

Molecular dynamics study of the dissolution of titanium nanoparticles in aluminum

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Abstract. The dissolution of a titanium particle in aluminum under the conditions of the crystalline and amorphous state of aluminum and titanium was studied by the molecular dynamics method. It is shown that the state of the aluminum structure has little effect on the intensity of titanium dissolution. This is due to the formation around a crystalline titanium particle, regardless of the initial aluminum structure, of a crystalline layer of aluminum with a thickness of about 1 nm, which repeats the titanium lattice. This layer affects the mechanism and intensity of mutual diffusion near the Ti–Al interface. In the case of the amorphous state of the titanium particle and the aluminum matrix, the dissolution occurred several times faster than in the crystalline state of titanium. That is, the reduction in the ignition temperature of the reaction of high-temperature synthesis in the Ti–Al system is much more efficiently achieved not by amorphization of aluminum, but by amorphization of titanium.

Keywords: molecular dynamics; diffusion; interphase boundary; titanium, aluminum

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Introduction

Intermetallic compounds of the Ti–Al system have a significant potential for their use as high-temperature structural materials for the aerospace and automotive industries. They have a combination of such properties as a high yield strength at elevated temperatures and good resistance to oxidation and corrosion, along with a relatively low density [1–7]. In practice, coarse-grained powders with grain sizes on the order of micrometers are usually used for the reaction synthesis of aluminides [8–10]. Currently, one of the promising methods for their preparation is preliminary mechanical activation treatment, which makes it possible to achieve the limiting degree of grain refinement in a mixture before the main synthesis reaction [11–13]. In the process of mechanoactivation, so-called mechanocomposites are formed, which are a matrix of a more plastic component (aluminum), in the volume of which there are nanosized particles of a more brittle component of the mixture (in this case, titanium) [12,13]. Such a system is characterized by a high degree of nonequilibrium due to

the high concentration of defects, interfaces, internal stresses, and the presence of an amorphous phase. It is noted that the onset of the combustion reaction in such a nonequilibrium system begins at temperatures significantly below the melting temperature of aluminum [12,13].

Earlier, in [14], using the molecular dynamics method, we studied the dependence of the melting temperature of titanium nanoparticles, as well as Ti_3Al , $TiAl$, and $TiAl_3$ particles, on their diameter in vacuum and in liquid aluminum. It has been shown that the melting point decreases as the particle size decreases in proportion to the ratio of the surface area of the particle to its volume. However, the decrease in the ignition temperature of the high-temperature synthesis reaction in mechanocomposites is obviously not associated with a decrease in the melting temperature of titanium nanoparticles, but is apparently due to the presence of internal stresses and an amorphous phase in the mixture, which can contribute to the intensification of mutual diffusion and the release of additional energy. To verify this, in the present work, a study was carried out using molecular dynamics simulation of the dissolution of titanium nanoparticles of different sizes in aluminum under the conditions of crystalline and amorphous states of aluminum and titanium.

Description of the model

The computational cell in the molecular dynamics model had the shape of a rectangular parallelepiped. Periodic boundary conditions were used along two axes, and free (or open) conditions were used along the third. The presence of an open surface allowed the computational cell to freely change the volume during the melting of aluminum or as a result of other processes during mutual diffusion. A round titanium particle was placed in the aluminum matrix at the center of the computational cell (Fig. 1). Aluminum and titanium were initially created in the crystalline state. Particles of three diameters were considered: 5, 7, and 9 nm. In our previous work [14], it was shown that the greatest influence of the particle size on its melting point is observed at a diameter less than about 7 nm. The number of atoms in the computational cell was 32427, 82401, or 179725, depending on the considered particle size. After introducing a titanium particle into an aluminum matrix and removing excess aluminum atoms, the structure was relaxed at a starting temperature of 0 K. After stabilization of the structure and temperature of the computational cell, it was again cooled to 0 K.

