PHYSICAL METALLURGY AND HEAT TREATMENT / METAΛΛΟΒΕДЕНИЕ И ТЕРМИЧЕСКАЯ ОБРАБОТКА

UDC 669.35: 539.89

https://doi.org/10.17073/0021-3438-2024-4-66-76

Research article Научная статья



Effect of annealing on the structure and properties formation of a copper alloy alloyed with palladium and silver

O.S. Novikova, Yu.A. Salamatov, A.E. Kostina, A.Yu. Volkov

M.N. Mikheev Institute of Metal Physics of Ural Branch of the Russian Academy of Sciences 18 Kovalevskaya Str., Ekaterinburg 620108, Russia

☑ Oksana S. Novikova (novikova@imp.uran.ru)

Abstract: A copper alloy with small additions of palladium and silver (Cu-1.5Pd-3Ag (at. %))—which has potential applications as a corrosion-resistant conductor of weak electrical signals—was studied using *X*-ray diffraction analysis, microhardness measurements, specific electrical resistivity, and tensile mechanical properties tests. Samples were examined in several initial states: quenched (from 700 °C) and deformed at room and cryogenic temperatures (with a 90 % reduction in cross-sectional area in both cases). To study the processes of structural reorganization and property evolution, the initial samples were annealed in the temperature range from 150 to 450 °C (in 50 °C increments), followed by cooling in water or air. The duration of the heat treatments ranged from 1 to 48 hours. It was established that annealing the Cu-1.5Pd-3Ag alloy at temperatures below 450 °C leads to the precipitation of silver-based phase particles in the Cu matrix. Annealing of the initially quenched alloy was found to slightly increase its specific electrical resistivity (ρ) from 3.55·10⁻⁸ to 3.8·10⁻⁸ Ohm·m (after 48 h at 250 °C). It was revealed that alloying copper with 1.5 at. % palladium and 3 at. % silver enhances the strength properties (the yield strength of the alloy reaches 500 MPa) and raises the recrystallization temperature, while the electrical conductivity of the alloy remains around 50 % IACS. The optimal combination of properties (strength, ductility, and electrical conductivity) is observed after annealing the pre-cryodeformed alloy at 250 °C for less than 18 h. Extending the annealing time causes overaging, resulting in softening. The results of this study can be applied in the development of a new high-strength material with reduced electrical resistivity.

Keywords: Cu-Pd-Ag alloys, resistometry, microhardness, microstructure, X-ray diffraction analysis, cryodeformation.

Acknowledgments: X-ray diffraction analysis and scanning electron microscopy were carried out using the equipment of the Center for Collective Use at the Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences.

This work was performed as part of the state assignment from the Ministry of Education and Science of Russia (project "Pressure", No. 122021000032-5).

For citation: Novikova O.S., Salamatov Yu.A., Kostina A.E., Volkov A.Yu. Effect of annealing on the structure and properties formation of a copper alloy alloyed with palladium and silver. *Izvestiya. Non-Ferrous Metallurgy.* 2024;30(4):66–76. https://doi.org/10.17073/0021-3438-2024-4-66-76

Влияние отжигов на формирование структуры и свойств сплава меди, легированного палладием и серебром

О.С. Новикова, Ю.А. Саламатов, А.Е. Костина, А.Ю. Волков

Институт физики металлов им. М.Н. Михеева УрО РАН Россия, 620108, г. Екатеринбург, ул. С. Ковалевской, 18

Оксана Сергеевна Новикова (novikova@imp.uran.ru)

Аннотация: Методами рентгеноструктурного анализа, измерения микротвердости, удельного электросопротивления и механических свойств при растяжении изучали сплав меди с малыми добавками палладия и серебра: Cu-1,5Pd-3Ag (ат. %), который может найти применение в качестве коррозионно-стойкого проводника слабых электрических сигналов. Исследованы образцы,

© 2024 O.S. Novikova, Yu.A. Salamatov, A.E. Kostina, A.Yu. Volkov

Ключевые слова: сплавы Cu-Pd-Ag, резистометрия, микротвердость, микроструктура, рентгеноструктурный анализ, криодеформация.

Благодарности: Рентгеноструктурный анализ, а также сканирующая электронная микроскопия проведены с использованием оборудования ЦКП ИФМ УрО РАН.

Работа выполнена в рамках государственного задания Минобрнауки России (тема «Давление», № 122021000032-5).

Для цитирования: Новикова О.С., Саламатов Ю.А., Костина А.Е., Волков А.Ю. Влияние отжигов на формирование структуры и свойств сплава меди, легированного палладием и серебром. *Известия вузов. Цветная металлургия*. 2024;30(4):66—76. https://doi.org/10.17073/0021-3438-2024-4-66-76

Introduction

Copper-based alloys are known for their low electrical resistivity, which has made them widely used in electrical engineering applications [1]. One approach to enhancing the mechanical properties of copper alloys without significantly reducing their electrical conductivity, while maintaining sufficient ductility, is alloying. For example, adding elements such as beryllium or niobium to copper can substantially improve its strength properties [2—4]. However, the toxicity and cost of beryllium, as well as the mutual immiscibility of copper and niobium in the solid state [5], limit the use of such alloys in industrial applications. The table below summarizes the physical and mechanical properties of various copper alloys used as electrical conductors [6].

Previous studies have shown [7] that alloying copper with palladium (less than 10 at. %) results in solid-

solution strengthening, while simultaneously increasing corrosion resistance. However, as the demand for high-strength electrical conductors continues to rise, strengthening by alloying with a single component may prove insufficient [8]. Therefore, to achieve superior functional properties, modern approaches utilize alloys with two or more alloying elements, as well as severe plastic deformation, including at cryogenic temperatures. This approach allows the combination of different strengthening mechanisms [9]. For example, the authors of [10] combined solid-solution and dispersion strengthening mechanisms to reinforce an Ag—Pd—Cu—Au alloy, while in [11], a method was proposed for strengthening the Cu—Pd—Ag alloy through the simultaneous occurrence of several phase transformations.

