

Effect of heat treatment on precipitation behaviour in a Cu-Ni-Si-P alloy

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The effects of applying different solution and ageing conditions on the electrical resistivity and precipitation behaviour of a Cu-1.3Ni-0.3Si-0.03P (wt%) alloy were studied. The electrical resistivity of solution-treated material is greatly reduced, by about 50%, by the ageing processes. The reduction in resistivity is due to depletion of solute atoms from the copper matrix by the formation of precipitates. Double ageing peaks appeared during isothermal ageing due to the formation of Ni₃P and Ni₂Si precipitates. The first maximum, due to the precipitation of Ni₃P, appeared at about 1 h of ageing time, while the second peak, due to Ni₂Si, appeared at around 10 h of ageing time when aged at 450°C. The precipitate Ni₃P forms early and the alloy starts to over-age before Ni₂Si precipitates and the alloy reaches maximum hardness. The maximum hardness produced by the precipitations of Ni₃P and Ni₂Si decreased with increasing ageing temperature from 450 to 550°C. The time to reach the maximum hardness due to Ni₃P precipitation became shorter, while that of Ni₂Si became longer, as the solution treatment temperature increased from 780 to 1020°C. The apparent activation energy for Ni₂Si precipitation was found to be about 80 kJ mol⁻¹ while that for Ni₃P precipitation was about 25 kJ mol⁻¹.

1. Introduction

Copper alloy strips used for semiconductor lead-frames to which silicon chips are bonded are required to possess high strength, good electrical conductivity and optimum elongation [1]. The requirement of high strength is becoming increasingly important with automation of the semiconductor packaging process. However, the typical penalty paid for increasing the strength is lower electrical conductivity and decreased elongation. The development of a new high performance copper-base alloy as a semiconductor lead-frame material possessing very high strength (610 MPa), good electrical conductivity, and optimum elongation (6%) has recently been reported [2, 3]. The nominal composition (wt%) of the alloy, PMC-102, is Cu-1Ni-0.2Si-0.03P. The electrical conductivity of the alloy exceeds 58% International Annealed Copper Standard (the value of 100% IACS at 20°C is equal to a resistivity of 0.017241 Ω mm² m⁻¹) [4]. The alloy is produced in usable condition by applying a series of thermomechanical processes after hot rolling.

The purpose of this work was to investigate the effect of applying different solution and ageing conditions on the precipitation behaviour in the alloy PMC-102. Electrical resistivity measurements, microhardness measurements, X-ray diffraction, differential thermal analysis (DTA), transmission electron micro-

scopic (TEM) examination, and energy-dispersive X-ray spectroscopy (EDS) were performed to characterize the precipitates and kinetics of the precipitation reactions in the alloy.

2. Experimental procedures

The alloy PMC-102 for this study was provided by the Poongsan Metal Corporation (Korea). Copper alloy plate 3 mm in thickness was received in the cold-rolled condition; this is an intermediate step in the manufacturing process. The chemical composition (wt%) of the alloy used in this work was Cu-1.3Ni-0.3Si-0.03P. The cold-rolled materials were solution treated at 1020, 900 and 700°C for 1 h, followed by water quenching. The solution-treated samples were aged at temperatures of 450, 500 and 550°C for different ageing times. The ageing time varied from 0.1 to 500 h.

The microstructures were examined by optical and electron microscopy. For optical examination, the polished samples were etched in a solution of 25 ml H₂O + 25 ml NH₄OH + 10 ml 3% H₂O₂. Thin foils for TEM examination were prepared by chemical thinning, followed by jet polishing. A solution of 60 ml HNO₃ + 40 ml H₂O was used for chemical thinning. Jet polishing was conducted in a solution of 70 ml H₃PO₄ + 30 ml H₂O at a current density of 0.5 to 1 A cm⁻² and 50 to 60 V.

