

The effect of Nb additive on Te-induced stress corrosion cracking in Ni alloy: a first-principles calculation (Postprint)

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Abstract

Nb can improve the resistance of Ni-based Hastelloy N alloy to Te-induced intergranular embrittlement. First-principles calculations are performed to research this mechanism by simulating the Ni(111) surface and the 5(012) grain boundary. The calculated adsorption energy suggests that Te atoms prefer diffusing along the grain boundary to forming the surface-reaction layer with Nb on surface of the Ni alloy. First-principles tensile tests show that the Nb segregation can enhance the cohesion of grain boundary. The strong Nb-Ni bonding can prevent the Te migration into the inside of the alloy. According to the Rice-Wang model, the strengthening/embrittling energies of Nb and Te are calculated, along with their mechanical and chemical components. The chemical bonds and electronic structures are analyzed to uncover the physical origin of the different effects of Te and Nb. Our work sheds lights on the effect of Nb additive on the Te-induced intergranular embrittlement in Hastelloy N alloy on the atomic and electronic level.

Full Text

Preamble

The Effect of Nb Additive on Te-Induced Stress Corrosion Cracking in Ni Alloy: A First-Principles Calculation

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Abstract: Niobium can improve the resistance of Ni-based Hastelloy N alloy to tellurium-induced intergranular embrittlement. First-principles calculations are performed to investigate this mechanism by simulating the Ni(111) surface and the $\Sigma 5(012)$ grain boundary. The calculated adsorption energy suggests that Te atoms prefer diffusing along the grain boundary rather than forming surface-reaction layers with Nb on the Ni alloy surface. First-principles tensile tests show that Nb segregation can enhance grain boundary cohesion. The strong Nb-Ni bonding can prevent Te migration into the alloy interior. According to the Rice-Wang model, the strengthening/embrittling energies of Nb and Te are calculated, along with their mechanical and chemical components. The chemical bonds and electronic structures are analyzed to uncover the physical origin of the different effects of Te and Nb. Our work sheds light on the effect of Nb additive on Te-induced intergranular embrittlement in Hastelloy N alloy at the atomic and electronic level.

Keywords: Nb, Hastelloy N, Te, First-principles calculations, Stress corrosion cracking, Molten salt reactor

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Introduction

The Molten Salt Reactor (MSR) is the only liquid-fueled reactor among the six most promising Generation IV reactor concepts [1]. As the structural material developed specifically for MSR, Hastelloy N—a Ni-based alloy—exhibits excellent corrosion resistance against molten salt and was used in the Molten Salt Reactor Experiment (MSRE) at Oak Ridge National Laboratory (ORNL, USA). However, MSRE revealed that the usefulness of Hastelloy N is limited by its susceptibility to stress corrosion cracking (SCC) induced by tellurium, which represents the most dangerous problem for Hastelloy N [2, 3]. Tellurium, a fission product in fuel salt, tends to diffuse along the surface grain boundaries (GBs) of Hastelloy N and eventually causes intergranular cracking, a phenomenon closely related to SCC.

To tackle this problem, a straightforward approach is to modify Hastelloy N through alloying additions. MSRE found that adding Nb (1%-2%) to Hastelloy N was beneficial in reducing intergranular Te cracking, though embrittlement still occurred [4, 5]. The mechanism of the Nb effect on Te-induced SCC remains unknown: Nb may form a stable and innocuous telluride compound, or Nb may hypothetically form surface-reaction layers with Te in preference to Te diffusion into the alloy along GBs, among other possibilities [4, 5]. Therefore, studies on

this mechanism would be helpful for developing more advanced Ni alloys with adequate resistance to Te for MSR applications.

First-principles calculation is suitable for mechanism investigations at the atomic level and has been used successfully to study effects of dopants or impurities in grain boundaries [6-9]. In this paper, we perform first-principles calculations to clarify this mechanism by simulating a $\Sigma 5(012)$ Ni GB [7, 10] and the Ni(111) surface with the coexistence of Te and Nb. The results regarding the effects of Te on Ni GB are in accordance with our previous work [9].

Computational Details

Figure 1 [Figure 1: see original paper] shows a schematic diagram of a $\Sigma 5(012)$ Ni GB unit cell, which contains two reversely oriented grains with 80 Ni atoms. The atom layers are distinguished by their distance from the GB plane. The GB0 layer represents the hollow sites, and there are four equivalent atomic sites in each layer. Geometry optimization calculations for the GB were performed including cell optimization. We adopted the GB model from Ref. [7] and performed further optimization (including cell optimization) to obtain a more accurate GB model.

The Ni(111) surface is modeled by a slab with a (4×4) surface periodic cell containing six layers of Ni atoms. The calculated lattice constant of bulk Ni used to construct the Ni(111) surface is 3.52 Å, which is in good agreement with experimental results. The bottom layer without Te or Nb is fixed to its optimal bulk position to mimic the bulk environment. The vacuum layer is approximately 12 Å thick. The Nb-Ni(111) surface, with a Nb atom substituted for a Ni atom in the topmost layer (Fig. 1(c)), is also calculated for comparison with the pure Ni(111) surface.

