

Grain-Boundary Diffusion of Nickel in Submicrocrystalline Molybdenum Processed by Severe Plastic Deformation

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Abstract—The depth–concentration profiles of nickel upon diffusion in submicrocrystalline (SMC) molybdenum processed by severe plastic deformation (SPD) have been studied by Auger electron spectroscopy. The coefficients (D_b) and activation energies of the grain-boundary diffusion of nickel in SMC molybdenum were determined in a 973–1123 K temperature interval. The results indicate that a difference between the D_b values in SMC and coarse-grained molybdenum is related to a nonequilibrium state of grain boundaries in the SPD-processed metal.

The creation of a new class of materials—nanostructural metals and alloys—in which a considerable fraction of substance occurs on the grain boundaries (GBs) and in the grain-boundary regions, increases the importance of knowledge about the laws and parameters of grain-boundary diffusion (GBD). This knowledge is especially important for volume nano- and submicrocrystalline (SMC) materials obtained by methods based on severe plastic deformation (SPD), in which GBs are characterized by a high density of strain-induced defects and, hence, occur in a nonequilibrium state [1].

A classical method for determining the GBD parameters (diffusion coefficients, diffusion activation energies, and diffusion widths of the GBs) is based on the measurement and analysis of the diffusant (impurity or isotope) depth–concentration profiles upon diffusion annealing of the samples. An analysis of the diffusant distribution in depth of a sample within the framework of an adopted model allows the GBD coefficients to be calculated as functions of the temperature.

At a relatively low temperature on the order of $(0.3–0.4)T_m$ (where T_m is the melting temperature), the diffusion mass transfer in a polycrystalline material proceeds predominantly via GBs, since the volume diffusion is “frozen” (the diffusion path is below 1 nm). In this temperature interval, the GBD proceeds in a regime of either type C (without any permeation of a diffusant into the grain body) or type B (with a minimum diffusant permeation into the grain body) [2]. In the former case, the depth of diffusant penetration via GBs into the

volume of a polycrystalline sample is determined entirely by the GBD parameters, while in the latter case, both GBD and bulk diffusion parameters are significant. According to a refined classification of the GBD regimes in fine-grained metals and alloys [3], the depth L_b of a diffusant penetration via GBs in regime C obeys the relation

$$L_b = (D_b t)^{1/2}, \quad (1)$$

where D_b is the GBD coefficient and t is the duration of the diffusion annealing. Thus, once the depth of diffusant penetration in regime C is determined using an experimental depth–concentration profile for the known diffusion time, the D_b value can be calculated.

In the present investigation, features of the GBD in SMC metals processed by SPD were studied for a Mo(Ni) system (here and below, the diffusant is indicated in parentheses). The SMC structure in the initial molybdenum with an average grain–subgrain structure element size of 0.45 μm was obtained by SPD using the method of torsion under pressure. The Mo(Ni) system is characterized by a unipolar solubility, whereby nickel is virtually not dissolved in the body of molybdenum grains and exhibits segregation at the GBs. In this system, the permeation of diffusant from GBs to the body of grains is insignificant even during the diffusion in regime B. Another specific feature of the Mo(Ni) system is the susceptibility of molybdenum to intergranular fracture, which allows the distribution of nickel concentration C_{Ni} in depth of a sample to be determined directly at the grain boundaries by studying

a transverse cross section of the sample fractured upon the diffusion annealing.

As is known [4], the diffusion in regime C is observed for nickel in GBs of coarse-grained molybdenum for a diffusion annealing time of 2–5 h at temperatures below 1273 K. For this reason, we have studied how the thermal stability of the SMC structure of SPD-processed molybdenum is influenced by the annealing at various temperatures in the interval of 973–1273 K. It was established that partial recrystallization and grain growth were observed in separate regions of a sample annealed for 1 h at 1273 K, while the annealing for 4–6 h at temperatures below 1173 K did not change the average element size in the grain–subgrain structure of molybdenum.

