ON THE POSSIBILITY OF FORMATION AND PROPERTIES OF COPPER–SILVER SOLID SOLUTIONS UNDER SEVERE PLASTIC DEFORMATION

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Mechanical alloying of Cu *and Ag powders in concentrations* Cu_{1-x}–Ag_x *(x at.% = 0.1, 0.2, ..., 0.9) under high-pressure torsion is investigated. The alloys obtained have a structure of nanograined nonequilibrium FCC solid solutions with positive deviation from Vegard's law. The hardness of the alloys is 4–6 times higher than of the initial components – copper and silver. The energy and power parameters of treatment of the solid solutions and stages of their formation are calculated from the shear stress measured in situ under high pressure. Thermally induced decomposition of the solid solutions begins from aging under normal conditions, is accelerated upon heating, and ends by short-term heating up to 500°C. It is accompanied by simultaneous development of the processes of gathering recrystallization.*

Keywords: Cu–Ag solid solution, sever plastic deformation, high pressure, mechanical solution, mechanical alloying, decomposition, nonequilibrium, nanocrystalline, nanostructure, hardness.

INTRODUCTION

Cu–Ag systems have a positive mixing enthalpy of 5 kJ/mol [1] and a limited solubility caused by violation of the second Hume–Rothery rule, since the relative deviation of ionic radii of these *d*-transition metals with close values of electron affinity is 23% [2]. For several reasons, the properties of the Cu–Ag systems, including similar physical and mechanical properties of their elements, absence of intermetallic compounds, electrical and medical applications, prospects for obtaining deformation-induced amorphous state of copper or silver based alloys stabilized by alloying, and good comprehension of microstructure and properties of pure components and their alloys are of great scientific and practical interest [3, 4]. Products of mechanical synthesis conventionally obtained by ball milling are in the powder state and have a number of disadvantages peculiar to the milling method: impurities, uncontrolled and undesirable heating, and methodological limitations on investigation of the structure and especially mechanical properties of powders [5]. For reliable structural attestation and measurements of physical and mechanical properties of synthesized solutions, they must be prepared as bulk solid samples by the method of high-pressure torsion in the Bridgman chamber with dies made from superhard cermets BK-6 and c-NB [6, 7]. This method allows megaplastic strain degrees to be achieved with simultaneous control over the treatment parameters, including pressure, temperature, and strain degree almost without sample contamination by the material used for treatment.
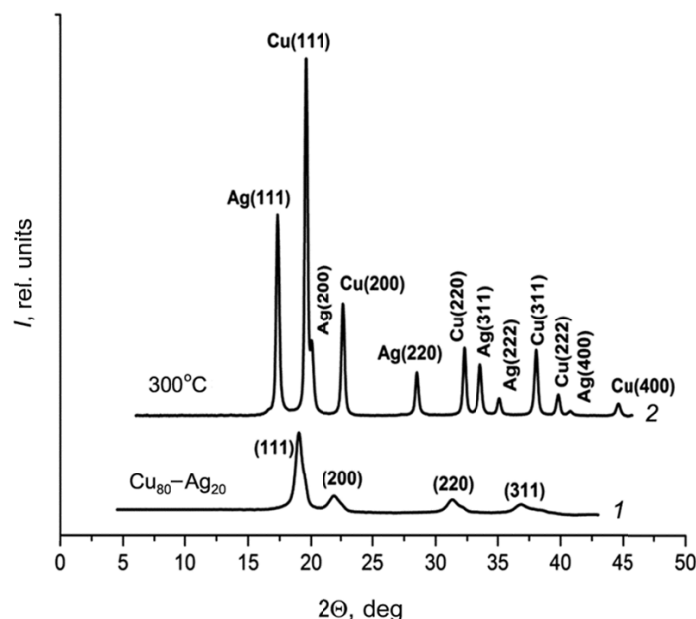
Fig. 1. X-ray diffraction patterns of the Cu_{80}–Ag_{20} samples. Here curve *1* is for the sample alloyed mechanically and treated in three steps at $T = 293$ K and curve *2* is for the sample alloyed mechanically and annealed at 300°C for 5 min.

