Investigation of superplasticity of ultrafine-grained copper alloys obtained using the ECAP

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Abstract. The paper describes the results of experimental studies of the superplasticity of ultrafine-grained (UFG) high-purity copper, as well as UFG copper alloys Cu-Ag and Cu-Cr. The study shows that the introduction of small (up to 0.1 wt.%) additives of alloying elements leads to an increase in the ductility of UFG copper at elevated temperatures. An increase in the concentration of alloying elements complicates the process of plastic flow of UFG copper at elevated temperatures due to the difficulty in grain-boundary sliding.

1. Introduction

Achieving superplasticity in alloys requires the following conditions: (i) high speed of grain boundary sliding (GBS); (ii) stable ultrafine-grained (UFG) structure [1-7].

Previously, the effect of superplasticity was successfully achieved using a large number of groups of materials, the most known of which being aluminum [8-10], magnesium [11-13], and titanium alloys [14-16]. Successful experiments with achieving superplasticity of UFG copper are less common (see, for example, [17-21]), with one exception being Cu-Zn alloys with a high (more than 20 wt.%) Zinc content.

This is due to the difficulty of achieving GBS in copper - grain boundaries of ordinary technical grade copper grains contain a large number of harmful impurities that significantly reduce ductility at elevated temperatures (for example, sulfur and bismuth in copper, which lead to ductility failures at strain temperatures of about 250 °C and 400-450 °C, respectively, at concentrations of 10⁻⁴%). In addition, most incoherent particles, which are released mainly along the grain boundaries of copper, which are necessary for stabilization of the UFG structure at elevated temperatures, also lead to "inhibition" of GBS.

However, in our opinion, the possibilities associated with the optimal alloying of UFG alloys are not yet fully exhausted and, first of all, are associated with new approaches in choosing the optimal processing modes involving intensive plastic deformation methods, as well as with the selection of small alloying element additives that impact, first of all, the diffusion properties of equilibrium and nonequilibrium grain boundaries in UFG materials.

A high-strength superplastic ultrafine-grained copper alloy can be created using several approaches. In our opinion, the most promising method for achieving GBS and reducing local grain-boundary concentration of harmful impurities is Equal Channel Angular Pressing (ECAP) [7]. Varying the ECAP
temperature should provide the necessary conditions for the diffusion-controlled redistribution of harmful impurities from the “old” grain boundaries to the “new” boundaries of deformational origin. This allows reducing the local concentration of harmful impurities in proportion to a change in the grain boundary area by \((d_1/d_2)^2\) times [15, 22-23]. Secondly, the speed of GBS can be increased by applying microadditives of alloying elements, which increase the coefficient of grain boundary diffusion [7].

In this paper we aim to study the effect of alloying elements on the superplasticity of UFG copper alloys.

2. Materials and methods
The object of study was the copper alloys microalloyed with silver (0.1, 0.25, 0.50 wt.% Ag) that were obtained by induction casting in vacuum, as well as chrome bronzes Cu-Cr with various chromium contents (from 0.05 to 0.5 wt.%).

The microalloyed copper alloys were obtained from the Russian industrial high-purity copper M00k. Samples 22×22×150 mm of copper alloys were obtained using INDUTHERM VTC-200 vacuum induction injection molding machine (Germany) equipped with a pyrometer for temperature control and a vibration casting system to increase the uniformity of the distribution of chemical elements in the melt. Microalloyed copper was not homogenized and quenched; Cu-Cr bronze samples were quenched from a temperature of 1040 °C (30 min) in water.

The UFG structure in copper alloys was formed using Ficep HF400L hydraulic press (400 tf). ECAP of copper and copper alloys was carried out at a temperature of 200-215°C at a strain rate of 0.4 mm/s. The first ECAP cycle was carried out at a temperature of 450°C.

To study the structure of copper alloys, we used Jeol JSM 6490 and TESCAN VEGA 2 LSU scanning electron microscopes with Oxford Instruments INCA 350, INCA Energy, INCA Wave microanalyzers, as well as an EBSD attachment.

Superplasticity tests were performed using Tinius Olsen H25K-S test machine. The heating time to the test temperature did not exceed 3-5 minutes; before the test, the sample was held at a set temperature for 5-7 minutes. After the test, the sample was cooled together with the furnace. The fractographic analysis of fractures of the samples after tensile tests was carried out using Jeol JSM-6490 SEM. Microstructure control was performed using Leica IM DRM metallographic microscope.

Samples were annealed in SNOL-1 625/11-43 air oven with a controlled heating system.

3. Experimental results

3.1. Study of thermal stability of the structure
The results of metallographic studies show that the samples have a dendritic structure, and the boundaries of the dendrites are characterized by a high content of alloying elements (the results of EDS microanalysis showed that the boundaries of dendrites contain about 2-3 times higher concentration of alloying elements compared to the volume of the crystal lattice). The obtained results confirm the literature data on the fact that the selected alloying elements tend to form segregations at the grain boundaries during casting.