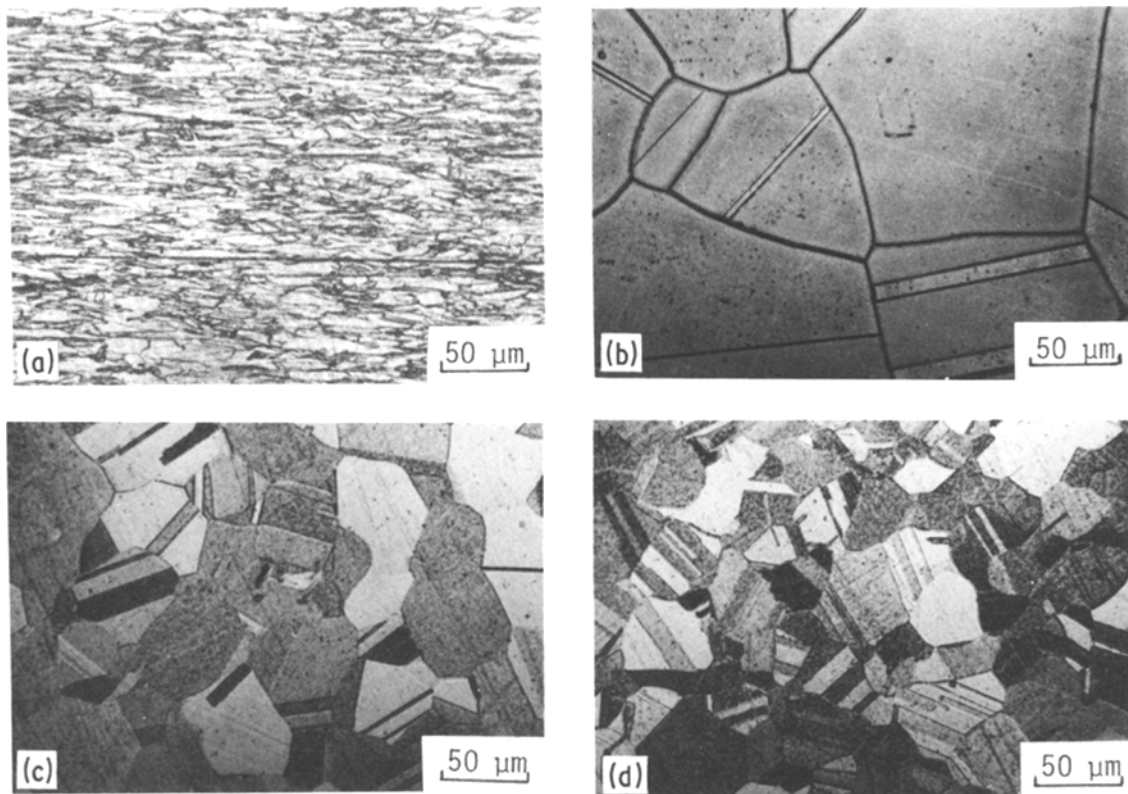


Figure 1 Optical microstructures of Cu–Ni–Si–P alloy: (a) cold-rolled state; (b, c, d) solution-treated at 1020, 900 and 780° C.

Specific electrical resistivity measurements were conducted as a function of ageing time for the various combinations of solution-treatment and ageing temperature. The electrical resistivity measurements were performed at -196°C using a four-probe potentiometric technique.

In order to study the formation of double ageing peaks, DTA was performed for samples with phosphorus (PMC-102 alloy) and without phosphorus. The phosphorus-free alloy (Cu–1.3Ni–0.3Si) was prepared by induction melting, followed by hot and cold rolling. DTA measurements were conducted from 0 to 1000°C at a heating rate of $5^{\circ}\text{Cmin}^{-1}$. The reference material used in the DTA study was α -alumina. X-ray diffraction studies were performed using nickel-filtered $\text{CuK}\alpha$ radiation at 30 kV and 20 mA at a scan rate of $2\theta = 0.5^{\circ}\text{min}^{-1}$. EDS was employed to analyse the relative spatial distribution of phosphorus and silicon after the ageing treatments. Microhardness measurements were made on the polished surfaces using a Vickers hardness tester for samples heat-treated at different solution and ageing temperatures as a function of ageing time.

