Reversible colour change in Cu–Al–Ni alloy ribbon associated with phase transformation

T. MINEMURA, H. ANDOH, I. IKUTA
Hitachi Research Laboratory, Hitachi Ltd, Hitachi 319-12, Japan

The colour change behaviour and its relation to phase transformation of Cu–14 wt% Al–4 wt% Ni alloy ribbon produced by the twin-roller type melt-quenching method were investigated by spectral reflectivity and X-ray diffraction, respectively. This ribbon turns copper-coloured around room temperature on quenching it from a temperature above 1020 K, and turns gold-coloured on ageing it between 670 and 970 K. By repeating these heat treatments, either of the two colours can be acquired interchangeably. The spectral reflectivity also changes with respect to the colour change. The copper-coloured alloy shows a DO_3 structure which is the β_1 phase. The gold-coloured alloy shows a mixed phase of γ_2 (cubic, Cu_9Al_4 compound), and α (fcc, Cu–Al–Ni solid solution) and/or γ_1' which is a martensite of the β_1 phase having a (1 2 1) twinning structure. Therefore, the colour change between copper and gold is due to the solid-state phase transformation between β_1 and γ_2 + (α and/or γ_1') on heat treatment.

1. Introduction

Metals and alloys are specially characterized by their colour and lustre. Due to these properties, some alloys such as the Cu–Zn system (e.g. [1]) are highly favoured as decorative materials. Their colours depend on the electron band structure determined by the crystalline structure [2]. In particular, the optical properties of β-phase alloys have been investigated for the purpose of determining their electron structure [3–5]. Therefore, it should be possible to determine the colour of alloys if their crystalline structure, that is, their phase is controlled by heat treatment. The authors have found that for some alloy systems, around room temperature, two colours can be reversibly produced by selected heat treatment. This paper presents the colour change behaviour of Cu–14 wt % Al–4 wt % Ni alloy, which is known to show the shape memory effect associated with thermal elastic martensitic transformation [6], and discusses it in relation to phase transformations caused by heat treatment.

2. Experimental procedure

A mixture of 99.99% Cu, 99.99% Al and 99.8% Ni was melted in a high-frequency induction furnace under an argon atmosphere to prepare a master alloy with the composition of Cu–14% Al–4% Ni. The melt was sucked up into quartz tubes (inner diameter: 4 mm) and solidified there. In order to discuss the colour change behaviour, Cu–20% Al–4% Ni, Cu–13% Al–4% Ni and Cu–3% Al–4% Ni alloys were also made by the same process.

The alloys were formed into a ribbon which can be rapidly quenched because of its small heat capacity and can be easily used for reflectivity measurements due to its flat surface. Ribbon specimens with a thickness of about 80 μm and width of 5 mm were produced by a twin-roller type melt-quenching apparatus [7], which is suitable for making ribbons of less formable materials. The chemical compositions of the ribbons are given in Table I.

After mechanical polishing to smooth the ribbon surfaces, specimens were aged at temperatures between 473 and 1073 K for 600 sec under an argon atmosphere, followed by quenching in water. The colours of the alloys were determined by spectral reflectivity. They were measured in the wavelength range of 200 to 1500 nm using a spectrophotometer with an intergrating sphere (diameter: 60 mm) normalized by the reflectance of MgO compound. The phases in the specimens were identified by X-ray diffractometry using Cu$K\alpha$ radiation and transmission electron microscopy (TEM). The thin films necessary for TEM were obtained by thinning the original specimens through electropolishing in a solution of 40% acetic acid, 30% phosphoric acid, 20% nitric acid and 10% water.

