

Formation of the $L1_2$ -type superstructure in Cu-5.9 at.%Pd and Cu-8 at.%Pd alloys

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Abstract. There was performed a resistometric study of the Cu-8 at.%Pd alloy during heating and cooling with a constant rate. There was made a comparison with the change in the electrical properties of the Cu-5.9 at.%Pd alloy. In the investigated Cu-Pd alloys, the anomalous behavior of electrical properties was revealed: long low-temperature annealing increased the electrical resistivity. It was concluded that nuclei of the ordered $L1_2$ phase were formed in the Cu-5.9 at.% Pd alloy. The obtained result is in contradiction with the currently known Cu-Pd phase diagram, where the Cu-5.9Pd alloy is the fcc-solid solution. The critical temperatures of the order→disorder phase transformation in the alloys were determined.

1. Introduction

Dilute Cu-Pd alloys have a great potential as corrosion-resistant conductors of electric current. However, their structure and properties are far from being sufficiently investigated. For example, abnormal annealing hardening was detected in the Cu-7 at.%Pd alloy [1]. The enhancement of the conductor strength is an important practical task. Therefore, it is of interest to understand the nature of the revealed phenomenon.

According to the phase diagram of Cu-Pd system [2], the content of palladium in the alloy should exceed 7.5 at% for the formation of the $L1_2$ superstructure. This means that a single-phase solid solution is formed in the alloy Cu-7 at.%Pd. Therefore, it is difficult to understand the reason for the increase in microhardness during annealing of the alloy. Nevertheless, several theoretical studies [3, 4] have recently shown that an ordered $L1_2$ -phase can be formed in the Cu-5 at.% Pd alloy. The results of theoretical calculations [3, 4] and experimental data [1] are matching each other well. Indeed, the formation of nuclei of a new phase will lead to a significant increase in strength of the material in the course of annealing.

The purpose of this work was to clarify the temperature boundary of the order↔disorder ($L1_2$ ↔A1) phase transformation in copper-palladium alloys with low palladium content.

2. Materials and methods

Cu-5.9 at.%Pd and Cu-8.0 at.%Pd alloys were prepared by melting Cu and Pd of 99.99% purity. For the sake of simplicity, the alloys were designated as Cu-5.9Pt and Cu-8Pd, respectively. Pure Cu was also melted and used as a reference material.

The selection of alloys was due to the following considerations. According to [2], the Cu-8Pd alloy is ordered with type $L1_2$ but the temperature of order-disorder transformation was not established. Before conducting our study, it was not known whether the ordered $L1_2$ phase was formed in the Cu-5.9Pd alloy and at what temperature this occurred.



Although the electrical resistivity of many superlattice alloys decreases with increasing degree of atomic order [5], in the Cu_3Pd alloy, the value of the electrical resistivity just below the order-disorder transition temperature (T_c) becomes higher than just above T_c [6]. This is ascribed to the fact that the temperature coefficient of electrical resistivity in the order state is larger than that in the disorder state. Therefore, the resistometric method of investigation was chosen as the main one in this work. We used resistometric measurements of the Cu-8Pd alloy to compare the results with the electrical properties of the Cu-5.9Pd alloy.

Ingots with a diameter of 5 mm were homogenized at 800 °C for 3 hours and then drawn to obtain thin wires with a diameter of 0.22 mm. Thus, drawing played the role of severe plastic deformation (SPD). Deformed wires were annealed at 700 °C for 1 hour followed by quenching in water. The following long low-temperature heat treatments were applied to form the nuclei of the ordered phase in the alloys. For the Cu-8Pd alloy, the heat treatment included multiple anneals in the temperature range of 200-300 °C followed by slow cooling to room temperature. The total heat treatment time was 3.5 months. Long-term low-temperature heat treatment of the Cu-5.9Pd alloy included annealing at 200 °C for 2 months.

Measurements of electrical resistivity were used as the principal method of investigation. This method was selected because it is known that the electrical resistivity of dilute Cu-Pd alloys changes noticeably during the disorder-order phase transformation [1, 6]. The electrical resistivity of thin wires was measured by the four-point method during heating and cooling in the temperature range of 20-550 °C under a low pressure of about 1×10^{-3} Pa. The rate of heating and cooling during the resistometric measurements was 120 °C/h. The electric current passing through the specimen was 20 mA.

3. Results and discussion

As has been established earlier [5,7], the rate of the ordering in the Cu-Pd system after SPD is higher than after SPD, followed by annealing and quenching. Therefore, at first we investigated the samples in two structural states: (1) after SPD and (2) after SPD, followed by annealing at 700 °C and subsequent water quenching. However, we had great difficulties in separating the effects of recrystallization and disordering on the electrical resistivity. Therefore, this paper deals only with the results obtained for the quenched samples.

The temperature dependence of the electrical resistance of the quenched Cu-8Pd alloy is shown in figure 1a.

