HYDROGEN EFFECTS ON THE CHARACTER OF DISLOCATIONS IN HIGH-PURITY ALUMINUM

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Abstract—The effect of hydrogen in solid solution on the edge/screw character of dislocations has been investigated by deforming samples of high-purity aluminum in a gaseous hydrogen environment in situ in a controlled environment transmission electron microscope. Solute hydrogen was found to stabilize edge segments of dislocations, which inhibited, and in some cases stopped dislocations from cross-slipping. Removal of hydrogen from the sample allowed the cross-slip process to continue. These observations provide an explanation for the macroscopic observation that hydrogen in solid solution can promote slip planarity.

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1. INTRODUCTION

Macroscopic observations of the effects of solute hydrogen on mechanical properties have shown that solute hydrogen can reduce the ductility and can change the fracture mode from ductile transgranular to transgranular cleavage to "brittle" intergranular. Microscopic observations have reported that solute hydrogen can cause the formation of new phases [1–5], increase the mobility of dislocations [6–20], and increase the propensity for planar slip and slip localization [21–26]. The most common mechanisms proposed to explain the macroscopic and microscopic effects associated with hydrogen embrittlement include hydrogen reducing the strength of atomic bonds, which facilitates bond breakage [27]; hydrogen adsorption at the crack tip or at surface imperfections, which reduces the energy for crack propagation or nucleation and injection of dislocations [8]; hydrogen shielding dislocations from interactions with other elastic obstacles, which allows dislocations to move at lower stresses [28]; hydrogen nucleating and growing a brittle hydride phase [29]; and hydrogen reducing the stacking-fault energy [20,24,30], which decreases the tendency for cross-slip by increasing the separation distance between partials. The diversity of the effects of hydrogen on the mechanical properties suggests that a single mechanism is unlikely to be responsible for all effects and, depending on the conditions, different mechanisms can operate in one system. The focus of this paper is not to review the arguments for and against the different mechanisms, as this has been done in numerous review articles [27,28,31,32], but rather to present direct experimental evidence for a new mechanism that accounts for the hydrogen-induced increase in slip planarity. Understanding this effect along with the concomitant increase in strain localization will potentially allow methodologies to be developed that will decrease the susceptibility of a material to hydrogen embrittlement.

From observations of slip lines on surfaces, it has been reported that solute hydrogen increases the propensity for planar slip in 310s stainless steel [25,33], spheroidized 1520 steel [34], single crystal nickel-based superalloy [35], Ni–Co [36], Al [23] and Ni [37]. The effect may, however, be restricted to the near surface [37]. To account for this effect it has been proposed that hydrogen causes a decrease in the stacking-fault energy. There are, however, only a few measurements of the effect of hydrogen on the stacking-fault energy, and these are restricted to steels with already low stacking-fault energies. Ferreira et al. [38] reported a decrease of about 20% in 310s stainless steel and Pontini and Hermida [39] a 40% reduction in AISI 304 steel. A lower stacking-fault energy will make cross-slip more difficult, although a lower stacking-fault energy does not in itself necessarily result in an increase in slip planarity.

Ulmer and Altstetter [25] suggested that solute hydrogen influenced the formation of edge character dislocations, which would also increase slip pla-
narity. No supporting experimental evidence for such an effect was, however, presented. In this paper, we provide the first direct experimental observations of hydrogen influencing the character of dislocations in high-purity aluminum.

2. EXPERIMENTAL PROCEDURE

Samples of high-purity aluminum with a composition of 99.999% were used. The material was received in the form of an ingot and was cold rolled, ground using 600 grit paper to a thickness of approximately 150 μm. Rectangular (10 × 3 mm²) samples were cut from the thin foil, annealed at 80°C for 30 min in a vacuum of approximately 10⁻⁶ Torr and quenched in vacuum oil. This anneal was sufficient to form a fully recrystallized structure in the high-purity aluminum. After heat treatment, the specimens were cleaned in acetone. Specimens were thinned to electron transparency by jet electropolishing in an electrolyte of 1:4 nitric acid/water at -10°C, at a voltage of 6/7 V, and a current of 0.6 A. Before TEM observation, the samples were coated with approximately 20 nm of Pd on each surface to enhance hydrogen adsorption from the gas phase; the electron transparent region was shielded during this procedure.

