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THE STUDY OF Cu/Nb INTERFACE DIFFUSION USING MOLECULAR DYNAMICS SIMULATION

The peculiarities of interfacial boundary diffusion where the boundary goes between nonmiscible metals with body-centered cubic (BCC) and face-centered cubic (FCC) lattices have been studied taking, as a case in point, the Cu/Nb system, and using the molecular dynamics method. The diffusion atomic displacements were shown to occur mainly near the mismatch dislocations and their intersections. The diffusion of the high-melting component was found to be characterized by high anisotropy with the predominant atomic displacement along the dense-packed direction in the interfacial boundary plane being common to FCC and BCC lattices with the Kurdyumov-Sachs mutual orientation.

INTERFACE DIFFUSION, COPPER-NIOBIUM, MOLECULAR DYNAMICS, KURDYUMOV-SACHS MUTUAL ORIENTATION.

1. Introduction

Materials on the basis of the copper-niobium system with dimensions of structural elements in the nanoscale such as nanolaminates and nanowires [1] represent the prototype of materials for advanced practical applications, due to the combination of high strength characteristics, good electrical conductivity, possible use as superconductors and radiation resistance [2–4]. The radiation resistance of nanolaminates grows with a decrease in the thickness of the component layers [3], which indicates a significant influence of interfacial boundaries on the processes of annihilation of radiation defects. The role of diffusion conductivity of the interphase boundary for annihilation of defects in the copper-niobium system was confirmed by a study of low-temperature diffusion under irradiation [5]. However, the details of this process are yet to be understood completely. In this paper, we study the Cu/Nb system by atomistic simulations to establish the mechanism of interfacial diffusion.

2. Research technique

To perform a molecular-dynamic modeling of diffusion, a sample of Cu/Nb nanolaminate containing an interfacial boundary was used. The prismatic sample contained 36,000 atoms and measured 8.9×9.8×6.0 nm. The copper and niobium layers were 3.0 nm thick. The layers of the Cu-Nb sample had Kurdyumov-Sachs mutual orientation observed experimentally [6]. An example of such a structure is shown in Fig. 1, where the face-centered cubic (FCC) Cu plane (111) is bordered by the body-centered cubic (BCC) Nb plane (110), and the Cu direction [110] is parallel to the Nb one [111]. Periodic boundary conditions are used.

A procedure for constructing samples and interatomic potentials was successfully used in [7–9]. The well-approved copper potentials constructed by Mishin [10] were used in the molecular dynamic modeling by the embedded-atom method (EAM). The EAM potentials for niobium and the pairwise copper-niobium potentials have been constructed on the base of the experimental data and results of *ab initio* calculations and presented in our papers [7–9].

A molecular dynamic experiment was carried out with the use of a Verlet algorithm in velocity form [11] and the molecular dynamic simulation step was 2 fs (femtoseconds).

The sample with the minimized interfacial boundary energy was used for modeling. Then the required temperature of the modeling experiment was set: from the beginning, within 2,000 molecular dynamic steps, using the

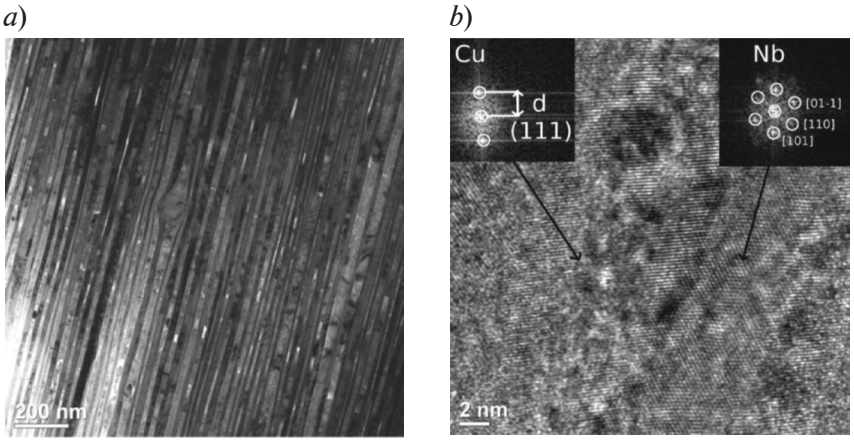

Fig. 1. An example of the structure under study:
a – microphotograph of nanolaminate Cu / Nb (18 nm thick averaged); *b* – Cu/Nb layers with the Kurdyumov-Sachs mutual orientation [13]

