

# Improvements to the Microstructure and Physical Properties of Pd-Cu-Ag Alloys

## ENHANCEMENT OF THE MECHANICAL AND ELECTRICAL PROPERTIES

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*Ordering and decomposition kinetics of Pd-Cu-Ag alloys having the B2-type superstructure that contain 0 to 30 wt.% silver have been studied. The results of investigations into the microstructure, electrical and mechanical properties are described. Different methods for improving the strength properties of ordered alloys are discussed.*

Ordered Cu-(35–50) at.% Pd alloys (B2-type superstructure) have a high corrosion resistance and are distinguished by possessing very low electrical resistivity  $\rho \approx (4–8) \times 10^{-8}$  ohm m (1), two properties which make them of interest to researchers developing functional materials. However, wide-scale use of these alloys is hindered by their relatively poor strength properties: the yield stress of Cu-40 at.% Pd (Cu-40Pd) alloy in the ordered state is only 400 MPa. While, for example, the ordered Cu-Au alloy ( $L1_0$ -type superstructure), used as electrical contact material, has a yield stress,  $\sigma_{0.2} = 800$  MPa.

Studies aimed at improving the functional properties of these Cu-Pd alloys have been undertaken and have resulted in the development of ternary Cu-Pd-Ni alloys with a nearly zero temperature coefficient of electrical resistivity over a wide temperature interval. Alloys Pd-Cu-Au and Pd-Cu-

Ag have also been developed and are in use; their yield stresses are in the range 900 to 1100 MPa. However the electrical resistivity of the ternary alloys is higher than that of the initial Cu-Pd binary ordered alloy.

This study will deal with possible methods for strengthening Cu-40Pd alloy and will consider changes in its ordering kinetics and its mechanical and electrical properties after alloying with silver. The results obtained may help towards developing methods to improve the mechanical properties of other ordered alloys.

## Materials and Experimental Technique

Various palladium-copper-silver alloys were prepared by vacuum melting palladium (99.98% purity), copper, and silver (99.99% purity), see Table. The alloys were subjected to various

Chemical Composition of the Palladium-Copper-Silver Alloys						
Alloy number	wt.%			at.%		
	Pd	Cu	Ag	Pd	Cu	Ag
1	53.00	47.00	–	40.24	59.76	–
2	50.00	40.00	10.00	39.42	52.80	7.78
3	50.00	35.00	15.00	40.52	47.49	11.99
4	50.00	30.00	20.00	41.68	41.88	16.44
5	50.00	25.00	25.00	42.91	35.93	21.16
6	50.00	20.00	30.00	44.21	29.62	26.17

mechanical and thermal treatments including annealing at 850°C, quenching in water, and deformation to 75%.

The atomic structure of the alloys was observed by field-ion microscopy (FIM) using wire samples of diameter 0.19 mm. The method of sample preparation and specific features of formation and interpretation of the images in an ion projector have been described in, for example, (2).

A standard heating holder was used when the microstructures of the alloys were being observed *in situ* in the column of a JEM-200CX transmission electron microscope. The thickness of the foil examined by transmission electron microscopy (TEM) was typically 0.1 mm.

Phase transformation kinetics were analysed from standard four-probe resistometric measurements performed on wire samples of ~ 150 mm long and 0.19 mm in diameter which were placed in an evacuated quartz tube. The device (that is, the quartz tube containing wire samples with four Cu wires as contacts) was placed in a furnace which was either heated to the assigned temperature at a specific rate or preheated, depending on what was required (3).

The strength properties of wire samples 1.5 mm in diameter and 30 mm long were checked by tensile testing.

## Methods for Strengthening Ordered Binary Systems

Atomic ordering within solid solutions has a huge effect on the physical and strength characteristics of alloys. In some cases atomic ordering is used to produce commercial alloys with a range of optimal properties. However, in-service, plastic deformation may disrupt the long-range atomic ordering, so ways to improve the mechanical properties of ordered alloys are of scientific and practical interest.

Binary alloys, in which planes and directions of dislocation slip become nonequivalent due to ordering (CuAu, CuPt, Ni<sub>2</sub>Cr, Ni<sub>4</sub>W, etc.), may acquire high strength properties, thanks to domain-boundary hardening (4). The main factor used for strengthening such alloys is the rearrangement of dislocations as they cross domain

boundaries, together with the related consumption of additional energy (5). Thus, refinement of the domain structure causes a big increase in the yield stress of ordered alloys. For example, the yield stress of the CuAu alloy can vary between 115 and 800 MPa depending on its domain structure (6).

A special feature of copper-palladium alloys with *B2* superstructure is the absence of domain boundaries. Therefore, only the traditional method of strengthening – grain refinement – can be used. After preliminary plastic deformation and subsequent annealing at 300 to 350°C the Cu-40Pd alloy forms an ordered structure with grains ~ 2 μm in size and yield stress  $\sigma_{0.2} \approx 500$  MPa. The strength properties may be improved a little further if the grains are refined more: by the careful selection of modifying agents.

