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Ageing of a Pd-35 at% Ag-25 at% Cu solid solution alloy[*]

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A palladium–35 at % silver–25 at % copper alloy has been prepared to simulate a succesful, commercial alloy. The commercial alloy is widely used because of its good corrosion resistance and formability and the fact that it develops good wear resistance and low electrical resistivity after ageing. However, little is known about the transformations which result from heat treatment of this alloy. Thus, the laboratory prepared material was used for determination of ageing transformations by means of resistance measurements, metallography, transmission microscopy, and X-ray diffraction. The following sequence of reaction was found to occur:

Supersaturated solid solution → Spinodal decomposition → Ordering and discontinuous precipitation

The transformations are quite similar to those occurring in several other solid solution systems whose initial spinodal decompositions are followed by discontinuous transformations with one or more ordered phases.

1. Introduction

A series of alloys based on ~40 at % palladium–35 at % silver–25 at % copper finds successful application as light-duty electrical contacts[†]. After a high-temperature solution treatment and water quench, these alloys are formable and can be aged to produce good wear properties and low electrical resistance.

The phase diagrams of binary pairs of the system are shown in Fig. 1 [1]. The palladium–silver system shows complete solubility, and the silver–copper system has a simple eutectic transformation at 40 at % Cu and 1052 K. The Cu–Pd binary exhibits complete solid solubility at temperatures above 873 K. With decreasing temperature, three ordered phases form at approximately 15, 25, and 40 at % Pd. The transformation in the region 30 to 50 at % Pd results in a change in crystal structure from disordered f c c to an ordered CsCl (B2) type. Ordering at lower Pd concentrations involves the formation of complex tetragonal structures whose exact descriptions remain unconfirmed [1].

The available literature on mechanical properties of Pd–Ag–Cu alloys concerns the more complex Paliney alloys. The manufacturer has made heat treatment suggestions, and Nordstrom [2, 3] has examined stress-relaxation and micro-deformation behaviour. However, to the author's knowledge, no studies have been made of the polymorphic transformations occurring during ageing. Since components of these alloys must be highly reliable and useable for long times it is important to know if the manufacturer's recommended heat treatment results in a stable material. Preliminary work on the commercial alloy indicated that the recommended solution treatment temperature was suitable, but that the solution time did not homogenize the sample and that the ageing time for a completely homogeneous sample may result

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[†] The given composition with minor additions of gold, platinum, zinc and nickel are marketed as Paliney alloys, a registered trade name of the J. M. Ney Company, Bloomfield, Ct, USA.

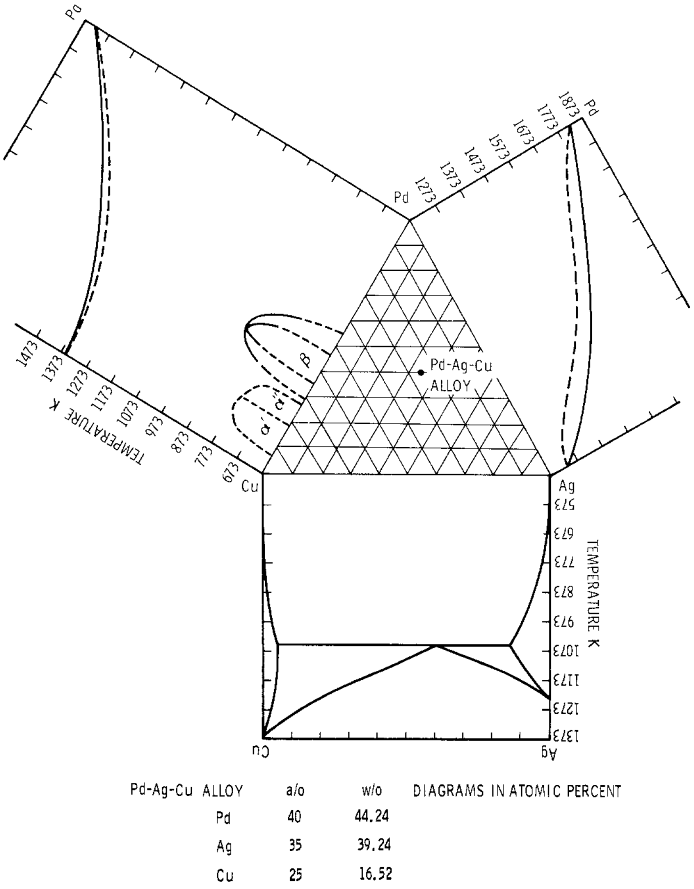


Figure 1 Component binary phase diagrams of the palladium–silver–copper system.

