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The formation of friction-induced nanocrystalline structure in submicrocrystalline Cu–Cr–Zr alloy processed by DCAP

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The paper studies the effect of high strain rate (10^5 s^{-1}) deformation by the method of dynamic channel-angular pressing (DCAP), annealing and quasi-static severe plastic deformation (SPD) under sliding friction on the evolution of the structure and properties of low-alloyed dispersion-hardened Cu–Cr–Zr alloys. It is shown that alloying of copper with chromium (0.09 – 0.14%) and zirconium (0.04 – 0.08%) microadditives changes mechanisms of submicrocrystalline (SMC) structure formation and elastic energy relaxation during DCAP: the cyclic character of structure formation associated with alternating of high-rate processes of fragmentation and dynamic recrystallization is changed to processes of fragmentation and partial strain aging resulting in precipitation of nanosized particles of the second-phase. The temperature-time regime of annealing (aging) of Cu–Cr–Zr SMC alloys processed by DCAP was established to improve the mechanical properties and electrical conductivity. In particular, for Cu–0.14 Cr–0.04 Zr SMC alloy it was shown that the optimal combination of microhardness (HV = 1880 MPa), electrical conductivity (80% IACS), strength ($\sigma_{0.2}$ = 464 MPa, σ_u = 542 MPa) and ductility (δ = 11%) can be obtained by DCAP and aging at 400°C for 1 h. The improved mechanical properties of the alloys as compared to copper are associated with extra hardening caused by precipitation of Cu_5Zr and Cr nanoparticles (5 – 10 nm) in the process of DCAP and aging. It was shown that low-alloyed Cu–Cr–Zr alloys possessed a high work-hardenability due to the methods of DCAP and SPD under sliding friction. By the example of Cu–0.09 Cr–0.08 Zr alloy it was established that the wear rate of samples with SMC structure obtained by the DCAP method decreased by a factor of 1.4 as compared to the coarse-grained state. It was also established that the combination of the treatment by DCAP, aging at 400°C, and SPD under friction of the alloy resulted in the formation of the friction-induced nanocrystalline structure with the grain size of 15 – 60 nm in the surface-layer material, which provided a high level of microhardness (3350 MPa) and low values of the friction coefficient (0.35).

Keywords: copper alloys, high strain rate and quasi-static deformation, submicro-and nanocrystalline structure, mechanical and functional properties.

1. Introduction

Development of deformation technologies to obtain nonequilibrium structures in structural and functional materials with the preset level of physical, mechanical, and functional properties and providing a high level of stability of the properties attracts attention of modern researchers [1 – 8]. In recent times, a lot of works have appeared on the study of regularities of SMC structure formation in dispersion-hardened copper-base alloys containing chrome and zirconium, used in electric-power and nuclear industries, in such quasi-static severe plastic deformation (SPD) processes as high-pressure torsion (HPT) and equal channel angular pressing (ECAP) [5 – 8]. However, the data on the effect of SPD and aging on functional and tribological properties of such alloys are scarce [7,8]. It is known that the values of the strain of surface layers of steels and alloys attained at SPD under friction are significantly higher than in the case of using bulk deformation methods [1 – 5, 9]. In this case, a friction-induced nanocrystalline structure is formed, which suggests that due to the friction effect extremely high values of plastic deformation [10,11] are realized in a thin (up to 10 μm) surface layer of metallic materials. The current study uses the dynamic channel-angular pressing (DCAP) method based on the shock-wave loading technique [9], which makes it possible to deform materials at rates by six orders of magnitude higher than when using ECAP [2 – 5]. It has been established before that the combined action of high strain rate deformation of simple shear, shockwave compression deformation, and temperature [12 – 14] is a characteristic feature of DCAP. The objective of the present study is to investigate the effect of DCAP, aging, and SPD under friction on the formation of SMC and nanocrystalline (NC) structures with high strain-strength and service properties in alloys based on the Cu–Cr–Zr system.

