



Evaluation of the structure and properties for the high-temperature phase of zirconium from the atomistic simulations

D.E. Smirnova^{a,b,*}, S.V. Starikov^{a,b}, I.S. Gordeev^{a,c}

^a Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia

^b Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr-University, Bochum, Germany

^c Moscow Institute of Physics and Technology, Moscow, Russia

ARTICLE INFO

Keywords:

Zirconium

Niobium

Zirconium alloys

Molecular dynamics

Diffusion

Interatomic potentials

Phase transitions

Heat capacity

ABSTRACT

We study peculiarities of phase transitions in zirconium and properties of the high-temperature β -Zr phase. To get a more detailed understanding of the structure and thermodynamic characteristics of zirconium, we perform atomistic simulations with two different interatomic potentials. Both potentials demonstrate an unstable behavior of β -Zr phase at low temperatures but explain this phenomenon by substantially different reasons. For one of the potentials, the mechanical instability takes place, and for the other potential the instability of β -Zr is purely dynamic. Review of the available experimental data shows that it is more correct to describe β -Zr through the low-temperature dynamic instability. The structure peculiarity discussed for β -Zr leads to a local non-cubic symmetry of this phase and low formation energy of the self-interstitial atoms. The latter leads to fast atomic self-diffusion that is consistent with existing data. We also perform deformation tests for the atomistic models of β -Zr-Nb alloys taking into account the studied details of α - β transition.

1. Introduction

Zirconium is a constituent of many alloys, which found their application in substantially different areas: from nuclear engineering to medical prosthetics. We can mention as an example for the former case the corrosion-resistant cladding alloy Zr-2.5%Nb [1,2]. As regards the medical applications, zirconium is mostly used as an alloying element. For example, it is part of the Ti-Nb-Zr medical alloys that can provide a combination of optimal elastic and mechanical properties with compatibility with biological tissues [3].

Huge diversity in the produced zirconium-containing alloys is caused by the phase variations observed for zirconium. According to the phase diagram [4], pure zirconium has three allotropic modifications existing at different temperatures T and pressures P . At the ambient pressure and low temperature, zirconium has a hexagonal close-packed (hcp) structure, α -Zr. At $T = 1136$ K, it transforms to body-centered cubic (bcc) β -Zr. At $T = T_m = 2128$ K bcc Zr melts [5]. The third possible crystal modification, ω -Zr, exists in the area of high pressures and has non-close-packed hexagonal symmetry. According to the reported data [4,6], the pressure boundary of α -Zr \rightarrow ω -Zr transition lies in a range between 2 and 6.5 GPa at the room temperature. If we consider some given alloy, its characteristics are strongly correlated with the properties of metal phase on which it is based. Therefore, determination

of the phase stability conditions is an essential issue in the materials science. At the same time, some controversies exist on the phase transitions in zirconium. The range of questions raised is wide, and topics vary from the uncertainty in zirconium melting line to disputes about details of the solid-solid phase transitions. Experimentally the phase diagram of pure zirconium has been studied in the work [4]. Zhang et al. used synchrotron X-ray diffraction and time-of-flight neutron scattering at temperatures up to 1273 K and high pressure. The experiments [4] considered only the solid phase stability regions since the upper-temperature limit is below the T_m . Except for the three known crystalline forms, Zhang et al. have found the extraordinary glass forming ability in zirconium at pressures between 6.4 and 8.6 GPa [4]. Phase diagram of zirconium was also calculated with the help of *ab initio* techniques [7–9]. For example, Ostanin and Trubitsin used the full-potential linear muffin-tin orbital method to estimate the thermodynamical Gibbs potentials and construct P - T phase diagram [7]. In the work [8], an emphasis was made on the determining of the phase diagram and the correct sequence of phases along the shock Hugoniot curve. To our knowledge, there is no reported data on experiments or theory on zirconium melting at high pressures.

Questions about self-diffusion in metals subjected to solid–solid phase transitions also gain significant interest. For example, the experiments performed for β -Zr by Lundy [10] revealed unusual non-

* Corresponding author at: Joint Institute for High Temperatures, Russian Academy of Sciences, Moscow, Russia.

E-mail address: d.e.smirnov@gmail.com (D.E. Smirnova).

Arrhenius temperature dependence of atomic self-diffusion in this phase. One of the hypotheses explaining this fact is related to the local atomic structure changes in the P - T vicinity of the phase transitions occurring in Zr [11]. Other possible reasons for this may include variation in the leading defect configuration (or its formation energy) or interaction with the impurities [12]. However, neither of these versions is supported with sufficient experimental or theoretical data, so the degree of their impact on the phenomena observed is unclear.

Many of the anomalies seen in the physical properties of zirconium are supposed to be a consequence of a very strong anharmonicity [13–15]. The phonon spectra obtained for β -Zr discovered highly anharmonic restoring force for the phonon distortion, which, in its turn, indicates that this phase is unstable at low temperatures [16]. High anharmonicity of the β -Zr also leads to difficulties when attempting to perform low-temperature *ab initio* calculations. It was shown for pure zirconium in [17] that at low temperature hcp structure is more energetically favorable than bcc, so the latter cannot be retained. Calculations made in [17] also showed that there is a possibility to stabilize β -Zr at low temperatures by addition of niobium.

To sum up, we can say that currently there is no fundamental description of zirconium that could accumulate all the existing data and describe a structure of the zirconium phases, their stability details, and phase transitions between them. In this work, we study peculiarities of phase transitions in zirconium and the properties of high-temperature β -phase. For a more detailed understanding of the structure and thermodynamic characteristics, we perform atomistic simulations with two different interatomic potentials. The paper is organized as follows. In Section 2 we examine differences between the used potentials. Section 3 contains information about the structure of β -Zr. In Section 4 we discuss results obtained from calculation of the self-diffusion coefficients in β -Zr. Section 5 is devoted to the investigation of zirconium phase diagram. In Section 6 we review the results of atomistic deformation tests made for the models of β -Zr-Nb alloys.

