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MOLECULAR DYNAMICS STUDY OF THE THERMAL STABILITY OF Ni_3Al NANONEEDLES

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Abstract. The study of the thermal stability of Ni_3Al nanoneedles in the dependence on the sharpness and crystallography orientation of the needle axis was held using molecular dynamics method. It is shown that the most stability nanoneedles in the conditions of thermal influence are the ones with the axis along [111] direction. Violation of the nanoneedles stability associated with their blunting, which is caused by surface diffusion. Stable radius of curvature of the needles at low temperatures, depending on the angle of the tip and orientation of the needle axis, is 0.6-1 nm.

1. Introduction

At present, the direction of researches related to the development of new materials and nano-devices allocated to one of the most important problems of modern materials science. At the sizes of functional devices that are comparable in size to the ensemble of atoms or molecules, the properties of materials based on nanoobjects are defined not only by physical and chemical characteristics related to the composition, but also with their geometrical sizes, structure and form. With a decrease in the size of the structural elements of the material is growing influence of interfaces (free surface, interphase and grain boundaries) on its properties.

One of the examples of such nanoobjects are needle-like nanocrystals of refractory metals which used, for example, as probes for high-resolution scanning tunneling microscopes, autoemission cathodes for vacuum electronics. Because of the small size, as other nanoobjects, the nanoneedles have a very high proportion of free surface, i.e. percentage of atoms contained in the surface layers and having more energy than atoms in the volume of material. Furthermore, the needles have a high curvature of the surface. Because of these two factors the form of the nanoneedle is relatively unstable under the conditions of thermal influence - the activation energy of surface diffusion is low [1, 2], so that at the increase of temperature the process of blunting of the nanoneedle is intensively occurs.

The present work is devoted to the study of the thermal stability of the nanoneedles made of Ni_3Al intermetallic, having $L1_2$ ordered structure, in the dependence on the crystallographic orientation of the axis of needles and its severity. Choosing Ni_3Al intermetallic is connected with its unique properties: high melting point, low density, heat resistance, high corrosion resistance [3]. The main issue decided in this paper was to find the most stable form and structure of the Ni_3Al nanoneedle.

2. Description of the model

The simulation was held using the method of molecular dynamics. The needle was created as a cone (Fig. 1), which was cut from the Ni_3Al ideal crystal. It was considered three orientation

of the axis of the nanoneedle: [100], [110] and [111] (it is known that the greatest strength of crystals is implemented along the directions with low indexes). The main variable parameters were two-dimensional angle of the needle tip Θ and height of the needle H (Fig. 1a). Fig. 1 shows examples of the starting structure of the nanoneedles with the tip angle of 45° and the axes along the [100] (Fig. 1a) and [111] (Fig. 1b) directions.

Several atomic planes in the base of the cone were rigidly fixed, i.e. motionless during molecular dynamics experiments (in Fig.1 fixed atoms are painted in dark gray color). It was necessary to hold the base form of the needle. There are no conditions were imposed on other atoms, i.e. side surfaces of the needles were free.

