JOURNAL OF MATERIALS SCIENCE 28 (1993) 3496–3500

Effects of pre-ageing and cold working on grain-interior and grain-boundary reactions of Ag–Pd–Cu 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 pre-ageing and cold working on grain-interior and grain-boundary reactions of Ag–Pd-Cu alloys were investigated by electrical resistivity measurements, hardness tests, and optical microscopic observations. Hardness values of the grain interior after the final thermo-mechanical treatment increased 20%–30% above the values after conventional ageing. The hardness values of alloys preaged at 400 °C for 1 min and then cold worked at 30% are the highest ($H_V = 320$).

1. Introduction

Thermo-mechanical treatment including age-hardening treatment and cold working is used to strengthen aluminium - [1–3] and copper-based [4] alloys. It is well known that the final thermo-mechanical treatment (FTMT), where precipitates are finely dispersed by preageing and cold working, strengthens ductile materials considerably [5].

It has been shown that grain-interior reactions which cause hardening, occur before the grain-boundary reaction in Ag–Pd–Cu alloys [6]. With age, grain-boundary precipitates ("nodules") are formed in the alloys, resulting in poorer corrosion resistance and poorer mechanical properties. If the maximum hardness value is reached by the final thermo-mechanical treatment before grain-boundary reactions occur, it is speculated that both strength and corrosion resistance may increase. Imai *et al.* [7] has reported the thermo-mechanical treatment of Ag–Pd–Cu alloys, but the mechanism of the strengthening has not been clearly established.

In this paper, the effects of both preageing and cold working on grain-interior and grain-boundary reactions of Ag–Pd–Cu alloys was investigated by electrical resistivity measurements, hardness tests, and optical microscopic observations.

2. Materials and methods

The alloys used in this study were Ag–25 mass % Pd–10% Cu. The alloys were prepared from materials of 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. As the weight loss in the melting process was less than 0.1%, chemical analysis after melting was not carried out. The ingots were cold worked slightly and homogenized at 900 °C for 2 h.

Block specimens, 5 mm × 5 mm × 10 mm, for optical microscopic observations and hardness measurements, and wire specimens of 1 mm × 100 mm for electrical resistivity measurements were prepared by cold working. For the solution treatment, the specimens were kept at 900 °C for 2 h before they were quenched in ice–water.

Fig. 1 describes the conditions of the final thermo-mechanical treatment and conventional ageing treatments. The two preageing treatments were selected to change the dispersed state of grain-interior precipitates widely. One preageing condition (150 °C, 7 days) was selected because the Guinier–Preston (G–P) zone and short-range order area were finely dispersed and the electrical resistivity reached a maximum. The other treatment (400 °C for 1 min) was selected because the precipitates were fully grown and the hardness was maximum according to a previous report [6]. The samples were cold worked 0%, 10% and 30% by a roller.

The specimens were finally aged at 300, 400 or 500 °C in a salt bath until the grains were surrounded by nodules.

Electrical resistivity was measured during continuous heating from room temperature to 850 °C at a constant rate of 2 °C min^{-1} by the potentiometric method. 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 25 g load using a micro-Vickers hardness tester to distinguish the grain interior from the nodules. The hardness values were averages of ten indentations. Area fractions of the nodules were measured digitally from microphotographs (× 400).