2. Interatomic potentials for simulation of zirconium phases

Molecular dynamics (MD) is often applied for the study of structural characteristics and physical properties of matter at the atomistic level, and advantages of this simulation technique were described in details in a number of works and reviews [18–20]. In case of zirconium, MD has been used previously for considering various topics, including self-diffusion [21], deformation behavior of polycrystalline Zr [22], the equation of state for Zr phases [23] and martensitic transformations in nanoclusters of pure zirconium [24]. During the last decade, several interatomic potentials were reported for simulation of zirconium [25,26,23]. These potentials have different methodological and physical backgrounds, hence, they reproduce the materials characteristics differently. In such case, comparison between the diverse models gives us an opportunity to look at the properties of zirconium in a broader perspective, as well as to compare the characteristics of the interatomic potentials.

In this work, we use two interatomic potentials: the one offered in 2007 by Mendeleev and Ackland [25], and the other developed by the authors of this work in 2017 [23]. The empirical potential formulated by Mendeleev et al. is based on the embedded-atom method (EAM) [27] and has been applied previously in numerous atomistic simulations of zirconium [28,29]. Originally, the work [25] contains a set of three potentials intended for simulation of different physical properties. As this work is mostly aimed at the study of phase transitions, we use here the potential EAM Zr#2, which was fitted, among other empirical parameters, towards the melting temperature. The potential [23] for a binary zirconium-niobium system has an angular-dependent form, which corresponds to that developed by Mishin et al. [30]. An angular-dependent potential (ADP) is an extension of the EAM model allowing one to take into account the angular dependence of energy. It was shown previously [31] that the use of such potential form might

Table 1

The properties of α -Zr and β -Zr at zero pressure. Results calculated with the interatomic potentials are given in comparison with the existing data for the following properties: average thermal expansion coefficient α_V (in K^{-1}); the energy difference between two phases $E_{\alpha\beta}$ (in eV); elastic constants C_{ij} of β -Zr (in GPa); stacking fault energies (in mJ/m^2) describing stable/unstable configurations.

	ADP	EAM	Experiments	<i>ab initio</i>
α -Zr				
I_2 SFE Basal	60/255	110/330	—	214/260 ^a
SFE Prismatic I	490/505	475/480	—	165/198 ^a
$\alpha_V \times 10^{-5}$	1.9	1.4	2.0 ^b	—
β -Zr				
$\alpha_V \times 10^{-5}$	2.5	2.6	2.9 ^{c,d}	—
C_{11} ($T = 0$)	100	96	—	87 ^e
C_{12} ($T = 0$)	62	109	—	92 ^e
C_{44} ($T = 0$)	38	42	—	27 ^e
C_{11} ($T = 1200$ K)	92	99	104 ^f	—
C_{12} ($T = 1200$ K)	87	85	93 ^f	—
$E_{\alpha\beta}$ ($T = 0$)	0.078	0.052	0.084 ^g , 0.057 ^h 0.076 ^k , 0.125 ^m	—
$E_{\alpha\beta}$ ($T = 1200$ K)	0.043	0.041	0.042 ^p	—

^{c,d} Experimental data from [36,34].

^a Calculations from [46].

^b Based on experiments [37,38].

^e Calculated elastic moduli from [43].

^f Experimentally based moduli from [35].

^g Data from [40].

^h Data from [44].

^k Data from [41].

^m Data from [42].

^p Data from [39].

increase the accuracy of description for the phases with the complex non-cubic symmetry. Besides the differences in the functional form, the potentials discussed here differ in their fitting: in contrast to the EAM Zr#2, ADP Zr-Nb was constructed using *force-matching* technique based on the use of *ab initio* data computed for a set of the reference structures [32,33].

The detailed verification of the potentials was given previously in the works [25,23]. Here, to expand the picture of the potentials capabilities, we report the additional verification results. Table 1 contains a set of properties calculated for α -Zr and β -Zr at zero pressure. For some characteristics of β -Zr, such as elastic constants and the energy difference between the phases, we give the values estimated at two different temperatures: $T = 0$ and $T = 1200$ K. Table 1 also contains information about stacking fault defects energies (SFEs) of the hcp zirconium. Here we should mention that the main assignment of the used potentials is description of thermodynamic properties and phase transitions. Such precondition leads to the fact that both mentioned potentials describe SFEs less precisely than the other potentials specially designed for this purpose: EAM Zr#3 [25] and COMB [26]. However, the summary given in Table 1 allows to make a general impression of the advantages and limitations attributed to the use of selected potentials. For a sake of comparison, we included in the Table 1 available experimental data [34–39] and results of *ab initio* calculations [40–44]. All classical MD simulation and static relaxation runs performed in this work were carried out using the LAMMPS code [45].

In case of zirconium, a question of phase stabilization gains significant interest. The main reason of crystal lattice instability is existence of the soft modes (i.e., imaginary frequencies) in phonon dispersion curves [47–50]. For example, the martensitic transformation from bcc to the hexagonal lattice (bcc \rightarrow hcp) is caused by the soft modes in [1 1 0] wave vector direction, see [48] for details. A special case of instability along [1 1 0] direction for long-wavelength phonons

Download English Version:

<https://daneshyari.com/en/article/7957100>

Download Persian Version:

<https://daneshyari.com/article/7957100>

[Daneshyari.com](https://daneshyari.com)