

Diffusion and Properties of Bulk Nanostructured Materials Processed by Severe Plastic Deformation

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Abstract

Thermostability of the structure, diffusion permeability and the features of the mechanical properties of nanostructured copper, nickel and composite Cu – 0.5 mass % Al_2O_3 were investigated. Using nanostructured nickel by way of example the influence of the grain boundary state on diffusion permeability of metallic materials in nanostructured state was studied. The role of dispersion strengthening in stabilisation of nanostructured and its properties during creep was analysed, including, the presence of the action of grain boundary diffusion fluxes of impurity atoms from the environment.

INTRODUCTION

During recent years, bulk nanostructured (NS) materials having size of 0.1–0.3 μm which are produced by severe plastic deformation [1–3] have been developed and studied intensively. These materials attract particular interest because of their unique mechanical and physicochemical properties. They possess high strength, while retaining sufficient plasticity; in certain situations, they may exhibit low-temperature or high-rate superplasticity [1, 4]. The basic properties of NS materials, *e. g.* elastic moduli, Curie and Debye temperature, specific heat, *etc.* [1, 5, 6], are found to vary. Thus it is found [7] that the grain boundary diffusion coefficients of NS materials are a few orders of magnitude higher relative to those of coarse-grain materials.

Wide application of NS materials obtained by severe plastic deformation (SPD) involves at least two main problems. One of these problems is the instability of non-equilibrium structure connected with high energy accumulated by severe plastic deformation [1]. It is well known that such instability is the cause of intense softening at relatively low

temperature. This temperature is close to 373 K for several NS materials, for example, copper [8]. An other problem is the increased diffusivity of material in NS state which leads to high sensitivity to the influence of environment [9].

One of the effective methods to enhance the thermostability of structure and mechanical properties of metals and alloys is dispersion hardening. In recent years, investigations have been begun on development nanostructured composites, where together with the matrix strengthening by high-stable oxide, carbide or some other nanosized phase (10–15 nm) the nanostructured state (grain size ~0.1–0.3 μm) by SPD is formed. The low solubility of strengthening phases and their high resistance to coagulation allow one to assume that the nanostructured composites will have high stability of structure and properties under simultaneous action of load and temperature.

In view of the above, complex investigations of the stability of structure and of physical and mechanical properties (including creep under grain boundary diffusion of copper and aluminium atoms from an external source (coat-

ing) [8]) of the NS nickel, copper and copper-based composites produced by SPD have been carried out.

EXPERIMENTAL

Nickel (99.95 %), copper (99.90 %) and Cu – 0.5 mass % Al_2O_3 composites (Glide Cop Al-25) in NS state (grain size $d \sim 0.3$ mm) were investigated. Coarse-grained (nickel ($d \sim 20$ mm), copper ($d \sim 10$ mm) and the composite in initial as-received state were studied for comparison. Cu – 0.5 mass % Al_2O_3 composite is produced by internal oxidation of mixture copper and aluminium powders [10]. Nanostructure in the materials investigated was obtained by torsion under high pressure and by equal-channel angular (ECA) pressing [1]

TEM studies of thin foils of the investigated materials were carried out on EM-125K microscopes. The distribution of Al_2O_3 particles in the composite matrix was studied by the replica method on an EM-125K microscope at 100 kV. Metallography studies were carried out on a Neophot-21 microscope.

Microhardness was measured with a PMT-3 device under load of 100 g. Specific electroresistivity was measured by a potentiometric four-point method on samples, $12 \times 0.09 \times 0.016$ cm in size at 77 K. The measurement error was 7 %.

Tensile and creep tests were carried out in vacuum at 10^{-2} Pa with a PV-3012M test machine in the temperature ranges of 293–673 and 398–673 K, respectively. A solubility of Al_2O_3 in the copper matrix in the investigated temperature interval does not exceed 10^{-18} atom fraction [11]. Double-spade shaped samples for the mechanical tests were cut by electric-spark method. Before the testing, the surface layer 50 mm thick was removed by mechanical polishing followed by electropolishing.

