Strengthening mechanism of ω-Zr

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ABSTRACT

The ω-zirconium (ω-Zr) is generally considered as the favorable strengthening phase in the application of Zr and its alloys. However, the intrinsic mechanism is still unclear. In this study, the elastic constants and anisotropic ideal shear strengths of ω-Zr and the common α-Zr phase are systematically studied by the first-principle calculations. Results reveal that the shear modulus of ω-Zr is 1.37 times that of α-Zr. The lowest shear strength of ω-Zr is 3.25 GPa along $(1\,0\,\bar{1}\,0)[0\,0\,0\,1]$, which is about 1.6 times the weakest shear strength (2.01 GPa) of α-Zr along $(1\,0\,\bar{1}\,0)[\bar{1}\,2\,\bar{1}\,0]$. In addition to the high strength, the critical strain of ω-Zr is 0.173, much larger than that (0.072) of α-Zr. The electron localization function (ELF) result shows that there are more electrons highly localized in ω-Zr than in α-Zr along their weakest shear directions, indicating the stronger metallic bonds of ω-Zr as the origin of the high shear strength and strain. In addition, based on the von Mises criteria, the dominating deformation mode for the polycrystalline material of ω-Zr is proposed along the $\{1\,0\,\bar{1}\,0\}\langle0\,0\,0\,1\rangle / \{1\,0\,\bar{1}\,\bar{1}\}\langle\bar{1}\,2\,\bar{1}\,0\rangle$ or $\{1\,1\,\bar{2}\,0\}\langle0\,0\,0\,1\rangle / \{1\,0\,\bar{1}\,\bar{1}\}\langle\bar{1}\,2\,\bar{1}\,0\rangle$ slips, which is helpful to the understanding of deformation behavior in polycrystalline ω-Zr.

1. Introduction

Zirconium (Zr) as a $4d$ transition metal has a small neutron-absorption cross section and excellent corrosion resistance, which has been paid a great deal of attention for its application as fuel rod materials in nuclear technology. The Zr and its alloys were also reported to have outstanding vitro biocompatibility; thus, they are promising for the surgical implants [1]. At ambient condition, Zr crystallizes in a hexagonal close-packed structure ($P63/mmc$), which is known as α phase. The ω phase, a simple hexagonal Zr ($P6/mmm$), has been observed through high-pressure phase transformation of α phase [2,3]. The Zr metal with single α phase commonly have a relatively low yield strength, and the formation of ω phase would greatly benefit the strength enhancement [4]. Up to now, the phase transition of Zr under high pressure and high temperature has been considerably studied [5–9], and the bulk nanocrystalline samples with mixed α and ω phases have also been fabricated by using various methods [3,4]. Catledge et al. [10] measured the hardness of ω phase through nanoindentation technology, the result revealed that ω phase has a hardness increase of 80% over α phase. As a result, the ω phase is widely accepted as the strengthening phase in Zr and its alloys.

To elucidate the mechanism underlying the unique mechanical properties of ω-Zr, several efforts have been made. Zhao et al. [4] pointed out that the non-spherical behavior in the charge density and the relatively bumpy atomic planes of ω-Zr should be responsible for its strengthening. Catledge et al. [10] inferred that the strengthening of ω-Zr can be attributed to the presence of trigonal bonds forming graphite-like nets in the $(0\,0\,0\,1)$ plane, which is expected to exhibit some covalent nature. A very recently study [11] reported that the ω-Zr possesses a ∼26% higher shear modulus and ∼60% higher ideal shear strength than the corresponding values of α-Zr, which are attributed to the relatively stronger component of directional bonding in the ω-Zr. However, the deformation path along the weakest direction in α-Zr was reported to be $\{1\,1\,\bar{2}\,0\}\langle1\,0\,\bar{1}\,0\rangle$ [11], which is inconsistent with the experimental observed prismatic slip system $\{1\,0\,\bar{1}\,0\}\langle1\,1\,\bar{2}\,0\rangle$ [12,13]. In addition, the reported weakest shear deformation path for ω-Zr is basal slip [11]. A texture of prismatic $\{1\,1\,\bar{2}\,0\}_\omega$ plane was observed in an in-situ high-pressure torsion (HPT) study, which can be due to the prismatic slip of $\{1\,1\,\bar{2}\,0\}$ plane in the $[0\,0\,0\,1]$ direction [14]. Therefore, these above discrepancies raise the questions that which is the truly weakest slip system in α-Zr and ω-Zr, and which is the deformation mode in polycrystalline ω-Zr.