The diffusion annealing of SPD-processed SMC molybdenum coated with a 5- to 7- μm -thick Ni film was performed in vacuum (residual pressure, 10^{-2} Pa) for 2–5 h at various temperatures in the interval of 973–1123 K. The penetration of nickel into the bulk of molybdenum (i.e., into the body of grains) due to the bulk diffusion from the surface at 1123 K (the bulk diffusion coefficient at this temperature is 7.1×10^{-24} m^2/s) for 5 h does not exceed 1 nm, so that the bulk diffusion during annealing in the regimes selected for this study can be considered “frozen.” Examination of the SMC structure in samples of the Mo(Ni) system showed that the diffusion annealing in these regimes did not change the dimensions of elements of the grain–subgrain structure of molybdenum, which was evidence for the absence of the migration of GBs in the course of diffusion annealing.

The distribution of C_{Ni} in the depth of molybdenum upon diffusion annealing was studied by Auger electron spectroscopy (AES) on the transverse cross section of fractured samples. The AES measurements of C_{Ni} in GBs were performed on a Shkhuna-2 setup with an ultrahigh-vacuum chamber (residual pressure, 10^{-7} Pa) equipped with an electron energy analyzer having an energy resolution of 0.7%. The spectra of Auger electron energies were measured in the regime of electron beam probing without scanning. The electron probe diameter was 1–1.5 μm ; the error of determining nickel concentration at the GB was within 20%.

Figure 1 shows the typical C_{Ni} profiles in GBs of SPD-processed SMC molybdenum upon diffusion annealing at various temperatures. From these data, the values of D_b were determined using Eq. (1) and the depth of nickel penetration into molybdenum via GBs for a given annealing time. The L_b value (maximum diffusant penetration depth) was determined as the maximum distance from the sample surface at which the nickel concentration decreased to 0.5 at. %, which corresponded to the limiting AES sensitivity with respect to nickel.

The results of calculations of D_b for the GBD of nickel in our samples are presented in the table in com-

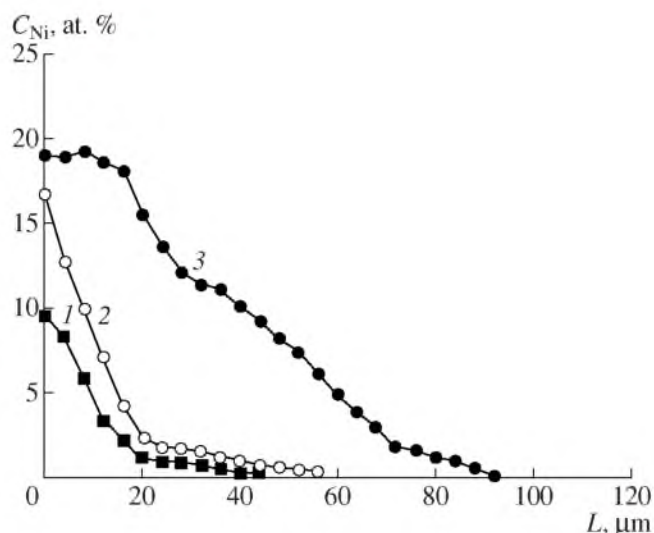


Fig. 1. Nickel concentration profiles in depth of SMC molybdenum upon the diffusion annealing for (1) 5 h at 973 K, (2) 2 h at 1073 K, and (3) 3 h at 1123 K.

parison to D_b values determined by AES for the diffusion of nickel in coarse-grained molybdenum [5]. As can be seen, D_b values for nickel in SMC molybdenum in the temperature interval of 1123–973 K are 2–3 orders of magnitude greater than the corresponding values in the coarse-grained metal. The difference between D_b values of coarse-grained and SMC molybdenum increases with decreasing temperature of the diffusion annealing.

Using data in the table, we have constructed a plot of the GBD coefficient D_b versus annealing temperature for nickel in SMC molybdenum (Fig. 2). The GBD diffusion activation energy ($Q_b = 121.3$ kJ/mol) determined from the slope of this plot is about half of the analogous value for coarse-grained molybdenum (245 kJ/mol [5]).

A specific feature of GBs in SMC materials processed by SPD methods is their nonequilibrium state. It

Grain-boundary diffusion coefficients for nickel in molybdenum

Temperature, K	D_b , m^2/s	
	Coarse-grained Mo	Submicrocrystalline Mo
1373	1.0×10^{-12}	
1273	1.9×10^{-13}	
1123	* 8.7×10^{-15}	7.8×10^{-13}
1073	* 2.6×10^{-15}	4.4×10^{-13}
973	* 1.5×10^{-16}	1.0×10^{-13}

* Values calculated from the experimental data for 1373 and 1273 K, assuming that the GBD obeys the Arrhenius law $D_b = D_{b0} \exp(-Q/RT)$.