The specimens were observed in a JEOL 4000 controlled environment transmission electron microscope [40-42]. The microscope was operated at 200 keV, which is above the threshold displacement voltage for Al, but no evidence of radiation damage was found. In this microscope a gas environment can be maintained around the sample, which permits in situ observations of the gas–solid reactions in real time and at high spatial resolution. Thus, with the environmental cell, it is possible to directly observe the effect of hydrogen on deformation processes. The procedure used in these experiments was to deform the specimen in vacuum to activate dislocations and then to gradually introduce hydrogen gas to the environmental cell. The movement and behavior of the dislocations was recorded on videotape for later analysis. Although the hydrogen content of the samples was not determined, previous studies [13, 14] established that under the conditions in the environmental cell, solute hydrogen is introduced into aluminum. In addition, Bond et al. [43] showed that the fugacity is several orders of magnitude higher than the externally measured gas pressure because of the dis-

Fig. 1. Series of bright-field images captured from videotape showing the locking of dislocations in a cross-slip configuration by hydrogen. Hydrogen gas pressure and lapsed time are indicated on each image. The arrows indicate the slip line traces on the surface of the sample with trace 1 corresponding to the initial slip plane, A, and trace 2 corresponding to the cross-slip plane, B.
sociation and ionization of the gas molecules by the electron beam.

3. RESULTS

The dynamic behavior of dislocations, especially when the reactions are complex is difficult to understand even when observed in real time. The problem becomes more complex when snapshots of the events are shown and the reactions described in words. Therefore, to assist in the visualization of the dynamics of the dislocation reactions, three views are presented. First, sequences of images captured directly from videotape at the indicated times and H₂ pressures are shown, then a series of comparison images formed by superimposing a positive and a negative image from the sequence is used to illustrate relative displacements, and finally, the complete reaction is summarized in a schematic diagram.

An example of hydrogen pinning dislocations in the process of cross-slip is shown in the time sequence in Fig. 1, the comparison images in Fig. 2, and schematically in Fig. 3. In Fig. 2, the black dislocations (positive image) show initial positions and white dislocations (negative image) final positions. Initially, the dislocations are moving on the primary slip system in the direction indicated by arrow 1, which marks the surface slip line trace. In Fig. 1(c), an abrupt change in line direction occurs for a segment of the dislocation (marked by arrowheads); this change is perhaps more apparent in the comparison image in Fig. 2(a), in which Figs 1(b) and (c) are compared directly. The change in line direction actually corresponds to a change in slip plane for this dislocation segment, see Fig. 3. Normally, the dislocation would continue the cross-slip process and then move on the cross-slip plane. However, maintaining 85 Torr of hydrogen gas in the cell stops the process, Fig. 1(d). That is, the presence of hydrogen in solid solution locks the dislocation in place with one segment on the primary and the other on the cross-slip plane. The locking action can be seen in the comparison image, Fig. 2(b), which compares Figs 1(c) and (d). The lack of image contrast for the dislocations in Fig. 2(b) shows that no movement has occurred. In this case the hydrogen pressure was maintained at this level for 27 s, but the dislocations can be pinned in this arrangement as long as the level of hydrogen is maintained above about 16 Torr [Figs 2(c) and (d)]. The cross-slip process continues after the hydrogen pressure in the environmental cell was reduced to less than 16 Torr as can be seen in Fig. 2(e), which compares the dislocation positions in Figs 1(f) and (g). The comparison in Fig. 2(f) compares the initial and final configuration of the dislocations; the
change in the line direction (slip system) is apparent.

