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Determining Temperature Boundary of the *A1→(A1+B2)* Phase Transformation in the Copper-55 at% Palladium Alloy Subjected to Severe Plastic Deformation

Higher temperature of phase transformation found for Cu-55 at% Pd alloy

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The changes in phase state, electrical properties and microhardness of copper-55 at% palladium alloy samples with different initial states (as-quenched and deformed *via* severe plastic deformation (SPD)) were studied during isothermal annealing. Ordered *B2*-phase formation in the disordered (*A1*) matrix was found to occur at a significantly higher temperature than is indicated in the generally accepted phase diagram of the Cu-Pd system. Corresponding electrical resistivity is also lower than reported elsewhere for alloys of similar compositions, at $\rho = (27.67 \pm 0.04) \times 10^{-8}$ Ωm, making this the lowest resistivity yet reported for a Cu-Pd alloy with 55 at% Pd.

Introduction

The physico-mechanical properties of Cu-Pd alloys vary significantly during atomic ordering (for example, resistivity is reduced, mechanical properties and corrosion resistance are improved). These alloys have long been used in dentistry, instrument making and jewellery.

There have been few studies on the kinetics of phase transformation in Cu-Pd alloys with Pd content higher than 50 at%. For instance, only three articles concerning alloys with a Pd content higher than 50 at% were mentioned in the most recent review on the Cu-Pd system (1). One of the reasons for this is the low transformation rate: it is mentioned (2) that only a 20% volume fraction of the ordered *B2* phase was observed in the Cu-55 at% Pd alloy after four months of continuous annealing with very slow cooling from 500ºC to 250ºC. For the same reason, the temperature of the start of the formation of the two-phase state in a disordered matrix, i.e., the boundary of *A1→(A1+B2)* transformation in the phase diagram (**Figure 1**), remains undetermined in this alloy. To the knowledge of the present authors, no more relevant literature data is available at the time of writing.

However, a study of Cu-Pd alloys with enhanced Pd content is both of scientific and practical interest: new perspectives in the use of these alloys in the capacity of exhaust gas catalytic converters and membrane materials for hydrogen separation from gas mixtures have recently been disclosed (3).

Earlier, it has been established that preliminary SPD leads to substantially accelerated kinetics of the *A1→B2* phase transformation in an equiatomic Cu-Pd alloy, which significantly reduced the formation time of an equilibrium state in this alloy (4). The aim of the present work is to study the phase composition of Cu-55 at% Pd (hereinafter Cu-55Pd) alloy samples in the course of isothermal annealing after preliminary SPD.

