Effect of high-speed dynamic channel angular pressing and aging on the microstructure and properties of Cu-Cr-Zr alloys

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Abstract. The microstructure, mechanical and functional properties, including electrical and wear resistances have been investigated for the Cu-0.09%Cr-0.08%Zr and Cu-0.14%Cr-0.04%Zr alloys subjected to high-speed dynamic channel angular pressing (DCAP) followed by annealing (aging). It was shown that DCAP led to the formation of a submicrocrystalline (SMC) structure ($d=200–400$ nm) with second-phase precipitates up to 5 nm in a size. The sequence of decomposition of a copper based α solid solution, accompanied by recrystallization and precipitation of second-phase nanoparticles during annealing (aging), was determined. DCAP and aging at 400-450 °C led to a decrease in the electrical resistance of the Cu-Cr-Zr alloys from 4.2 to 2.1 $\mu\Omega\cdot cm$ and to a drastic increase in their strength properties ($\sigma_u$ from 197 to 542 MPa, $\sigma_{0.2}$ from 94 to 464 MPa), while retaining reasonable ductility. It was revealed that the SMC structure processed by DCAP and annealing (aging) at 400 °C can be additionally strengthened after sliding friction tests due to the formation of a nanocrystalline structure in the surface layer.

1. Introduction
Copper alloys with small additions of chromium and zirconium belong to the group of precipitation-hardenable low-alloyed alloys characterized by a good combination of strength and electrical conductivity [1-3]. They are widely used in the electrical and atomic-energy industries. 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 [1-5]. In this study, we used a new SPD method, namely, dynamic channel-angular pressing (DCAP) [6], which is a high-rate (~$10^5$ s$^{-1}$) version of ECAP [5]. The advantage of the DCAP method consists in the use of the energy of gun-powder gases instead of energy-consuming pressing equipment and the short duration (~$5\times10^4$ s) of one pressing cycle. In the case of the DCAP, the deformation by simple shear is a high-strain-rate process. In addition, upon DCAP, high-speed shock-wave compressive strain takes place, which creates an additional source of deformation-induced hardening [7, 8]. The aim of the work was to study the changes in the microstructure and properties of Cu-Cr-Zr alloys processed by DCAP and the thermal stability of the produced SMC structures.

2. Experimental
The alloys Cu-0.09% Cr-0.08% Zr and Cu-0.14% Cr-0.04% Zr (wt. %) were selected for the study.
The alloys were melted from pure components. The as-cast rods were quenched from 1000 °C in icy water, and DCAP samples with a size of Ø16×65 mm were cut from the quenched material. The samples were accelerated in a gun to a velocity of 230 m/s and were directed to a die with channels with a diameter of 16 and 14 mm, which intersect each other at an angle of 90°. The strain rate was \( \sim 10^5 \text{s}^{-1} \), the time for one pass was 5×10^{-4} s, and the number of passes was \( n=4 \). The samples were analyzed in the as-quenched and DCAP states and after annealing (aging) at 300-700 °C for 1 hour. The TEM observations were performed using a JEM-200CX microscope. The electrical resistance, \( \rho \), was measured by the potentiometric (compensation) method on samples of 0.3×2.0×15 mm, and the error did not exceed \( \Delta \rho/\rho = 1\% \). Microhardness was determined at a load of 0.49 N. Uniaxial tensile tests were carried out at room temperature with an initial strain rate of 10^{-2} \text{s}^{-1}. Tribological tests by sliding friction were carried out without lubrication at a normal load of 196 N and a sliding velocity of 0.014 m/s, the number of cycles was 1000, and the sliding distance was 9 m. The friction force was continuously measured and registered. The friction coefficient \( f \) was determined as the ratio of the integral values of the friction force to the normal load.

3. Results and discussion

3.1. Microstructural changes after DCAP and annealing (aging)

The grain size of the alloys in the initial quenched state was in the range of \( d=200-400 \mu \text{m} \). A fragmented structure consisting of subgrains 200-400 nm in size with an internal dislocation structure was formed indicating occurrence of dynamic polygonization during DCAP. Second-phase precipitates with a size up to 5 nm are visible at the boundaries and in the interior of subgrains (figure 1 a). One can conclude that the coarse-grained structure of the alloys was transformed into a SMC structure due to high-rate processes of fragmentation, dynamic polygonization and strain aging.