3. Results

3.1. Reversible changes in spectral reflectivity

A photograph of Cu–14% Al–4% Ni alloy ribbon is reproduced in Fig. 1. The left half-part was heated with a gas burner and quenched in water. The ribbon

TABLE I Chemical compositions (wt %) of melt-quenched Cu–Al–Ni alloy ribbons (balance Cu)

Alloy	Al	Ni	Si
Cu–14% Al–4% Ni	13.9	4.00	< 0.01
Cu–20% Al–4% Ni	19.7	3.98	< 0.01
Cu–13% Al–4% Ni	13.1	3.96	< 0.01
Cu–3% Al–4% Ni	2.8	4.01	< 0.01

0022–2461/87 $03.00 + .12

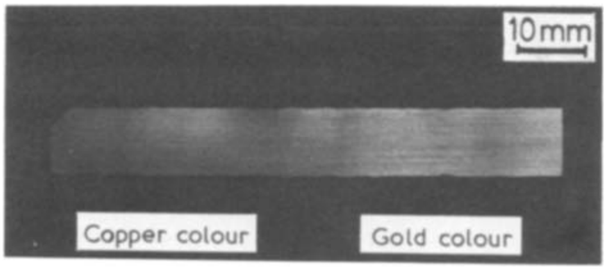

Figure 1 Photograph of Cu–14% Al–4% Ni alloy ribbon showing copper and gold colours.

acquires two colours, copper and gold at room temperature, and the boundary between them is very clear. Furthermore, the copper colour can be changed to gold by selecting the heating conditions. The spectral reflectivities of these two colours are shown in Fig. 2. The reflectivities clearly differ at the wavelengths of around 500 nm and at wavelengths above 700 nm. From these qualitative observations, it may be said that the colour of Cu–14% Al–4% Ni alloy ribbon is reversibly changed between copper and gold by selected heat treatment, and the two colours can be distinguished by the spectral reflectivity. Then, for the purpose of investigating the colour change behaviour of this alloy, the spectral reflectivities of the ribbon aged at various temperatures between 473 and 1073 K were measured.

Fig. 3 shows the change in the spectral reflectivities of Cu–14% Al–4% Ni alloy ribbons quenched from 1073 K with ageing temperatures between 473 and 673 K. The quenched ribbons acquires the copper colour, which remains unchanged by ageing at 473 K; its spectral reflectivity is the same as that of the copper-coloured ribbon as shown in Fig. 2. By ageing at temperatures above 573 K, the reflectivities increase around 500 nm and decrease at wavelengths above 700 nm. the ribbon aged at 673 K shows the same spectral reflectivity as the gold-coloured ribbon of Fig. 2.

The spectral reflectivities of Cu–14% Al–4% Ni alloy ribbons aged at temperatures above 870 K are

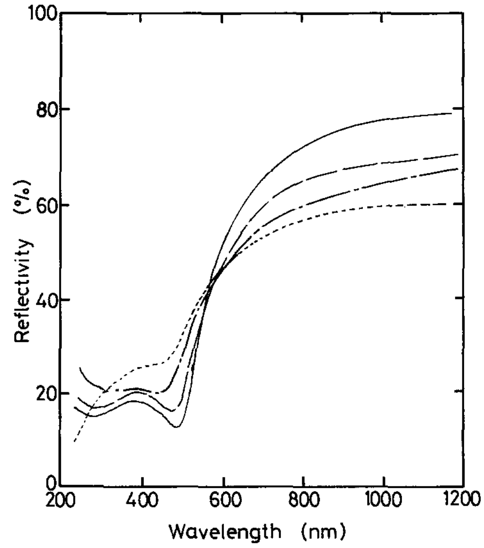

Figure 3 Change in spectral reflectivity of Cu–14% Al–4% Ni alloy ribbons aged for 600 sec at temperatures of (——) 473 K, (– – –) 573 K, (–·–) 623 K, (···) 673 K.

shown in Fig. 4. The ribbon aged at 873 K has the same reflectivity as that aged at 400° C. On ageing between 920 and 970 K, the reflectivities change only slightly, showing deceases at wavelengths lower than 500 nm and increases at wavelengths above 700 nm. It is almost impossible to distinguish the colours of these ribbons visually from the gold colours of the ribbons aged between 670 and 870 K, due to the small differences in their reflectivities in the visible wavelength range (380 to 780 nm). The spectral reflectivity is like that of copper again on ageing above 1023 K. From these results, it is confirmed that Cu–14% Al–4% Ni alloy ribbon acquires the copper colour on ageing above 1020 K and turns gold-coloured on ageing between 620 and 1020 K. By repeating these heat treatments, either of these two colours can be acquired interchangeably.