in an unstable microstructure. Thus, non-repeatable mechanical behaviour may be anticipated. Clarification of phase stability and ageing response of the Pd–Ag–Cu alloys is in order. The objective of the present investigation was, therefore, to elucidate the phase transformations and mechanisms occurring in a typical Pd–Ag–Cu alloy (40 at% Pd–35 at% Ag–25 at% Cu) during ageing.

2. Experimental procedure

2.1. Material

The chemical composition of the alloy used in the present investigation is given in Table I. Ingots 10 cm × 2.5 cm × 1.5 cm were prepared from 99.9 + % purity Pd and Ag and 99.9 % pure Cu by arc melting a 41.7 at% Cu–58.3 at% Ag master alloy with appropriate additions of Pd.

The analysis of the finished alloy is given in Table I.

The ingots were cold rolled 17% and homogenized for 96 h at 1133 K in a flowing argon atmosphere. Final samples were then prepared by cold rolling to a thickness of 0.3 cm (for metallographic samples), 0.1 cm (for resistance samples) or 0.004 cm (for X-ray and transmission electron microscopy samples) and solution-treated again.

Based upon metallographic evidence of suitable homogenization, the solution treatment was standardized to 1133 K for 1 h followed by water quenching.

TABLE I Chemical composition of the Pd–Ag–Cu alloy

Element	wt%	at%	p.p.m.* (by weight)
Ag	38.3	34.0	
Cu	17.0	25.7	
Pd (by difference)	44.7	40.3	
Fe			700
Mn			30
Mg			30
Si			150
Pt			200
Ti			100
Ca			90
Ni			2000

*Results from emission spectroscopy.

2.2. Electrical resistance measurements

The technique of monitoring changes in electrical resistance was used to determine temperature regimes where significant microstructural alterations may be occurring. Resistance measurements were made using a 4-terminal reversing-polarity apparatus with a constant current of 0.1 A flowing through the sample. The specimens were 0.1 cm x 0.1 cm x 10 cm length with Pt current and voltage measurement leads welded at each end. The voltage leads were located approximately four wire diameters inside each of the current leads.

Measurements of the per cent change in resistance were made either during thermal cycling between 298 K and 1133 K or after water-quenching and during isothermal ageing at selected temperatures. The per cent change in resistance, A, was determined using the equation given below for every point:

$$A = \frac{R_i - R_T}{R_0 - R_T} \times 100$$

The value R_i is the instantaneous resistance at any time, R_0 is the resistance at the beginning of ageing and R_T is the resistance at 1133 K just prior to quenching. This method of normalization eliminated dimensional effects. Since these results only served to delineate those temperature and time regimes to be investigated more fully with microscopy and X-ray diffraction techniques, no attempt was made to obtain absolute resistivity values.

2.3. Metallography

Optical metallography and microhardness samples were prepared using standard techniques. Final etching of samples for metallography utilized a freshly prepared aqueous solution of 10 wt % KCN and 10 wt % $(NH_4)_2S_2O_7$. The Knoop hardness results are the averages of at least five indentations at 100 g loads.

Transmission electron microscopy samples were prepared using the window technique, and thinning was accomplished with an electrolyte of 6 vol % $HClO_4$ in methanol at 16 to 20 V and a bath temperature of 213 to 223 K. Careful washing in methanol followed initial foil perforation after which a segment was cut to fit the 3 mm grid sample holder.

Two electron microscopes were used during this investigation, a JEM 200 A and a JEM 100 C operated at 200 and 100 kV, respectively. Both microscopes were equipped with double tilt stages and cold fingers to reduce contamination.