It has been found [12] hat small additions of silver (3 at. %) have a negligible effect on the electrical con-

Physical and mechanical properties of low-alloyed copper alloys for electrical conductors [6]

Физические и механические свойства низколегированных медных сплавов для проводников электрического тока [6]

Alloy	ρ, 10 ⁻⁸ Ohm·m	σ _u , MPa	
		Deformation	Deformation + annealing
Cu + 0.4Zr	2.0	_	270
Cu + 0.3Mg	2.2	530	300
Cu + 0.4Cr + 0.2Sn + 0.8Ti	2.6	_	650
Cu + 0.1Ag	1.7	340	200

ductivity of Cu—Pd alloys while significantly enhancing their strength and recrystallization temperature. For instance, the yield strength and ultimate tensile strength of the ternary Cu—3Pd—3Ag (at. %) alloy are higher, while its electrical conductivity is comparable to that of the Cu—3Pd alloy. It is of particular interest to investigate the properties of a ternary Cu—Pd—Ag alloy with a lower palladium content and to determine the effect of cryodeformation on its strength and electrical conductivity.

The aim of the present work was to study the structure and properties of the Cu-1.5Pd-3Ag (at. %) alloy in various initial states, as well as after annealing in the temperature range of 150-450 °C.

Materials and methods

The Cu-1.5Pd-3Ag (at. %) alloy was melted from copper, palladium, and silver with purities of 99.98 %, 99.99 %, and 99.99 %, respectively. The melting was performed under a vacuum of at least 10^{-2} Pa, with the alloy cast into a graphite crucible.

A 5 mm diameter ingot was homogenized at 800 °C for 3 h, then quenched by water cooling and cut into two parts. From one part of the ingot, a wire with a diameter of 1.5 mm was produced through drawing, and samples for tensile testing were cut from this wire. Further drawing to a diameter of 0.22 mm produced thin wire for resistometry. The other part of the ingot was rolled into plates with a thickness of 0.3 mm, which were used to characterize the phase composition at various stages of processing and to measure microhardness.

Cryodeformation of the samples was carried out between two stainless steel plates. This assembly was immersed in liquid nitrogen for about one minute, after which the rolling step was performed. The process was then repeated. The massiveness of this sandwich-like structure ensured the stability of the cooled sample's temperature. Some of the wires and plates deformed at room temperature were annealed at 700 °C (for 1 h) and then quenched in water. Thus, the study investigated samples in several initial states: quenched (from 700 °C), deformed at room and cryogenic temperatures (in both cases, with a 90 % reduction in cross-sectional area).

Both the wire and plate samples had the same degree of preliminary deformation. As we previously demonstrated for various ordered systems, setting aside some differences in microstructure and texture between the samples, the mechanism of deformation-induced structural reorganization, in general, does not depend on whether the preliminary deformation is performed by rolling or drawing [13]. Therefore, the results obtained provide a comprehensive picture of the effect of deformation on the structure and properties of the Cu—1.5Pd—3Ag alloy.

To study the processes of structural reorganization and property evolution, the initial samples were annealed in the temperature range from 150 to 450 °C (in 50 °C increments), followed by cooling in water or air. The duration of the heat treatments ranged from 1 to 48 h. All heat treatments were performed in vacuum-sealed glass or quartz ampoules. In further descriptions of the heat treatment process, including its characteristics (temperature, holding time, etc.), the term "annealing" is used. When emphasizing changes in properties due to the formation of a new phase, the term "aging" is applied.

The specific electrical resistivity (ρ) was measured using the standard four-point probe method (with a constant current of I = 20 mA). Measurements of the specific electrical resistivity at room temperature were conducted on wire samples with a diameter of 0.22 mm and a length of 250 mm, fixed in a special conductor as previously described [13]. The absolute measurement error of ρ was $\pm 0.04 \cdot 10^{-8}$ Ohm·m.

Mechanical tests were carried out using a ZD 10/90 tensile testing machine at a strain rate of 3 mm/min. The working length of the samples was 30 mm. At least five samples were tested for each structural state. The absolute measurement error for the yield strength was ± 10 MPa, and for elongation to failure, it was ± 0.5 %.

X-ray diffraction analysis (XRD) was conducted on alloy plates with a thickness of 0.3 mm. The X-ray diffraction measurements were performed using a PANalytical Empyrean Series 2 laboratory diffractometer (Netherlands) equipped with a three-axis Eulerian cradle. Measurements were made in parallel beam geometry using CoK_{α} radiation with a wavelength of 0.179 nm. The microstructure was studied using a Tescan MIRA LMS scanning electron microscope (SEM) (Czech Republic) with an accelerating voltage of up to 30 kV, magnifications ranging from 20^{\times} to $160\,000^{\times}$, and a resolution of 1.2 nm. Structural images were obtained in both backscattered and secondary electron modes. The chemical composition of the samples (Cu-2.4Pd-5.2Ag (wt. %) / Cu-1.5Pd-3Ag (at. %)) was monitored using an EDAX energy-dispersive X-ray spectrometer (USA) with a resolution of 160 eV.

Vickers microhardness was measured using a PMT-3 device (JSC LOMO, St. Petersburg, Russia) under a load of 50 g with a holding time of 30 s. At least 10 measurements were taken for each structural state.

Results and discussion

Fig. 1 shows the changes in mechanical properties after holding quenched and room-temperature-deformed samples of the Cu—1.5Pd—3Ag alloy for 1 h in the temperature range of 150 to 450 °C.

