DEFORMATION BEHAVIOR IN MATERIALS SUSCEPTIBLE TO HYDROGEN EMBRITTLEMENT

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ABSTRACT

The effects of dissolved hydrogen on dislocation motion in stainless steel have been studied in an attempt to understand how hydrogen impacts deformation, which is important for understanding hydrogen embrittlement in these alloys. Indentation tests of stainless steels before and immediately after exposure to high hydrogen gas pressures have been conducted to examine the effects of dissolved hydrogen on indentation induced slip steps. No significant changes have been noted on the slip step patterns or the amount of out of plane material pile-up around indentations, indicating that dissolved hydrogen does not change the general deformation mechanisms. In regions where slip steps result from a single slip system, the step spacing decreases after hydrogen charging. Also after charging, increased numbers of slip steps are observed on secondary slip systems in the regions where they are present. These more subtle changes indicate that hydrogen does impact deformation at the level of individual dislocations. Hydrogen enhanced localized plasticity (HELP) has evolved as a prominent theory for describing how hydrogen might affect plasticity. Since dislocations are presumed to initiate at or near the indenter tip and initially glide down into the bulk, a secondary mechanism must be required for dislocations to emerge at the free surface. This could be the result of dislocation cross-slip or activation of new dislocation sources. In the first case, decreased spacing between dislocations piled up at a boundary, as described by the HELP theory, could account for decreased spacing between cross-slip events and thereby lead to decreased spacing between surface slip steps. For the latter case, increased localized stress, also predicted by the HELP theory, would allow for the activation of an increased number of sources. As more sources become activated the spacing between slip steps observed on the surface would be expected to decrease.

1 INTRODUCTION

Hydrogen in metals has been extensively studied using both microscopy and mechanical testing, and it has been shown in many alloys to lead to embrittlement and premature fracture of ferrous alloys such as stainless steels (Hirth[1), Oriani[2], Teter[3]). However, the actual mechanism by which hydrogen embrittles metals is still a subject of debate. Since it is generally understood that some amount of plasticity must precede even brittle fracture, some research has attempted to determine the effect of hydrogen on dislocations (Katz[4], Ferreira[5]). Some of this work, primarily that involving *in situ* transmission electron microscopy (TEM) studies of various FCC metals has led to the development of the hydrogen enhanced localized plasticity (HELP) theory (Ferreira[5], Birnbaum[6]). Some outcomes of the HELP theory show that hydrogen may shield dislocation stress fields, which results in decreased glide stresses and closer spacing between dislocations in pile-ups. Additionally, edge segments become energetically preferential to screw segments leading to increased planar slip.

The study of both fracture and plasticity is important to understanding hydrogen embrittlement. Since the HELP theory presumes failure occurs as a result of highly localized plasticity, the goal of this research is to examine the effect of dissolved hydrogen on the motion of dislocations produced during indentation. The original TEM studies involving *in situ* testing in an environmental cell clearly showed hydrogen to increase the mobility of edge dislocations, but complementary experimental research on larger, bulk samples which demonstrates this phenomenon is limited (Teter[3]). Micro- and nano-indentation testing have the advantage of testing materials on length scales intermediate between TEM and bulk testing.

Indentation testing has long been used to measure hardness and elastic modulus, but more recently has been demonstrated as an effective method for qualitative measurements of strain hardening exponent and stacking fault energy (SFE). The height and extent of out-of-plane material pile-up around indentations relates to strain hardening and yield stress, respectively (Johnson[7]). Larger pile-up heights correspond to low strain hardening while small pile-up heights, no pile-up and even sink-in around the indentation indicates large amounts of strain hardening. When combined with Atomic Force Microscopy (AFM) and Orientation Imaging Microscopy (OIM), slip traces in the deformed material around indentations can be imaged and correlated with specific slip planes (Nibur[8]). The waviness and thickness of these slip lines can provide qualitative comparisons of SFE (Nibur[8]).

