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Hydrogen-induced softening in nanocrystalline Ni investigated by nanoindentation

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ABSTRACT

The influence of hydrogen on the plastic deformation of nanocrystalline nickel was analysed by recourse to nanoindentation on the uncharged and hydrogen-charged samples. It was revealed that, in nanocrystalline Ni, hydrogen significantly decreases hardness but does not alter the strain rate sensitivity. Through thermal desorption spectroscopy measurement, charged hydrogen was expected to reside in face-centred cubic lattice, grain boundaries (GBs) and vacancies rather than dislocations. The hydrogen-induced softening behaviour is discussed in terms of the possible roles of hydrogen in GB-assisted dislocation flow mechanism.

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1. Introduction

Over the past two decades, mechanical behaviour of nanocrystalline (nc) metals and alloys has been one of the extensive research topics in structural materials community [1–3]. Now it is well accepted that their outstanding mechanical performance, compared to conventional coarse-grained materials (e.g. ultra-high yield and fracture strengths, superior wear resistance and enhanced superplastic formability at lower temperatures and faster strain rates) basically originates from the large volume fraction of grain boundaries (GBs).

One of the practically important issues in the applications of structural materials is the influence of hydrogen (H) on mechanical behaviour (especially, H-induced degradation such as embrittlement), since structural materials are easily exposed to H which is known to seriously affect the mechanical properties of most metals and alloys [4–6]. Therefore, it is somewhat surprising that, although nc metals are often considered as a promising next-generation structural material, almost no systematic research has been performed on the H effects on the mechanical behaviour of nc metals. Up to date, most H studies on nc materials have been limited to H storage property [7], H diffusivity [8] and H-induced phase transformation [9]. In addition to the technological purpose, as the GB-mediated plasticity

substitutes for conventional dislocation nucleation and motion as the dominant deformation mechanism in nc materials [1], the possible breakdown of classical H embrittlement mechanisms provides another scientific motivation for studying H effects on mechanical behaviour of nc materials.

With this in mind, here we explore the mechanical behaviour of electrochemically hydrogenated nc-Ni using a series of nanoindentation experiments using two different indenters. The influence of H on the plastic deformation, strain rate sensitivity and activation volume was systematically investigated, which revealed an interesting phenomenon for the first time (to the best of our knowledge); i.e. H-induced softening in nc metal.

2. Experimental

The examined material was electrodeposited nc-Ni foil with an average grain size of ~ 30 nm, as reported elsewhere [2]. H was introduced into the sample by cathodic charging at room temperature in 1N H_2SO_4 solution including 0.25 g/l As_2O_3 (for avoiding H atom's recombination) for 24 h under a constant current density of 100 mA/cm². The H desorption behaviour was studied by a thermal desorption spectroscopy (TDS) equipped with a quadrupole mass spectroscopy (EX0014, R-DEC Company, Tsukuba, Japan). After charging, the samples were immediately immersed into a liquid nitrogen container and kept there while they were moved to the TDS measurement place. During TDS, hydrogenated samples were put into a vacuum glass tube and heated at a constant rate of 5 °C/min. The flow of H_2 gas that desorbs from the specimen is recorded with an accuracy of 0.01 weight ppm (wppm).

For subsequent nanoindentation tests, the specimen surface was mechanically polished with fine SiC paper (grit number up to 2000) and 0.05- μm colloidal silica to a mirror finish. Nanoindentation tests were conducted using Nanoindenter-XP (formerly MTS; now Keysight Technologies, Oak Ridge, TN, USA) at a peak load of 100 mN under constant indentation strain rates of $\dot{\epsilon} = (dh/dt)/h = 0.01, 0.025, 0.5$ and 0.125 s^{-1} [10]. Two different three-sided pyramidal indenters, Berkovich and cube corner, having different centreline-to-face angles, ψ , of 35.3° and 65.3°, respectively, were used for the tests. More than 20 indentations were conducted for each condition. To minimise the amount of out-gassing that possibly occurs during surface preparation, tests were started within 1,800 s after charging [3,11,12]. After nanoindentation, indentation impressions were profiled with an atomic force microscope (AFM; XE-100, Park Systems, Suwon, Korea).

