Self-Diffusion Parameters of Grain Boundaries and Triple Junctions in Nanocrystalline Materials

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Keywords: self-diffusion, nanocrystalline materials, triple junction, grain boundary, molecular dynamics

Abstract. Suggested methods describe the process of self-diffusion along grain boundaries and triple junctions in polycrystals without using geometric models of the grain boundaries structure. The calculation method introduced diffusion characteristics along grain boundaries derived from the results of molecular dynamic simulations of nanocrystalline materials. The diffusion experiments were imposed to establish relationship between introduced diffusion characteristics and the diffusion parameters along grain boundaries and triple junctions of the Fisher's grain boundary diffusion model. By the example of copper for the first time the characteristics of self-diffusion along grain boundaries of nanocrystalline materials and coarse grained analog defined in the same temperature range was compared for the first time. It was found that values of the self-diffusion characteristics along grain boundaries in high purity nanocrystalline and polycrystalline copper are equal at the same temperatures.

Introduction

Diffusion along grain boundaries (GB) in polycrystals is a process of atoms displacements with energy barriers overcoming in the grain boundary area, which forms the basis of the mechanisms of grain boundary migration, grain growth, the allocation of secondary phases at grain boundaries, Coble creep and other diffusion-controlled processes in polycrystals. Therefore, the introduction of parameters for quantitative description of grain boundary diffusion and their definition are of great interest in both theoretical and practical aspects. So far, the Fisher's model of diffusion along grain boundaries was the basis for processing results of diffusion experiments, despite the fact that it uses a simplified representation of the grain boundary as a plate of a homogeneous phase. Using this approach, a significant progress has been made in understanding the processes of diffusion along grain boundaries. Significantly greater rate of diffusion along grain boundaries in comparison with the diffusion in the bulk of the crystal grains was found, the classification of regimes of grain boundary diffusion and grain boundary diffusion processes was studied in many polycrystals. Creation of nanocrystalline materials (NC) in which intergranular atoms represent a significant part of the material raised new questions for the quantitative description of diffusion in the intergranular area. There are primarily two questions: 1) Are the parameters of intergranular diffusion in nanocrystalline and coarse materials (the influence of the size factor) differs? and 2) What is the value of triple junctions (TJ) contribution? It can be substantial, because there are a significant part of triple junctions in the intergranular area and they can have greater permeability in comparison with grain boundaries. It should be noted that there is a problem with direct comparison of grain boundary diffusion characteristics in nanocrystalline and coarse state. To avoid recrystallization in NC samples during the diffusion experiments, they are conducted at low temperatures, while in the coarse-crystalline samples experiments conducted at high temperature to obtain sufficient information for analysis.

Molecular dynamics simulation allows to identify characteristics of diffusion processes in NC materials at high homologous temperatures. This is possible due to detailed information about displacements of atoms during the short times in comparison with characteristic times of structure

changes in the simulated NC material. However, comparison of these results with data from diffusion experiments in coarse grained analogues is difficult for two main reasons. First, molecular dynamic simulation of atoms diffusion displacements at distances of more than 10 nm along grain boundaries (as in real experiments) is impossible because of the limited maximum computer simulation time. Secondly, the information about displacements of atoms in the grain boundaries and triple junctions depends from synthetically chosen criterion of atoms accessories to intergranular area.

The suggested analysis showed that existing problems of diffusion description in the grain field of nanocrystalline materials connected to the lack of methods for interpreting results of diffusion experiments and molecular dynamics simulation based only on the characteristics of intergranular diffusion, but not on the geometric models of grain boundaries and triple junctions. That is why in this paper we set problems (i) to develop a description of the self-diffusion along grain boundaries and triple junctions that are not tied to an effective diffusion coefficient and the thickness of the grain boundary parameters of the Fisher's model of grain boundary diffusion, (ii) to establish the self-diffusion characteristics of the grain boundaries and triple junctions in the nanocrystalline state by the example of molecular dynamics simulations of nanocrystalline copper.

Methods

Diffusion characteristics of grain boundaries and triple junctions are described by the excesses of sum of squared diffusion atomic displacements with respect to the crystalline state, shared per unit area of grain boundaries (marked as ζ_{GB}) and unit length of the triple junction (ζ_{TJ}). Description of defects by the excesses of the additive values makes introduced intergranular diffusion characteristics independent from the choice of geometrical model of grain boundaries. We can extract GBs and TJs contributions from the excesses of sum of squared diffusion atomic displacements in nanocrystalline materials by analogy of division of excess of thermodynamic additive quantities described in [1]. Introduced characteristics and relative contributions of GB and TJ in the intergranular diffusion are calculated by the example of molecular dynamics simulation of NC copper at temperatures from 700 to 1200 K. We derive relations between these diffusion characteristics and effective self-diffusion coefficients grain boundaries and triple junctions, based on the Fisher's model. The results are compared with the literature data about grain-boundary diffusion, obtained from diffusion experiments in well-annealed high purity coarse copper in the temperature range of 723-1066K [2]. The contribution of triple junctions in intergrain diffusion, depending on the average grain size is defined. The effective coefficients of diffusion along grain boundaries and triple junctions are compared from the simulation results.