The quenched sample has a very low yield strength ($\sigma_{0.2} = 70\,$ MPa), which remains almost unchanged after aging in the temperature range below 300 °C (Fig. 1, *a*). After heat treatment of the quenched alloy at 400 °C, the yield strength increases significantly to ~170 MPa, while aging at temperatures above 400 °C causes a slight decrease. The increase in strength during aging of quenched Cu—Ag alloys has been observed multiple times before and is attributed to the decomposition of the supersaturated solid solution, accompanied by the precipitation of fine silver particles along grain boundaries and within the grains [14; 15]. The elongation to fracture of the initially quenched Cu—1.5Pd—3Ag alloy is almost independent of the heat treatment temperature and remains at ~40 %.

After 90 % deformation at room temperature, the yield strength of the alloy increases to $\sigma_{0.2} = 520$ MPa (Fig. 1, b), which is about seven times higher than that of the initially quenched sample. Annealing the initially deformed alloy at temperatures below 250 °C does not significantly change its strength properties. Above 250 °C, there is a sharp decline in yield strength due to recrystallization. Since the onset of recrystallization depends on temperature and time conditions [16], comparing this characteristic in different alloys should be done under similar heat treatment conditions. In previous

experiments with deformed pure copper samples, it was established that the decrease in strength due to recrystallization begins after annealing for 1 hour at 150 °C [8]. Thus, the recrystallization temperature of the investigated alloy is approximately 100 °C higher than that of pure copper.

After annealing the previously deformed alloy at 425-450 °C, its elongation to failure increases from the initial 2 % to 46-48 %. Notably, after annealing within this temperature range, the mechanical properties of the samples are very similar and practically independent of their initial state. This result suggests that annealing at 425-450 °C creates similar structural states in both quenched and deformed samples. Based on the obtained data, it can be concluded that heat treatment of the initially deformed Cu-1.5Pd-3Ag alloy for 1 h in the temperature range of 200-250 °C provides sufficiently high strength ($\sigma_{0.2} \approx 520$ MPa) and ductility ($\delta = 8 \div 14 \%$). It is worth noting that the Cu-1.5Pd-3Ag alloy deformed by 90 % does not show the anomalous increase in strength after annealing in the 150-250 °C range that was observed in the mechanical tensile tests of the Cu-3Pd-3Ag alloy. In that case, we detected a 40 MPa increase in $\sigma_{0,2}$ after annealing the initially deformed alloy, and in cryodeformed alloy, the yield strength anomalously increased by ~100 MPa, reaching $\sigma_{0.2} \approx 720$ MPa) [12].

We also noted that during the aging process, Cu—Ag alloys are typically cooled in air [17; 18]. To ensure a correct comparison with the literature data, subsequent experiments in our study were conducted using this cooling method. Fig. 2 shows the resistometry re-

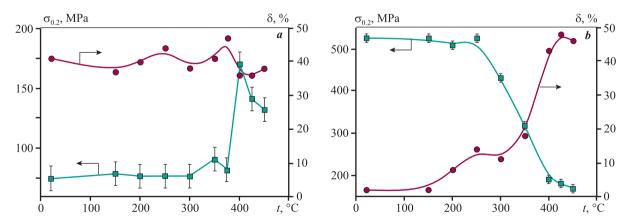


Fig. 1. Dependences of the yield strength ($\sigma_{0.2}$) and elongation to failure (δ) on annealing temperature of Cu-1.5Pd-3Ag alloy samples in the initially quenched (\boldsymbol{a}) or pre-deformed (\boldsymbol{b}) states

Holding time at each temperature -1 h, cooling in water

Рис. 1. Зависимости предела текучести ($\sigma_{0,2}$) и удлинения до разрушения (δ) от температуры обработки образцов сплава Cu-1,5Pd-3Ag, находящихся в исходно закаленном (a) или предварительно деформированном (b) состояниях

Время выдержки при каждой температуре – 1 ч, охлаждение в воде

sults for quenched and deformed wire samples of the Cu-1.5Pd-3Ag alloy after annealing in the temperature range of 150 to 450 °C. The holding time at each temperature ranged from 1 to 48 h.

Aging for 1 hour does not lead to significant changes in the specific electrical resistivity of the quenched alloy (Fig. 2, a); throughout the entire investigated temperature range, ρ remains at ~3,55·10⁻⁸ Ohm·m with a slight decrease at 450 °C. Extending the heat treatment duration (up to 48 h) results in an increase in the resistivity of the initially quenched samples, with a maximum observed in the 200-250 °C temperature range. The increase in resistivity during aging aligns well with the processes of decomposition in the alloy, as discussed above. As is known [19-21], fine second-phase particles act as scattering centers for charge carriers, leading to an increase in specific electrical resistivity. A precise solution to this problem is considered in quantum mechanics, specifically in the theory of single-channel particle scattering (see, for example, [22]). To simplify, the smaller the effective size of the interaction potential, the less it distorts the trajectory of passing charge carriers. Fewer charge carriers are affected, and distortion of their paths due to scattering processes is macroscopically observed as electrical resistivity (or its inverse, electrical conductivity). Individual atoms of alloving elements distort the trajectories of charge carriers far less than large dispersed particles, and therefore, they have a smaller impact on electrical conductivity. The increase in the size of precipitates at

elevated processing temperatures leads to the disappearance of this effect's contribution to the material's overall resistivity. Indeed, after aging at 450 °C, the specific resistivity of the alloy samples does not exceed $\rho \sim 3.5 \cdot 10^{-8}$ Ohm·m.