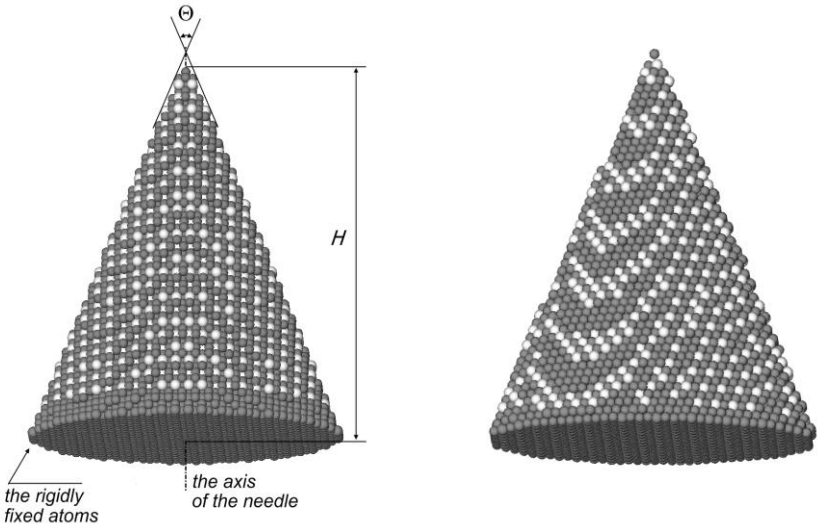


Fig. 1. Examples of the starting structure of the nanoneedles with the tip angle of 45° and the axes along the [100] (a) and [111] (b) directions. Ni – dark atoms, Al – light ones. Dark gray atoms in the base of the cones are the atoms which during the computer experiment remained motionless.

For a description of the interatomic interactions in the present paper the pair Morse potential function was used. Parameters of the potentials were taken from [4]. Experience of application of these potentials shows that with their help is possible to describe various properties of metals and alloys [5-8]. Parameters of potentials describing the interaction of atoms of one type (Ni-Ni and Al-Al), in [4] were determined from the properties of the pure metals by the values of the sublimation energy, lattice parameter and bulk modulus. When determining the parameters of the interaction of atoms of different types (Ni-Al) as an energy characteristic the values of the energies of formation of shear antiphase boundaries in Ni_3Al intermetallide was used. These Morse potentials satisfy the condition of the equilibrium of the alloy lattice, correctly describe the anisotropy of the energies of antiphase boundaries and basic property of intermetallide - to keep order until the melting temperature [4].

The temperature in the model was set by the initial velocity of the atoms according to the Maxwell-Boltzmann distribution [6]. In this case the total kinetic energy was corresponded to predetermined temperature, and the total momentum of the calculation block was zero. The time step in the molecular dynamic experiments was 5 fs ($5 \cdot 10^{-15}$ s).

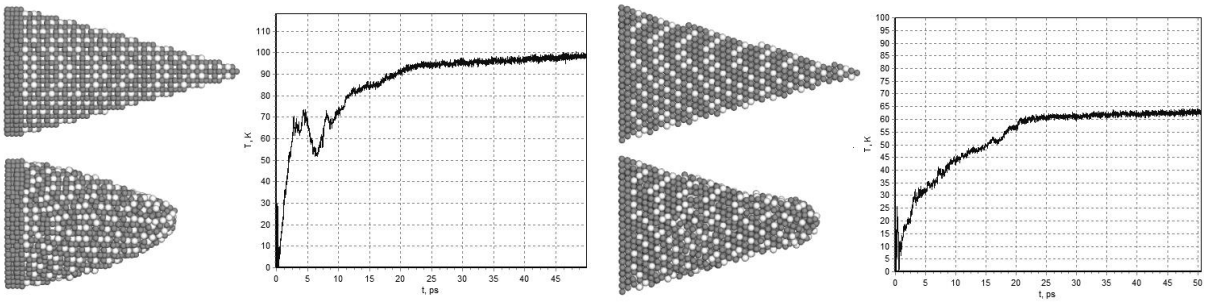
3. Results and discussion

Stability of the nanoneedles, as mentioned above, it was investigated for the three orientations of the axes: [100], [110] and [111]. Two-dimensional angle of the tip was varied from 30° to

90°. Thermal stability was determined on the graph of dependence of the nanoneedle temperature *T* on the time of computer experiment *t*. Structural transformation, consisting in the needle blunting, accompanied by an increase in temperature, and the more intensively the blunting occurred, the more intensively the temperature raised.