The main equation is based on the following: First we use above mentioned characteristics ζ_{GB} and ζ_{TJ}, Second the increase rate of ΔZ, which is the excesses of sum of squared diffusion atomic displacements, accumulated in the NC sample during time t is the sum of the GB and TJ contributions:

$$(\Delta Z/t)= \zeta_{GB}A_{GB} + \zeta_{TJ}l_{TJ} \quad (1)$$

$(\Delta Z / t)$ is the slope of ΔZ dependence from t, and can be obtained from the computer simulation. According this expression, we need to know the area of grain boundary, the length of the triple junction in nanocrystalline samples and we must establish relation between these values to obtain ζ_{GB} and ζ_{TJ} from $(\Delta Z / t)$. We can get the value A_{GB} from stereometrical identity [3] $A/V=2/\langle L\rangle$, where A is the total area of grain boundaries in nanocrystalline sample without accounting of triple junctions. The real area of grain boundaries A_{GB} is less than A by δA , which is determined by triple junctions region. The expression for δA can be obtained by investigating conditions of local thermodynamic equilibrium (LTE) between the average energies of the triple junction and the adjacent n GBs: $nR\gamma_{GB}=2\gamma_{TJ}$. Here we assume that the triple junction area is a homogeneous phase

in the form of a cylinder of radius R [1]. Assuming that the shrinkage of grain boundary δA is equal to nRl_{TJ}, using (1) and stereometrical identity we derive equation for calculating ζ_{GB} and ζ_{TJ} [4]:

$$(\Delta Z / t)\frac{< L >^2}{V} = 2\zeta_{GB} < L > +\lambda(\zeta_{TJ} - \frac{2\gamma_{TJ}}{\gamma_{GB}}\zeta_{GB}) \tag{2}$$

The diffusion parameter ζ_{GB} in the GB is determined from the slope of linear dependence: $((\Delta Z/t)/V <L>^2$ from <L>. The diffusion parameter ζ_{TJ} in the TJ is calculated from the intersection of this equation with a vertical axis.

If we want to use developed method to determine the diffusion characteristics ζ_{GB} and ζ_{TJ} from the results of molecular dynamic simulations and compare these results with the real diffusion experiments, we must made additional consideration. It is necessary to circumvent one of the mentioned earlier problems of computer simulation. In the real diffusion experiments the atomic displacements in grain boundaries are much greater then distances considered in molecular dynamics simulation (1 nm) even for relatively high homologous temperatures.

It must be empathized, that GBs have many barriers for atoms displacements with different values. It leads to dependence of activation energy of displacements from atoms shifts (even in case of bounds series). More the shift is more the barrier controlling this shift. Saturation occurs only when shifts are rather big, following which all shifts are controlled by the same value of barrier.

To solve the marked problem the technique of calculating the diffusion characteristics based on the convergence of diffusion values with increasing distance l_{min} was suggested. If atom displacement bigger than l_{min} it will be taken into account when calculating the diffusion parameters. Usually l_{min} is used to eliminate contribution of atomic displacements due to thermal vibrations during the analysis of molecular dynamics simulation results [5] and it is chosen equal to ~ $0{,}5r_1$, where r_1 is the nearest distance between atoms in the equilibrium lattice of the studied material. This paper considers l_{min} shifts from $0.5r_1$ to $2.0r_1$. At $l_{min} \sim 1.5r_1$ (0.38 nm in the case of copper) is achieved fast convergence of diffusion parameters. For comparison with the actual results of diffusion experiments and with qualitative estimations from the Einstein expression for diffusion coefficient we demonstrate that the introduced GBs and TJs characteristics are associated with the corresponding effective D_{GB} and D_{TJ} diffusion coefficients with the following ratios:

$$(D_{GB} - D_V)\delta = \frac{\Omega}{6}\zeta_{GB} \quad \text{and} \quad (D_{TJ} - D_V)R^2 = \frac{\Omega}{6\pi}\zeta_{TJ}, \tag{3}$$

