The effect of Cr and Zr content on the microstructure and properties of the Cu-Cr-Zr system alloy

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Abstract. This article investigates the effect of various contents of Cr and Zr on the microstructure and properties of the alloy of the Cu-Cr-Zr system. It has been defined that an increase in the content of Zr leads to a decrease in the grain size both in the initial state and after severe plastic deformation. The increase in the content of Zr significantly enhances the strength of the alloy.

1. Introduction
Cu-based alloys are considered to be good conductors and are widely used in different branches of industry: in heat exchange units, in resistance welding machines (electrodes and other fittings), in the electrical engineering, electronics engineering, instrument engineering and etc. [1, 2]. However, coarse-grained Cu-Cr-Zr alloys exhibit low strength that limits their application.

The traditional way to improve the strength properties of metallic materials is the application of plastic deformation and/or the addition of alloying elements. For example, the addition of Cr significantly reinforces the Cu alloy and increases the level of high-temperature strength. The inclusion of a small percentage of Zr leads not only to an increase in strength properties, but also to a considerable improvement of ductility at elevated temperatures. Alloys of the Cu-Cr-Zr system are dispersion-strengthened materials [2]. The strength of Cu alloys can be further increased due to the formation of an ultrafine-grained structure by the methods of severe plastic deformation. [3-6].

The aim of this work is to investigate the influence of Cr and Zr additions on the structure and properties of the alloys of the Cu-Cr-Zr system during severe plastic deformation.

2. Experimental methods
In this work, the experiments were carried out on Cu-0.5%Cr-0.2%Zr, Cu-1.8%Cr-0.8%Zr, Cu-0.8%Cr-0.08%Zr (wt. %) alloys. The alloys were subjected to high-temperature treatment at T=1000 °C during τ=30 minutes with a subsequent quenching in 5% NaCl solution to form a supersaturated solid solution, thereby forming the initial state. Hereafter, the samples with a size of 12×12×80 mm in the form of rectangular parallelepipeds were deformed by equal channel angular
pressing at room temperature with a rate of 0.2 mm/sec with an interior angle of the fitting \( \psi = 120^\circ \) and an exterior angle \( \varphi = 0^\circ \) for equal channel angular pressing via route A. The number of passes was 4. The degree of deformation for each pass was 0.8.

To study the microstructure, we used an OLIMPUS GX51 optical microscope, a JEOL JSM-6490LV scanning electron microscope, and a JEOL 2100 transmission electron microscope. X-ray structural analysis of the samples was performed by a Rigaku Ultima IV (Bragg-Brentano geometry) diffractometer using the Cu\( \text{K}_\alpha \) monochromatic radiation at the reflected beam (parabolic graphite monochromator). The measurements were conducted along the area of \( 2 \times 2 \text{ mm}^2 \) located in the center of the samples.

The microhardness of the investigated samples was measured by a “Micromet” with a load of 100 g and a holding time under load of 10 seconds. The investigations of electrical conductivity were performed at the temperature \( T = 23 \, ^\circ \text{C} \) by the eddy current method. The measurement error was \( \pm 2\% \).

3. Results and discussion

The structure of the alloys was investigated in the initial state and after severe plastic deformation. Figure 1 a, b, c shows rounded inclusions with a size of several microns (table 1) in the initial state against the matrix of the \( \alpha \)-solid solution. These inclusions are excessive Cr and Zr, which are formed during solidification of the alloy and are not dissolved during quenching of the solution, since the solubility of Cr at a temperature of 1000 °C in the copper matrix is only 0.4-0.45 wt. %, and Zr – 0.15 wt. % [2, 7]. The size of large inclusions is 4.3±0.1 \( \mu \text{m} \) in the Cu-0.5Cr-0.2Zr alloy, 3.2±0.2 \( \mu \text{m} \) in the Cu-0.8Cr-0.08Zr alloy, 2.6±0.2 \( \mu \text{m} \) in the Cu-1.8Cr-0.8Zr alloy. It can be said that an increase in the content of Zr leads to a decrease in the size of the inclusions. An increase in the degree of alloying by Zr leads to a decrease in the grain size. In particular, the grain size is 260±11 \( \mu \text{m} \) in the Cu-0.8Cr-0.08Zr alloy, 140±8 \( \mu \text{m} \) in the Cu-0.5Cr-0.2Zr alloy, 110±4 \( \mu \text{m} \) Cu-1.8Cr-0.8Zr alloy. This is due to the particles of the non-dissolved Zr. Thus, the alloys in the initial state are characterized by a coarse-grained microstructure, in which with increasing Zr content the average grain size decreases.

![Figure 1. Scanning electron microscopy. The microstructure of the alloys in the initial state: the Cu-0.8Cr-0.08Zr alloy (a), the Cu-0.5Cr-0.2Zr alloy (b), the Cu-1.8Cr-0.8Zr alloy (c).](image_url)

The implementation of severe plastic deformation leads to a decrease in the size of the inclusions (\( d_{\text{av}} \) in table 1). Besides, the average distance (\( L_{\text{av}} \)) between the inclusions decreases resulting in an increase in the density of their distribution. The latter could be explained by mechanical fragmentation of particles.