MATERIALS AND EXPERIMENTAL TECHNIQUE

Mixtures of the Ag (99.99%) and Cu (99.70%) powders (see Fig. 1) in concentrations Cu_{1-x}–Ag_x ($x = 0.0, 0.1, …, 0.9, 1.0$) where subjected to high-pressure torsion with angular velocity of 1.0 rpm at 20°C to plastic strain degrees $0.5 \leq \varepsilon \leq 8.1$ on the true deformation scale, $\varepsilon = \ln\left(1 + \varphi^2 R^2 / h^2\right)^{1/2}$, where R is the radius counted from the anvil rotation axis, φ is the rotation angle, in radians, and h is the thickness of the disk samples [6]. The metal powder mixtures consisted of sawdusts with sizes of 100–500 μm sawn from silver ingots and of particles of chemically reduced copper with sizes of 30–100 μm. After deformation, disc-shaped samples with thickness of 100–140 μm and diameters of 5.0 or 10.0 mm were prepared. The torsion shear force F was measured *in situ* under high pressure as a function of the rotation angle $\varphi = 2\pi n$, where n is the number of rotations. The shear stress τ for the anvil radius $R = 2.5$ mm was calculated from the formula $\tau = \dfrac{3l}{2\pi R^3} F$, where l is the length of the lever that transmits force from the anvil to an electronic dynamometer ACDS-1I-1 with signal recording on a PC. The mixtures were treated at angles $\varphi = 2\pi n$, $n = 1.0, 3.0, 10.0$, and 40.0 corresponding to strain degrees $\varepsilon = 4.1, 5.9, 7.1$, and 8.1, respectively. The method allows high strain degrees to be obtained, but has a special feature – inhomogeneity of the deformation along the sample radius (anvil platforms). For this reason, to decrease the inhomogeneity of the deformation, treatment was performed in three steps $n = 10 + 10 + 10$ [6, 7]. After that three-step treatment, the samples acquired a monochromatic color determined by the initial concentration of the components in the charge with hardness values that remained unchanged along the sample diameter. The structural and phase compositions of the samples were investigated by a complex of methods: transmission electron microscopy (TEM) using a JEM-200 CX electron microscope, x-ray diffraction (XRD) with CuK_α radiation using a DRON-1 diffractometer, and in transmitted synchrotron radiation (SR) at $\lambda = 0.03685$ nm with registration using a MAR345 image plate detector. Integrating over all directions the lauegrams in SR, they were transformed into plots of the intensity dependence on the diffraction angle 2θ, and the parameter a (nm) of the alloy
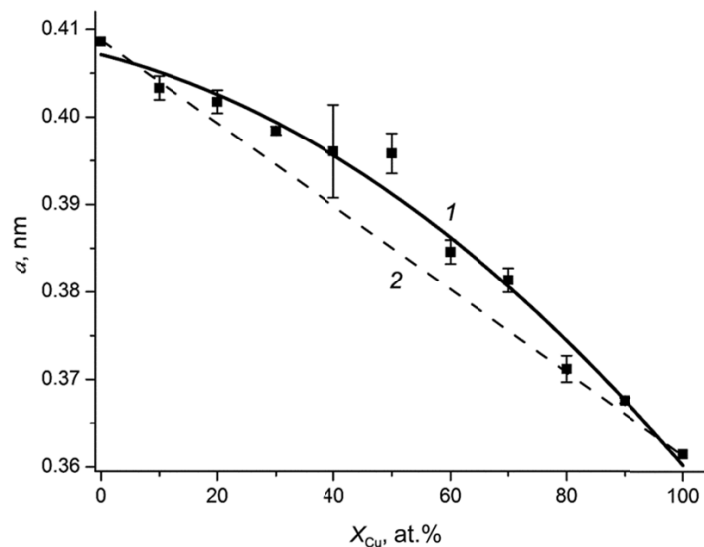
Fig. 2. Dependence of the lattice parameter (curve *1*) of the mechanically synthesized Cu$_{1-x}$–Ag$_x$ (x = 0.0, 0.1, …, 0.9, 1.0) alloys and linear dependence (curve *2*) of the lattice parameter (Vegard's law).

lattice was calculated from positions of the peak centers of gravity. The Vickers microhardness H_μ was measured using a PMT-3 microhardness tester with a load of 0.5 N. The structure was investigated and H_μ was measured for fresh samples prepared mechanically no later than 3–4 hours ago. In the case of longer time period between the sample preparation and measurements, they were held in liquid nitrogen at a temperature of 78 K. To investigate the thermal stability of alloys, the samples were held at room temperature for two–three weeks or were annealed in steps at 300, 400, and 500°C for 5 min.