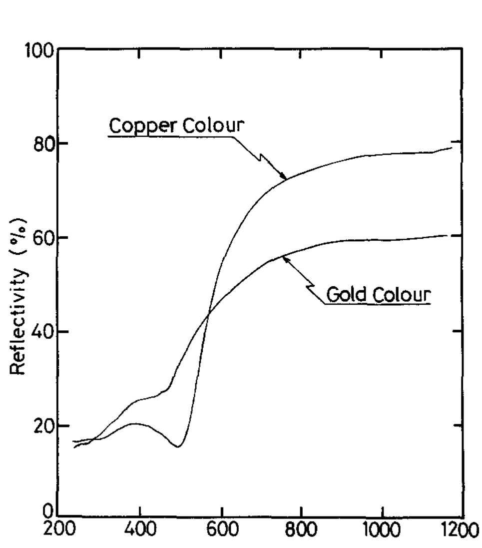

Figure 2 Spectral reflectivities of Cu–14% Al–4% Ni alloy ribbons with copper and gold colours.

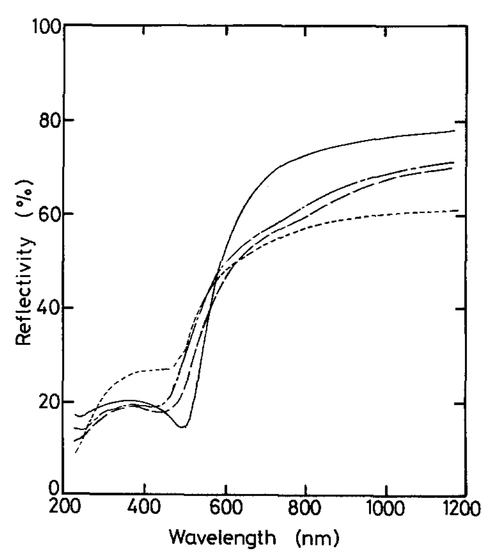

Figure 4 Change in spectral reflectivity of Cu–14% Al–4% Ni alloy ribbons aged for 600 sec at temperatures of (···) 873 K, (–·–) 923 K, (– – –) 973 K, (——) 1023 K.

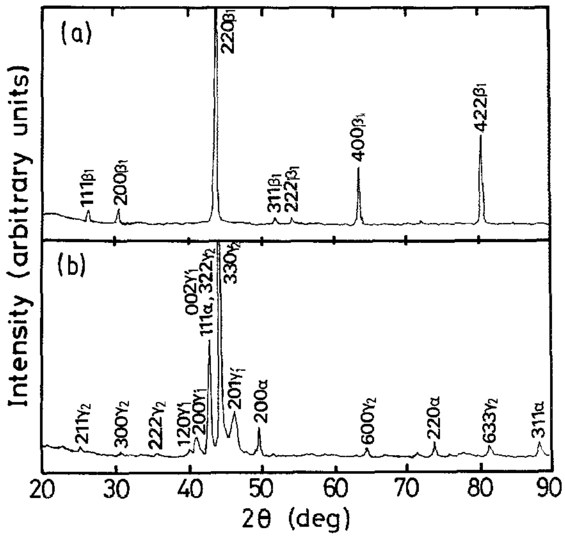

Figure 5 X-ray diffraction patterns of Cu–14% Al–4% Ni alloy ribbons with (a) copper and (b) gold colours.