Grain-boundary diffusion coefficients were obtained using concentration profiles of copper penetration into nickel during diffusion annealings. Diffusion anneals of copper-coated nickel were performed in vacuum at 10^{-2} Pa for 3 to 5 h at the following temperatures: 423, 573, 773, 823 and 873 K. In addition, NS nickel samples were annealed at 373 K for 95 h in air. The concentration of copper in nickel

was measured by the method of secondary ion mass-spectroscopy (SIMS) using a MC-7201 device. The measurement error was about 20 %.

The effect of grain boundary diffusion fluxes of impurity atoms from environment on the creep of NS materials was studied using copper-covered nickel (Ni(Cu) system, diffusion impurity is indicated in brackets), and aluminium-covered copper and composite (Cu(Al) and Cu – Al_2O_3 (Al) systems) as an example. Copper layer having 12–15 mm in thickness was electrodeposited on the surface of the nickel samples. Aluminium layer 10 mm in thickness was ion-plasma sprayed on the copper and composite samples.

RESULTS AND DISCUSSION

The TEM studies of thin foils of investigated materials reveal that the microstructure of nickel and copper subjected to SPD has an intricate diffraction contrast which prevents one from distinguishing dislocation structure details (Fig. 1). Extinction contours are frequently observed in grain volume, which suggests the existence of internal stresses on grain boundaries [12]. The average grain size as determined from dark-field images is (0.26 ± 0.08) mm for NS nickel and (0.30 ± 0.06) mm for NS copper. A great number of reflexes arranged circle-wise are observed in electron-diffraction patterns obtained for an area of 1 mm^2 , some of the reflexes showing azimuthal smearing which is indicative of the existence of high-angle misorientations among nanostructural components and of elastic stresses in individual grains.

The anneals of NS nickel performed in the temperature interval of 398–548 K result in no significant structural changes (including grain size) which could be measured by electron microscopy. However anneals conducted at 523 and 548 K bring about a 10–20 % increase in the number of grain boundaries having a streaky contrast and disappearance of the extinction contours within the grains surrounded by such grain boundaries. The same structural changes of NS copper are observed in the temperature interval of 373–448 K. This is evidence for the evolution of the processes of