In practice, electrical conductivity, measured according to the IACS (International Annealed Copper Standard), is increasingly used instead of the specific electrical resistivity of a conductor. According to this standard, the conductivity of any material is expressed as a percentage of the conductivity of pure copper. According to our data, the electrical conductivity of the Cu—1.5Pd—3Ag alloy is 49 % IACS. It is worth noting that the cathode copper used in this study has a lower conductivity than the standard, at 97 % IACS.

The high defect density in the structure of the initially deformed alloy slightly increases its resistivity compared to the quenched state: $\rho \sim 3.7 \cdot 10^{-8}$ Ohm·m. During annealing at temperatures up to 250 °C, regardless of the duration, there is a gradual decrease in the resistivity of the pre-deformed alloy (Fig. 2, *b*). Annealing above 250 °C causes a sharp drop in ρ , which is attributed to recovery/recrystallization processes. Extending the annealing duration increases the rate of resistivity reduction. After holding at 450 °C for 48 h, the resistivity of the alloy reaches $\rho \sim 3.25 \cdot 10^{-8}$ Ohm·m (53 % IACS). Thus, annealing the deformed alloy results in a reduction in its resistivity by approximately 12 %. As is known [16], a reduction in defect density during recrystallization leads to a 3–4 % decrease in

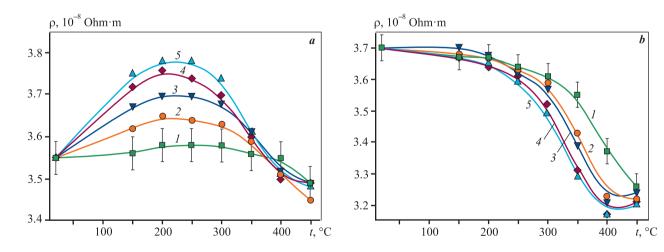


Fig. 2. Dependences of the electrical resistivity of Cu-1.5Pd-3Ag alloy samples quenched form 700 °C (a) and deformed by 90 % (b) on temperature (t) and heat treatment duration (τ) τ , h: I-1, 2-6, 3-12, 4-24, 5-48

Рис. 2. Зависимости удельного электросопротивления закаленных от 700 °C (a) и деформированных на 90 % (b) образцов сплава Cu-1,5Pd-3Ag от температуры (t) и продолжительности термообработки (τ) τ , ч: I-1, I=1, I

resistivity. Since in our case, annealing the deformed alloy reduces its resistivity by approximately 12 %, it is likely that structural changes related to the redistribution of silver in the material also contribute to the specific resistivity values. The obtained ρ values, alongside sufficient strength and ductility, may be of interest for using the alloy as an electrical signal conductor. It is well known that preliminary cryodeformation is an effective method for strengthening copper and copper alloys [18; 23; 24].

The change in microhardness after annealing in the temperature range of 150 to 450 °C for deformed Cu—1.5Pd—3Ag alloy samples is shown in Fig. 3. The microhardness of the samples after room and cryogenic deformation is 2000 and 2200 MPa, respectively (Fig. 3, *a*, *b*). The higher microhardness of the pre-cryodeformed alloy is observed across the entire annealing temperature range. It is worth noting that the microhardness of the cryodeformed sample increases particularly noticeably after annealing at 250 °C: a distinct "step" appears in the microhardness vs. temperature plot (Fig. 3, *b*).

Regardless of the temperature-time treatment conditions, all diffractograms of the Cu—1.5Pd—3Ag alloy (Fig. 4) show intense peaks from the matrix, which represents a face-centered cubic (FCC) solid solution of palladium in copper, along with much weaker reflections from an FCC phase enriched with silver. Notably, the (111) peak of this phase is already present in the alloy quenched from 700 °C (diffractogram *1* in Fig. 4, *a*). After cryodeformation, the peaks become less intense and

broader (diffractogram 3 in Fig. 4, a), due to increased internal stresses and grain refinement [25].

As shown in the XRD data of the studied alloy (Fig. 4, a), the addition of palladium and silver increases the lattice parameter of both the quenched and deformed alloy across various temperatures to a = 0.3644 nm (compared to the lattice parameter of pure copper at a = 0.3619 nm). Heat treatments of the alloy samples (in all initial states) at 250 °C and 400 °C result in a reduction of the lattice parameter of the matrix (to 0.3639 nm and 0.3625 nm, respectively), causing the peaks to shift to the right (Fig. 4, b, c).

When heated to 700 °C, the formation of a silver-enriched phase begins, which is retained after subsequent quenching (diffractogram 1 in Fig. 4, a). Considering that the solubility of silver in copper is very low, it can be assumed that this phase consists of regions of pure or nearly pure silver. The most favorable regions for the precipitation of this phase are grain boundaries, dislocations, and other defects, as these areas have a lower concentration of solvent atoms. However, X-ray diffraction analysis, being an integral method, does not allow for precise determination of where the precipitates form. Deformation leads to the fragmentation and breakdown of the precipitated clusters, resulting in a more uniform distribution of silver in the matrix. During heat treatment at 250 °C, noticeable diffusion does not occur: the volume of the silver-enriched phase remains approximately the same as before the heat treatment (Fig. 4, b). The lattice parameter of the silver-based phase in the initially

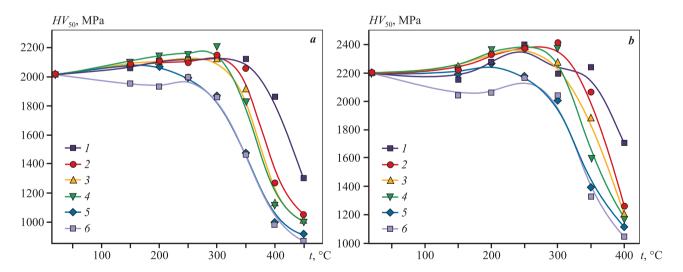
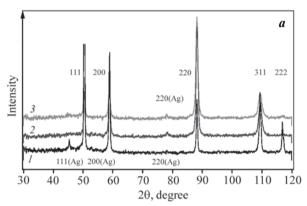