3. Results and discussion

For understanding the H effects, information about the content of H that is charged into the specimen is essential. Figure 1 exhibits the TDS results where the H content was found to be ~ 4.46 wppm. In addition to H content, Figure 1 also provides information about the interactions between H and microstructures since a distinction can be drawn between different H traps based on the different peak temperatures for H desorption during heating; i.e. each H desorption peak represents the H desorbed from different trapping sites, and if the peak occurs at a higher temperature, it means that the H-trapping sites bind H in a stronger manner and hence require higher temperature so as to release the trapped H [11,13]. In Figure 1, there are three peaks, which indicate three different sites with distinct binding energies for H residing. Although it is not judged in a quantitative way currently,

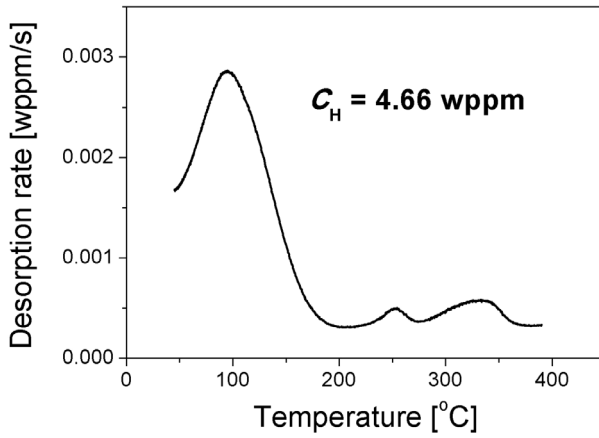


Figure 1. TDS curve of H-charged nc-Ni specimen.

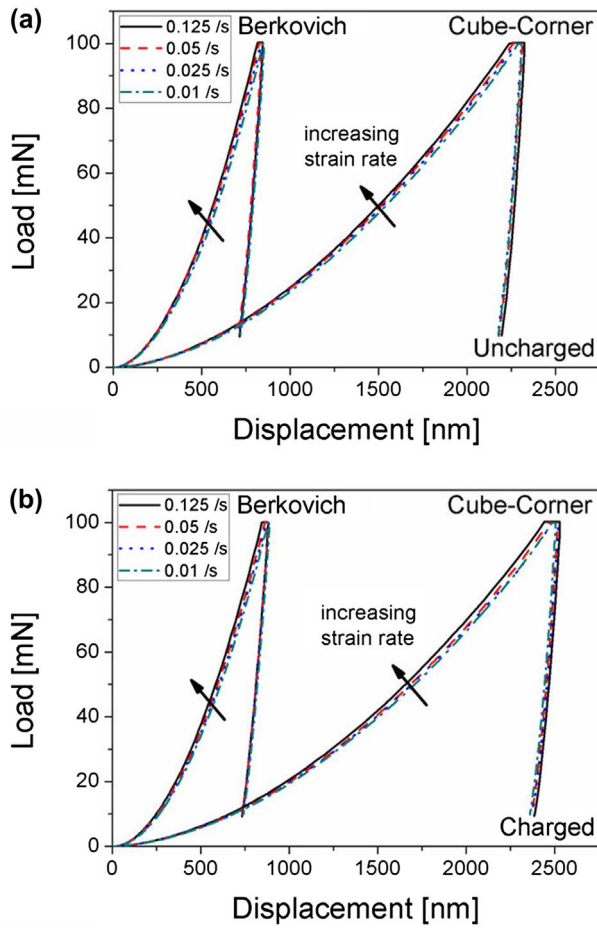


Figure 2. (colour online) Representative load–displacement curves at different $\dot{\epsilon}$ of (a) uncharged and (b) charged specimens.

