INFLUENCE OF ALLOYING WITH PALLADIUM ON ANNEAL HARDENING EFFECT OF COPPER ALLOY

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ABSTRACT
This paper reports results of investigations carried out on sintered copper and copper-palladium alloy (with 4at%Pd). The Cu-Pd alloy and pure copper for the sake of comparison were subjected to the same thermomechanical treatment with finally reduction of 25 %, 50 % and 75 %. Annealing up to the recrystallisation temperature was performed, followed by hardness and electrical conductivity measurement. This investigation shows that the hardness and electrical conductivity of cold deformed Cu-Pd alloy increase after annealing in the temperature range of 160-450 °C due to anneal hardening effect. It is shown that the amount of strengthening, caused by anneal hardening effect increase with increasing degrees of finally deformation.

Keywords: copper-palladium, anneal hardening effect, thermomechanical treatment

1. INTRODUCTION
Palladium alloys are important for catalysts, automobile exhaust gas cleaning, thermocouples, electrical contacts, capacitors, permanent magnetic alloys, and for the production of high purity hydrogen [1] because of its high activity and excellent chemical stability. Palladium is expensive so researchers have been focused on decreasing the Pd content. Alloying of less expensive metal with noble metals like palladium is a potential way to achieve this goal [2]. The Cu-Pd system has recently received a lot of attention because of the existence of three particular superstructures (Cu$_3$Pd, 1D-LPS and 2D-LPS) and order–disorder transition between the ordered structures and f.c.c. solution [3].

In some cold deformed copper based solid solutions annealed below the recrystallization temperature, a hardening effect - anneal hardening effect is produced through the interaction of solute atoms with lattice defects. This hardening effect cause a considerably increase of mechanical properties, where solute locking to dislocations has the most important role, although solute segregation to stacking faults has important role [4,5]. Vitek and Warlimont [6] studied anneal hardening effect in copper-based binary systems with Al, Au, Ga, Ni, Pd, Rh and Zn and confirmed the increase of spring bending limit (measure of annealing hardening intensity) in the Cu–Pd system.

The goal of this paper is to study the effect of anneal hardening in the alloy of the Cu–Pd system, and investigation of the alloy properties improvement in the comparison with pure copper.

2. EXPERIMENTAL
Samples of pure copper and Cu-4at.%Pd (Cu–4Pd) alloy were prepared by powder metallurgy technic. Electrolytic copper powder with 99.7 % purity and chemical palladium with 99.9 % purity were used as the starting materials. Green compacts with dimensions: 6-7 mm in height, 30 mm in length and 12 mm in width were prepared by a one-sided pressing with the pressure of 300MPa. Green compacts were sintered at 790 °C in a horizontal tube furnace under an atmosphere of high purity dry hydrogen for 1h. After sintering, the samples were subjected to cold rolling with reduction of 25 %, 50 % and 75 %. Cold rolled samples of pure copper and Cu-4Pd alloy were annealed in the temperature range 160 °C - 600 °C in 30 minutes intervals. Vickers hardness (applying load of 50 N) and electrical
conductivity were measured after each annealing. The results were averaged and reported as a single data set.

3. RESULTS AND DISCUSSION

Fig. 1, fig. 2 and fig. 3 show the dependence of hardness on the annealing temperature of the cold rolled (25%, 50 %, and 75 %, respectively) sintered copper and Cu-4Pd alloy.

![Fig. 1 Dependence of hardness on the annealing temperature of the cold rolled (ε=25%) samples](image1)

![Fig. 2 Dependence of hardness on the annealing temperature of the cold rolled (ε=50%) samples](image2)

![Fig. 3 Dependence of hardness on the annealing temperature of the cold rolled (ε=75%) samples](image3)

When the cold rolled (ε=25%) Cu-4Pd alloy is annealed at some temperature from 160 °C to 300 °C, an increase in hardness is noticed due to anneal hardening effect. Hardness value of cold rolled (ε=25%) Cu-4Pd alloy was 121 HV and it increased to 138 HV after annealing at 260 °C. After annealing at the higher temperature than 350 °C, the hardness values decrease due to recrystallization. The recrystallization temperature for cold rolled (ε=25%) sintered copper is about 250 °C. Hardness of cold rolled (ε=25%) sintered Cu-4Pd alloy achieved the maximum increase on that temperature. For the cold rolled (ε=50%) Cu-4Pd alloy, hardness value increased from 154 HV to 166 HV after annealing at 200 °C. After annealing at the higher temperature than 250 °C, the hardness values decrease due to recrystallization. The maximum hardness increase, caused by the anneal hardening effect was obtained in Cu-4Pd alloy deformed with the highest deformation degree (ε=75%), it was about 26 HV(at temperature 200 °C). The amount of strengthening due to anneal hardening effect, increases with increasing degree of predeformation as result of larger number of defects, more intensive partial dislocations recombination and interactions of solute atoms with lattice defects during the annealing [7,8].
Fig. 4, fig. 5 and fig. 6 show the dependence of electrical conductivity on the annealing temperature of the cold rolled (25%, 50 %, and 75 %, respectively) sintered copper and Cu-4Pd alloy.

It can be seen that the electrical conductivity of all Cu-Pd cold deformed alloys slowly increases with annealing in the temperature range of 160 °C – 300 °C where the anneal hardening effect appears, due to the segregation of the palladium atoms to the lattice defects, which contributed to the solid solution weakening on the alloying element. If the palladium atoms are dissolved into the copper matrix, the copper matrix lattice parameter increases. Thus, as palladium segregation to lattice defects occurs, the copper lattice becomes similar to that of pure copper, and the electrical conductivity increases [9]. During further annealing at higher temperature, electrical conductivity of Cu-Pd alloy increases due to recovery and recrystallisation [10]. The best combination of properties (166 HV, 23.5 MSm⁻¹), was achieved after annealing at 200 °C of cold deformed (ε =50 %) Cu-4Pd alloy. This material can be applied for electrical contacts.

4. CONCLUSION
The study of the anneal hardening effect of cold rolled sintered Cu-4Pd alloy was described using hardness and electrical conductivity measurement. In the annealing temperature range of 160 °C-300 °C, the hardness of cold rolled Cu-4Pd alloy increased due to the anneal hardening effect. The increase in cold rolling results increasing of anneal hardening intensity. In the annealing temperature range, where the anneal hardening effect is observed, the electrical conductivity of Cu-4Pd alloy
increases. The best combination of properties such as hardness of 166 HV, electrical conductivity of 23.5 MSm$^{-1}$, was achieved after annealing at 200°C of cold deformed ($\varepsilon = 50 \%$) Cu-4Pd alloy, this material can be applied for the electrical contacts. The properties of Cu-4at%Pd alloy are significantly improved in comparison with pure copper.

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6. REFERENCES