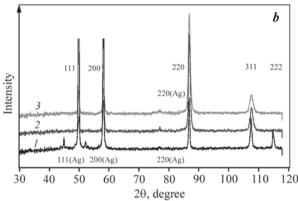
Fig. 3. Dependence of microhardness of Cu-1.5Pd-3Ag alloy samples on annealing temperature a - 90 % deformation at room temperature, b - 90 % deformation at cryogenic temperature τ , h: 1 - 1, 2 - 6, 3 - 12, 4 - 18, 5 - 24, 6 - 48

Рис. 3. Зависимости микротвердости образцов сплава Cu-1,5Pd-3Ag от температуры отжига a – деформация на 90 % при комнатной температуре, b – деформация на 90 % при криогенной температуре τ , ч: I – 1, I – 2, I – 3, I – 18, I – 24, I – 48

quenched alloy is 0.4027 nm, and after heat treatment at 250 °C, it remains nearly unchanged at 0.4023 nm.

After annealing at 400 °C, silver again forms clusters in the material initially deformed at various temperatures





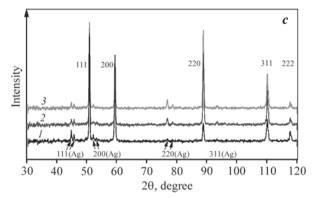


Fig. 4. *X*-ray diffraction patterns of Cu-1.5Pd-3Ag alloy samples

a – initial state: I – quenching from 700 °C, 2 – 90 % deformation at room temperature, 3 – 90 % deformation at cryogenic temperature; b – initial state + 250 °C, 48 h, air cooling;

c – initial state + 400 °C, 48 h, air cooling

Рис. 4. Дифрактограммы образцов сплава Cu-1,5Pd-3Ag

a — исходное состояние: I — закалка от 700 °C, 2 — деформация на 90 % при комнатной температуре, 3 — деформация на 90 % при криогенной температуре;

b — исходное состояние +250 °C, 48 ч, охлаждение на воздухе; **c** — исходное состояние +400 °C, 48 ч, охлаждение на воздухе

(diffractograms 2 and 3 in Fig. 4, c). Here, the splitting of weak peaks of the silver-enriched phase is observed. This may indicate that during annealing, silver segregation occurs, forming regions with different levels of palladium enrichment. Some regions may consist of clusters of nearly pure silver. Indeed, the lattice parameter of the silver-based phase (for the peaks on the left) after annealing at $400\,^{\circ}\text{C}$ (0.4080 nm) becomes close to that of pure silver (0.4077 nm).

The lattice parameter of the second silver-based phase (for the peaks on the right) after annealing at 400 °C is 0.4007 nm. These regions may correspond to silver clusters that additionally contain dissolved palladium. For example, in study [26], field ion microscopy, which allows direct observation of atoms on the surface of solids, showed that during the early stages of decomposition in the Cu—50Pd—20Ag (at. %) alloy, the precipitate phase represents a solid solution of palladium in silver. However, this phase may also consist of small silver clusters within the original matrix that have not yet coalesced into larger formations. A definitive conclusion regarding the nature of this phase cannot be drawn based solely on X-ray diffraction analysis.

The diffractograms of the samples deformed at various temperatures, as well as after annealing at 250 °C, show a pronounced texture: the intensity of the (220) peak is an order of magnitude higher than the others (diffractograms 2 and 3 in Fig. 4, a, b). As is known, during cold rolling of face-centered cubic (FCC) alloys, the main rolling texture develops with the {110} plane parallel to the rolling plane and the <112> direction parallel to the rolling direction [27]. Additionally, even after prolonged annealing of the initially deformed samples at 250 °C, the width of the X-ray peaks does not decrease. This indicates that the recrystallization process is still far from complete at this stage of heat treatment. A similar conclusion was previously drawn from resistometry data and microhardness measurements.

Since the optimal set of functional characteristics (strength, ductility, and electrical conductivity) is observed after annealing at 250 °C, SEM analysis was performed on a sample annealed at this temperature.

Fig. 5 shows an SEM image of the microstructure of the Cu-1.5Pd-3Ag alloy after cryodeformation and annealing at 250 °C for 48 h. One of the detected precipitates is highlighted with an oval in Fig. 5, *a*. The particle of the new phase has an elongated "lenslike" shape, with a thickness of $\sim 10~\mu m$ and a length of $\sim 45~\mu m$. The formation of such a large particle is caused by so-called overaging, where prolonged heat

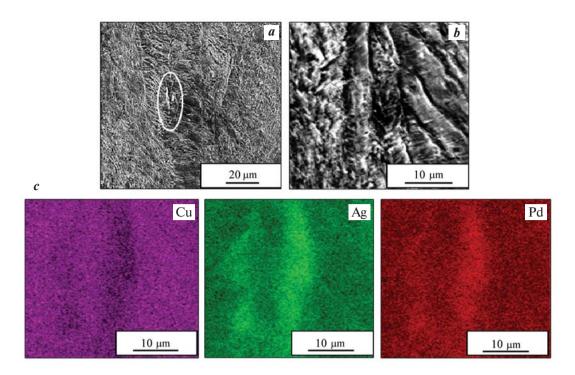


Fig. 5. Microstructure of the Cu–1.5Pd–3Ag alloy after annealing (t = 250 °C, $\tau = 48$ h) and air cooling after cryodeformation by 90 %

a – an elongated silver precipitation is shown by an oval; b – area from which distribution maps of chemical elements were obtained (c)

Рис. 5. Микроструктура сплава Cu-1,5Pd-3Ag после отжига ($t=250\,^{\circ}$ C, $\tau=48\,^{\circ}$ ч) и охлаждения на воздухе после криодеформации на 90 %

- а участок, на котором овалом показано вытянутое выделение серебра
- b участок, с которого были получены карты распределения по химическим элементам (c)

treatment leads to the coalescence of small precipitates. It is well known that at this stage, the strength properties of aging alloys significantly decrease [28]. Indeed, as seen in the results in Fig. 3, *b*, the maximum microhardness values are observed after annealing at 250 °C for no more than 18 h.