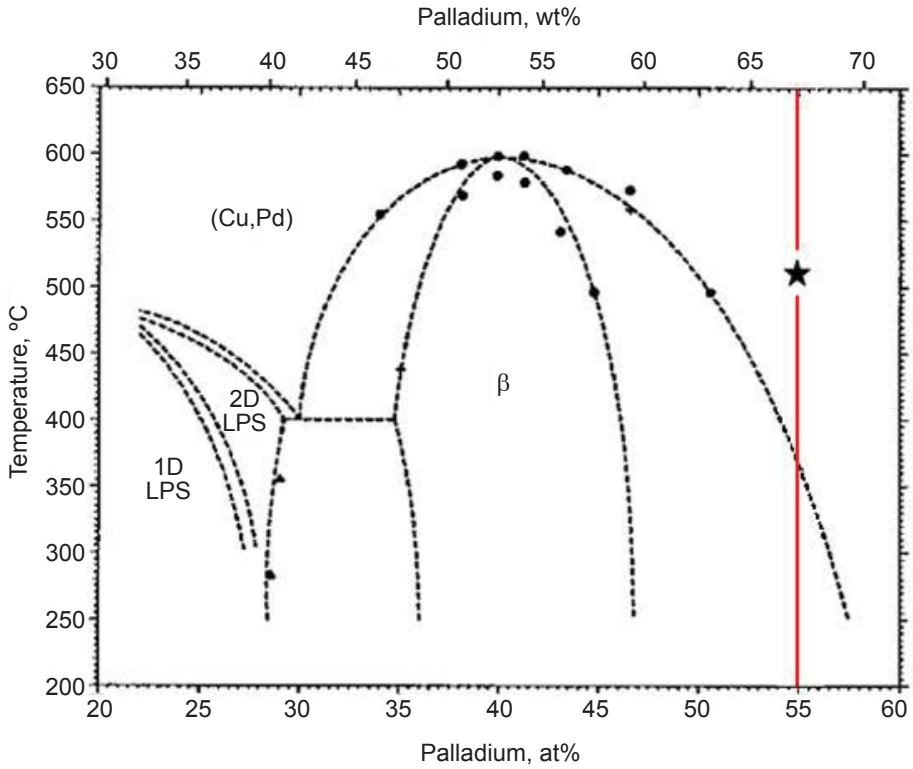

Fig. 1. Portion of the phase diagram of the Cu-Pd system (1). The vertical line denotes the alloy composition studied. The sign "★" marks the temperature boundary of the *A1→(A1+B2)* transformation of the Cu-55Pd alloy that was determined in this study

Experimental Procedure

The initial components taken for the alloy preparation were of 99.98% purity. Melting was performed in a vacuum of at least 10^{-2} Pa and the alloy was poured into a graphite crucible.

An alloy ingot 8 mm in diameter was homogenised at 850ºC for 3 h and quenched in water. Deformation was carried out at room temperature in two stages without intermediate annealing. First, the ingot was drawn from its initial diameter of 8 mm up to a rod with 3 mm diameter. Part of the rod was then drawn to a wire 0.22 mm in diameter (for resistivity measurements). The rest of the rod was cold rolled to plate samples 0.2 mm thick (for X-ray diffraction (XRD), transmission electron microscopy (TEM) and microhardness measurements). After SPD, the wire samples have a degree of true deformation of $\varepsilon \approx 7.1$ and plate samples were deformed up to $\varepsilon \approx 3.8$. Some experiments were carried out on as-quenched alloy samples in the disordered state fixed by quenching from 750ºC in water. This was necessary to compare rates of phase transformation depending on initial alloy state.

The chemical composition of all samples studied in this paper was analysed using a JEOL JCXA-733 microprobe instrument (accelerating voltage of 25 kV, probe current of 50 nA). The analysis showed that the sample composition was slightly lower in Pd than expected, at 66.9 wt% Pd, with the balance 33.1 wt% Cu. The measurement error did not exceed 0.4 wt%. The impurity content in the alloy was less than the lower limit of instrument sensitivity at 0.05 wt%. The major impurity detected was platinum. Thus the exact composition for the alloy studied was 45.3 at% Cu-54.7 at% Pd, which is referred to in this paper as Cu-55Pd.

The electrical resistivity ρ of the samples was measured by the standard four-probe technique, at a direct current of I = 10 mA. Samples were first subjected to isothermal annealing of different durations followed by quenching in water. All of the heat treatments were carried out in evacuated quartz or glass ampoules. Resistometric investigations were carried out at room temperature. The absolute deviation of the electrical resistivity measurements was found to be $\Delta\rho = \pm 0.04 \times 10^{-8}$ Ω m (for experiment details, see (5)).

Standard θ-2θ XRD scans were collected using a Rigaku D/MAX-2200/PC diffractometer. The CuK_α radiation was monochromatised by a graphite single crystal. An estimation of lattice parameters of disordered and ordered phase was carried out by the precise lattice parameter determination software of the diffractometer. Uncertainty of the estimation did not exceed 0.00007 nm.

Measurements of samples' microhardness were carried out by the standard method on the PMT-3 device, with a 50 g load.

The microstructure was investigated by TEM using a JEM 200 CX microscope with accelerating voltage of 160 kV. The foils for TEM investigations were made out of the plate samples by electroetching.

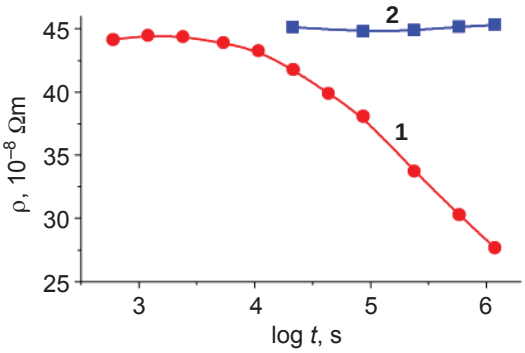

Fig. 2. The dependence of resistivity on the holding time at 350ºC of Cu-55Pd alloy in different initial states: after SPD (curve **1**) and after quenching from 750°C (curve **2**)

Results and Discussion

Electrical resistivity as a function of holding time at 350ºC was measured for different initial states of the Cu-55Pd alloy (**Figure 2**). Samples were subjected to preliminary SPD ($\varepsilon \approx 7.1$) (curve **1**) or quenching (750ºC) (curve **2**). The maximum duration of heat treatment was 306 h.