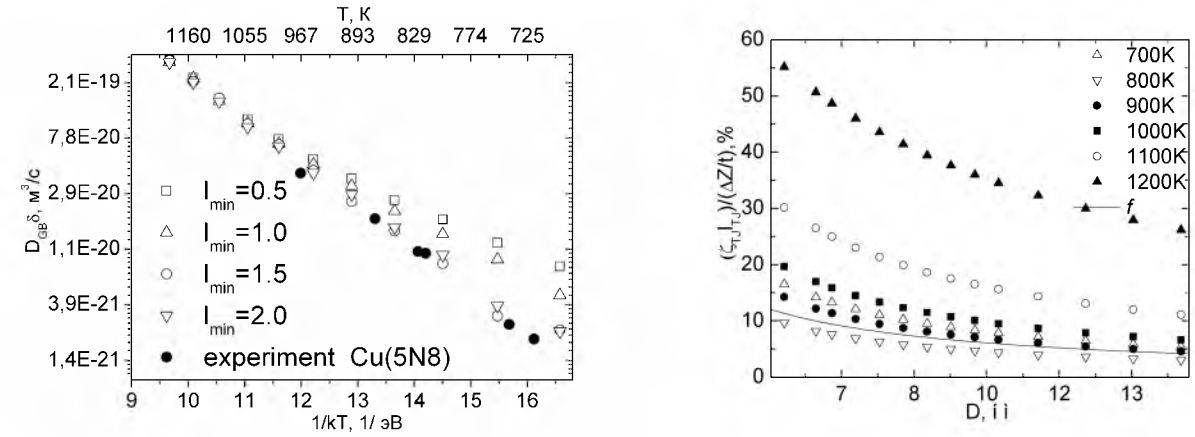
In the case GB and TJ are homogeneous phases in the form of a plate of thickness δ and the cylinder of radius R, respectively. D_V is diffusion coefficient in the bulk of grains and Ω is the average volume per atom. Further we consider only such cases, where diffusion in the bulk of grains is small compared to diffusion in intergranular area, so the diffusion coefficient D_V sets equal to zero. This analysis is valid for diffusion in nanocrystalline materials at low homologous temperatures and for computer simulation of diffusion process in nanocrystalline metals at times over which concentration of vacancies in the grain bulk is negligible and the diffusion by a vacancy mechanism does not have time to develop. Equations (3) allow us to compare diffusion characteristics obtained in the model approach (D_{GB} and D_{TJ}) and without such (ζ_{GB} и ζ_{TJ}). Equations (3) also show that the products of $D_{GB}\delta$ and $D_{TJ}R^2$ have a physical meaning independent from model representations of the GB and TJ structure and are accurate within a multiplier factors the increase rates of sum excesses of squared diffusion atomic displacements with respect to the crystalline state in the GB and TJ respectively (in case of D_V=0). It is interesting to note, that we can determine only $D_{GB}\delta$ product when we use Fisher's model to analyze results of experiments in which implemented B regime of grain-boundary diffusion. In this case, the approach of Fisher's model is only required at the intermediate stage of processing the results of diffusion experiments. The final description of the

diffusion $D_{GB}\delta$ does not depend on the choice of model, and coincides with ζ_{GB} (within a multiplier factor), which is free from this approximation.

The establishing of sum of squared diffusion atomic displacements in 14 NC copper samples was carried out by molecular dynamics method. The embedded atom method potentials for Cu were used [6]. The molecular dynamics (MD) step was 3 fs. Before the model experiment, each sample was kept at a given temperature and zero pressure for 24 ps by molecular dynamics method. Following which effects on the model samples were switched off and the simulation was conducted by NVE (constant number of particles, volume and total energy) MD scheme. The sum of squared diffusion atomic displacements ΔZ (the displacement at distances over than lmin) accumulated over time t was averaged over 20 initial moments of time, separated by intervals of 0.3 ps. The slope of (ΔZ/t) was determined in the range of t values from 60 to 120 ps by using a linear interpolation method of least squares. This time interval was chosen because the function ΔZ(t) becomes a linear dependence for all used samples and considered temperatures after the time of 60 ps.

Results

The main results of molecular dynamic simulation are shown in Fig. 1, where you can see calculated dependences $D_{GB}\delta$ from (1/kT) for different l_{min} compared with published data on grain-boundary diffusion in high purity copper [2]. Also you can see established contribution from TJ in (ΔZ/ t) according to the formula (1) in comparison with the contribution evaluated by composite model of NC materials [7].