3.2. Phase changes accompanied by colour change

The X-ray diffraction patterns of typical copper and gold-coloured ribbons of Cu–14% Al–4% Ni alloy are shown in Fig. 5. The copper-coloured ribbon quenched from 1073 K has a DO_3 structure which is the β_1 phase obtained by quenching of β [8]. On the other hand, the gold-coloured ribbon aged at 673 K has a mixture of phases which consists of γ_2 (cubic, Cu_9Al_4 compound), α (fcc, Cu–Al–Ni solid solution) [9] and γ_1' which is a martensite of the β_1 phase. It is known that the β_1 phase transforms to two types of martensite, γ_1' and β_1', in Cu–Al alloys [10, 11]. The former has a twinning structure and the latter has a stacking-fault one. Some peaks in the X-ray diffraction pattern are almost identical to those of the Cu_2Ti-type structure of γ_1' in Cu–14.2% Al–4.3 % Ni alloy with the lattice parameters of a = 0.4382 nm, b = 0.5356 nm and c = 0.4222 nm as reported by Otsuka and Shimizu [12]. Furthermore, TEM observations of the martensite in the ribbon aged at 673 K show a (1 2 1) twinning structure (Fig. 6), which verifies it as the γ_1' phase.

Fig. 7 shows the changes in X-ray diffraction patterns of Cu–14% Al–4% Ni alloy ribbons aged at various temperatures. The ribbons are quenched from 1073 K beforehand. Accompanying the change in colour from copper to gold, γ_2 and γ_1' phases appear in the ribbons aged at temperatures above 570 K, while β_1 disappears on ageing above 620 K. The α phase appears above 670 K, and γ_1' disappears between 770 and 870 K. On ageing at temperatures between 920 and 970 K, the ribbons again indicate a mixture of γ_2 and γ_1' phases. Finally, the ribbons show the β_1 single phase, which accompanies the colour change from gold to copper. The TEM observations identify all of the martensites in these heat-treated ribbons as the γ_1' phase, due to their twinning structure.

4. Discussion

It is known that the colours of metals and alloys depend on the band structure determined by the crystalline structure [2]. Therefore, it can be expected that colour changes are closely related to phase transformations in Cu–14% Al–4% Ni alloy. As shown in Figs 2 to 4, the spectral reflectivities of the two colours differ at wavelengths around 500 nm and at wavelengths above 700 nm, and the colour changes due to ageing appear there also. Then, for the purpose of discussing the relationship between colours and phases in this alloy, the changes in reflectivities at 500 and 700 nm with ageing temperature are shown in Fig. 8 together with the phases identified in the ribbons. The reflectivities of copper-coloured alloys transitionally turn to gold on appearance of a mixture of γ_2 and γ_1' phases by ageing between 520 and 620 K, whereas the reflectivities increase at 500 nm and decrease at 700 nm. They are almost unchanged by ageing at temperatures between 400 and 600° C, where β_1 transforms to a mixture of γ_2 and α. However, when β_1 transforms to a mixture of γ_2 and γ_1', the reflectivities show almost no change on ageing between 920 and 970 K. But they dramatically turn copper-