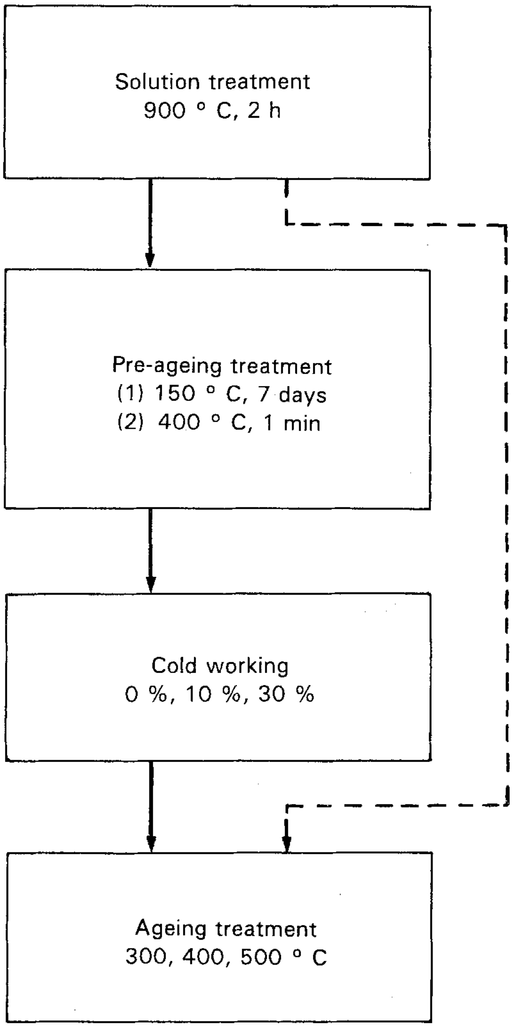

Figure 1 Flow chart of the final thermo-mechanical treatment of Ag–Pd–Cu alloys. (– – –) Conventional treatment.

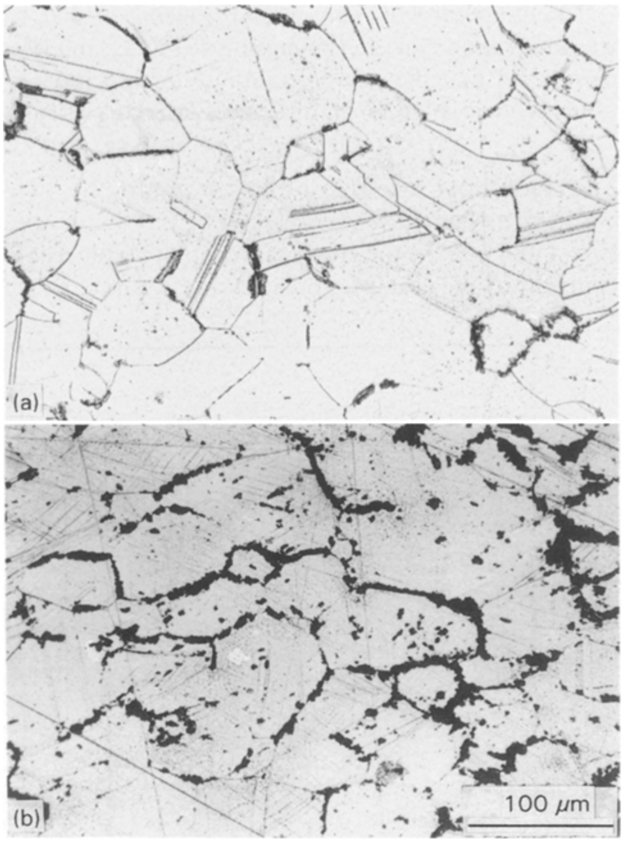

Figure 2 Microstructure of alloys finally aged at 300 °C for 10^3 min. (a) No cold working after 400 °C preageing. (b) 30% cold worked after 400 °C preageing.

3. Results and discussion

3.1. Optical microstructures

Fig. 2 shows the microstructures of alloys that were preaged at 400 °C for 1 min, and finally aged at 300 °C for 10^3 min (a) without cold working and (b) with 30% cold working. In Fig. 2a, the growth rate of the nodules is different at each grain boundary and depends on its inclination. In Fig. 2b, however, the nodules appear at all grain boundaries and also in grain interiors. The changes in the microstructures of alloys preaged at 150 °C was similar to the 400 °C preageing treatment.