technique of velocity scaling, and then within 3,000 steps using a Nose-Hoover algorithm [12]. Temperatures were set in the range from 700 to 1200 K in increments of 50 K. After setting the required temperature, the sample was kept within 5,000 steps without affecting the system. At this time, temperature was controlled in the modeling process. The temperature fluctuation near the constant values with an amplitude not exceeding 0.08 % indicated the establishment of the thermodynamic equilibrium in the system under the specified conditions of the modeling.

Further, the diffusion experiment was carried out according to our developed procedure for a molecular dynamics computer experiment which was described in Ref. [14]. 20 starting positions of atoms for the states were separated by 5,000 molecular dynamics steps. Then, within 1.5 million molecular dynamic steps, the sum of squares for diffusion displacements of atoms for each of the initial moments was calculated. 300 points of the time dependence for the sum of squares of atom displacements on the modeling time were recorded. For each of these points, there was an averaging of 20 starts to reduce the impact of random fluctuations. As diffusion displacements of atoms, we took into account the displacement that was more than 1.5 the average distance between the nearest atoms in ideal copper lattice and 1.0 of the average distance between nearest atoms in the case of niobium. We showed the adequacy of such an approach for the diffusion characteristics of interfacial boundaries in Ref. [15]. We took the time interval of modeling the diffusion experiment as equal to 3 ns.

The molecular dynamic investigation of the diffusion characteristics in nanocrystalline materials through the sum of squared atomic displacements has been successfully used by us in the studies in grain boundary self-diffusion in the high-purity copper and the diffusion of copper along the grain boundaries of niobium and achieved good agreement with the experimental data [9, 14]. This confirms the high reliability of the results obtained by this method.

3. Results and discussion

On the basis of the obtained time-dependence of the sum of squares of atomic displacements at various temperatures, the rate of diffusion displacements $\Delta Z/t$ for copper and niobium atoms was determined in the sample under study. The time-dependent sum of the squared atomic displacements is shown as an example in Fig. 2.

The growth rates $\Delta Z/t$ of the sum of atomic displacements squared as a function of $1/kT$ (k is the Boltzmann constant and T is the sample temperature), are logarithmically plotted for Cu and Nb (see Fig. 3). The construction procedure for these plots was presented in Refs [14, 15]. The activation energy of the diffusion processes at the interfacial boundary was found to be 0.7 ± 0.1 eV/atom for copper and

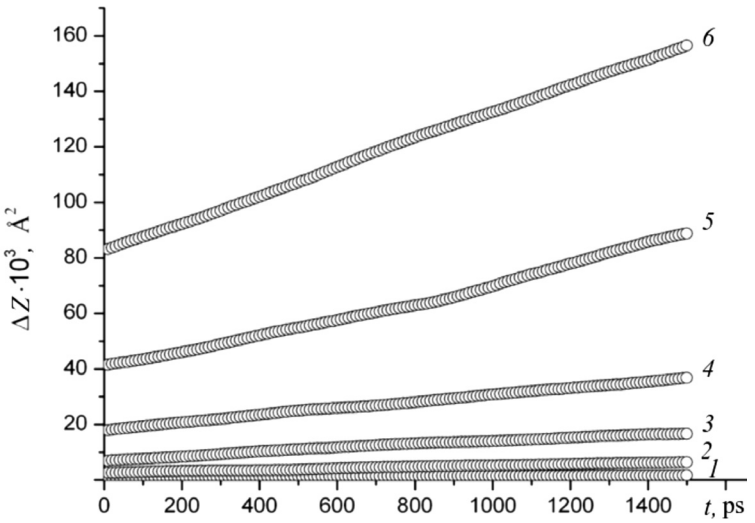

Fig. 2. The plots of ΔZ sum of Cu-atomic displacements squared in the Cu/Nb interfacial boundary versus the simulation time at various temperatures (in K): 700 (*1*), 800 (*2*), 900 (*3*), 1000 (*4*), 1100 (*5*), 1200 (*6*); obtained by molecular dynamics

1.1 ± 0.1 eV/atom for niobium (using the diagrams in Fig. 3).