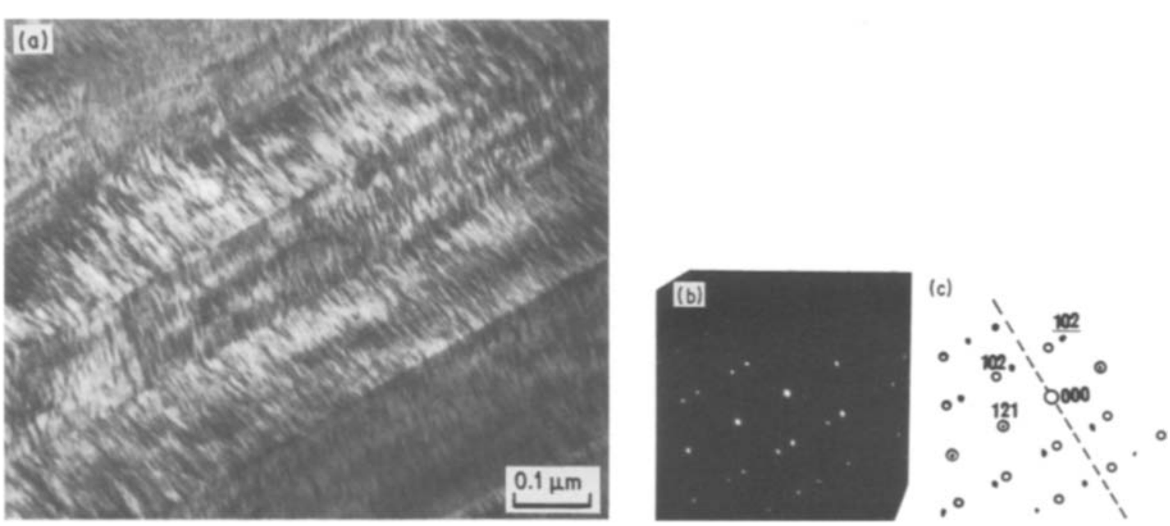

Figure 6 (a) Transmission electron micrograph and (b, c) selected-area diffraction pattern of Cu–14% Al–4% Ni alloy ribbon aged at 673 K for 600 sec. In (c) the dashed line denotes (1 2 1) twinning.

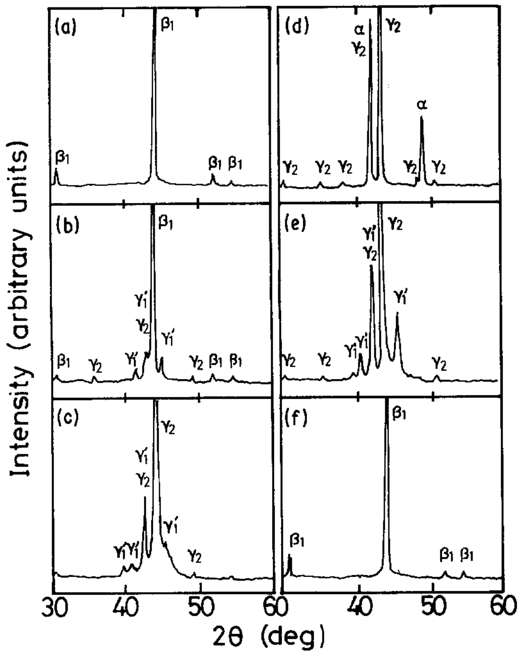

Figure 7 Changes in X-ray diffraction pattern of Cu–14% Al–4% Ni alloy ribbons aged for 600 sec at temperatures of (a) 473 K, (b) 573 K, (c) 623 K, (d) 873 K, (e) 923 K, (f) 1023 K.

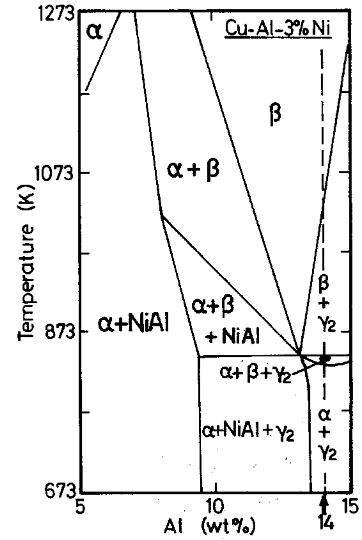

Figure 9 Equilibrium phase diagram of pseudo-binary Cu–Al–3% Ni alloy system (from [13]).

coloured again by ageing above 1020 K where β_1 is observed.