2. Materials and experimental methods

The materials used in this work are low-alloyed Cu–0.09% Cr–0.08% Zr and Cu–0.14% Cr–0.04% Zr (mass percents) 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 quenched in ice water from 990 – 1000°C to get a supersaturated solid solution of copper. 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 up to the speed of 230 m/s and entered the die with 16 and 14 mm diameters intersecting at a 90° angle [9, 12 – 14]. 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 $n = 3 – 4$. Some samples were annealed at 400 – 700°C after quenching and DCAP. The samples were separated into series and each series was annealed at a definite temperature for 1 or 4 hours followed by cooling in ice water.

Vickers microhardness was determined using PMT-3M equipment with the indentation load of 0.49 N. Uniaxial tensile tests were performed on an INSTRON 3382 device at strain rates of $10^{-3} – 10^{-2}$ s^{-1} on samples with a length of 25 mm and a working part with dimensions $2.0\times2.0\times1.5$ mm, the measurement error σ_u, and $\sigma_{0.2}$ was no more than 10 MPa, and the relative strain δ amounted to 1%. Electrical resistance was measured using the potentiometric method on $0.3\times2.0\times15$ mm samples. The error of measurements $\Delta\rho/\rho$ was no more than 1%. The values were converted to electrical conductivity and presented in percentage ratio to the value of conductivity of annealed copper according to the International Annealed Copper Standard (% IACS) [15].

Tribological tests were carried out under sliding friction conditions following the scheme "plate (sample)-indenter" with the latter made of VK-8 alloy and having a cylinder shape with diameter of 4 mm and a height of 4 mm on an experimental equipment described in [10,11]. The unlubricated friction was carried out in air at the load of 196 N and sliding velocity of 0.014 m/s; the number of cycles (double passes of the indenter) amounted to 1000, the sliding distance was 9 m. The friction force was continuously measured and recorded in the process of wear. Friction coefficient f was determined as a ratio of the value of the friction force averaged over the test time to the normal load. The error of measurement of f amounted approximately to 5%. The wear rate Ih was calculated according to the formula:

$$Ih = \Delta Q/(\rho\cdot l\cdot s),$$

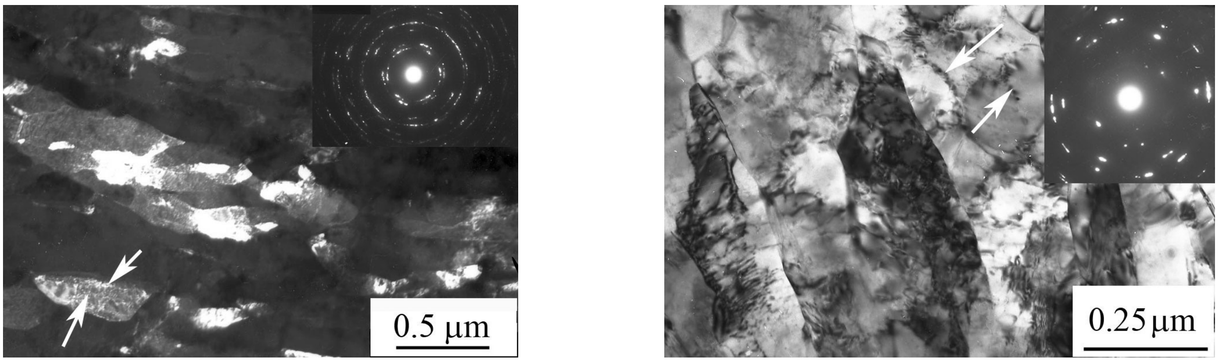
where ΔQ is the mass loss of the sample, ρ the density, s the geometric area of the contact, and l represents the sliding distance. Electron microscope investigation was conducted using a JEM– 200CX microscope. Foils to study the structure of the samples after DCAP and annealing were made using double-side electropolishing. Foils to study the structure of the material of the thin (up to 10 μm) surface layer after SPD under sliding friction were made using single-side electropolishing [10].

