STRUCTURE, PHASE TRANSFORMATIONS, AND DIFFUSION

Evolution of Structure of Cu−Nb Composite under High-Pressure Torsion and Subsequent Annealing

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Abstract—The evolution of structure of a multicore in situ Cu-18Nb composite under high-pressure torsion (HPT) by one, three, and five anvil revolutions was investigated by scanning and transmission electron microscopy, and microhardness measurements. Thermal stability of the HPT deformed structure was studied after annealings in the 300−800°C temperature range. The combined use of repeated cold drawing and HPT made it possible to refine the structure and thereby to obtain equiaxed grains with a size of 10−30 nm, which sharply increased the microhardness (to 4800 MPa). Under the subsequent annealing the nanocrystalline structure is retained and; the microhardness remains considerably higher than that of the composite not subjected to HPT. Thus, the combination of repeated cold drawing with further high-pressure torsion provided substantial strengthening and higher thermal stability of the composite in comparison with niobium and copper nanostructured by severe plastic deformation.

INTRODUCTION

Nanostructured materials showing high strength, good plasticity, elevated resistance to fatigue and corrosion, and low-temperature superplasticity are of great interest [1−3]. Bulk nanostructured materials can be produced by currently well-known methods of severe plastic deformation (SPD) [4, 5], particularly by high pressure torsion (HPT) [6]. This method allows us to continuously deform the materials including brittle and strengthened ones up to high degrees in a wide temperature range [7−10].

The structure refinement caused by SPD is limited by a dynamic recrystallization and an achievement of saturation stage, in which an increase in the degree of deformation does not lead either to further refinement of the structure or to strengthening of the material [11]. At this stage, the density of generated dislocations is so high that their motion is blocked in all existing slip systems and there comes an equilibrium between the deformation-induced strengthening and the recovery processes. In addition, the obtained nanostructures possessing special properties are characterized by low thermal stability, especially in pure metals [12]. One way to overcome these problems is alloying leading to a change in the energy of stacking faults, deformation mechanism, and the temperature range of recrystallization [13].

The combined use of various SPD methods (for example, hot extrusion or equal-channel angular pressing (ECAP) and HPT) is a relatively new direction to obtain more dispersed and stable structures [14]. The processing of copper-based composites after rolling or drawing with application of SPD is of great interest [15]. After deformation with high degrees, composites whose second component (Nb, Fe, Cr, Ag, and W) has an extremely low solubility in the matrix become so-called microcomposites with unique properties, in particular, extremely high strength while maintaining good electrical conductivity [16]. The subsequent action of severe plastic deformation (ECAP or HPT) allows us to gain additional knowledge about nanostructuring, saturation stage, mechanical alloying, interdiffusion, thermal stability, and the maximum achievable strength of materials.

Cu−Nb composites demonstrate the highest strength characteristics while maintaining high electrical conductivity and are used in the creation of superconductors based on Nb_3Sn [17]. The structure and properties of the individual components of the Cu−Nb composite, copper and niobium, after high-pressure torsion have been studied in many publications [18−22].

The aim of this work was to study the evolution of the structure of a multicore Cu−Nb composite under the action of HPT followed by annealing and to carry out a comparison with the behavior of its constituents treated in the same way.
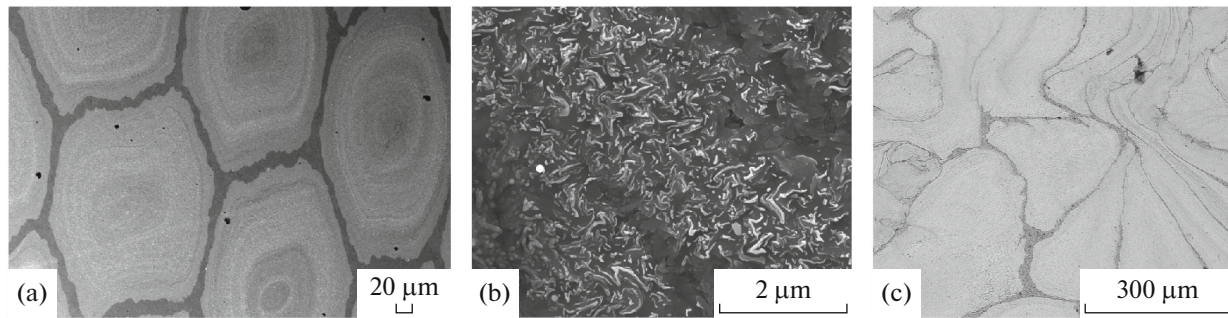
Fig. 1. SEM images of the structure of the Cu—18Nb composite (a, b) in the initial state and (c) after HPT with one revolution (at half radius).

