Embrittlement of Metal by Solute Segregation-Induced Amorphization

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Impurities segregated to grain boundaries of a material essentially alter its fracture behavior. A prime example is sulfur segregation-induced embrittlement of nickel, where an observed relation between sulfur-induced amorphization of grain boundaries and embrittlement remains unexplained. Here, $48 \times 10^6$-atom reactive-force-field molecular dynamics simulations provide the missing link. Namely, an order-of-magnitude reduction of grain-boundary shear strength due to amorphization, combined with tensile-strength reduction, allows the crack tip to always find an easy propagation path.

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The modification of chemical bonds due to a small amount of impurities segregated to grain boundaries (GBs) controls the mechanical properties of materials [1]. Despite decades of intense experimental [2,3] and theoretical [4–6] efforts, however, mechanisms of such GB mechanochemistry [7] are not well understood. In the case of sulfur (S) segregation-induced embrittlement of nickel (Ni), which is important for the development of next-generation nuclear reactors [8], Heuer et al. performed tensile tests of notched specimens with varying amount of S segregation to GBs [3]. (The maximum range of S segregation was determined to be 0.5 nm on either side of a GB.) They observed a transition from transgranular ductile fracture to intergranular brittle fracture at a critical S concentration of $15.5 \pm 3.4\%$ at GBs. In addition, they measured another critical S concentration for amorphization of Ni face-centered cubic (fcc) crystal during $S^+$-ion implantation [3]. The critical S concentration of $14.2 \pm 3.3\%$ for amorphization coincides with the critical S concentration for GB embrittlement within experimental error. These experiments clearly demonstrate an essential relation between amorphization and embrittlement. The central question is: What are the atomistic mechanisms that relate amorphization to embrittlement?

Answering this question poses a so called multiscale simulation challenge [9], i.e., coupling quantum-mechanical accuracy to describe solute chemistry with large length scales to incorporate long-range stress fields and microstructures such as grains and amorphous GB phases. Recent developments in chemically reactive atomistic simulation methods and parallel computing technologies that are scalable over $10^5$ processors (see [10], Fig. S1) [11], combined with those in nanomechanical experiments [12], have set the stage to address this challenge. Namely, simulations and experiments can now study the mechanical properties of nanoscale materials at the same length scale. Here, we perform large molecular dynamics (MD) simulations (see [10], Supplementary Methods) based on reactive force fields (REAXFF) [13,14], which are trained and validated (Supplementary Tables S1 and S2, [10]) by quantum-mechanical calculations based on the density functional theory [15], in order to study the effect of S segregation in nanocrystalline Ni.

We first investigate the effect of S doping on the structure of Ni crystal. Here, we perform REAXFF MD simulation of fcc Ni, where a fraction of Ni atoms in the range of $0\%–24\%$ is randomly substituted by S atoms. The system is a cube of side 3.52 nm with periodic boundary conditions. For each S concentration, the system is relaxed by a steepest-descent procedure and is further relaxed for 5 ps at 10 K, before it is gradually heated up to 300 K. Figure 1(a) compares the radial distribution functions, $g(r)$, for 0% and 24% S substitutions. We observe broadening of the peaks in the latter, which represents the disordering of the fcc structure due to S doping. The FWHM of the first peak of $g(r)$ as a function of S concentration in Fig. 1(b) exhibits a sudden increase at 16%, which is close to the experimental threshold ($14.2 \pm 3.3\%$) for amorphization [3]. In fact, Fig. 1(c) shows that the bond angle distribution at 24% S substitution closely resembles that of amorphous Ni prepared by a melt-quench procedure. The amorphization threshold, 16%, is close to the percolation threshold [16], 14%, for randomly substituted S in fcc Ni, considering the connectivity up to the second nearest-neighbor S atoms at 0.35 nm. In the light of strong S-S interaction in Ni up to 0.33 nm as pointed out in Ref. [4], it is reasonable to identify the amorphization as a percolation transition with 0.35 nm connectivity. In contrast, the 16% amorph-
Crossover from mixed transgranular and intergranular fracture in NC-Ni [Fig. 2(b)] to purely intergranular fracture in NC-Ni + 20%S [Fig. 2(c)]. In NC-Ni, the crack propagates through both grains [transgranular fracture indicated by white arrows in Fig. 2(b)] and GBs (intergranular fracture), resulting in 56% intergranular fracture. Common ductile fracture behaviors such as crack-tip blunting, void formation in front of the crack tip and its coalescence with the main crack, and necking are observed in NC-Ni, in agreement with experimental observations [19]. Figure 2(b) also shows a void extending several GBs, which may explain dimple microstructures observed in fractured NC-Ni surfaces [19]. In contrast, the crack in NC-Ni + 20%S propagates in a cleavage manner only through GBs, resulting in 100% intergranular fracture, in agreement with experiments [3].

