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A study of spinodal decomposition in Ni–30 at% Cu and Cu–46 at% Ni–4 at% Fe alloys using electrical resistivity measurements

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The spinodal decomposition in Ni 30 at% Cu and Cu 46 at% Ni 4 at% Fe alloys has been investigated using electrical resistivity measurements. The electrical resistivity results, for ageing temperatures between 423 and 823 K, were analysed from the equation of change of electrical resistivity for spinodal decomposition in binary alloys proposed by Kolometz and Smirnov, together with the classical spinodal decomposition theory of Cahn. This analysis enabled us to obtain a plot of the amplification factor, $R(\beta)$, as a function of temperature. From this plot, the coherent spinodal temperatures for Ni–30 at% Cu and Cu–46 at% Ni–4 at% Fe alloys were found at 590 and 790 K, respectively, and are in good agreement with experimental and theoretical values reported by other authors.

1. Introduction

The miscibility gap in the Cu–Ni system has been predicted to appear at temperatures lower than 600 K based on thermodynamical data [1–3]; however, it has been difficult to determine its existence experimentally because of the low atomic diffusivity in this temperature range.

Wagner *et al.* [4] used neutron irradiation to enhance the atomic mobility in a Ni–41 at % Cu alloy, and determined the temperature of coherent spinodal to be at 525 K for this composition.

Aalders *et al.* [5] pointed out that the phase decomposition in Cu–Ni alloys can be enhanced by adding a third alloying element, such as iron. Later, Poerschke *et al.* [6] determined the coherent spinodal temperature to be at 795 K in a Cu–46 at % Ni–4 at % Fe alloy based on neutron scattering data.

Kolometz and Smirnov [7] have proposed that the change in electrical resistivity of a binary alloy due to the spinodal decomposition can be expressed by

$$\rho_0 - \rho(t) = \alpha A^2(t) \qquad (1)$$

where $\rho(t)$ and ρ_0 are the electrical resistivity of the alloy aged isothermally at a temperature lower than the spinodal temperature for a time t, and that of the homogeneous alloy, respectively, α is a constant and $A(t)$ is the amplitude of concentration modulation at a time t formed by spinodal decomposition.

In the classical theory of spinodal decomposition, Cahn [8] has defined the amplitude of concentration modulation, $A(t)$, as follows

$$A(t) = A_0 \exp[R(\beta)t] \qquad (2)$$

where A_0 is the initial amplitude of concentration modulation, and $R(\beta)$ the amplification factor of the concentration modulation. This factor is a function of the wave number, β, defined by $2\pi/\lambda$, λ being the wavelength of the amplitude. Substituting Equation 2 into Equation 1, the following equation is obtained

$$\ln[\rho_0 - \rho(t)] = \ln[\alpha A_0^2] + 2R(\beta)t \qquad (3)$$

This modified Kolometz–Smirnov equation has been used to evaluate the interdiffusion coefficient in an artificially modulated foil of Au–Ag alloy [9]. From Equation 3, it could be also possible to determine the amplification factor, $R(\beta)$, for different ageing temperatures. The plot of $R(\beta)$ versus temperature could enable us to estimate the coherent spinodal temperature, because $R(\beta)$ is equal to zero at the coherent spinodal [8].

The aim of this work was to study the spinodal decomposition in Ni–30 at % Cu and Cu–46 at % Ni–4 at % Fe alloys based on the analysis of electrical resistivity measurements by the modified Kolometz–Smirnov equation.

2. Experimental procedure

Ni–30 at % Cu and Cu–46 at % Ni–4 at % Fe alloys were vacuum-melted in an alumina crucible using pure copper (99.99%), nickel (99.97%) and iron (99.6%). Ingots of about 14 mm diameter were encapsulated in a quartz tube, evacuated and filled with pure argon gas, and then homogenized at 1273 K for 1 week (604.8 ks). Wires of 0.4 mm were obtained by

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a sequence of hot forging, swaging and wire drawing. Samples were solution treated at 1173 and 1123 K for 1 h (3.6 ks) for Ni–30 at % Cu and Cu–46 at % Ni–4 at % Fe alloys, respectively, and subsequently quenched into water. As-quenched samples were aged at temperatures from 373–823 K for various periods of time. Electrical resistance measurement of aged samples was carried out by the standard potentiometric method using a wire sample, 0.4 mm diameter and 500 mm length, mounted on a quartz support. All measurements were performed with samples kept at liquid nitrogen temperature.

