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Effect of nonmetallic solutes on the ductility of zirconium from first-principles calculations

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Abstract. The effect of nonmetallic solutes on the ductility of Zr-X (X= H, N, O and C) by calculating the generalized stacking-fault energies (GSFEs) of {0001} <10-10> and {11-22} <11-23> and (0001) surface energies of Zr-X binary systems using first-principles calculations. Calculation results show that all nonmetallic solutes considered here reduce both the basal and pyramidal SFEs. However, based on values of ductility parameter D , all nonmetallic alloying elements herein have not exhibited the ductility. This work provides a basis for investigating the effect of nonmetallic alloying elements on mechanical properties of zirconium alloys.

1. Introduction

Zirconium alloys are widely used in nuclear power reactors in view of their special properties: good corrosion resistance, adequate mechanical properties, and a low capture cross section for thermal neutrons [1-3]. The addition of alloying elements is useful to modify the comprehensive mechanical properties of zirconium alloys. However, the understanding of alloying effects on the deformation mechanisms of zirconium alloys is insufficient. The stacking fault energies (SFEs) can be predicted by using First-principles calculation based on density functional theory (DFT), which may increase the understanding of responsibility for doped solutes for the deformation modes [4,5].

The generalized stacking-fault energy (GSFE) can exhibit the effect of unstable SFE on the nucleation tendency of dislocations. Zhang *et al.* [6] proposed that solutes Si, O, and N can improve considerably the ductility of magnesium by calculating the ductility parameters D . Our previous calculation [4] demonstrated that alloying elements such as Sn, Fe, Cr and Nb have exhibited great potentials in improving comprehensively mechanical properties of zirconium.

Theoretical study suggest that oxygen is likely to play a critical role in the observed strain-rate and time dependence of (10-12) twinning [7]. More recently, oxygen as nonmetallic elements can considerably enhance the mechanical properties of α -Ti, which are confirmed by both experimental [8] and theoretical [9] investigations. C. Domain, *et al.* [10] reported that the effect of hydrogen on mechanical properties of Zirconium. Furthermore, Chen, *et al.* [11] identified the effect of content of oxygen on the hardness of Zr-Sn-Nb-Fe-Cu alloys. Y. Udagawa, *et al.* [12] clarified that hydrogen in zirconium can reduce both the brittleness and ductility of zirconium. However, the influence of nonmetallic solutes such as N, O, and C on mechanical properties of zirconium has rarely reported,



especially, for that of theoretical investigations. The nonmetallic elements stay at an interstitial site due to differences between atomic sizes of non-metallic elements and zirconium are remarkable. In the present work, we carry out first-principles calculations based on DFT of GSFEs for $\{0001\} \langle 10-10 \rangle$, $\{11-22\} \langle 11-23 \rangle$ slip systems, and (0001) surface energies of Zr-X (X= H, N, O and C). Thus, based on the calculation results above, it may explore the effect of nonmetallic solutes on the ductility of zirconium alloys.

2. Methodology

The calculations were performed using the Vienna Ab initio Simulation Package (VASP) [13], with the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form [14]. The plane-wave cut-off energy was set as 400 eV. The first-order Methfessel-Paxton with smearing of 0.2 eV was used for the structural relaxation until the total energy changes within 10^{-6} eV. Then, the total energy was calculated using linear tetrahedron method with Blöchl correction [15]. The Brillouin zone was sampled using a Monkhorst-Pack mesh of k -points [16] were as follows: $7 \times 9 \times 3$ for both the (0001) basal surface and basal $\{0001\} \langle 10-10 \rangle$ slip system, and $4 \times 7 \times 3$ for the pyramidal $\{11-22\} \langle 11-23 \rangle$ slip system. The electron configurations of each of the elements are as follows: Zr ($4d^2 5s^2$), H ($1s^1$), N ($1s^2 2s^2 2p^3$), O ($1s^2 2s^2 2p^4$), and C ($1s^2 2s^2 2p^2$).

The atomic positions were relaxed only along the direction perpendicular to the slip plane. The supercell contained 49 atoms, and consisted of 12 layers and a vacuum gap of 10 Å between periodically repeated slabs. Two atomic layers close to the upper and lower free surfaces of the cell were fixed, and all atomic positions, except in these two layers, were optimized.