EXPERIMENTAL RESULTS AND DISCUSSION

The Cu and Ag powders and their mixtures were deformed by axial compression at 8.0 GPa and by combination of compression and torsion that led to the transformation of a compact into disc-shaped samples. XRD analysis demonstrated that the deformation of the pure Cu and Ag powders and Cu$_{1-x}$–Ag$_x$ mixtures (x = 0.0, 0.1, …, 0.9, 1.0) monotonically increasing under constrained conditions caused the structural-phase changes in them, which affected the relative intensities, profiles, and positions of lines in diffraction patterns (curve *1* in Fig. 1).

When the deformation of mixtures increased, mutual shear of the copper and silver peaks on the scale of angles 2θ was observed. Severe deformation caused their complete merging into one wide symmetrical peak of the first-order reflection. For higher-order reflections, the peak profiles approach to, but do not reach full symmetry (curve *1* in Fig. 1). Based on the XRD analysis, we can conclude that cold mechanical alloying of Cu and Ag into FCC substitutional solid solutions took place with concentrations of the composition of the initial discharge. A positive deviation of the parameter a (nm) of alloys from Vegard's law was observed (Fig. 2). Error in measuring a (nm) was higher for equiatomic composition and compositions close to it due to strong diffraction peak broadening as a consequence of lower stability of solutions with these concentrations. Annealing at 300 and 400°C for 5 min caused separation of X-ray reflections from copper and silver and their narrowing that testified to the thermally initiated decomposition of the solid solutions obtained by mechanical alloying and the decrease of internal stresses (curve *2* in Fig. 1). Heating at 500°C for 5 min led to complete decomposition of solutions and initiated gathering recrystallization and appearance of copper oxide.
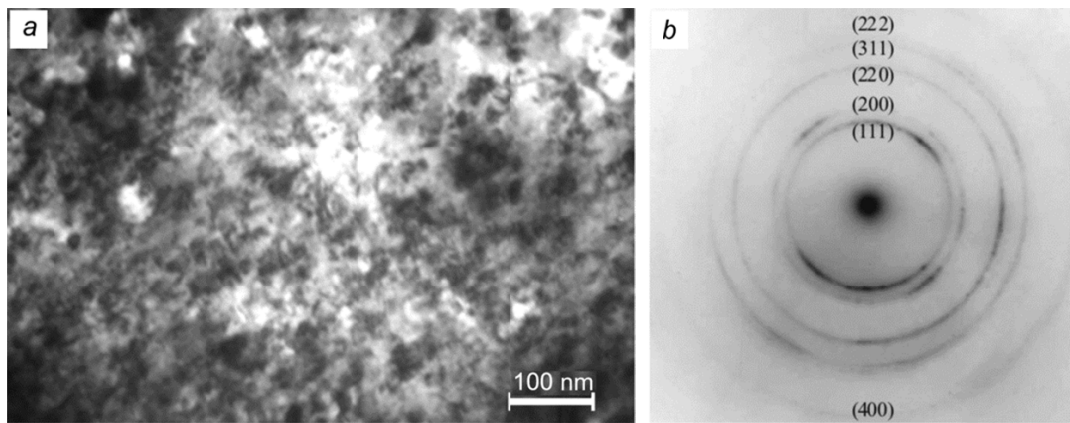
Fig. 3. Microstructure of the mechanically alloyed mixture of Cu_{80}–Ag_{20} powders after the three-step treatment at $\varepsilon = 8.1$. Here case *a* is for the bright field TEM image, and case *b* is for the electron microdiffraction pattern. The low sharpness was caused by decomposition upon exposure to the electron beam of the microscope.

