

The Effect of Dispersion Hardening on the Regularities and Mechanisms of the Creep of Copper with Submicron Grain Sizes

G. P. Grabovetskaya^a*, I. P. Mishin^a**, and Yu. R. Kolobov^b***

^a*Institute of Strength Physics and Material Science, Siberian Branch, Russian Academy of Sciences, Akademicheskii pr. 2/4, Tomsk, 632055 Russia*

^b*Center of Nanostructure Materials and Nanotechnologies, Belgorod State University, ul. Pobedy 85, Belgorod, 308015 Russia*

**e-mail: grabg@ispms.tsc.ru*

***e-mail: mishinv1@yandex.ru*

****e-mail: kolobov@bsu.edu.ru*

Abstract—Regularities and mechanisms of the creep of submicrocrystalline copper and Cu–1.1 vol % Al₂O₃ dispersion-hardened powder composite in a temperature range of $(0.2–0.35)T_{m\text{ Cu}}$ have been investigated. The role that the grain-boundary state and dispersion-hardening material with Al₂O₃ nanosized (10–40 nm) particles plays in the development of plastic deformation during creep is analyzed.

Key words: submicrocrystalline structure, dispersion-hardened composite, creep, grain boundaries, grain-boundary creeping, localization of deformation.

INTRODUCTION

Many studies [1, 2] show that the submicrocrystalline (SMC) structure of metallic materials, which was formed by methods of intensive plastic deformation (IPD), is, in addition to their small grain sizes, characterized by the nonequilibrium state of their boundary (GB). These grains have a heightened energy and excess volume in comparison with the crystallographic necessary one under given conditions and form long-range fields of elastic stresses and distortions of the lattice in the boundary region. It is known [1, 3, 4] that the heightened diffusion permeability, the reduced migration resistance, and the reduced shearing resistance are inherent in nonequilibrium GBs and not to equilibrium ones. Therefore, the nonequilibrium state of GBs can still negatively affect the development of plastic deformation in SMC polycrystals, which have a great extension of grain boundaries, in the course of the creep even at low homologous temperatures.

One effective way to enhance the migration resistance of GBs and the creeping resistance over them is dispersion hardening [5]. This suggests that the dispersion-hardened SMC-metals with nonequilibrium GBs can have a stable structure and a high level of mechanical properties under the conditions of the creep.

Therefore, it is of interest to study the effect of the dispersion hardening with nanosized (10–40 nm) particles

of the second phase upon the regularities and mechanisms of the creep of SMC-metals obtained by IPD methods.

MATERIALS AND INVESTIGATION TECHNIQUES

As objects to investigate, we use copper (99.97%) and the dispersion-hardened composite material (CM) of Cu–1.1 vol % Al₂O₃ composition, which is produced by the consolidation and internal oxidation of Glide Cop Al-25 (US) powders [6]. The SMC-structure in copper and the composite was obtained by torsion (5 rotations) under pressure (5 GPa). Electron-microscopic studies of fine foils showed [7, 8] that, as a result of the mentioned treatment, in copper and the CM, a SMC-structure is formed whose averaged size of the elements of the grain–subgrain structure is ~0.25 μm. In the SMC-composite, particles of Al₂O₃ 10–40 nm in size are uniformly distributed throughout the volume and are contained both on boundaries and within grains. Also, single coarser (50–100 nm) particles of Al₂O₃ are observed, which is inevitable with powder method for obtaining dispersion-hardened CMs. The SMC-structure of copper is stable up to a temperature of 473 K; one of the copper matrixes of the composite is stable to 673 K. In the course of pre-recrystallization annealings in them, return processes develop intensively, which is evidenced by the variation of the specific resistivity [1]. Annealings in a range of $T = 293–$

