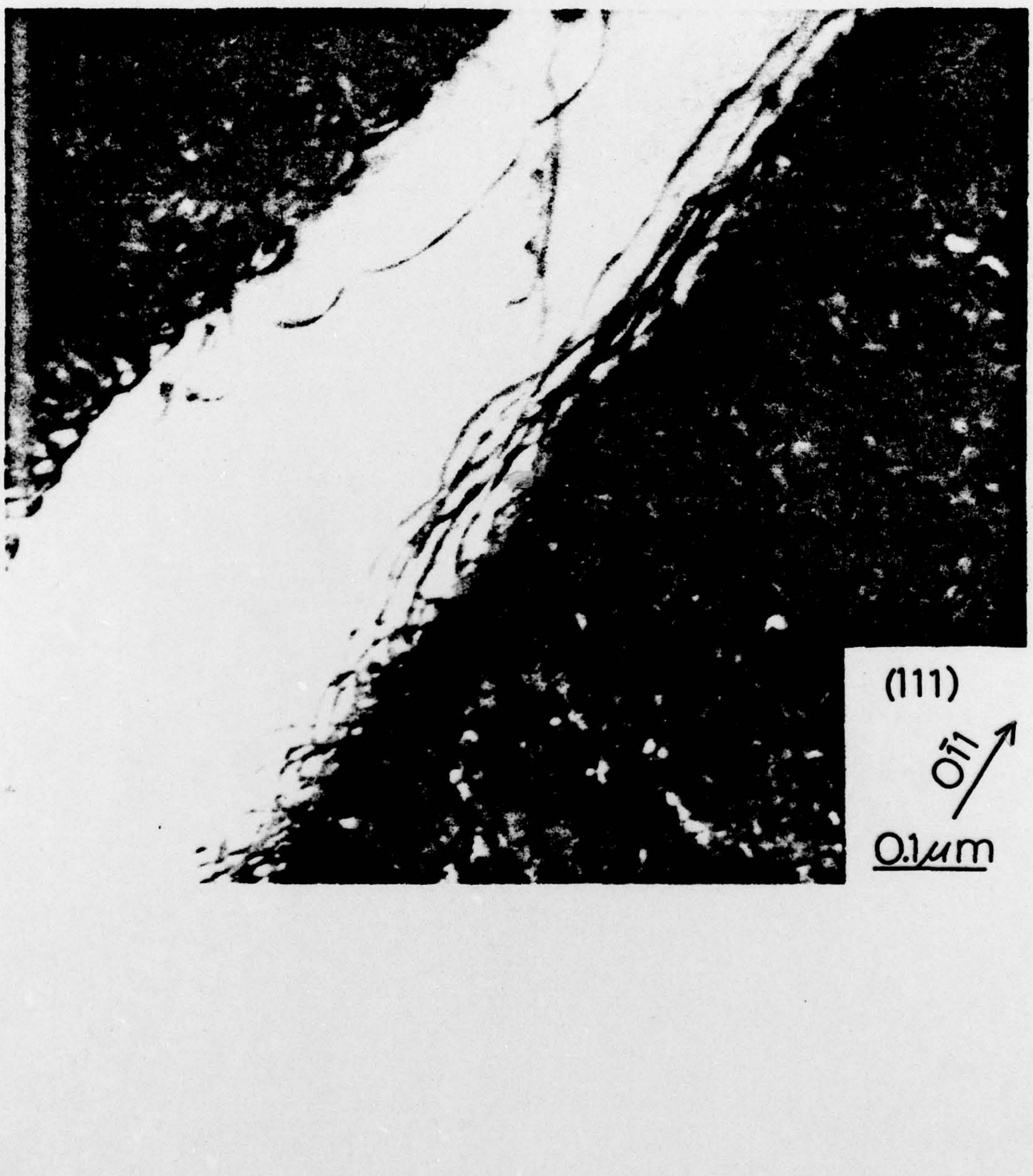




Gahr, Makenas, Birnbaum Fig. 2



Gahr, Makenas, Birnbaum Fig. 3 a



Gahr, Makenas, Birnbaum Fig. 3b

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

University of Illinois
Dept. of Metallurgy & Mining Eng.

2a. REPORT SECURITY CLASSIFICATION
unclassified

2b. GROUP

3. REPORT TITLE

Hydrogen Embrittlement - Hydride Fracture

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Technical Report

5. AUTHOR(S) (First name, middle initial, last name)

S. Gahr, B. J. Makenas and H. K. Birnbaum

6. REPORT DATE
July 1979

7a. TOTAL NO. OF PAGES
17

7b. NO. OF REFS
25

8a. CONTRACT OR GRANT NO.
USN 00014-75-C-1012

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

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11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

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13. ABSTRACT

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Hydride						
Fracture						

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