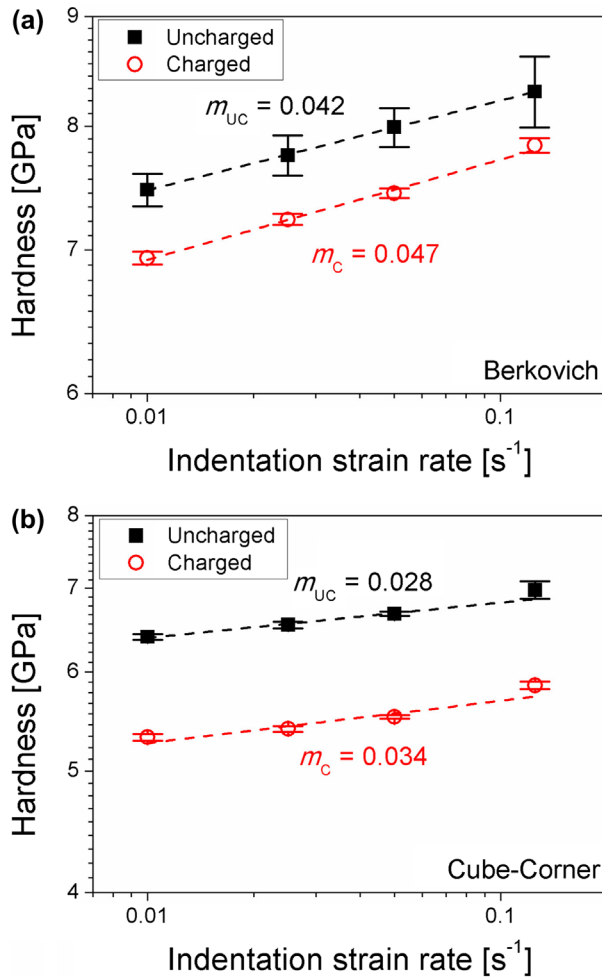


Figure 3. (colour online) Double logarithmic plots of hardness vs. strain rate for estimating strain rate sensitivity; (a) Berkovich and (b) cube corner indentation.

each peak may correspond to lattice sites, GBs [13] and vacancies [14], respectively, in the order from low to high temperature.

Representative load–displacement (P – h) curves of both uncharged and charged samples obtained at various $\dot{\epsilon}$ are given in Figure 2, where two important trends are noticeable: first, at any given $\dot{\epsilon}$, the peak–load displacement (h_{max}) increases after H charging, indicating an H-induced softening; second, there is a non-negligible rate dependency on the h_{max} . From the P – h curves, nanoindentation hardness was estimated according to so-called Oliver–Pharr method [15,16]. Hardness changes with $\dot{\epsilon}$ are summarised in Figure 3 as double logarithmic plots.

From the relation between hardness and indentation strain rate $\dot{\epsilon}$ in Figure 2, one can estimate strain rate sensitivity, m , which is a quantitative measure for the rate dependency of the strength, by $m = \partial \ln \sigma / \partial \ln \dot{\epsilon}$ (σ is uniaxial flow stress and can be replaced by hardness in this calculation according to Tabor relation). The estimated m values are also indicated

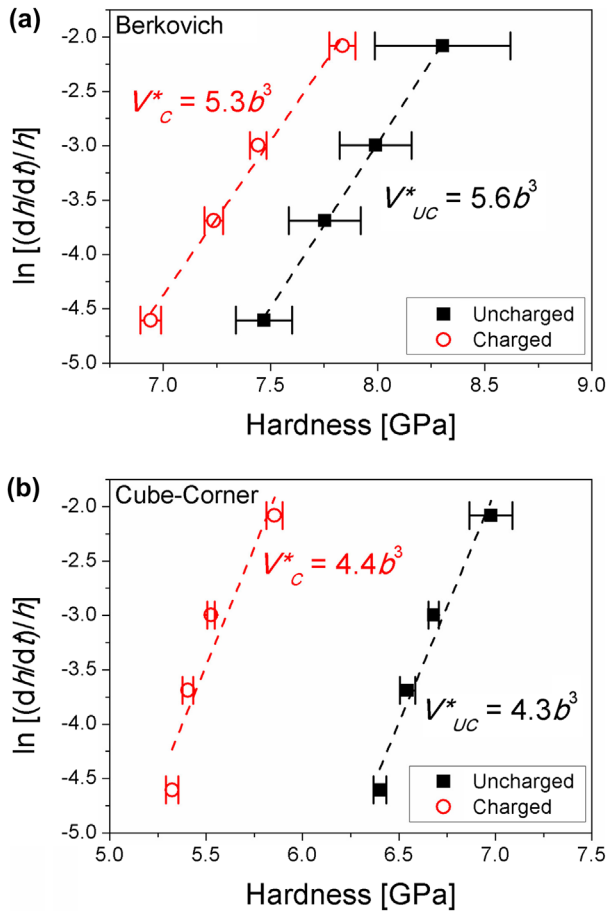


Figure 4. (colour online) Plots of logarithmic strain rate vs. hardness for calculating V^* ; (a) Berkovich and (b) cube corner indentation.