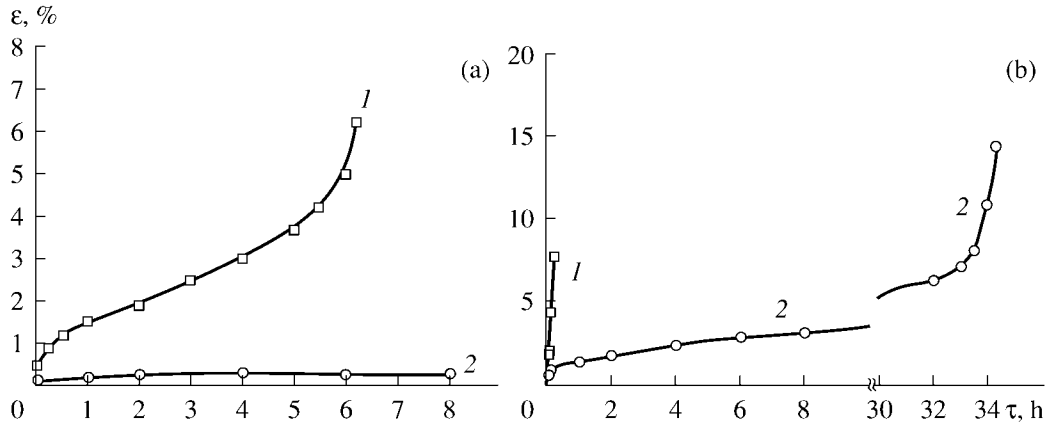


Fig. 1. Curve of the creep of submicrocrystalline (1) copper and (2) Cu-1.1 vol % Al₂O₃ composite at $T = 423$ K and (a) $\sigma = 150$ and (b) 285 MPa.

1073 K do not vary the sizes of hardening particles of Al₂O₃ or their distribution on the volume of the CM.

Creep tests in a temperature range of $(0.2-0.35)T_{m\text{Cu}}$ were performed in vacuum (10^{-2} Pa) with a PV-3012M testing machine. The samples were cut out by the electro-spark method to obtain the shape of a double shovel. Before the test, the ~ 50 - μm -thick layer was removed from the sample surface by mechanical grinding and electrolytic postpolishing. The relative deformation was measured using a KM-6 optical cathetometer with an accuracy of no worse than 0.1%. The deformation relief of the sample surface after creep was studied with the use of a Philips SEM 515 scanning electron microscope.

The value of the apparent activation energy (Q_c) of creep was determined by the method of the temperature jump ($\Delta T = 10$ K) in the course of tests, and its value was computed by the formula [9]

$$Q_c = R \ln(\dot{\epsilon}_2/\dot{\epsilon}_1)/(1/T_1 - 1/T_2), \quad (1)$$

where $\dot{\epsilon}_1$ and $\dot{\epsilon}_2$ are rates of the stable creep before and after the temperature change, respectively; R is the gas constant; and T_1 and T_2 are absolute temperatures.

RESULTS AND DISCUSSION

Figure 1a shows a typical curve of the creep for submicrocrystalline copper and a Cu-1.1 vol % Al₂O₃ composite at $T = 423$ K and the stress $\sigma = 150$ MPa ($0.4\sigma_{0.2}$ of SMC-copper). On the graph corresponding to SMC-copper, three stages of creep are observed: transitional, stationary, and accelerated. For the SMC-composite under the mentioned conditions of the test, the creep is not stated by the used method of the measurement of its rate. With the increase of the applied stress to 285 MPa ($0.4\sigma_{0.2}$ of the SMC-CM), only the accelerated stage of creep is on the curve for SMC-copper (see Fig. 1b); for the composite, all three are characteristic: transitional, stationary, and accelerated. From Fig. 1b it is evident that, at $T = 423$ K and $\sigma = 285$ MPa, the time and defor-

mation before the destruction of the SMC-CM are a factor of ~ 90 and 2, respectively, more than for SMC-copper.