3. Result and discussion

The formula of E_S is as follows [17]: $E_S = (E_{crack} - E_0) / A$, where E_{crack} is the energy of the supercell with a crack and E_0 is the energy of the bulk one, and A is the cross-sectional area of the supercell. The formula of GSFE is as follows [4]: $\gamma_{GSFE} = (E - E_0) / A$, where E is the total energy of faulted supercell, E_0 is the total energy of the original supercell, and A is the cross-sectional area of the supercell. The ductility parameter D for evaluating the intrinsic ductility of materials is as follows [6]: $D = (0.3E_S / \gamma_{us})$, where E_S is the surface energy of two cleavage surfaces and equals to the energy needed for the propagation of a crack, γ_{us} is the unstable SFE which characterizes the resistance to the nucleation of a dislocation and γ_{us} is chose the largest one. The calculated E_S , GSFE and D values are listed in Table 1, respectively. Figure 1 shows the typical supercells for the (0001) surface, $\{0001\} \langle 10-10 \rangle$ and $\{11-22\} \langle 11-23 \rangle$ of Zr-X (X= H, N, O and C).

3.1. GSFE for (0001) $\langle 10-10 \rangle$ basal slip system

Intrinsic stacking faults I_2 is computed due to I_2 is directly determined the partial dislocations from the dissociation of perfect basal $\langle a \rangle$ dislocation. Figure 2a shows the GSFE curves for the (0001) $\langle 10-10 \rangle$ basal slip system of Zr-X binary alloys. The intrinsic SFEs (γ_{is}) and unstable SFEs (γ_{us}) for basal slip are listed in Table 1. Both γ_{is} and γ_{us} are decreased with the addition of nonmetallic elements herein, and the potential to decrease γ_{is} in the order H > C > N > O. The γ_{is} for Zr-C and Zr-H are all positive compared to the γ_{is} for Mg-C and Mg-H (two of the γ_{is} are negative, it indicate that C and H doped in the Mg alloys can exhibit superior strength.) [6]. Thus, it can be found that all the nonmetallic solutes doped in Zr alloys have not enhanced the superior mechanical properties of these alloys.

3.2. GSFE for $\{11-22\} \langle 11-23 \rangle$ pyramidal slip system

Based on pyramidal $\langle c+a \rangle$ slip system can accommodate strain along $\langle 0001 \rangle$ direction is supported by five independent slip systems, thus the ductility of zirconium may enhance. The calculated GSFE curves for the pyramidal $\{11-22\} \langle 11-23 \rangle$ slip system are shown in Figure 2b. Both the unstable and

intrinsic SFEs of pyramidal $\{11\text{-}22\}$ $\langle 11\text{-}23 \rangle$ slip system are decreased with the addition of all the nonmetallic elements herein.

According to Ref. [18], the ductility parameter D is to evaluate the intrinsic ductility of materials under “Mode I” loading for tensile stress perpendicular to the cleavage. The brittle and ductile behaviors can be exhibited by the concentrated stress can be relieved either by propagation of a pre-existing crack or generation and motion of dislocations, respectively, which can be distinguished by calculating the ductility parameter D . It may deduce that the competition between the propagation of a pre-existing crack on the (0001) plane and emission of a pyramidal $\langle c+a \rangle$ dislocation under the load is set along [0001] direction in zirconium alloys. The potential to enhance the intrinsic ductility in the order decreases $O > N > C > H$. It is thus expected that none of the nonmetallic alloying elements herein have improved the ductility of zirconium alloys due to the value of the ductility parameter $D < 1$ for all nonmetallic alloying elements herein [18].

