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An interatomic potential for simulation of Zr-Nb system

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A B S T R A C T

We report a new attempt to study properties of Zr-Nb structural alloys. For this purpose we constructed an angular-dependent many-body interatomic potential. The potential functions were fitted towards the *ab initio* data computed for a large set of reference structures. The fitting procedure is described, and its accuracy is discussed. We show that the structure and properties of all Nb and Zr phases existing in the Zr-Nb binary system are reproduced with good accuracy. The interatomic potential is appropriate for study of the high-pressure hexagonal ω-phase of Zr. We also estimated characteristics of the point defects in α-Zr, β-Zr and Nb; results are proven to correlate with the existing experimental and theoretical data. In case of α-Zr the model reveals anisotropy of the vacancy diffusion, in agreement with previous calculations and experiments. The potential provides an opportunity for simulation of Zr-Nb alloys based on α-Zr and β-Zr. This conclusion is illustrated by the results obtained for the alloys with different niobium concentrations: up to 7% in case of hcp alloys and up to 50% for bcc alloys.

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1. Introduction

Zirconium alloys are widely chosen for structural applications in nuclear reactors. Originally, these alloys found their use as a material for fuel cladding tubes in water-cooled reactor. The choice was made due to low neutron absorption cross-section of zirconium, suitable corrosion resistance in water and appropriate mechanical characteristics [1]. Additionally, it was found that alloying with small amount of niobium (less than 5%) improves the corrosion resistance of the material without increase of the capacity for hydrogenation [2], the latter can cause formation of fragile hydride phase [3]. According to these requirements several alloy compositions are designed and manufactured. The most significant here are dilute Zr-Nb alloys, such as Zr-1%Nb (also marked as E110) and Zr-2.5%Nb (or E125).

Structure of the given alloy is determined by its manufacturing procedure, which can include different heat-treatment and/or deformation [4,5]. Moreover, it has been observed that the Zr-Nb alloys can demonstrate microstructure changes under working conditions [6]. One of the reasons is that pure zirconium has three allotropic modifications existing at different pressures P and temperatures T. At ambient pressure and low temperature zirconium has a hexagonal close packed (hcp) structure, α-Zr. At $T = 1135$ K it transforms to body centred cubic (bcc) β-Zr. At $T = 2128$ K bcc

Zr melts. The third crystal modification, ω-Zr, exists in the area of high pressures and has a hexagonal symmetry. According to the reported data, the pressure boundary of $\alpha \leftrightarrow \omega$ transition lies in a range between 2 and 6.5 GPa at room temperature [4].

One of the most discussed cases related to the structure changes in alloys concerns formation of the precipitates of different phases, for example, β-Nb or metastable β-Zr and ω-Zr. At the same time, characteristics of the material (e.g. corrosion resistance) are strongly correlated with the alloys structure, so its deviations from the intended phase composition cause a change for the worse in durability. Understanding of these relations is required for extension of the materials lifetime, as well as for development of modified zirconium alloys with improved properties. To date many experimental and theoretical approaches have been used to investigate the correlation between structure changes and behaviour of the alloys. It has been stated that some of the precipitates have a positive impact on the alloys durability. For example, Ribeiro et al. [7] have mentioned that the configuration of Zr-1%Nb that consists of α-Zr matrix containing Nb in solid solution and fine β-Nb precipitates provides a combination of high creep resistance and small dimensional changes caused by irradiation. Experimental investigations of the role of precipitates in dilute Zr-Nb alloys have been also done in many works [6,8,9]. For example, the authors in [6] have established dependence of corrosion behaviour of Zr-Nb alloys on Nb content and cooling rate. It has been summarized (from the microstructural study and corrosion test) that the equilibrium Nb concentration below solubility limit (0.6 at.%Nb)

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in a matrix plays more important role to enhance the corrosion resistance than the supersaturated Nb, the β-phase, and the precipitates. Thereby, many aspects can provide an impact on the resulting alloys characteristics. Nevertheless, one should keep in mind that experiments require material resources to determine nature of the exact precipitates in the given alloy. In such cases, it may be useful to involve theoretical approaches to support the experimental study.

Previously several works have been aimed at theoretical investigations of structure of Zr-based alloys. Kharchenko and Kharchenko [2] have reported results of *ab initio* calculations that determined the structural properties of hcp and bcc Zr-Nb alloys with different Nb concentration. CALPHAD approach has been also applied for investigation of the Zr-Nb system. For example, Wang et al. [10] used CALPHAD model to trace concentration dependences of elastic constants of bcc solid solutions of Nb in Zr. The model parameters used in [10] have been based on available experimental and first-principles data. Molecular dynamics (MD) simulation has also found its application in investigation of Zr-Nb system. Previously MD has shown its advantages for study of structural characteristics and physical properties of matter at the atomistic level [11–14]. However, to apply this method to a specific material an appropriate interatomic potential is required [15]. In case of Zr-Nb system several interatomic potentials have been reported up to date. Most of them are aimed at study of pure Zr [16–18] and Nb [19]. Nonetheless, to our knowledge, two interatomic potential models have been developed for study of the binary alloys. Liang, Li and Liu have reported the potential for Zr-Nb system in a series of works [20,21]. In 2008 this research group has proposed a long-range empirical potential for Zr-Nb system, the model parameters have been summarized in [20]. The purpose of this potential was to investigate amorphization in Zr-Nb alloys and an interaction between Zr and Nb layers. The potential model adopted in [21] can reproduce melting temperatures of pure elements along with lattice and elastic constants, which have been used directly for fitting. The fitting base contains no data about point defects, results for defects energies were not presented. In 2013 Lin et al. developed an N-body potential for Zr-Nb system [22] on the basis of the embedded-atom method [23], the latter is also referred to as EAM. The test calculations show that the potential [22] is able to reproduce static properties of α-Zr, β-Zr and Nb, including characteristics of point defects (e.g. vacancies). However, the melting temperatures T_m and thermal expansion coefficients of pure elements reported in [22] are underestimated in comparison with the experimental data. Thereby, it can be said that the potential models reported up to date for Zr-Nb system have different limitations. For example, they were not intended to be appropriate for study of high-pressure ω-Zr. Also, previous MD works [20–22] did not pay significant attention to the behaviour of self-interstitial atoms (SIAs) in Zr and Zr-Nb alloys, while MD investigations of pure zirconium affirm the importance of both types of point defects [24].

