JOURNAL OF MATERIALS SCIENCE 28 (1993) 3957–3961

Effects of tin addition on the ordering process of PdCu ordered alloys

I. KAWASHIMA, Y. ARAKI, H. OHNO
Department of Dental Materials Science, School of Dentistry, Higashi Nippon Gakuen University, 1757 Kanazawa, Ishikari-Tobetsu, Hokkaido, Japan

The effects of tin additions on the ordering process of PdCu ordered alloys were investigated by electric resistivity measurements, optical microscopic observations, hardness tests, X-ray diffraction, and electron probe micro-analysis. The ordering process was found to be acccelerated by addition of tin, 1.0% addition being the most effective. This acceleration of ordering by the addition of tin may be explained by assuming that the formation of ordered nuclei becomes easier. The β-phase is stable up to 900 °C with 1.5% Sn addition.

1. Introduction

Grain-boundary precipitates ("nodules") in Ag–25 mass % Pd–10% Cu alloys are nodules of two phases, a silver-rich solid solution (α-phase) and a PdCu ordered lattice of the CsCl type (β-phase) [1–3]. It was shown previously [4], that grain-boundary reactions in Ag–25 mass % Pd–10% Cu alloys are retarded with 1% Sn addition. To determine the retardation mechanism by tin addition in Ag–Pd–Cu alloys, it is necessary to investigate the phase of which the nodules are composed. (Silver-rich and PdCu ordered phases).

The isothermal ordering process in PdCu alloys was investigated by Shiraishi [5], but the effect of the added element on the ordering process in this alloy was not reported. In the present work, the effects of tin addition on the ordering process in PdCu ordered alloys were investigated by electrical resistivity measurements, optical microscopic observations, hardness tests, X-ray diffraction, and electron probe micro-analysis.

2. Materials and methods

The ordered alloys (55.12 mass % Pd–44.88% Cu) were used with 0, 0.5, 1.0, and 1.5% Sn added [6]. The alloys were prepared from metals of a purity better than 99.99% in an alumina Tamman tube under an argon atmosphere in a high-frequency induction furnace, and then cast in a stainless steel mould. The melted mass of each alloy was 50 g. The weight loss in the melting process was less than 0.1%, and chemical analysis after melting was not carried out. The ingots were cold worked slightly and homogenized at 950 °C for 3 h.

Block specimens, 5 mm × 5 mm × 10 mm, for optical microscopic observations and hardness measurements, and 1 mm × 100 mm wire specimens for electric resistivity measurements, were prepared by cold working. For the solution treatment, the specimens were kept at 950 °C for 2 h before they were quenched in ice–water.

The specimens were finally aged at 220, 300, 350 or 400 °C in a salt bath until the grains were surrounded by nodules.

The electrical resistivity was measured during continuous heating from room temperature to 850 °C at 2 °C min^{-1} by the potentiometric method with a direct current of 50 mA. Variation of electrical resistivity with isothermal ageing was measured by the four-terminal potentiometric method with a direct current of 20 mA at room temperature.

Hardness tests were performed with a 1 kg load using a Vickers hardness tester. The hardness values were averages of ten indentations.

Identification of phases was made by X-ray diffraction. The X-ray diffraction measurements were conducted as follows: The target was copper with a 35 kV tube voltage and 20 mA current. The volume fraction of β-phase was determined from the ratio of the 1 1 0 peak area for the β-phase to the 1 1 1 peak area for the α-phase. The lattice constants of the α- and β-phases were determined from the 0 2 4 and 2 3 1 peak sites, respectively, and the diffraction peak sites were corrected with a sample plate stained with annealed copper powder.

Concentration profiles of each element were obtained by electron probe micro-analysis (EPMA).

3. Results and discussion

3.1. Electrical resistivity measurements with rising temperature

Fig. 1 shows the electrical resistivity for solution-treated samples at 950 °C. The temperature where ordering reactions start shifts to lower values with the addition of tin.