EXPERIMENTAL

In this paper, we studied a multicore Cu—18Nb composite developed and manufactured at the Bochvar High-Technological Research Institute of Inorganic Materials [23]. A rectangular bar (3 × 5.8 mm in size) consisting of 600 in situ single-core Cu—18Nb microcomposites placed in a matrix of high-purity copper was used. The true drawing strain was $e = 12.5$. The structure of this composite was studied previously in [24].

Disks 0.5 mm thick cut from the rod were deformed by high-pressure torsion. The deformation was performed in open Bridgman anvils with a diameter of 10 mm at room temperature using one, three, and five anvil revolutions under a pressure of 6 GPa with an angular velocity of 0.3 rpm. To study the thermal stability of the structure formed, the deformed samples were annealed at temperatures from 300 to 800°C for 1 h. The annealing was carried out using a vacuum tube furnace under a pressure of $10^{-2}–10^{-3}$ Pa.

The structure was studied by scanning electron microscopy using Quanta-200 and Inspect F microscopes and transmission electron microscopy using a JEM-200CX microscope.

Microhardness was measured using a special attachment in a Neophot-21 optical microscope and calculated as $H = 18192P/L^2$ MPa, where P is the load (50 g) and L is the indentation diagonal (µm). Each value L was calculated as an average of no less than nine indentations. The microhardness measurement error was 2–3% and no higher than 5% at a reliability level of 0.95.

RESULTS AND DISCUSSION

The initial (undeformed) rectangle sample is seen in Fig. 1a to present hexagonal Cu—Nb composite strands in a copper matrix. Inside the strands, there are alternating brighter and darker rings. EDS analysis showed that in the brighter rings, Nb filaments are located more closely to each other. Their transverse section is seen (Fig. 1b) to have a curved shape. This

morphology was observed in in situ Cu—Nb composites and is attributed to the peculiarities of sliding systems in bcc niobium and the effect of the fcc copper matrix [17, 25, 26].

Under the action of HPT, the rectangle sample is flattened into a round disk. In this case, the strands approach each other, the copper layer between them becomes thinner and gradually disappears, and then strands are curled in the direction of rotation of the anvil (Fig. 1c). After HPT with one revolution, the structure is inhomogeneous along the radius of the sample, which is typical of this deformation method and was noted in [6—10, 22]. In the center of 1-revolution HPT sample, the strands are flattened, but retain the shape of polyhedrons, and at the edges they are elongated and curled. After five revolutions, the strands are curled over the entire cross section and the copper layer between them is not visible.

Let us consider the evolution of the fine structure under HPT. After one revolution of anvils, the structure is inhomogeneous. In the central part and at the half radius of the sample, there are ribbon-like Nb filaments with a fragmented structure consisting of fine equiaxed grains (Fig. 2a). After HPT by three revolutions, the structure becomes more homogeneous and is represented by a mixture of fine (20—30 nm) equiaxed grains over the entire cross section. Increasing the number of revolutions (up to five) results in even more homogeneous and dispersed (grain size of 10—20 nm) structure (Fig. 2b). In this case, the electron diffraction pattern in Fig. 2c is seen to consist of Debye rings corresponding to copper and niobium. The reflections are located close to each other, making the rings almost continuous.

