Letters on Materials 9 (4), 2019 pp. 400-404 www.lettersonmaterials.com

https://doi.org/10.22226/2410-3535-2019-4-400-404 PACS: 61.46.-w, 82.40.Fp

Investigation of Cu_5Zr particles precipitation in Cu-Zr and Cu-Cr-Zr alloys subjected to quenching and high strain rate deformation

I. V. Khomskaya†, V. I. Zel'dovich, N. Yu. Frolova, D. N. Abdullina, A. E. Kheifets

†khomskaya@imp.uran.ru

M. N. Miheev Institute of Metal Physics Ural Branch of RAS, 18 S. Kovalevskaya St., Ekaterinburg, 620108, Russia

The paper studies the decomposition of a supersaturated solid solution with a precipitate of particles of the copper-zirconium phase in the Cu-0.06 wt.% Zr and Cu-0.21 wt.% Cr-0.20 wt.% Zr alloys in two initial states, i. e. after solid-solution quenching and after high strain rate deformation (10^5 s^{-1}) by the method of dynamic channel-angular pressing (DCAP). It has been shown that the decomposition of the supersaturated solid-solution of zirconium in copper in the quenched micro-alloyed Cu-Zr and low-alloyed Cu-Cr-Zr alloys occurs in two stages. At the first stage, nanoparticles of a metastable copper-zirconium phase are formed. The crystal structure of the nanoparticles is close to the structure of the copper matrix. At the second stage, particles of the equilibrium Cu_5Zr phase are formed in the form of rods. Annealing (aging) of the alloys deformed by DCAP is characterized by the predominance of heterogeneous precipitation of Cu_5Zr nanoparticles at sub-grain boundaries and dislocations, and the decomposition begins at a lower temperature. The particle size is less by an order of magnitude than that in the quenched state. The precipitation of nanoparticles at dislocations retards the formation of recrystallization centers. It has been shown that the treatment including DCAP and annealing at 450°C for 1 h substantially increases microhardness of the micro-alloyed Cu-0.06%Zr alloy by a factor of 2.7 as compared to the initial quenched state. This behavior is related to substantial structure refinement during DCAP and decomposition of the supersaturated α-solid solution of copper.

Keywords: copper alloys, high strain rate deformation, decomposition of the supersaturated solid solution.

1. Introduction

Copper alloys with small additions of chromium and zirconium belong to the group of precipitation-hardenable micro- and low-alloyed alloys, characterized by a good combination of strength and electrical conductivity [1–5]. They are widely used in the electrical and atomic-energy industry. To obtain a submicrocrystalline (SMC) structure in copper alloys, methods of severe plastic deformation (SPD), such as high-pressure torsion, equal-channel angular pressing (ECAP), multidirectional forging have been used [5–9]. In this investigation, we used a new method of SPD, namely, the dynamic channel-angular pressing (DCAP) [10–12], which is a high-strain-rate (with strain rates of 10^4–10^5 s^{-1}) variant of ECAP. The advantage of the DCAP method is in the use of the energy of gunpowder gases instead of the energy-consuming pressing equipment, the short duration ($5\cdot10^{-4}$ s) of one pressing cycle, and the opportunity of obtaining bulk SMC metals and alloys using only two to four cycles [10–14].

It is important to emphasize that, in the case of DCAP, the simple shear deformation, which produces the structure upon ECAP, is a high-strain-rate process; moreover, upon DCAP, a high-speed shock-wave compressive strain takes place, which creates an additional source of deformation-induced work hardening. It was previously established that the strength of precipitation-hardenable copper alloys with 0.2–0.5 wt.% Cr and Zr can be additionally increased by optimizing the temperature-time parameters of post-deformation annealing [1–5,13,14]. The process of solid solution decomposition in Cu-Cr-Zr alloys has been investigated repeatedly [1–4,13–16]. The morphology and microstructure of precipitating chromium particles has been studied in much detail; however, information about the morphology of copper-zirconium phase precipitation is scarce. The decomposition of a solid solution in Cu-Zr alloys has been studied in less detail than the ternary alloys. It was established that the strengthening phase in Cu-Zr alloys is the intermetallide phase Cu_5Zr, which participates in the eutectic reaction with an α-solid solution copper-based at 967°C [1,4,15].