The temperature where transformation from the ordered to the disordered state occurs, becomes higher, the greater the amount of added tin. This

0022–2461 © 1993 Chapman & Hall

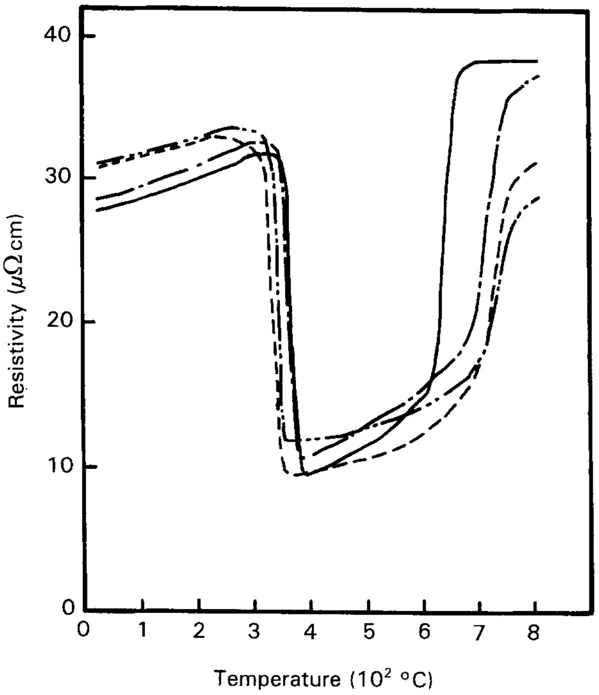

Figure 1 Electrical resistivity changes during continuous heating at 2 °C min^{-1}. Tin content: (——) 0%, (—·—) 0.5%, (– – –) 1.0%, (- · · -) 1.5%.

suggests that the addition of tin makes the ordered state stable at higher temperatures.

3.2. Optical microstructure

Fig. 2 shows the microstructure of alloys solution treated at 950 °C, and aged at 300 °C for 30 min. In Fig. 2, the irregular-shaped ordered phase (arrowed) appears from the grain boundary and widens into the grain interior with ageing time [5]. The mode of precipitation is similar in all samples and ageing treatments.

3.3. Electrical resistivity, hardness, and volume fraction of β-phase with isothermal ageing

Figs 3–5 show the changes in electrical resistivity, f, hardness, H_v, and volume fraction of the β-phase, C_β, after ageing at 300 °C. In Fig. 3, f is given by

$$f(\%) = 100(\rho - \rho_f)/(\rho_0 - \rho_f) \qquad (1)$$

where ρ_0, ρ and ρ_f are specific resistivities with the solution treatment, ageing, and long-term ageing, respectively. The electrical resistivity decreased most rapidly with 1.0% Sn addition. This agrees with the results of the electrical resistivity measurement with rising temperatures.

Fig. 4 shows that the hardness with solution treatment increases with tin content, indicating solution hardening.

The volume fraction of β-phase in Fig. 5 was determined from the ratio of the 0 1 1 peak area of β-phase and the 1 1 1 peak area of α-phase.

The decrease in electrical resistivity in each alloy corresponds to the increase in hardness.