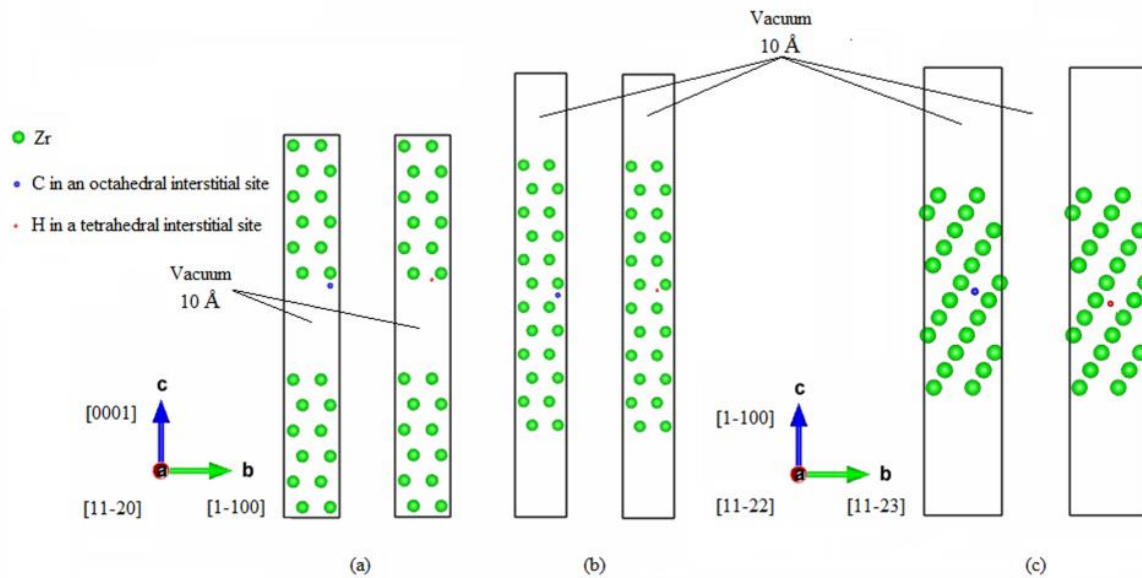


Figure 1. Supercells used in the calculation of (a) (0001) surface energy, (b) $\{0001\} \langle 10\text{-}10 \rangle$ and (c) $\{11\text{-}22\} \langle 11\text{-}23 \rangle$ GSFE curves for the solute staying at a tetrahedral interstitial position and an octahedral interstitial position.

Table 1. The (0001) surface energies (mJ/m^2) and intrinsic SFEs (γ_{is} , mJ/m^2) and unstable SFEs (γ_{us} , mJ/m^2) for Zr_{48}X_1 in (0001) $\langle 10\text{-}10 \rangle$ and $\{11\text{-}22\} \langle 11\text{-}23 \rangle$ slip systems and the ductility parameter D .

	$E_{S(0001)}$	SFE (0001) $\langle 10\text{-}10 \rangle$		SFE $\{11\text{-}22\} \langle 11\text{-}23 \rangle$			D
		γ_{is}	γ_{us}	γ_{is}	γ_{us1}	γ_{us2}	
Zr	968	110	145	228	686	518	0.423
Zr_{48}H_1	935	85	124	166	620	458	0.452
Zr_{48}N_1	1002	98	141	180	610	444	0.493
Zr_{48}O_1	994	100	140	112	582	437	0.512
Zr_{48}C_1	997	97	144	184	625	452	0.479

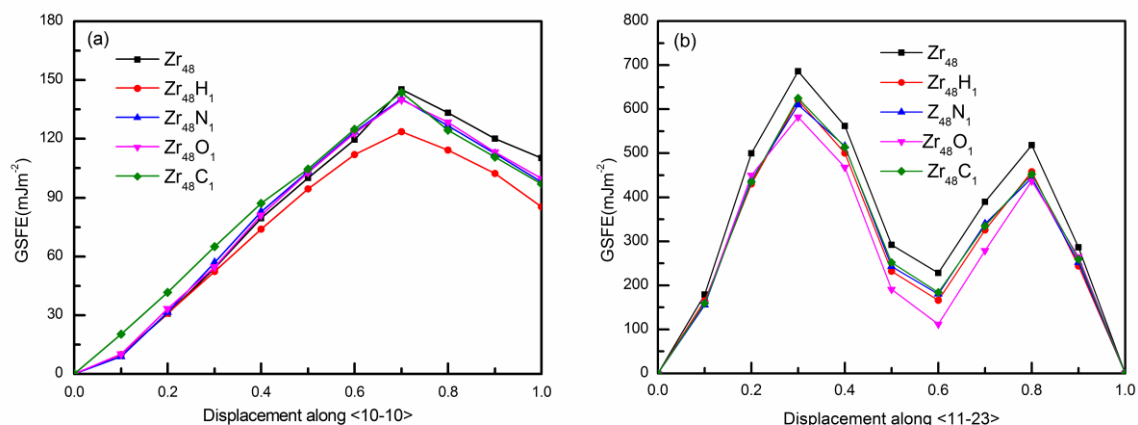


Figure 2. GSFE curves on a (a) basal (0001) <10-10> and (b) pyramidal {11-22} <11-23> slip systems for Zr and its alloys.

4. Conclusions

The GSFEs of Zr₄₈X₁ (X= H, N, O and C) for the basal (0001) <10-10>, pyramidal {11-22} <11-23> slip systems, and (0001) surface energies are computed using first-principles calculations. Both the unstable and intrinsic SFEs for the basal and pyramidal slip systems are decreased with all nonmetallic elements doped herein in Zr. However, Zr-C and Zr-H alloys do not exhibit superior strength as that of Mg-C and Mg-H alloys. It can predict that none of the nonmetallic elements herein exhibit the potential to improve the ductility of zirconium alloys by calculating the ductility parameter *D*. This work provides one approach for judging the role of nonmetallic elements doped in the zirconium which influence the mechanical properties of zirconium alloys.

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