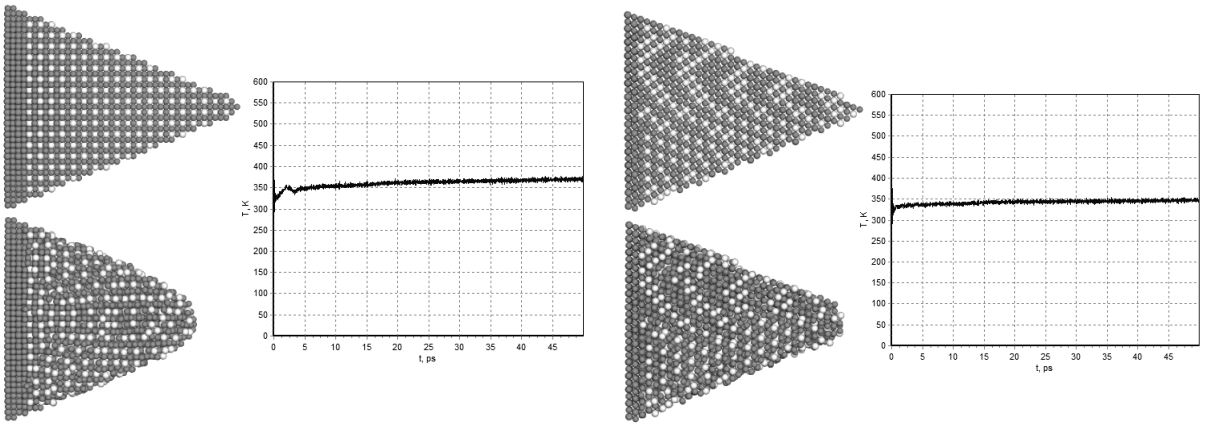
Figures 2-4 shows changes in the shape of the needles with the tip angle of 30°, 45°, 60° in the process of the computer experiment during 50 ps and the corresponding dependences of the temperature on the time *T(t)*. The figures present results only for the needles with the axes along [100] and [111] directions. Needles with the [110] axis were significantly less stable than the [100] and [111] needles for all considered angles of the tip. Blunting of [110] needles took place without any additional initiation (without thermal influence), even for large values of the tip angle Θ.

At the tip angle of 30° the needles with the axes along the [100] and [111] directions also became blunt spontaneously without additional initiation. In Fig. 2 can be seen that during the whole 50 ps computer experiment temperature increase occurred: first an intensive, then more gradual. Moreover, the relatively larger increase in temperature and change in the needle shape was observed in the case of the needle with the axis along [100]. Needles with the axis along [111] were the most stable, as with other values of the tip angle.



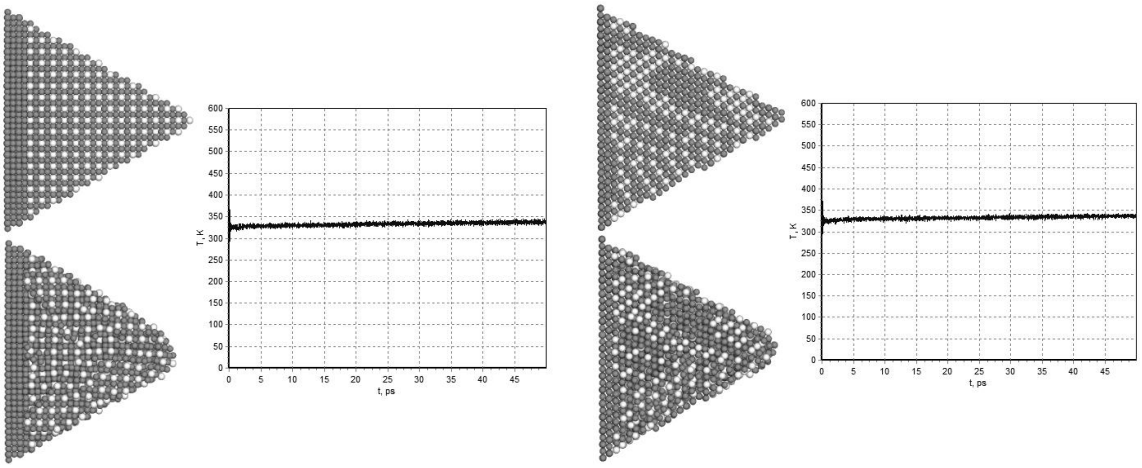
a) b)