3. Results and discussion

3.1. Evolution of the structure of alloys under DCAP and aging

In the initial quenched condition the grain size of Cu–0.09 Cr–0.08 Zr and Cu–0.14 Cr–0.04 Zr alloys amounted to 200 – 400 μm. After DCAP with $n = 3 – 4$, a fragmented structure consisting of grains and subgrains with a size of 0.2 – 0.3 μm with the internal dislocation structure (Fig. 1a) is formed in the alloys. Nano-sized precipitates of second-phases with a diameter from 2 to 5 nm (shown by arrows in Fig. 1a) are seen 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. This means that under DCAP the coarse-crystalline (CC) structure of alloys is transformed into a SMC one as a result of high strain rate processes of fragmentation and partial deformation aging. It should be noted that in copper a cyclic character of the structure formation under DCAP is observed, which is associated with an alternation of high strain rate processes of fragmentation and dynamic recrystallization [14]. Therefore, alloying of copper with Cr and Zr microadditives results in the change of the mechanism of SMC structure formation and elastic energy relaxation under DCAP, which is related to the different stacking fault energies in copper and copper alloys.

Annealing at temperatures of 300 – 350°C does not cause any changes in SMC structure formed under DCAP. Annealing at temperatures of 400 – 450°C results in a further decomposition of the supersaturated α-solid solution of copper. A previously carried out analysis of the data obtained by dark-field, diffraction, and crystallographic studies of the low-alloyed Cu–0.09 Cr–0.08 Zr, Cu–0.14 Cr–0.04 Zr alloys [16,17] and microalloyed Cu–0.06 Zr alloy [18] showed that a precipitation of Cu_5Zr particles with a diameter of 5 to 10 nm occurred under DCAP and annealing (aging) at



a b

Fig. 1. SMC structure of Cu–Cr–Zr alloys after DCAP (a) and DCAP + aging at 400°C (b); (a) — dark-field image in reflection 002_α and (b) — bright-field image.

350 – 400°C. The Cu_5Zr nanoparticles (shown by arrows in Fig. 1b) precipitating on the dislocations and boundaries of subgrains contribute to their pinning and immobilization. As a result, the process of formation of recrystallization centers which requires a rearrangement of the dislocation structure slows down. The increase in aging temperature up to 450 – 500°C results in a more complete decomposition of the solid solution. In Cu–Cr–Zr alloys, in addition to Cu_5Zr, Cr particles are precipitated [16,17]. Recrystallization of the alloy starts at the temperature of 500°C and is completed at 600°C. Under annealing at temperatures of 600 – 700°C, chromium particles grow in size up to 100 nm and acquire an elongated shape [16], Cu_5Zr globular particles scarcely grow and their diameter does not exceed 10 nm. This results in the formation of a structure with a grain size of 1 – 5 μm containing a large number of Cr and Cu_5Zr nanoparticles in Cu–Cr–Zr alloys.

3.2. Microhardness and mechanical behavior of SMC alloys

Microhardness of the alloys in the initial quenched CC state is approximately equal to 680 MPa (Fig. 2, curve 1). Annealing at temperatures of 300 – 350°C for 1 h almost does not change the microhardness of the CC alloy while annealing at 400 and 450°C increase its value up to 850 and 1000 MPa (that is by 170 and 320 MPa), respectively, which is associated with the process of decomposition of the supersaturated α-solid solution of copper.

DCAP of the alloy increases its microhardness up to 1600 MPa, that is 2.4-fold as against the initial one (Fig. 2, curves 1 and 2), which is associated with a significant (from 200 – 300 μm to 0.2 – 0.3 μm) structure refinement and partial deformation aging in the process of DCAP. Annealing of SMC alloys at temperatures of 200 – 300°C for 1 and 4 hours does not result in the change in microhardness. Its growth up to 1700 – 1780 MPa is observed when annealing at 350 – 450°C for 1 h and is associated with the processes of decomposition of the solid solution. It should be noted that the change in the aging time at 400°C from 1 to 4 hours increases the microhardness of the SMC alloy from 1780 MPa to 1880 MPa. Annealing at 550 – 600°C results in a decrease in microhardness (Fig. 2, curve 2), which is caused by the process of recrystallization.