The Cu_5Zr phase has a complex face-centered cubic lattice of the Be_5Au type with a lattice parameter of 0.687 nm [1,4,14]. According to [1,4,16], the limited solubility of zirconium in copper at 967°C is 0.15 wt.%; 850°C is 0.073 wt.% and at 600°C — 0.01 wt.%. Structural investigations of the precipitation of the Cu_5Zr phase in Cu-Zr and Cu-Cr-Zr alloys are not numerous. Electron-microscopic observations of structural changes upon aging in the Cu-1.07 wt.% Zr alloy subjected to solid-solution quenching and plastic deformation were performed in [17]. The authors of [5,7–9] judged the processes of the dissolution of the Cu_5Zr phase in Cu-Cr-Zr and Cu-Zr alloys upon severe plastic deformation (SPD) and precipitation of this phase in the course of annealing (aging) by changing the properties: microhardness, strength characteristics, electrical conductivity and others, however, the observations of the microstructure of this phase are absent. The aim of the present study is to investigate the effect of the initial structural state on the morphology and microstructure of Cu_5Zr particles precipitated during decomposition of a supersaturated solid solution in Cu-0.06 wt.% Zr and Cu-0.21 wt.% Cr-0.20 wt.% Zr alloys.

2. Materials and experimental methods

The materials used in this work are micro-alloyed Cu-0.06% Zr and low-alloyed Cu-0.21% Cr-0.20% Zr (wt.%) alloys melted out of pure components in a vacuum induction furnace. 0.5–1 kg ingots were forged into rods with a diameter of 18 mm. The rods were solid solution treated at 1000°C for 30 min and quenched in 5% water solution of NaCl. Then a part of the rods was used as DCAP samples with a diameter of 16 mm and a length of 65 mm. The samples were accelerated in a special gun and entered the die with two channels (16 and 14 mm diameters) intersecting at an angle of 90° [10–14]. As the energy source for accelerating the samples, the combustion products of gun powder were used [11]. Being accelerated to speeds of 230–250 m/s, the samples passed 30 mm along the first (inlet) channel almost without resistance; further, they were pressed through the second channel under the effect of inertia forces due to the kinetic energy stored upon the acceleration. The pressure of the gun-powder gases and the rate of the acceleration of the samples were regulated by changing the charge and the grade of the gun powder. To guarantee the pass of the sample through the zone of intersection of the die channels, the powder charge was taken so that the pressure onto the front butt end of the sample would substantially exceed the dynamic yield stress of the material [12]. The strain rate of the material amounted to 10^5 s^{-1}, the single pass time was $5\cdot10^{-4}$ s, the pressure in the region of the channels' intersection was 1.5–2 GPa, and the number of passes totaled $n=3-4$. Samples were analyzed in the as-quenched and DCAP states and after annealing at 300–700°C for 1 or 4 hours. Vickers microhardness was determined using PMT-3M equipment with an indentation load of 0.49 N. The structure was studied using transmission electron-microscopy, micro-X-ray spectral and local energy-dispersive analyses. The investigations were conducted using JEM 200CX (at a voltage of 160 kV), TECNAI G230 Twin (at a voltage of 300 kV) with a scanning system of an EDAX energy-dispersive spectrometer (resolution of the spectrometer EDAX 160 eV), and a Quanta-200 scanning electron microscope with an energy-dispersive X-ray spectrometer.

3. Results and discussion

3.1. Evolution of the microstructure of alloys under quenching and annealing

The grain size of the Cu-0.06% Zr and Cu-0.21% Cr-0.20% Zr alloys in the initial quenched state was 300–400 μm. The process of precipitation of particles upon annealing (aging) was investigated by the methods of electron microscopy. The particles precipitated in the initial quenched state of the alloys are only observed after annealing at temperatures 500–550°C. The precipitation of Cu_5Zr particles occurs homogeneously, as was found previously in [1–3]. After annealing at 550°C for 1 h, the precipitation of particles of the copper-zirconium phase of four orientations in the Cu-0.06% Zr alloy is observed. Fig. 1a demonstrates a dark-field image of particles of the copper-zirconium phase with one orientation. The particles have the shape of thin disks with a diameter of up to 100–150 nm and thicknesses — 10–20 nm. This shape of particles minimizes the energy of elastic-stress fields created by the particle [18]. Dark-field image and diffraction analysis showed that the disk plane is parallel to the {111} planes of the copper matrix. The precipitation of such disk-shaped Cu_5Zr particles were observed in the quenched Cu-0.30% Zr alloy [2]. The morphology of the precipitates resembles Widmanstatten precipitates revealed in the quenched Cu-1.07% Zr alloy after annealing (aging) at 500°C [17]. The oriented arrangement of the particles indicates the existence of an orientation relation between the crystal lattices of the particles and the matrix. It is important to note that the point reflections from particles in the electron-diffraction patterns almost coincide with the diffuse reflections from the matrix (Fig. 1a). This means that zone axes (011) for the matrix and the particles nearly coincide and the corresponding planes of the {111} and {002} types of the crystal lattices of the copper matrix and the particles also almost coincide. The similarity of the crystal structures of the particles and the matrix and their orientation connection at this aging stage provide the minimum surface energy of the particle/matrix interfaces. Consequently, the disk-shaped particles present particles of the metastable phase, the structure and the strength properties of which are close to the structure and the properties of the copper matrix. These particles must have a higher copper concentration than the equilibrium phase.