It is interesting to note that the calculated activation-energy value for diffusion of Cu at the Cu/Nb interfacial boundary corresponds to that of the grain-boundary self-diffusion of Cu equal to 0.71 ± 0.01 eV/atom and the Cu diffusion along grain boundaries of Nb equal to 0.69 ± 0.07 eV/atom at appreciable concentrations of Cu in grain boundaries of Nb [9]. The activation energy for Nb diffusion at the Cu/Nb interface within the error coincides with the activation energy of Cu diffusion equal to 1.2 ± 0.3 eV/atom in grain boundaries of niobium at a small concentration of copper. This indicates the crucial role of the less refractory metal Cu in the diffusion process at the grain boundaries of the Nb as well as at the interface of the Cu/Nb.

Analysis of the structure of the Cu/Nb interface boundary after the diffusion experiment (see Fig. 4) shows that the diffusion displacements of copper atoms occur only near the mismatch dislocations (see also Fig. 6 ,*a*)

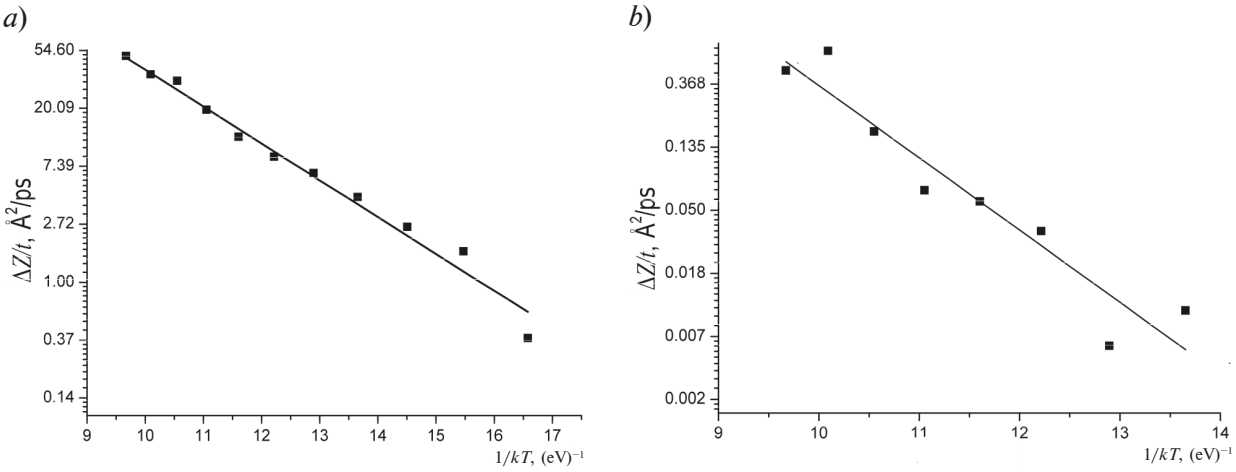

Fig. 3. The plots of the growth rate $\Delta Z/t$ of the sum of atomic displacements squared versus $1/kT$ for the interfacial diffusion of Cu (*a*) and Nb (*b*) in the Cu/Nb system obtained by molecular dynamics simulations