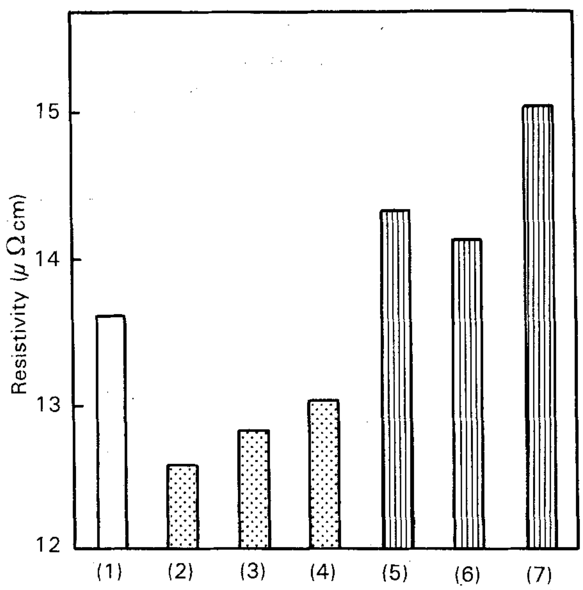

Figure 3 Electrical resistivity before final ageing of various samples: (1) quenched only, (2) preaged at 400 °C, (3) 10% cold worked after preageing at 400 °C, (4) 30% cold worked after preageing at 400 °C, (5) preaged at 150 °C, (6) 10% cold worked after preageing at 150 °C, (7) 30% cold worked after preageing at 150 °C.

3.2. Electrical resistivity before final ageing

Fig. 3 shows the electrical resistivity of each alloy before the final ageing, column 1 is the value with solution treatment. The electrical resistivity values with 0%, 10% and 30% cold working after preageing at 400 °C are shown in columns 2–4, respectively. The electrical resistivity after preageing at 400 °C was lower than the values after solution treatment and increased with increasing degree of cold working. The values of 0%, 10% and 30% cold working after preageing at 150 °C are shown in columns 5–7, respectively. Electrical resistivity without cold working is higher than the values with the solution treatment. However, the electrical resistivity is lower after 10% cold working and higher after 30% cold working. As shown by columns 2 and 5, the electrical resistivity after preageing at 150 °C is higher than the values with the solution treatment. This is considered to be caused by the G–P zone and short-range ordering, as will be discussed later.

The electrical resistivity after preageing at 400 °C was lower than that after preageing at 150 °C, and it is considered that the size of grain-interior precipitates of the former is larger than those of latter.

3.3. Electrical resistivity measurement with rising temperatures

Figs 4 and 5 show the electrical resistivity with rising temperatures for samples preaged at 150 and 400 °C,

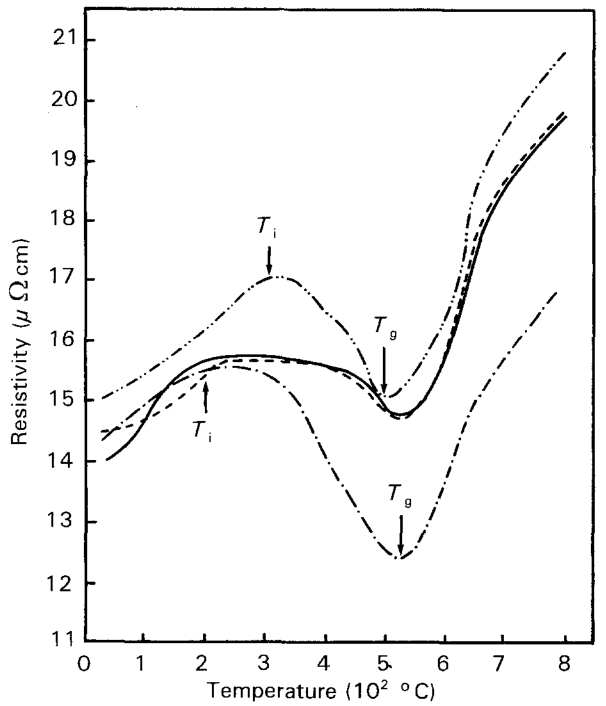

Figure 4 Electrical resistivity changes with increasing temperature in alloys preaged at 150 °C. For key, see Fig. 3: (——) (1), (– – –) (5), (— · —) (6), (— · · —) (7). Grain-interior reactions begin at T_i. Grain-boundary reactions become active at T_g.