3. Results and discussion

The optical microstructure of the as-received material is shown in Fig. 1a. Since it was in the cold-rolled state the material had a high degree of preferred orientation. Figs. 1b, c and d show the microstructures after solution treatment at 1020, 900 and 780°C , respectively. Complete recrystallization followed by grain growth occurred, the grain size increasing with increasing solution-treatment temperature. The ASTM grain sizes were found to be 5, 7, and 8 for the solution treatment temperatures of 1020, 900 and

780°C , respectively. Numerous annealing twins formed during solution treatment.

Fig. 2 shows the specific electrical resistivity as a function of ageing time for ageing at 500 and 550°C . The electrical resistivity decreased continuously with ageing time. It decreased by about 50% upon ageing at 500°C after 128 h of ageing, as shown in Fig. 2a. The effect of solution-treatment temperature on the resistivity change was more pronounced at 550°C than at 500°C , as shown in Fig. 2b.

Precipitation hardening is an important strengthening process in leadframe alloys since it generally increases the electrical conductivity as well as the strength. The mechanism of increasing electrical conductivity upon ageing in precipitation-hardened alloys was explained early by Geisler [5]. Electrical conductivity depends on the mobility of free electrons in the lattice. The increase of electrical conductivity on ageing is due to the removal of dissolved solution elements from the copper matrix by the formation of precipitates. The conductivity depends on the rate of transport of solute atoms from the matrix to the precipitates. It also depends on the change of strain energy between the matrix and precipitates during the ageing process. It is worthwhile here to point out that in Fig. 2 there is an inflection point at about 1 h of ageing time. This phenomenon may indicate that more than one reaction takes place in the Cu–Ni–Si–P alloy.

The results of the microhardness measurements as a function of ageing time at 450, 500 and 550°C are shown in Fig. 3. Double ageing peaks occurred upon ageing, independently of the different solution treatment temperatures. The first peak formed after 1 h of ageing time, and the second one appeared at about

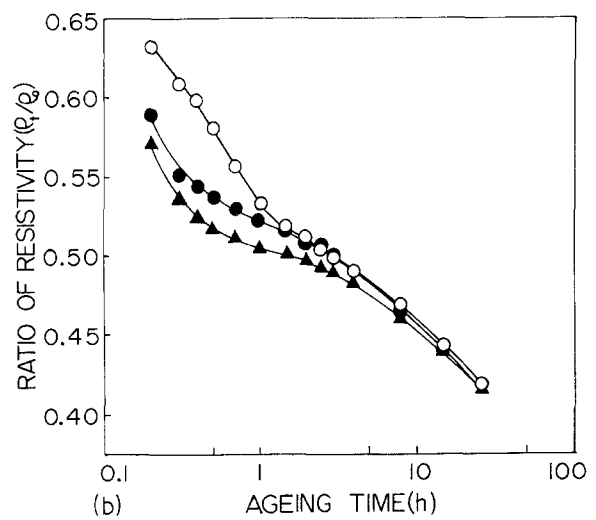
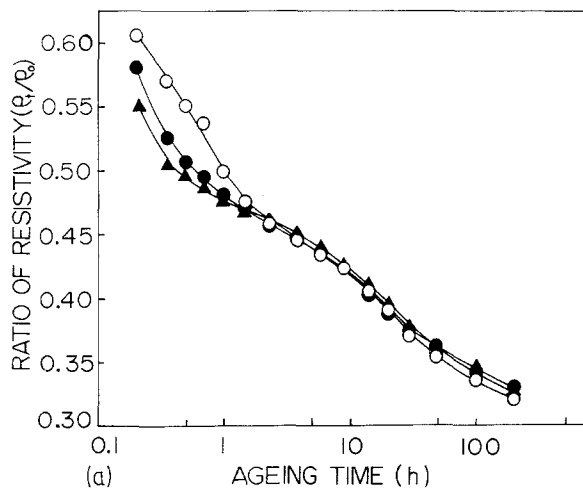


Figure 2 (a) Specific electrical resistivity against ageing time, aged at 500°C, after solution treatment at (▲) 1020, (●) 900 and (○) 780°C; (b) as (a) but aged at 550°C.

10 h of ageing at 450°C, as shown in Fig. 3a. The magnitude of the first peak decreased with increasing ageing temperature. The time to reach the first maximum became shorter, while the time to reach the second maximum became longer, as the solution-treatment temperature increased from 780 to 1020°C. The double hardness peaks may be related to the formation of two different kinds of precipitates during ageing.