These characteristics have allowed indentation testing to emerge as a promising way to study the interaction of hydrogen with dislocations. Micro- and nano- indentation have the ability to probe intermediate volumes of material that are large enough to contain many dislocations on many slip systems, yet small enough to eliminate the uncertainty resulting from the simultaneous deformation of many different grains that occurs during bulk testing of polycrystalline samples. AFM images of indentations show slips steps on the surface, which form very repeatable patterns dependent primarily on the crystal orientation of the grain and somewhat on the geometry of the indenter tip (Nibur[8]). This paper will explore qualitative and quantitative comparisons of the slip steps produced around indentations made in a stainless steel alloy before and after exposure to hydrogen.

2 EXPERIMENTAL PROCEDURE

An FCC stainless steel alloy with an approximate composition of 19.1%Cr, 6.9%Ni, 9.5%Mn, .26%N (referred to as 21-6-9) was annealed at 1200^{o}C for 5 hours to produce a large, equiaxed grain structure with many grains larger than 1mm in diameter. Orientation imaging microscopy (OIM) was performed to identify the crystal orientation of many grains from which a few were selected with orientations near (100), (110), and (111). Conical indentations with loads ranging from 50 to 550 mN were made with a Nanoinstruments Nanoindenter II in each grain and imaged using AFM. The sample was then placed in a controlled environment of 138 MPa H_2 at 300^{o}C for 7 days. This resulted in a total concentration of about 15000 appm H. Immediately following charging, a second set of indentations was made in the same grains and with the same loads as before charging. AFM images of all indentations were used to examine the patterns formed by the steps, to measure the height and spacing between steps and to measure indentation size.

3 RESULTS

AFM images of the indentations were used to measure indentation size, which yields hardness values, as well as a variety of quantities not available from load vs. depth curves. After charging with hydrogen, the hardness increased by 10%. The height of out of plane material pile-up (h/a) and radius of the plastically deformed region around the indentation (c/a) were measured and normalized to the indentation diameter. Table 1 shows that the values for these measurements did not change significantly for indentations of different loads nor after hydrogen charging.

Figure 1 shows AFM topography images of two indentations in a grain with $[7\ \overline{11}\ \overline{1}]$ surface normal. No significant changes are noticeable in the general deformation pattern. Some differences become apparent at higher magnification of the slip steps. AFM deflection images of the deformation lobe on the left side of the indentations is shown in Figure 2. The lobe contains parallel slip steps resulting from dislocations moving on $(1\bar{1}1)$ slip planes determined by methods previously developed (Nibur[8]). These planes are oriented such that dislocations traveling away from the indenter would emerge at the surface as expected. The spacing between steps in this area before hydrogen charging was ~ 140nm and decreased to 75nm after charging.

AFM deflection images of the opposite deformation lobe, corresponding to the right side of the indentations in Figure 1, are shown in Figure 3. These images show slip steps resulting from the $(1\bar{1}1)$, $(\bar{1}11)$, and $(11\bar{1})$ slip planes, with the $(1\bar{1}1)$ plane appearing to be responsible for most of the deformation. After hydrogen charging the spacing of steps on the $(1\bar{1}1)$ planes increased slightly and the number of steps on the $(\bar{1}11)$ planes doubled.

4 DISCUSSION

The fact that the slip step patterns, c/a, and h/a in this alloy did not change significantly after hydrogen charging suggests that the general deformation mechanisms were not affected by the presence of hydrogen. The increase in hardness and the changes in step spacing and distribution, however, are evidence that hydrogen has an effect on dislocation motion.

It has often been suggested that dislocations produced during indentation are generated in the very small volume of material directly below the tip of the indenter where the stresses are significantly higher and that the dislocations are initially directed down into the bulk of the material (Zielinski[9]). For this to be the case, the slip lines visible on the surface must be due to dislocation activity on slip systems which differ from those of the original dislocations generated at the tip. This can happen in one of two ways. The dislocations can cross-slip onto a new slip

Table 1: Indentation measurements

	Normalized plastic radius (c/a)	Normalized pile-up height (h/a)	Hardness (MPa)
No hydrogen	3.22 ± 0.16	0.057 ± 0.006	657 ± 83
15000 appm hydrogen	3.21 ± 0.16	0.059 ± 0.005	735 ± 47

