Electron irradiation of palladium-copper alloy

S V Simakov, A A Ashmarin, N A Vinogradova, O N Nikitushkina
Baikov Institute of Metallurgy and Materials Science, 49 Leninskiy prospect, Moscow

Abstract. The process of high-energy electron irradiation of the Cu – 40 Pd alloy in air under 350 °C is considered. After irradiation, a layer of copper oxide CuO was formed on the alloy surface, which under normal thermal conditions forms at the temperature of 400 – 500 °С. Reflections of the ordered β-phase disappeared in the surface layer. The elemental composition of the alloy changed along the distance from irradiated surface of the metal. Phases with low degree of long-range order and an increased palladium content formed. The presence of these phases is caused by selective oxidation of copper.

E-mail: simakov-sv@mail.ru

1. Introduction
Palladium alloys have long been considered as functional materials for various applications in electrical engineering, as catalysts, etc. [1]. Among these alloys is the alloy of the Pd-Cu system. It was shown, for example, that this alloy can be used to develop a low-resistance resistive alloy, with high strength and plastic properties. The study of the palladium – copper alloy [2] - showed that on the phase diagram there are areas of solid solution decomposition with the formation of ordered phases. Above the temperature of 600 °C, according to the phase diagram, there is a continuous series of Pd – Cu solid solutions with an FCC lattice. The dependence of the lattice parameter on the Pd content is additive. Phase transition occurs for the Cu – 40 Pd alloy at the temperature below ~ 600 °C. During the decomposition of a solid solution with FCC structure and the lattice parameter of the order of 0.37 nm, an ordered phase forms with a BCC structure of the CsCl type and the lattice parameter of the order of 0.296 nm.

The diffusion transition will occur at temperatures below the existence curve of the disordered FCC phase, or the FCC – BCC transition. According to [2], the maximum temperature for the existence of the BCC phase for the composition with 40 at% Pd is 598 °C. With the decrease and increase in the concentration of Pd, the transition temperatures will decrease. Together with the decrease in temperature, the difference in the free energies of the two phases increases, however the diffusion mobility for the realization of the phase transition also decreases. In [3], C-shaped temperature – conversion curves for the FCC – BCC transition were constructed and optimal temperatures were estimated for which there is a maximum gradient in the free energies of the two phases and, at the same time, there is sufficient diffusion mobility. The stability of the FCC phase will decrease with decreasing temperature and an increase in supercooling, however the diffusion process will slow down. According to these data, the optimal annealing temperatures for the quenched FCC phase, at which the FCC – BCC conversion time is minimal, were 400 – 450 °C.

In a number of works, for example [4], a deformation mechanism was used to stimulate the phase transformation process. Thus, in [5] it was shown that an increase in the degree of deformation leads to a decrease in the ordering temperatures to 300 and even 200 °C.
The processes of accelerating phase transformations, decomposition of dilute and supersaturated solid solutions were studied under the influence of radiation [6]. In this regard, it is of interest to study the possible processes of phase transformations in alloys of the palladium-copper system under high-energy irradiation.

The aim of this work is to study the effect of irradiation with high-energy electrons on structural-phase changes in the alloy of the Cu – 40 Pd system.

2. Methods and materials
The Cu – 40 Pd alloy was used as the object of the study. This composition corresponds to the region on the phase diagram with the maximum temperature, where the decomposition of the solid FCC solution and the formation of the BCC phase can occur. The sample was a 0.8 mm thick foil disk with a diameter of approximately 12 mm. Before irradiation, the sample was annealed at 950 °C in a vacuum during 1.5 h. The sample was mounted on a copper substrate cooled by water. The sample was heated by an electron beam, and the excess heat was removed by a copper substrate. Irradiation was carried out in air under temperature 350 ± 20 °C, which was controlled by a thermocouple. The sample was irradiated on U-10 type electron accelerator. The electron energy was 1.8 MeV, the electron beam current — 180 – 200 μA, and the distance to the sample was ~ 10 cm. For these geometric parameters, the sample was completely covered by an electron beam. The irradiation intensity was ~ 1.2·10^{15} \text{cm}^{-2}\text{s}^{-1}, and the maximum accumulated radiation dose was 3·10^{19} \text{cm}^{-2}.

X-ray phase analysis was performed on a Shimadzu XRD-6000 vertical 2θ -θ X-ray diffractometer at room temperature, normal atmospheric pressure, and humidity in monochromatized copper radiation with the wavelength of λ_{Kαav} = 1.54184 Å. Phases were identified by ICDD PDF-2 2004 data base.

3. Results and discussion
As a result of irradiation of the alloy sample by the above method, it is found that the color of the sample changed from ordinary metal to black. This result is associated with the oxidation processes that occurred on the surface of the alloy.

The examination of the surface of the sample after irradiation by X-ray diffraction showed the presence of black copper oxide CuO reflexes in the diffractogram. Under ordinary thermal conditions, this oxide is formed at temperatures of 400 – 500 °C. Although the irradiation temperature was 350 °C, this result can be explained by the processes of radiation acceleration of diffusion processes equivalent to the actual increase in temperature.