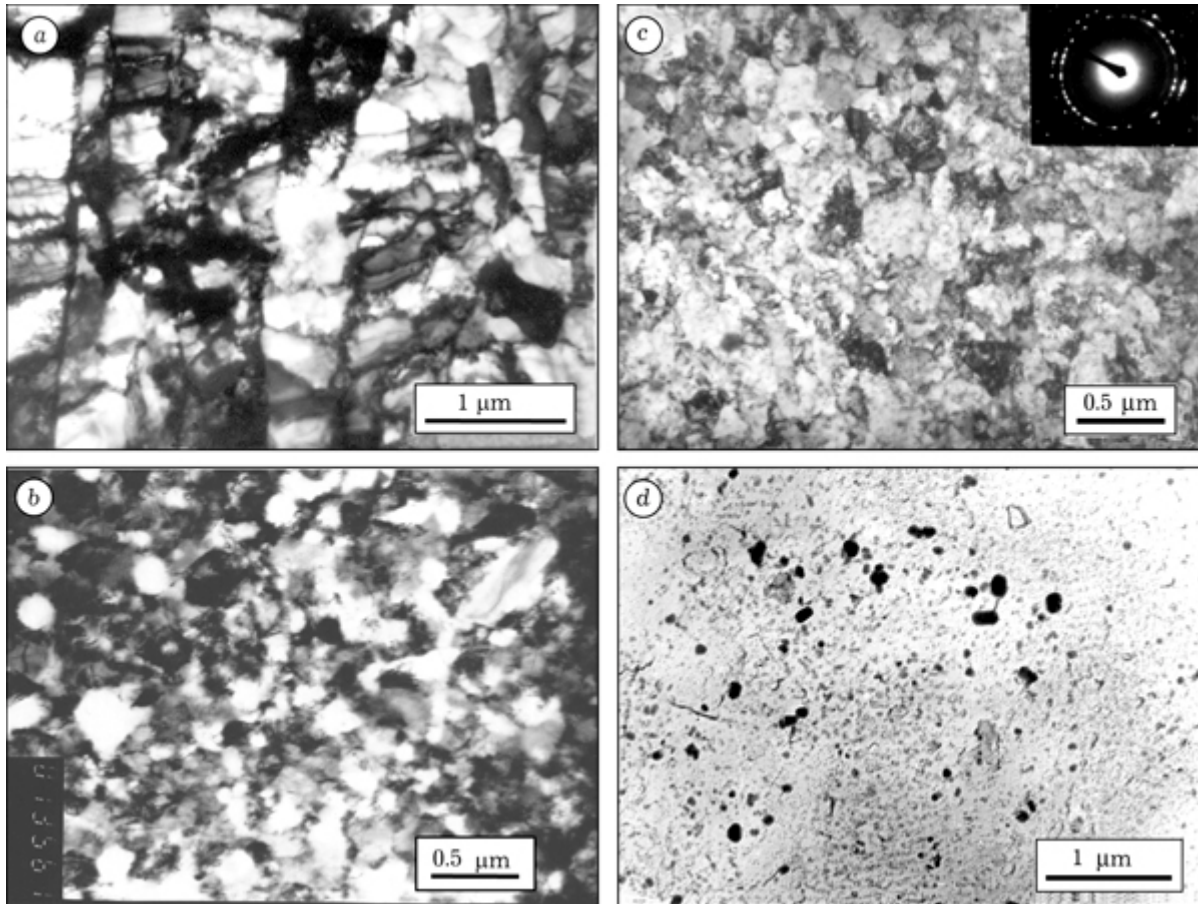


Fig. 1. Microstructure of nanostructured nickel (a), copper (b) and composite Cu - 0.5 mass % Al₂O₃ (c - thin foil [9], d - replica with extracted particles).

stress relaxation on the above grain boundaries, with the grain size remaining unchanged. Recrystallization of NS nickel and copper occurs at 573 and 473 K, respectively.

The nanostructured Cu - 0.5 mass % Al₂O₃ composite has ultrafine-grained structure ($d \sim 0.2 \mu\text{m}$). It is established by the extraction replica method that dispersed particles of Al₂O₃ having size less than 20 nm are homogeneously distributed in the composite volume. There are individual areas containing bigger Al₂O₃ particles (50–100 nm).

Anneals carried on in the temperature interval of 423–1073 K influence neither the size of Al₂O₃ strengthening particles nor their distribution in the composite volume but lead to structural changes in the copper matrix. These data are correlated with the literature data [11] where it was established that Al₂O₃ particles size and their distribution in copper matrix are not changed by annealing up to 1273 K.

Anneals conducted at the temperatures below 673 K cause no changes in the grain size of the copper matrix; however, relaxation processes occur intensively. The decrease of the level of internal stresses may be due to re-distribution and annihilation of dislocations in the grain boundaries and near-boundary regions [13]. The first recrystallized areas arise in the structure of the composite after annealing at 673 K (1 h). The recrystallization process occurs slowly and a temperature increase from 673 up to 873 K does not result in complete recrystallization. Complete recrystallization of the copper matrix occurs during annealing at 1073 K for 1 h, the average grain size of the copper matrix is 2.5 μm. For comparison, the recrystallization temperature of NS copper is 448 K.