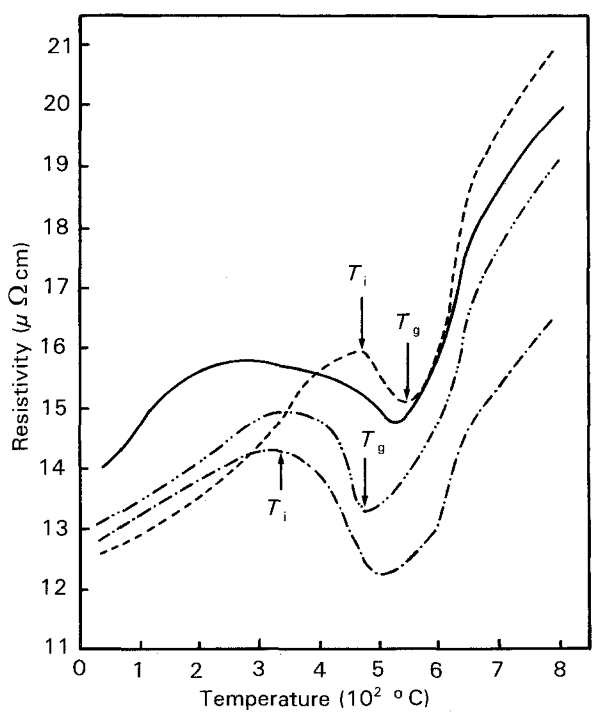

Figure 5 Electrical resistivity changes with increasing temperature in alloys preaged at 400 °C. For key, see Fig. 3: (——) (1), (– – –) (2), (— · —) (3), (— · · —) (4). Grain-interior reactions begin at T_i. Grain boundary reactions become active at T_g.

and then cold worked. The temperature where grain-interior reactions begin is about 200 °C (T_i) at 0% and 10% cold working in Fig. 4, and with 30% cold working it is about 300 °C (T_i). This indicates that the temperature at which grain-interior reactions begin, becomes higher with more cold working following preageing at 150 °C. It suggests that the grain-interior reaction is retarded by cold working.

The minimum temperature reflecting active grain-boundary reactions are about 520 °C (T_g) with no cold working, and 500 °C (T_g) with 30% cold working. This indicates that the grain-boundary reaction is accelerated by cold working.

In Fig. 5, the temperature where deviation from linearity begins is about 450 °C (T_i) with no cold working, and with 10% cold working it is about 320 °C (T_i). The minimum temperature (T_g) reflecting active grain-boundary reactions is below 500 °C (T_g) and shifts to lower temperatures with more cold working. This suggests that both grain-interior and grain-boundary reactions are accelerated in alloys preaged at 400 °C.

3.4. Electrical resistivity, hardness, and area fraction of nodules

Fig. 6 shows change in (a) electrical resistivity, (b) hardness, and (c) area fraction of nodules, after final ageing at 300 °C. The case for conventional ageing treatment is also shown. In Fig. 6a, ρ_0 and ρ are specific resistivities with the solution treatment and at the final ageing, respectively. The time when the electrical resistivity rapidly decreased shifted to the very beginning (10^0 min) with increasing degree of cold working in the alloys preaged at 150 °C. In Fig. 6b, the initial hardness of grain interiors with solution treatment is about 130 (= H_V). The hardness of grain interiors with 400 °C preageing was about 290 (= H_V) by 30% cold working only, and this hardness increased to about 320 (= H_V) by the final ageing treatment. The maximum hardness with the conventional ageing treatment was 260. The samples which were preaged at 150 °C without cold working age-hardened quickly from 195 to 260 (= H_V). With 150 °C preageing, the hardness increased by cold working, while grain-interior hardening was retarded at the start of ageing. This contrasts with the shift in the deviation from linearity on the electrical resistivity curve to higher temperatures and the retardation of grain-interior reactions (Fig. 5). The hardness of the nodule area of all the samples was about 190, and this value was not influenced by preageing or cold working.

The area fraction of nodules (Fig. 6c), the grain boundary reaction, is accelerated by increasing degree of cold working and there is a little effect of preageing. But, even though the final thermo-mechanical treatment has some effect, it is not difficult to harden grain interiors without the growth of nodules and it is simple to apply in practice.