A new interatomic potential that was developed in the present work is aimed on simulations of properties of different phases existing in Zr-Nb system, including binary alloys and ω-Zr. For this purpose we use many-body interatomic potential model in an angular-dependent form. The paper is organized as follows. Section 2 contains information about the potential development technique and discussion about its accuracy. In Section 3 we show results obtained from simulations of zirconium phases with the constructed potential. Section 4 is devoted to study of pure niobium properties. In Section 5 the potential is validated by applying it for investigation of point defects characteristics and self-diffusion in Zr and Nb. In Section 6 we evaluate the potential application for simulation of the Zr-Nb binary alloys.

2. Development of a new interatomic potential for Zr-Nb

In this work we develop the interatomic potential for Zr-Nb system based on the form of Angular-Dependent Potential (ADP) [25]. For the ADP the total potential energy U is given by the following formula:

$$U = \sum_{i>j}\varphi_{\alpha\beta}(r_{ij}) + \sum_i F_\alpha(\bar{\rho}_i) + \frac{1}{2}\sum_{i,k}(\mu_i^k)^2 + \frac{1}{2}\sum_{i,k,l}(\lambda_i^{kl})^2 - \frac{1}{6}\sum_i \nu_i^2, \tag{1}$$

where

$$\bar{\rho}_i = \sum_{j\neq i}\rho_\beta(r_{ij}), \quad \mu_i^k = \sum_{j\neq i}u_{\alpha\beta}(r_{ij})r_{ij}^k,$$
$$\lambda_i^{kl} = \sum_{j\neq i}w_{\alpha\beta}(r_{ij})r_{ij}^k r_{ij}^l, \quad \nu_i = \sum_k \lambda_i^{kk}. \tag{2}$$

Here indices i and j enumerate atoms, while superscripts $k, l = 1, 2, 3$ refer to the Cartesian components of vectors and tensors. Indices α and β denote the element types of atoms. The first term in Eq. (1) represents pair interactions between atoms *via* a pair potential φ. The summation is over all j-th neighbours of i-th atom within the cut-off distance $r_{cut} = 6.2$ Å. The second term F is the embedding energy that is a function of the total electron density $\bar{\rho}$. The two first terms in Eq. (1) give principal contribution to the system energy. Additional μ and λ terms introduce non-central interactions through the dipole vectors and quadrupole tensors. They are intended to penalize deviations of local environment from the cubic symmetry. The ADP potential form has been previously applied for study of various binary systems, such as, for example, Al-Cu [26], U-Mo [27] and U-N [28]. The ADP appears to be more sensitive, especially in case of non-cubic structures, compared with the original EAM potential. This conclusion is supported by the recent simulations that revealed local tetragonal distortions in the crystal structure of γ-U and γ-U-Mo alloys [29]. Thereby, we suppose that application of the angular-dependent model can improve accuracy of description for phases with hexagonal, tetragonal, orthorhombic, or more complex symmetry.

In this work we constructed the potential for Zr-Nb system using the force-matching method [30]. This method provides a way to construct physically justified interatomic potentials from the fitting database, which does not contain experimental data. The idea is to adjust the interatomic potential functions to optimally reproduce per-atom forces (together with total energies and stresses) computed at the *ab initio* level for a fine-tuned set of reference structures. In this work optimization of the potential functions was performed with the help of the *Potfit* code [31,32]. The reference *ab initio* data were calculated using the DFT code VASP 5.2 [33]. Each of the reference structures (or so-called *configurations*) contains approximately 200 atoms in a simulation box with periodic boundary conditions (PBC). The exact number of atoms depends on the phase structure, density, and the number of defects included. The Brillouin zone was sampled with the $2 \times 2 \times 2$ Monkhorst-Pack **k**-point mesh [34]. We tested the convergence of the energy in the studied structures using different **k**-points meshes, such as: $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $3 \times 4 \times 4$. According to these tests in our case the $2 \times 2 \times 2$ mesh is suitable for bcc and hcp structures. The same setting is also extended to the case of hexagonal ω-phase. The cut-off energy of a plane-wave basis set was equal to 520 eV. We use projector augmented wave pseudopotentials [35] included in the VASP package and the exchange-correlation functional within generalized-gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof. Twelve electrons $4s^2 4p^6 5s^1 4d^3$ for zirconium and eleven electrons