Fig. 4 shows the X-ray diffraction patterns taken from the sample heat-treated at 1020°C and aged at 450°C for different ageing times. The X-ray diffractometer traces showed the presence of orthorhombic

Ni₂Si precipitate, but no other precipitates were detected. Revina *et al.* [6] reported the formation of disc-shaped orthorhombic Ni₂Si precipitates in a Cu-2.8Ni-1.38Si alloy aged at 500°C for 4 h. Voloshko *et al.* [7] have recently reported the formation of Ni₃P and Ni₂P precipitates in a Cu-1.1Ni-0.13P alloy aged at around 500°C. It is possible that some kinds of Ni-P precipitate formed in the Cu-1.3Ni-0.3Si-0.03P alloy, but their presence might not be detected by X-ray diffractometry due to the very small phosphorus content (0.03%) in the alloy.

The results of DTA studies of the phosphorus containing Cu-alloy, PMC-102, and the phosphorus-free alloy (Cu-1.3Ni-0.3Si) are given in Fig. 5. The samples for DTA were solution-treated at 1020°C followed by water quenching. Curve 1 (solid line) is for the phosphorus-containing alloy, and curve 2 (dashed line) for the phosphorus-free alloy. Curve 1 reveals two strong exothermic peaks, while Curve 2 reveals only one exothermic peak at high temperature. The result indicates that the low-temperature peak of Curve 1 corresponds to some kind of phosphorus

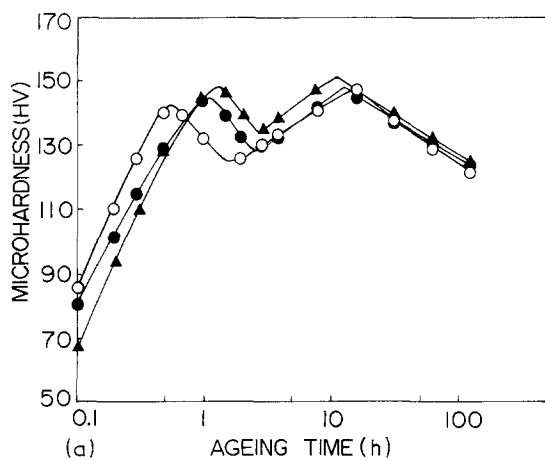
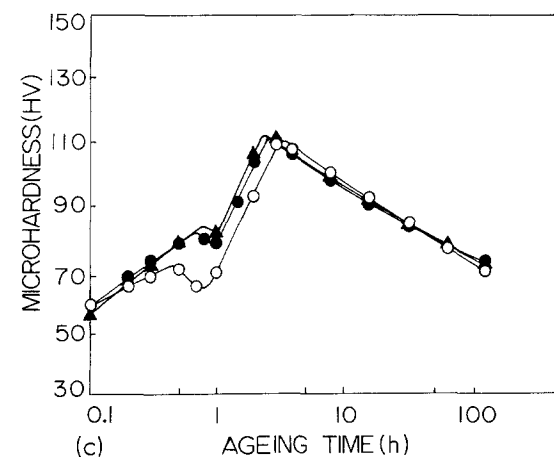
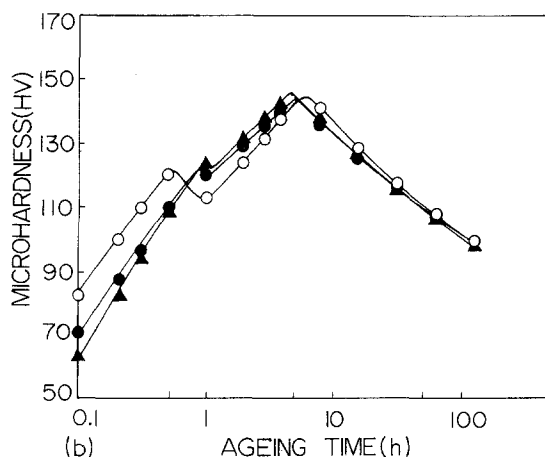


Figure 3 (a) Microhardness against ageing time, aged at 450°C, after solution treatment at (○) 1020, (●) 900 and (▲) 780°C; (b) as (a) but aged at 500°C; (c) as (a) but aged at 550°C.