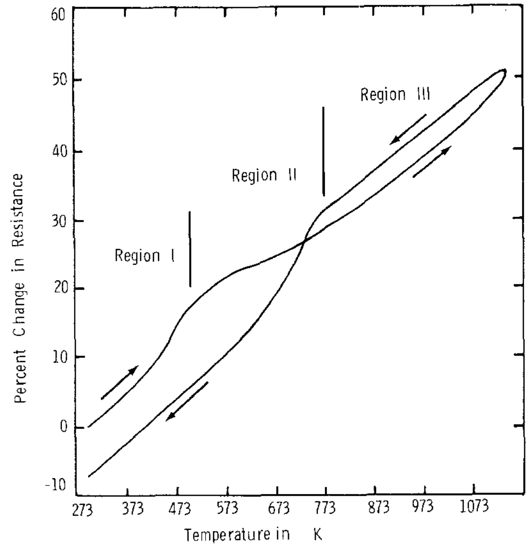


Figure 2 Summary of Pd–Ag–Cu resistance survey.

2.4. X-ray diffraction

The lattice parameters of the various phases, which resulted from ageing the Pd–Ag–Cu alloy, were determined using Ni-filtered CuKα radiation. The samples, having been previously thinned for electron microscopy, were mounted in a 114.6 cm diameter Debye–Scherrer camera, and treated as powder aggregates.

3. Results

3.1. Results of a heating and cooling survey

An initial series of slow heating and cooling excur-

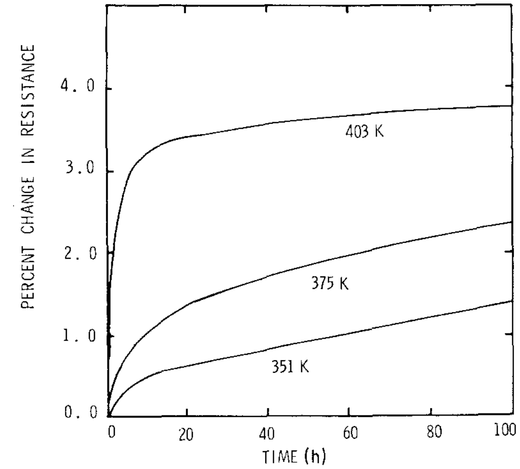


Figure 3 Isothermal ageing behaviour of Pd–Ag–Cu alloy in Region I. Aged at indicated temperatures after solution treatment at 1133 K for 1 h and water quenched.

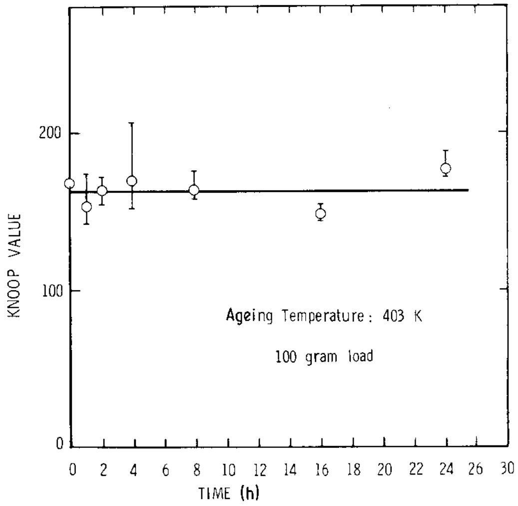
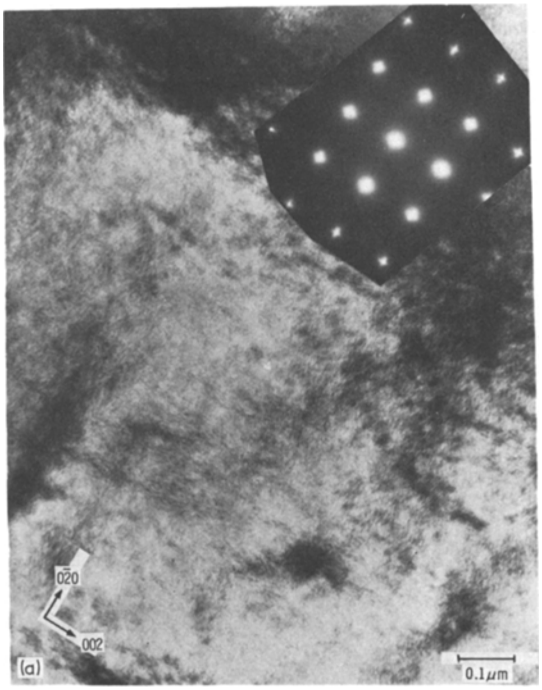


Figure 4 Influence of ageing time in Region I on the hardness of Pd–Ag–Cu alloy.

sions on solution-treated and quenched samples was performed to identify temperature regimes having significant changes. Examination of such a survey shown in Fig. 2 indicated that there were three regions of differing resistance behaviour:

Region I – Room temperature up to 493 K where a rapid resistance increase with temperature was observed.

