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Resolving the hydrogen effect on dislocation nucleation and mobility by electrochemical nanoindentation

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Electrochemical nanoindentation is used to study the in situ effect of electrochemically charged hydrogen on the mechanical properties of austenitic stainless steel (ASS). In addition to the observed reduction of the pop-in load and the increase of the hardness, a novel analysis method based on the Taylor assumption and the indentation size effect is used to calculate the effect of hydrogen on lattice friction. The reduction of the pop-in load is explained within the framework of the defactant model.

Keywords: Hydrogen embrittelement; Dislocation; Stainless steel; Nanoindentation; Indentation size effect

A large number of experimental studies of hydrogen/deformation interactions in ASS show significant effects of hydrogen on the plasticity of this family of alloys [1–6]. A thorough literature survey shows that the experimental conditions (e.g. hydrogen charging conditions, geometry of the sample and stability of the γ structure) must be carefully controlled to justify the apparent inconsistency of some results and to explain the origin of the large contradiction that can be observed in the magnitude of the hydrogen-induced degradation of the mechanical properties. For example, hydrogen charging at high temperature may provide a relatively uniform distribution of hydrogen in ASS, which possesses a relatively low diffusion coefficient for hydrogen at room temperature [7]. However, ex situ mechanical tests on these samples are always affected by the hydrogen gradient in the sample that is produced by the outgassing of hydrogen during the tests. Similarly, conventional mechanical tests with in situ hydrogen charging at room temperature suffer from hydrogen gradients from the surface to the bulk of the sample. In the case of in situ electrochemical hydrogen charging in the presence of hydrogen, recombination poisons like As_2O_3 may lead to lattice distortions of the austenite and an increase of the defect density [8]. Although these observations reflect a strong degradation of the mechanical properties, they cannot account for the hydrogen plasticity interactions, and they cannot be used for the characterization of the hydrogen embrittlement mechanism or the study of the dislocation hydrogen interactions during plastic deformation. A reliable study of the effect of hydrogen on the plasticity of ASS requires (i) charging conditions that do not alter the austenite and (ii) a uniform hydrogen concentration within the probed volume of the material. A moderate charging condition (i.e. electrochemical charging at low current densities and without hydrogen recombination poisons) guarantees the stability of the austenite [9]. However, because of the relatively low diffusion rate and high solubility of hydrogen in austenite at room temperature [10], it is nearly impossible to achieve a uniform hydrogen concentration in a macroscopic sample at room temperature. One possible solution requires a reduction of the sample size [11]. However, scale reduction may introduce complexities to the mechanical testing that are not easy to solve. Another possibility is scaling the reduction of the mechanical test to within the depth of uniform hydrogen concentration at room temperature. This approach is possible by application of the nanoindentation technique [12]. However, it should be noted that the probing depth using this technique is limited to a few tens of nanometers; therefore, testing an ex situ hydrogen charged sample with this technique encounters uncertainties in the hydrogen concentration within the tested volume. Electrochemical nanoindentation introduces the possibility of simultaneous electrochemical hydrogen charging and nanomechanical testing within a very small volume close to the surface, where the hydrogen concentration becomes uniform within a very short time. This technique is already applied for the study of the mechanism of hydrogen embrittlement and hydrogen dislocation interaction in aluminum, copper, nickel [13], iron

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aluminides [11,14] and Fe–3 wt.% Si [15]. In these studies, the effect of hydrogen on dislocation nucleation was studied by focusing on the dislocation nucleation process through the observation of pop-in during nanoindentation. In this paper, we have used electrochemical nanoindentation to study the effect of hydrogen on dislocation nucleation and mobility in AISI 316L ASS (316L-SS).

A cylindrical sample (∅10.6 mm and 1 mm thickness) was cut from a 316L-SS slab. In order to achieve large grains and a fully annealed low-dislocation-density microstructure, the sample was heat treated at 1150 °C for 8 days in a vacuum better than 10^{-5} mbar, followed by cooling in the furnace. Standard surface preparation was used, including mechanical polishing to 1 μm with diamond paste followed by electropolishing in H_2SO_4/methanol [16]. Electropolishing is an important step in the study of metastable ASS because the mechanically deformed layer on the sample surface can undergo a phase transformation from austenite to martensite [17] and the electropolishing step guarantees a fully austenitic sample. A Hysitron TI 750 Ubi™ scanning nanoindentation system with a Performech™ control unit was used to perform the nanomechanical tests. All indents were made with a Berkovich diamond tip, which was used to image the surface of the sample prior to and after indentation, using the in situ imaging option of the nanoindentation system. The hardness and elastic modulus were calculated from load–displacement (L–D) curves, according to the Oliver–Pharr method (Supplementary data). The tip area function was carefully calibrated by indentation on fused quartz within the range 25–300 nm. In order to avoid the orientation effect, all tests were performed on a single large grain. Only indents made far from the grain boundary are considered in the analysis to avoid any influence of the grain boundary on the mechanical properties.