The dislocation behavior presented in Figs 1 and 2 is shown schematically in Fig. 3. The dislocations have a mixed character on the primary slip plane, Plane A; the Burgers vector indicated was inferred from the direction of intersection of the slip planes involved in the reaction. The screw segment of the dislocation cross-slips to Plane B and the remainder of the dislocation attempts to follow; dislocation position 2 corresponds to the situation in Fig. 1(c). If the cross-slip were to continue unimpeded, the

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**Fig. 4.** Series of weak-beam dark-field images captured from videotape comparing the effect of environment on the dislocation motion. Hydrogen pressure and lapsed time are indicated on each image. The arrows indicate the trace on the surface of the sample with trace 1 corresponding to slip on the initial slip plane, A, and trace 2 to slip on the cross-slip plane, B.
process would proceed as indicated by dislocation position 3 where the length of the screw segment is increased. As cross-slip continues the mixed nature of the dislocation on Plane B is recovered as shown in dislocation position 4. However, hydrogen halts the process with the dislocation in a position similar to that of dislocation in position 2. In this configuration, segments on the primary and cross-slip planes have an edge component. Removal of hydrogen from the sample allows the dislocation segment on the primary slip plane to reorient towards the screw orientation and to complete the cross-slip process.

A second example of hydrogen affecting the character of dislocations during the cross-slip process is shown in the series of weak-beam dark-field images presented in Fig. 4. The comparison images are presented in Fig. 5 and a schematic of the reaction in Fig. 6. In this series of comparison images the white dislocations show the initial position (positive image) and the dark dislocations the final position (negative image). The motion of dislocations a, b, c, and d in vacuum is initially parallel to the direction indicated by arrow 1, Figs 4(a)–(c). Dislocations b, c, and d cross-slip as seen by the change in dislocation line direction between Figs 4(a) and (c); these images are compared in Fig. 5(a). The cross-slip plane is steeply inclined to the beam direction in this example and, hence, the line length of the cross-slipped segment is short, see Fig. 6. The cross-slipped segment now moves in a direction parallel to arrow 2. With the introduction of hydrogen into the environmental cell, the cross-slipped segment of dislocations b and c continues to move on the
cross-slip plane as evidenced by the decrease in line length of the segment on the primary slip plane, Figs 5(c) and (d). At a later time and in a higher hydrogen concentration [Figs 4(g) and (h)], dislocation \( b \) remains locked between the primary and cross-slip planes; dislocation \( b \) is not visible in the comparison image Fig. 5(d) because of the cancellation of contrast by the superposition. Dislocation \( c \) cross-slips completely and moves in the cross-slip plane and dislocation \( d \) cross-slips back to the primary slip plane; compare Figs 4(g) and (h) or see the comparison image Fig. 5(d). With 78 Torr of hydrogen gas in the cell, Fig. 4(i), dislocation \( b \) remains locked and dislocations \( c \) and \( d \) now move on the primary slip plane: compare the curvature of the dislocations in Figs 4(i) and (a). New dislocations, \( e \), \( f \) and \( g \), moving on the primary slip plane, enter the field of view from the upper right. Dislocations \( c \), \( d \) and \( e \) move on the primary slip plane in the presence of hydrogen [Figs 4(i)–(k) and Fig. 5(f)], but as hydrogen is removed [Figs 4(l)–(o)] and the deformation continues in vacuum dislocations \( e \), \( f \) and \( g \) cross-slip readily and move on the cross-slip plane [Fig. 5(i)]. In the presence of hydrogen slip is confined to the primary slip plane and cross-slip is restricted.

### 4. DISCUSSION

Analysis of the dislocations in the above examples showed that during the cross-slip process the length of the screw component at the intersection of the two slip planes increased and the length of the mixed (largely edge) components decreased. The effect of introducing solute hydrogen is to stop the cross-slip process (Figs 1–3) or in some cases reverse it (Figs 4–6). These observations can be explained by two effects:

1. Solute \( H \) forms an atmosphere primarily around the edge dislocation components. Relative to the dislocations in a uniformly dispersed solute \( H \) distribution, the formation of a \( H \) atmosphere around the edge component decreases the energy of the system. This does not occur at the screw dislocation components.

2. As the edge dislocation components are converted to screw components during cross-slip, the \( H \) solutes from the atmosphere return to a higher energy configuration in the solid solution. Hence, any process, such as cross-slip, that increases the screw component length at the expense of the edge component length will be made more difficult by the presence of hydrogen.