Region II – From ~493 to 803 K where the resistance change with the temperature was observed to be anomalously low.



Region III – Above ~803 K where the resistance increased linearly with temperature as expected from a metal.

Isothermal resistance monitoring, hardness, optical and transmission microscopy, and X-ray analysis were used to characterize the transformations in Regions I and II. Since the resistance behaviour above 803 K was normal, this region presented no special further interest.

3.2. Changes in Region I

In Fig. 3 are shown resistance versus time plots for a series of isothermal anneals. The resistance in this region increased with time and did so at an accelerating rate at higher temperatures. The influence of ageing time in Region I on the microhardness of the alloy is illustrated in Fig. 4. No increase in hardness was detected after the heat treatment even though there is a consistent small increase in resistance. The hardness test is apparently not sufficiently sensitive to delineate small changes in microstructure that are presumably evidenced in the isothermal resistance data.

Optical microscopy indicated that the alloy, solution-treated at 1133 K and water-quenched, is a single-phase, solid solution. However, transmission microscopy showed that the solution-treated condition really consisted of an extremely fine modulated structure, Fig. 5a. Selected area diffraction patterns of the [1 0 0] zone taken from regions similar to Fig. 5a indicate that the matrix reflections are accompanied by satellite reflections. These satellites become more apparent as the order of the matrix reflections increases as shown in

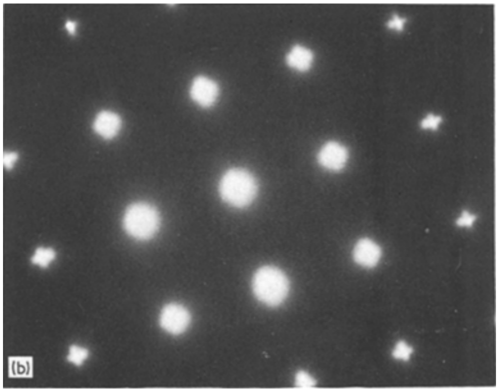


Figure 5 (a) Transmission electron micrograph of Pd–Ag–Cu alloy showing modulated structure. Solution-treated 1 h at 1133 K and water-quenched. (b) Selected area diffraction pattern of structure of Fig. 5a showing satellites. [1 0 0] zone axis.

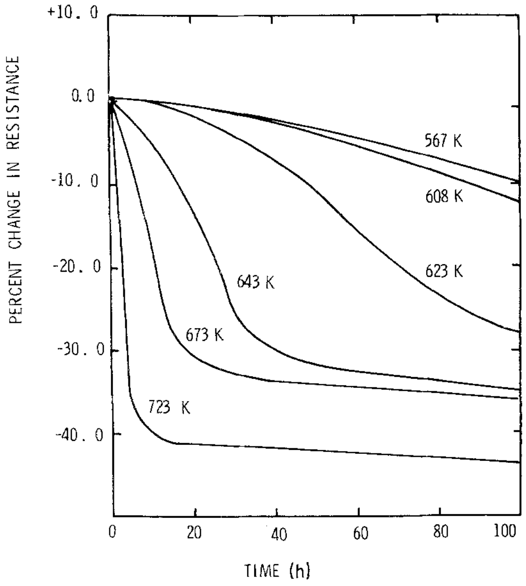


Figure 6 Isothermal ageing behaviour of Pd–Ag–Cu in Region II. Aged at indicated temperatures after solution treatment at 1133 K for 1 h and water-quenched.

Fig. 5b. Ageing within Region I for extended times did not result in any noticeable change in the microstructure from that observed in the quenched specimens.