It should be noted that the interplanar distances for both phases correspond to the referenced values. Thus, as a result of HPT process there are no distortions of the niobium lattice and no amorphous regions as differentiated from initial state [24]. There is no noticeable dissolution of these phases in each other. According to [27], under the action of HPT, the mutual solubility of Cu—Nb composite components increases and reaches 1.5 at % Nb in Cu and 10 at %
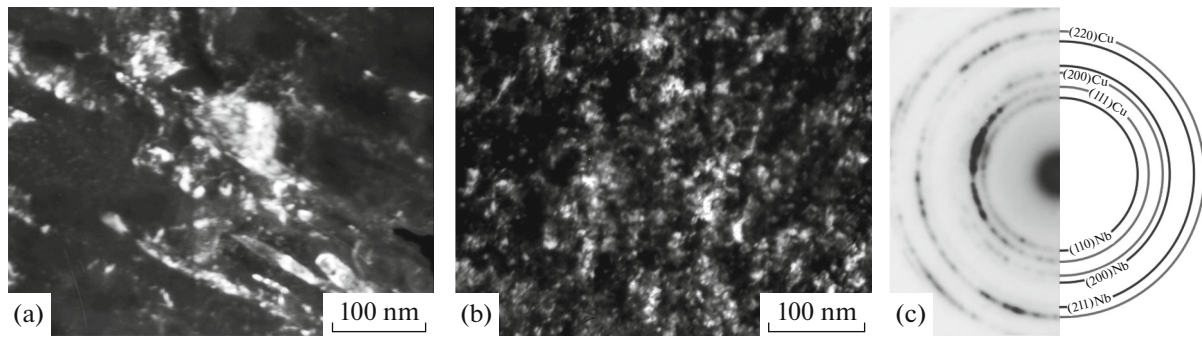
Fig. 2. Structure of the Cu−18Nb composite after HPT with (a) one and (b) five revolutions: (a, b) dark-field images in the $(111)_{Cu}$ and $(110)_{Nb}$ reflections; (c) electron diffraction pattern.
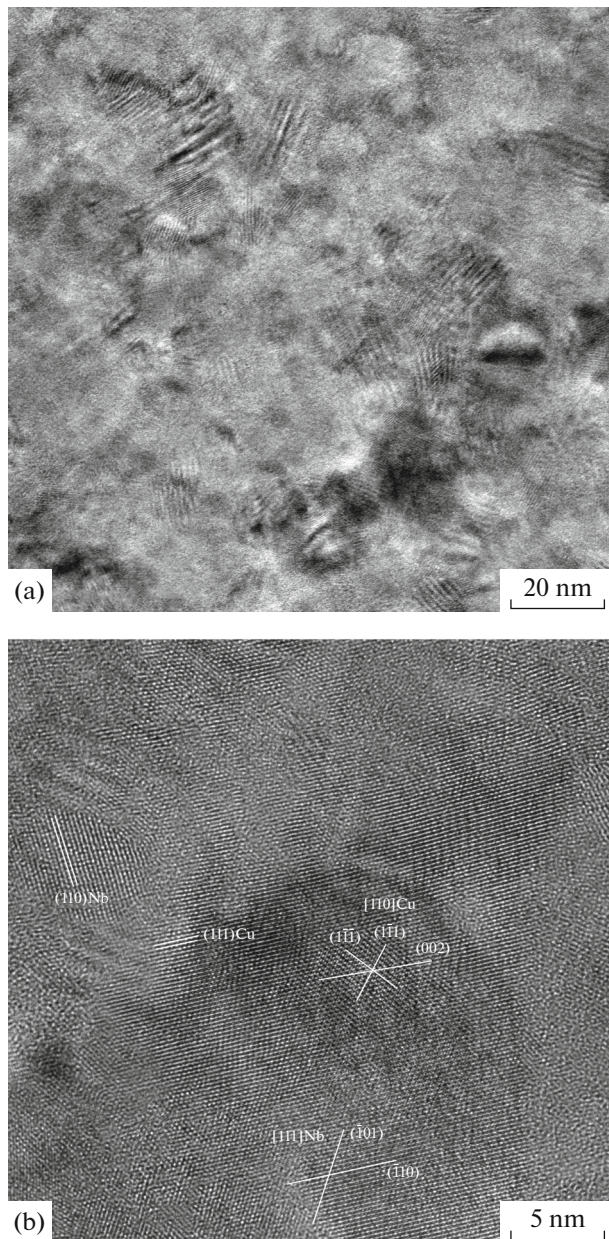

Fig. 3. High-resolution TEM images of the Cu−18Nb composite after HPT with five revolutions: (a) overall view of grains; (c) niobium and copper grains with indicated planes.