These changes in the phase transformations of β_1 with ageing temperatures can be predicted using an equilibrium phase diagram. Fig. 9 shows the phase diagram of the pseudo-binary Cu–Al–3% Ni alloy system reported by Alexander [13]. From this diagram, it can be predicted that Cu–14% Al–4% Ni alloy exhibits several phases, ($\gamma_2 + \alpha$), ($\gamma_2 + \alpha + \beta$), ($\gamma_2 + \beta$) and β as temperature rises. β_1, which is a metastable phase formed by quenching of β [8], may transform to ($\gamma_2 + \alpha$) or ($\gamma_2 + \alpha + \beta$) below the eutectoid temperature of about 850 K. Therefore, it is concluded that the ($\gamma_2 + \alpha$) phase in the gold-coloured alloys aged between 670 and 870 K in this work results from the eutectoid decomposition of β_1.

In the transition range from copper to gold colour (ageing temperature: 520 to 620 K), eutectoid decomposition may not occur because α could not be identified. It is thought that γ_2 precipitates in the β_1 phase, which is one reason for formation of γ_1' in this ageing temperature range. That is, the β_1 phase with γ_2 precipitation should transform to its martensite at room temperature. Because the amount of aluminium in β_1 becomes lower due to the precipitation of γ_2 with a higher amount of aluminium than β_1, this results in the M_s temperature rising. But it is suggested that this decrease in the amount of aluminium is less than 1% because the martensite has been identified as γ_1' which is formed alone by 13% Al [10, 11]. This change in the amount of aluminium in the β_1 phase is sufficient for the transformation to martensite at room temperature: the M_s point of β_1 in Cu–14% Al–4% Ni alloy is very sensitive to the amount of dissolved

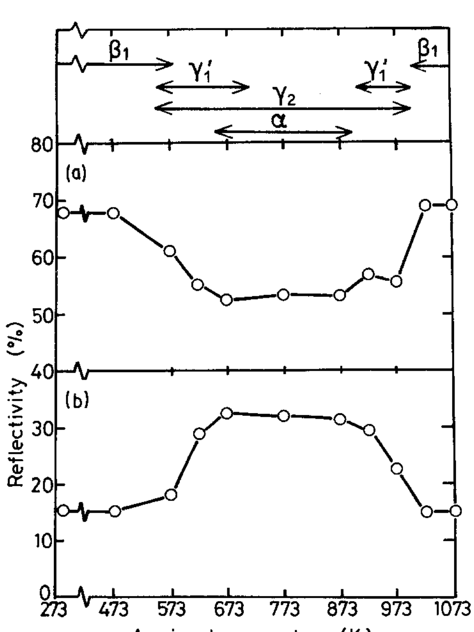

Figure 8 Changes in reflectivities at 700 and 500 nm of Cu–14% Al–4% Ni alloy ribbons aged for 600 sec together with phases identified.

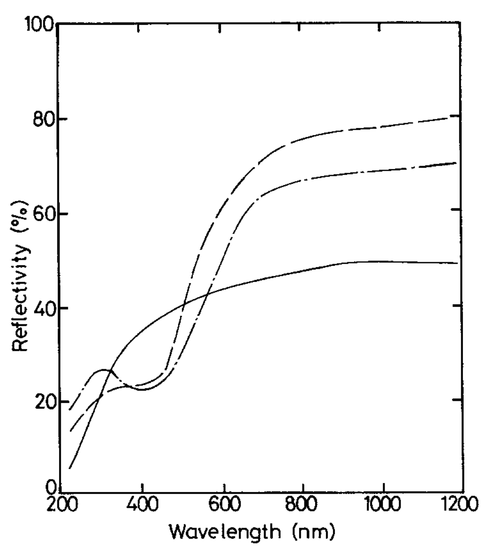

Figure 10 Spectral reflectivities of (——) Cu–20% Al–4% Ni (γ_2), (–·–) Cu–13% Al–4% Ni (γ_1') and (– – –) Cu–3% Al–4% Ni (α) alloy ribbons.

aluminium, that is, it rises about 45 K when aluminium is decreased by 1% in the parent phase [14].