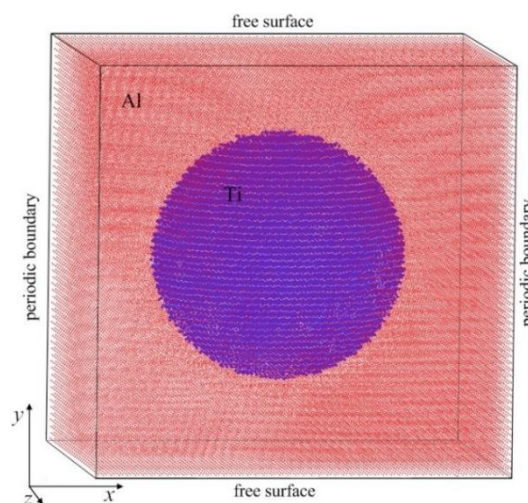


Fig. 1. Computational cell with the round titanium particle in aluminum

To describe interatomic interactions in the Ti–Al system, EAM potentials from [15] were used, where they were obtained based on comparison with experimental data and ab initio calculations for various properties and structures of metals Ti, Al and intermetallic compounds Ti_3Al and TiAl . These potentials have proven themselves well in various studies and have been successfully tested in a wide range of mechanical and structural-energy properties of alloys of the Ti–Al system [14–19]. In particular, the potentials used quite well describe the melting points of Ti and Al: in our molecular dynamics model, they turned out to be 1995 and 990 K, respectively (reference values: 1943 and 933 K).

In addition to the crystalline state of aluminum and titanium, in this work we considered the cases of dissolution of crystalline titanium in amorphous aluminum and amorphous titanium in amorphous aluminum. The amorphous structure of aluminum or titanium was created by heating in the model of the corresponding phase to a temperature significantly higher than the melting point of the metal, holding for some time for the final destruction of the crystalline structure, and subsequent rapid cooling, during which crystallization did not have time to occur. In carrying out this procedure, we sought to minimize the initial mutual diffusion of titanium and aluminum. The quality of the amorphous structure was verified not only by the diagrams of the radial distribution of atoms, but also by the absence of crystallization during the subsequent simulation in the considered phase. For the occurrence of homogeneous crystallization in the molecular dynamics model, as a rule, longer computer experiments were required to be compared to those considered in the present work [18–22].

The temperature in the main computer experiments was set in terms of the initial velocities of the atoms according to the Maxwell distribution. A Nose-Hoover thermostat was used to keep the temperature constant during the simulation. The time integration step in the molecular dynamics method was 2 fs.

Results and discussion

To analyze the intensity of the dissolution of titanium atoms in aluminum, a special characteristic was used – the difference in the number of dissolved titanium atoms ΔN at the current and initial moments of time. A Ti atom was considered dissolved if the number of Al atoms in its nearest environment (within a radius of 3.7 Å) exceeded 50 %. Figure 2(a) shows the time dependences of the percentage of dissolved titanium atoms for particles with a diameter of 5, 7, and 9 nm at a constant temperature of 1200 K, that is in molten aluminum. In all cases, as can be seen in the figure, the dissolution at first proceeded intensively, then the rate decreased and subsequently remained approximately constant. The same character of particle dissolution was noted by other researchers, for example, in [23,24], and is apparently explained by the formation at the first stage of a diffusion zone saturated with atoms of both components.

The ratio of the surface area of a particle to its volume increases as the particle diameter decreases. In this regard, the proportion of dissolved titanium atoms is higher for particles of smaller size than for particles with a large diameter (Fig. 2(a)). Next, we used a value that is universal for particles of different sizes – the specific number of dissolved atoms $\Delta N/S$, which was defined as the ratio of the number of dissolved atoms to the surface area of a particle. Figure 2(b) shows the dependences of $\Delta N/S$ on time at a constant temperature of 800 K for the considered particles in the cases of crystalline Ti and Al, crystalline Ti and amorphous Al, and amorphous Ti and Al.

The first thing that attracts attention is the coincidence of the graphs obtained for the crystalline and amorphous states of aluminum (lower graphs in Fig. 2(b)). The titanium particle in both cases was crystalline. This is an interesting result, indicating that the intensity of titanium dissolution in aluminum is almost independent of the state, crystalline or amorphous, of the aluminum structure. Here it should be emphasized that we are talking about

dissolution at a constant temperature below the melting point of aluminum. Structural transformations and partial crystallization of amorphous aluminum can lead to the release of additional heat in real materials, which can accelerate dissolution. However, at a constant temperature, as the simulation showed, there is almost no difference for the crystalline and amorphous states of aluminum. Small differences in the values of $\Delta N/S$ for particles of different sizes are due to the fact that the interphase boundary has a certain effective thickness, which was also discussed in [14] when studying the effect of particle diameter on their melting temperature.