Methods of scanning electron microscopy found no isolation of particles of the second phase in ingots. The results of measuring the specific electrical resistivity (SER) show that the SER value to a rather high degree (±0.05μΩ·cm) corresponds to the theoretical SER value calculated using the additivity rule (Mattissen rule). The cumulative data obtained suggests that during the casting process, all alloying elements are completely dissolved in the volume of the copper crystal lattice.

The results of electron microscopy studies of misorientation spectra showed that ECAP leads to emergence of a highly fragmented mixed grain-subgrain structure (Figures 1, 2). The average fragment size varies from 0.4 to 1 μm (depending on the ECAP mode). The results of EDS microanalysis showed that after ECAP, the difference in the concentration of alloying elements between the grain boundaries (grain dendrites) and the volume of the crystal lattice decreases and, on the whole, lies within the range of natural dispersion. Thus, it can be assumed that the ECAP (probably, the first ECAP cycle, which is
carried out at a temperature of 450 °C) results in deformation-induced redistribution of alloying elements from “old” dendritic grain boundaries to “new” grain boundaries of deformational origin and, in part, into the volume of the crystal lattice of copper. The value of electrical resistance of all alloys after ECAP increased by 0.03-0.1 μΩ·cm.

Figure 1. Microstructure of UFG copper alloy Cu-0.5Ag after N = 2 ECAP cycles

Figure 2. Microstructure of UFG copper alloy Cu-0.5Ag after N = 4 ECAP cycles

Figure 3. Microstructure of UFG copper alloy Cu-0.5Ag after ECAP (N = 4) and annealing at 260 °C

Studies of thermal stability showed that the recrystallization point during 30-minute annealing of high-purity UFG copper M00k (ECAP, N = 4) is 100-125 °C. Doping UFG copper with horophilic alloying elements (Ag, Cr) leads to a decrease in the grain growth migration rate, a decrease in the volume fraction of the recrystallized structure (at a given annealing temperature), and an increase in the temperature of the onset of T1 and the end of T2 of recrystallization. The temperature T1 in silver microalloyed UFG copper rises to 300-325 °C (the maximum values of the recrystallization point were recorded for UFG Cu-0.25Ag and Cu-0.5Ag alloys). We should note that microalloying changes the
nature of the processes of recrystallization in UFG copper - while annealing of high-purity UFG copper leads to the formation of a pronounced structure with varied grain sizes, which is typical for primary recrystallization, the recrystallization annealing of micro-alloyed UFG copper renders a noticeably lower degree of grain size variability.

The experimental dependences of the volume fraction of the recrystallized structure on the time of isothermal annealing were analyzed using the Avrami equation: \( f_r = 1 - \exp\left(-\left(t/t_r\right)^n\right) \), where \( n \) is the numerical experiment (Avrami coefficient), \( t \) is the annealing time, \( t_r \) is the diffusion time scale, determined using the standard equation: \( t_r = t_0 \exp\left(-\frac{Q_R}{kT}\right) \), where \( t_0 \) is the preexponential factor, \( Q_R \) is the activation energy of recrystallization (in kT_m), \( k \) is the Boltzmann constant, \( T \) is the annealing temperature (in K), \( T_m = 1356 \) K is the melting point of copper [24]. To determine the activation energy of recrystallization \( Q_R \) for each UFG alloy in the temperature range from \( T_1 \) to \( T_2 \), we plotted the dependences of the volume fraction of the recrystallized structure against the annealing time at three constant annealing temperatures \( f_r (t) \). Based on the slope of the dependence \( f_r (t) \) replotted in double logarithmic coordinates \( \ln(\ln(1-f_r)) \) – \( \ln(t) \) for each annealing temperature (\( T \)), we determined the coefficient \( n \); using the value of the free coefficient, we determined the value \( n \cdot \ln(t_r) \) for each annealing temperature (see Figure 4). The activation energy \( Q_{R1} \) was determined from the slope of the dependence \( \ln(t_r) - T_m / T \) (see Figure 5).