The measurements of microhardness, H_m , performed for NS nickel and copper show that nanostructure formation by SPD enhances H_m relative to coarse-grained counterparts. Varia-

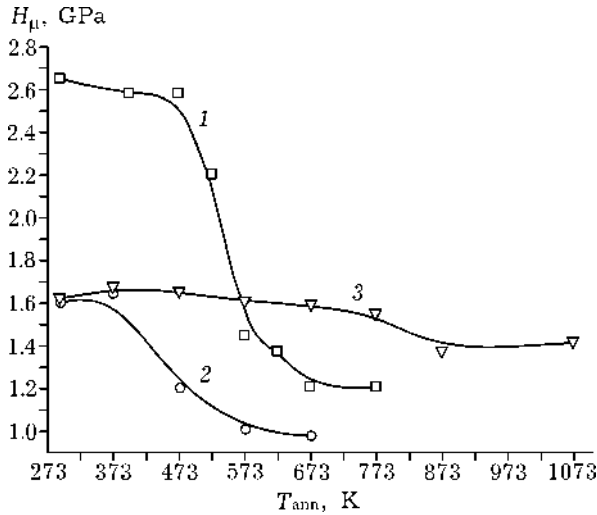


Fig. 2. Microhardness vs. the temperature of preliminary annealing: 1 – NS nickel, 2 – NS copper, 3 – NS Cu – 0.5 mass % Al_2O_3 composite.

tion in this quantity with annealing temperature occurs non-monotonically (Fig. 2). After annealing is performed in the range of temperatures close to recrystallization temperatures, H_m decreases sharply. With increasing annealing temperature, H_m gradually decreases to the value characteristic for coarse-grained state.

An important feature of the NS composite investigated is high thermal stability of H_m relative to pure coarse-grained and NS copper (see Fig. 2). For example, the NS composite subjected to SPD and to annealings in the temperature interval of 673–873 K has microhardness of 1.60–1.67 GPa. After annealings at higher temperatures (973–1073 K), H_m decreases down to 1.40 GPa; however, the quantity remains 3 times higher than that of recrystallized copper (0.5 GPa).

The other physical and mechanical properties of NS nickel and copper also change non-monotonically with annealing temperature. Figure 3 shows the plots of variation in the relative specific resistance (τ/τ_0 ; τ_0 is specific resistance of non-annealed material) against the temperature of preliminary annealing. As is seen from Fig. 3, a sharp reduction in the specific resistance of NS nickel and copper, which become close to those of the coarse-grained counterparts, is observed in the temperature interval in which no grain growth takes place, with only the processes of recovery

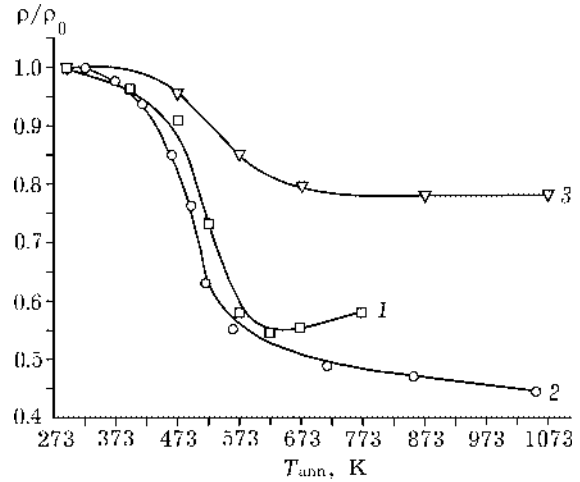


Fig. 3. Specific resistivity vs. the temperature of preliminary annealing: 1 – NS nickel, 2 – NS copper, 3 – NS Cu – 0.5 mass % Al_2O_3 composite; τ_0 – specific resistivity of the as-processed NS samples.

occurring in the grain-boundary structure. A significant decrease (by 20 %) in the resistance of the NS composite is observed in same temperature interval as in the case of NS copper (see Fig. 3).

The dependence of s_B , $s_{0.2}$ and d on annealing temperature obtained for NS nickel (Fig. 4) reveals that an essential decrease of $s_{0.2}$ is observed in the temperature interval where there is no grain growth, while a decrease of s_B and d mainly occurs after the beginning of grain growth.