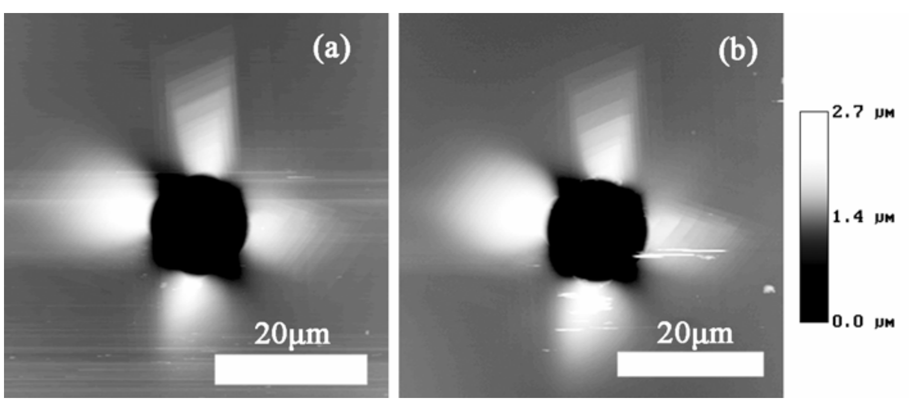

Figure 1: AFM topography images of 550mN indentations in the same grain of material before (a) and after (b) gas phase hydrogen charging show that the general deformation around the indentations does not change.

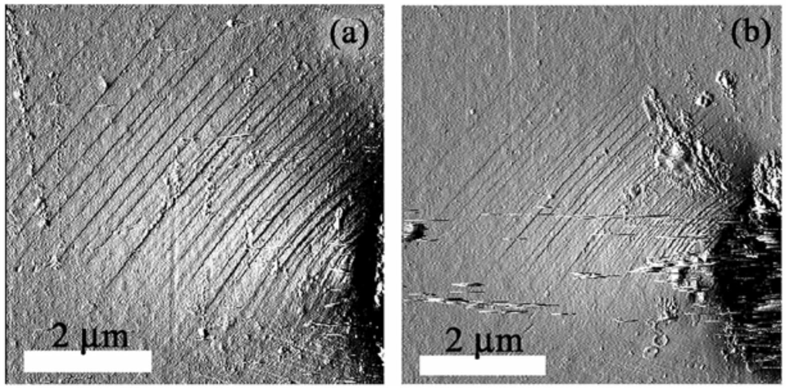

Figure 2: AFM deflection images showing that the spacing between slip steps decreases after hydrogen charging. Before charging (a) steps are spaced an average of 140nm between steps. After charging (b) the spacing decreases to an average of 75 nm.

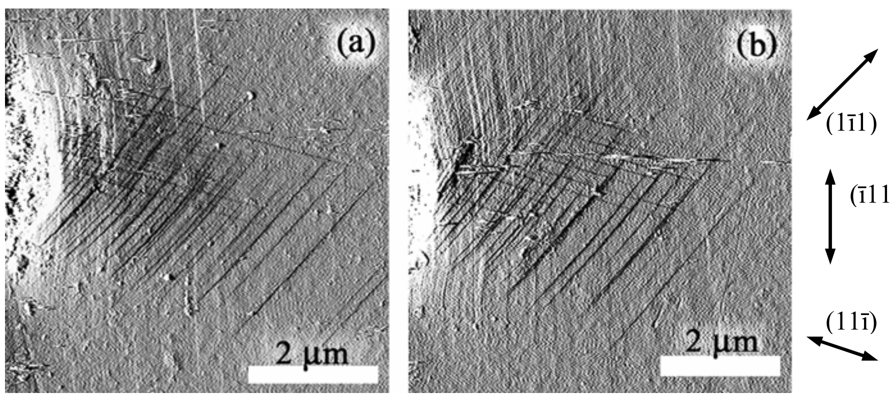

Figure 3: AFM deflection images showing details of the right side deformation lobe from 50 mN indentations in the same grain reveal a single prominent slip system before charging (a) and increased number of slip steps on other slip systems after charging (b). Arrows at right indicate the three slip planes associated with the slip steps.

plane such that the existing Burgers vector will allow dislocations to emerge at the free surface. Alternatively, as compressive stresses under the indentation increase, sources on new slip systems may be activated producing dislocations capable of emerging at the free surface.