In considering the formation of \( H \) atmospheres around the dislocations, two elastic interactions need to be considered [44]. A “first order” interaction, \( W_{\text{int}} \), results from the interaction of the distortion field around the \( H \) solute, \( e^H_{ij} \), and the stress field of the dislocation, \( \sigma_{ij}^{\text{disl}} \):

\[
W_{\text{int}} = -e^H_{ij} \sigma_{ij}^{\text{disl}} \tag{1}
\]

where the summation is taken over repeated indices. This interaction varies as \( 1/r \) where \( r \) is the distance
from the dislocation. Hydrogen solutes also interact with the dislocations via a “second order” elastic interaction, resulting from the hydrogen-induced change of the local moduli

$$W^2_{\text{int}} = \left( \frac{1}{3} \right) \sum_{i<j} \left( C_{ijkl} - C_{ijkl}^0 \right) V_H$$

where $C_{ijkl}$ and $C_{ijkl}^0$ are the dislocation strain components, $V_H$ is the volume over which a H solute changes the elastic moduli, and $C_{ijkl}^0$ and $C_{ijkl}^0$ are the elastic stiffness in the presence of H and in pure Al, respectively. The second order interaction varies as $1/r^2$. This “second order” interaction can lead to a weak, short-range H atmosphere if $(C_{ijkl} - C_{ijkl}^0) < 0$ or a short-range depletion of H if $(C_{ijkl} - C_{ijkl}^0) > 0$.

Interstitial H occupies an octahedral site in f.c.c. Al and hence its distortion field has cubic symmetry. This results in a “first order” interaction only with the normal stress components of the dislocation and hence, in a H atmosphere around the edge dislocation components but not with screw components. While the effect of H on the elastic moduli of Al has not been measured, any H atmosphere due to the “second order” interaction is likely to be very small in H density and extent.

In a system containing solute H and dislocations, the formation of the atmosphere around the dislocation reduces the energy of the system. This decrease in energy is given by

$$\Delta E = (E_{\text{disl}} + E^\text{uniform}_H) - (E_{\text{disl}} + E^\text{atmospheric}_H)$$

where $E^\text{uniform}_H$ is the energy of the H in uniform solid solution and $E^\text{atmospheric}_H$ is the energy of the H in solution after the formation of the atmosphere at the dislocation. This energy change was calculated using the methods employed by Sofronis and Birnbaum [45] with the result that $\Delta E = 0$ for screw dislocations and the results shown in Fig. 7 for edge dislocations. There is a decrease in the energy of the the system at significant H concentrations — a decrease that is small relative to the energy difference between edge and screw dislocation components. This small energy gain can, however, influence the stability of a dislocation configuration during cross-slip. Hence this $\Delta E$ favors the formation of edge components and decreases the tendency for cross-slip. The experimental observations of decreased cross-slip caused by solute hydrogen can be accounted for by the above concepts.

A decrease in the tendency for cross-slip can increase slip planarity although other factors may also be important. It has been suggested that hydrogen in solid solution can significantly decrease the stacking-fault energy and thereby increase the slip planarity [20, 24, 30]. However, it is only recently that the magnitude of the decrease in the stacking-fault energy due to solute hydrogen has been reported. Ferreira et al. [38] have studied the effect of hydrogen on the stacking-fault energy of 310 stainless steel by measuring the dimensions of dislocation nodes, and reported that hydrogen reduces the stacking-fault energy from 34 to 27 mJ/m$^2$, a decrease of at most 20%. A larger decrease was reported by Pontini and Hermida [39], who used X-ray diffraction to measure a 40% reduction in the stacking-fault energy of AISI 304 steel. The stacking-fault energy of aluminum has been reported to be 166 mJ/m$^2$ [46]. A 40% reduction would not be sufficient to explain the increased slip planarity that has been observed [23]. In addition, no widely spaced dislocation partials were observed in the present TEM studies or in other TEM studies of Al containing large concentrations of hydrogen.

5. CONCLUSIONS

In situ environmental cell TEM observations have shown that cross-slip in high-purity aluminum is inhibited by solute hydrogen. Analysis of the energy changes due to formation of H solute atmospheres at edge and screw dislocations has shown that the energy change stabilizes the edge components. Stabilization of the edge components during cross-slip has the effect of decreasing cross-slip in accord with experimental observations.

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