In the current work, we systematically investigated the intrinsic mechanical behavior of α- and ω-Zr by analyzing their elastic constants and anisotropic ideal shear strengths via first-principles cal-

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culations. The origin for the high shear strength and strain for ω-Zr has been clearly presented from the change of electron localization distribution during shearing process, and the dominating deformation mode for the ω-Zr polycrystalline material is proposed based on the von Mises criteria.

2. Computational methods

The first-principles calculations based on the density functional theory (DFT) were performed using the Vienna Ab initio Simulation Package (VASP) code [15], with the projector augmented wave (PAW) method [16] for core-valence electron interaction. The Perdew–Burke–Ernzerhof (PBE) [17] form of the generalized gradient approximation (GGA) was employed to describe the exchange–correlation potential. A plane wave energy cut-off of 500 eV was used and the valence electrons for zirconium were in the $4s^2 4p^6 4d^2 5s^2$ configuration throughout the calculation. The selected calculation parameters were all tested to ensure energy convergence less than 1 meV per atom. During the elastic constant calculation, the Γ-centered k point-meshes in the Brillouin zone (BZ) were sampled by $18 \times 18 \times 16$ and $16 \times 16 \times 18$ grids for the primitive hexagonal cells of α-Zr and ω-Zr (Fig. 1), respectively, according to the Monkhorst-Pack method [18]. The Voigt-Reuss-Hill approximations [19] was adopted to obtain the average bulk modulus B and shear modulus G for the presupposed polycrystalline material.

During the ideal shear strength calculation, the orthorhombic cell with 4 atoms was reselected for α phase and the primitive hexagonal cell with 3 atoms are adopted for ω phase (see the green cells in Fig. 1). Monkhorst-Pack grids of $18 \times 16 \times 16$ and $16 \times 16 \times 18$ were used for α-Zr and ω-Zr, respectively. The structure was strained incrementally along the applied shear direction [20]. At each step, the lattice parameter a, b, c, and atomic coordinates in structure were fully relaxed, and the shearing angle was fixed. The structural relaxations were stopped until all the forces on atoms were converged to less than 0.01 eV/Å and all the stress components orthogonal to the applied stress were less than 0.05 GPa. The configuration during shearing process was constructed based on the relaxed structure in the previous strain step, ensuring the continuous strain path at simulation. The corresponding stress for each strain is estimated based on the Nielsen-Martin scheme [21–23]. The current calculation method for the ideal shear strength is fundamentally consistent with those in previous works [11,20,21,24].

Notably, the current calculations were carried out at 0 K and pressure of 0, 5, and −5 GPa. Actually, for the solid materials such as metals, the predicted properties at ground state, i.e. 0 GPa and 0 K, are commonly comparable to those at ambient condition, i.e. 10^{-4} GPa and 300 K. The reason can be due to that: in the free electron gas model, the contribution of temperature (T) to the electron energy (E) can be expressed as E = 1.5K T, where K is the Boltzmann constant. As a result, for the room temperature (300 K), E = 0.039 eV, and this contribution is very small relative to the binding energy of metal. In other words, for most metals, their ground-state lattice parameters and mechanical properties are consistent with those at ambient condition. This situation has been verified by many published calculation works. The previously calculated ground-state lattice parameters and elastic constants for α-Zr were all comparable with those in experimental observations (see Table 2). In addition, the ω-Zr has been experimentally proved to be recovered to ambient condition [3,25]. Based on the above analysis, it is reasonable and of practical significance for the current ground-state calculations of the mechanical properties of α-Zr and ω-Zr.