It has been shown previously that alloys with the *L1<sub>0</sub>* superstructure can acquire an optimal structural state, characterised by high strength and plastic properties (7). This state can be formed by a ‘quick ordering’ of predeformed alloys during annealing over a certain temperature-time interval below  $T_c$  ( $T_c$  is the critical temperature of ordering). In this case, dislocations inherited from the initial deformed state do not have time to redistribute themselves in the superlattice and so they form a kind of a framework.

The possible ‘inheritance’ of this dislocation framework by *B2* superstructures has been discussed earlier, taking Fe-Co-Cr as the example (8). It was shown that recrystallisation was retarded when a predeformed alloy was annealed over the temperature interval of fast ordering (9). This treatment may be able to cause strengthening in other ordered alloys with the *B2* superstructure. In practice the method reduces to short annealings over the temperature interval of the maximum ordering rate. This paper will describe tests of this treatment for enhancing strength properties of Cu-40 at.% Pd alloy.

A kinetic ‘C-curve’ describing the rate of ordering processes in Cu-40Pd alloy was plotted using resistometric measurements on wire samples of the alloy immersed in a salt melt, see Figure 1 (3). The results were used to select temperature-time parameters of annealings for ‘fast ordering alloy’.

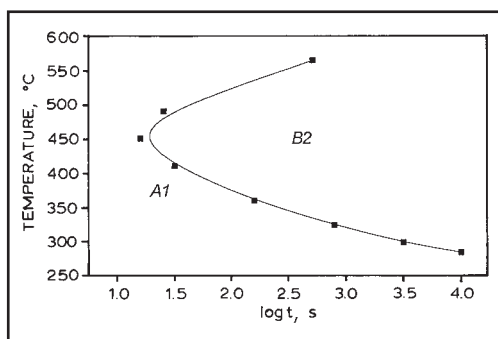


Fig. 1 Kinetic 'C-curve' of the A1→B2 phase transformation in the Cu-40Pd alloy in the initial deformed state (annealings in a salt bath)

Results of mechanical tests on Cu-40Pd alloy pre-deformed to 75% after various treatments are given in Figure 2. Curve 1 corresponds to the initial state of the alloy, that is, after preliminary deformation by drawing to 75%. Curve 4 shows the alloy in the disordered recrystallised state, fixed after annealing at 850°C for 1 hour and subsequent quenching. Curve 3 represents annealing treatment which ends with slowly cooling the sam-

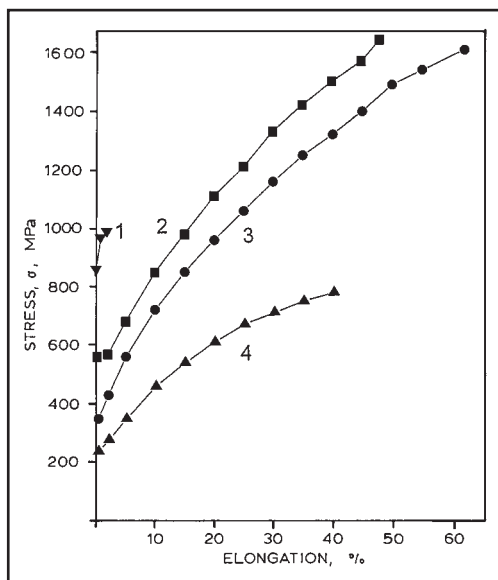


Fig. 2 Stress-strain curves for the Cu-40Pd alloy in different states:  
 1 – 75% deformation (initial state);  
 2 – 850°C, 90 s, quenching (ordered, non-recrystallised);  
 3 – 850°C, 1 h, cooling at 100°C h<sup>-1</sup> (ordered, recrystallised);  
 4 – 850°C, 1 h, quenching (disordered, recrystallised)

ples in the furnace and results in an alloy in a well-ordered recrystallised state. Curve 2 corresponds to a non-recrystallised ordered state. The yield stress of the ordered alloy with non-recrystallised structure (Curve 2) was nearly 250 MPa higher than that of the ordered alloy with recrystallised structure (Curve 3).

From Figure 2 it appears, that we have succeeded in hardening the Cu-40Pd alloy thanks to the dislocation framework inherited from the preliminary plastic deformation. Although the strength properties produced by this method are smaller than analogous values for alloys with L1<sub>0</sub>-type superstructure (7), both types of alloys have high plasticity.

While several methods have been proposed and developed for improving the yield stress of ordered alloys, more work needs to be undertaken to find new approaches to hardening.