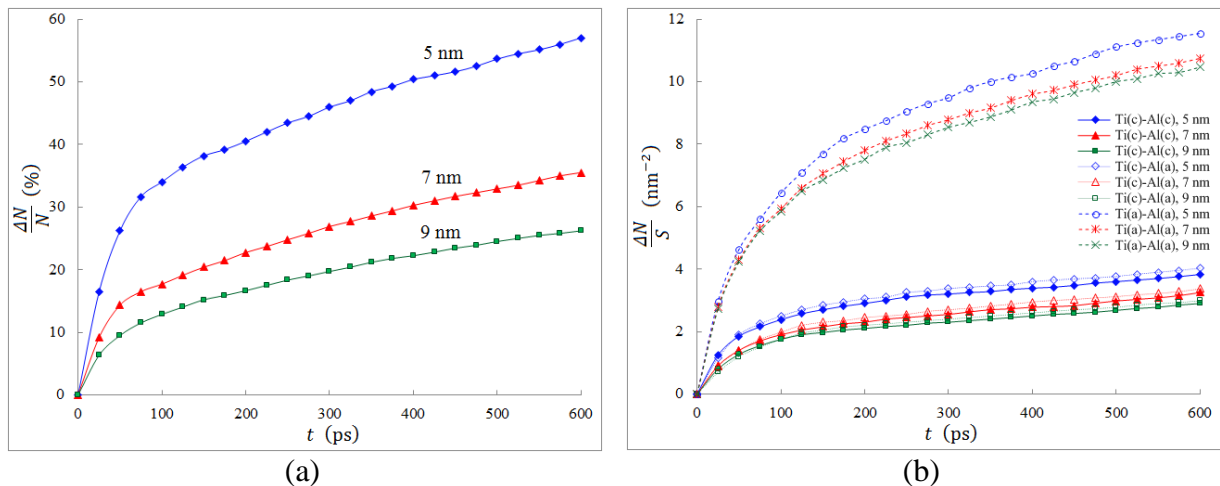


Fig. 2. Dissolution of Ti particles in Al at a constant temperature: (a) time dependence of the percentage of dissolved Ti atoms at a temperature of 1200 K for particles with a diameter of 5, 7, and 9 nm; (b) time dependences of the specific amount of dissolved Ti atoms at a temperature of 800 K for the considered particles in the cases of crystalline Ti and Al, crystalline Ti and amorphous Al, and amorphous Ti and Al

The fact is that, as we noted earlier in [19], when studying the effect of the orientation of the interphase boundary on the intensity of mutual diffusion, regardless of the type of aluminum structure and its orientation, a crystalline aluminum layer several atomic planes thick is formed on the Ti–Al interphase boundary, repeating the crystal lattice of titanium. This layer was observed by us in [19] even at temperatures above the melting point of aluminum and had a significant effect on the mechanism of mutual diffusion at the Ti–Al interface. Figure 3 shows an example of the formation of a crystalline layer in initially amorphous aluminum around a titanium particle 9 nm in diameter. It should be noted that further crystallization of aluminum during the modeling process, as a rule, did not occur, mainly due to the mismatch between the parameters and types of titanium and aluminum crystal lattices. The formation of a crystalline layer of aluminum near the interface with a titanium particle primarily depended on the orientation of the titanium crystal lattice. The thickness of this layer was not the same in different areas of the particle surface (Fig. 3).

When modeling the dissolution of an amorphous titanium particle in amorphous aluminum, the situation changed drastically and, in contrast to the cases with a crystalline titanium particle, the dissolution proceeded much faster (upper plots in Fig. 2(b)). The specific amount of dissolved atoms $\Delta N/S$ for amorphous titanium was several times greater than for a particle with a crystalline structure at the same temperature. Thus, the decrease in the ignition temperature is achieved much more efficiently not by aluminum amorphization, but by titanium amorphization.