An increase in the aging temperature up to 700°C results in a more complete decomposition of the α-solid solution of copper in Cu-0.06% Zr and Cu-0.21% Cr-0.20% Zr alloys the initial quenched state. Coarse Cu_5Zr particles in the shape of rods with a length to 2–3 μm and a thickness of about 0.2–0.3 μm are formed in alloys. Figs. 1b and 2a demonstrates photographs of rod-shaped Cu_5Zr particles formed in Cu-0.06% Zr and Cu-0.21% Cr-0.20% Zr alloys. The particles consist of thin twin-like layers with a thickness of 6–7 nm. The electron-diffraction patterns of such particles (Figs. 1b, 2a) substantially differ from the electron-diffraction patterns obtained from the structures with the disk-shaped particles (Fig. 1a). The reflections become elongated in the direction perpendicular to the layers; i.e., the elongated shape of the reflections is caused by the lamellar structure of the particles. The size of the coarse particles made it possible to carry out the local chemical analysis of the energy-dispersion and estimate the ratio of the concentrations of copper and zirconium in the particles. Figs. 1c and 2b show the energy-dispersion spectrum from the coarse rod-shaped particles.

The ratio of atomic concentrations of copper and zirconium in this particle was 5.6:1 and 6:1 that is close to the stoichiometry of the equilibrium Cu_5Zr phase.

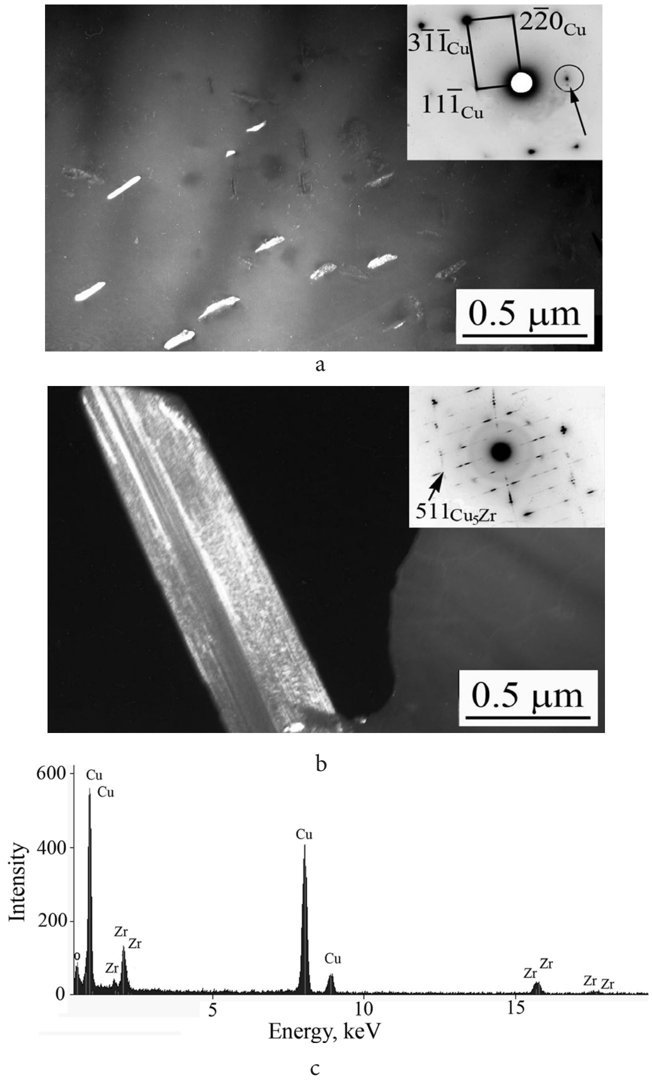


Fig. 1. Microstructures of Cu-0.06% Zr alloy after quenching and annealing at 550°C, 1 h (a); 700°C, 1 h (b) and energy-dispersion spectrum obtained from the rod-shaped particle (c).