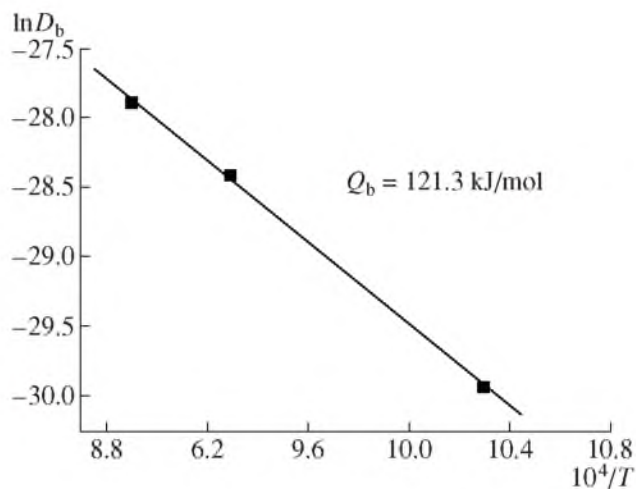


Fig. 2. Temperature dependence of the GBD coefficient for nickel in SMC molybdenum.

can be suggested that an increase in the D_b values for nickel in SMC molybdenum as compared to the corresponding values in a coarse-grained metal is related to a change in the state of GBs during the SPD processing. As is known [6], pre-recrystallization annealing leads to a transition of the GBs in SPD-processed SMC molybdenum to the equilibrium state. In order to elucidate the effect of the state of GBs on the D_b value for nickel diffusion in SMC molybdenum, we have changed the state of GBs by annealing the samples at 1073 K for 2 h prior to depositing nickel on the surface of molybdenum. Figure 3 shows the C_{Ni} profiles in GBs of the initial (SPD-processed) and preannealed SMC molybdenum samples upon a diffusion annealing for 2 h at 1073 K. As can be seen, the maximum penetration depth of nickel via GBs in the preannealed SMC molybdenum is decreased by a factor of approximately 4.5 as compared to the depth reached by the diffusant in the initial SMC state. The D_b value in the preannealed sample decreases to $6.8 \times 10^{-15} \text{ m}^2/\text{s}$, which is close to the value in coarse-grained molybdenum ($3.3 \times 10^{-15} \text{ m}^2/\text{s}$).

Thus, the results obtained for the Mo(Ni) system show that the GBD coefficients in the temperature interval of $(0.3-0.4)T_m$ in SMC metals processed by SPD methods are increased by several orders of magnitude as compared to the corresponding values for a coarse-grained state. The GBD activation energy for a metal in the SMC state is approximately about half of the value for the same metal in a coarse-grained state. An increase in the GBD coefficients in SMC metals is

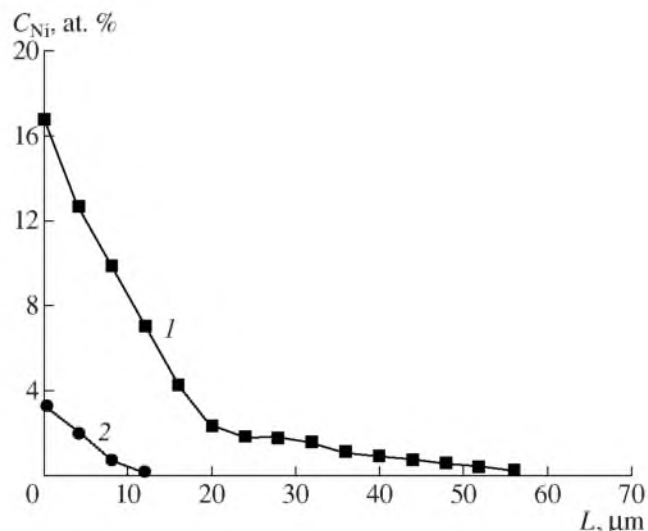


Fig. 3. Nickel concentration profiles in depth of SMC molybdenum upon diffusion annealing for 2 h at 1073 K: (1) SMC molybdenum upon SPD processing; (2) SMC molybdenum upon SPD processing followed by annealing for 2 h at 1073 K.

related to a nonequilibrium state of GBs formed in metals during the SPD processing.

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