Spin-polarized electronic state calculations were performed within density functional theory (DFT) [11, 12] using the Vienna Ab-initio Simulation Package (VASP) [13]. Projector-augmented plane-wave (PAW) methods [14] were employed with the PBE generalized gradient approximation (GGA) [15]. The wave functions were expanded in a plane-wave basis set with a cutoff energy of 350 eV. The Brillouin zone was sampled using a $3 \times 3 \times 1$ k-point mesh.

First-principles tensile tests were carried out to study the GB strength with Te or Nb in the GB region. To simplify calculations, the lattice dimensions in the GB plane were fixed to neglect Poisson's ratio effects. A uniaxial tensile strain was applied in the GB normal direction (i.e., the [012] direction). At each strain step, the starting atomic configuration was taken from the relaxed configuration of the preceding step with an increment of 2% to ensure a continuous strain path.

Results and Discussion

A. Adsorption Energy of Te

The adsorption energies of Te, E_{ad} , on the Ni(111) and Nb-Ni(111) surfaces are calculated by:

$$E_{\text{ad}} = E_{\text{Te-sub}} - E_{\text{atom,Te}} - E_{\text{sub}}$$

where $E_{\text{Te-sub}}$, $E_{\text{atom,Te}}$, and E_{sub} refer to the calculated total energies of the optimized substrate with the adsorbate (i.e., a Te atom), one isolated Te atom, and the clean substrate, respectively. A strongly negative value of E_{ad} indicates intense binding between the Te atom and the substrate.

As shown in Fig. 1, the top, bridge, hexagonal close-packed (hcp), and face-centered cubic (fcc) sites were considered for adsorption. Table 1 shows the calculated adsorption energies (in eV) of Te at each site on the Ni(111) and Nb-Ni(111) surfaces. The two data groups for the three site types are roughly the same, indicating that this kind of Nb substitution for Ni does not change the Te adsorption energy significantly. However, the hcp site of Nb-Ni(111) is unstable for Te adsorption due to the presence of the Nb atom, and the Te atom is repelled to move from the hcp site to a more distant site (Site 5 in Fig. 1(c)). Consequently, Te atoms do not preferentially form strong binding with Nb atoms on the surface of Ni-Nb alloy. Therefore, the resistance of Nb to Te-induced SCC in Hastelloy N cannot be attributed to the hypothetical formation of surface-reaction layers between Te and Nb. Instead, Te would prefer to diffuse into the alloy along the GBs. The Nb effect in GBs with coexisting Te will be discussed later.

B. First-Principles Tensile Tests

To further understand how the Nb additive affects the Ni GB in the presence of Te, first-principles tensile tests were carried out to investigate the maximum strength of the GB and its fracture process. Te and Nb atoms, which are larger than Ni, prefer to occupy substitution sites (Site 1 in Fig. 1) rather than interstitial sites (Site 0 in Fig. 1) on the GB plane. Therefore, only the substitution case is considered. There are four sites in Layer 1. For simplification, the comparison was made among the clean GB, the GB + Nb layer (4 Nb atoms in Layer 1), the GB + mixed layer of Nb and Te (2 Nb and 2 Te atoms in Layer 1), and the GB + Te layer.

As shown in Fig. 2 [Figure 2: see original paper], the GB + Nb layer exhibits the largest tensile strength (21.3 GPa) at a strain of 28%, while that of the clean GB case is slightly lower. In contrast, the maximum strength of the GB + Te layer is approximately one-half of that for the GB + Nb layer. However, when the four sites in Layer 1 are occupied by 2 Nb and 2 Te atoms, the maximum GB strength increases to 16.4 GPa at a strain of 20%, which represents

a significant improvement compared with the GB + Te layer. Clearly, Nb segregation enhances Ni GB cohesion, while Te in the GB region induces Ni GB embrittlement, thus demonstrating the inhibition of Te-induced SCC in Ni GB by segregated Nb atoms.

In the strain region below 28%, elastic deformation occurs for the GB + Nb layer. From strain = 32%-36%, this GB undergoes plastic deformation, and the positions of atoms in the GB cell are no longer layer-by-layer. For the clean GB, GB + Te layer, and GB + 2(Nb + Te), the fracture surface is indeed the GB plane. However, the fracture surface of the GB + Nb layer is not the GB plane but the plane between Layers 2 and 3 (see Fig. 1). As a result, the Nb(1)-Ni(2) bonds are stronger than the Ni(2)-Ni(3) bonds in the GB + Nb layer and the corresponding Ni(1)-Ni(2) bonds in the clean GB.

C. Strengthening/Embrittling Energy

According to the Rice-Wang model [16], the effects of various elements on GB cohesion can be determined by the strengthening/embrittling energy, ΔE , defined as:

$$\Delta E = (E_{\text{GB,doped}} - E_{\text{GB}}) - (E_{\text{FS,doped}} - E_{\text{FS}})$$

where $E_{\text{GB,doped}}$, E_{GB} , $E_{\text{FS,doped}}$, and E_{FS} represent the total energies of the doped GB, clean GB, doped free surface (FS), and clean FS, respectively. A positive ΔE value indicates GB embrittlement, while a negative value indicates GB enhancement.