![Figure 4](image1.png)

**Figure 4.** Dependences \( \ln(\ln(1-f)) \) – \( \ln(t) \) for UFG alloys with 0.1Ag (a) and 0.25Ag (b)

![Figure 5](image2.png)

**Figure 5.** Dependences \( \ln(t_r) - T_m / T \) for UFG alloys with 0.1Ag (a) and 0.25Ag (b)

The analysis shows that an increase in the content of alloying elements leads to an increase in the activation energy \( Q_R \) from 6.0-6.5 kT_m, which is typical for pure UFG copper M00k, to 10.4-11.5 kT_m in UFG alloys Cu-0.25Ag and Cu-0.5Ag. The resistivity measurements showed that during the recrystallization annealing, the resistivity decreases by 0.05-0.1 \( \mu \Omega \cdot \text{cm} \) (increase in electrical conductivity by \( (1.5-2) \times 10^{-6} \) S/m, see Figure 6), which corresponds to the scale of the influence of defects (lattice dislocations, grain boundaries) on the resistivity of metals. Thus, it can be argued that during the annealing, the solid solution does not decompose and no particles are released, and therefore, the increased thermal stability of the UFG structure of copper is due to the influence of alloying elements on the diffusion properties of nonequilibrium grain boundaries.
Studies of the thermal stability of UFG alloys Cu-Cr showed that, starting from chromium concentration of 0.1 wt%, they decompose a solid solution, which manifests as a sharp decrease in SER (increase in difference \( \Delta \rho = \rho_{\text{init}} - \rho(t, T) \), see Figure 7). We should point out that during the first cycle of high-temperature ECAP, which is required to eliminate the liquidation heterogeneity, a partial decomposition of the solid solution is observed, and the degree of this decomposition, measured as the difference between the theoretical and experimental values of the electrical resistivity, increases with increasing chromium content in the alloy. The most intense release of particles during ECAP is observed in alloys with 0.5 wt% chromium - the degree of decomposition in them reaches 25-30%.

To determine the mechanism of the separation of chromium particles at various temperatures, we plotted the dependences of SER against annealing time \( \Delta \rho(t) \) (see Figure 7a), based on which, using the model of coherent decomposition of a solid solution [25], we calculated the dependences of the volume fraction of precipitated particles on the annealing time \( f_v(t) \). To analyze the obtained dependences, we used the Avrami-Mel-Jones-Kolmogorov equation: 

\[
f_v = f_{v0}(1-\exp(-t/t_{v0}^n))
\]

where \( f_{v0} \) is the maximum volume fraction of chromium particles released at a given temperature, \( n \) is a numerical coefficient characterizing the intensity of the solid solution decomposition process, \( t_v = t_{v0}\exp(Q_s/kT) \) is the diffusion time scale (\( Q_s \) is the activation energy of the diffusion-controlled process, \( t_{v0} \) is the preexponential factor). As shown in [25, 26], the set of parameters \( (n, Q) \) allows identifying the decomposition mechanism of a solid solution. To determine the values of \( n \) and \( Q \), the dependences \( f_v(t) \) were replotted in double logarithmic coordinates: 

\[
\ln(\ln(1-f_v/f_{v0})) - \ln(t)
\]

(see Figures 7b, c). The slope of this dependence determines the value of the coefficient \( n \), and the free coefficient determines the value \( n\ln(t_v) \). The slope of the dependence \( \ln(t_v) - T_m/T \), was used to determine the activation energy of the decomposition of the solid solution \( Q_s \). Studies of solid solution decomposition showed that the dependences \( \ln(\ln(1-f_v/f_{v0})) - \ln(t) \) have a two-stage character, which indicates that the kinetics of solid solution decomposition in UFG alloys Cu-Cr is controlled by the simultaneous occurrence of two quasi-independent processes characterized by their sets of parameters: process I \( (n_1 \approx 1.5, Q_1 \approx 18kT_m) \) and process II \( (n_2 \approx 0.2-0.35, Q_2 \approx 12-14kT_m) \). Based on the analysis of the results obtained, we can conclude that the process of solid solution decomposition during annealing of UFG alloys Cu-Cr is controlled by simultaneously occurring processes of particle separation in the volume of the crystal lattice (process I) and at grain boundaries of UFG copper (process II).
3.2. Superplasticity tests

An analysis of the results showed that the deformation curves of UFG copper at room temperature have a form typical for a strongly deformed metal (see Figure 8). The maximum elongation to fracture (δ) in UFG copper is does not exceed 32-34%. An increase in the test temperature from 20 to 300 °C led to a decrease in the ductility of UFG copper from 32-34% to 15%. This is a rather unexpected result, since it is traditionally assumed that an increase in the test temperature should lead to an increase in the ductility of the material. An analysis of the results of the study of the grain structure of the tested images showed that heating of UFG copper is accompanied by an intensive grain growth and the formation of a structure of varying grain size. This probably caused a simultaneous decrease in the flow stress from 390 to 255 MPa and a decrease in the ductility of UFG copper.

A further increase in the test temperature to 400 °C leads to an increase in the ductility of copper to 85% and a decrease in flow stress to 125 MPa (see Figure 9). The tensile curve of UFG copper at a temperature of 400 °C has the form typical for a highly ductile material. The results of structural studies showed that the average grain size in UFG copper after testing at a temperature of 400 °C was quite large.