The relatively large size of the precipitate allows for the determination of its elemental composition (Fig. 5, b, c). Energy-dispersive analysis performed using SEM revealed the following chemical composition of the particle (wt. %): 54.8 Cu, 1.2 Pd, and 44.0 Ag. The high copper content in the precipitated particle raises doubts and is more likely due to electrons reflected from the Cu matrix reaching the detector. Indeed, in a previous study [26] using field ion microscopy, it was established that in the Cu-50Pd-20Ag (at. %) alloy, Pd-Ag particles precipitate during the atomic ordering of the Cu-Pd matrix. Additionally, mathematical analysis of the X-ray peak shapes performed in [12] suggested that after cryodeformation and annealing at 250 °C in the Cu-3Pd-3Ag (at. %) alloy, two regions form: one enriched in silver and the other depleted.

Conclusions

- 1. Alloying copper with palladium (1.5 at. %) and silver (3 at. %) enhances the strength properties through the combination of two mechanisms: solid-solution strengthening and decomposition. Preliminary cryodeformation provides an additional strengthening effect of about 10 %.
- **2.** Annealing the Cu—1.5Pd—3Ag alloy at temperatures below 450 °C leads to the precipitation of silver-based phase particles in the Cu matrix. The optimal combination of properties (high strength, adequate ductility, and electrical conductivity) is observed after annealing the preliminarily cryodeformed alloy at 250 °C for less than 18 hours. Prolonging the annealing time results in overaging.
- **3.** In its optimal structural state, the Cu—1.5Pd—3Ag alloy exhibits a yield strength of ~500 MPa, a higher recrystallization temperature compared to copper (by ~100 °C), and electrical conductivity of 50 % IACS. The set of properties found in this alloy may be of interest for practical applications.

References

- 1. Osintsev O.E., Fedorov V.N. Copper and copper alloys. Domestic and foreign brands: Reference book. 2-nd ed., rev. and add. Moscow: Innovatsionnoe mashinostroenie, 2016. 360 p. (In Russ.).
 - Осинцев О.Е., Федоров В.Н. Медь и медные сплавы. Отечественные и зарубежные марки: Справочник. 2-е изд., перераб. и доп. М.: Инновационное машиностроение, 2016. 360 с.
- Valova-Zakharevskaya E.G., Deryagina I.L., Popova E.N., Khlebova N.E., Pantsyrnyi V.I. Special characteristics of the microstructure of high-strength multifiblamentary Cu—18Nb composites. *Diagnostics, Resource and Mechanics of materials and structures*. 2018;5:116—126. (In Russ.).

https://doi.org/10.17804/2410-9908.2018.5.116-126

Валова-Захаревская Е.Г., Дерягина И.Л., Попова Е.Н., Хлебова Н.Е., Панцырный В.И. Особенности микроструктуры высокопрочного многоволоконного композита Cu—18Nb. *Diagnostics, Resource and Mechanics of Materials and Structures*. 2018;5:116—126.

https://doi.org/10.17804/2410-9908.2018.5.116-126

3. Chzhigan Ch., Tszyunvey L., Shitsyan L., Yanni S., Yuan M. Mechanisms of high-temperature deformation of the Cu—Be alloy in the high-elastic annealed state. Fizika Metallov i Metallovedenie. 2018;119(1):73—80. (In Russ.). https://doi.org/10.7868/S0015323018010096 Чжиган Ч., Цзюньвэй Л., Шицянь Л., Янни С., Юань М. Механизмы высокотемпературной деформации сплава Си—Ве в высокоупругом отожжен-

ном состоянии. Физика металлов и металловедение.

https://doi.org/10.7868/S0015323018010096

2018;119(1):73—80.

- Loginov P.A., Vorotilo S., Sidorenko D.A., Lopatina Yu.V., Okubaev A., Shvyndina N.V., Levashov E.A. The effect of Ti and TiH₂ additives on structure and mechanical properties of copper alloys for diamond cutting tools. *Izvestiya. Non-Ferrous Metallurgy.* 2020;(3):51—58. (In Russ.). https://doi.org/10.17073/0021-3438-2020-3-51-58 Логинов П.А., Воротыло С., Сидоренко Д.А., Лопатина Ю.В., Окубаев А., Швындина Н.В., Левашов Е.А. Влияние добавок Ті и ТіН₂ на структуру и свойства медных сплавов для алмазного режущего инструмента. *Известия вузов. Цветная металлургия.* 2020;(3):51—58.
 - https://doi.org/10.17073/0021-3438-2020-3-51-58
- Rajarshi Banerjee, Sangita Bose, Arda Genc, Pushan Ayyub. The microstructure and electrical transport properties of immiscible copper-niobium alloy thin films. *Journal of Applied Physics*. 2008;103(3):033511. https://doi.org/10.1063/1.2836970