Abraham and Altstetter studied slip traces that formed on the faces of thin foil tensile bars in 310 stainless steel before and after hydrogen charging to various hydrogen concentrations and clearly noted an increase in spacing and height of the slip steps after hydrogen charging (Abraham[10]). The result was attributed to an increase of slip localization caused by hydrogen. The decrease in spacing shown in Figure 2 appears to be in direct contradiction to Abraham and Altstetter's results, but the difference could be due to deformation mechanisms that occur during tensile tests versus those of indentation tests. Around an indentation, the deformation seen on the surface does not result from dislocations originally produced at the tip but rather from cross slip or nucleation of additional sources.

If the slip steps visible on the surface are the result of new sources being activated, then the observation can be explained in the following manner. Hydrogen leads to slip localization and increased macroscopic shear stress during dislocation motion, which is consistent with an increased hardness(Birnbaum[6], Altstetter[10]). Each slip step on the surface must result from a dislocation source, and the source must experience some minimum stress to activate. As the macroscopic and localized stresses that evolve during dislocation motion increase, so will the stress acting on each source. As a result, more sources will be activated for a given amount of deformation in the case with hydrogen. On the left side of the indent (Figure 2), with steps resulting from a single slip system, this would result in a decrease in slip step spacing whereas on the opposite side (Figure 3) it would cause increased slip activity on secondary slip systems, as has been observed.

If the surface slip steps are the result of dislocation cross slip, it may be a result of decreased spacing between dislocations in a pile-up. Ferreira et al observed that the equilibrium spacing between dislocations at a pile-up decreases in the presence of hydrogen (Ferreira[5]). As the stress field under the indenter transitions from favoring downward dislocation motion to upward dislocation motion, the dislocations in pile-ups would cross-slip onto a new slip plane before moving to the free surface. Figure 4 demonstrates how the decreased spacing between dislocations at a pile-up could result in a decreased spacing between cross-slip events. This would be manifested in decreased spacing between slip steps as observed in Figures 2 and 3.

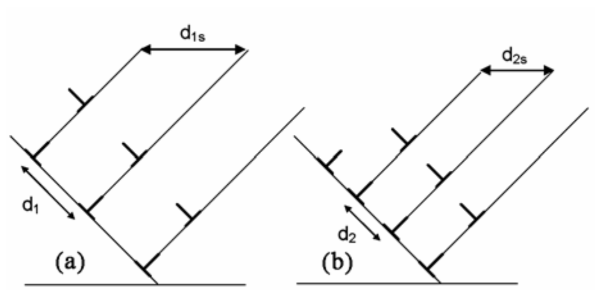

Figure 4. The spacing of dislocations in a pile-up (d_1 and d_2) may directly affect the spacing between slips steps observed on the free surface (d_{1s} and d_{2s}). Without hydrogen (a) the distance between cross slip events observed on the surface would be greater than after hydrogen charging (b).

5 SUMMARY

Observations of slip steps around indentations in FCC stainless steel before and after hydrogen charging indicate that hydrogen does not change the general deformation mechanisms during indentation but does affect deformation at the dislocation level. Hydrogen is shown to cause a decrease in spacing between surface slip steps around indentations in regions where a single slip plane orientation is primarily responsible for the surface steps. This could be the result of the activation of an increased number of dislocation sources or a decrease in spacing between dislocation cross-slip events. HELP theory can be used to explain either case. A decrease in spacing between dislocations at a pile-up, as predicted by HELP theory, could decrease the distance between cross-slip events, while increased macroscopic and localized stresses, also predicted by HELP theory, could result in the activation of more sources.

6 ACKNOWLEDGEMENTS

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