The same transformation process may occur in alloys aged at temperatures between 920 and 970 K. The (γ_2 + β) phase exists in this temperature range above the eutectoid point in the phase diagram. If this β phase is quenched to room temperature it should transform to its martensite due to the precipitation of γ_2. This mechanism results in the formation of γ_2 and γ_1' in this ageing temperature range.

Therefore, the colour change from copper to gold in Cu–14% Al–4% Ni alloy is due to the martensitic transformation from β_1 to γ_1' accompanied by the precipitation of γ_2 and/or to the eutectoid decomposition from β_1 to (γ_2 + α). Conversely it can be said that the change from gold to copper is due to the dissolving of γ_2 in the matrix phases of γ_1' and/or α.

From the above discussion it is suggested that γ_2, γ_1' and/or α phases indicate the spectral reflectivity of the gold colour. Fig. 10 shows the spectral reflectivities of Cu–20% Al–4% Ni (quenched from 1073 K), Cu–13% Al–4% Ni (773 K) and Cu–3% Al–4% - Ni (773 K). These heat-treated alloys have γ_2, γ_1' and α phases, respectively. The γ_2 of Cu–20% Al–4% Ni shows a dark silver colour for which the spectral reflectivity does not fall at wavelengths around 500 nm. On the other hand, the spectral reflectivities of γ_1' and α fall significantly there. Visual observation shows a gold-like colour. But the α phase is more reddish than γ_1' because the reflectivities between 600 and 800 nm are higher than those of γ_1'. Therefore, the gold colour of the mixture of γ_2, γ_1' and/or α in Cu–14% Al–4% Ni ribbon is due to γ_1' and α.

5. Conclusions

The Cu–14% Al–4% Ni alloy ribbon turns copper-coloured at room temperature on quenching from temperatures above 1020 K, and turns gold-coloured on ageing between 670 and 970 K. By repeating these heat treatments, either colour can be acquired interchangeably. The spectral reflectivity also reversibly changes with respect to the colour change. The colour change between copper and gold is due to the solid-state phase transformation between β_1 and γ_2 + (α and/or γ_1'). This shape memory alloy is a new functional material having a reversible colour-change property.

Acknowledgements

The authors would like to thank Dr M. Suwa, Mr K. Tanno and Mr T. Tamamura for their suggestions and encouragement. They are indebted to Mr Y. Miura and Mr Y. Kato for experimental help.

References

1. L. E. PRICE and G. J. THOMAS, *J. Inst. Metals* **64** (1938) 21.
2. M. F. MOTT and H. JONES, "The Theory of the Property of Metals and Alloys", (Oxford, London, 1936) p. 105.
3. H. AMER, K. H. JOHNSON and K. P. WANG, *Phys. Rev.* **12** (1966) 148.
4. J. P. JAN and S. S. VISHNUBHATLA, *Can. J. Phys.* **45** (1967) 2505.
5. S. S. VISHNUBHATLA and J. P. JAN, *Phil. Mag.* **16** (1967) 45.
6. K. OTSUKA and K. SHIMIZU, *Scripta Metall.* **4** (1970) 469.
7. J. ISHIHARA and I. IKUTA, in Proceedings of 5th International Conference on Rapidly Quenched Metals, Sendai, August 1981, edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, Sendai, 1982) p. 19.
8. D. R. F. WEST and D. L. THOMAS, *J. Inst. Metals* **83** (1954) 505.
9. M. HANSEN, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) p. 87.
10. P. R. SWANN and H. WALIMONT, *Acta Metall.* **11** (1963) 511, 1099.
11. *Idem, ibid.* **11** (1963) 1099.
12. K. OTSUKA and K. SHIMIZU, *Trans. Jpn Inst. Metals* **15** (1974) 103.
13. W. O. ALEXANDER, *J. Inst. Metals* **64** (1938) 163.
14. L. DELAEY, *Z. Metallkde* **58** (1967) 388.

Received 21 April
and accepted 10 July 1986