The TEM investigations of the samples after three-step treatment at $\varepsilon = 8.1$ ($n = 10 + 10 + 10$) demonstrated the presence of a specific microstructure. In the bright-field image, the structure consists of individual light and dark roundish fragments with sizes of 10–25 nm. However, sections of highly defective microstructure were observed in the form of individually indistinguishable high-density dislocation pileups. The average fragment size in the Cu_{80}–Ag_{20} composition was about 20–25 nm (Fig. 3*a*), and its maximal size reached 50 nm. Clusters of 5–20 light and dark roundish fragments that were in contrast with the surrounding sections were detected in addition to individual fragments. The contrast can be explained by different values of absorption of the electron beam passing through the foil due to different concentrations of copper and silver in clusters. In sections enriched with silver compared to its average content in the initial mixture, the intensity of the transmitted beam decreased; it increased in sections depleted in silver and enriched with copper compared to their average concentrations. In microstructures, dark and light clusters were formed. The TEM and XRD data suggested that the deformation-induced single-phase state of the FCC solid solution was observed (Fig. 3*b*). Wherein, sections from which the doublet Debye rings were observed in the electron microdiffraction patterns were detected in foils. During TEM investigations modification of Cu_{80}–Ag_{20} alloy foil sections upon exposure to electron beam was observed, namely, fragments under the beam acquired a more rounded shape when observed through the microscope with exposure time of 15–20 s or longer. Changes of the microstructure upon uncontrolled local heating by the electron beam were due to a very nonequilibrium state of the concentration of solutions and their imperfection. This circumstance also hindered obtaining a sharp TEM image of the structure of nonequilibrium alloys upon heating by an electron beam (Fig. 3). Aging of the samples obtained by deformation and of their foils at a temperature of 20°C for up to 2 weeks and longer also led to the formation of the microstructure consisting of clusters of globular contrast fragments. On the electron microdiffraction patterns of such sections, the doublet Debye rings were observed with superimposed more intensive point reflections from larger crystallites.

The dependence of the *in situ* measured force F and the torsion shear stress τ of the samples calculated for it on the strain degree for pure silver and copper powders demonstrated comparatively fast saturation at angles $\varphi = \pi/2$ for silver and $\varphi = \pi$ for copper (Fig. 4).

Saturation of τ for pure copper and silver without subsequent growth of hardening can be explained by the dynamic equilibrium established between the competing processes of hardening and dynamic recovery. The Cu–Ag mixtures of powders demonstrated higher shear strain with a more delayed saturation of τ. This was caused by superposition of the strain processes not only of the structural fragmentation, but also of the solid solutions of Ag and Cu components and hence by manifestation of solid solution hardening. The work and power spent for deformation were calculated from the measured torsion shear strain force and the mass of the samples. The specific power per atom of the Cu_{80}–Ag_{20} mixture deposited in the stage close to saturation, that is, in the stage of maximal refinement of the
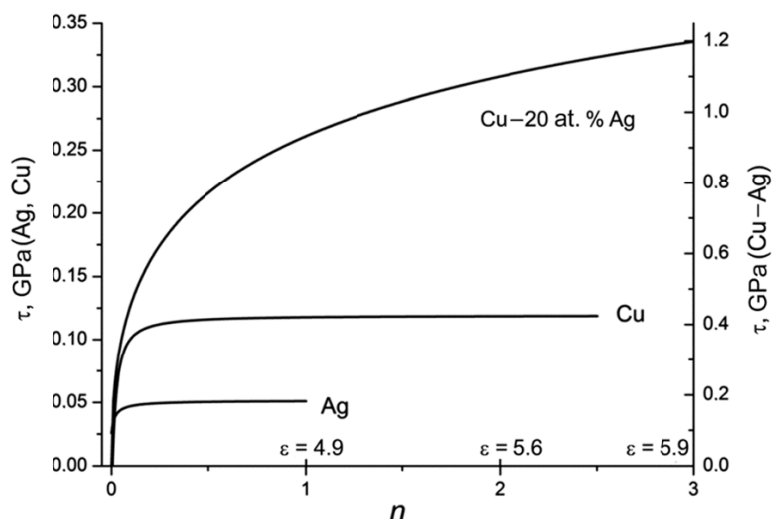
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Fig. 4. Dependence of the *in situ* torsion shear stress of pure silver and copper and Cu_{80}–Ag_{20} mixture on the strain degree.
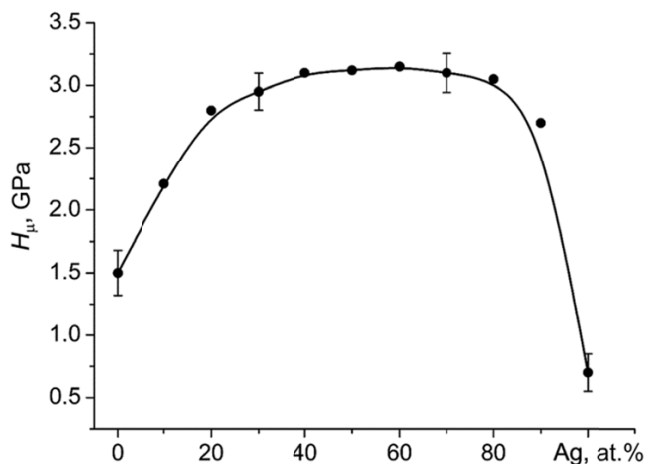