The change in electrical resistivity is clearly shown in **Figure 2** to be fixed only in the strongly deformed sample (curve **1**). After an incubation period, the resistivity of the sample after SPD starts to decrease, which indicates the beginning of the phase transition. After holding for 306 h the resistivity of this alloy sample changed to $\rho = 27.67 \times 10^{-8}$ Ω m. Note that this is the first time such a low resistivity has been recorded for the Cu-55Pd alloy. The minimum electrical resistivity value previously reported for the Cu-55.31Pd alloy was $\rho = 43.5 \times 10^{-8}$ Ω m (6).

From the shape of curve **1** in **Figure 2** it can be concluded that holding at a temperature of 350ºC for 306 h is obviously insufficient for reaction completion. Indeed, the rate of resistivity decrease was still significant in the later stages of this experiment and, consequently, the formation of the structure had not yet been terminated by the end of the experiment. Thus, the electrical resistivity of the studied alloy in the equilibrium state at 350ºC is expected to be considerably lower than that which has already been attained.

As was shown earlier (7–9), a change in physico-mechanical properties is closely connected with structure related phase transformations (*A1*↔*B2*) that take place in Cu-Pd alloys. For instance, in the course of atomic ordering of the Cu-50Pd alloy its resistivity virtually falls by an order of magnitude (10). In terms of these experimental results (**Figure 2**) it can be concluded that after preliminary SPD the atomic ordering process in the investigated alloy occurs quite actively at 350ºC. However, this conclusion contradicts the phase diagram (**Figure 1**). In order to check the resistometry data, XRD analysis was employed (**Figures 3(a)** and **3(b)**).

The θ-2θ XRD scan for the sample after quenching from 750ºC only contains lines of the *A1* (face-centred cubic (fcc)) phase (**Figure 3(a)**, XRD pattern **1**). The lattice parameter of the alloy in the disordered state was measured to be $a = 0.3779$ nm. The phase state after annealing of the quenched alloy for 306 h at 350ºC does not appear to change (XRD pattern **2**). In comparing XRD scans in **Figure 3(a)**, a redistribution of peak intensities should be noted. Moreover, the lattice parameter of the alloy after annealing for 306 h remains unchanged at $a = 0.3779$ nm. This is close to the corresponding literature value $a = 0.3781$ nm for an alloy of similar composition (1).

The XRD scan of the alloy subjected to SPD ($\varepsilon \approx 3.8$), as well as of the alloy after quenching from 750ºC, contains lines of only the *A1* (fcc) phase (**Figure 3(b)**, XRD pattern **1**). The lattice parameter of the alloy after SPD is $a = 0.3783$ nm, which is a little larger in comparison with the lattice parameter of this alloy in the quenched state. There is no reported data on the lattice parameter for Cu-55Pd alloy subjected to SPD. A distinction between the lattice parameters of the fcc-phase of Cu-Pd alloys after quenching and SPD has been observed earlier (10) and had the same order of magnitude. The increase in the lattice parameter of