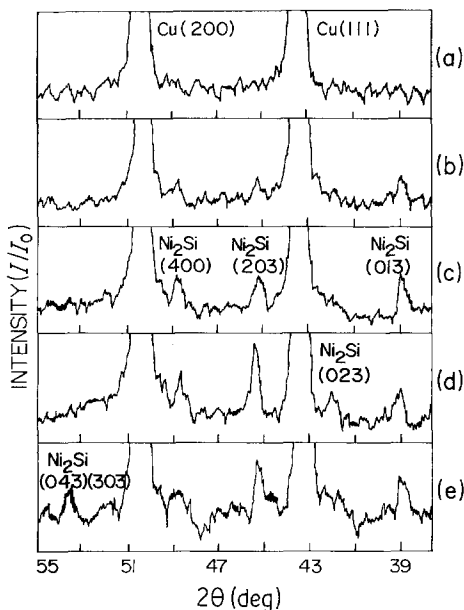


Figure 4 X-ray diffractometer traces of Cu-Ni-Si-P alloy. (a) Solution-treated at 1020°C; also aged at 450°C for (b) 1 h, (c) 8 h, (d) 128 h and (e) 500 h.

precipitate, and the high-temperature peak corresponds to the Ni₂Si precipitate.

In order to identify the precipitates, thin foils were examined by TEM. Fig. 6a is from TEM of a sample water-quenched after solution treatment at 1020°C. Fig. 6b is a dark-field TEM image of a sample aged at 450°C for 1 h. The electron diffraction pattern of the sample is shown in Fig. 6c. Analysis of the diffraction pattern (Fig. 6d) shows that the precipitate reflections present were consistent with those expected from body-centred tetragonal Ni₃P. The orientation relationship is (100)_{Cu} || (111)_{Ni₃P}, [011]_{Cu} || [132]_{Ni₃P}. Fig. 6e is from TEM of a sample aged at 450°C for 127 h, and its diffraction pattern is shown in Fig. 6f. The electron diffraction analysis (Fig. 6g) showed that the major precipitate was orthorhombic Ni₂Si, confirming the results of X-ray diffractometry.

The results of the DTA thermograms and analyses of the precipitates indicate that the double ageing peaks result from the formation of Ni₃P and Ni₂Si precipitates at different ageing times. Ni₃P forms early and over-ages before the precipitation of Ni₂Si produces maximum hardness. For Ni₃P the time to reach maximum hardness decreases as the solution-treatment temperature increases, as shown in Fig. 3. On the other hand, the time to reach the maximum hardness due to Ni₂Si precipitation becomes longer as the solution-treatment temperature increases. The maximum hardness associated with Ni₂Si was not greatly affected by the different solution-treatment temperatures, but that due to Ni₃P decreased with increasing solution-treatment temperature.

Fig. 7 is an Arrhenius plot of time to reach maximum hardness as a function of ageing temperature for the Ni₂Si and Ni₃P precipitates. The apparent activation energies for Ni₂Si precipitation were found to be 84.0, 79.4 and 75.5 kJ mol⁻¹ for solution-treatment temperatures of 1020, 900 and 780°C, respectively. The activation energies for the precipitation of Ni₃P

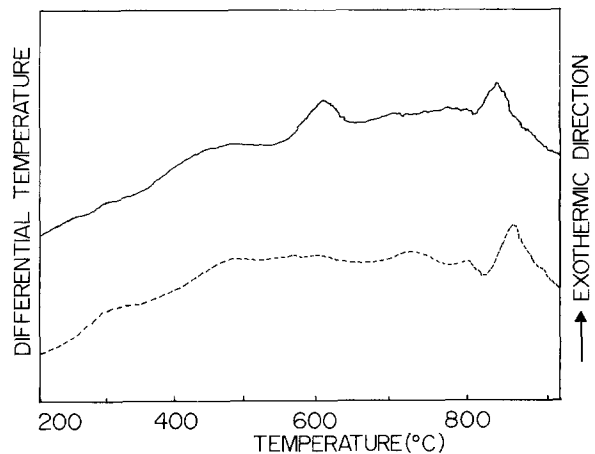


Figure 5 DTA thermograms of Cu-Ni-Si-P and Cu-Ni-Si, solution-treated at 1020°C and water-quenched. (—) Curve 1, Cu-Ni-Si-P; (---) Curve 2, Cu-Ni-Si.