Figure 2 demonstrates the microstructure of the alloy after severe plastic deformation in the longitudinal section of the samples. Severe plastic deformation leads to the formation of an elongated fragmented structure with an ultrafine size in the transverse direction. The longitudinal axis of the elongated fragments is oriented at an angle of 35 degrees in respect to the axis of the sample. Due to the high elongation, only the transverse dimension of this structure can be defined. Its average transverse size is 170±10 nm in the Cu-0.8Cr-0.08Zr alloy, 160±7 nm in the Cu-0.5Cr-0.2Zr alloy, 155±10 nm in Cu-0.2Cr-0.8Zr. As reported above, in the initial state of these alloys, the same, but more pronounced tendency was observed.

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Along with large inclusions observed in images of scanning electron microscopy, observations by the method of transmission electron microscopy revealed small particles about 7-11 nm in size (figure 2). The paper [8] reports the presence of Cr and Cu₅Zr phases in these alloys. Small particles are generated as a result of dynamic ageing implemented during severe plastic deformation. This is demonstrated by the change in the lattice parameter in the alloys (table 1) towards the parameter of the pure Cu lattice (0.3615 nm) associated with the impurity depletion of the main matrix. On the other hand, severe plastic deformation considerably increases the concentration of defects (table 1) that leads to acceleration of diffusion processes, i.e. to the kinetics of ageing.

![Figure 2. Transmission electron microscopy. The microstructure of the alloys after severe plastic deformation: the Cu-0.8Cr-0.08Zr alloy (a), the Cu-0.5Cr-0.2Zr alloy (b), the Cu-1.8Cr-0.8Zr alloy (c)](image)

Figures 2 a and 2 c demonstrate the presence of twins (indicated by arrows). With an increase in the degree of alloying, the number of twins grows due to the decrease in the stacking fault energy, which is consistent with [9].

Table 1. Microstructure parameters of the alloys

| State | Cu-0.8Cr-0.08Zr | Cu-0.5Cr-0.2Zr | Cu-1.8Cr-0.8Zr |
|-------|-----------------|----------------|----------------|
|       | Solid solution  | Severe plastic deformation | Solid solution  | Severe plastic deformation | Solid solution  | Severe plastic deformation |
| $H_v$, MPa | 750±20 | 1460±30 | 950±20 | 1500±40 | 1030±60 | 1650±40 |
| IACS, % | 32.0±0.7 | 33.0±0.7 | 29.0±0.6 | 30.0±0.6 | 30.0±0.6 | 29.0±0.6 |
| $D_{av}$, mkm | 260±11 | 0.17±0.01 | 140±8 | 0.160±0.007 | 110±4 | 0.155±0.010 |
| $d_{av}$, mkm | 3.2±0.2 | 1.0±0.1 | 4.3±0.1 | 2.5±0.2 | 2.6±0.2 | 1.9±0.1 |
| $L_{av}$, mkm | 38 | 11 | 34 | 21 | 20 | 21 |
| Lattice parameter, nm | - | ±0.000001 | ±0.00005 | ±0.00002 | ±0.000029 | ±0.00015 |
| Lattice strain, % | - | 0.23 | 0.074 | 0.2400 | 0.037 | 0.20 |
| Crystallite size, nm | - | 39±3 | 145±22 | 32±3 | 229±59 | 34±4 |
| Disl.dens, 10¹⁵ m⁻² | - | 6.7±0.6 | - | 4.6±0.3 | - | 3.8±0.6 |

Table 1 shows the increase in microhardness after severe plastic deformation. In particular, the microhardness value of all three ultrafine-grained alloys dramatically increased in comparison with the initial state (table 1). Besides, the highest microhardness is achieved in the Cu-1.8Cr-0.8Zr alloy with a high content of alloying elements.

It is known that Cr and Zr atoms dissolved in the Cu matrix scatter the electrons responsible for the conductivity, and, consequently, significantly degrade the electrical conductivity. Table 1 shows that the electrical conductivity of the Cu-0.5Cr-0.2Zr and Cu-1.8Cr-0.8Zr alloys is about 30% IACS (International Annealed Copper Standards). This indicates that almost the same number of atoms is dissolved in the matrix. However, the electrical conductivity in the Cu-0.8Cr-0.08Zr alloy is slightly lower.
higher after severe plastic deformation. Firstly, this is due to the fact that the Cu-0.8Cr-0.08Zr alloy contains a smaller amount of Zr, and, secondly, the dynamic aging and the formation of new precipitates take place during severe plastic deformation. Nevertheless, a small amount of Cr and Zr elements still remains in the matrix leading to low conductivity.

4. Conclusions
1. The increase in the content of Zr in the alloy and the implementation of equal channel angular pressing allow achieving the structure with the smallest transverse cross section of fragments equal to 155 nm.
2. The increase in the content of Zr in the alloy and the implementation of equal channel angular pressing activate twinning processes.
3. The process of dynamic ageing is implemented in the alloy during severe plastic deformation. As a result, the particles of Cr and Cu$_2$Zr precipitate in the matrix mainly in the form of a sphere and with a mean radius of 7-11 nm.
4. The increase in the content of Zr in the alloy and the implementation of equal channel angular pressing significantly increase the microhardness. The highest microhardness of 1650 MPa is achieved in the Cu1.8Cr-0.8Zr alloy that is 1.6 times higher compared to the initial state.

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