To gain deeper understanding, the strengthening/embrittling energy can be decomposed into mechanical and chemical components. The decomposition procedure from Refs. [10, 17-19] was used for this analysis. The calculated ΔE and its mechanical and chemical components for Te and Nb are listed in Table 2. According to the calculated strengthening/embrittling energy, Te (with a positive value) is an embrittler, while Nb (with a negative value) is a cohesion enhancer. The mechanical components of both Te and Nb are positive, which arises because their larger atomic sizes cause GB expansion. In contrast, the chemical component of Nb is strongly negative and plays a dominant role in the strengthening/embrittling energy. However, Te has a small chemical component value, which has little effect on the strengthening/embrittling energy. Therefore, the contrary effects of Te and Nb are mainly attributed to differences in their chemical components. Our results agree well with previous calculations [10, 20] (Table 2).

D. Chemical Bonds and Electronic Structures

The atomic and electronic structures were studied to elucidate the mechanisms underlying the different effects of Te and Nb on Ni GB. The calculated interatomic distances in the GB region are shown in Fig. 3 [Figure 3: see original

paper] for comparison. Being larger than Ni in atomic radius, both Te and Nb induce GB expansion. For example, compared with the clean GB, the Ni(3)-Ni(-3) distances in the GB + Te layer and GB + Nb layer are elongated by 0.58 Å and 0.24 Å, respectively. This expansion can impair GB cohesion, which is consistent with the positive mechanical components of the strengthening/embrittling energies for Te and Nb. Additionally, Fig. 3 shows that Te-induced GB expansion is more severe than Nb-induced expansion, as evidenced by the larger positive mechanical component for Te compared to Nb.

The chemical component of the strengthening/embrittling energy is thought to arise from charge redistribution due to the presence of doped atoms [10]. While the mechanical components for Te and Nb differ only slightly (see Table 2), their chemical components show significant differences. Figure 4 [Figure 4: see original paper] shows the calculated charge density distributions for the clean GB, GB + Te layer, and GB + Nb layer. The Te(1)-Ni(2)/Ni(-2) bond in Fig. 4(b) and the Nb(1)-Ni(2)/Ni(-2) bond in Fig. 4(c) are stronger than the corresponding Ni(1)-Ni(2)/Ni(-2) bond in Fig. 4(a), as judged by the charge densities along these bonds. However, these strong Te-Ni bonds cannot significantly enhance GB cohesion since the bond directions are almost parallel to the GB plane. In contrast, the Ni(2)-Ni(-2) and Ni(1)-Ni(4)/Ni(-4) bonds are normal to the GB plane and provide the main cohesive force holding the two grains together, as shown in Fig. 4(a). Replacing Ni with Te in Fig. 4(b) makes the Ni(2)-Ni(-2) bond much weaker than the corresponding Ni(2)-Ni(-2) bond in Fig. 4(a). However, for the GB with a Nb layer in Fig. 4(c), the Ni(2)-Ni(-2) bond is slightly weaker than the corresponding Ni(2)-Ni(-2) bond in Fig. 4(a), but the Nb(1)-Ni(4)/Ni(-4) bond is obviously stronger than the Ni(1)-Ni(4)/Ni(-4) bond in Fig. 4(a). Consequently, the remarkable differences between the chemical components of the strengthening/embrittling energies for Te and Nb are induced by these charge redistributions. The charge density for the GB + Te layer in Fig. 4(b) is consistent with the result in Ref. [10].

As the conjugation interface between two misoriented grains, GBs serve as ideal channels for migration of corrosive elements (e.g., Te in our case) that induce SCC. As an alloy additive, Nb can segregate to the GB and enhance GB cohesion, which can reduce intergranular Te cracking. The strong Nb-Ni bonds in the GB region can also prevent Te migration along the GB into the alloy interior. Meanwhile, MSRE found that Nb can improve the resistance of Ni-based Hastelloy N to irradiation embrittlement, though this effect may not be useful at operating temperatures much above 650 °C [4, 5]. Our work sheds light on the effect of Nb additive on Te-induced SCC in Hastelloy N at the atomic and electronic level and is very helpful for designing modified Hastelloy N with new additives that can simultaneously improve resistance to both Te-induced intergranular embrittlement and irradiation embrittlement at elevated temperatures.

Conclusion

First-principles calculations were performed to investigate the effect of Nb additive on Te-induced GB embrittlement in Ni alloy. Energetic studies have shown that Te atoms do not tend to form surface-reaction layers with Nb on the Ni alloy surface, and Nb atoms on the surface cannot prevent the preferred diffusion of Te atoms along GBs. However, first-principles tensile tests have demonstrated that Nb segregation in GBs can inhibit Te-induced GB embrittlement. The strong Nb-Ni bonds in the GB region can improve GB cohesion and prevent Te migration along GBs. The strengthening/embrittling energies of Nb and Te were calculated, and the chemical bonds and electronic structures were analyzed to uncover the physical origin of the mechanical and chemical components of the strengthening/embrittling energies.

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