Figs 7 and 8 show changes in (a) electrical resistivity, (b) hardness, and (c) area fraction of nodules aged at 400 and 500 °C. The hardness values of the grain

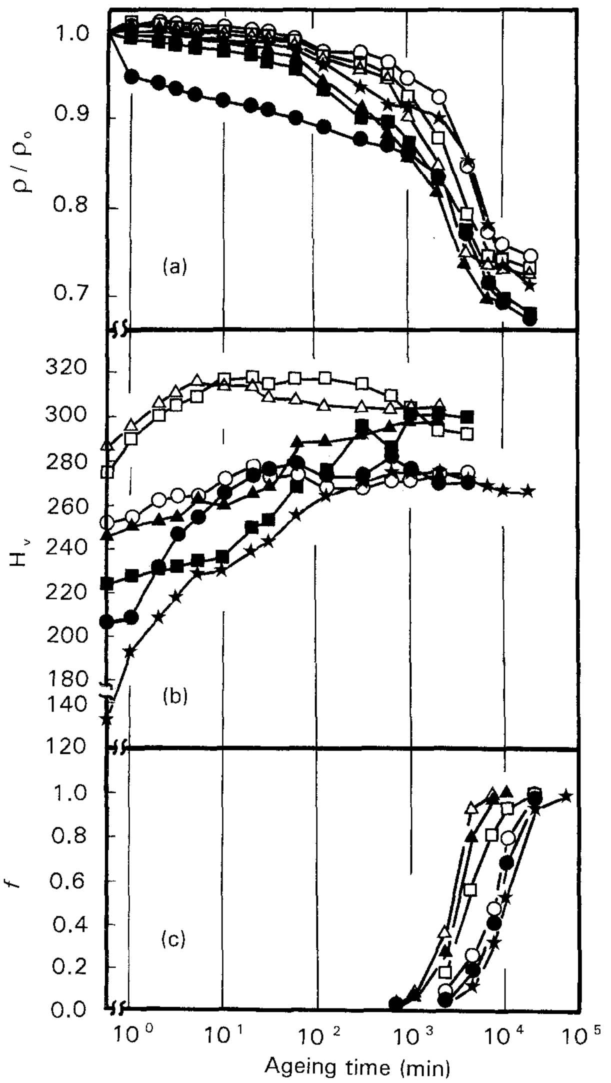

Figure 6 (a) Electrical resistivity, (b) hardness, and (c) area fraction of nodules at 300 °C final ageing and various degrees of cold working after preageing. Samples as in Fig. 3: (★) (1), (○) (2), (□) (3), (△) (4), (●) (5), (■) (6), (▲) (7).