Preliminary pre-recrystallization annealings lead to an increase in the rate of the steady-state creep ($\dot{\epsilon}$) for submicrocrystalline copper and composite; however, it appears differently for them. For example, after preliminary annealing at $T = 423$ K for $\tau = 1$ h, the value of $\dot{\epsilon}$ for SMC-copper at $T = 423$ K and $\sigma = 150$ MPa increases from 1.4×10^{-6} to $6.3 \times 10^{-6} \text{ s}^{-1}$; for the SMC-composite at the same temperature and $\sigma = 285$ MPa, it increases from 4.3×10^{-7} to $8.3 \times 10^{-7} \text{ s}^{-1}$.

The results of experimental investigations for determining the stress dependence of the rate of the steady-state creep of SMC-copper in double logarithmical coordinates $\log \dot{\epsilon} - \log \sigma$ are presented in Fig. 2, where, for comparison, we give similar dependences computed by Koble models [10], grain-boundary creeping (GBC) [11], and dislocation creep [12]. From data of Fig. 2, it follows that the experimental σ dependence of the value $\dot{\epsilon}$ for SMC-copper is described by a power law with the factor $n \sim 6.5$ of the stress sensitivity; this is close to the value $n \sim 7$, which is characteristic for coarse-grained copper under the conditions at which the creep is achieved through the dislocation motion and controlled through diffusion along dislocation tubes [12]. However, the rates of the steady-state creep of SMC-copper, which are observed by the experimental method, are higher than values predicted by the Koble theory of dislocation creep and GBC.

The parameter that indicates the deformation mechanism and determines the value $\dot{\epsilon}$ is the activation energy of creep. Further, we give the values of the apparent activation energy of creep (Q_c and Q_c^*) and the activation energies of volume diffusion (Q_v) and diffusion along dislocation tubes (Q_d) and on grain boundaries (Q_b and Q_b^*) for coarse-grained (CG), nanocrystalline (NC), and

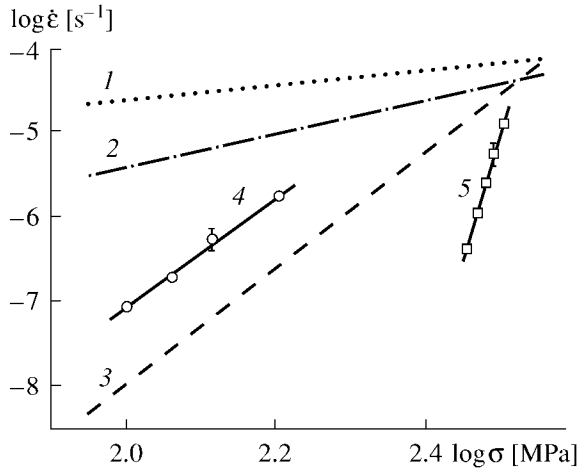


Fig. 2. (1–3) Theoretical and (4, 5) experimental stress dependences of steady-state creep for (1–4, $T = 398$ K) submicrocrystalline copper and (5, $T = 423$ K) Cu–1.1 vol % Al_2O_3 composite.

submicrocrystalline (SMC) copper at $T = 373$ – 423 K, which are expressed in kJ/mol:

Q_c^* (SMC) [exp. data]	71–75
Q_c (CG) [10–12]	117–186
Q_v (CG) [10]	196
Q_d (CG) [10]	117
Q_b (CG) [10]	104
Q_b^* (NC) [14]	61.8

It is evident that the measured values of Q_c^* are a factor of 1.5–2.5 less than Q_c , which is evidence of the change of either the main mechanism of deformation on creep or the diffusion process governing them during the transfer from the coarse-grained structure to the SMC-one.

In the considered temperature interval, copper deformation in the CG-state on creep happens due to the dislocation motion and is governed, according to different data [9, 12–14], by the volume diffusion or diffusion along dislocation tubes. In this case, the value Q_c is close to the activation energy, either that of the volume self-diffusion (Q_v) of copper or the diffusion (Q_d) along dislocation tubes, respectively. The comparison of measured values of Q_c^* with known Q_v and Q_d and, consequently, a decrease in Q_c^* can be related only to the change in the diffusion mechanism governing the dislocation motion from the volume diffusion to the diffusion along dislocation tubes.