Therefore, DCAP results in the structure refinement of Cu–Cr–Zr alloys by three orders (from 200 – 300 μm to 0.2 – 0.3 μm) and a 2.4-fold increase in microhardness. DCAP and aging at 400°C for 1 and 4 hours increase microhardness of SMC alloys by factors of 2.6 and 2.8 as compared with CC state, respectively.

Of a significant interest is the study of mechanical properties of the SMC alloy obtained by DCAP, which exhibited the best microhardness after aging. The results of measurements of the properties are presented in Table 1. The alloy has low values of the yield stress (94 MPa), ultimate strength (196 MPa), and a high ductility of 37% in the initial quenched CC state. Aging of the alloy at 450°C for 1 h results in an increase in yield stress up to 139 MPa, ultimate strength up to 237 MPa. Such an increase in strength characteristics is caused by a decomposition of the supersaturated solid solution with precipitation of Cr particles retaining coherent bond with the copper matrix [16].

High strain rate deformation by DCAP method results in 2.6 to 3.3-fold increase in the strength properties of the alloy: ultimate strength increases from 196 to 507 MPa, the yield stress from 94 to 312 MPa (Table 1). For a comparison, the strength properties of copper underwent a 1.2 – 1.4-fold increase after DCAP [14]. A more considerable hardening of Cu–0.14 Cr–0.04 Zr alloy as against copper is associated with a significant strain hardening and deformation aging related to the precipitation of nanoparticles of second-phases in the process of DCAP, as discussed above. Even more strongly, as compared to the CC state, the strength properties of the SMC alloy are enhanced after aging at 400 – 450°C (a 2.8 – 5.1-fold increase), which is due to the development of the processes of decomposition of the solid solution with precipitation of Cu_5Zr and Cr nanoparticles.

Thus, the treatment that includes successive DCAP and annealing at 400°C for 1 hour results in obtaining an alloy with high microhardness (1780 MPa) and strength (σ_u = 542 MPa, $\sigma_{0.2}$ = 464 MPa), while the ductility remains on a satisfactory level (δ = 11%). It should be noted that to reach the same level of properties in higher-alloyed Cu–Cr–Zr alloys 8 passes of ECAP were applied [5].

3.3. The effect of aging on the change in electrical conductivity of SMC alloys

Electrical conductivity of Cu–0.14 Cr–0.04 Zr alloy in its quenched state is about 40% IACS (Fig. 3, curve 1). The decrease in electrical conductivity of copper alloyed with chrome and zirconium microadditives in quenched CC state is associated with the fact that when α-solid solution

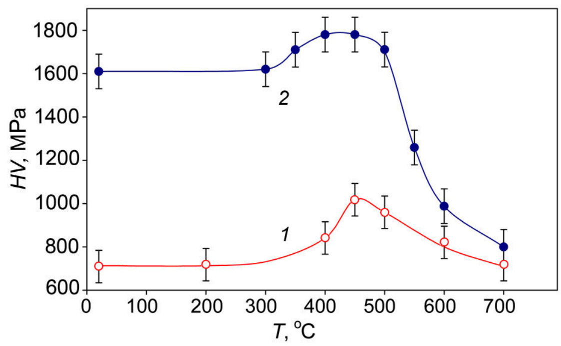


Fig. 2. Effect of aging temperature on the microhardness of Cu–0.14% Cr–0.04% Zr alloy in the quenched state (1) and after DCAP (2).

