Structure and properties of Cu-based alloys diluted by Pd and Ag

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Abstract. The microstructure, mechanical and electrical properties of Cu-Pd alloys (with Pd content not more than 8 at.%) and triple Cu-Pd-Ag alloys with 5 at.%Ag were studied. It was established that the strength and the recrystallization temperature of the Cu-Pd alloys increased with palladium content. A comparison of the electrical properties of these alloys when Pd content was increased from 0 to 8 at.%Pd was done. An anomaly was revealed in the Cu-5.9Pd and Cu-8Pd alloys: the plastic deformation does not lead to an increase in the electrical resistivity. It is due to the destruction of short range atomic order in the quenched Cu-Pd alloys under deformation. The alloying with silver leads to a further increase in strength with a constant electrical conductivity. It was found that annealing of the deformed Cu-Pd-Ag alloys at 200-300°C led to an increase in strength. It was shown that the effect was not related to the Pd-content and was due to silver only.

1. Introduction
Supersaturated solid solutions based on Cu-Ag alloys have high strength properties, acceptable ductility and low electrical resistivity. Such an optimal combination of functional properties allows using these alloys in practice. However, the search for ways to further improve the strength properties of copper-based alloys without losing their electrical conductivity is an important scientific and practical task.

Earlier, we showed [1] that the introduction of even a small amount of palladium (less than 10 at.%) into copper led to a significant increase in strength, which was caused by solid-solution hardening and grain refinement. Furthermore, the addition of palladium increases the corrosion properties of copper. Thus, it has been suggested that palladium in copper solid solutions can be used as a matrix for additional strengthening of copper with silver. The implementation of this idea can result in obtaining high-strength corrosion-resistant Cu-Pd-Ag alloys with a sufficiently high electrical conductivity that are in demand by the industry.

The purpose of this work was to study the structure and physical and mechanical properties of binary Cu-Pd alloys (with palladium content from 0 to 8 at.%) and ternary alloys based on them Cu-3Pd-5Ag and Cu-5Pd-5Ag (at.%).

2. Materials and methods
The alloys under investigation were prepared by melting Cu, Pd and Ag of 99.98, 99.99 and 99.99% purity, respectively. The metals were melted in vacuum of at least 10⁻² Pa, and the alloys were poured
into a graphite crucible. The chemical composition of samples was analyzed using a JEOL JXA-733 microprobe. In total 5 binary Cu-Pd alloys were melted (with palladium contents 1.5, 3.0, 4.5, 5.9, and 8.0 at.% Pd) and two ternary alloys Cu-3Pd-5Ag and Cu-5Pd-5Ag (at.%). Further, for the sake of brevity, we omit “at.\%” in the alloy names, for example: Cu-3Pd-5Ag. The pure Cu was also melted and used as a reference material.

The ingots 5 mm in diameter were homogenized at 800°C for 3 hours and then cut into two pieces. One piece of the ingot was to a 0.25 mm diameter thin wire (it was then cut to obtain samples for the resistometric study). The other piece of the ingot was rolled to obtain 0.3 mm thick plates (they were used as samples for the X-Ray analysis and microhardness measurements). We also carried out cryodeformation experiments. For this purpose, the sample was placed between two plates of stainless steel 18/10 and this “assembly” was then soaked for about 1 min in liquid nitrogen prior to each rolling pass. Although the rollers of the rolling mill had room temperature, we believe that the alloy samples inside this “assembly” were deformed at a temperature close to cryogenic one.

Some of these wires and plates were annealed at 700°C for 1 h and then were immediately quenched in cold salt water. As a result, we studied the samples that were in three structural states: hardened, deformed at room temperature and subjected to deformation at a low temperature.

The room-temperature electrical resistivity was measured by the four-point method at DC 20 mA. Vickers microhardness values were determined using the PMT-3 tester with 0.05 kg load and dwelling time of 30 s. Each microhardness value was the average of at least ten measurements.

3. Results and discussion

3.1. Binary Cu-Pd alloys

It is well known that plastic deformation leads to an increase in the electrical resistivity of metals and alloys. It is caused by the formation of different scattering centers such as dislocations, point defects, and stacking faults due to deformation [2]. As an example, curve 1 in figure 1 shows the dependence of the electrical resistivity of pure copper on the deformation strain (e). This experiment was carried out using wires and their deformation strain was defined by the common equation: \( e = \ln \left( \frac{S_o}{S_f} \right) \), where \( S_o \) and \( S_f \) are the initial and final cross section areas, respectively [3].

![Figure 1. Dependences of the electrical resistivity on the deformation strain of pure copper (1), Cu-5.9Pd (2) and Cu-8Pd (3) alloys.](image)

Because of severe plastic deformation (SPD), the electrical resistivity of copper increases approximately by 4%. It is clear that the deformation strain of copper higher than \( e \approx 4.0 \) does not lead to any change in its electrical resistivity. In this case, there is a dynamic equilibrium between the
generation of defects through SPD and their disappearance due to the processes of dynamic recovery/recrystallization [4].

However, the dependences of the electrical resistivity obtained during the deformation of the initially quenched Cu-5.9Pd and Cu-8Pd alloys significantly differ from the behavior of copper. Indeed, the electrical resistivity of the Cu-8Pd alloy even slightly decreases at the initial stages of deformation (curve 3 in figure 1). The effect of SPD on the electrical resistivity of these alloys has never been investigated before. However, as it was established in [5], the electrical resistivity of the Cu-19.5Pd alloy abnormally decreases under plastic deformation.