Fig. 5. Microhardness of the Cu_{1-x}–Ag_x (x = 0.0, 0.1, …, 0.9, 1.0) mechanically alloyed samples.

structure and formed mixtures, was 4.7 and 3.8% of the binding energy of the silver and copper lattice, respectively. The energy characteristics of high-pressure deformation of the powder mixtures refer to intensive deformation treatment, and only extreme processes of substance modification, for example, by a shock wave, are more intensive [8]. To proceed to the extreme processes for which the energy comparable to the lattice binding energy is deposited into the system, in the case of the employed treatment, deformation by torsion with angular velocity greater by 2 orders of magnitude is required. Direct measurements of sample heating using a copper-constantan thermocouple in different deformation stages demonstrated that the temperature of macroscopic heating exceeded the room temperature by no more than 10–12°. Low macroscopic heating is caused by intensive two-side removal of heat liberated upon deformation from the thin samples to the massive anvils and by high thermal activity of the sample materials and the Bridgman dies.

Measurements of the microhardness H_μ in the center of the radius of all disk samples allowed the dependence of the microhardness on the concentration of components to be established (Fig. 5). Values of H_μ of the alloys were higher than H_μ of pure Cu and Ag samples and were comparable with the hardness of tempered austenite steels, for

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example, 12Cr18Ni10Ti stainless steel. The Cu–Ag samples alloyed mechanically had increased brittleness compared to the pure components, which was also due to their strong fragmentation, high nonequilibrium concentration of the obtained solid solutions, and high level of internal stresses.

A set of data on the structure, thermal stability, and mechanical properties of the alloy samples allows us to analyze the processes and physical mechanisms of forming the Cu–Ag nonequilibrium solid solutions and to determine the degree of their homogeneity. By the present time, the stage changes in the structure of single-phase pure metals during cold and low-temperature deformation have been established [9, 10]. In this case, the processes of saturation of the lattice by different defects whose concentration is determined by the specific thermobaric conditions and deformation rate, are observed in metals. As a result, metals reach the nanostructured state that corresponds to anomalously high self- and heterodiffusion and regimes of dynamic saturation of the shear stress $d\tau/d\varepsilon = 0$. The complex character of the dynamic behavior is complicated even greater for mixtures of chemically dissimilar metals subjected to structural fragmentation and heterogeneous stress-diffusion initiated by severe deformation. The deformation on the meso- and microlevels caused the shape of metal particles to change: their laminar stretching in thin layers is observed with subsequent turbulent eddies, torsions, rotations, and breaking of layers. These processes lead to strong – by several orders of magnitude – increase in the contact areas of the elements. Interlayers of mixed states that thicken and, in their turn, are also subjected to structural changes and fragmentation to the nanocrystalline state, are formed on the boundaries of contacts of the dissimilar metals due to stress-diffusion. The complexity of the processes of joint deformation of the mixtures allows only qualitative models [5, 11–13] of mass transfer by flows of nonequilibrium point defects, vacancies, and interstitial atoms formed in the process of dragging of vacancy and interstitial jogs by crossing dislocations [14, 15] to be used. In the process of severe deformation of the Cu–Ag mixtures, the equilibrium *formation – decomposition of the solid solution* is established with dynamical equilibrium $d\tau/d\varepsilon = 0$. As mentioned above, the concentration and structural equilibrium in dynamics corresponds to certain thermobaric conditions and treatment rate. Thus, first, the state is extremely saturated with defects, and the volume fraction of atoms in the intercrystallite space with $d_{aver} = 20$ nm is about 25–30% [16]. Second, the solid solution on the crystallite scale significantly exceeds the chemically equilibrium state with almost zero equilibrium mutual solubility of Cu and Ag at 293 K [2]. The homological temperature $T_{hom} = T_{def} / T_{melt}$, where T_{def} is the deformation temperature and T_{melt} is the melting temperature, is 0.24 for silver and 0.22 for copper at 293 K. Therefore, room temperature is comparatively low for the activation of conventional diffusion, although it is well known that the processes of dynamic and post-dynamic recrystallization occur in pure copper upon severe deformation at 80 and 293 K [9], whereas the processes of gathering recrystallization occur in it upon aging and heating to 100°C. This demonstrates the saturation of the structure with high-density defects and the increase of the internal energy. In our case, just after intensive treatment the system is far from equilibrium both in saturation by lattice defects of various topologies and in strong excess of the equilibrium concentration of the mutually mixed copper and silver atoms. When the treatment is finished, the system is shifted from the dynamic equilibrium *formation – decomposition of the solid solution* toward the decomposition of the solid solution. Manipulations with samples after deformation treatment – relieve from shear and compressive axial stresses, preparation of foils, and temporal aging under normal conditions – require time that leads to decomposition of nonequilibrium solid solutions and system transition to the stable state. Moreover, globules having different contrasts enriched with copper and silver are formed. Therefore, the state of the samples with the sections of still preserved nonequilibrium solution and sections in which decomposition has already started was registered by the TEM method. It should also be noted that the microstructure of the Cu–Ag alloys obtained differs from the microstructures of severely deformed pure metals and stable alloys [9, 10] or solid solutions mechanically alloyed for systems with negative shear enthalpies, for example, Cu–Ni or Cu–Zn systems [6]. In the latter, globular nanocrystallites were absent after identical intense deformation treatment, since the decomposition processes do not proceed in these systems with negative shear enthalpy.