Comparative tensile testing of the Cu – 0.5 mass % Al_2O_3 composite in NS and as-received states reveals that the formation of na-

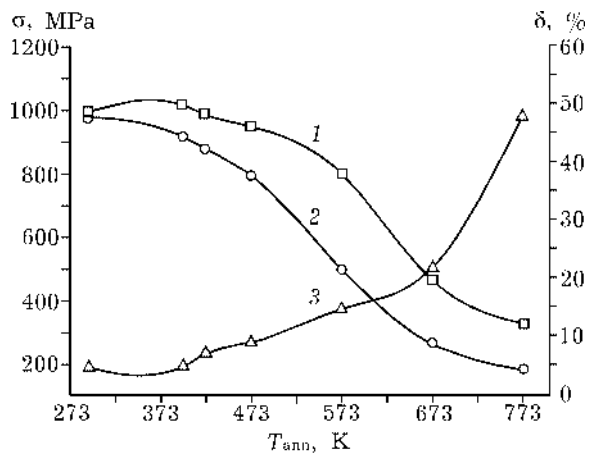


Fig. 4. Strength (1), yield strength (2) and elongation up to failure (3) vs. the preliminary annealing temperature for nanostructured nickel. $T_{\text{tests}} = 293$ K.

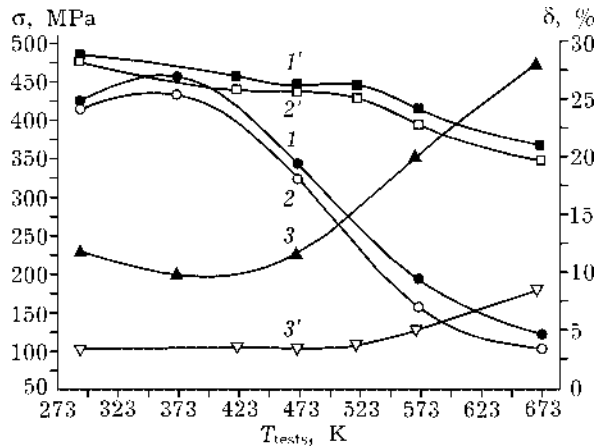


Fig. 5. Strength (1, 1'), yield strength (2, 2') and elongation up to failure (3, 3') vs. the tests temperature for nanostructured copper (1-3) and Cu - 0.5 mass % Al_2O_3 composite (1'-3').

nostructure results in an enhancement of strength and yield strength by 20 and 35 %, respectively. Deformation up to failure decreases by 4 times. The anneals of the NS composite conducted at 673 and 873 K for 1 h. lead to a decrease of s_B and $s_{0.2}$ and to an increase of d . But even after annealing at 873 K, the strength properties of the composite in a NS state are higher than those of NS copper.

Figure 5 represents the temperature dependence of strength, s_B , yield strength, $s_{0.2}$, and elongation up to failure, d , obtained for NS copper and for the Cu - 0.5 mass % Al_2O_3 composite. Evidently, at ambient temperature the values of s_B and $s_{0.2}$ obtained for NS copper are close to those of the composite and exceed the respective values obtained for coarse-grained copper by 1.6 and 2 times, respectively (Table 1). The values s_B and $s_{0.2}$ decrease monotonously with temperature while plasticity, d , grows. It should be noted that s_B

and $s_{0.2}$ observed for the composite decrease more slowly with temperature than those of NS copper. The high thermal stability of the mechanical properties of the composite is probably due to Al_2O_3 particles, dispersed in the composite volume. Al_2O_3 particles may block dislocations and grain boundary migration and thus impede material recrystallization, which leads to material softening.