It is known [15] that, in materials in the nonequilibrium state (submicrocrystalline obtained by IPD methods fall into this category), the dislocation motion is difficult; therefore, the largest contribution to total deformation should be the mesoscopic mechanisms of the plastic

flow: the grain-boundary creeping and the development of localized deformation bands, along the boundary of which the cooperative GBC is possible. As is known, GBC is governed by diffusion along grain boundaries, the activation energy (Q_b) of which for coarse-grained polycrystals is less than the corresponding values for the diffusion along dislocation tubes (Q_d) by a factor of 1.2–1.3. For copper in the SMC-state, the difference between values Q_b^* and Q_d is evidently higher than for coarse-grain one. For example, the value Q_b^* of NC-copper is approximately half Q_d [16]. Because of this, an increase in the contribution of the GBC in the total deformation of SMC-copper on creep should lead to a decrease in Q_c^* up to a value close to the value of the activation energy for grain-boundary diffusion, which is supported by foregoing data: $Q_c^* \sim Q_b^*$ (71–75 and 61.8 kJ/mol). This gives grounds to suppose that the GBC make a significant contribution to the total deformation of SMC-copper on the creep in the temperature range of $(0.2$ – $0.35)T_{m\text{Cu}}$.

The possibility of a noticeable contribution of GBC in the total deformation of NC- and SMC-materials at low homologous temperatures ($T < 0.3T_m$) was shown theoretically by authors [17]. The development of the GBS in the course of deformation at the room temperature of SMC-copper obtained by the IPD was established experimentally in paper [18], where the contribution of GBC was $\sim 20\%$.

Figure 3a presented the typical view of the deformation relief of the surface of SMC-copper after creep at the steady-state stage at $T = 423$ K. You can see clearly the formation of regions of localized deformation bands with steps (shown by arrows) on the boundaries indicating the development of the cooperative GBS. After pre-recrystallization annealings that lead to a decrease in degree of nonequilibrium of grain boundaries, and the evolution of the deformation tensor of the surface of the SMC-copper is qualitatively retained; however, the density and degree of relief of the bands of localized deformation decrease. After recrystallization of the SMC-structure, the formation of deformation bands in the course of creep at the copper surface is not observed (see Fig. 3b) and the value of the apparent activation energy of creep increases to 102 kJ/mol.

In conditions of the inhibitory effect of particles of the hardening phase on the developme Al_2O_3 SMC-composite, localized deformation bands on the sample surface also don't appear (see fig. 3c). In this case, the value of Q_c^* is 127 kJ/mol, which is a factor of ~ 1.7 larger than for SMC-copper (71 kJ/mol).

The stress dependence of steady-state creep for the Cu–1.1vol % Al_2O_3 SMC-composite, like for SMC-copper, is described by the power law of creep; however, its sensitivity factor of $n \sim 30$ is higher by a factor of 4.5 than for SMC-copper. To explain the

