Effect of cooling rate on structural transformations in Ti-Al-V nanoalloy: molecular dynamics study

N Yu Sdobnyakov, V M Samsonov, V S Myasnichenko, P M Ershov, A N Bazulev, S A Veresov, S S Bogdanov and K G Savina

Tver State University, Tver, Russian Federation

E-mail: nsdobnyakov@mail.ru

Abstract. Using the isothermal molecular dynamics and the tight-binding potential, crystallization of Ti6Al4V nanodroplets was simulated. The objects of the research consisted of 2869 atoms, including 172 Al atoms and 115 V ones. The OVITO program was employed to recognize local structures and nanophases arisen in the course of cooling nanoalloy with the cooling rates of 0.1 and 0.4 K/ps. We have found that the cooling rate effect on the structure of the Ti6Al4V nanoalloy and the thermally induced structural transformations is much more pronounced than the size effect.

1. Introduction

Compared with single-component nanoparticles (NPs), employing binary and multi-component ones significantly expands the range of possible practical applications in catalysis, energetics, optics, electronics, medicine and material science. On the one hand, binary and multi-component NPs, often referred to as nanoalloys, inherit properties of their components. On the other hand, synergism and other unusual tuning effects are possible due to interactions between the nanoalloy components. So, for the last decade nanoalloys attract the attention of many researchers. First of all, bimetallic and trimetallic NPs are intensively studied. Following to other authors [1, 2], we will distinguish between the terms ‘binary’ and ‘bimetallic’, ‘ternary’ and ‘trimetallic’ assuming that in bimetallic and trimetallic nanoalloys components are, to a greater or lesser extent, separated or ordered as, for example, in the core-shell and Janus structures. The variety of possible bimetallic and, especially, trimetallic nanoalloys is very wide. So, entirely empirical experimental research of their properties, as well as search of possible applications do not seem relevant. For this reason, computer simulation methods and, first of all, atomistic simulations [3-6] successfully complement efforts of experimentalists. Among trimetallic nanoalloys the Ti–Al–V systems, including Ti6Al4V [7-9] are of special interest. Being allotropic, titanium has two basic crystalline modifications, i.e. exhibits a martensitic transformation between hcp (α-modification) and bcc (β-modification) structures. Besides, the hexagonal (ω-modification) structure is possible. Other elements added to Ti may be divided into α- and β-stabilizers as they increase or decrease the α → β transition temperature T0, which is (for the bulk Ti) of 1155 K. Of course, T0 should be size dependent, i.e. its value for a nanoalloys of the chosen composition and structure should differ from the bulk value T0(∞) =1155 K.

In our previous paper [5] molecular dynamics (MD) simulation was performed of spherical ternary Ti–Al–V NPs consisting of 2869 atoms (including 172 Al atoms and 115 V atoms) employing the
tight-binding potential [10]. We have found that the structure of the $Ti-Al-V$ nanoalloy is very sensitive to the cooling rate used to reproduce crystallization of the $Ti-Al-V$ nanodroplets. In the present paper the effect of the cooling rate is studied in more detail. Besides, a special attention is paid to structural transformations in the cores of the simulated trimetallic NPs.

2. Approaches to MD simulations and processing MD simulation results

The isothermal MD simulations (NVT-ensemble) were performed by employing our own computer program. NPs under investigation were put into a large enough simulation box of 216 nm$^3$ in volume. Spherical fragments of the bulk $Ti6Al4V$ lattice were used as the initial nanoalloy configurations. Structural transformation were induced by the NP cooling from 1500 K down to almost zero value of 0.001 K with the temperature increment of 3 K between the constant temperature relaxations (annealings). The overall cooling rates from 0.1 to 100 K/ps were reproduced in the performed MD experiments. The choice of the interatomic interaction potential and determination of its parametrization seems to be the central problem of the multi-component nanoalloy simulation. In [11, 12] parametrizations of the tight-binding potential [10] are proposed for Ti, Al and V. So, we determined the cross parameters for the $Ti-Al-V$ alloys as the geometric mean values found in accordance with the Lorentz-Berthelot rules. All the values of parameters necessary for MD simulations are tabulated in our previous paper [5]. The OVITO program [13] was employed to involve the polyhedral template matching [14] (PTM) to identify (recognize) fcc, hcp, bcc and ico local structures and corresponding nanosized phases. Step by step the PMT algorithm compares the local surrounding of the chosen atom with a pattern, i.e. a geometric object of an ideal shape. If an ideal surrounding is recognized, the root-mean-square deviation (RMSD) is calculated. Finally, a structure type with the lowest value of RMSD is attributed to the atom.

3. Results and discussion

In figure 1 some recognized structures of the core of a ternary $Ti6Al4V$ NP are presented corresponding to temperature $T=700$ K and different values of the RMSD cut-off parameter $\xi$.

![Identified structures of a ternary Ti6Al4V NP corresponding to $\xi=0.06$ (a), $\xi=0.09$ (b), $\xi=0.15$ (c), $\xi=0.23$ (d) and $\xi=0.34$ (e). Green color corresponds to fcc atoms, blue to hcp, red to bcc and yellow to ico.](image-url)
Variation of the $\xi$ parameter makes it possible to reveal structures recognized in the NP core and, therefore, to better predict physical and chemical properties, which then may be studied in real (laboratory) experiments.

In comparison with our previous paper [5], we have more accurately taken into account the temperature range corresponding to crystallization. In our MD simulations we used low enough cooling rates of 0.1 K/ps and 0.4 K/ps. In figure 2 diagrams are presented which demonstrate variation of the $Ti6Al4V$ core structure.

**Figure 2.** Variation of the ternary $Ti6Al4V$ NP composition at different cooling rates: 0.1 K/ps (a) and 0.4 K/ps (b). The chosen value of the RMSD parameter $\xi$ was 0.15.

One can see that the phase composition of the $Ti6Al4V$ nanoalloy depends rather on the cooling rate than on temperature (see the shape of the envelope line in figure 2). In the temperature range corresponding to crystallization temperature, variation of the cooling rate makes it possible to tune the final structure of the ternary NP (see the phase composition just after crystallization).
In figure 3 recognized structures are presented, which were formed after crystallization at different values of cooling rate. We have found two nanophases (ico cores and bcc) absent in the final nanoparticle configurations cooled down to 0 K. These phases appear at the early stages of crystallization and correspond to cores of an icosahedra with higher density as well as to bcc areas formed at the grain boundaries inside the nanoalloy.

No doubt that the choice of the interaction potential model for each component affects regularities of the structural transformations in NPs [5, 15]. The effect of the cross-parameters variation seems to be much more pronounced [16].

4. Conclusion
The obtained results seem to be of interest from both scientific and applied points of view. Scientific aspects relate, first of all, to the unusual allotropic nature of Ti, i.e. its transformations from α- to β-modifications. Other components of the Ti6Al4V nanoalloy, being α- and β-stabilizers, make it possible to tune the structural transformations in the nanoalloy under consideration and, respectively, its physical properties. The applied aspect relates to the industrial applications of the Ti6Al4V alloy. It is well known that β-phase in α-matrix increases performance of the Ti6Al4V materials and, in particular, their mechanical properties. So, the Ti6Al4V nanoalloy should also be of interest because of possible applications in nanotechnology.

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