## The Effect of Silver on the Structure and Properties of Cu-Pd Alloy

Above we considered possible methods for hardening ordered binary compounds. Their strength properties can be further improved by alloying. For example, the yield stress of silver-loaded Cu-Au alloy rises to 1000–1400 MPa (from 800 MPa) when a silver-rich phase precipitates on thermal antiphase domain boundaries (10).

Silver alloying of Cu-Pd alloys (B2 superstructure) also improves their strength. In this case, Pd-Cu-Ag alloys are of interest as a functional material for a wide range of applications from stomatology (11) to fabrication of musical instruments (12).

## Initial Stages of Ordering and Decomposition in Pd-Cu-Ag Alloys

When alloys of the Pd-Cu-Ag system are annealed at a temperature below the critical ordering temperature,  $T_c$ , long-range atomic order is established and the supersaturated solid solution decomposes (13). The ordering kinetics may be estimated most rapidly from an analysis of the temperature behaviour of the electrical resistivity.

Data of the variation of electrical resistivity with temperature for the alloys given in the Table

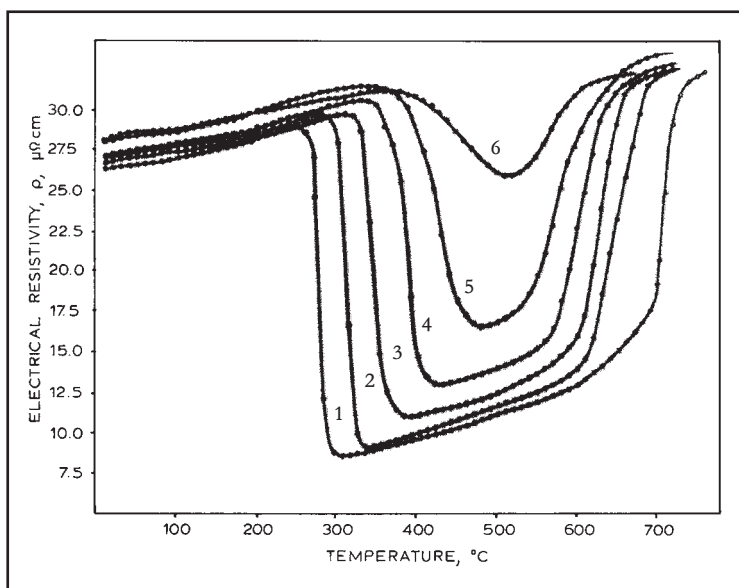


Fig. 3 The temperature dependence of the electrical resistivity of palladium-copper (1) and palladium-copper-silver (2–6) alloys in the initial deformed (75%) state. The heating rate was  $60^{\circ}\text{C h}^{-1}$ . The alloys are marked in accordance with the Table (14)

are shown in Figure 3 (14). These alloys had been deformed to 75% in their initial state. At the beginning of the experiment, electrical resistivity increases a little on heating. However, as temperature continues to increase, ordering within the alloy causes a sharp drop in resistivity. On further heating, the resistivity again increases as the materials become disordered at temperatures above the critical point  $T_c$ . It appears that electrical resistivity is enhanced and the kinetics of phase transformation are decelerated with an increasing percentage of silver in the alloys.

Structural studies are needed to gain a better understanding of the transformations taking place in the alloys. The initial stages of the processes are of special interest and require analysis by a high-resolution method, such as FIM.

The phase transformation investigated by FIM in the Pd-Cu-Ag alloys (see Table), is one that leads to the formation of a PdCu phase with an ordered b.c.c. lattice and to a silver-rich solid solution (AgPd) with an f.c.c. lattice (11). Our studies of the precipitate microstructure during early stages of the phase transformation, performed using layer-by-layer evaporation of surface atoms, have never shown the formation of just a single phase during the decomposition of a ternary solid solution. On every occasion two phases have pre-

cipitated simultaneously and the PdCu phase has always had atomic structure with a high degree of long-range order. The minimum size of particles in both phases was 4–5 nm. As can be seen during evaporation of the atomic layers, the particles had lamellar form.

The progress of ordering and decomposition at later stages may be followed if the alloy foil is heated directly *in situ* in the column of an electron microscope. For this, a Pd-Cu-Ag alloy containing 20 wt. % silver, 'Alloy 4', was used. The boundary between two grains near the edge of the foil was examined, see Figure 4. The test alloy had been initially disordered by quenching after annealing at  $950^{\circ}\text{C}$  for 1 hour. Figure 4(b) shows an electron diffraction pattern for one of the grains in Figure 4(a); it includes satellites near structural reflections (which become more pronounced with the increasing order of the reflection) and splittings in the positions of the superstructural reflections.