3.3. Changes in Region II

Fig. 6 is a plot of the changes in resistance upon isothermal annealing at a series of temperatures in Region II. The plots show that the resistance falls with time and at an accelerated rate at higher temperatures. At high ageing temperatures in this range, the resistance tends to approach an asymptotic value. The hardness results representative of samples aged in Region II are given in Fig. 7. In Region II it appears that the hardness may go through a maximum. This maximum value of Knoop 345 occurred after 4 h ageing at 673 K, and levelled at approximately 321 for the duration of the ageing (100 h) at that temperature.

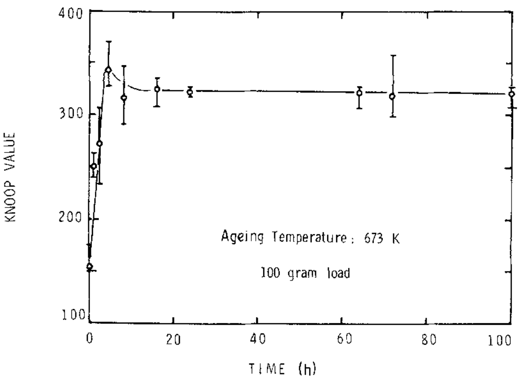


Figure 7 Influence of ageing time in Region II on the hardness of Pd–Ag–Cu alloy.

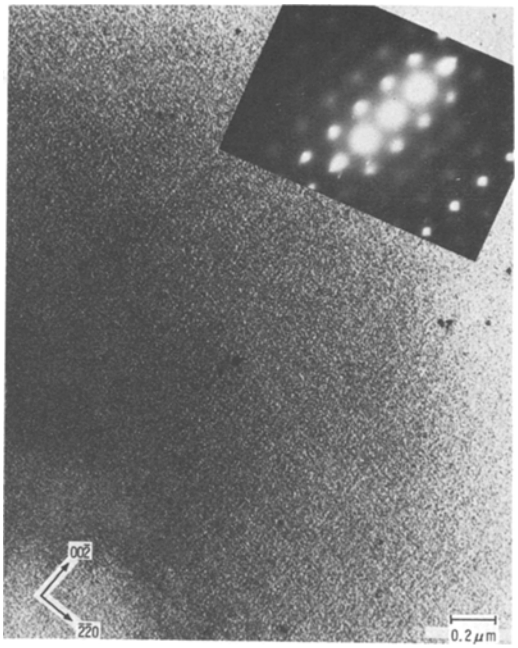


Figure 8 Transmission electron micrograph of Pd–Ag–Cu alloy showing modulated structure. Water-quenched and aged for 1 h at 673 K. [1 1 0] zone axis.

Optical metallography on samples aged for 1 and 2 h showed only a single phase, but transmission microscopy showed that the modulated structure developed upon quenching gradually coarsened, as shown in Figs. 8 and 9.

In Region II, small amounts of the discontinuous structure were visible in transmission microscopy at grain boundaries even at short ageing times. After 4 h, the volume fraction of the discontinuous structure was significant and easily detected in optical metallography and the amount increased with further ageing. Fig. 10 shows an island of the discontinuous structure produced after ageing for 8 h at 673 K. Typically, precipitation has initiated at a grain boundary triple point with subsequent growth tending to be restricted to only one of the three adjacent grains. Increases in ageing time resulted in an increase in the volume fraction of the discontinuous transformation until it had consumed the entire matrix (Fig. 12).

The transmission micrograph, Fig. 11, shows, at high magnification, the very fine interconnected nature of the discontinuous structure, after 12 h at

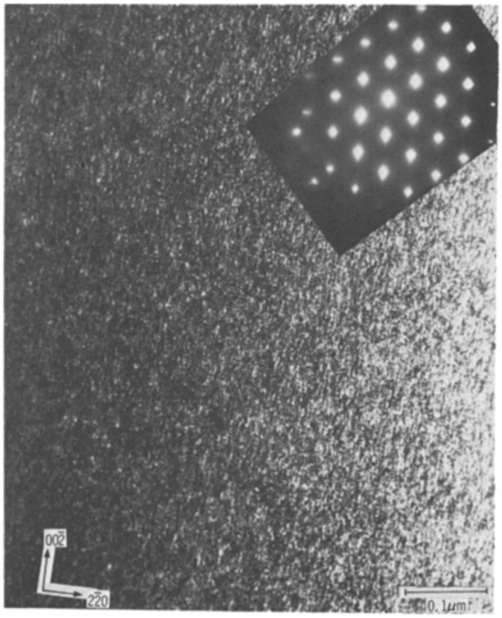


Figure 9 Transmission electron micrograph of Pd–Ag–Cu alloy showing modulated structure. Solution-treated at 1133 K for 1 h, water-quenched and aged 2 h at 673 K. [1 1 0] zone axis.