A specially designed three-electrode electrochemical configuration for the Hysitron TI 750 Ubi™ with a platinum counter electrode and an Ag/AgCl reference electrode was used to electrochemically H-charge the sample during nanoindentation. The parameters of the electrochemical cell are described elsewhere [15]. All potentials are reported against the Ag/AgCl reference electrode. The electrochemical H-charging was performed in a 0.5 M Na_2SO_4 aqueous solution, without the addition of any hydrogen recombination poison, by polarizing the sample to −1100 mV.

Typical L–D curves obtained during nanoindentation of the sample under both H-free and H-charged conditions are shown in Figure 1. All of the L–D curves in the figure show three stages: (i) elastic loading, (ii) a pop-in at the onset of plasticity, followed by (iii) elasto-plastic deformation. Interestingly, hydrogen charging clearly affects all of these three stages.

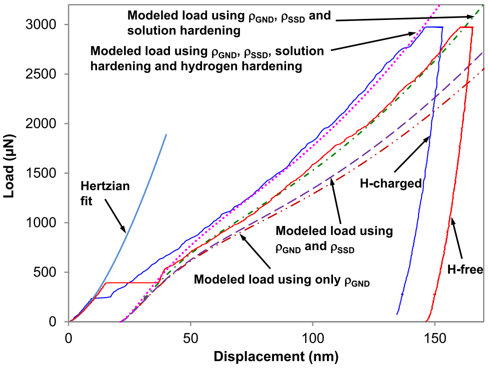

Figure 1. Typical L–D curves of the sample in H-free and H-charged conditions. The solid line is a fit of the initial elastic loading segment to the Hertzian contact model. The elastic–plastic parts of the L–D curves are fitted to the Taylor dislocation model considering different parameters, as stated in the graph.

The initial elastic portion of the loading curves is fitted with the Hertzian elastic response,

$$P = 1.33 E_r \sqrt{R} h^{1.5} \tag{1}$$

in which h is the indentation depth and E_r is the reduced modulus (equal to 192 GPa for 316L-SS) [18]. The radius of the Berkovich tip was found to be 700 nm from the Hertzian fits to the elastic portion of the L–D curves in Figure 1. Typical dislocation densities in an annealed metal are in the range of 10^{10} to 10^{12} m^{-2}, with dislocations spaced between 1 and 10 μm apart. A typical indentation test in the elastic regime probes a lateral region with a maximum size of a couple of hundred nanometers, to the point where pop-in is noted. This suggests that the volume of material sampled by the indentation test at this depth is smaller than the average dislocation spacing, so that an indentation placed randomly on the surface would have a significant probability of sampling a region that contains no pre-existing dislocations. The absence of dislocations means that the material continues to load elastically until the shear stress under the tip reaches a value near the theoretical shear strength τ_{th} of the material, well above that necessary to activate an existing dislocation source [19,20]. At this point, dislocations are homogeneously nucleated, followed by subsequent glide and multiplication events. It can be assumed that the applied shear stress that nucleates a dislocation is the maximum shear stress beneath the indenter during the pop-in. According to continuum mechanics, the maximum shear stress acts on a point located 0.48 times the contact radius (a) below the sample surface and is given by the following expression:

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

This maximum shear stress is responsible for the homogeneous dislocation nucleation (HDN) below the tip. Classic dislocation theory predicts that the free energy required for HDN of a circular dislocation loop with radius r under the action of a uniform shear stress τ is given by the following [21]:

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

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

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

where b is the Burgers vector (0.254 nm), μ is the shear modulus (80 GPa), ν is the Poisson's ratio (0.3) and ρ_{core} is the dislocation core radius ($\sim b/2$).

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 this assumption is