The superstructural reflections, divided into pairs in the positions of 100 types and quadruples in the positions of 110 types, have been repeatedly observed in quenched Cu-Pd binary alloys (16), and explained by short-range atomic order. However, it should be emphasised that formation of a structure with short-range order does not lead to the appearance of satellites near structural

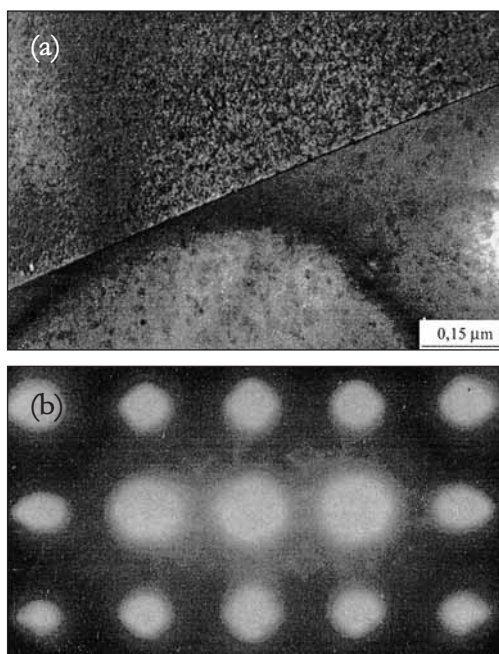


Fig. 4 Initial state of the Pd-Cu-20Ag alloy after annealing at 950°C, 1 h, quenching:  
 (a) microstructure;  
 (b) diffraction pattern of the upper grain

reflections. Such satellites have been observed in a Pd-25Cu-35Ag alloy (at.%) (17) and appeared as a result of a small difference in lattice constants in the two new phases formed from the matrix. Note that the Pd-25Cu-35Ag alloy did not have an ordered state.

Thus, from the electron diffraction pattern in Figure 4(b) it follows that decomposition was already present in the initial state of the alloy. The alloy contained, on the one hand, microregions enriched with and depleted of the precipitation phase and, on the other hand, groups of copper and palladium atoms having a certain number of neighbours of each species in the nearest coordination spheres.

When the Pd-Cu-20Ag sample (of Figure 4) was heated, the atomic ordering and the decomposition reaction were enhanced. Temperatures and 'holding times' for this alloy are given in Figures 5(a)–5(c). The 'holding times' at certain temperatures were to allow the transmission electron microscope screen image to stabilise and clear, as the image moved and became blurred

upon heating the sample. Thermal treatment in the transmission electron microscope column is thus in steps: nearly instantaneous heating to some temperature; a holding period (images and diffraction patterns were taken at the end of the period); heating to the next temperature; another holding period, etc.

The study demonstrated that the silver-enriched

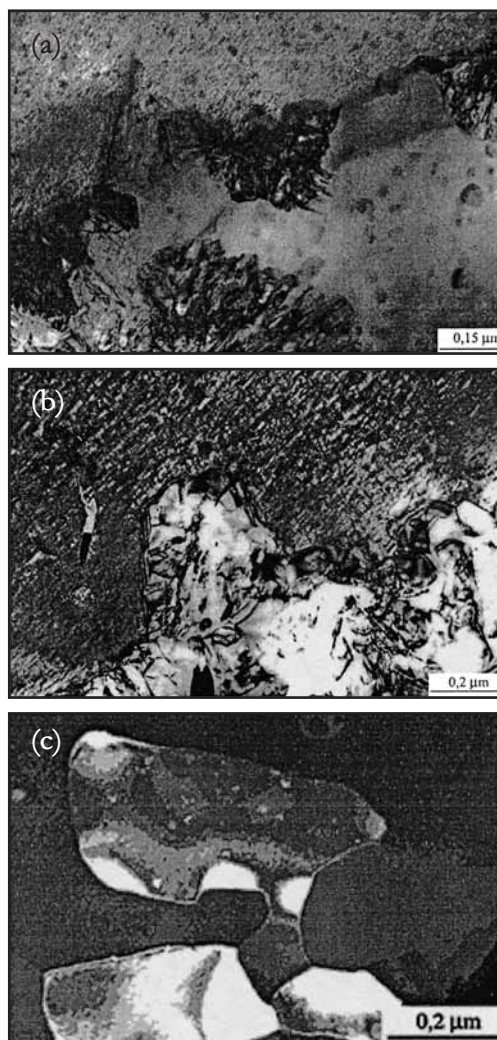


Fig. 5 Evolution of the microstructure shown in Figure 4 during heating:  
 (a) initial state + 250°C, 5 min + 360°C, 15 min + 400°C, 5 min;  
 (b) state (a) + 400°C, 15 min + 440°C, 5 min + 550°C, 15 min;  
 (c) state (a) + heating to 600°C and cooling in the microscope column



