Mechano-structural characteristics of Cu$_{72}$Au$_{24}$Ag$_4$ alloy subjected to severe plastic deformation combined with subsequent heat treatment

N. V. Gokhfeld$^1$, A. V. Okulov$^1$, O. S. Iusupova$^1$, V. G. Pushin$^1$, and V. P. Pilyugin$^1$

$^1$Institute of Metal Physics, Ural Branch of the RAS, 18 S. Kovalevskaya Street, Ekaterinburg, 620108, Russia

Abstract. Mechano-structural characteristics of the synthesized Cu$_{72}$Au$_{24}$Ag$_4$ and commercial Cu$_{59}$Au$_{33}$Ag$_7$Fe$_1$ alloys subjected to preliminary severe plastic deformations (SPDs) by high-pressure torsion combined with subsequent annealings at different temperatures and holding times were studied by means of scanning and transmission electron microscopy as well as durometry. Due to SPDs, it was possible to refine the structure of the investigated alloys to submicro- and nanostructural state. As a result of certain annealing regimes, the atomic ordering processes began to occur in the alloys. The microstructural features and mechanical properties after preliminary SPDs and subsequent annealings were compared for the studied alloys. Influence of the deformation degree and subsequent annealing regimes on the kinetics of atomic ordering and changes in mechanical properties was shown. In addition, it was found the inhibition effect of the nanograin growth due to the barrier action of dispersed precipitates.

1 Introduction

Electroresistive Cu$_3$Pd- and Cu$_3$Au-based alloys are of great importance in the electronics industry due to the ability to change their structure, electrical and mechanical properties depending on the regimes of thermomechanical treatment and alloying [1–6].

The aim of the work was to study and compare the features of the structural and mechanical characteristics of synthesized Cu$_{72}$Au$_{24}$Ag$_4$ and commercial Cu$_{59}$Au$_{33}$Ag$_7$Fe$_1$ alloys after preliminary severe plastic deformations (SPDs) and subsequent annealings, as well as alloying with a third component. In addition, one of the main tasks was to obtain submicro- and nanostructural state in the above alloys in order to maximize grain refinement and, accordingly, strengthening.

* Corresponding author: gokhfeld@imp.uran.ru
2 Materials and methods

Synthesized Cu\textsubscript{72}Au\textsubscript{24}Ag\textsubscript{4} and commercial Cu\textsubscript{59}Au\textsubscript{33}Ag\textsubscript{5}Fe\textsubscript{1} alloys were studied in the initial state and after SPDs with subsequent annealings. The Cu-Au ingots were manufactured by vacuum melting using high-purity Cu and Au (99.98–99.99%). The alloys were subjected to recrystallization annealing at 800 °C for 3 h in vacuum. The atomic disordered state was fixed by quenching in water from 640 °C. The samples for SPDs by high-pressure torsion were disk-shaped with a diameter of 10 mm and a thickness of 0.4 mm. The pressure was 6 GPa and the number of revolutions (n) varied from 1/2 to 5. The SPD samples were subjected to isothermal or stepwise annealings in quartz ampoules evacuated to 10\textsuperscript{–4} mm Hg at temperatures of 350 °C, 370 °C, 430 °C up to 24 hours.

The microstructure of the alloys was studied at the Collective Use Center of IPM UB RAS by means of scanning (Quanta 200 Pegasus coupled with energy-dispersive X-ray (EDX) and electron backscatter diffraction (EBSD) detectors) and transmission (JEM-200CX, Tecnai G² 30 and Philips CM 30) electron microscopy. The microhardness tests were carried out on the PMT-3 device from the center to the periphery in 3 directions with the step of 500 μm and load of 50 g.

3 Results and discussion

The study of the initial Cu\textsubscript{72}Au\textsubscript{24}Ag\textsubscript{4} alloy after recrystallization annealing by scanning electron microscopy (SEM) showed that the grain size was in the range of 30–70 μm (the average size ~50 μm) (Fig. 1).

![Fig. 1. SEM image of the initial Cu\textsubscript{72}Au\textsubscript{24}Ag\textsubscript{4} alloy](image)

By the means of the electron microscopic studies, it was shown that after SPDs, the coarse-grained structure (average grain size ~100 μm) gradually transformed into a nanostructure consisting of nanosized (10–50 nm) crystallite grains with a high dislocation density. At the initial stages of SPD, the grain refinement in the Cu\textsubscript{72}Au\textsubscript{24}Ag\textsubscript{4} alloy was practically not observed. There was the accumulation of dislocations and the formation of a network or spiral dislocation substructure. The grain refinement process starts with n = 1/4 revolution. It was also evidenced by the appearance of annular reflections in the microelectron diffraction pattern (Fig. 2a). However, the grain refinement was still very inhomogeneous. This state persisted even after SPD for n = 1 revolution, although the tendency to a more pronounced annular continuity increased.
The increase in the number of revolutions during SPD up to \( n = 5 \) led to intensive grain refinement. In turn, the increase in the density of annular reflections in the electron diffraction patterns was a clear confirmation of the grain refinement process and indicated the predominance of high-angle misorientations between nanocrystals (Fig. 2b). The absence of superstructural reflections indicated the absence of long-range order. The study of the microstructure of the Cu\(_{72}\)Au\(_{24}\)Ag\(_{4}\) alloy after SPD showed that the grains had a size from several nanometers to several tens of nanometers (Fig. 2b).