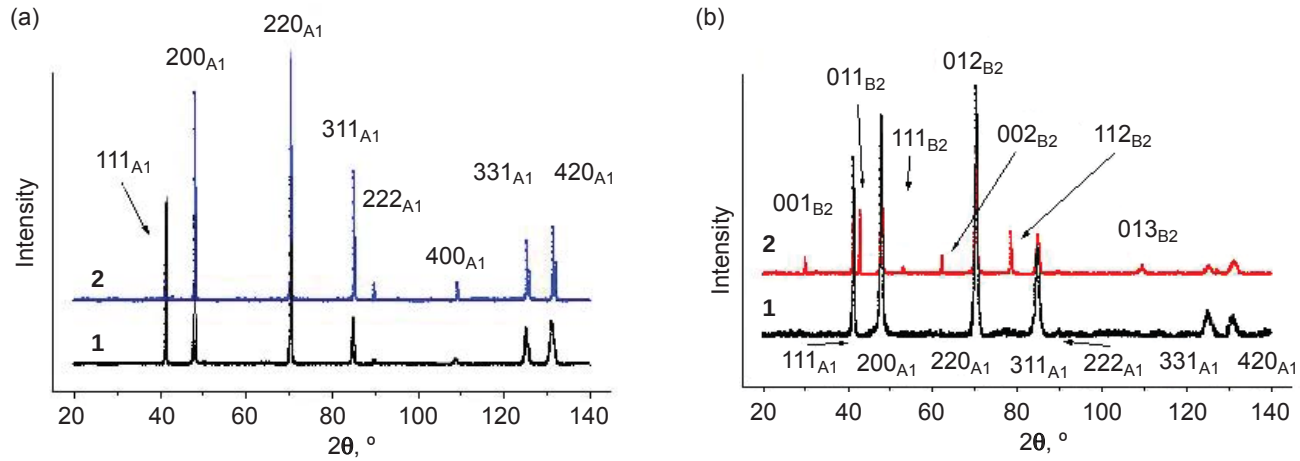

Fig. 3. XRD patterns from the alloy Cu-55Pd in the initial state (pattern **1**) and after annealing (pattern **2**) at a temperature of 350ºC for 306 h (2): (a) quenched; (b) subjected to SPD

Cu-Pd alloys after SPD can be assumed to result from the formation of a nanocrystalline state. In this state, the crystal lattice parameter is determined by the proximity of boundaries and the large value of their relative volume. The size of the regions of coherent scattering, *d*, of the Cu-55Pd alloy after SPD has been estimated by the Williamson-Hall method (11) and is determined as d = 56 nm.

After annealing of the Cu-55Pd alloy preliminarily subjected to SPD ($\varepsilon \approx 3.8$) for 306 h at 350ºC, the two-phase state (*A1*+*B2*) is observed (**Figure 3(b)**, XRD pattern **2**). In the XRD pattern **2** (**Figure 3(b)**), well-pronounced lines from an ordered *B2* phase (a = 0.2980 nm) are revealed in the background of reflections from a disordered *A1* phase (a = 0.3781 nm). The value of the lattice parameter a of the Cu-55.3Pd alloy in the ordered state is reported to have been equal to 0.2978 nm (1). It can be noted that the values of the lattice parameters a = 0.3781 nm (*A1*-phase) and a = 0.2978 nm (*B2*-phase) (1) were not of experimental origin but were calculated on the basis of earlier data (2).

As follows from the phase diagram (**Figure 1**), the annealing temperature chosen in the present experiment belongs to the boundary of the phase transition *A1*↔(*A1*+*B2*) for the Cu-55Pd alloy. However, proceeding from all the results obtained (**Figures 2** and **3(b)**), a true boundary of the existence of a single-phase disordered state that is characteristic of the alloy under investigation exists at a higher temperature. As was already mentioned above, a determination of the boundary temperature was earlier performed on the quenched alloy, where the rate of ordered phase formation is very low. A preliminary SPD considerably accelerates the phase transformation in the studied alloy in the course of subsequent heat treatments. This can be seen in **Figure 2**.

On the basis of the results obtained, an attempt was made to determine a temperature interval for the boundary between the two-phase (*A1*+*B2*) and completely disordered (*A1*) states characteristic of the alloy under investigation. All further experiments were carried out on the samples subjected to SPD. Annealings were performed in the temperature interval from 350ºC to 550ºC with a step of 50 K.

A set of XRD patterns taken from the alloy samples after annealing in the specified temperature interval for 336 h is presented in **Figure 4(a)**. In the spectra distinct reflections from the *B2* phase are observed in the background of reflections from the fcc matrix after annealing between 400ºC and 450ºC. Moreover, in the sample annealed at 500ºC, traces of an ordered structure are also present. In this XRD pattern, elevations above background intensity in the regions of $2\theta \approx 43^\circ$ and $2\theta \approx 79^\circ$ angles exhibit clear distinction and are in correspondence with the peaks from the *B2* phase (marked with a circle).