Fig. 2. Changes in the shape of the needles with the tip angle of 30° and axes along [100] (a) and [111] (b) directions in the process of the computer experiment during 50 ps and the corresponding dependences of the temperature on the time *T(t)*.



a) b)

Fig. 3. Changes in the shape of the needles with the tip angle of 45° and axes along [100] (a) and [111] (b) directions in the process of the computer experiment during 50 ps and the corresponding dependences of the temperature on the time *T(t)*.



a) b)

Fig. 4. Changes in the shape of the needles with the tip angle of 60° and axes along [100] (a) and [111] (b) directions in the process of the computer experiment during 50 ps and the corresponding dependences of the temperature on the time *T(t).*

With the growth of the tip angle Θ, as expected, the stability of the needle increased. Figure 3 and Figure 4 depict changes in the shape of the needles for the angles 45° and 60° at the starting temperature of 300 K, i.e. at room temperature. In the case of the [100] 45° needle (Fig. 3) shape of the needle still unstable - for all of the computer experiment there was an increase in temperature and blunting of the needle, but in other cases the temperature is practically not changed. Some blunting, especially at the beginning of the simulation, there took place, but then it (as well as surface diffusion) was relatively slow, due to what can be said about the relative stability of these forms of the needles. First blunting of the needles with the angle Θ=60° to the radius of curvature of about 0.7-1 nm remained unchanged in subsequent molecular dynamic experiments within 50 ps at higher temperatures: for needles with the [100] axis up to 500 K for [111] - up to 800 K.

About a perfect stability of the needles can speak clearly only when considering the already slightly blunted the needles to the radius of curvature of about 0.6-1 nm, such as those depicted in Fig. 4, at low temperature conditions. Already at normal temperature stability and sharpness of the needle with considered sizes cannot be guaranteed. The activation energy of surface diffusion is comparatively very low [1, 2], it proceeds intensively even at normal temperatures. In this connection, the radius of the needle tip for industrial cantilevers for scanning microscope is in the range of 5-90 nm, laboratory - a maximum from 1 nm [9, 10].

The smallest radius of curvature of the needles (i.e. minimum blunting) was observed in the simulation of the needles having the tip angle close to the "geometrically ideal" when the tip was created on the basis of the pyramid, that is the following atomic plane was created by one monatomic step less than the previous. For the needles with [100] axis is 90°, for [111] – 78.37°. Such needles are the most stable and resistant to the thermal influence.

4. Conclusion

In the present work using the molecular dynamics simulations it is shown that the most stability nanoneedles in the conditions of thermal influence are the ones with the axis along [111] direction. Needles with the [100] axis are relatively less stable, and needles with [110] axis are the least stable of the considered. In all cases with the growth of the angle of the tip the stability increased. It was found that the tip angles corresponding to the highest thermal stability are close to the "geometrically ideal" angles, when the following atomic plane was created by one monatomic step less than the previous. For the needles with [100] axis is 90°,

for [111] – 78.37°. In this case the surfaces of the needles have fewer movable atoms which are capable of participate in the surface diffusion. Violation of the nanoneedles stability associated with their blunting, which is caused by surface diffusion, which in turn, is more intensive with increasing in density of monatomic steps and breaks on them at the free surfaces of the nanoneedles. Due to the active process of surface diffusion it is practically very difficult to achieve the atomic sharpness of the nanoneedles. According to the results of this work, stable radius of curvature of the needles at low temperatures, depending on the angle of the tip and orientation of the needle axis, is 0.6-1 nm. In practice [9, 10] the nanoneedles laboratory prepared with a radius of curvature from a few nanometers.

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