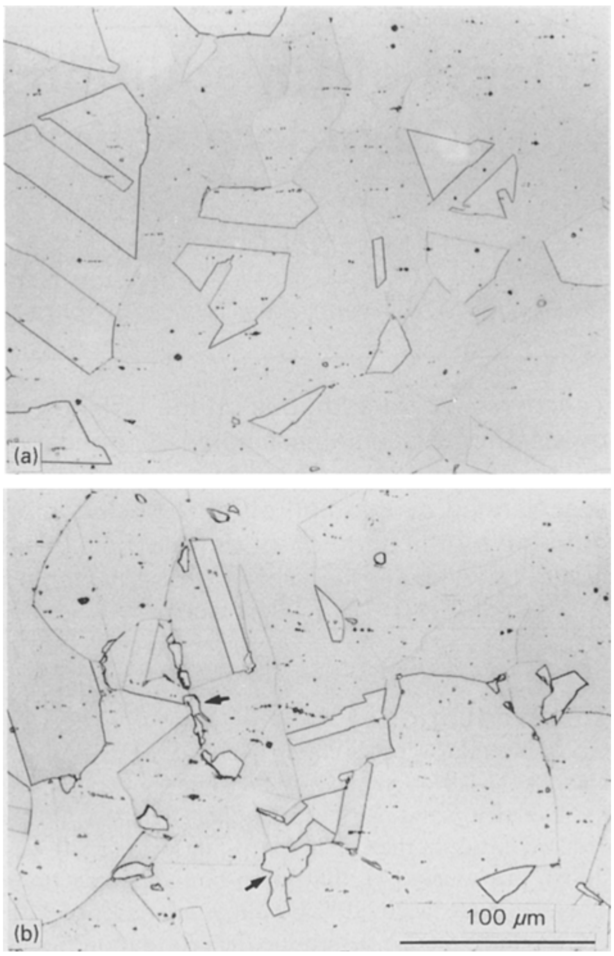

Figure 2 Microstructure of (a) solution treated and (b) samples aged at 300 °C for 30 min, in alloys with the addition of 1.5% Sn.

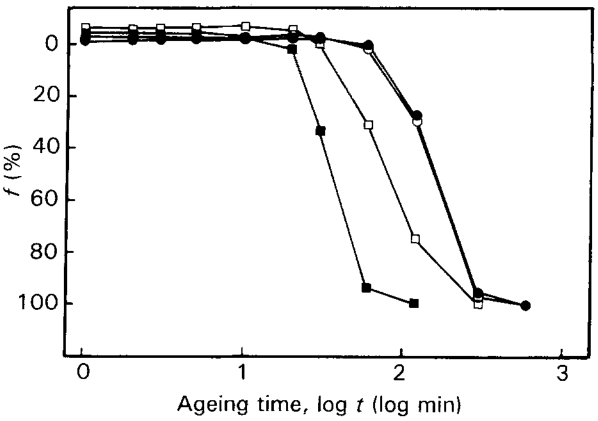

Figure 3 Changes in electrical resistivity in samples aged at 300 °C. Tin content: (●) 0%, (○) 0.5%, (■) 1.0%, (□) 1.5%.

Figs 6 and 7 show changes in electrical resistivity after ageing at 350 and 400 °C, respectively. The addition of 1% Sn accelerates the ordering most with the higher temperature. Fig. 8 shows changes in electrical resistivity for samples aged at 220 °C for short periods. The maximum value of electrical resistivity increases with tin content. This is also the case at other ageing temperatures, except at 400 °C, and is more marked with lower ageing temperatures. The increase in electrical resistivity with faster ageing originates in the formation of a Guinier–Preston (G–P) zone or short-range ordering [7]. The increase in electrical resistivity at the very beginning of ageing is caused by the

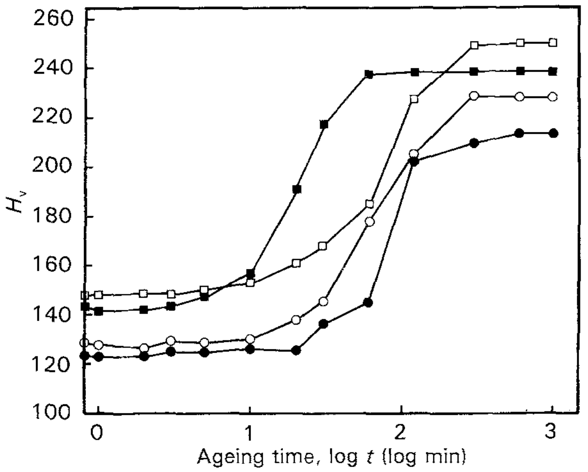

Figure 4 Changes in hardness in samples aged at 300 °C. For key, see Fig. 3.

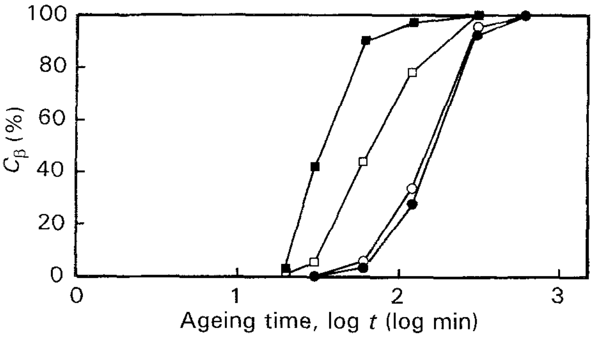

Figure 5 Changes in volume fraction of β-phase in samples aged at 300 °C. For key, see Fig. 3.