Figure 4(b) shows a set of XRD patterns taken from the alloy samples after annealing at 500ºC, 520ºC, 540ºC and 550ºC for 336 h (2θ ranged from 42º to 44º). After annealing the sample at 500ºC, the peak from the *B2* phase at $2\theta \approx 43^\circ$ is seen to be the most intense (lowest XRD pattern, **Figure 4(b)**). With increasing annealing temperature the intensity of the reflection decreases.

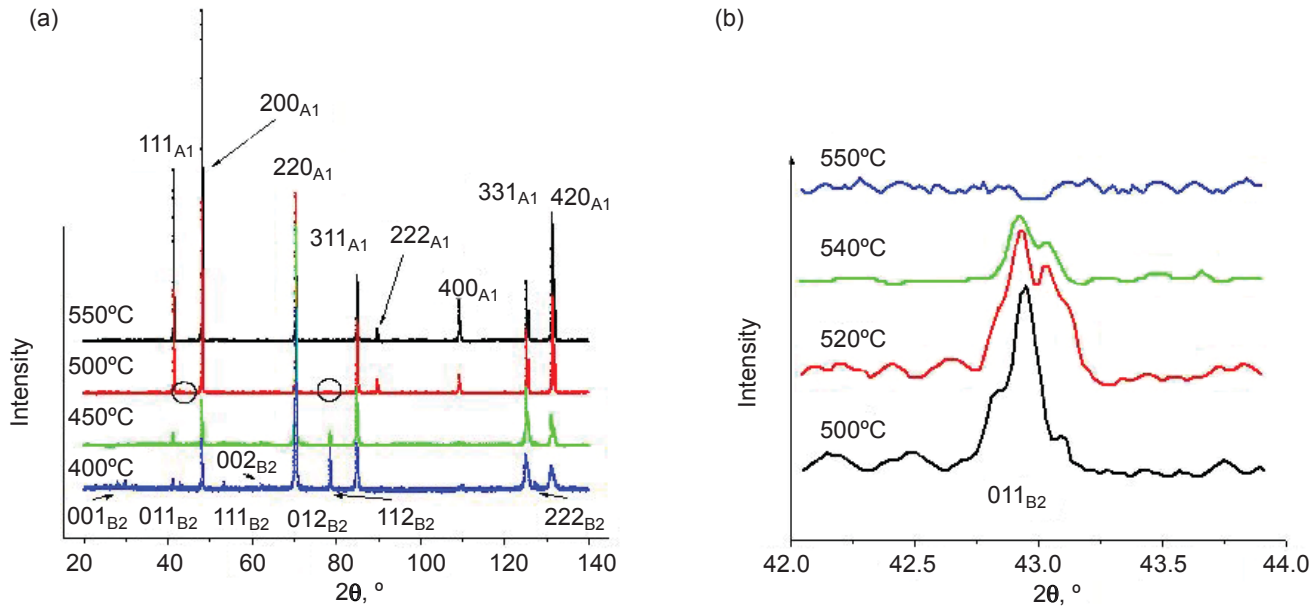

Fig. 4. XRD patterns from the studied alloy subjected to SPD and subsequent holding at various temperatures for 336 h: (a) 400°C –550°C; (b) 500°C –550°C (2θ = 42° –44°)

No ordered phase was detected in the alloy subjected only to annealing at a temperature of 550°C (upper XRD pattern, **Figure 4(b)**). The revealed temperature boundary of the *A1*→(*A1*+*B2*) transformation of the Cu-55Pd alloy is located significantly higher than is expected from the conventional phase diagram (**Figure 1**).

As has been demonstrated elsewhere (5, 8, 9), it is possible to study the kinetics of phase transformation in Cu-Pd alloys with the help of resistivity measurements. In **Figure 5** it can be seen that during the course of the experiments the electrical resistivity of virtually all the alloy samples decreased. This unambiguously testifies to the occurrence of the processes of atomic ordering in the material. And it is noteworthy that after annealing at temperatures below 450°C for 336 h the electrical resistivity of the alloys studied exhibited a notable decrease. A heat treatment at 500°C for 96 h led to an insignificant change in ρ; further increases in the annealing duration hardly affected the resistivity of the alloy. In the course of holding the alloy at a temperature of 550°C, some increase in its resistivity can be observed. In this case, the growth of the electrical resistivity of an initially deformed alloy is caused by recrystallisation that develops in the course of annealing and by the formation of the short-range order under subsequent quenching. The obtained resistometric data are in full agreement with the XRD analysis.

