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Correlation between the hydrogen chemical potential and pop-in load during in situ electrochemical nanoindentation

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ABSTRACT

The variation in the pop-in load during electrochemical nanoindentation of Fe 3 wt.% Si alloy at different cathodic polarizations was measured. It is clearly shown that a higher hydrogen chemical potential results in a lower pop-in load, which is an indication of easier dislocation nucleation below the tip. Classic dislocation theory and defactant model are used to analyze the data and calculate the excess hydrogen on the dislocation line at different electrochemical potentials.

It is now well established that the hydrogen interaction with dislocations plays a crucial role during hydrogen embrittlement, through both experimental observation [1–10] and theoretical computation [11–17]. Apart from transmission electron microscopy, one of the most successful recent methods delivering direct evidence for dislocation activity in the metals is nanoindentation [18–27]. During the nanoindentation of perfectly prepared samples with a very low dislocation density, it is possible to observe a homogeneous dislocation nucleation (HDN) below the surface in the volume. The small size of the indenter used during the nanoindentation confines the sheared volume below the surface to a region smaller than the mean dislocation spacing, i.e., ~1 μm for a sample with a dislocation density of $10^{12}m^{-2}$. Then plasticity starts under this condition by HDN within this small sheared volume beneath the tip, and manifests itself in the form of a sudden jump in load–displacement curves, which is usually called pop-in or the yield point phenomenon [28–31]. There have been attempts to study the effect of hydrogen on dislocation nucleation by means of nanoindentation [32–34]. However, in all these attempts, the samples are charged ex situ and then tested with nanoindentation. This limits the testing to metals and alloys which have a very high solubility for hydrogen, like austenitic stainless steels [33], or for which the hydrogen desorption is inhibited by an oxide layer as in vanadium [34]. For most other alloys and metals, it is not possible to study the hydrogen effect on dislocation nucleation after ex situ hydrogen charging. The main reason is the depletion of the hydrogen or the formation of a hydrogen concentration gradient close to the surface of the sample as a result of hydrogen outgassing and desorption from the surface within a short time after the ex situ hydrogen charging. Hence, within the HDN site, which is a few tens of nanometers below the surface, the hydrogen is already depleted or reduced to a very low concentration and no effect will be registered with the nanoindenter. Therefore, we have developed the so-called in situ electrochemical nanoindentation (ECNI) setup by integrating a three electrode miniaturized electrochemical cell into a nanoindentation instrument so the samples can be electrochemically charged in situ with hydrogen [35,36]. The ECNI has been intensively used for studying the hydrogen effect on HDN in different alloys and metals charged in situ with hydrogen evolved from aqueous electrolytes [37–40]. It should be noted that one big shortcoming of aqueous solutions is their high solubility for oxygen. Due to the limited volume of our cell, it is not possible to remove the oxygen by bubbling with inert gas. This dissolved oxygen can interact with the surface and as a result, corrosion and out-of-control reactions can take place locally on the sample surface, which in turn contaminate the electrolyte and roughen the surface through localized corrosion. Therefore, a typical ECNI test in aqueous solution is limited to a few hours of testing, which in turn limits the number of different conditions (cathodic and anodic) that can be tested. In this paper, we report the very first attempts to perform ECNI inside a glycerol based electrolyte. The advantage of this electrolyte is its extremely low solubility and diffusivity for oxygen [41,42]. This makes it possible to perform ECNI over a very long time without any alteration

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of the sample surface and its impact on the nanoindentation measurements. The sample we used was a commercial Fe-3 wt.% Si alloy received in coil form with 1 mm thickness. The composition of the alloy is given in Table 1, as provided by the producer. A circular Fe-3 wt.% Si sample was cut from the coil by spark erosion and heat treated at 1200 °C for one week in order to achieve big grains in the range of a few millimeters. Nanoindentation tests at all cathodic and anodic conditions were confined to a single grain to exclude any orientation effects. The specimen was mechanically and electrochemically polished according to the procedure given in [43]. The details of the experimental setup are given elsewhere [44].

The experiments were performed with a Hysitron Tribo-Indenter®. The indenter tip, designed specially for testing in liquid, was a Berkovich diamond tip. The load function used for the indentation consisted of a loading segment with a 12.5 mN/s loading rate and a 0.5 s holding time at the peak value of 2500 μN, with an additional 0.25 s holding time at 10% of the peak value during unloading for drift correction [39].