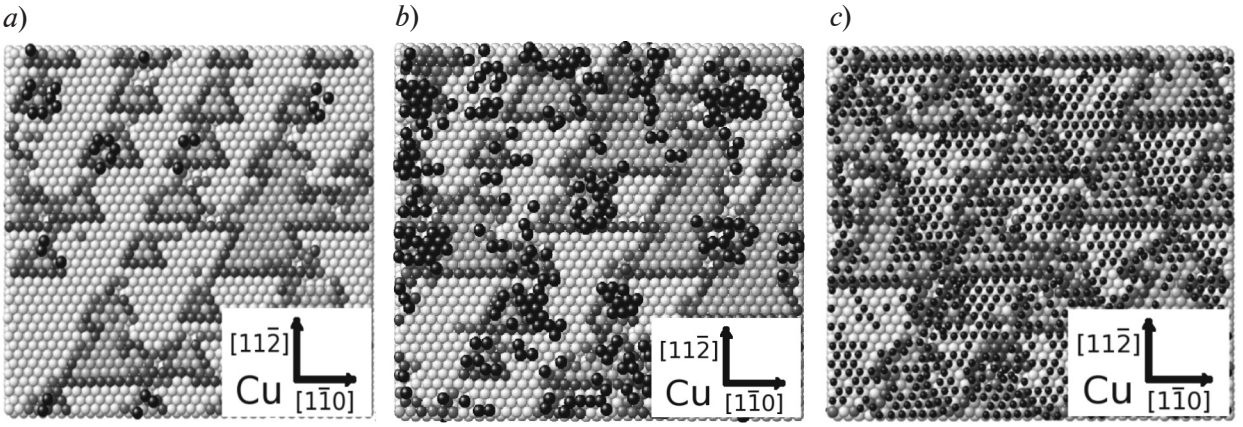

Fig. 4. Cu atoms in the boundary layer shifted at a distance of more than 3.83 Å (are given in black) on a background of the second Cu layer starting with the Cu/Nb interfacial boundary after the diffusion experiment at various temperatures, K: 700 (*a*), 950 (*b*), 1200 (*c*).
The white, the light gray, and the dark gray indicate Cu atoms with local environments which are typical of FCC, HCP, and defect structures, correspondingly

and their intersections, which limit the area of diffusion shifts of atoms. In Fig. 4 these areas are displayed by hexagonal close-packing (HCP) of atoms of the second layer, relative to the layer of copper atoms lying at the interface boundary. This leads to an inhomogeneous distribution of the copper atoms involved in the diffusion process in the boundary layer up to the temperature of ~950 K (0.75 of copper's melting point).

At higher temperatures, the diffusion displacements encompass all copper atoms which are in the boundary layer. In the case of the niobium diffusion (Fig. 5*a*,*b*), an inhomogeneous distribution of the diffusion processes is marked at all examined temperatures, including the highest temperature of 1200 K (0.4 of Nb melting point). It can be explained by the higher melting point of niobium in comparison with that of the copper. The analysis of diffusion displacements of niobium (Fig. 5,*b*) permitted to identify two mechanisms of diffusion. The former is the vacancy mechanism implemented by structural vacancies formed in the boundary niobium layer. The latter is a new mechanism implemented by displacements of niobium atoms along the mismatch dislocations, which form channels with less dense arrangement

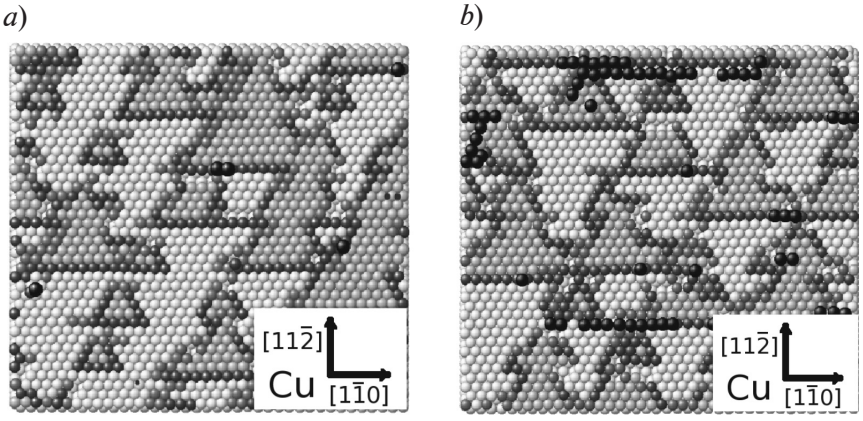

Fig. 5. Nb atoms in the boundary layer shifted at a distance of more than 2.85 Å (are highlighted in black) on a background of the second layer of Cu starting with the Cu/Nb interfacial boundary after the diffusion experiment at two temperatures, K: 950 (*a*), 1200 (*b*).
The white, the light gray, and the dark gray balls indicate the Cu atoms with local environments which are typical of FCC, HCP, and defect structures, correspondently