The subsequent annealing of the plastically deformed Cu\(_{72}\)Au\(_{24}\)Ag\(_{4}\) alloy led to the elimination of dislocations and the coarsening of nanograins to a size of more than 100 nm. The stepwise annealing was chosen to restore the long-range atomic order in the Cu\(_{72}\)Au\(_{24}\)Ag\(_{4}\) alloy: 350 °C for 10 h + 370 °C for 10 h (Fig. 3a). The conventional regime of atomic ordering of the Cu\(_{72}\)Au\(_{24}\)Ag\(_{4}\) alloy was chosen for comparison: cooling from 430 °C to 200 °C at a rate of 10 °C per day for 23 days (Fig. 3b). As a result, the growth of the thermal domain structure and the splitting of superstructural reflections were observed. This also confirmed the process of atomic ordering.

![Fig. 2. TEM images of the Cu\(_{72}\)Au\(_{24}\)Ag\(_{4}\) alloy after SPD at P = 6 GPa and (a) \( n = 1/2 \), (b) \( n = 5 \) revolutions and corresponding microelectron diffraction patterns](image)

![Fig. 3. TEM images of the Cu\(_{72}\)Au\(_{24}\)Ag\(_{4}\) alloy after SPD at P = 6 GPa, \( n = 5 \) revolutions: (a) stepwise annealing (350 °C for 10 h + 370 °C for 10 h), (b) atomic ordering during annealing from 430 °C to 200 °C (10 °C per day for 23 days) and corresponding microelectron diffraction patterns](image)
uniform grain refinement. In addition, the presence of superstructural reflections after additional annealing indicated the atomic ordering in the Cu$_{59}$Au$_{33}$Ag$_7$Fe$_1$ alloy (Fig. 4a). In this case, the thermal stability of the nanostructure was persisted up to $T_C$ [7].

![Fig. 4. TEM images of the Cu$_{59}$Au$_{33}$Ag$_7$Fe$_1$ alloy after SPD at P = 6 GPa, n = 5 revolutions: (a) stepwise annealing (300 °C for 1h + 290 °C for 1h + 280 °C for 1h + 270 °C for 1h), (b) annealing at 250 °C for 4 h and corresponding microelectron diffraction patterns](image)

During annealing the Cu$_{59}$Au$_{33}$Ag$_7$Fe$_1$ alloy at 250 °C for 4 h, the recrystallization process proceeded very intensively with the formation of coarser grains. In some cases, the grains with sizes of several hundred nanometers were observed. According to microelectron diffraction patterns, the reflections formed dotted networks which also indicated the increase in the average grain size (Fig. 4b).

The microhardness values of the Cu$_{72}$Au$_{24}$Ag$_4$ alloy after SPD and heat treatment are presented in Table 1.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>SPD, n</th>
<th>Heat treatment</th>
<th>Microhardness, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{72}$Au$</em>{24}$Ag$_4$</td>
<td>–</td>
<td>The initial state*</td>
<td>1460</td>
</tr>
<tr>
<td>Cu$<em>{72}$Au$</em>{24}$Ag$_4$</td>
<td>–</td>
<td>430–200 °C, 23 days</td>
<td>2190</td>
</tr>
<tr>
<td>Cu$<em>{72}$Au$</em>{24}$Ag$_4$</td>
<td>5</td>
<td>370 °C, 1 hour</td>
<td>3510</td>
</tr>
</tbody>
</table>

As shown in Table 1, the microhardness of the Cu$_{72}$Au$_{24}$Ag$_4$ alloy increased significantly depending on the regime of thermomechanical treatment. The similar dynamics was also observed for the Cu$_{59}$Au$_{33}$Ag$_7$Fe$_1$ alloy.

**Conclusion**

The synthesized Cu$_{72}$Au$_{24}$Ag$_4$ and commercial Cu$_{59}$Au$_{33}$Ag$_7$Fe$_1$ alloys with submicro- and nanocrystalline structure were obtained by SPDs and subsequent annealings.

It was established that in the above alloys, the inhibition effect of the nanograin growth during annealing is additionally realized due to the barrier action of nanodispersed precipitates. The annealings after SPDs in both alloys leads to their atomic ordering and, consequently, to improvement in mechanical and electrical characteristics. Thus, the thermomechanical treatment method can be effectively used to obtain high-strength nanostructured resistive and electrocontact materials.
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References