Diffusivity of NS metals was investigated using Ni(Cu) system as an example. Figure 6 shows the temperature dependence of grain-boundary diffusivity of copper in NS nickel. Additionally, the self-diffusion coefficients in coarse-grained and nanocrystalline (produced by powder consolidation method) nickel are represented [14]. The grain-boundary diffusion coefficients were calculated using the concentration profiles of copper penetration into nickel. It was taken into account that, according to TEM, grain boundaries in NS nickel do not migrate and volume diffusion is «frozen» [15]. Calculating the grain boundary diffusivity (D_b) for coarse-grained nickel, one takes account of the migration of grain boundaries at 773-873 K.

It is seen from Fig. 6 that the grain boundary diffusivity observed for NS and nanocrystalline nickel at the same temperature may differ by 1-5 orders of magnitude. In addition, the above values obtained for NS nickel in different experiments are found to scatter by 2-3 orders. Such scattering may be due to various production methods and to different purity grades of the samples. Moreover, the diffusion processes occurring in NS nickel depend on the grain boundary state.

The steady-creep rates of NS nickel, copper and the Cu - 0.5 mass % Al_2O_3 composite

TABLE 1

The dependence of the mechanical properties of NS copper and Cu- 0.5 mass % Al_2O_3 composite on the annealing temperature

Material	State	$s_B \pm 10$, MPa	$s_{0.2} \pm 10$, MPa	$d \pm 0.5$, %
Copper	NS	369	352	7.2
	NS + annealing (353 K, 1 h)	358	309	8.3
	Coarse-grained	225	180	5.0
Cu-0.5 mass % Al_2O_3	NS	510	475	6.2
	NS + annealing (673 K, 1 h)	474	429	11.8
	NS + annealing (873 K, 1 h)	423	355	21.6

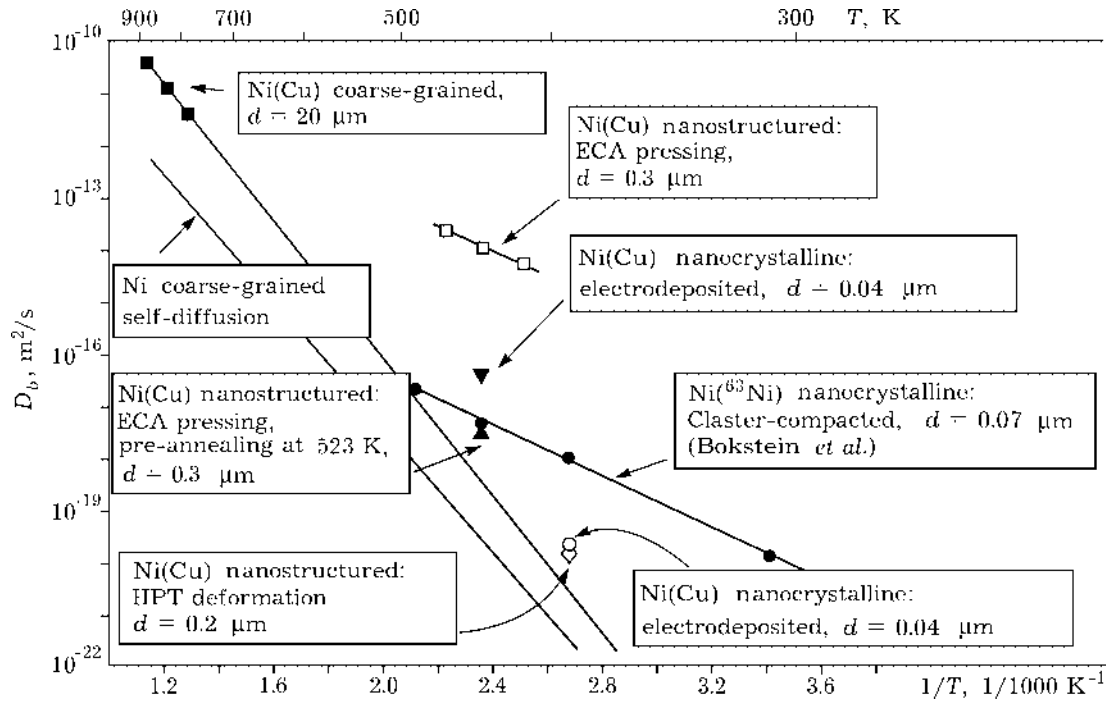


Fig. 6. Arrhenius plot of copper grain boundary diffusivities in nickel in different states.