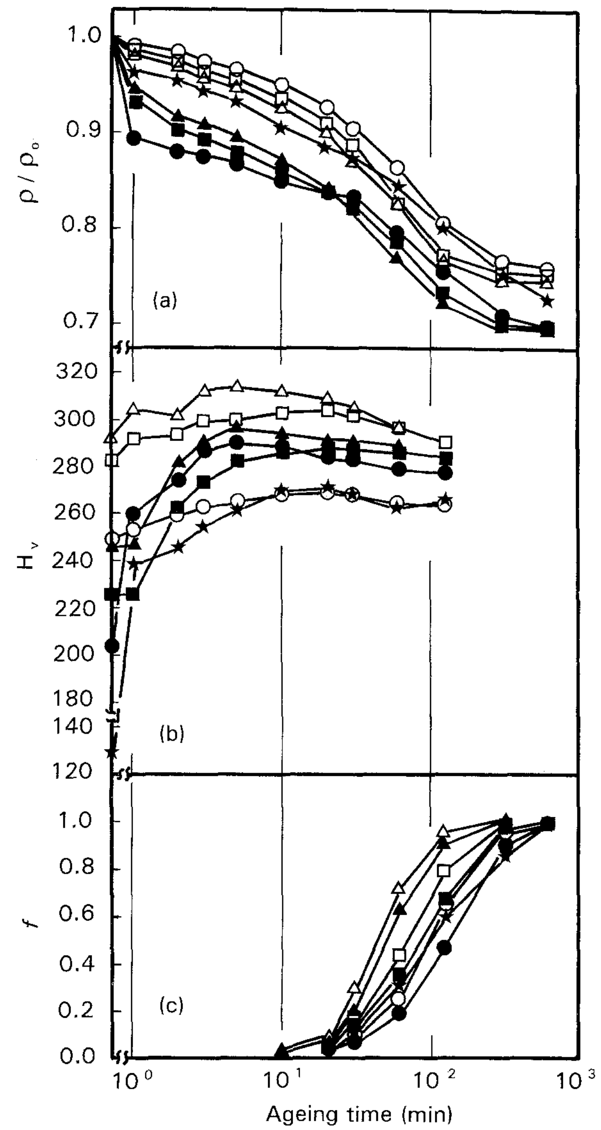

Figure 7 (a) Electrical resistivity, (b) hardness, and (c) area fraction of nodules at 400 °C final ageing and various degrees of cold working after preageing. For key, see Fig. 6.

interiors subjected to the final thermo-mechanical treatment increased about 20%–30% above the values after the conventional ageing treatment.

The grain-boundary reaction is accelerated for all the ageing temperatures with increasing degree of cold working. With higher final ageing temperatures, there is some slowing down in the acceleration of grain-boundary reactions by preageing.

3.5. Effects of preageing and cold working on the grain-interior reaction

The electrical resistivity of samples preaged at 150 °C without cold working is higher than the values after the solution treatments (Fig. 3). Here, it is considered that the increase in electrical resistivity was caused by the G–P zone and short-range ordering [8, 9]. Although electrical resistivity of the alloys may generally be increased by cold working, the alloys with 10% cold working after preageing at 150 °C showed a decrease (Fig. 3).

There are a few reports [4, 10] where electrical resistivity of alloys was decreased by cold working, and one reason suggested by Osamura *et al.* [10] relates to the relationship between the zone radius of the G–P zone or the short-range ordering and the numbers per unit volume.

The decrease in electrical resistivity by 10% cold working is also explained by their model. The conditions of preageing treatments (150 °C, 7 days) were set to achieve the maximum effect, as indicated by preparatory experiments of electrical resistivity, which is related to the G–P zones, the short-range ordering, and the dispersion state. When the structures with the dispersed state are cold worked they become more finely dispersed by motion and by a multiplication of dislocations. As a result, it is considered that the electrical resistivity decreased.

The lack of increase in hardening during final ageing at 300 °C within the first 10 min for alloys with cold working after preageing at 150 °C can be explained similarly (Fig. 6b). That is, the slowing down of hardening occurs as the G–P zone and short-range order area, that is finely dispersed by cold working, starts to grow again to a size where dislocations are effectively obstructed from movement.