Figure 7. The dependence of the change in SER on the time of isothermal annealing of the UFG alloy Cu-0.4Cr at various temperatures (a); dependences of the volume fraction on the annealing time in double logarithmic coordinates at the annealing temperature of 450 °C (b) and 400 °C (c)

Figure 8. Tension diagrams at different temperatures of samples of UFG copper M00k (a), Cu-0.1Ag alloy (b), Cu-0.25Ag alloy (c), Cu-0.5Ag alloy (d), and UFG Cu-0.4Cr alloy (e)
(more than 50 µm), and the microstructure itself was completely recrystallized and remained quite uniform. (In our opinion, the recrystallization process was fully completed even at the stage of preliminary heating of the sample - the superplasticity test procedure involves heating of the sample in the grips to the test temperature and holding it at this temperature for 5-7 min to establish thermal equilibrium). The fractographic analysis shows that the fractures of the UFG copper samples are viscous (see Figure 10).

![Figure 9](image1.png)

**Figure 9.** Dependences of flow stress ($\sigma_f$) and ultimate elongation to failure ($\delta$) on the test temperature of UFG copper alloys of various compositions

![Figure 10](image2.png)

**Figure 10.** Fractographic analysis of fractures of UFG copper M00K after tensile tests at room temperature (a), 200 °C (b), 350 °C (c)

An analysis of the influence of alloying shows that the positive effect of alloying elements is observed only in the case of low concentration (not more than 0.1 wt.%) - in this case, it is possible to provide 1.5-2 times greater ductility compared with UFG copper. As an example, Figure 8 shows the tensile diagrams of UFG alloys Cu-Ag with different silver contents. As can be seen, the strain hardening curves of the UFG alloy Cu-0.1Ag reveal a plastic flow stage already at a temperature of 300 °C, the ductility of the UFG alloy in this case reaches 135-140%, which significantly exceeds the ductility of pure UFG copper at the same temperature (32-34%). With an increase of the test temperature to 350-400 °C, the difference between the ductility of UFG copper and UFG alloy Cu-0.1Ag becomes smaller (at a temperature of 400 °C, the ductility of Cu-0.1Ag alloy is 140-150%, which is 1.7 times higher than the ductility of pure UFG copper (80-85%), see Figure 9).

The fractures of the UFG alloy Cu-0.1Ag samples after tensile tests are also viscous (see Figure 11). The study of strain-induced grain growth showed that the average grain size in the fracture zone after testing for superplasticity at a temperature of 350-400 °C is 3-5 µm. The grains are elongated, but the elongation coefficient is relatively small.
It is interesting to note that an increase in silver concentration leads to a significant decrease in the deformation-induced grain growth intensity (average grain size of 1-2.5 μm after testing at a temperature of 350-400 °C), which, in accordance with the theory of structural superplasticity [1-6, 27-30], should lead to an increased ductility of metal. At the same time, the test results show that the ductility of UFG alloys with a high silver content is quite low even at a temperature of 400 °C: for UFG Cu-0.25Ag alloy the elongation is 37-40%, and for UFG Cu-0.5Ag alloy it is 15-20%. This is a rather unexpected result. In our opinion, the most likely reason for the decrease in ductility of alloys with a high content of alloying elements is the inhibition of GBS due to a decrease in the coefficient of grain boundary diffusion included in the equation for GBS [7].

Fractographic analysis of fractures (see Figures 12, 13) shows that the failure of UFG alloys with a high silver content has a mixed brittle-viscous nature, and with an increase in the silver content, the share of the brittle constituent increases.

The results of tests of the superplasticity of the UFG alloy Cu-0.4Cr samples show that the dependence of the relative elongation on the test temperature is nonmonotonic in nature with a maximum (85-90% at a temperature of 300 °C). A further increase in the test temperature to 400 °C leads to a decrease in the ductility of UFG chromium bronze Cu-0.4Cr to 45-47%. Studies of the structure show
that chromium particles ensure the stability of the UFG structure when tested for superplasticity only up to a temperature of 250-300 °C, and a further increase in the test temperature leads to a sharp increase in the average grain size by more than an order of magnitude. The fractographic analysis of fractures showed that tests at high temperatures (350-400 °C) are accompanied by an increase in the share of the brittle constituent, which is probably due to the intensive grain growth and the release of chromium particles at the grain boundaries.

4. Conclusions
Our team conducted the superplasticity tests of UFG microalloyed copper samples with different silver and chromium contents. Our study shows that microalloying of UFG copper leads to a significant reduction of the rate of deformation-induced grain growth and to further increase the superplastic characteristics of UFG copper. Fractographic analysis of fractures showed that failure of the samples is viscous in nature. It has been established that in high concentrations, alloying elements negatively affect grain-boundary sliding, which leads to a decrease in the ductility of UFG copper at elevated temperatures (despite their positive effect on the stabilization of the UFG structure).

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