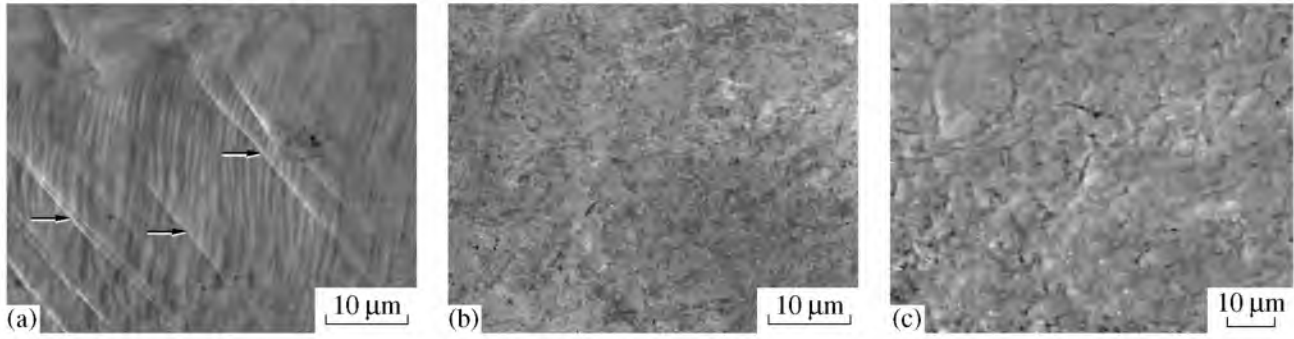


Fig. 3. Deformation relief of the sample surface of (a) submicrocrystalline and (b) recrystallized copper and (c) the Cu-1.1 vol % Al_2O_3 SMC-composite at the steady-state stage of creep at $T = 423$ K, $\varepsilon = 4\%$, and (a) $\sigma = 130$, (b) 80, and (c) 285 MPa.

anomalously high values of n for dispersion-hardened CMs, paper [19] suggests a creep model; in accordance with it, their plastic deformation happens due to the motion of lattice dislocations. At the same time, the σ dependence of $\dot{\varepsilon}$ is presented by the power law of creep and determined through the thermally active separation of the dislocation of the hardening phase from particles. Based on the model [19], authors [20] suggested the following equation to describe the rate of the steady-state creep of ultra-fine-grained dispersion-hardened CMs:

$$\dot{\varepsilon} = \frac{6D_v l \rho_d}{b} \times \exp\left\{-\frac{Gb^2 r}{kT} [(1 - k_b)(1 - \sigma/\sigma_d)]^{3/2}\right\}, \quad (2)$$

where D_v is the coefficient of volume diffusion; ρ_d is the density of mobile dislocations; b is the Burgers vector; G is the shear modulus; r is radius of particles of the hardening phase; k_b is the parameter describing stress relaxation close to the particle–matrix surface; σ is the applied normal stress; $2l$ is the distance between disperse particles; $\sigma_d = \sigma_0 \sqrt{1 - k_b^2}$ is the stress of the separation of the dislocation from a particle; and σ_0 is the yield stress of the composite material by Orowan.

In paper [21], in the considered dependence of $\dot{\varepsilon}(\sigma)$ for ultra-fine-grained dispersion-hardened composites, they suggest, in addition to the Orowan stress, that the long-distance athermic component of stress (σ_a), which prevents the dislocation motion, should be taken into account. For this case, Eq. (2) was written in the following form:

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp\left\{-2T_r \left[(1 - k_b) \left(1 - \frac{\sigma - \sigma_a}{\sigma_d}\right)\right]^{3/2} (kT)\right\}. \quad (3)$$

where $\dot{\varepsilon}_0 = 3D_v l / (Mb)$, $M = 3$ is the Taylor factor; T_r is the linear stress of dislocation; and $\sigma_a = aGbm\rho_d^{1/2}$, $a = 0.2$ is the elastic interaction coefficient.

The computation results for the stress dependence of the rate of steady-state creep for the Cu-1.1vol% Al_2O_3 SMC-composite by Eqs. (2) and (3) at $T = 423$ K are presented in Fig. 4 in double logarithmical coordinates. (The computations were carried out under the assumption that the creep of the studied SMC-composite is governed by diffusion along dislocation tubes because, using the volume self-diffusion coefficient, Eqs. (2) and (3) have no solution for the CM of the given composition in the considered temperature interval.) To compute, we used the equation

$$\sigma_0 = \sigma_{0.2(m)} + [45Gb/(2r)]f, \quad (4)$$

where $f \sim 0.84\%$ is the volume part of Al_2O_3 particles in the material without taking the great precipitations of this oxide, which don't contribute to hardening [7], into account $\sigma_{0.2(m)} = 352$ MPa is the stress yield of the SMC-matrix without particles at $T = 423$ K; $b = 2.56 \times 10^{-10}$ m is the Burgers vector of dislocation in copper [12]; $r = 20$ nm is the radius of Al_2O_3 particles; and $G = 4.0 \times 10^4$ MPa is the shear modulus at $T = 423$ K.