![Figure 1. Diffraction patterns before and after irradiation.](image)

After irradiation, the β-phase reflexes, i.e., the BCC structure of CuPd, were absent on the diffractogram. In addition to the initial FCC phase with narrow reflexes, satellites with wide reflexes appeared, i.e., a low degree of long-range order, with the lattice parameter of 3.819 Å, instead of 3.752 Å of the FCC phase lattice before irradiation.
A cross-section sample is cut from the irradiated sample, on which further studies of the microstructure of metal from irradiated surface to volume are carried out. On the surface area from the irradiation side, there is black copper oxide CuO. Behind it, at the depth of less than 1 μm, a dark gray sublayer with a metallic sheen is observed. The diffraction patterns showed traces of, presumably, palladium oxide. All phases of the sublayer are characterized by a lower degree of long-range order. It can be assumed that in this sublayer there is more palladium oxide.

After that, an analysis of the structure and composition are made in the volume of the alloy at various depths from the surface. Figure 2 shows the image of the cross-section of the sample.

![Figure 2. The structure of the Cu - 40 Pd alloy.](image)

Below is a dark gray sublayer with palladium oxide, after which there is a metal matrix. The analysis of the composition at five points, at different distances from the oxide – Cu-Pd alloy interface, showed that the concentration of the components changes with the distance from the irradiated surface.

| Расстояние, нм | О ат% | Pd ат% | Cu ат% |
|---------------|-------|--------|--------|
| 130           | 13    | 37     | 47.5   |
| 390           | 10    | 38     | 48.7   |
| 565           | 9     | 38     | 51     |
| 1150          | 6     | 40     | 53     |
| 1500          | -     | 43     | 56     |

From the results of this analysis, it follows that in the surface layer the concentration of Pd and especially Cu decreased and at the same time a significant oxygen content appeared. At the depth of 1500 nm, the oxygen concentration decreased to zero, and the metal content almost returned to its original content in the alloy before irradiation.

A similar result is due to the oxidation of metals and, especially, selective oxidation of copper. According to this dependence, the formed phase with a low degree of long-range order corresponds to the existence of a number of solid solutions with a high palladium content. The presence of these phases is caused by selective oxidation of copper.

Thus, after irradiation, the following changes in the structure of the alloy occurred. Copper oxide CuO was formed on the surface, the β phase disappeared, part of the FCC phase remained unchanged, and the FCC phase with an increased Pd content appeared.

The results showed that irradiation of Pd – Cu alloy with high-energy electrons leads to the change of initial composition of the alloy components at the distance about ~ 1500 nm from the surface. The oxidation processes, mainly selective oxidation of copper, became the dominant influence factor of irradiation. As a result of this, in comparison with the initial composition, a structure with an increased
Pd content was formed in the irradiated volume, i.e., the alloy composition shifted along the phase diagram. This occurred due to the release of some copper atoms from the solid solution to the surface with the formation of CuO oxide.

For further studies of the effect of high-energy irradiation on structural-phase changes in the Pd – Cu alloy, it is necessary to exclude the influence of oxygen during radiation exposure.

4. Conclusion
1. Experiments on high-energy electron irradiation in air of the Cu – 40 Pd alloy under 350 °C is carried out.
2. As a result of irradiation an oxide layer of copper CuO is formed on the alloy surface, as well as palladium oxides in the surface layer.
3. It is shown that at the depth of penetration of the electron beam, selective oxidation of copper resulted in the change in the chemical composition of the alloy with an increase in the concentration of Pd. So the main effect of irradiation in this conditions was process of oxidation.

Acknowledgement
This research was provided in the frame of the state task no. № 075-00746-19-00.

Reference
[1] Savitsky Ye M, Polyakova V P, Tylkina M A 1967 Palladium alloys (Moscow Nauka Publ) p 215 (in Russ)
[2] Subramanian, P.R., Laughlin D.E. Cu-Pd (Copper-Palladium) 1991 Journal of Phase Equilibria 12(2) 231-243
[3] Balina E A, Geld P V, Andreyeva L P, Zelenin L P 1990 Kinetics of the processes of ordering and disordering of Cu-Pd binary alloys Physics of metals and metal science 12 144-148 (in Russ)
[4] Kim M J and Flanagan W F 1967 The effect of plastic deformation on resistivity and Hall effect of copper-palladium and gold-palladium alloys Acta Metallurgica 15 735-745
[5] Antonova O V, Volkov A Yu 2012 Changes of microstructure and electrical resistivity of ordered Cu-40Pd (at.%.) alloy under severe deformation Intermetallics 21 1-9
[6] Ivanov L I, Volkov M G, Platov Yu M et al. 1988 Mechanism of decomposition of Cu-Ni alloy under irradiation Physics and Chemistry of Materials Treatment 1 28 (in Russ)