3.2. Evolution of the microstructure of alloys under DCAP and annealing

As it has been established earlier, after DCAP with $n = 3 - 4$, a fragmented structure consisting of grains and sub-grains with a size of 0.2 – 0.4 μm with the internal dislocation structure is formed in the alloys. Nanoparticles of the second-phase with a diameter from 2 to 5 nm are precipitated on the boundaries and inside individual crystallites, which suggests that a partial decomposition of the supersaturated α-solid solution of copper occurs in the process of DCAP [13,14]. Fig. 3 a represents the sub-grained SMC structure obtained after DCAP and annealing (aging) at 400°C for 4 h in the Cu-0.06% Zr alloy. The heterogeneous precipitation of particles at the boundaries of sub-grains and at dislocations is indicated by arrows. A similar heterogeneous precipitation of nanoparticles was observed in the Cu-0.21% Cr-0.20% Zr alloy. The electron-diffraction pattern contains reflections of the Cu_5Zr phase (Fig. 3 a). Often around heterogeneous precipitated nanoparticles, a deformation contrast was visible. Observation of this contrast indicates the existence of a coherent (or partially coherent)

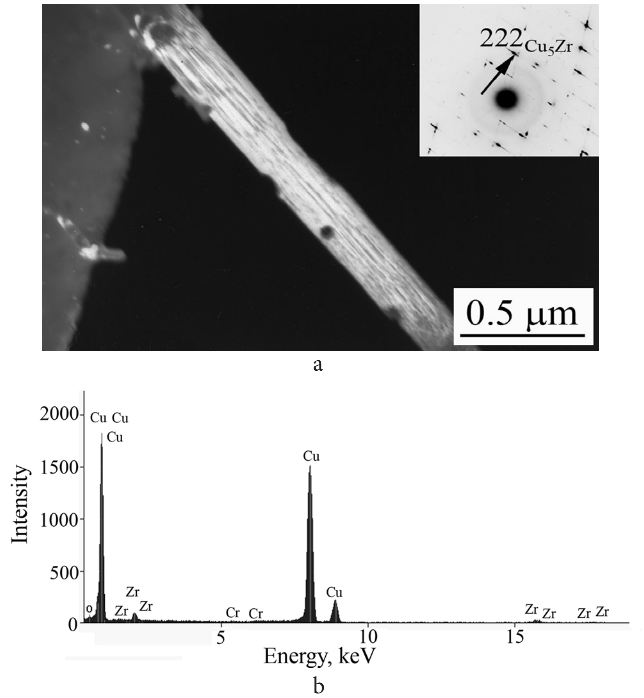


Fig. 2. Rod-shaped particle of Cu_5Zr formed in Cu-0.21%Cr-0.20% Zr alloy after quenching and annealing at 700°C, 1 h (a) and energy dispersion spectrum obtained from the rod-shaped particle (b).

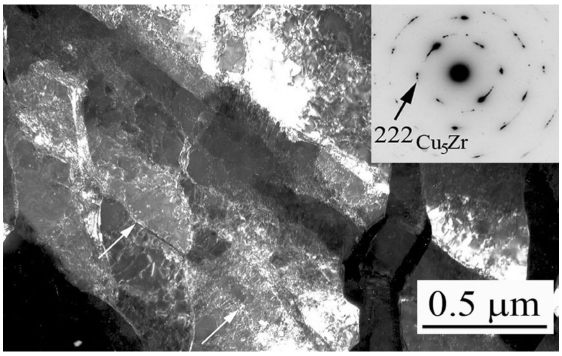
connection between the lattices. Apparently, these particles are metastable phases, just as the disk-shaped particles formed during aging in the quenched state (Fig. 1a).