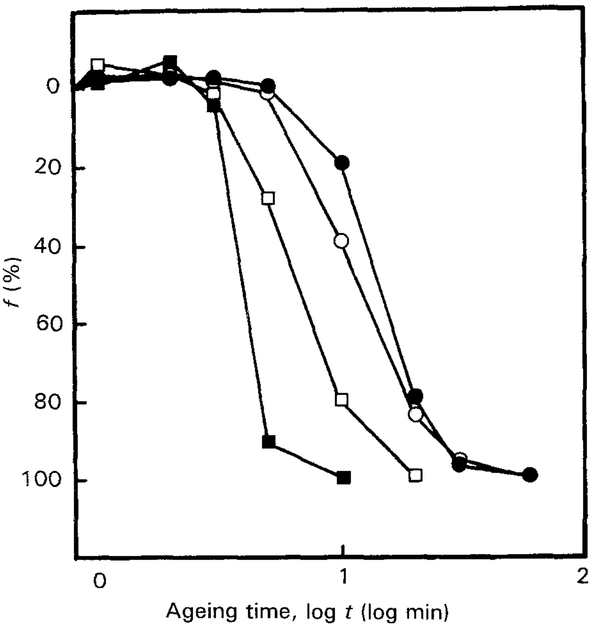

Figure 6 Changes in electrical resistivity in samples aged at 350 °C. For key, see Fig. 3.

appearance of a short-range ordered area where tin concentrates; this is because the alloy used here is a typical ordered alloy, and the maximum reached by the alloy (Fig. 8) increases with tin content.

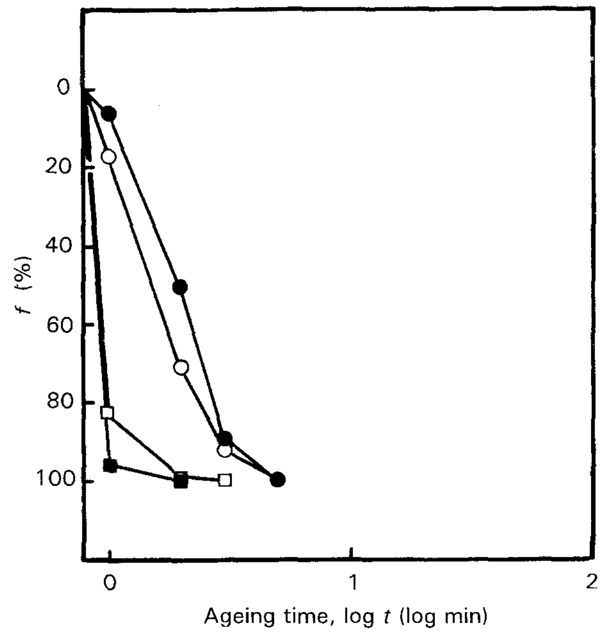

Figure 7 Changes in electrical resistivity in samples aged at 400 °C. For key, see Fig. 3.

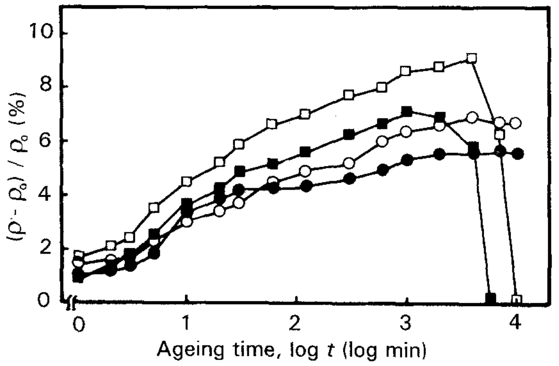

Figure 8 Changes in electrical resistivity in samples aged at 220 °C for short periods. For key, see Fig. 3.