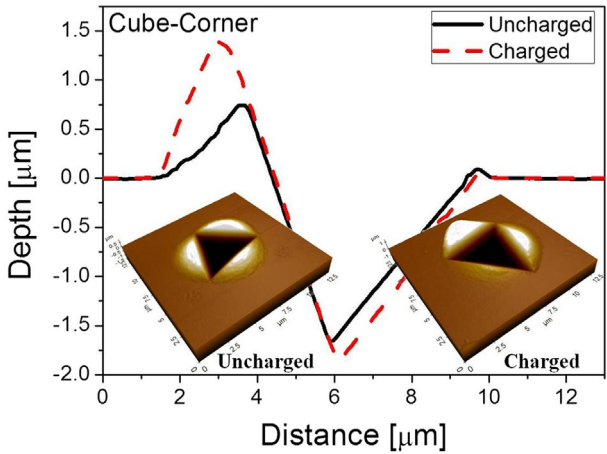


Figure 5. (colour online) Representative AFM images and profiles of nanoindentation pile-ups with cube corner indenter at $\dot{\epsilon}$ of 0.025 s^{-1} in both uncharged and charged nc-Ni specimens.

in Figure 3. For both Berkovich and cube corner indentations, it is clear that, despite the H-induced softening, H-charging induces no significant change in m . Note that m is slightly higher in Berkovich indentation than in cube corner, which can be attributed to the higher strain produced with the cube corner indenter [17] because as m is known to be a function of deformation strains in fcc nc metals [18].

The rate sensitivity of hardness substantially provides a clue for the dominant physical deformation mechanism, as revealed by calculating the activation volume, $V^* = \sqrt{3}kT(\partial \ln \dot{\epsilon} / \partial \sigma)$ [19], where k is the Boltzmann constant, T is absolute temperature, σ can be estimated by Tabor relation for nc-Ni (i.e. hardness is $\sim 4\sigma$) [2,20]. The calculated V^* is illustrated in Figure 4. For uncharged nc-Ni, m is ~ 0.03 – 0.04 and V^* is ~ 4 – $5b^3$ (where b is the Burgers vector of Ni, 0.249 nm) with two indenters, which is in a good agreement with literature data on nc-Ni [21]. Such low V^* for dislocation-mediated flow in nc metals is due to the change in predominant dislocation nucleation sources in nc metals from Frank–Read-type sources (which are typical in coarse-grained metals) to GBs [18]; i.e. in nc metals, a full dislocation or a complete set of partial dislocations are generally emitted from the GB and traversing a grain [1,18].

Similar to the trend of m , it is obvious in Figure 4 that V^* is barely affected by H charging, implying that predominant deformation mechanism (i.e. GB-assisted dislocation flow) remains unchanged in hydrogenated samples. Also, no detectable change in microstructure by hydrogenation was found during observations of optical microscope and scanning electron microscope; for example, no change in grain size. Therefore, the absorbed hydrogen does not change microstructure and deformation mechanism but only softens, which indicates that the hydrogen facilitates the given deformation mechanism.

In conventional coarse-grained metals, H-induced softening has been attributed to the H-assisting dislocation motion either through modifying the Peierls potential to increase screw dislocation mobility (especially, for body-centred cubic metals [22]) or through elastic shielding effect of H on the interactions between dislocations (for both body-centred and face-centred cubic metals [4]). In nc metals, however, these models may not be applicable because of abovementioned different deformation mechanism induced by large volume fraction of GBs.