both in a NS SPD state and in an annealed state obtained at $T = 423$ K and $s \sim (0.60-0.65) s_{0.2}$ (s is stress) are represented in the Table 2. For comparison, the creep rates obtained for the composite in as-received extruded state are also listed. Obviously, the creep resistance of the NS materials decreases after non-recrystallization anneals, which may be caused by the relaxation of the defect structure of the matrix. Incorporation of dispersed particles of Al_2O_3 into the NS matrix of the composite results not only in an essential enhancement of creep resistance, but also increases its thermal stability.

As was noted above, the decrease of diffusivity in NS state results in high sensitivity of such structure to the influence of environment.

Thereupon, investigation of the effect of impurity atoms diffusion from coating on the creep of NS materials is of great interest. Creep studying of Ni(Cu) and Cu(Al) systems in the temperature interval of 373–523 K reveals that diffusion impurity fluxes moving from the surface into the bulk of the NS metals tested in the narrow temperature interval (398–473 K) bring about a significant enhancement of the materials' creep rates and growth of deformation up to the materials failure. It was previously found [1] that an analogous effect is observed for coarse-grained nickel and copper in the temperature intervals of 773–923 K and 573–673 K, respectively. Thus the effect of creep activation is observed for SPD NS metals under the action of diffusion impurity fluxes

TABLE 2

Steady-state creep rates of NS nickel, copper and Cu – 0.5 mass % Al_2O_3 composite at 423 K

Material	s , MPa	State	$\dot{\epsilon}$, s^{-1}
Nickel	630	NS	2.8×10^{-7}
		NS + annealing (398 K, 1 h)	1.1×10^{-6}
Copper	130	NS	2.3×10^{-7}
		NS + annealing (353 K, 1 h)	2.2×10^{-6}
Cu-0.5 mass % Al_2O_3	285	NS	4.3×10^{-7}
		NS + annealing (353 K, 1 h)	6.2×10^{-7}

from external sources at significantly lower temperatures relative to the respective coarse-grained counterparts, which may be due to the enhanced diffusivity of the NS materials.

The creep tests of the NS composite conducted in vacuum under the action of diffusion aluminium fluxes from the surface show that the creep curves obtained remain unaffected by the above fluxes. It has been shown elsewhere [9] that the effect of creep activation of polycrystals by the influence of grain boundary impurity diffusion fluxes is stipulated by the activation of grain-boundary sliding and by greater contribution of the latter process to the overall deformation. It is contended that the absence of the above effect during the creep of the Cu – 0.5 mass % Al₂O₃ composite might be attributed to the well-known effect of breaking of grain-boundary sliding by dispersed particles arranged along the grain boundaries [16].

CONCLUSIONS

1. Severe plastic deformation methods enable one to form in polycrystalline materials a nanostructure having grain size less than 0.5 μm . Such materials possess superior mechanical properties relative to their coarse-grained counterparts.

2. Using grain-boundary diffusion of copper in nickel by way of an example, it has been shown that the diffusivity of nanostructured materials processed by severe plastic deformation is by 1–5 orders of magnitude higher relative to their coarse-grained counterparts.

3. The effect of creep activation is observed for nanostructured copper and nickel under the action of diffusion grain-boundary impurity fluxes from external sources in the interval of temperatures, which are significantly lower relative to those of coarse-grained counterparts. This might be due to an essential enhancement of diffusivity of metals in the nanostructured state relative to the same coarse-grained materials.

4. Incorporation into the nanostructured copper matrix of strengthening nano-sized phase results in superior mechanical properties and enhanced thermostability of the material. In so doing, the effect of creep activation associated with the activation of grain-boundary diffusion fluxes from the environment is virtually eliminated.

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