Cu in Nb, but, nevertheless, both phases are retained in contrast to the Cu−Fe composite, in which a supersaturated solid solution of Fe in copper is formed upon HPT [28]. Since the Debye rings of $(110)_{Nb}$ and $(111)_{Cu}$ are close to each other, they fall into the aperture together when obtaining dark-field images, and thereby, dark-field images contain grains of both copper and niobium.

Grains of both phases can be distinguished only by HREM. These studies were carried out by V. Popov Jr. using a Titan Themis 60−300 FEG-S/TEM microscope [29, 30]. In Fig. 3, grains of niobium and copper are seen in Fig. 3 to have an equiaxed almost spherical shape and are approximately the same in size. Note that their sizes in the initial composite were significantly different. Copper grains had the shape of polyhedrons with a size of 200−300 nm and were surrounded by oddly shaped Nb interlayers with a thickness of 30−40 nm [24]. After HPT, the grains are located randomly without predominant mutual orientations of copper and niobium (Fig. 3b).

The grain size (10−20 nm) obtained in the composite under study is an order of magnitude finer than that of the initial pure metals by this method at room temperature (150−200 nm for copper [9, 31, 32] and 100−150 nm for niobium [22, 33−35]). Such a significant refinement of the structure should be accompanied by a significant increase in the microhardness. Indeed, the microhardness of the composite in the initial state was 3200 MPa, and its values (at the half radius of the sample) increased to 3700, 4250, and 4800 MPa after HPT by one, three, and five anvil revolutions, respectively.

When creating materials with special properties by severe plastic deformation methods, it is important to create a homogeneous ultrafine-grained (UFG) structure with high strength and to ensure its stability at elevated temperatures. Therefore, much attention is paid to the behavior of UFG materials upon annealing, that is, to the study of the thermal stability of the structure formed by SPD.
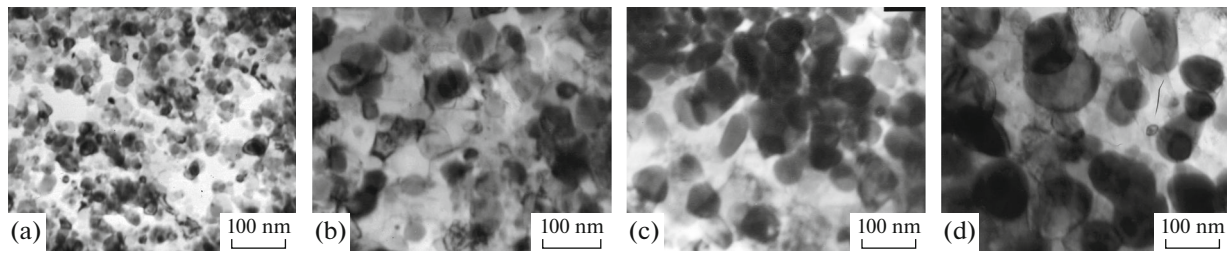
Fig. 4. TEM images of the Cu−18Nb composite after HPT with five revolutions and subsequent annealing at (a) 500, (b) 600, (c) 700, and (d) 800°C.

Figure 4 shows the TEM images of the Cu−Nb composite after HPT by five anvil revolutions and subsequent annealing. The structure after annealing at 300°C remains practically unchanged and is still represented by fine Cu and Nb polyhedral crystallites. It can be noted that the crystallite boundaries become clearer, which indicates relaxation processes. An insignificant increase in the grain size is observed after annealing at 400°C; however, the polyhedral shape of grains is retained. Starting from 500°C, the crystallites noticeably increase and their shape changes (Fig. 4a). Niobium grains acquire a spherical shape and are embedded in a copper matrix whose grains are still polyhedral. In bright-field images presented in Figs. 4b−4d, niobium grains are seen as dark round spots against the background of copper matrix. With increasing the annealing temperature, the grain sizes noticeably increase. However, after annealing at 800°C, the sizes of both Nb particles and Cu grains do not exceed 100 nm. Thus, after the completion of recrystallization, the nanocrystalline structure in the Cu−Nb composite is retained, since the Nb and Cu crystallites inhibit the growth of each other.