The phase transformation in a previously deformed alloy is accompanied by one additional solid-state reaction, namely, by recrystallisation (12). Thus, in the course of heat treatment, in the bulk of material there simultaneously coexist three structural components, namely: an initially deformed matrix, recrystallised grains of a disordered phase and nuclei of a new, ordered phase. Based on the data presented above, the temperature interval of the phase transformation (**Figure 4**) and its kinetics (**Figure 5**) can be assessed.

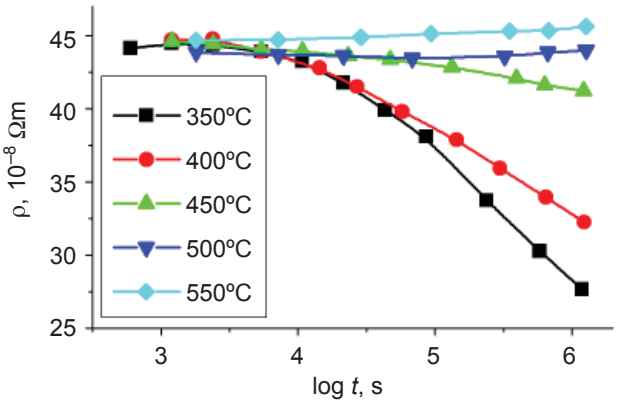

Fig. 5. The dependence of the electrical resistivity of Cu-55Pd on the holding time at different temperatures

The plot of microhardness *vs.* treatment temperature allows the origin of the recrystallisation processes in the alloy under consideration to be assessed (**Figure 6**).

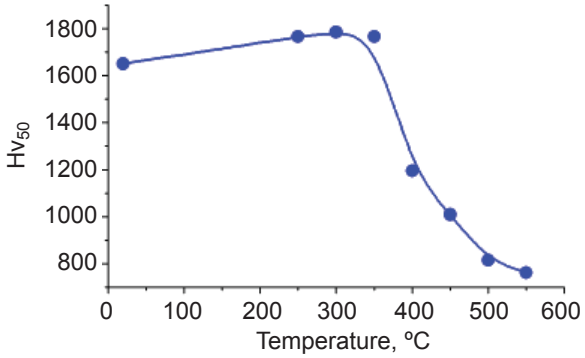

Fig. 6. The dependence of microhardness on the holding temperature for 336 h of samples of Cu-55Pd alloy subjected to SPD

After annealing at temperatures from 250°C to 350°C, the microhardness of the studied alloy increases. As shown in **Figures 2** and **3(b)**, the process of atomic ordering develops in this temperature interval. Thus, the increase in strength is governed by the appearance of a large quantity of nuclei of the ordered phase in a highly deformed matrix. An analogous phenomenon was observed earlier after low-temperature annealing of the SPD-treated alloy Cu-40Pd (7). It has been established that in this case a fine-grain structure (grain size of 2 μm–3 μm) is formed in the material with approximately equal volume amounts of the ordered and disordered phases.

Annealing in the temperature interval from 400°C to 450°C causes a considerable reduction in the hardness of the alloy (**Figure 6**), which can be explained as a result of the development of recrystallisation processes. Increasing the temperature of heat treatment to 550°C is accompanied by decreasing microhardness to very low values typical of a perfectly recrystallised, disordered state of the alloy. **Figure 4** shows that at this temperature the recrystallised grains of only one, disordered, phase grew in the severely deformed matrix of the alloy studied; the formation of an ordered phase does not take place.