phase could precipitate in the given alloy by two mechanisms: continuous and discontinuous (18). The structure of the interface, which was the preferred nucleation site for new phases, changed little at the first stage. Then, at temperatures up to 400°C discontinuous precipitate plates grew in one of the grains (the lower grain in Figure 5(a)). At temperatures from 400 to 500°C signs of the phase precipitation via the continuous mechanism were enhanced in unreacted regions of the matrix: a parallel Moiré pattern appeared in some regions of the upper grain (Figure 5(b)). The Moiré pattern was due to electron beam diffraction on ensembles of mutually parallel planes having similar interplanar spacings in two superimposed crystals. At temperatures above 500°C (but below  $T_c \approx 600^\circ\text{C}$ ) continuously precipitated particles grew smoothly and became coarser. They were located in two mutually perpendicular directions of the  $\langle 100 \rangle$  type of the initial grain. At elevated temperatures changes also took place in the foil bulk, which decomposed via the discontinuous mechanism. An almost complete grain structure can be seen in Figure 5(b) instead of classical colonies of discontinuous precipitates, which are present in Figure 5(a).

Figure 5(c) presents a two-phase structure, which was formed in the test alloy after heating to 600°C and cooling in the transmission electron microscope column. This structure had grains 0.2–0.3  $\mu\text{m}$  in size. The ability to refine such grains may be a useful method to improve the mechanical properties of Pd-Cu-Ag alloys.

### Changes in the Electrical and Mechanical Properties of Pd-Cu-Ag Alloys during Ordering

Turning now from the structural evolution of Pd-Cu-Ag alloys to the electrical and mechanical properties, we are especially interested in the Pd-Cu-10Ag alloy, Alloy 2. This is because its electrical resistivity differs least from that of the initial Cu-40Pd binary alloy (see Figure 3).

Figure 6 shows ordering kinetics for Pd-Cu-10Ag, depending on its initial state (heating rate of  $600^\circ\text{C h}^{-1}$ ). The initial disordered state was produced either by deformation, by drawing to 75%,

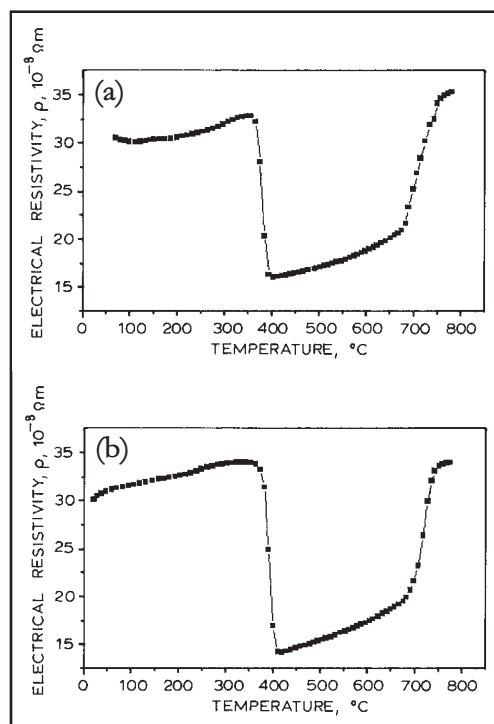


Fig. 6 Temperature dependence of the electrical resistivity of the Pd-Cu-10Ag alloy disordered by different methods (heating rate of  $600^\circ\text{C h}^{-1}$ ): (a) deformation by drawing to 75%; (b) annealing at  $850^\circ\text{C}$ , 1 h, quenching

(Figure 6(a)) or by quenching after an anneal for 1 hour at  $850^\circ\text{C}$  (Figure 6(b)). From the curves it can be seen that the ordering rate in the predeformed alloy is a little larger than in the alloy disordered by quenching from a high temperature. Indeed, the drop in electrical resistivity caused by ordering stopped at  $375^\circ\text{C}$  on heating the deformed material. However, the electrical resistivity of the initial quenched alloy was a minimum at  $420^\circ\text{C}$  under similar treatment.

It is known that establishment of both the long-range order and the decomposition process affects electrical resistivity. The variation in the kinetic characteristics of phase transformations depending on the initial state of the alloy can be better determined if the electrical conductivity is measured at some annealing temperature. Such experiments were performed with the Pd-Cu-10Ag alloy in one of two initial states: after preliminary plastic deformation or after quenching from a high temperature