The round shape of niobium grains is inherited from the structure of the composite not subjected to HPT. As noted above, Nb filaments in the composite after cold drawing acquire the shape of thin curved ribbons; as a result of annealing, their structure becomes bamboo-like with a round transverse section [24, 36, 37]. Possible mechanisms of such an evolution of the structure of the composite upon annealing were discussed in [37]. Spheroidization of Nb occurs due to the destruction of the Cu/Nb interfaces, as well as due to the coalescence of adjacent Nb particles to reduce the surface energy.

Figure 5 shows the microhardness values of the Cu−Nb composite after drawing and HPT as a function of annealing temperature. These dependences are practically symbatic. The microhardness is seen to decrease slightly after annealing at 300°C. Within the range of 400−700°C, there is a significant drop in the microhardness values. With a further increase to 800°C, the falling of curve is retarded.

A similar three-step decrease in the microhardness was observed in pure niobium subjected to HPT [8, 33]. The first stage corresponds to the processes of recovery, which favor a decrease in the internal elastic stresses and density of dislocations. At the second stage, there is an active recrystallization with a significant increase in the grain size. The third stage is the growth of recrystallized grains. Although the temperature ranges of these stages are practically the same in the composite after both drawing and HPT, it can still be argued that the thermal stability of the structure after HPT is higher. Despite a sharp drop in the microhardness, the curve remains at a much higher level than that after drawing and annealing. This also corresponds to the evolution of the microstructure, which, as shown above, remains submicrocrystalline even after annealing at 800°C.

Thus, the application of HPT to composites consisting of two practically insoluble phases after repeated cold drawing makes it possible to additionally refine and stabilize the nanocrystalline structure. Such materials demonstrate significant strengthening and retain high strength characteristics after anneal-
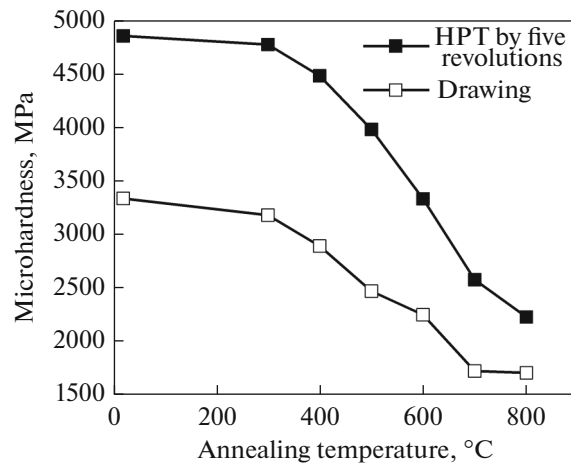

Fig. 5. Microhardness of the Cu−18Nb composite after drawing (□)) and HPT (■) as a function of annealing temperature.

ing, while their pure constituents are characterized by coarser structure and loss of strength.

CONCLUSIONS

The effect of high-pressure torsion on the structure of a multicore in situ Cu−18Nb composite has been studied. Under the action of HPT, the ribbon shape of Nb filaments is destroyed and a mixture of equiaxed copper and niobium grains is formed. The size of formed grains is 10−20 nm that is an order finer than that of pure Cu and Nb subjected to the same deformation.

Such a significant refinement of the structure is accompanied by an increase in the microhardness by 1.5 times as compared to its value of the composite after repeated cold drawing with a true strain of 12.5. The subsequent annealing in the temperature range of 400−800°C leads to a grain growth and a decrease in the microhardness. Nevertheless, the structure remains nanocrystalline with grain sizes less than 100 nm; the microhardness values are higher than that in the composite after drawing and similar annealing. Thus, the combined use of cold drawing and high-pressure torsion enables us to produce a nanocrystalline structure which is more dispersed and thermally stable than in the composite after drawing, as well as in pure copper and niobium subjected to HPT.

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Translated by O. Golosova