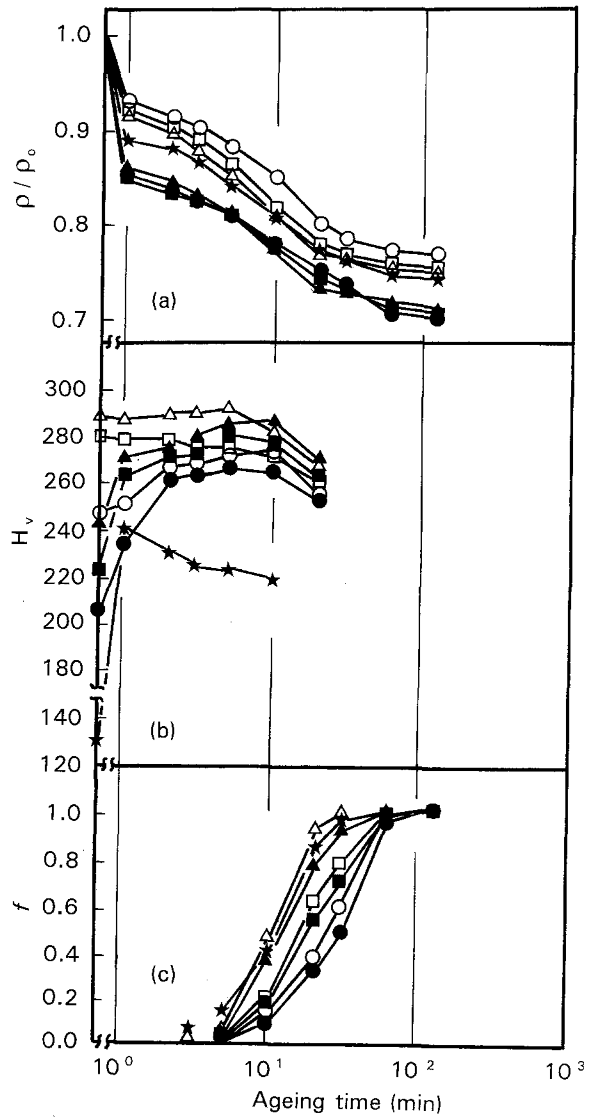

Figure 8 (a) Electrical resistivity, (b) hardness, and (c) area fraction of nodules at 500 °C final ageing and various degrees of cold working after preageing. For key, see Fig. 6.

3.6. Effect of cold working on the grain-boundary reaction

The electrical resistivity measurements with rising temperatures show clearly that the minimum electrical resistivity, where the grain-boundary reaction is active, shifts to lower temperatures (Figs 4 and 5) with cold working. The change in area fraction of nodules, also showed that the grain-boundary reaction was accelerated with increased cold working (Fig. 7). This allows a discussion of the reasons for the grain-boundary reaction acceleration caused by cold working.

A previous paper [6] has shown that internal strains resulting from precipitation in grains is not the driving force for nucleation of nodules and that the grain-boundary reaction is independent of the stress generated internally. Therefore, it may be considered that the strain energy generated by cold working is not the driving force for the grain-boundary reaction either.

It has been reported [11] that the nodules grow more easily at high angles to the grain boundary, where the potential energy is higher than at low grain-boundary angles or at coincident lattice areas. It is considered that the potential energy of the grain boundary changes from low values, where nodules nucleate with difficulty, to high values with more dislocations as the degree of cold working increases. In addition, the dislocations occur both at the subgrain boundary and as microdefects in the grain-interior. Therefore, the interfacial energy increases with cold working, and it is considered that this makes nucleation of nodules in the grain interior easier.

4. Conclusions

The effects of preageing and cold working on grain-interior and grain-boundary reactions of Ag–Pd–Cu alloys were investigated by electrical resistivity measurements, hardness tests, and optical microscopic observations. The following results were obtained.

1. Hardness values of the grain interior after the final thermo-mechanical treatment increased about 20%–30% above the values of aged-only specimens.
2. The grain-boundary reaction was accelerated by cold working after 150 °C preageing, but here the grain-interior reaction was retarded.
3. The hardness of the alloys which were preaged at 400 °C for 1 min and then 30% cold worked was the highest ($H_V = 320$) of all.

References

1. T. UNO and Y. BABA, *J. Jpn Inst. Metals* **45** (1981) 405.
2. M. SUGAMATA, J. KANEKO, and K. AOKI, *ibid.* **48** (1984) 655.
3. E. DI RUSSO, M. CONSERVA, F. GATTO and H. MARKUS, *Met. Trans.* **4** (1972) 1133.
4. H. TONDA, M. NAGAHISA, O. IKEGAMI, and T. KAWASAKI, *J. Jpn Inst. Metals* **47** (1983) 1075.
5. H. KOSUGE and K. TAKEUCHI, *Bull. Jpn Inst. Metals* **21** (1982) 104.
6. I. KAWASHIMA, Y. KANZAWA, Y. ARAKI and H. OHNO, *J. Jpn Inst. Metals* **53** (1989) 14.
7. M. IMAI, Y. KANZAWA, K. YASUDA and H. ISAKA, *J. Jpn Soc. Dent. Appar. Mater. Special Issue* (1969) 11.
8. M. OHTA, K. HISATSUNE and M. YAMANE, *J. Less-Common Metals* **65** (1979) 11.
9. K. YASUDA, *J. Jpn Soc. Dent. Appar. Mater.* **10** (1969) 156.
10. K. OSAMURA, M. KITAGAWA, M. TAKEDA and Y. MURAKAMI, *J. Jpn Inst. Metals* **42** (1978) 986.
11. PETER HAASEN, "Physickalische Metallkunde", 1st Edn (AGUNE, Tokyo, 1981) p. 300.

Received 7 February and accepted 8 December 1992