- Loginov Yu.N. Copper and deformable copper alloys: textbook. Ekaterinburg: UGTU-UPI, 2004. 136 p. (In Russ.).
 - Логинов Ю.Н. Медь и деформируемые медные сплавы: Учеб. пос. Екатеринбург: УГТУ—УПИ, 2004. 136 с.
- Volkov A.Yu., Novikova O.S., Kostina A.E., Antonov B.D. Effect of alloying with palladium on the electrical and mechanical properties of copper. *Physics of Metals and Metallography*. 2016;117(9):945—954.

https://doi.org/10.1134/S0031918X16070176

- Волков А.Ю., Новикова О.С., Костина А.Е., Антонов Б.Д. Изменение электрических и механических свойств меди при легировании палладием. *Физика металлов и металловедение*. 2016;117(9):977—986. https://doi.org/10.7868/S0015323016070172
- 8. Maki K., Ito Yu., Matsunaga H., Mori H. Solid-solution copper alloys with high strength and high electrical conductivity. *Scripta Materialia*. 2013;68:778—780. https://doi.org/10.1016/j.scriptamat.2012.12.0217
- Gorsee S., Ouvrard B., Goune M., Poulon-Quintin A. Microstructural design of new conductivity — high strength Cu-based alloy. *Journal of Alloys and Compounds*. 2015;633:42—47.
 - https://doi.org/10.1016/j.jallcom.2015.01.234
- Ohta M., Shiraishi T., Hisatsune K., Yamane M. Agehardening of dental Ag-Pd-Cu-Au alloys. *Journal of Dental Research*. 1980;59(11):1966-71.

https://doi.org/10.1177/00220345800590110701

- 11. Iwamoto C., Adachi N., Watanabe F., Koitabash R. Microstructure evolution in Cu—Pd—Ag alloy wires during heat treatment. *Metallurgical and Materials Transactions A.* 2018;49:4947—4955.
 - https://doi.org/10.1007/s11661-018-4800-3
- 12. Novikova O.S., Kostina A.E., Salamatov Yu.A., Zgibnev D.A., Volkov A.Yu. The influence of deformation at cryogenic or room temperature followed by annealing on the structure and properties of copper and its Cu—3Pd and Cu—3Pd—3Ag (at. %) alloys. *Frontier Materials & Technologies*. 2023;(2):77—87. (In Russ.).

https://doi.org/10.18323/2782-4039-2023-2-64-6

Новикова О.С., Костина А.Е., Саламатов Ю.А., Згибнев Д.А., Волков А.Ю. Влияние деформации при криогенной или комнатной температуре с последующим отжигом на структуру и свойства меди и ее сплавов Cu—3Pd и Cu—3Pd—3Ag (at. %). Frontier Materials & Technologies. 2023;2:77—87.

https://doi.org/10.18323/2782-4039-2023-2-64-6

13. Volkov A.Yu., Novikova O.S., Antonov B.D. The kinetics of ordering in an equiatomic CuPd alloy: A resistometric study. *Journal of Alloys and Compounds*. 2013;581: 625—631.

http://dx.doi.org/10.1016/j.jallcom.2013.07.132

- Gong X., Wei B., Teng J., Wang Z., Li Yu. Regulating the oxidation resistance of Cu—5Ag alloy by heat treatment. *Corrosion Science*. 2021;190: 109686.
 - https://doi.org/10.1016/j.corsci.2021.109686
- Straumal B.B., Kilmametov A.R., Baretzkyet B., Kogtenkova O.A., Straumal P.B., Litynska-Dobrzynska L., Chulist R., Korneva A., Zieva P. High pressure torsion of Cu—Ag and Cu—Sn alloys: Limits for solubility and dissolution. *Acta Materialia*. 2020;195:184—198. https://doi.org/10.1016/j.actamat.2020.05.055
- Freudenberger J., Kauffmann A., Klaub H., Marr T., Nenkov K., Subramanya S.V., Schultz L. Studies on recrystallization of single-phase copper alloys by resistance measurements. *Acta Materialia*. 2010;58:2324—2329. https://doi.org/10.1016/j.actamat.2009.12.018
- Shakhova I., Sakai Y., Belyakov A., Kaibyshev R. Microstructure evolution in a Cu—Ag alloy during large strain deformation and annealing. *Materials Science Forum*. 2011;667—669:493—498. https://doi.org/10.4028/www.scientific.net/MSF.667-669.493
- Kada S., Vadlamani S.S., Kauffmann A., Hegedus Z., Gubicza J., Lechner M., Freudenberger J., Wilde G. High strength and ductile ultra-grained Cu—Ag alloy through bimodal grain size, dislocation density and solute distribution. *Acta Materialia*. 2013;61:228—238.
 - https://doi.org/10.1016/j.actamat.2012.09.053
- Wang H., Zhang Z., Zhang H., Hu Z., Li S., Cheng X. Novel synthesizing and characterization of copper matrix composites reinforced with carbon nanotubes. *Materials Science and Engineering A*. 2017;696:80—89. https://doi.org/10.1016/j.msea.2017.04.055
- 20. Fine structure and properties of solid solutions: Collection of articles. Eds. V. Kester, I.Ya. Bokshitsky, Ya.P. Selissky. Moscow: Metallurgiya, 1968. 223 р. (In Russ.). Тонкая структура и свойства твердых растворов: Сб. статей. Пер. с нем. под ред. В. Кестера, И.Я. Бокшицкий. Ред. Я.П. Селисский. М.: Металлургия, 1968. 223 с.
- 21. Islamgaliev R.K., Nesterov K.M., Valiev R.Z. Structure, strength, and electric conductivity of a Cu—Cr copperbased alloy subjected to severe plastic deformation. *Physics of Metals and Metallography*. 2015;116(2):209—218. https://doi.org/10.1134/S0031918X14090063
 Исламгалиев Р.К., Нестеров К.М., Валиев Р.З. Структура, прочность и электропроводность медного сплава системы Си—Сг, подвергнутого интенсивной пластической деформации. *Физика металлов и металловедение*. 2015;116(2):219—228. https://doi.org/10.7868/S001532301409006X