Generation of nonequilibrium point defects upon plastic deformation of initial mono- and polycrystalline FCC metals was modeled in a number of works (for example, see [17, 18]). According to the results of calculations presented in [18], the concentration of nonequilibrium vacancies of deformation origin increased by 5–6 orders of magnitude from $5 \cdot 10^{-12}$ to $5 \cdot 10^{-7}$ for $\varepsilon = 0.4$–0.8; it increased from $5 \cdot 10^{-13}$ to $7 \cdot 10^{-7}$ for bivacancies [18]. The concentration of the interstitial atoms increased even stronger: from 10^{-22} to 10^{-13}. The calculated data are in a good agreement with *in situ* experimental measurements [19] in copper mono- and polycrystals during deformation, where it was demonstrated that

the orders of magnitudes of the local vacancy concentrations for $\varepsilon = 0.4$–0.6 reached 10^{-7} in monocrystals and 10^{-6} in polycrystals. Moreover, the change in the concentration of the grain boundaries having deformation origin from 10^{-5} to 10^{-4} for $\varepsilon = 0.4$, which is initial for the present work, was also established in [19]. Therefore, the concentration of grains significantly increased up to 10^{-3} with the deformation, which caused further fragmentation of the structure [20], with a considerable increase in the excessive volume. The set of theoretical and experimental data on the effect of severe deformation on the structural changes of the metal allows alloying of the elements and hence the formation of nonequilibrium solid solutions together with their microstructures to be explained qualitatively.

To accelerate the mutual penetration and spreading of atoms, including dissimilar ones, throughout the crystal, multiple acts of generation, migration, and annihilation of nonequilibrium point defects should be modeled. Upon cold deformation, generation and annihilation of vacancies and interstitial atoms occur during annihilation of dislocation dipoles, climbing dislocation jogs, dragging elementary and long jogs during intersection of forest dislocation, their climbing, etc. [14, 15]. The resulting nanostructural state of the system is achieved via multiple elementary acts of plastic deformation leading to nanofragmentaion of the structure accompanied by the formation of solid solution in the conditions of cold plastic deformation under high pressure.

CONCLUSIONS

The Cu–Ag alloys with the structure of nanocrystalline FCC nonequilibrium solid solutions have been obtained in the process of severe cold deformation under high pressure. The solid solutions obtained were chemically homogeneous on the scale of spherulites with sizes 20–25 nm and of their clusters and had high hardness and brittleness. The alloys obtained by deformation were unstable and decomposed during aging, heating, and upon exposure to an electron beam of the microscope. The special features of the formation, microstructure, and thermal stability established for the nonequilibrium solid solutions consisting of pure components of the Cu–Ag system should be considered in their preparation and application as solid lubricants or additives.

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