TABLE II d-spacings obtained from powder pattern of Pd–Ag–Cu sample solution treated at 1133 K, water-quenched, and aged 64 h at 673 K

d for palladium (Å)	Intensity (%)	d observed for alloy (Å)	Intensity estimate
		2.98	W
2.246	100	*2.30**	S
		2.18	VW
		2.12	M
1.945	42	*1.98*	M
		1.72	VW
		1.49	W
		1.41	VW
1.376	25	1.33	W
		1.22	W
1.1730	8	1.053	VW
		1.152	W
1.1232	8	1.053	VW
		0.996	VW
0.9723	3	0.966	VW
		0.913	W
0.8924	13	*0.892*	W
0.8697	11	0.863	VW
		0.817	W
		0.796	VW

*Italicized d-spacings judged to be related to the matrix.

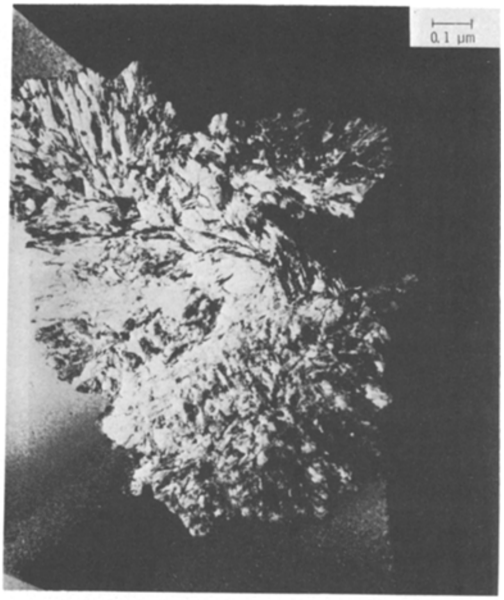


Figure 10 Transmission micrograph of an island of the discontinous structure after solution treatment and ageing for 8 h at 673 K.

673 K, which did not change appreciably after continued ageing to 64 h.

Table II summarizes the results of X-ray diffraction measurements of a sample solution treated at 1133 K, water-quenched, and aged 64 h at 673 K. More lines are present than are allowed by an f c c structure.

A solid solution of palladium–silver–copper should have an f c c lattice and such a structure with $a_0 = 3.96$ Å was calculated from the pattern

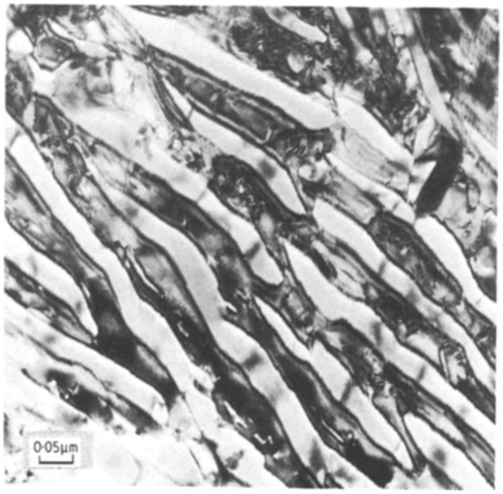


Figure 11 Transmission electron micrograph showing the interconnected structure after solution treatment and ageing for 12 h at 673 K.

Figure 12 Transmission electron micrograph of Pd–Ag–Cu alloy solution treated at 1133 K, water-quenched and aged 24 h at 673 K showing the discontinuous structure.

using the *d*-spacings italicized in Table II. These values are just slightly larger than those for Pd. The residual lines were subjected to fitting on a Bunn chart, and ratios of c/a of 1.03, 0.70, and 0.99 were found to be solutions. The 1.03 to 0.99 values suggest slight tetragonality and the 0.7 value is also such a derivative, provided that the $h + k + l = 2n$ rule is obeyed for a body-centred rearrangement of a face-centred cell.