(a) (b)

Figure 1. (a) dependence of $D_{GB}\delta$ from (1/kT) for different l_{min} compared with experiment [2]; (b) contribution TJ diffusion on integrated intergranular diffusion

For quantitatively description of the convergence of numerical results by l_{min} and comparison with experimental data, ΔE_{GB} and P_0 parameters were compared according to Arrhenius's equations: $D_{GB}\delta=P_0\exp(-\Delta E_{GB}/k_BT)$. The equations were calculated from the ζ_{GB} quantities at different values of l_{min} and obtained from diffusion experiments. The convergence of calculated values ΔE_{GB} and P_0. with increasing l_{min} was established. They did coincide within the error of calculations for l_{min} = 1.5 r_1 and l_{min} = 2.0 r_1. Therefore, we selected diffusion characteristics of grain boundaries in copper when l_{min} = 1.5 r_1 for comparison with experiment. Fig. 1a and table 1 illustrate very good agreement of grain boundary self-diffusion characteristics in copper, obtained by two independent methods: from the diffusion experiments and molecular dynamics simulation. This shows that, firstly, the characteristics of grain boundary diffusion in nanocrystalline and coarse grained copper at temperatures of 700K and higher temperatures are equal, and secondly, confirms the reliability of computer simulation data and the results of diffusion experiments in pure copper of 99.9998%.

Table 1. The calculated and experimental values of the parameters of the Arrhenius dependence $D_{GB}\delta=P_0\exp(-\Delta E_{GB}/k_BT)$ for high-purity copper for different temperatures.

		ΔE_{GB} (eV/atom)	P_0 (m^3/s)
Experiment 784-973K		Cu (99.999 %)	
		0,87	$1.16\cdot10^{-15}$
Experiment 720-1066K		Cu (99.9998 %)	
		0.75	$3.89\cdot10^{-16}$
Modeling		Cu (100 %)	
$l_{min}=2.0r_1$	700-1200K 1000-1200K	0.71±0.01 0.79±0.03	$(2.6\pm0.5)\cdot10^{-16}$ $(6\pm2)\cdot10^{-16}$
$l_{min}=1.5r_1$	700-1200K 1000-1200K	0,73±0,02 0.79±0.03	$(3.4\pm0.9)\cdot10^{-16}$ $(6\pm2)\cdot10^{-16}$
$l_{min}=1.0r_1$	700-1200K 1000-1200K	0.60±0.02 0.77±0.02	$(8\pm2)\cdot10^{-17}$ $(5\pm1)\cdot10^{-16}$
$l_{min}=0.5r_1$	700-1200K 1000-1200K	0.53±0.02 0.74±0.02	$(4\pm1)\cdot10^{-17}$ $(4.0\pm0.9)\cdot10^{-16}$
[4]	950-1200K	0.70±0.3	$(2.4\pm0.9)\cdot10^{-16}$
[8]	700-1100K	0.71±0.2	$(1\pm0.2)\cdot10^{-16}$

As the table shows, decrease of copper purity from 99.9998 to 99.999% leads to a significant increase of activation energy for grain boundary self-diffusion from 0.75 to 0.87 eV/atom. The agreement of calculated value ΔE_{GB}=0.73 eV for 100% purity Cu with that derived from experiments ΔE_{GB} = 0.75 eV for 99.9998% purity Cu indicates the absence of segregation influence on the activation energy of grain boundary self-diffusion only in high-purity copper (99.9998%). As you can see from Fig. 1b, the contribution of TJ in intergranular diffusion can significantly exceed values derived from simple estimates based on geometric representations of triple junctions as the intersection of intergranular homogeneous phases. TJ contribution for D = 10 nm grains is 4 times higher than that predicted by composite model in the temperature region near 1200 K. Increasing of the TJ contribution at 800-1200 K can be explained by a much greater influence of high temperatures on the thermal disordering of TJ than GB. The estimating ratio of the effective diffusion coefficients D_{TJ}/D_{GB} made from calculated ζ_{GB} and ζ_{TJ} values is below 10 in the considered range of temperatures.

References

[1] A.G. Lipnitskii: Materialovedenie (Materials Science) No. 2 (2009), p. 2.

[2] T. Surholt and Chr. Herzig: Acta Materialia V. 45 (1997), p. 3817.

[3] J.C. Russ and R.T. Dehoff, in: *Practical Stereology*, 2nd Ed. (Plenum Press, NY, 1999).

[4] Yu.R. Kolobov, A.G. Lipnitskii, I.V. Nelasov, and G.P. Grabovetskaya: Russ. Phys. J. Vol. 51, No. 4. (2008), p. 385.

[5] B. Schonfelder, G. Gottstein, and L.S. Shvindlerman: Acta Materialia. V. 53 (2005), p. 1597.

[6] Y. Mishin, M.J. Mehl, D.A. Papaconstantopoulos, A.F. Voter, and J.D. Kress: Physical Review B Vol. 63 (2001), p. 224106.

[7] H.S. Kim, Y. Estrin, and M.B. Bush: Acta Materialia Vol. 48 (2000), p. 493.

[8] T. Frolov and Y. Mishin: Physical Review B Vol. 79 (2009), p. 174110.

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