Although the detailed scenario of H-induced softening in nc metal is not fully understood at this point, some possible mechanisms may be proposed as follows. As shown in the first peak of the TDS results, the majority of H may reside in the lattice, which has been found to lower the stacking fault energy (SFE) in fcc metals and alloys [23,24]. Such SFE reduction caused by interstitial elements (e.g. C and N) has been one of well-known solid solution strengthening mechanisms in conventional coarse-grained metals and alloys (that is referred to as ‘Suzuki effect’ [25]); i.e. in which the lowered SFE increases the separation of the partial dislocations and thus a certain amount of strengthening can be achieved by the limited activity of partial dislocation motion and cross-slip. In nc materials, however, due to the extremely short dislocation movement path, the role of cross-slip may become less important and a pair of partial dislocations are known to move more easily. Partial dislocations can nucleate at stresses lower than that required for the equivalent perfect dislocation source [26,27]. Therefore, the partial dislocations that are emitted from GBs may play an important role in plastic flow in nc-Ni due to the effect of lattice H to reduce the SFE, causing the observed H-induced softening.

A possible mechanism that could also contribute to the softening may be the H-vacancy interaction that is often utilised for rationalising H-enhanced local plasticity (HELP) theory. In crystalline metals and alloys, the attraction between interstitial H and vacancy has been thought to derive higher level of equilibrium vacancy concentration in H-containing metals than in uncharged metals because the formation energy of a vacancy is reduced by trapping H atoms [28]. In this regard, there is a possibility that H and vacancies can accumulate as defect clusters at GBs, which may subsequently facilitate the dislocation emission from the GBs by destabilising the GBs. This possibility is supported by recent first principal calculations [29] suggesting that H stabilises vacancies at GBs and the H-vacancy clusters accumulated at GBs significantly reduce the tensile strength of GBs. Such H-vacancy interaction can also be understood under a thermodynamic frame ‘defactants (DEFect ACTing AgeNTS)’; i.e. H atoms segregating at defects play roles as ‘defactants’ that lower the formation energy of defects such as dislocation loops or vacancies, resulting in HELP [30,31]. Therefore, the drastic enhancement of vacancy creation induced by H and the H-vacancy clusters accumulated at GBs may also contribute to the H-induced softening behaviour observed in nc-Ni.

Another clue for supporting this H-induced softening behaviour is the material pile-up behaviour around hardness impressions. Surface profiles around the indents were examined using AFM. Note that the pile-up observed from cube corner indentations was mainly investigated here since the cube corner tip produces much larger strain underneath the indenter and thus more pronounced pile-up than Berkovich indenter. Indeed, for impressions produced during Berkovich indentation, no obvious change in pile-up was generated by hydrogenation. From the representative line-scan profile from the tests at $\dot{\epsilon}$ of 0.025 s^{-1} (see Figure 5), it can be clearly seen that the material pile-up around the indentation is much more pronounced in the charged sample than that in the uncharged one. It is well known that there are two important material parameters affecting the pile-up behaviour, strain hardening exponent n and the ratio of effective modulus to yield strength E_{eff}/σ_y ; that is, pile-up becomes more developed for a material having smaller n and larger E_{eff}/σ_y [16]. While E_{eff} change by H (which has been reported for single crystal Ni [32,33]) remains as an unclear issue for nc-Ni, H-induced hardness reduction observed in current study is ~ 7 and $\sim 17\%$ for Berkovich and cube corner tip, respectively. Thus, it is reasonable to expect that H may increase the value of E_{eff}/σ_y . In addition, one can imagine that the above-mentioned softening mechanism can make strain hardening more difficult, resulting in decreasing n . These increased E_{eff}/σ_y and decreased n are in good agreement with the more pronounced pile-up in hydrogenated sample, which indirectly support that the possibility suggested above may hold valid.

4. Conclusion

The effects of H charging on the plastic deformation of nc-Ni were examined using the nanoindentation technique. It was expected from TDS analysis that the H mainly resides in fcc lattice, GBs and vacancies. Subsequent nanoindentation experiments revealed that H charging reduces the hardness and enhances the pile-up around indentation. This H-induced softening behaviour of nc metal could be explained by H-enhanced activity of partial dislocations emitted from GBs and/or abundant H-vacancy cluster formation around GBs.

Disclosure statement

No potential conflict of interest was reported by the authors.

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