The recrystallization and growth of particles occur as the aging temperature increases to 500 – 600°C in the Cu-0.06% Zr and Cu-0.21% Cr-0.20% Zr alloys. In the recrystallized grains, globular Cu_5Zr particles with a size from 0.05 to 0.2 μm were observed. Fig. 3 b demonstrates the dark-field image of three particles obtained in the reflection $(311)Cu_5Zr$ in the Cu-0.06% Zr alloy after DCAP and aging at 550°C for 1 h. With a further increase in the aging temperature to 700°C globular and elongated particles with a size from 0.1 to 0.5 μm were observed. Apparently, the elongated particles are similar to the rod-shaped particles formed at high temperatures of aging in the initially quenched alloy. Fig. 4 a shows the microstructure obtained in the Cu-0.21% Cr-0.20% Zr alloy after DCAP and annealing at 700°C for 1 h. Micro-X-ray spectral analysis showed that the globular particles are particles of the copper-zirconium phase (Fig. 4 b).

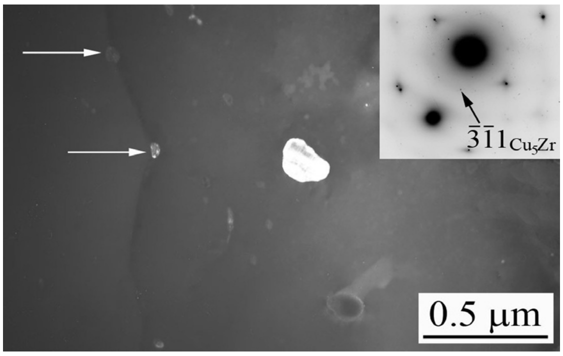
Thus, after DCAP, the decomposition of the solid solution begins by 100 – 150°C earlier than in the quenched state. In the quenched state, the precipitation of particles of the Cu_5Zr phase occurs mainly homogeneously; in the deformed state, heterogeneous precipitation at sub-boundaries and dislocations prevails, although the homogeneous precipitation is also observed in the bulk of the sub-grains. The size of particles precipitated in alloys after DCAP is less by an order of magnitude than that in the quenched state.

3.3. Effect of annealing temperature on the microhardness of alloys subjected to quenching and DCAP

The microstructural changes affected the properties of the alloys. The microhardness of the micro-alloyed Cu-0.06% Zr

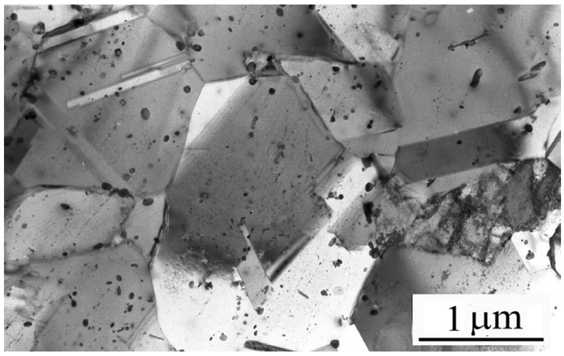


a

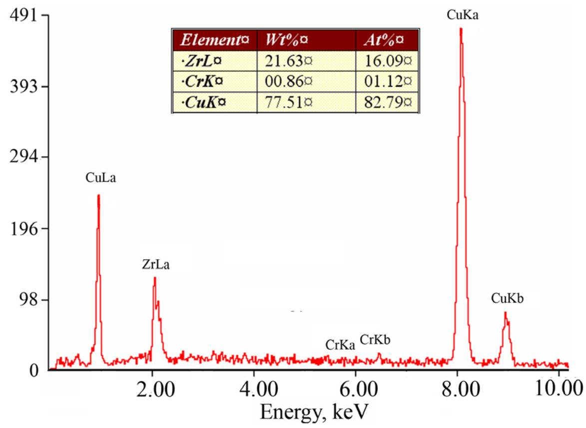


b

Fig. 3. Microstructures of Cu-0.06% Zr alloy after DCAP and annealing at 400°C, 4 h (a); 550°C, 1 h (b).