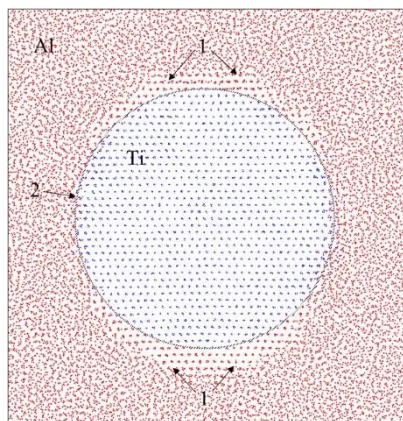


Fig. 3. Formation of a crystalline layer (marked with 1) in initially amorphous aluminum around a particle 9 nm in diameter (particle boundary is marked with 2) at a temperature of 750 K. The figure shows a layer 2 nm thick cut from the computational cell

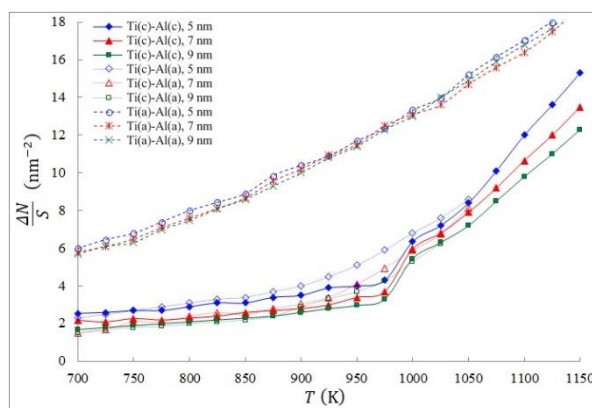


Fig. 4. Temperature dependences of the specific amount of dissolved Ti atoms after simulation for 200 ps for particles 5, 7, and 9 nm in diameter in the cases of crystalline Ti and Al, crystalline Ti and amorphous Al, and amorphous Ti and Al

To further confirm this thesis, we studied the dependence of the specific amount of dissolved Ti atoms on temperature for the same duration of a computer experiment of 200 ps. Figure 4 shows the dependences obtained for the three considered particle sizes and the cases of crystalline Ti and Al, crystalline Ti and amorphous Al, and amorphous Ti and Al.

On Fig. 4 for the case of crystalline Ti and Al, the "ignition temperature" is well identified by a sharp increase in the value of $\Delta N/S$ at a temperature coinciding with the melting point of aluminum. For the potentials used, it is slightly higher than the reference value of 933 K and is approximately 990 K. In addition, it can be seen that the diameter of the particle does not affect the position of the jump in the value of $\Delta N/S$ and coincides for all considered particles. Thus, another important result is the absence of an effect of the titanium nanoparticle diameter on the ignition temperature of the high-temperature synthesis reaction in the Ti–Al system. It should be emphasized that this refers specifically to the temperature at which there is a sharp acceleration of mutual diffusion, and not to the intensity of dissolution, which is proportional to the total area of the interphase boundary and will obviously be higher with a smaller diameter of titanium particles.

In the amorphous state of aluminum, no jumps were observed in the dependences of the $\Delta N/S$ value in the region of the melting temperature. However, these dependences otherwise coincided with the dependences obtained for the case of crystalline aluminum. The absence of a jump in the dependences was obviously due to the absence of a phase transition in aluminum – aluminum in this case was initially amorphous.

In the amorphous state of the titanium particle and the aluminum matrix, the dissolution occurred much more intensively (upper graphs in Fig. 4). In this case, the dependences of the $\Delta N/S$ value did not contain any breaks or jumps. In the entire considered temperature range, the behavior of the dependences had the classical form of the Arrhenius temperature dependence.

Conclusion

The dissolution of a titanium particle in aluminum under the conditions of the crystalline and amorphous state of aluminum and titanium was studied by the molecular dynamics method. It is shown that the state of the aluminum structure has practically no effect on the intensity of titanium dissolution. This is due to the formation around a crystalline titanium particle,

regardless of the initial aluminum structure, of a crystalline layer of aluminum with a thickness of about 1 nm, which repeats the titanium lattice. This layer affects the mechanism and intensity of mutual diffusion near the Ti–Al interface.

In the case of an amorphous state of a titanium particle and an aluminum matrix, the dissolution occurs much more intensively than in the crystalline state of titanium. The intensity of dissolution in the first case already at a temperature of 700 K corresponds to the melting temperature of aluminum in the case of a crystalline titanium particle. That is, a decrease in the ignition temperature of the high-temperature synthesis reaction in the Ti–Al system is achieved much more effectively not by aluminum amorphization, but by titanium amorphization.

The diameter of titanium nanoparticles, as was found in the work, affects the intensity of dissolution of titanium in aluminum, but does not affect the ignition temperature of the high-temperature synthesis reaction.

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