3.4. The mechanism accelerating ordering with tin addition

The phase diagram of the pseudo-binary phase of the PdCu–Sn system was established to determine the mechanism accelerating ordering on the addition of tin. Fig. 9 shows part of the pseudo-binary phase diagram of the PdCu–Sn system made by X-ray diffraction. There is β-phase at higher temperatures with higher tin contents, up to 900 °C with 1.5% Sn. This is contrasted by the shift towards higher temperatures for the deviation from linearity in the electrical resistivity curve in Fig. 1.

Fig. 10 shows a line analysis of a two-phase area with 1.5% Sn at 800 °C, where tin is clearly concentrated in the β-phase. This indicates that tin is concentrated in and stabilizes the β-phase.

Tin has the lowest melting point of all the alloying elements concerned, and so most easily diffuses into the alloy elements. The maximum electrical resistivity increases with tin content, and may be a result of clusters of tin-rich compounds at the grain boundary, resulting in acceleration of the ordering reaction.

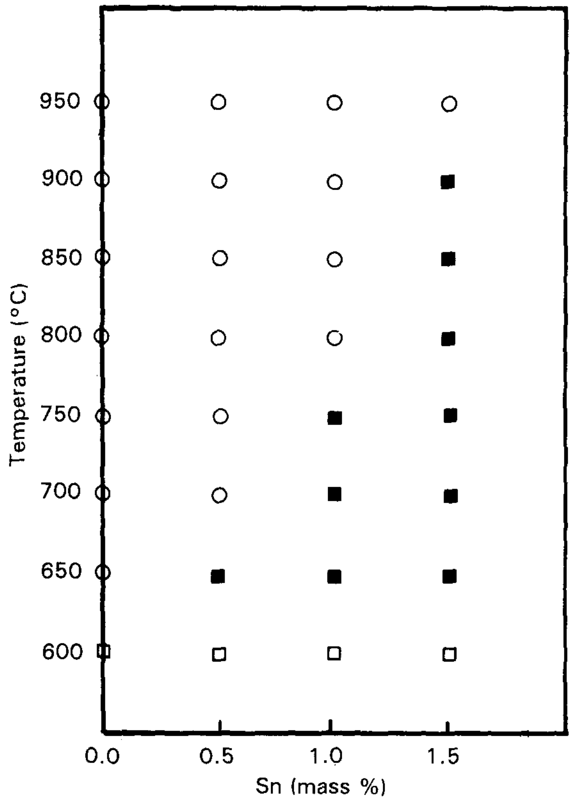

Figure 9 The phase diagram of the pseudo-binary phase diagram of the PdCu–Sn system. (○) α, (■) α + β, (□) β.

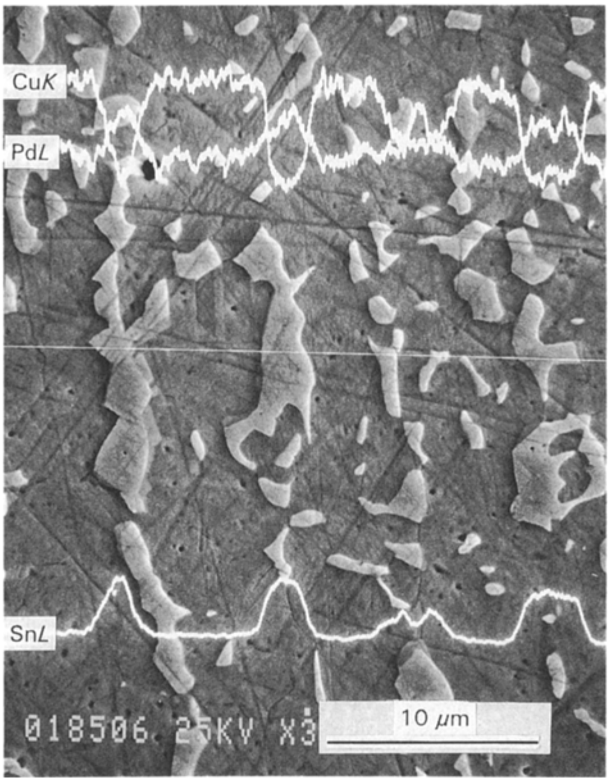

Figure 10 Line analysis of the two-phase area in alloys with 1.5% Sn added, at 800 °C.