Table 1. Mechanical properties of Cu–0.14 Cr–0.04 Zr alloy after treatment under various conditions

Treatment modes	$\sigma_{0.2}$ MPa	σ_u, MPa	δ, %
Quenching from1000°C	94	196	37
Quenching + aging at 450°C, 1 h.	139	237	18
DCAP	312	507	10
DCAP + 400°C, 1 h.	464	542	10
DCAP + 400°C, 4 h.	464	536	13
DCAP + 450°C, 1 h.	477	520	11

is formed, electric field of the lattice of solvent, i.e. copper, is distorted and scattering of conduction electrons increases [15]. High strain rate deformation increases the electrical conductivity of the alloy as compared to that in the quenched state (compare curves 1 and 2, Fig. 3). This is related to a partial decomposition of the supersaturated α-solid solution of copper in the process of DCAP that is confirmed by structural studies and the results of changes in mechanical properties.

The electrical conductivity of the quenched alloy when annealed at 200 – 300°C for 1 h practically does not change, it increases up to 43% IACS when annealed at 350°C, and increases from 48 to 70% IACS when heated within the range of temperatures of 350 – 500°C (Fig. 3, curve 1), which is associated with the decomposition of the supersaturated α-solid solution of copper. Electrical conductivity of the alloy with the SMC structure formed by DCAP does not change when annealed at 200°C, then it increases from 43 to 48% IACS× (Fig. 3, curve 2) when annealed within the range of temperatures of 200 – 300°C, which is associated with the processes of recovery, and increases significantly (from 48 to 80% IACS) when annealed within the range of 350 – 600°C, which is caused by the decomposition of the α- solid solution with precipitation of nano-sized particles of second-phases. It should be noted that the increase in electrical conductivity of the alloy after DCAP starts at a lower temperature and reaches higher values than after quenching (compare curves 1 and 2, Fig. 3), i.e. the process of decomposition of the solid solution of copper after DCAP proceeds more intensively. Moreover, the increase in electrical conductivity occurs at a lower temperature than the temperature at which the microhardness increases (compare Figs. 2 and 3). That means that the depletion of the alloying elements in the solution occurs earlier that particles of an optimum size necessary to increase the microhardness are formed.

3.4. The effect of SPD under sliding friction on the formation of NC structure in the surface layer and tribological properties of SMC alloy

In the initial quenched CC state the values of wear rate (*Ih*) and friction coefficient (*f*) of Cu–0.09 Cr–0.08 Zr alloy amounted to 3.1×10^{-7} and 0.5, respectively. After DCAP with $n = 3$, the value of *Ih* of the alloy dropped to 2.3×10^{-7}, which is 1.4 times less than the wear rate of the alloy in CC state, while *f* increased up to 0.62. Aging at 400°C results in the increase in *Ih* of the alloy up to 8.3×10^{-7}. At the same time, *f* decreases and reaches its minimum value 0.35. Diffractional and dark-field analyses of the structure of the surface layer showed that SPD under friction of a bulk SMC alloy obtained by DCAP results in formation of NC structure with a crystallite size of 40 – 50 nm in the material of the surface layer (Fig. 4a). Rings with a great number of point reflections belonging to FCC of the copper matrix on the electron diffraction pattern indicate that a NC structure is formed (Fig. 4a). Such a dispersion of the structure expectedly results in the increase in microhardness of the alloy (up to 3200 MPa), i.e. in a 2-fold hardening of the surface layer as compared to the hardening attained by DCAP (1600 MPa, see Fig. 2). Therefore, the SMC structure formed by DCAP is transformed into a NC structure with a high hardness after SPD under friction.

Presented in Fig. 4b is the structure of a surface layer of the alloy after a combined treatment including DCAP, annealing at 400°C for 1 h, and SPD under friction. One can see that such a treatment results in an even more intensive dispersion of the surface layer structure than the one consisting of DCAP and SPD under friction. The size of the crystallites decreases from 40 – 50 to 15 – 30 nm. Microhardness of the alloy after DCAP and annealing at 400°C amounts to 1800 MPa (see Fig. 2, curve 2). Microhardness increases up to 3350 MPa after SPD under friction. That is, the combined treatment including DCAP, aging at 400°C for 1 h, and SPD under friction results in extra hardening of the material of the surface layer: microhardness increases from 3200 to 3350 MPa, which is 5 times higher than that of the alloy in its initial CC state.