FIG. 2 (color). Crossover of fracture modes caused by amorphous sulfide intergranular phases in nanocrystalline Ni. (a) A snapshot of MD simulation, where prenotched nanocrystalline Ni is fractured by applying uniaxial strain. (b) and (c) are close-ups of the fracture simulations for NC-Ni and NC-Ni + 20%S, respectively, where gray, blue and yellow colors represent Ni atoms inside grains (>0.5 nm from GBs), Ni atoms within 0.5 nm from GBs, and S atoms, respectively. White arrows in (b) point to transgranular fracture surfaces.
To determine the mechanism of S-induced transitions of fracture behavior, we first adopt a theoretical framework by Rice and Wang [6], which explains GB embrittlement from the energetics of solute segregation. We perform a tensile test, where the energy required to separate a Ni $\Sigma 5(012)$ symmetric tilt GB is computed with and without a monolayer of segregated S atoms using REAXFF (see [10]). The calculated work of interfacial separation is reduced from 1.65 J/m² for pure Ni GB to 1.20 J/m² with segregated S. From the derivative of the energy-separation relation with respect to separation, we also estimate the tensile stress required to separate the GB. The results show the reduction of tensile (cohesive) strength from 22.0 GPa to 15.5 GPa due to S segregation (Fig. S2. [10]). This suggests S-induced reduction of GB tensile strength as part of the embrittlement mechanism in agreement with Yamaguchi et al. [4]. However, this mechanism alone cannot explain the role of amorphization for embrittlement.

A clue for additional embrittlement mechanism lies in a generalized stacking fault energy (GSFE) [20], i.e., the energy required to slide Ni $\Sigma 5(012)$ GB, without S segregation [Fig. 3(a)], with a monolayer of segregated S atoms [Fig. 3(b)], and with 0.5 nm-thick amorphous sulfide (Ni$_{0.8}$S$_{0.2}$) GB layers [Fig. 3(c)]. The GSFE is calculated by displacing the upper grain with respect to the lower grain, while atoms are allowed to relax only in the vertical direction [Fig. 3(g)]. In Figs. 3(d)–3(f), shear stress is calculated from the derivative of the three GSFEs [Figs. 3(a)–3(c)] with respect to displacement along the [100] direction. The GB shear strength (i.e., the maximum shear stress) drastically decreases from 17.3 GPa [without S, in Fig. 3(d)] to 2.5 GPa [with amorphous sulfide GB phase, in Fig. 3(f)], due to GB amorphization. In contrast, the S monolayer does not decrease the GB shear strength much [Fig. 3(e)] [21]. This amorphization-induced GB shear-strength reduction provides a hitherto missing link between GB amorphization and embrittlement. As Fig. 3(h) illustrates, the shear-strength reduction provides sliding (mode II) fracture paths in front of the crack tip if the GB ahead of the crack tip is not perpendicular to the tensile direction, while the S-induced tensile-strength reduction provides crack-opening (mode I) paths as in the Rice-Wang model [4,6]. Together, the two mechanisms always provide weak cleavage paths right in front of the crack tip, obviating the void opening that is a signature of ductile fracture in pure Ni [Fig. 2(b)], and making the fracture with S segregation purely intergranular and brittle. Sliding of unaccommodated GBs has been postulated as a failure mechanism of NC-Ni [19], which is made easy here by the soft amorphous intergranular phases. Such GB phases endow broad materials with unique mechanical properties, e.g., superhard nanocrystalline ceramics [22].

Because of the reduction of GB shear strength by amorphization, plastic activity within grains [23] is suppressed. We use a common neighborhood parameter (CNP) [24] to identify topological defects such as dislocations and twins during the fracture simulations in NC-Ni and NC-Ni + 20%S. In NC-Ni, dislocations formed at a GB (dislocation source) are absorbed by another GB (dislocation sink). Figure 4(a) is a snapshot (color-coded by CNP) of ductile fracture in NC-Ni, where the green stripes show grains that have deformation twinning. The atomic configuration of the twinning structure in Fig. 4(b) is similar to those observed experimentally [25], and such localized plasticity in NC-Ni is consistent with experimental observations [19]. These plastic activities inside grains are largely suppressed in NC-Ni + 20%S, where plastic deformations are confined in soft amorphous GB phases because GBs fail under shear before dislocations within grains nucleate. The number of intragrain defect atoms (as identified by the CNP) is plotted as a function of time in Fig. 4(c). The number of intragrain defect atoms (as identified by the CNP) is plotted as a function of time in Fig. 4(c).

Another signature of embrittlement is the reduction of toughness, which is a consequence of reduced plastic activity. Figure 4(d) compares the stress-strain relations calculated ahead of the notch for NC-Ni and NC-Ni + 20%S. The toughness (the area under the stress-strain curve) is 0.101 GJ/m³ and 0.0898 GJ/m³ for NC-Ni.
and NC-Ni + 20% S, respectively. Furthermore, the stress-strain curve for NC-Ni + 20% S exhibits the characteristics of brittle fracture, i.e., a sudden drop of the stress to zero at a critical strain. In contrast, the stress-strain curve of NC-Ni exhibits nonzero stress up to much larger strains—a characteristic ductile behavior [26].

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[17] As expected, with 20% S doping, GB sulfide layers have amorphized during sample preparation.
[21] Quantum-mechanical calculation based on density functional theory confirms that a monolayer of S at GB does not reduce the shear strength.
[26] The plasticity of nanocrystalline Ni is known to be reduced compared with that of Ni single crystal, see D. Farkas, S. van Petegem, P. M. Derlet, and H. van Swygenhoven, Acta Mater. 53, 3115 (2005).

FIG. 4 (color). Ductility of nanocrystalline Ni with and without S segregation. (a) Close-up of fractured NC-Ni, where the atoms are color-coded according to the common neighborhood parameter (blue represents atoms with perfect fcc structure). Green stripes represents twinning boundaries. (b) The inset magnifies a deformation twinning in one of the grains, where yellow and blue colors denote the twinning boundary and perfect atoms, respectively. (c) Number of intragrain defect atoms for NC-Ni (red) and NC-Ni + 20% S (blue). (d) Stress-strain relation ahead of the notch for NC-Ni (red) and NC-Ni + 20% S (blue).