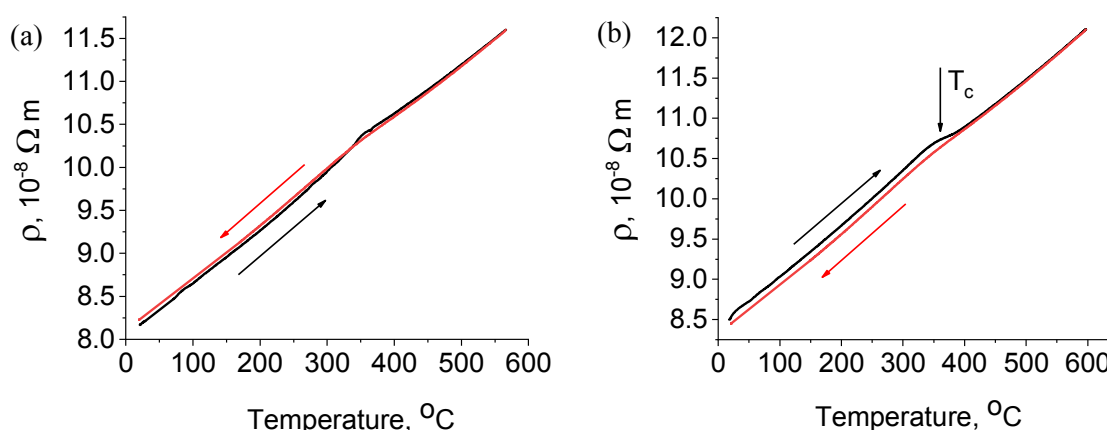


Figure 1. Temperature dependences of the electrical resistivity of the Cu-8Pd alloy: the initial quenched state (a) and the state after long-term low-temperature heat treatment (b).

The temperature dependence of the electrical resistivity of the Cu-8Pd alloy within the range from 300 to 400 °C has a nonlinear form. It is seen that the rate of the electrical resistivity change increases

in temperature range from 300 to 350 °C, but further it decreases between 350 and 400 °C. With further heating, the temperature dependence of the electrical resistivity becomes linear. It should be noted that after the heating-cooling cycle, the electrical resistivity of the alloy under investigation slightly increased at room temperature. This is in full compliance with the results of work [6]. Indeed, in the course of slow cooling from a temperature above T_c , the $L1_2$ -superstructure is formed in this alloy, which increases the electrical resistivity. As a result, after cooling to room temperature, the electrical resistivity of the alloy becomes higher.

The quenched samples of the Cu-8Pd alloy were subjected to the long-term low-temperature heat treatment to obtain a two-phase state with a maximum volume fraction of the ordered $L1_2$ -phase. We were guided by the following considerations when selecting the heat treatment conditions. As is known, diagrams of temperature-time-transformation of diffusion controlled reactions have a C-shaped form [8]. Thus, there is some optimal temperature at which the rate of formation of a new phase is maximal. Above this temperature, the rate of nuclei formation of the ordered phase will be slower. Below the optimal temperature, the rate of the nuclei formation of the ordered phase will be reduced due to lower diffusivity.

Based on the phase diagram of the Cu-Pd system [2], we assumed that the temperature of the phase order-disorder transformation in the Cu-8Pd alloy lies in the range from 350 to 400 °C. Therefore, we used the following heat treatment conditions. First, the quenched samples of the alloy were annealed at the temperature of 300 °C for 1 month, then cooled to the temperature of 250 °C and annealed for 1 month. Then, the temperature was lowered to 200 °C and the samples were annealed again for 1 month. After that, the alloy was cooled to room temperature at a rate of 50 °C/week. The total heat treatment time was 3.5 months. As shown by a TEM study [7], after such a long treatment, fine grains with an ordered $L1_2$ phase were found in the disordered matrix of the Cu-8Pd alloy.

Figure 1b shows the temperature dependence of the electrical resistivity of the Cu-8Pd alloy after long-term low-temperature annealing. It is seen that the electrical resistivity of the alloy has increased as compared with the initial quenched state (figure 1 a, b). This is explained by the formation of some volume of the ordered $L1_2$ phase in the alloy. The greatest interest in figure 1 b is the presence of a kind of “step” on the graph during heating. The end point of this “step” and the transition of the graph to a linear dependence is sufficiently accurate to indicate the temperature of the order-disorder phase transition (T_c). It was reliably established earlier by various methods in the study of Cu-Pd alloys containing from 12 to 18 at.% of palladium [6]. Thus, the critical temperature of the order-disorder phase transition in the Cu-8Pd alloy is $T_c \approx 380$ °C (figure 1b).

We also attempted to elucidate whether the ordered $L1_2$ phase can be formed in the Cu-5.9Pd alloy. Note that most investigators believe that this alloy is a single-phase fcc-solid solution [2, 6, 9]. The possibility of atomic ordering with the formation of the $L1_2$ phase is discussed only in [3, 4] by the results of computer simulation. In addition, in our previous study [10] there were noted anomalies of electrical properties, which were explained by the formation of nanosize nuclei of the new phase.