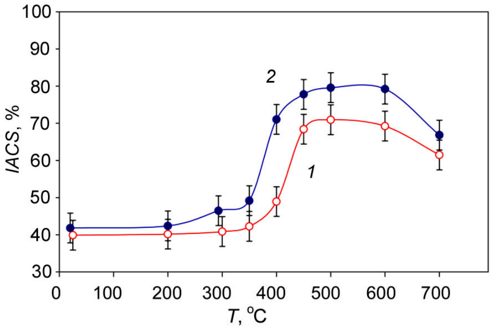


Fig. 3. Effect of aging temperature on the electrical conductivity of the Cu–0.14% Cr–0.04% Zr alloy in the quenched state (1) and after DCAP (2).

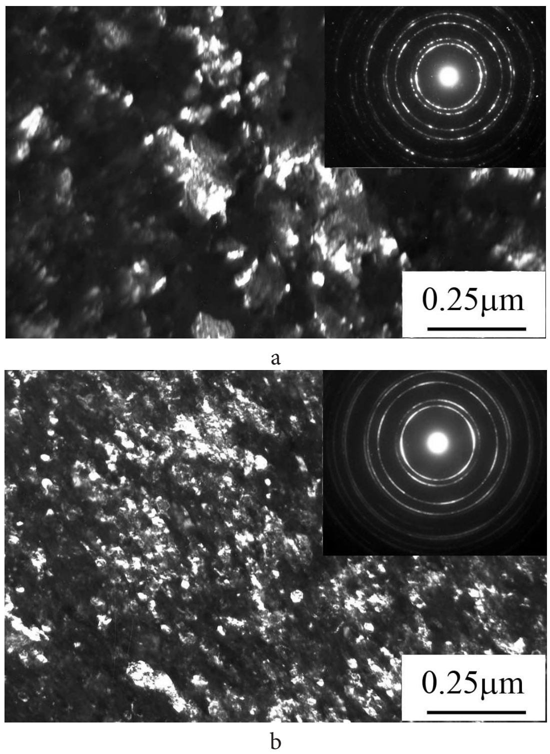


Fig. 4. Friction-induced NC structure of Cu–0.09% Cr–0.08% Zr alloy after DCAP (a) and DCAP + aging at 400°C (b); (a),(b) — dark-field images in reflection $\{111\}_{\alpha}$.

4. Conclusions

Temperature and time regimes of aging of low-alloyed dispersion-hardened Cu–Cr–Zr alloys with a SMC structure formed by the DCAP method aimed to obtain high strength and electrical conductivity have been established. It has been shown that for SMC Cu–0.14% Cr–0.04% Zr alloy the optimum combination of microhardness (HV = 1880 MPa), electrical conductivity (80% IACS) and strength ($\sigma_{0.2}$ = 464 MPa, σ_u = 542 MPa) while maintaining a satisfactory ductility (δ = 11%) can be attained using the treatment consisting of DCAP and aging at 400°C for 1 h. The increased level of mechanical properties of the alloys as compared with those of copper is associated with extra hardening caused by the precipitation of nano-sized Cu_5Zr and Cr particles in the process of DCAP and aging. It has been established that low-alloyed alloys exhibit high hardenability due to the DCAP method, subsequent aging and SPD under sliding friction. By an example of Cu–0.09% Cr–0.08% Zr alloy it has been shown that maximum microhardness (3350 MPa) after SPD under friction is achieved in the alloy exposed to DCAP and aging at 400°C for 1 h. Its value is 5 times higher than the hardness of the CC alloy. Wear rate of the samples with SMC structure obtained by DCAP decreases 1.4 times less than that in the CC state. It has been established that the combination of the treatment by DCAP, aging at 400°C, and SPD under friction results in the formation of a NC structure with a crystallite size of 15 – 30 nm, which provides a high level of hardness and good tribilogical properties, i.e. a low value of the friction coefficient (0.35) on retention of a satisfactory wear rate of the alloy.

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