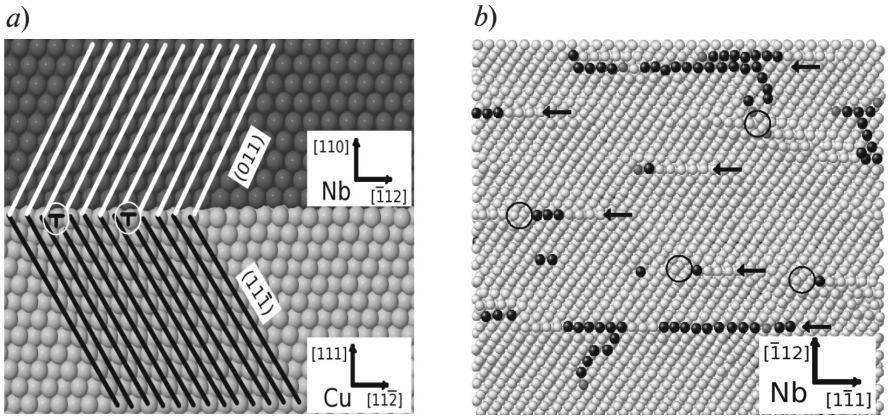

Fig. 6. The Cu/Nb interface boundary at 1200 K after the diffusion experiment; *a* – the mismatch dislocations (see the text), *b* – the boundary Nb layer. The black balls indicate the Nb atoms shifted at a distance of more than 2.85 Å, the gray ones do the Cu atoms introduced in a close-packed row of Nb atoms near the mismatch dislocations, the black ones indicate vacancies in the boundary layer of Nb

of the copper atoms in the boundary copper layer. Chains of shifted atoms in Fig. 5,*b* are located in these channels, but the mechanism is implemented only in case of the introduction of a number of copper atoms in the close-packed rows of niobium atoms, which, thanks to the smaller radius of the copper atom, make an additional free volume in rows of niobium atoms (see Fig. 6,*b*). Figs. 5,*b* and 6,*b* show that the second diffusion mechanism of niobium in the Cu (111)/Nb (110) interfacial boundary with the Kurdyumov-Sachs mutual orientation is the primary one at temperatures up to 1200 K.

4. Summary

A new niobium diffusion mechanism at the copper-niobium interfacial boundary characterized by the displacement of atoms along the mismatch dislocations has been established. Diffusion processes in niobium are activated by the introduction of a number of copper atoms in the rows of niobium atoms near the mismatch dislocations. The activation energy of the process within the error corresponds to that of the copper diffusion along the high-angle grain boundary of niobium. Up to the temperature of 1200 K, the vacancy mechanism of diffusion at the Cu/Nb boundary does not play a significant role.

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Неласов И.В., Липницкий А.Г. ИССЛЕДОВАНИЕ ДИФФУЗИИ ПО МЕЖФАЗНОЙ ГРАНИЦЕ МЕДЬ – НИОБИЙ МЕТОДОМ МОЛЕКУЛЯРНОЙ ДИНАМИКИ.

Особенности диффузии по межфазной границе несмешиваемых металлов имеющих гранецентрированную кубическую (ГЦК) и объемноцентрированную кубическую (ОЦК) решетки, изучены на примере системы медь–ниобий методом молекулярной динамики. Показано, что диффузионные смещения атомов происходят преимущественно вблизи дислокаций несоответствия и их пересечений. Было установлено, что диффузия тугоплавкого компонента характеризуется высокой анизотропией с преимущественным смещением атомов вдоль плотно упакованного направления в плоскости межфазной границы, которое является общим для ГЦК- и ОЦК- решеток с взаимной ориентацией Курдюмова – Закса.

МЕЖФАЗНАЯ ДИФФУЗИЯ, МЕДЬ–НИОБИЙ, МОЛЕКУЛЯРНАЯ ДИНАМИКА, ВЗАИМНАЯ ОРИЕНТАЦИЯ КУРДЮМОВА – ЗАКСА.

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