The Cu-Pd alloys in vicinity of Cu₃Pd stoichiometry are known to form L₁₂-superstructure and the Cu-19.5Pd alloy has the maximum rate of the disorder→order phase transformation among them [6]. Quenching of ordered alloys leads to the formation of a short range atomic order (SRO) in them. Clusters of SRO are effective centers of electron scattering, but plastic deformation destroys them. That is why the electrical resistivity of the quenched Cu-19.5Pd alloy is more than that of the deformed one [5].

The L₁₂-type superstructure is also formed in Cu-8Pd alloy, but its ordering rate is significantly lower compared with the Cu-19.5Pd alloy. As shown in [7], the formation of the SRO in both Cu-8Pd and Cu-19.5Pd alloys increases their electrical resistivity as the result of quenching. The destruction of the SRO at the first step of plastic deformation leads to a decrease in the electrical resistivity of these alloys. When the deformation strain increases, the mean free path of the electron will decrease due to the rise in the number of different scattering factors such as grain boundaries, dislocations, vacancies, etc. As a result, the dependence of the electrical resistivity from the deformation strain of the initially quenched Cu-8Pd alloy has a parabolic shape.

It is shown in figure 1 (curve 2) that the electrical resistivity of the Cu-5.9Pd alloy remains almost constant during SPD (we had not sufficient quantity of this alloy, so this graph has no intermediate points). As follows from the phase diagram of the Cu-Pd system, only a solid solution of palladium in copper should form in the Cu-5.9Pd alloy. However, our results do not confirm that. The electrical resistivity of the solid solution should increase during the deformation, as it happens in pure copper [8]. However, the result is quite in agreement with our assumption about low degree of SRO, which forms in the Cu-5.9Pd alloy as the result of the quenching from high temperatures [7]. In this case, during the deformation of the quenched alloy, short-range order clusters are destroyed and new defects are generated. However, if the oppositely directed contributions from these processes to the electrical resistivity are comparable, it will remain almost unchanged.

The experiments carried out once again showed that the existing phase diagram of the Cu-Pd alloys needed further refinement. Indeed, our experimental data (see figure 1 and our works [1, 7]), as well as the results of the theoretical evaluation in [9], suggest that the region, where the L₁₂-superstructure exists in the Cu-Pd system, is somewhat wider than it follows from the generally adopted phase diagram.

3.2. Triple Cu-Pd-Ag alloys

It was established before [10] that the preliminary cryogenic deformation suppressed the processes of dynamic recovery/recrystallization, increased the dislocation density and activated the mechanical twinning. It leads to the formation of an ultrafine-grained structure during annealing of the alloys that increases their mechanical properties. It was found in [11] that the application of moderate annealing after cryo-rolling allowed achieving an optimal combination of high strength and good ductility in the Cu-3Ag alloy. As these results may be applied for practical purposes, the study of cryo-deformed alloys is of doubtless scientific interest. However, until now, the effect of the preliminary cryo-deformation on the evolution of the structure and properties during annealing has been studied in detail mainly in pure metals (Cu, Al, Nb etc.). For example, changes in the structure, texture, and properties during long low-temperature annealing of cryo-deformed copper was studied in [12]. However, the efficiency of preliminary cryogenic deformation for increasing the strength of dilute Cu-Pd and Cu-Pd-Ag alloys is still not clear.
The study has shown that the introduction of silver into the copper-palladium matrix leads to a significant increase in microhardness (figure 2). Moreover, during the study, we found a temperature anomaly: the strength properties of pre-deformed Cu-Pd-Ag alloys grow after low-temperature annealing. This phenomenon is particularly pronounced after the preliminary cryodeformation. The study found that the detected anomaly did not depend on the amount of palladium in the alloy and was determined exclusively by the silver content. The nature of this anomaly is known: low-temperature annealing leads to the decomposition of the supersaturated solid solution with the precipitation of submicrocrystalline particles of the new phase on all defects (dislocations, twin boundaries, etc.) [13]. We assumed hereabove that the $L1_2$-superstructure might be formed in dilute Cu-Pd alloys. However, our TEM investigation did not help to detect the ordered $L1_2$ phase due to its small content in the Cu-5.9Pd alloy. From this point of view, a detailed study of the microstructure of Cu-Pd-Ag ternary alloys is of particular interest. As is known, the simultaneous implementation of the atomic ordering and decomposition processes in ternary alloys leads to a significant acceleration of both reactions. We showed it earlier in Cu-Pd-Ag alloys heavily doped with palladium and silver [14]. A recent study of precipitate growth at reduced temperatures during ordering by $L1_0$-type in deformed Au-Cu-Ag alloys confirmed this conclusion [15]. Therefore, it is of interest to carry out a detailed study of the microstructure of dilute Cu-Pd-Ag alloys after long low-temperature annealing. Indeed, the antiphase domain boundaries will splash with the particles of the precipitated phase, facilitating the detection of the the ordered phase. Thus, it is necessary to continue the study of the structure and properties of dilute Cu-based alloys with Pd and Ag.

4. Conclusion
The results of this study give reason to doubt that the Cu-5.9Pd alloy is a solid solution. Since the short-range atomic order is observed in the quenched alloy, it is possible that the long-range atomic order can be formed in it. Thus, the results obtained in this work necessitate further studies of low-alloyed copper-palladium alloys in order to clarify the position of the thermal-concentration boundary of the existence of the ordered $L1_2$ phase on the phase diagram of the Cu-Pd system. The high physical and mechanical properties of Cu-Pd-Ag alloys make it possible to consider them as promising high-
strength conductors of electric current. The detected anomalous increase in strength properties during low-temperature annealing of Cu-Pd-Ag alloys can be used in practice for their further strengthening. The preliminary cryodeformation causes an increase in the strength properties of all investigated alloys.

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