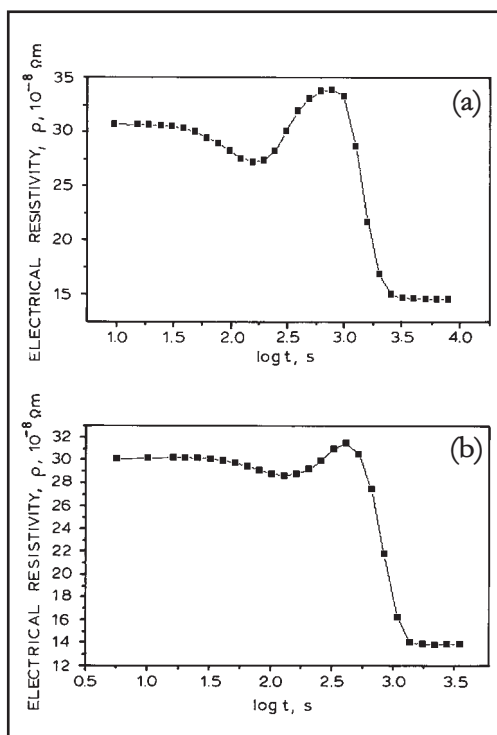


Fig. 7 The electrical resistivity of Pd-Cu-10Ag alloy vs. the annealing time:  
 (a) initial state: 75% deformation, annealing temperature 335°C;  
 (b) initial state: quenching from 850°C, annealing temperature 370°C

(Figure 7). To separate effects due to ordering of the matrix and decomposition of the supersaturated solid solution, and to increase the length of time of this reaction, treatments were performed at the low temperatures of 335°C for predeformed alloys (Figure 7(a)) and 370°C for quenched alloys (Figure 7(b)). Both curves are very similar.

It could be thought that the increase in electrical resistivity at the initial stages of annealing in Figure 7 is due to the appearance of both an ageing phase and short-range atomic ordering. Indeed, the electrical resistivities of binary Pd-W, Pd-Mo, and Pd-Co alloys are known to increase due to short-range atomic ordering. Short-range atomic ordering at initial stages of ordering in Pd-Cu and Pd-Cu-Ag alloys has been observed more than once (11, 16). The electrical resistivity of precipitation-hardened alloys also increases during initial ageing due to the appearance of interfaces

between regions of different concentrations. The biggest effect was observed for local regions of different composition, of about 1 nm in size (20). These findings are very similar to our results: namely that as seen by FIM, the size of nuclei in the ageing-phase was about 4–5 nm.

X-ray diffraction (XRD) was used to confirm our findings of the structural and phase transformations in Pd-Cu-10Ag. After preliminary plastic deformation by drawing to 75% the alloy initially had a disordered f.c.c. structure, which was preserved for some time at the initial stage of annealing at 335°C. About 75% of the alloy had an ordered b.c.c. structure after annealing for 35 minutes. The decomposition process was completed when the alloy was kept in the furnace for longer. Thus, the behaviour of electrical resistivity in Figure 7 clearly correlates with structural changes seen in the XRD data of the alloy. Similar results were obtained for the alloy in the initial quenched state.

Figure 8 shows how the electrical resistivity of the alloy depends on the holding times at different temperatures. The shapes of the curves change with increasing temperature; the increase in resistivity immediately before ordering, which is characteristic of low temperatures (see Figure 7), vanishes. The curves in Figure 8 also suggest that the long-range ordering rate was large and that at temperatures above 400°C the ordering process ended before the sample reached the required temperature. This is seen as a rise in resistivity in the curve 'tails', connected with increases in electrical resistivity on heating the ordered material, showing a resistivity dependence on growing temperature. For example, from the trend of Curve 2 in Figure 8 it follows that at the furnace temperature of 530°C the ordering processes in Pd-Cu-10Ag were complete 4 minutes after the start of heat treatment (that is, the curve drops to a minimum). However, our measurements showed that the sample had a temperature of  $\sim 450^\circ\text{C}$  at that moment and heated to the preset temperature in 7 minutes. In this time interval the resistivity increased in the resistometric curves before they flattened out.

The speed of heating the sample in the vacuum

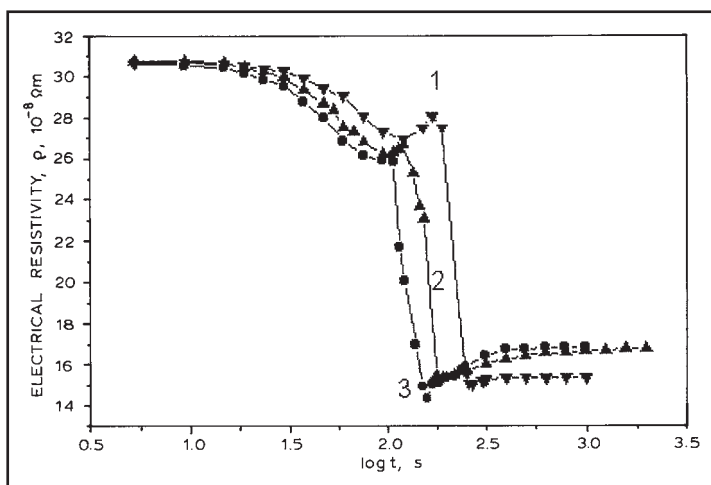


Fig. 8 Electrical resistivity of the initial deformed Pd-Cu-10Ag alloy vs. the annealing time at: 1 450°C, 2 530°C, and 3 570°C