3. Results

Fig. 1 gives the relative change of electrical resistivity as a function of time for the Ni–30 at % Cu alloy during isothermal ageing at 423, 473, 573, 623, 673, 723 and 773 K. A decrease of electrical resistivity with time can be observed, as expected by the analysis of Equation 1, considering that the value of $R(\beta)$ is positive when spinodal decomposition occurs.

On the other hand, a similar decrease of electrical resistivity with time is observed in the Cu–46 at % Ni–4 at Fe alloy aged at 473, 523, 573, 623, 673, 723, 773 and 823 K as shown in Fig. 2.

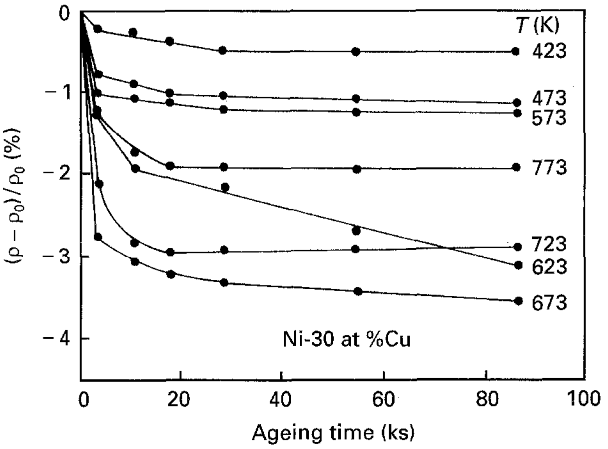

Figure 1 Isothermal ageing curves of electrical resistivity of Ni–30 at % Cu alloy.

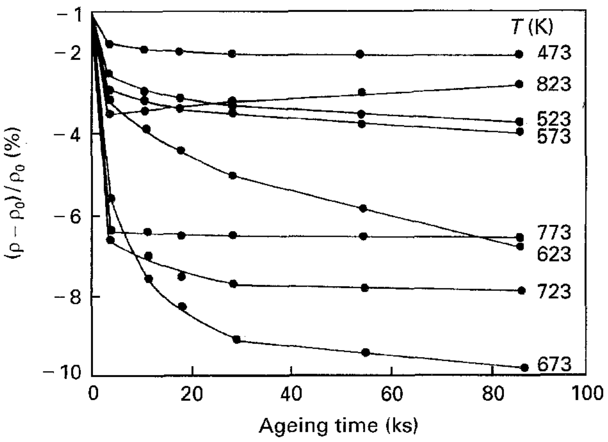

Figure 2 Isothermal ageing curves of electrical resistivity of Cu–46 at % Ni–4 at % Fe alloy.

Isochronal curves of electrical resistivity change (86.4 ks) for both alloys are shown in Fig. 3. A maximum decrease of electrical resistivity at 673 K can be observed in both alloys. This has been attributed to an atomic clustering and magnetic effects in Cu–Ni alloys [10, 11]. However, the decrease in resistivity originating from phase decomposition might be overlapped by those of atomic clustering and/or magnetic moment.

In order to clarify the origin of the decrease of resistivity, an analysis of electrical resistivity results was conducted for both alloys using Equation 3. Cu–46 at % Ni–4 at % Fe alloy was assumed to be a pseudobinary alloy, because the phase decomposition produces a mixture of copper- and nickel-rich phases in this alloy system [6]. Corresponding to Figs 1 and 2, the plots of $\ln[\rho_0 - \rho(t)]$ as a function of time for different ageing temperatures are shown in Figs 4 and 5 for Ni–30 at % Cu and Cu–46 at % Ni–4 at % Fe alloys, respectively. In general, for both alloys, the value of $\ln[\rho_0 - \rho(t)]$ increased rapidly with ageing time. This means a sudden decrease of $\rho(t)$ with time which could be caused by the elimination of quenched-in vacancies during ageing. The value of $\ln[\rho_0 - \rho(t)]$ then increased linearly for times longer than 18 ks in most cases; however, a decreasing tendency of this value with time can be observed