Though the contribution of ambient temperature to the electron energy is insignificant, the high temperature can significantly affect the materials' properties, for example, the lattice expansion. Prediction of materials' properties at elevated temperatures is still a big challenge for the first-principle calculation. Here we use an alternative method to describe the possible effect of temperature on the mechanical properties of ω-Zr. Because the temperature-generated lattice expansion can also induced by the negative pressure and the simple pressure effect on the energy can be definitely determined by the DFT calculation, we have considered and added the negative pressure (−5 GPa) to ω-Zr, and calculated the corresponding ideal shear strength for the simulation of possible temperature effect.

3. Results and discussion

Table 1 shows the calculated lattice parameters, elastic constants, and elastic moduli of α-Zr and ω-Zr, respectively. The experimental and other previous theoretical results are also listed for comparison. The equilibrium lattice parameters are a = 3.238 Å, c/a = 1.599 for α-Zr and a = 5.054 Å, c/a = 0.624 for ω-Zr. It can be seen that our calculated lattice parameters and elastic constants for the two zirconium allotropes agree well with the experimental data [29–31] and other available theoretical calculations [26–28]. A preliminary comparison of mechanical properties for α-Zr and ω-Zr were made by analyzing their elastic moduli constants. From Table 1, it can be seen that the shear modulus G of ω-Zr is 45 GPa, which is about 1.37 times that of α-Zr. Generally, the higher shear modulus of ω-Zr represents its larger resistance to shear deformation. Moreover, the classical criteria of Pugh's modulus ratio (G/B) [33] separates ductile and brittle materials. A G/B value larger than 0.571 suggests the brittle property, while a smaller one is corresponding to the ductile property. Seen from Table 1, the G/B ratio of α-Zr is 0.343, which is smaller than that of ω-Zr (0.464). This finding indicates that both α-Zr and ω-Zr are ductile in nature, while ω-Zr is relatively more brittle than α-Zr.

The calculated ideal shear strengths as well as the corresponding shear strains for both α-Zr and ω-Zr were obtained from the stress-strain relationships (Fig. 2 and Table 2). Our simulations included the most common slip systems in α-Zr (see the colored planes in Fig. 1). The result shows that the shear strength along $(10\bar{1}0)[\bar{1}2\bar{1}0]$ in α-Zr has the minimum value of 2.01 GPa, indicating that the prismatic slip $(10\bar{1}0)[\bar{1}2\bar{1}0]$ is easiest to start. In comparison, the shear strength along $(10\bar{1}1)[11\bar{2}]$ slip system is 2.19 GPa, slightly higher than that along the prismatic slip, and the start of basal slip $(0001)[\bar{1}2\bar{1}0]$ needs the larger shear stress of 2.75 GPa. The ideal shear strength for another potential basal
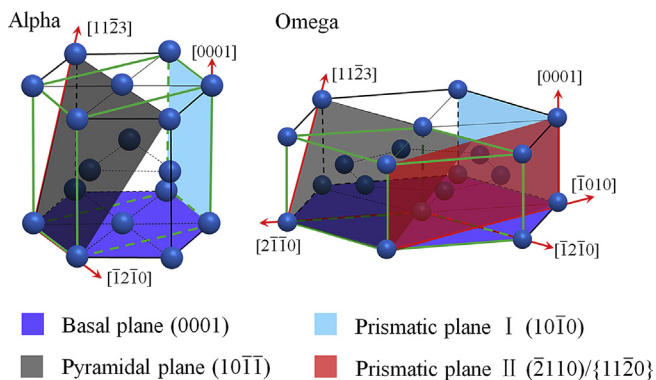

Fig. 1. Crystal structures of α-Zr and ω-Zr. The crystalline planes and orientations are illustrated by colored planes and red arrows, respectively. To simplify the strength calculation, the green orthorhombic cell for α-Zr and primitive cell for ω-Zr are selected, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)