tube is low. We placed our device (at room temperature) into the hot furnace and from that moment the temperature of the sample increased and phase transformation started. The phase transformations finished before the sample reached the required temperature. For this reason Curve 2 in Figure 8 again shows an increase in resistivity between 4 and 7 minutes. The plateau for the Curves in Figure 8 appears only after this maximum. Analogous effects connected with a high ordering rate have been detected earlier in Cu-40Pd (6). In order to avoid such effects it is necessary to accelerate the heating of the sample. For example, we used immersion of the sample in the salt melt for drawing the kinetic 'C-curve' in Figure 1.

Further experiments were performed to examine transformations in deformed Pd-Cu-10Ag alloy at even higher temperatures. The electrical resistivity again dropped after the start of the experiment, including the case when the alloy was placed in a furnace heated to 850°C. It was not thought earlier that a disordered material placed in a furnace at 250°C higher than  $T_c$ , had time to become ordered during heating. Moreover, at temperatures just a little higher than  $T_c$  the  $B2 \rightarrow A1$  transformation rate was small: only partial ordering took place at 630°C after a 3-hour anneal.

The relationship between changes in electrical resistivity during heat treatment and the formation of mechanical properties was also investigated. To

this end, the samples underwent mechanical tests in the states when the electrical resistivity curves (Figure 7) included singularities (the minima and maxima on curves  $\rho(t)$  and points where  $d\rho/d(t) = 0$ ).

Mechanical and electrical properties usually depend on different structural features of alloys (21). For example, recrystallisation has little effect on electrical resistivity, but causes considerable loss in their strength properties and the growth of plasticity. Ordering will probably not affect mechanical properties, but will lead to a considerable change in electrical resistivity. Figure 3 shows that the electrical resistivity dropped by nearly 3 times. Actually, only small local regions of different concentration may both change the mechanical properties and cause an increase in electrical resistivity.

Figure 9 shows the dependence of: (a) yield stress,  $\sigma_{0.2}$ , and (b) plasticity,  $\delta$ , on the annealing time at 335°C for the initial deformed state and at 370°C for the quenched recrystallised state. The mechanical properties of the alloy in the two states changed in completely different ways with annealing time, although their resistivity curves (Figure 7) are similar. When the alloy in the initial deformed state (Curves 1 in Figure 9) was annealed, the yield stress depended little on the heat treatment time: it increased slightly and then dropped at the holding times of 1 and 3 hours (Figure 9(a)). Plasticity increased from 2 to 4% (Figure 9(b)). When the



quenched alloy was annealed for a short time (3 and 7 minutes), the yield stress increased slightly, while plasticity was preserved at a high level (45%). The quenched alloy embrittled sharply (to 0% elongation) on longer heat treatment.

Obviously, the main processes responsible for the deformation behaviour took place during ordering. This is seen by comparing the results of Figure 7 with the mechanical test data in Figure 9. In Figure 9(b), over the time for alloy ordering Curve 1 rises while Curve 2 descends steeply. This again confirmed that the behaviour of the electrical resistivity cannot clearly show the structural changes in the alloy. Indeed, the resistivity curves in Figures 7(a) and 7(b) are similar, but there are different mechanical properties.

Thus, further experiments are needed to improve the plastic properties in the ordered state of the initial deformed Pd-Cu-10Ag alloy. Results of mechanical tests on Pd-Cu-10Ag alloy are given in Figure 10. Curves 1 and 5 show the mechanical properties of the alloy in states: plastic deformation to 75% (Curve 1) and the recrystallised disordered state produced by quenching from 850°C (Curve 5). Curve 4 is given for comparison and shows the variation in mechanical properties when a well-ordered recrystallised state is formed. Curve 2 reproduces one of the results in Figure 6 and describes properties of the initial deformed alloy after annealing at 335°C for 35 minutes.

Curve 3 shows the mechanical properties for alloy annealed at 570°C for 1 hour after a prelimi-

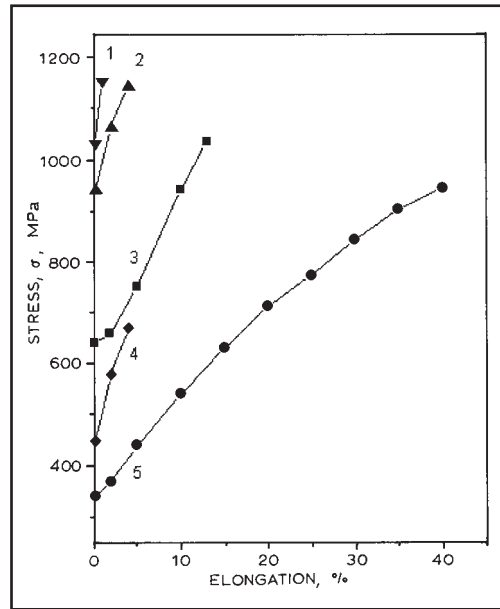


Fig. 10 Stress-strain curves for the Pd-Cu-10Ag alloy after different treatments:

- 1 75% deformation (initial deformed state);
- 2 335°C, 35 min, quenching;
- 3 570°C, 1 h, cooling in furnace;
- 4 850°C, 1 h, cooling in furnace;
- 5 850°C, 1 h, quenching (initial quenched state)

nary plastic deformation by drawing to 75%. The alloy became ordered and its plasticity was 12%, which is the highest value among the samples in Figure 10 in which transformation occurred. When this alloy was stretched, the yield stress was followed by a very long plateau and, consequently, Curve 3 has a slightly different trend. All tests of

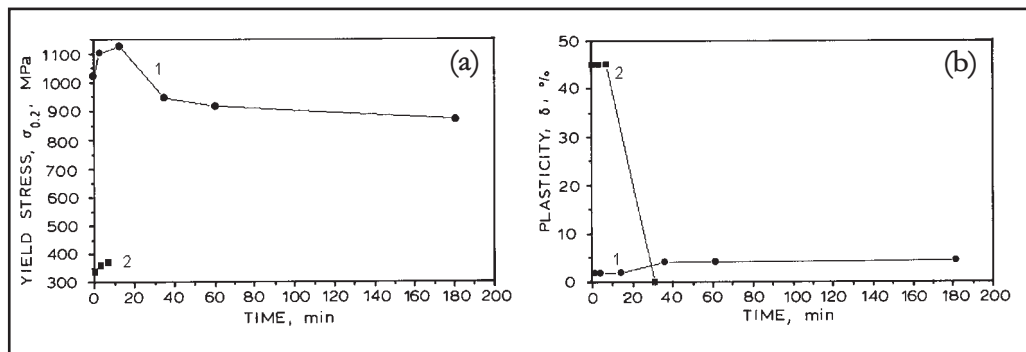


Fig. 9(a) The yield stress and (b) plasticity of the Pd-Cu-10Ag alloy:  
 1 initial state: 75% deformation, annealing temperature of 335°C;  
 2 initial state: quenching from 850°C, annealing temperature of 370°C

the alloy samples in the initial quenched state were a failure as ordering caused total embrittlement of the material.

## Conclusions

Using this data, it is possible to solve the problem of enhancing the strength properties of ordered alloys in the copper-palladium system. One possible variant was discussed at the beginning of this paper; it involves heating the initially quenched Pd-Cu-Ag alloy (containing 20–25 wt.% Ag) to 600°C and subsequent cooling. The two-phase fine-grain structure formed may have a combination of relatively high strength and plastic characteristics.

Another method for strengthening Pd-Cu-Ag alloys containing less than 10 wt.% Ag involves solving the same task considered earlier in (7). Strength properties can be largely improved if an appropriate reinforcing framework is chosen for the plastic matrix. This means the dislocation framework inherited from the preliminary plastic deformation and which is 'built into' the ordered matrix. Fine particles of the silver-based phase, formed on the framework dislocations, considerably improve the strength properties of the alloy.

## Acknowledgement

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## Luminescent Osmium(II) Carbonyls

Osmium (Os) atoms are highly effective in promoting spin-orbit interactions due to their heavy molecular weight and could thus make efficient phosphorescent materials.

Researchers from Taiwan have now prepared a new series of octahedral Os(II) carbonyl complexes [Os(CO)<sub>3</sub>X(dbm)] (X = CF<sub>3</sub>CO<sub>2</sub>, Cl, Br, I, SCN; dbmH = dibenzoylmethane) by using both solid-state pyrolysis and ligand exchange reactions (Y.-L. Chen, C. Sinha, I.-C. Chen, K.-L. Liu, Y. Chi, J.-K. Yu, P.-T. Chou and T.-H. Lu, *Chem. Commun.*, 2003, (24), 3046–3047). The skeletal arrangement consists of one β-diketonate chromophore (dmb)H to balance the +2 formal charge on the Os, one anionic ligand X and three orthogonal CO ligands located at the octahedral coordination site.

At room temperature, in CH<sub>2</sub>Cl<sub>2</sub>, the Os complexes exhibit prominent <sup>3</sup>π-π\* phosphorescence, with unusually long lifetimes (29–64 μs) and high quantum yields (0.08–0.13). These complexes have excellent photophysical and electrochemical properties, and may be employed in a variety of photochemical applications, such as organic light emitting diodes or photovoltaic devices.