![TEM images of the Cu-0.14Cr-0.04Zr (a, b) and Cu-0.09Cr-0.08Zr (c) alloys after: DCAP (a), DCAP and aging at: 400 °C (b) and 600 °C (c). Note second-phase precipitates (arrowed) at boundaries and in the interior of subgrains.](image)

Figure 1. TEM images of the Cu-0.14Cr-0.04Zr (a, b) and Cu-0.09Cr-0.08Zr (c) alloys after: DCAP (a), DCAP and aging at: 400 °C (b) and 600 °C (c). Note second-phase precipitates (arrowed) at boundaries and in the interior of subgrains.

The microstructure of the alloys obtained after DCAP remained almost the same after annealing at 300 °C. Annealing (aging) at 350-400 °C caused the decomposition of the supersaturated \( \alpha \) solid solution of copper, which led to the precipitation of \( \text{Cu}_5\text{Zr} \) nanoparticles (5-10 nm) (figure 1 b). \( \text{Cu}_5\text{Zr} \) nanoparticles precipitated at dislocations (and subgrain boundaries) and promoted their pinning. This impeded the formation of recrystallization centers. An increase in the annealing (aging) temperature to 450-500 °C caused further decomposition of the supersaturated \( \alpha \) solid solution and Cr-containing particles precipitated in the Cu-Cr-Zr alloys along with \( \text{Cu}_5\text{Zr} \) particles. The recrystallization of the alloys started at 500 °C and ended at 700 °C. After annealing (aging) at 600 °C, Cr-containing particles grew up to 100 nm in size and often had an elongated shape. \( \text{Cu}_5\text{Zr} \) globular precipitates, grouped in stripes, grew more slowly and gained around 10 nm (figure 1c). As a result, a disperse microstructure, which consisted of grains with a size of \( d=1-5 \mu \text{m} \) containing a large number of Cr-containing and \( \text{Cu}_5\text{Zr} \) nanoparticles was obtained in the Cu-Cr-Zr alloys. After annealing (aging) at 700 °C the grain size did not exceed 5-10 \mu \text{m} [9].
3.2. Mechanical properties after DCAP and annealing (aging)

The microstructural changes affected the properties of the alloys. The microhardness of the investigated alloys in the initial coarse-grained state was 700 MPa (figure 2). After DCAP, the microhardness increased to 1600 MPa (in 2.3 times) as compared to the initial values. This is associated with a substantial microstructure refinement (by three orders of magnitude) and the strain aging of the alloys during DCAP. Annealing of the deformed alloys at 300 °C did not change their microhardness. After annealing (aging) at 400-450 °C, the microhardness increased up to 1,800 MPa in contrast to the deformed state (figure 2). This behavior is related to the decomposition of the supersaturated α solid solution of copper [1-3]. 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 no appreciable grain growth occurred.

As expected, the high-speed DCAP led to a significant increase (in 2.6-3.3 times) in the strength properties of the Cu-0.14Cr-0.04Zr alloy (figure 3). It should be noted that the strength properties of copper after the same treatment increased only in 1.2-1.4 times [8]. The strength properties of the deformed alloy increased even more significantly (in 2.8-5.1 times) after annealing (aging) at 400 °C (figure 3). Thus, using the combined treatment, DCAP (n=4 passes) and aging at 400 °C, we can fabricate an alloy with superior microhardness (1800 MPa) and strength properties (σu=542 MPa, σ0.2=464 MPa) while retaining reasonable ductility (δ=11%). Note that ECAP and n=8-12 passes were required to achieve near the same level of strength properties in the Cu-0.44%Cr-0.2%Zr alloy [1].