were found to be significantly lower. The apparent activation energies for Ni₃P precipitation were 12.9, 24.0 and 27.2 kJ mol⁻¹ for solution-treatment temperatures of 1020, 900 and 780°C, respectively. The earlier formation of Ni₃P precipitates during isothermal ageing is related to the lower activation energy for Ni₃P precipitation, compared to that of Ni₂Si. The diffusivity of phosphorus in copper is reported to be $1.4 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ [8] and that of silicon in copper is reported to be $4.2 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$ [9] in the vicinity of 500°C. The higher mobility of phosphorus relative to silicon in copper is thus consistent with the earlier formation of Ni₃P relative to Ni₂Si. However, the apparent activation energies for Ni₃P and Ni₂Si precipitations are found to be significantly lower than those of the activation energies of diffusion for phosphorus in copper [7] and silicon in copper [8], 96.2 [8] and 171.6 kJ mol⁻¹ [9], respectively. The reason for the greatly lower values of the apparent activation energies for Ni₃P and Ni₂Si precipitation is unclear at this time.

A qualitative evaluation of the spatial distribution of phosphorus and silicon in the samples was obtained by EDS. The samples solution-treated at 1020°C and water-quenched were aged at 500 and 550°C for 1 and 5 h, respectively. The relative distribution of phosphorus and silicon at grain boundaries (GB), twin boundaries (TB) and in the matrix (MT) was evaluated. Fig. 8a is a diagram showing the relative distribution of phosphorus among GB, TB, and MT under the conditions of ageing at 500°C for 1 h. It shows that Ni₃P formed preferentially at twin boundaries rather than at grain boundaries or in the matrix. In order to find possible nucleation sites in the matrix, the sample was examined by TEM. TEM of a sample water-quenched from 1020°C is shown in Fig. 6a, where dislocations and dislocation loops are visible in the matrix. The dislocations were most likely generated by thermal contraction during rapid quenching from 1020°C. It is possible to form dislocation loops by condensation of excess vacancies existing at the high temperature [10]. The dislocations and prismatic loops could be effective nucleating sites for precipitates in the matrix. As the solution-treatment temperature