- 22. Babikov V.V. Phase function method in quantum mechanics. 2-nd ed., rev. and add. Moscow: Nauka, 1976. 287 p. (In Russ.).
 - Бабиков В.В. Метод фазовых функций в квантовой механике. 2-е изд., испр. и доп. М.: Наука, 1976. 287 с
- Kon'kova T.N., Mironov S.Y., Danilenko V.N., Korznikov A.V. Effect of low-temperature rolling on the structure of copper. *Physics of Metals and Metallography*. 2010:110(4):318—330.

https://doi.org/10.1134/S0031918X10100029

Конькова Т.Н., Миронов С.Ю., Даниленко В.Н., Корзников А.В. Влияние низкотемпературной прокатки на структуру меди. *Физика металлов и металловедение*. 2010;110(4):336—348.

https://doi.org/10.1134/S0031918X10100029

- 24. Guo S., Liu S., Liu J., Gao Z., Liu Z. Investigation on strength, ductility and electrical conductivity of Cu—4Ag alloy prepared by cryorolling and subsequent annealing process. *Journal of Materials Engineering and Performance*. 2019;28:6809—6815.
 - https://doi.org/10.1007/s11665-019-04448-7
- Umansky Ya.S., Skakov Yu.A., Ivanov A.N., Rastorguev L.N. Crystallography, X-ray diffraction and electron microscopy. Moscow: Metallurgiya, 1982. 632 p. (In Russ.).
 - Уманский Я.С., Скаков Ю.А., Иванов А.Н., Расторгуев Л.Н. Кристаллография, рентгенография и электронная микроскопия. М.: Металлургия, 1982. 632 с.
- 26. Syutkin N.N., Ivchenko V.A., Telegin A.B., Volkov A.Yu. Field emission microscopy of the early stages of ordering and decomposition of a palladium—copper—silver alloy. *Fizika Metallov i Metallovedenie*. 1986;62(5):965—969. (In Russ.).
 - Сюткин Н.Н., Ивченко В.А., Телегин А.Б., Волков А.Ю. Полевая эмиссионная микроскопия ранних стадий упорядочения и распада сплава палладий—медь—серебро. Физика металлов и металловедение. 1986;62(5):965—969.
- Honeycomb R. Plastic deformation of metals. Moscow: Mir, 1972. 408 p. (In Russ.).
 Хоникомб Р. Пластическая деформация металлов. М.: Мир, 1972. 408 с.
- 28. Toschi S., Balducci E., Ceschini L., Mørtsell E., Morri A., Di Sabatino M. Effect of Zr addition on overaging and tensile behavior of 2618 aluminum alloy. *Metals*. 2019;9:130.
 - https://doi.org/10.3390/met9020130

Information about the authors

Oksana S. Novikova — Cand. Sci. (Phys.-Math.), Senior Research Scientist, M.N. Mikheev Institute of Metal Physics of Ural Branch of the Russian Academy of Sciences (IMP UB RAS). https://orcid.org/0000-0003-0474-8991

E-mail: novikova@imp.uran.ru

Yuriy A. Salamatov — Cand. Sci. (Phys.-Math.), Senior Research Scientist, IMP UB RAS.

https://orcid.org/0000-0002-3857-2392

E-mail: salamatov@imp.uran.ru

Alina E. Kostina — Postgraduate Student, Junior Research Scientist, IMP UB RAS.

E-mail: alina 30 93@mail.ru

Aleksey Yu. Volkov – Dr. Sci. (Eng.), Head of the laboratory, IMP UB RAS.

https://orcid.org/0000-0002-0636-6623

E-mail: volkov@imp.uran.ru

Информация об авторах

Оксана Сергеевна Новикова — к.ф.-м.н., ст. науч. сотрудник Института физики металлов им. М.Н. Михеева (ИФМ) УрО РАН.

https://orcid.org/0000-0003-0474-8991

E-mail: novikova@imp.uran.ru

Юрий Александрович Саламатов — к.ф.-м.н., ст. науч. сотрудник ИФМ УрО РАН.

https://orcid.org/0000-0002-3857-2392

E-mail: salamatov@imp.uran.ru

Алина Евгеньевна Костина — аспирант, мл. науч. сотрудник И Φ М УрО РАН.

E-mail: alina 30 93@mail.ru

Алексей Юрьевич Волков — д.т.н., заведующий лабораторией ИФМ УрО РАН.

https://orcid.org/0000-0002-0636-6623

E-mail: volkov@imp.uran.ru

Contribution of the authors

O.S. Novikova – conceptualization, methodology, participation in SEM studies, resistometry, manuscript writing.

Yu.A. Salamatov – processing of *X*-ray diffraction data, discussion of results.

A.E. Kostina – sample preparation, microhardness measurements, mechanical tensile testing, discussion of results.

A.Yu. Volkov – supervision, validation, review, and editing of the manuscript.

Вклад авторов

О.С. Новикова — концептуализация, методология, участие в СЭМ-исследовании, резистометрия, написание статьи.

Ю.А. Саламатов — обработка данных рентгеноструктурного анализа, обсуждение результатов

А.Е. Костина — подготовка образцов, измерение микротвердости, проведение механических испытаний на растяжение, обсуждение результатов.

А.Ю. Волков — курирование, проверка, анализ и редактирование статьи.

The article was submitted 25.12.2023, revised 22.03.2024, accepted for publication 25.03.2024
Статья поступила в редакцию 25.12.2023, доработана 22.03.2024, подписана в печать 25.03.2024