3.3. Electrical resistance and wear resistance after DCAP and aging

The electrical resistance (ρ) of the Cu-0.14Cr-0.04Zr alloy in the quenched state was ρ ≈ 4.3 μΩ·cm (figure 4). The DCAP resulted in a decrease of the ρ value as compared to that of the quenched state (figure 4). This is associated with a partial decomposition of the supersaturated α solid solution of copper after DCAP, which is confirmed by the microstructural observations and the measured properties (figures 1 b, 2 and 3). The ρ value of the quenched alloy decreased significantly with increasing the annealing (ageing) temperature in the range of 350-500 °C (figure 4), which was caused by the decomposition of the α solid solution of copper. The ρ value of the deformed alloy began to decrease in the range of 200-300 °C, which is related to the recovery processes, and decreased significantly in the range of 350-450 °C (figure 4). The latter can be ascribed to the extensive precipitation of the second-phase particles. It should be noted that the decrease in the ρ value after DCAP took place at a lower temperature than after quenching, since the decomposition of the solid solution after DCAP was more extensive than after quenching. Note that the increase in microhardness
started at higher temperatures than the decrease in the $\rho$ value (figures 2 and 4). This finding suggests that the depletion of the solid solution by the alloying elements occurred earlier than the precipitates were formed, which led to increasing the microhardness. It is interesting that the $\rho$ value of the alloy after DCAP and aging at 500 °C decreased to 2.1 $\mu$Ω·cm. This should be ascribed to the almost complete decomposition of the $\alpha$ solid solution. Note that the $\rho$ value of the alloy after quenching and aging at 500 °C was 2.5 $\mu$Ω·cm, which indicated an incomplete decomposition of the $\alpha$ solid solution.

The samples of the Cu-0.09Cr-0.08Zr alloy were subjected to sliding friction tests after different treatments. In the quenched state, the wear rate ($Ih$) and the coefficient of friction ($f$) of the samples were 3.1·10$^{-7}$ and 0.5, respectively. After DCAP, the $Ih$ value decreased to 2.3·10$^{-7}$, and the $f$ value increased to 0.62 (figure 5). The microhardness of the deformed by DCAP alloy after testing for sliding friction increased from 1600 to 3200 MPa. As was earlier shown [9], this was the result of the formation of a nanocrystalline microstructure with a grain size of $d=40-50$ nm in the surface layer of the tested samples.

![Figure 4. Dependences of electrical resistance on the aging temperature obtained for samples of the Cu-0.14Cr-0.04Zr alloy after (1) quenching and (2) DCAP](image1)

![Figure 5. Dependences of the wear rate, $Ih$, and friction coefficient, $f$, on the aging temperature after DCAP obtained for samples of the Cu-0.09Cr-0.08Zr alloy](image2)

Annealing (aging) at 400 °C led to an insignificant increase in the $Ih$ value as compared to the DCAP state. When this happens, the $f$ value decreased and reached its minimum value of 0.35, the microhardness increased to 3350 MPa. This was the result of microstructural refinement down to 15-30 nm [8] and decomposition of a supersaturated $\alpha$ solid solution of copper followed by precipitation of particles of the second-phase. The elevation of the aging temperature to 500 °C resulted in a significant growth (in near 30 times) of the $Ih$ value and an increase of the $f$ value from 0.35 to 1.0. At higher aging temperatures, 600 and 700 °C, the $Ih$ and $f$ values returned to the values close to those obtained after DCAP and DCAP and annealing (aging) at 400 °C (figure 5).

4. Summary

In the present work, two Cu-Cr-Zr alloys of near the same composition have been studied. It was shown that DCAP and annealing (aging) of the Cu-Cr-Zr alloys under study led to a refinement of the microstructure and to the decomposition of the $\alpha$ solid solution followed by precipitation of nanosized particles. This resulted in a significant improvement of their mechanical and functional properties. DCAP and aging at 400 °C of the alloys provided an increase in the ultimate strength in 2.6-3.3 times and the yield stress in 2.8-5.1 times as compared to those in the initial coarse-grained state, while retaining reasonable ductility.

DCAP and aging at 400-500 °C led to a decrease in the electrical resistance of the Cu-Cr-Zr alloys to 2.1 $\mu$Ω·cm. Tests for sliding friction of samples subjected to DCAP and aging at 400, 600, and 700 °C gave rise to the formation of the nanocrystalline microstructure in the surface layer. That provided a high level of the microhardness and acceptable tribological properties.
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