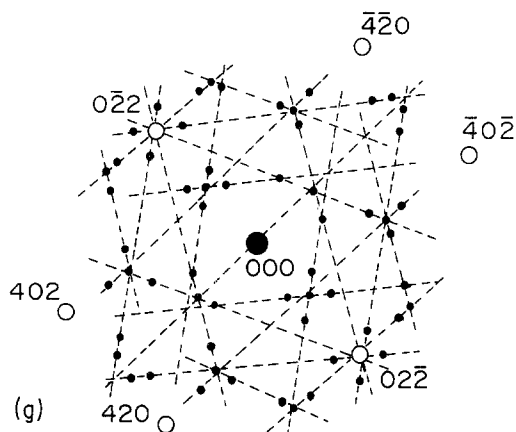
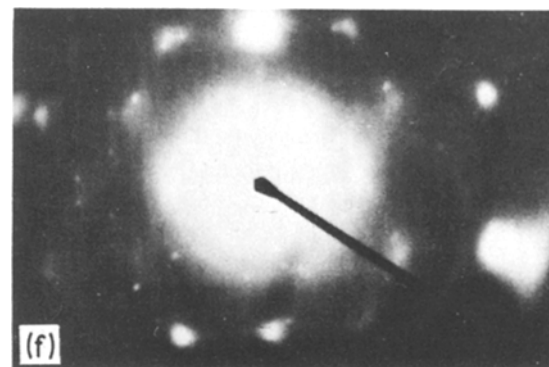
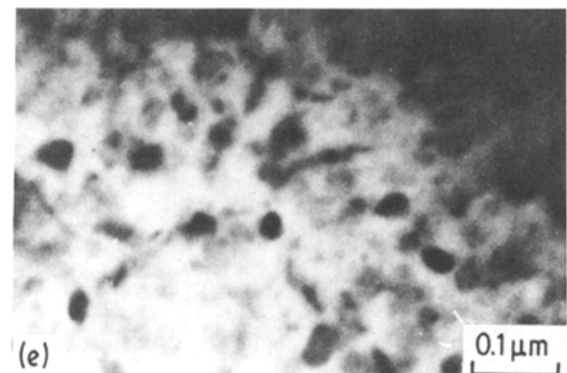
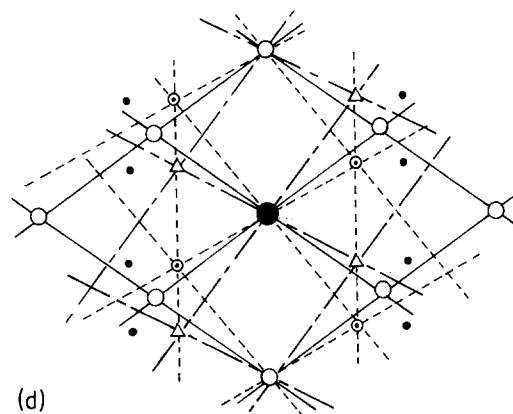
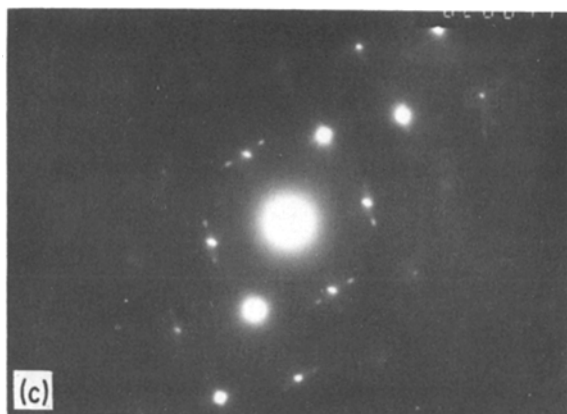
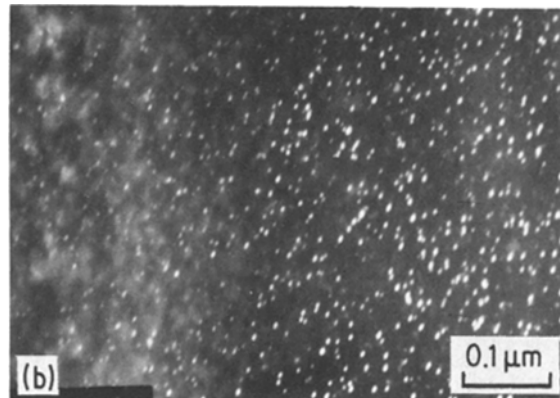
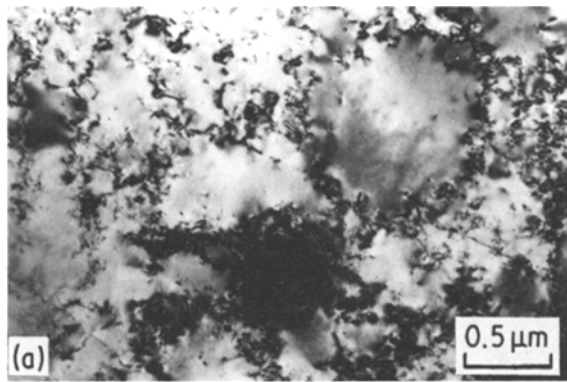


Figure 6 TEM of thin foil samples. (a) Solution-treated at 1020° C and water-quenched. (b) Aged at 450° C for 1 h. (c) Electron diffraction pattern of precipitates in (b). (d) Analysis of the diffraction pattern of (c): (●) double diffraction spot, (○) Ni₃P with [1 3 2] zone axis, (Δ) Ni₃P with [3 1 2] zone axis, (○) [0 1 1] Cu. (e) TEM of sample aged at 450° C for 127 h. (f) Electron diffraction pattern of precipitates of (e). (g) Analysis of the diffraction pattern of (f); (○) [1 2 2], (●) Ni₂Si.

increases from 780 to 1020° C, precipitation of Ni₃P could be expedited (Figs. 3a and b) due to a higher population of heterogeneous nucleation sites.