The lattice constants of the disordered solid solution, and the ordered phase, were measured to determine why ordering in the alloy with 1.0% Sn is accelerated the most.

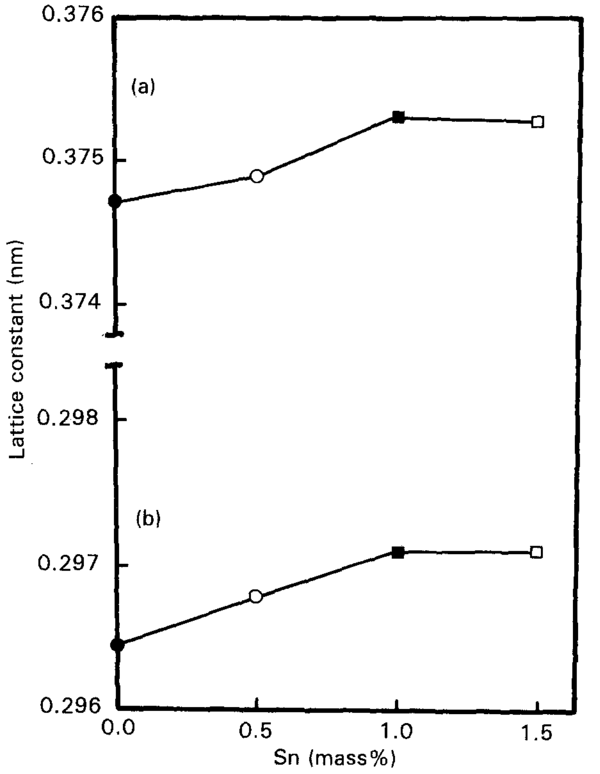

Figure 11 Change in the lattice constant of (a) solution-treated alloys (α-phase), and (b) alloys aged at 300 °C for 3 h (β-phase).

Fig. 11 shows the lattice constants of the solution-treated alloy, and that aged at 300 °C for 3 h. The lattice constant of the solution-treated alloy has a 0 2 4 peak of f c c type, and the β phase aged at 300 °C for 3 h has a 2 3 1 peak of CsCl type. The lattice constants of both phases increase up to 1.0% Sn, after which they remain stable. Here the theoretical lattice constants of the α- and β-phases with 1.5% Sn added should be larger than the values for 1.0% Sn (Fig. 9); the experimental result was the same. This is considered to be due to precipitation of β-phase during quenching with the solution treatment. The β-phase precipitated during quenching is copper-poor concentrated tin as shown in Fig. 10. It may be assumed that the composition of the disordered solid solution is copper-rich. Therefore, the composition of the disordered solid solution shifts to the two-phase area on addition of 1.5% Sn. It is reported that the ordering of the two phase area of PdCu ordered alloy is retarded [5].

4. Conclusions

The effects of tin addition on the ordering process in PdCu ordered alloys were investigated by electrical resistivity, optical microscopy, hardness tests, X-ray diffraction, and electron probe microanalysis.

1. The ordering process is accelerated by tin addition, and greatest acceleration being with 1.0% Sn.
2. The effect of tin addition on the ordering process may be explained by the easier formation of ordered nuclei.
3. The phases are stable up to 900 °C with 1.5% Sn added.

References

1. I. KAWASHIMA, Y. KANZAWA, Y. ARAKI and H. OHNO, *J. Jpn. Inst. Met.* **53** (1989) 14.
2. H. ISAKA, *J. Jpn. Soc. Dent. Appar. Mater.* **28** (1977) 137.
3. S. TANAKA, *ibid.* **21** (1980) 263.
4. I. KAWASHIMA, Y. ARAKI and H. OHNO, *J. Mater. Sci.* **26** (1991) 1113.
5. T. SHIRAISHI, *J. Jpn. Soc. Dent. Appar. Mater.* **22** (1981) 229.
6. M. HANSEN, "Constitution of Binary Alloys", 2nd Edn (McGraw-Hill, New York, 1958) p. 612.
7. K. OSAMURA, M. KITAGAWA, M. TAKEDA and Y. MURAKAMI, *J. Jpn. Inst. Met.* **42** (1978) 986.

Received 11 August 1992
and accepted 4 January 1993