4. Discussion

A mode of transformation is postulated in view of the above experimental evidence which coordinates observations in both Regions I and II. The transformations in this system may be divided into three stages as follows:

Stage 1 – A spinodal reaction begins during the quench. In Region I this stage, with extended ageing, is the only transformation proceeding. A spinodal reaction is postulated for several reasons: (1) The thermal energy is quite small at the low temperatures of Regions I and the spinodal reaction requires no activation energy [4]. (2) The structural modulations occur along the [1 0 0] planes, typically the preferred, soft directions for f c c materials. (3) The striations maintain an essentially constant spacing with ageing. The nearly-constant spacing and an accompanying increase in intensity or amplitude at a given temperature are characteristics of the spinodal reaction [4]. (4) The presence of satellite spots about the matrix spots in the electron diffracition pattern (a result of the slightly different lattice parameters of the two new phases developing from the matrix). (5) The absence of grain boundary denudation expected to accompany compound formation. (6) The absence of overageing (at least within the observed time periods >100 h) as as would accompany GP zone formation. (7) The slight increase in resistance indicative of slight departure from the solid solution structure. All of these features together point to spinodal decomposition.

Stage 2 – In Region II later stages of spinodal decomposition occur concurrently with two other processes; ordering and discontinuous precipitation. Both ordering and discontinuous transformation are believed to be responsible for the large drop in resistance observed experimentally. The ordering process observed is considered comparable to ordering in the Pd–Cu binary system. Growth of discontinuous reaction regions increased from the beginning of Region II.

The evidence for ordering lies in two aspects;. (1) the X-ray data which indicate the development of another phase of very similar structure and (2) the large decline in resistance. Westbrook [5] indicates that "a well-ordered alloy usually exhibits very low electrical resistivity compared to that same alloy in the disordered state due to the near ideality of the periodicity of the atomic lattice... so very characteristic is this behaviour that surveys of electrical resistance have been used to search for the existence of order–disorder transformations. ."

Ceresara [6] has recognized that "clustering" and ordering can proceed simultaneously as predicted by the theory of Richards and Cahn [7]. Moreen *et al.* [8] consider that a continuous ordering process can proceed as described by Cook *et al.* [9] in which a wave of interatomic wavelength causes long range order and a wave of longer wavelength develops the domains. Ceresara suggested in the case of the Al–Li alloy that the resistivity decrease arising from ordering dominated an increase due to small grain size or the formation of nearly equal amounts of two slightly different phases.

Discontinous transformation occurs concurrently with and independently of spinodal decomposition as in the Al–Zn [10] and Au–Pt [11, 12] systems.

Stage 3 – In Region II this stage is correlated with the hardness maximum and is associated with with the formation of the discontinuous structure which was observed after ageing of 8 h at 673 K. No new transformations occur in this stage only the culmination of the changes from Stage 2. This structure is made up of two phases; one, a silver-enriched palladium–silver–copper f c c matrix and the other, a copper-enriched palladium–silver–copper ordered structure, f c c or b c t with a c/a ratio very close to 1.

Several other systems demonstrate similar behaviour. One of these systems, even more complex than the palladium–silver–copper system, is the Cu–Ti system, as described by Cornie *et al.* [13]. That system shows the following transitions:

Supersaturated solid solution → Modulation of the matrix by periodic redistribution of solute along [1 0 0] → Formation of β', a coherent or semi-coherent tetragonal phase

↓

Equilibrium Cu_3Ti (cellular precipitation)

This behaviour was confirmed by Dutkiewicz [14]. He indicated that either spinodal decomposition or nucleation and growth mechanisms may operate depending upon the composition and the ageing temperature.

5. Summary

The ageing behaviour of a Pd–Ag–Cu alloy has been studied by resistometric, X-ray and metallographic techniques. The transformation process in this solid solution alloy as derived from the experimental observations may be described as follows:

Supersaturated solid solution → Spinodal decomposition modulation of the matrix by periodic redistribution along [1 0 0] directions

↓

Simultaneous formation of ordered phase and growth of discontinuous structure

↓

Final equilibrium of very fine discontinuous structure

In Region I, only the spinodal reaction has been observed. The final equilibrium structure after ageing in Region II is characterized by lower electrical resistance and higher hardness than in the quenched matrix. This tranformation mode is consistent with the observations and is analogous to transformation in several other systems.

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