In order to avoid any Cl ion contamination of the electrolyte, a double junction $Hg/HgSO_4$ reference electrode was used and all potentials are reported versus this electrode. The resulting representative load–displacement (L–D) curves at different potentials are shown in Fig. 1. The topography of the sample surface during the course of the test was continuously inspected by means of imaging the sample surface using the same tip as for nanoindentation. The topography images from the sample surface at three different conditions are also shown in Fig. 1, where the alteration in the surface RMS roughness was less than 1 nm over 1 μm^2. This ensures that the observed changes in the pop-in load are not due to the change of the surface, but the dissolution of hydrogen in the metal at cathodic polarizations. The variation of the mean pop-in load at different potentials together with its standard deviation are given in Fig. 2. During nanoindentation, the shear stress resulting in HDN can be assumed to be the maximum shear stress beneath the indenter at the onset of a pop-in. According to continuum mechanics, the position and value of the maximum shear stress, $z_{(\tau_{max})}$ and τ_{max}, are given by [39].

$$z_{(\tau_{max})} = 0.48\left(\frac{3PR}{4E_r}\right)^{\frac{1}{3}} \quad (1)$$

$$\tau_{max} = 0.31\left(\frac{6E_r^2}{\pi^3 R^2}P\right)^{\frac{1}{3}} \quad (2)$$

where P is the applied load, R is the radius of the tip curvature, and E_r is the reduced modulus [39]. A more realistic analysis of the shear stress and its position below the surface can be done by considering the grain orientation, the anisotropic elastic properties of the materials, and resolving the shear stress on probable slip systems below the tip [2]. Here, for the sake of simplicity, we only consider the simple isotropic continuum approach. For Fe-3 wt.% Si and a diamond tip, E_r is equal to 201 GPa [45]. The tip radius was found to be 1750 nm by fitting a Hertzian model to the elastic loading part of the L–D curves. If we insert this tip radius into Eq. (2), we obtain a maximum shear stress for each pop-in load. This maximum shear stress is responsible for the HDN at $z_{(\tau_{max})}$ below the tip. Classic dislocation theory predicts that the free energy required for HDN of a

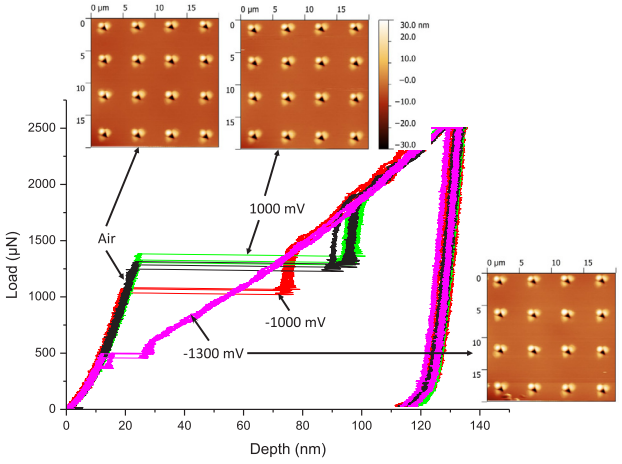

Fig. 1. Representative load–displacement curves in air (Black), at −1000 mV cathodic potential (Red), at −1300 mV cathodic potential (Magenta), and at 1000 mV anodic potential (Green). Insets show the topography of the surface at the respective conditions. All topography images have the same height color scale and are directly comparable with each other. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

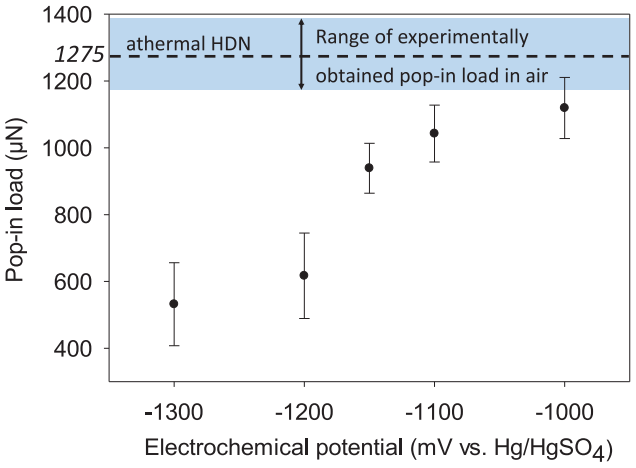

Fig. 2. Variation of the mean pop-in load by potential for Fe-3 wt.% Si alloy

circular dislocation loop with radius r under the action of a uniform shear stress τ is given by the following [46]:

$$\Delta G = 2\pi r\gamma_{dis} - \pi r^2 b\tau \quad (3)$$

The elastic self-energy, γ_{dis}, of a full circular dislocation loop in an infinite isotropic elastic solid is given by

$$\gamma_{dis} = \frac{2-\nu}{1-\nu}\frac{Gb^2 r}{4}\left(\ln\frac{4r}{\rho_{core}} - 2\right) \quad (4)$$

where b is the Burgers vector (0.25 nm), G is the shear modulus (85 GPa), ν is Poisson's ratio (0.3), and ρ_{core} is the dislocation core radius. We can assume that the maximum shear stress in Eq. (2) acts uniformly on a small volume in the range of several Burgers vectors. The isotropic continuum mechanics calculation shows that

Table 1
Composition of Fe-3 wt.% Si alloy used in this study.

Element	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Al	Ti	Nb	V	B	Zr	Ce
Weight%	0.003	2.383	0.202	0.013	0.012	0.033	0.048	0.015	0.020	0.365	0.005	0.020	0.002	0.0008	0.005	0.009

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