The density of mobile dislocations was determined in the following way [22]:

$$\rho_d^{-1/2} = 0.6Gb/\sigma \quad (5)$$

at applied stresses $\sigma = 270\text{--}320$ MPa.

Values of l were determined on the assumption of the ideal location of particles on angles of a square by formula [13]

$$f = [r/(2l)]^2. \quad (6)$$

From Fig. 4, it is evident that the dependence $\log \dot{\varepsilon} - \log \sigma$ for the 1.1 vol % Al_2O_3 CM (curve 1), which was computed by Eq. (2), doesn't agree with the experimental one (curve 3). The value of the factor n , which was determined by the slope of curve 1 at $k_b = 0.75$, exceeds its measured value approximately by a factor of 3 (~ 98 against ~ 30). (With the variation of k_b , the difference between them is even greater.) The dependence $\log \dot{\varepsilon} - \log \sigma$ computed by Eq. (3) at $k_b = 0.95$ satisfactorily agrees with the experimental one (curve 2), and the

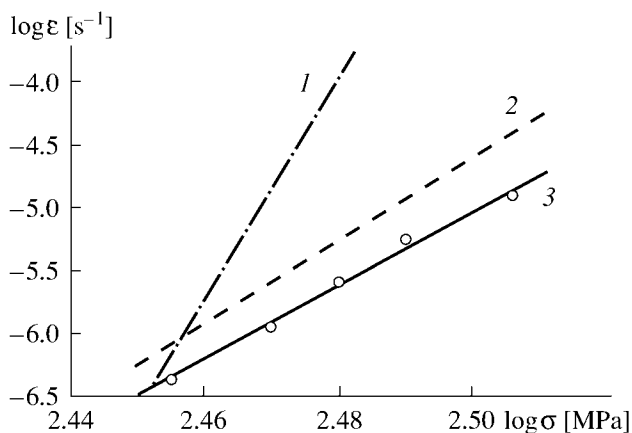


Fig. 4. Comparison of models of the creep of dispersion-hardened CMs with the experimental stress dependence of the rate of steady-state creep of the Cu-1.1 vol % Al₂O₃ SMC-composite. (1) computation by Eq. (2) at $k_b = 0.75$; (2) computation by Eq. (3) at $k_b = 0.95$; (3) experiment at $T = 423$ K.

values of factor n in both cases are similar: ~ 35 and ~ 30 , respectively.

CONCLUSIONS

It was established that the largest peculiarity of the deformation mechanism of submicrocrystalline copper with nonequilibrium boundaries of grains at the steady-state stage of creep in the temperature interval $(0.2-0.35)T_{m,Cu}$ —unlike with the deformation of copper with equilibrium boundaries—is the development of grain-boundary creeping and bands of localized deformation. The presence of hardening nanosized oxide particles at nonequilibrium boundaries of grains in the course of creep prevents not only the development of GBC, but also the localization of plastic deformation in the dispersion-hardened SMC-copper. This leads to an increase in the resistance to creep and deformation before disruption. In conditions of the inhibitory effect of nanosized oxide particles on the development of the GBC, the most likely mechanism of the deformation of dispersion-hardened SMC-copper with nonequilibrium boundaries of grains in the temperature interval $(0.2-0.35)T_{m,Cu}$ is dislocation creep governed by diffusion along dislocation tubes. At the same time, the mechanism that determines the stress dependence of the rate of steady-state creep is local creeping and the consequent thermally active separation of dislocations from hardening particles.

ACKNOWLEDGMENTS

This work was supported by the Siberian Branch of the Russian Academy of Sciences (project SO RAN no. 3.6.2.2) and the Federal Special Program (grant no. 02.513.11.3198). We thank R.Z. Valiev for granting the materials to study.