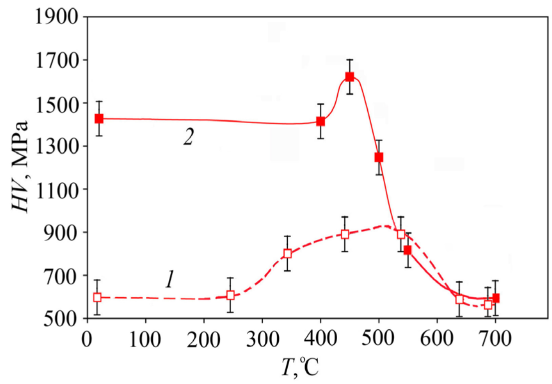
a



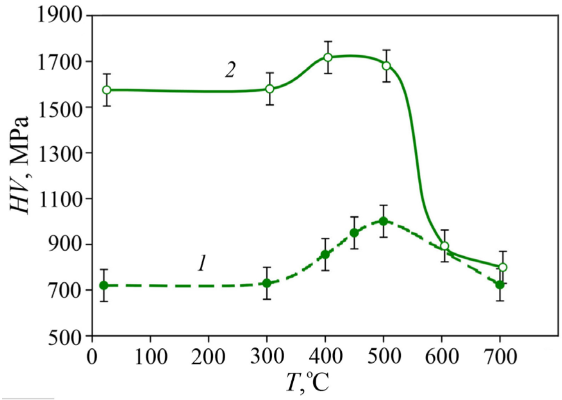
b

Fig. 4. Microstructures of Cu-0.21% Cr-0.20% Zr alloy after DCAP and annealing at 700°C, 1 h (a) and micro-X-ray spectral analysis of the particle of Cu_5Zr (b).

and low-alloyed Cu-0.21% Cr-0.20% Zr alloys in the initial quenched coarse-grained state was 600 and 720 MPa, respectively (Fig. 5, curves 1). Annealing at temperatures of 250–300°C for 1 h almost does not change the microhardness of the investigated alloys. Annealing at 400 and 500°C increases its value up to 850 and 900 MPa (Cu-0.06% Zr) and up to 870 and 1000 MPa (Cu-0.21% Cr-0.20% Zr) i.e., by 1.3 and 1.5 times as compared to the initial values, which is associated with the process of decomposition of the supersaturated α-solid solution of copper. DCAP of the alloys increases its microhardness up to 1400 and 1600 MPa, that is 2.3-fold as against the initial one (Fig. 5, curves 1 and 2), which is associated with a significant (from 300–400 to 0.2–0.4 µm) structure refinement and partial deformation aging in the process of DCAP [13,14]. Annealing of the deformed Cu-0.21% Cr-0.20% Zr alloy at temperatures of 300°C for 1 h (at 400°C for 1 h for the Cu-0.06% Zr alloy) did not change their microhardness (Fig. 5, curves 2). After annealing (aging) at 400 and 450°C, the microhardness of the Cu-0.21% Cr-0.20% Zr alloy increased up to 1720 MPa (and up to 1630 MPa in Cu-0.06% Zr alloy) in contrast to the deformed state (Fig. 5, curves 2). This behavior is related to the decomposition of the supersaturated α-solid solution of copper [13,14]. An increase in the annealing (aging) temperature to 500–600°C led to a decrease in the microhardness, which is explained by the development of recrystallization. Annealing (aging) at 650–700°C did not cause further softening of the investigated alloys because appreciable grain growth did not occur. The microhardness of the micro-alloyed Cu-0.06% Zr alloy (as well as low-alloyed Cu-0.21% Cr-0.20% Zr) can be substantially increased by the treatment including DCAP and annealing at 450°C for 1 h by a factor of 2.7 as compared to the initial quenched state.



a



b

Fig. 5. Effect of annealing temperature on the microhardness of alloys Cu-0.06%Zr (a), and Cu-0.21% Cr-0.20% Zr (b) in the quenched state (1) and after DCAP (2).

4. Conclusions

Decomposition of the supersaturated solid solution of zirconium in copper in the quenched Cu-0.06% Zr and Cu-0.21% Cr-0.20% Zr alloys occurs in two stages. The first stage is the precipitation of particles of the metastable copper-zirconium phase in the shape of thin disks. This shape of particles minimizes the energy of the elastic-stress fields created by the particle. The crystal structure of the particles is close to the structure of the copper matrix. The similarity of the crystal structures of the particles and of the matrix and their orientation connection at this aging stage provide the minimum surface energy of the particle/matrix interfaces. At the second stage, particles of the equilibrium Cu_5Zr phase are formed in the shape of rods. The preliminary high strain rate deformation by the DCAP method results in a change from homogeneous nucleation of particles of the Cu_5Zr phase to mainly heterogeneous nucleation and substantially accelerates the decomposition of the supersaturated solid solution. The precipitation of nanoparticles of the Cu_5Zr phase in the deformed alloys occurs at lower temperatures than in the quenched alloys. Thus, the heterogeneous nucleation, the number of Cu_5Zr phase of nucleation centers are increasing at low temperatures, which results in an increase in the amount of particles and a decrease in their sizes. The precipitation of nanoparticles Cu_5Zr at dislocations decelerates the formation of recrystallization centers. The microhardness of the micro-alloyed Cu-0.06% Zr alloy (as well as low-alloyed Cu-0.21% Cr-0.20% Zr) can be substantially increased by the treatment including DCAP and annealing at 450°C for 1 h by a factor of 2.7 as compared to the initial quenched state.