Figure 7(a) shows a typical TEM image of the microstructure of the Cu-55Pd alloy after SPD and annealing at 500°C for 336 h. After such treatment the alloy forms a two-phase (*A1*+*B2*) state: precipitations of the ordered body-centred cubic (bcc)-phase (*B2*) are observed in the fcc-matrix (*A1*). Precipitations of the *B2* phase generally have a rounded shape and their most probable size is less than 0.2 μm. Bright-field image of the microstructure containing the *B2*-phase coarse precipitation and the selected area diffraction pattern

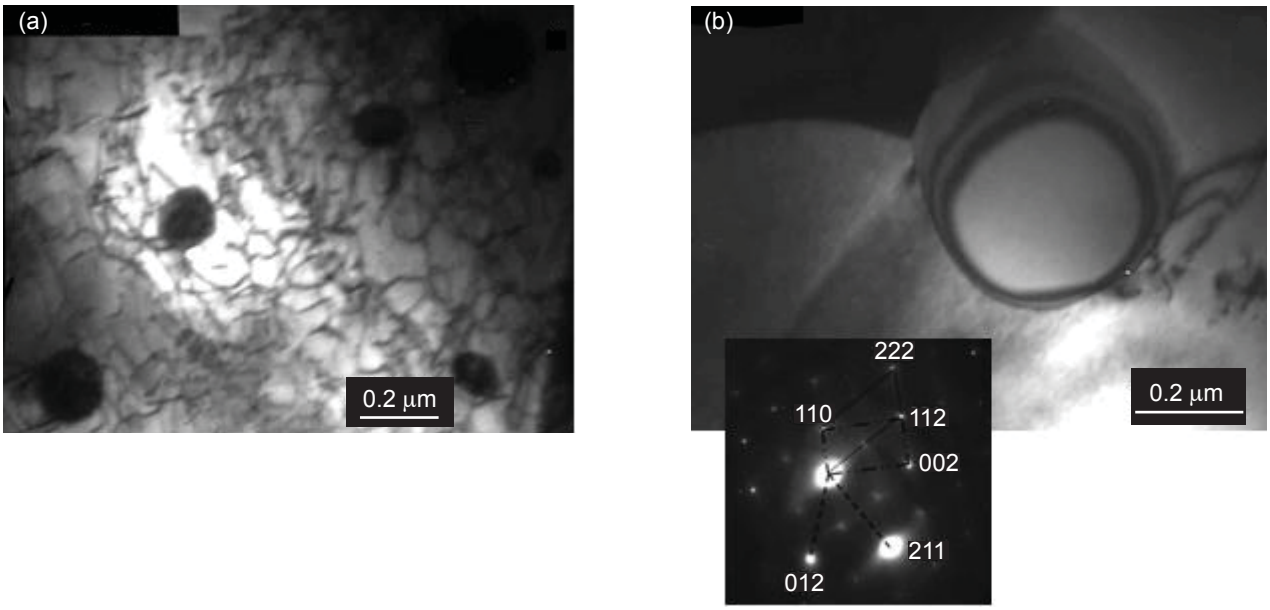

Fig. 7. The bright-field images of Cu-55Pd alloy after SPD to $\varepsilon \approx 3.8$ (the plate 0.2 μm thickness) and annealing at 500°C for 336 h: (a) a typical microstructure; (b) the microstructure containing *B2*-phase precipitation (the inset shows a selected area diffraction pattern of the precipitation)

of the precipitation are shown in **Figure 7(b)**. The selected area diffraction pattern is a superposition of two cross-sections of the reciprocal lattice of the *B2* phase and does not have additional reflections. The general picture of the microstructure in **Figure 7** is in good agreement with the results of XRD analysis (see lowest XRD pattern, **Figure 4(b)**).

It can also be noted that, despite the high temperature and the long annealing time, a residual dislocation density remains (**Figure 7(a)**) which is caused by the incomplete recrystallisation process. More detailed TEM investigation would be beyond the scope of this paper.

Conclusions

In summary, the temperature boundary of the *A1*→(*A1*+*B2*) transformation of the Cu-55Pd alloy takes place at around 550ºC, approximately 200ºC higher than expected from the generally accepted Cu-Pd phase diagram. Preliminary SPD has been shown to greatly accelerate phase transformation in the Cu-55Pd alloy. However, after annealing for 336 h at temperatures below 450ºC, the equilibrium phase state had not been reached. The room temperature electrical resistivity of the Cu-55Pd alloy in the annealed state obtained while holding at 350ºC for 306 h after preliminary SPD is $\rho = (27.67 \pm 0.04) \times 10^{-8}$ Ωm. This resistivity is much lower than that indicated elsewhere as the minimum value for alloys with similar compositions.

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