Fig. 8b shows the relative spatial distribution of silicon among GB, TB and MT under conditions of

ageing at 550° C for 5 h. This corresponds to full precipitation of Ni₂Si (Fig. 3b). The distribution of silicon was relatively uniform compared with that of phosphorus (Fig. 8a), although grain boundaries and twin boundaries were found to be more favourable sites for Ni₂Si precipitates than in the matrix.

4. Conclusions

1. The electrical resistivity of solution-treated material decreases significantly upon ageing.
2. The decrease in resistivity is due to the depletion

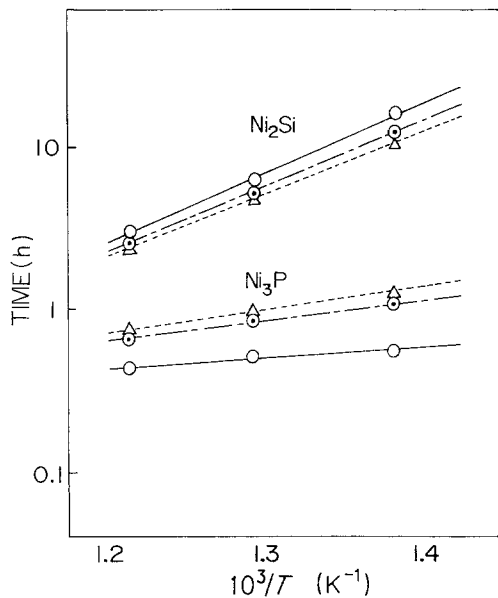


Figure 7 Time to reach maximum hardness against $1/T$ for different ageing temperatures: (○) 1020, (◻) 900 and (△) 700°C.

of solid-solution elements from the matrix by the formation of precipitates.

3. The precipitates are orthorhombic Ni_2Si and body-centred tetragonal Ni_3P in the $\text{Cu-1.3Ni-0.3Si-0.03P}$ alloy.

4. Double ageing peaks appeared during isothermal ageing; the first peak was due to the precipitation of Ni_3P , and the second one was due to that of Ni_2Si .

5. The first peak, due to Ni_3P , formed at around 1 h of ageing time, while the second one, due to Ni_2P , formed at around 10 h in samples aged at 450°C.

6. The maximum hardness associated with the precipitation of Ni_3P decreased with increasing ageing temperature from 450 to 550°C, and the time to reach the maximum became shorter as the solution-treatment temperature increased from 780 to 1020°C.

7. The maximum hardness associated with the precipitation of Ni_2Si also decreased with increasing ageing temperature, but the time to reach the maximum increased as the solution temperature increased.

8. The apparent activation energy for Ni_2Si pre-

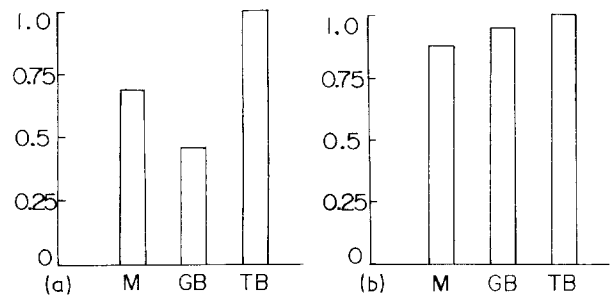


Figure 8 (a) Relative distribution of phosphorus among matrix (MT), grain boundary (GB) and twin boundary (TB) regions aged at 500°C for 1 h. (b) Relative distribution of silicon among MT, GB, and TB, aged at 550°C for 5 h.

cipitation was about 80 kJ mol^{-1} , while that of Ni_3P was about 25 kJ mol^{-1} .

9. Ni_3P formed preferentially at annealing twin boundaries and in the matrix, but the distribution of Ni_2Si precipitates was relatively uniform.

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