Acknowledgements. Electron microscopic studies were carried out using the equipment of Collaborative Access Center "Testing Center of Nanotechnology and Advanced Materials" at the Institute of Metals Physics of Ural Branch of RAS. The present work was accomplished according to the State Assignment theme "Structure" (reg. № AAAA-A18-118020190116-6).

References

1. O. E. Osintsev, V. N. Fedorov. Copper and Copper Alloys: Domestic and Foreign Grades. A Handbook. Moscow, Mashinostroenie (2004) 336 p. (in Russian).
2. H. Suzuki, M. Kanno. J. Jpn. Inst. Metals. 36, 363 (1972). Crossref
3. T. Nagai, Z. Henmi, T. Sakamoto, S. Koda. J. Jpn. Inst. Metals. 36, 564 (1972). Crossref
4. P. Forey, J.-L. Glimois, J.-L. Feron, G. Develey, C. Becle. Compt. Rendue Acad. Sc. Paris, Ser. C. 291, 177 (1980).
5. A. Vinogradov, V. Patlan, Y. Suzuki, K. Kitagawa, V. I. Kopylov. Acta Mater. 50, 1639 (2002). Crossref
6. R. R. Mulyukov, R. M. Imayev, A. A. Nazarov. J. Mater. Sci. 43, 7257 (2008). Crossref
7. S. V. Dobatkin, D. V. Shangina, N. R. Bochvar, M. Janeček. Mater. Sci. Eng. A. 598, 288 (2014). Crossref
8. G. Purcek, H. Yanar, D. V. Shangina, M. Demirtas, N. R. Bochvar, S. V. Dobatkin. Journal of Alloys and Compounds. 742, 325 (2018). Crossref
9. A. P. Zhilyaev, A. Morozova, J. M. Cabrera, R. Kaibyshev, T. G. Langdon. J. Mater. Sci. 52, 305 (2017). Crossref
10. V. Zel'dovich, E. Shorokhov, N. Frolova, I. Zhgiliev, A. Kheifetz, I. Khomskaya. Int. J. Mat. Res. 100, 830 (2009). Crossref
11. I. G. Brodova, E. V. Shorokhov, A. N. Petrova, I. G. Shirinkina, I. V. Minaev, I. N. Zhgilev, A. V. Abramov. Rev. Adv. Mater. Sci. 25, 128 (2010).
12. I. V. Khomskaya, E. V. Shorokhov, V. I. Zel'dovich, A. E. Kheifets, N. Yu. Frolova, P. A. Nasonov, A. A. Ushakov, I. N. Zhgilev. The Physics of Metals and Metallography. 111, 612 (2011). Crossref
13. V. I. Zel'dovich, I. V. Khomskaya, N. Yu. Frolova, A. E. Kheifets, E. V. Shorokhov, P. A. Nasonov. The Physics of Metals and Metallography. 114, 411 (2013). Crossref
14. I. V. Khomskaya, A. E. Kheifets, V. I. Zel'dovich, L. G. Korshunov, N. Yu. Frolova, D. N. Abdullina. Letters on Materials. 8, 410 (2018). Crossref
15. Phase Diagrams of Binary Metal Systems. A Handbook. Vol. 2 (ed. by N. P. Lyakishev). Moscow, Mashinostroenie (1997) 1024 p. (in Russian).
16. M. E. Drits, N. R. Bochvar, L. S. Guzei, et. al. Binary and Multicomponent Copper-Based Systems. A Handbook. Moscow, Nauka (1979) 248 p. (in Russian).
17. V. A. Phillips. Metallography. 7, 137 (1974). Crossref
18. Physical metallurgy. Vol. 2 (ed. by R. W. Cahn, P. Haasen). Elsevier SciencePublisher BV, Amsterdam (1983) 624 p.