REFERENCES

1. Kolobov, Yu.R., Valiev, R.Z., Grabovetskaya, G.P., et al., *Zernogranichnaya diffuziya i svoystva nanostrukturnykh materialov*, (Grain-boundary Diffusion and Properties of Nanostructure Materials), Novosibirsk: Nauka, 2001.
2. Noskova, N.I. and Mulyukov, R.R., *Submikrokristallicheskie i nanokristallicheskie metally i splavy*, (Submicrocrystalline and Nanocrystalline Metals and Alloys), Yekaterinburg: Ural Division, Russ. Acad. Sci., 2003.
3. Bokstein, B.S., Kopetskii, I.V., and Shvindlerman, L.S., *Termodinamika i kinetika granits zeren v metallakh*, (Thermodynamics and Kinetics of Grain Boundaries in Metals), Moscow: Metallurgiya, 1986.
4. Chuvil'dyaev, V.N., *Neravnovesnye granitsy zeren v metallakh. Teoriya i prilozhenie*, (Nonequilibrium Grain Boundaries in Metals. Theory and Application), Moscow: Fizmatlit, 2004.
5. Kolobov, Yu.R., *Diffuzionno-kontroliruyemye protsessy na granitse zeren i plastichnost' metallicheskih polukristallov*, (Diffusion-controlled Processes at Grain Boundaries and Plasticity of Metal Semicrystals), Novosibirsk: Nauka, 1998.
6. Schilling, W.F. and Grant, N.J., *Metal. Intern.*, 1973, no. 5, p. 117.
7. Kolobov, Yu.R., Grabovetskaya, G.P., Ivanov, K.V., and Ivanov, M.B. *Khim. Interesakh Ustoichivogo Razvitiya*, 2002, vol. 10, p. 111.
8. Islamgaliev, R.K., Buchgraber, W., Kolobov, Yu.R., et al., *Mater. Sci. Eng.*, 2001, vol. A 319–321, p. 874.
9. Garofalo, F., *Zakony polzuchesti i dlitel'noi prochnosti metallov i splavov*, (Laws of Creep and Creep Rupture Strength of Metals and Alloys), Moscow: Metallurgiya, 1968.
10. Cobl, R.L., *J. Appl. Phys.*, 1963, vol. 34, no. 7, p.1679.
11. Grabskii, M.V., *Strukturnaya sverkhplastichnost' metallov*, (Structural Superplasticity of Metals), Moscow: Metallurgiya, 1975.
12. Frost, G. J. and Ashby, M.F., *Karty mekhanizmov deformatsii*, (Deformation Mechanism Map), Chelyabinsk: Metallurgiya, 1989 (in Russian).
13. Honeycomb, R., *Plasticheskaya deformatsiya metallov*, (Plastic Deformation of Metals), Moscow: Mir, 1972 (in Russian).
14. Raj, S.V. and Langdon, T.G., *Acta Metal.*, 1989, vol. 37, no. 3, p. 843.
15. Panin, V.E., *Fiz. Mezomekhanika*, 2000, vol. 1, no. 6, p. 5.
16. Larikov, L.N., *Metallofiz. Noveishie Tekhnol.*, 1995, vol. 17, no. 1, p. 3.
17. Pozdnyakov, V.A. and Glezer, A.M., *Fiz. Tverd. Tela*, 2002, vol. 44, issue 4, p. 705.
18. Valiev, R.Z., Kozlov, E.V., Ivanov, Yu.F., et al., *Acta Metal. Mater.*, 1994, vol. 42, no. 7, p. 2467.
19. Rösler, J., Joos, R., and Arzt, E., *Acta Metal. Mater.*, 1990, vol. 38, no. 4, p. 671.
20. Sauer, C., Weisgraber, T., Dehm, G., et al., *Z. Metallk.*, 1998, Bd. 89, no. 2, p. 119.
21. Grundmann, U., Gerner, M., Heilmaier, M., et al., *Mater. Sci. Eng.*, 1997, vol. A234–236, p. 505.
22. Harrison, L.G., *Trans. Faraday Soc.*, 1961, vol. 57, no. 7, 9. 1191.