Figure 2 a shows the temperature dependence of the electrical resistance of the quenched Cu-5.9Pd alloy. It is seen that the graph in figure 2 a differs from the temperature dependence of the quenched alloy Cu-8Pd (figure 1a). Moreover, based on this result, it is very difficult to make an unambiguous conclusion whether the ordered phase can be formed in the Cu-5.9Pd alloy.

To verify the possibility of ordering in the Cu-5.9Pd alloy, we also used a long low-temperature annealing. We assumed that the temperature of the phase order-disorder transformation of this alloy is about 300 °C. Therefore, the annealing of the alloy was carried out at a temperature of 200 °C for two months. Figure 2 b shows the temperature dependence of the electrical resistivity of this alloy in the obtained structural state. In general, the temperature dependences obtained for the Cu-8Pd and Cu-5.9Pd alloys after long-term low-temperature heat treatment are very similar (figures 1 b and 2 b). Thus, the critical temperature of the order-disorder phase transformation in the Cu-5.9Pd alloy is $T_c \approx 350$ °C.

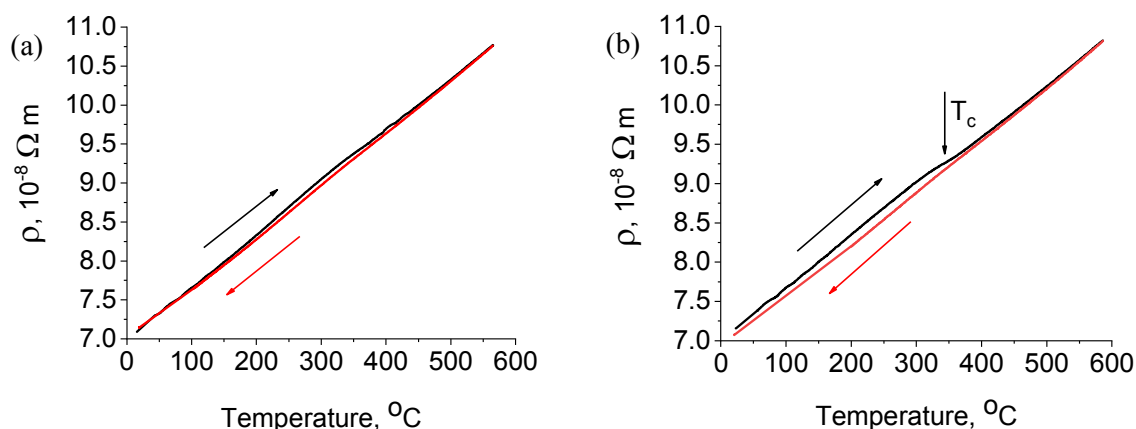


Figure 2. Temperature dependences of the electrical resistivity of the Cu-5.9Pd alloy: the initial quenched state (a) and the state after long-term low-temperature annealing (b).

4. Conclusions

- 1) The temperatures of the order→disorder phase transformation (T_c) in the Cu-8Pd and Cu-5.9Pd alloys were found to be $T_c \approx 380$ °C and $T_c \approx 350$ °C, respectively.
- 2) The results of first-principle calculations of the $L1_2$ phase stability in binary Cu-Pd alloys obtained in refs. [3, 4] were experimentally confirmed.
- 3) Addressing to the abnormal annealing hardening in the quenched Cu-7Pd alloy [1], one can conclude that this was caused by the formation of nuclei of the ordered $L1_2$ -phase.

Acknowledgments

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References

- [1] Marcovic I, Ivanov S, Stamenkovic U, Todorovic R and Kostov A 2018 *J. Alloys Comp.* **768** 944
- [2] Subramanian P R and Laughlin D E 1991 *J. Phase Equil.* **12** 231
- [3] Li M, Guo C and Li C 2008 *Comp. Coupl. Phase Diagr. Thermochem.* **32** 439
- [4] Freudenberger J, Kauffmann A, Klaub H, Marr T, Nenkov K, Subramanya Sarma V and Schultz L 2010 *Acta Mater.* **58** 2324
- [5] Volkov A Yu 2004 *Platinum Metals Rev.* **48** 3
- [6] Mitsui K 2001 *Phil. Mag. B* **81** 433
- [7] Volkov A Yu, Kostina A E, Volkova E G, Novikova O S and Antonov B D 2017 *Phys. Metals Metallogr.* **118** 1236
- [8] Christian J W 2002 *The Theory of Transformations in Metals and Alloys* parts I and II 3ed (Pergamon) p 1200
- [9] Huang P, Menon S, de Fontaine D 1991 *J. Phase Equil.* **12** 3
- [10] Volkov A Yu, Novikova O S, Kostina A E and Antonov B D 2016 *Phys. Metals Metallogr.* **117** 945