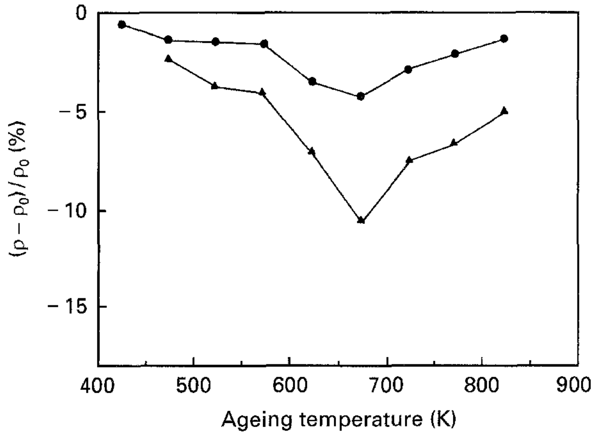

Figure 3 Isochronal ageing curves of electrical resistivity of (●) Ni–30 at % Cu and (▲) Cu–46 at % Ni–4 at % Fe alloys.

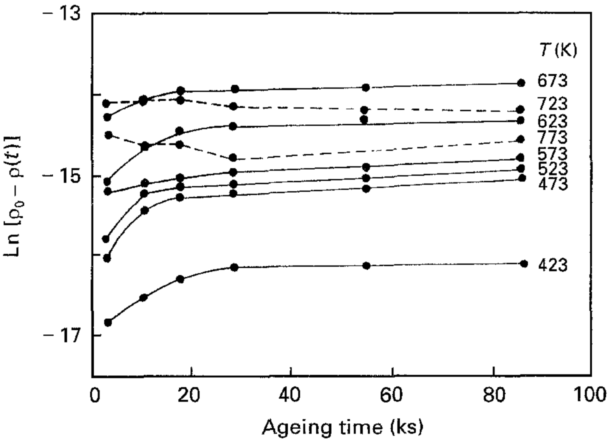

Figure 4 Plot of $\ln[\rho_0 - \rho(t)]$ versus ageing time for Ni–30 at % Cu alloy.

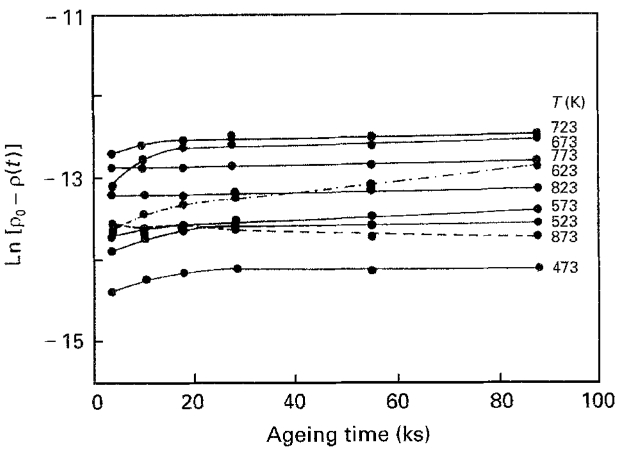

Figure 5 Plot of $\ln[\rho_0 - \rho(t)]$ versus ageing time for Cu–46 at % Ni–4 at % Fe alloy.

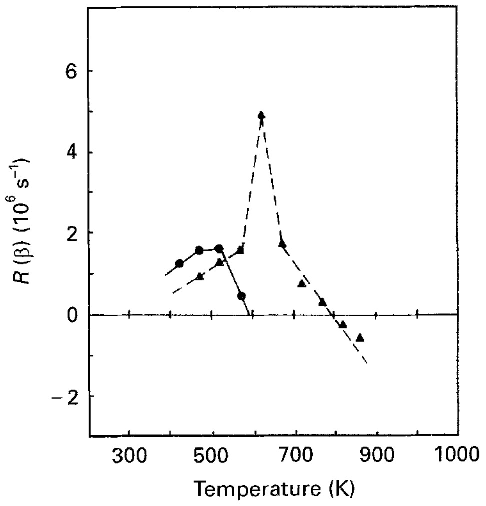

Figure 6 Plot of the amplification factor $R(\beta)$ as a function of temperature for (●) Ni–30 at % Cu and (▲) Cu–46 at % Ni–4 at % Fe alloys.

for temperatures higher than 673 and 773 K in Ni–30 at % Ni and Cu–46 at % Ni–4 at % Fe alloys, respectively.

According to Equation (3), the amplification factor, $R(\beta)$, can be obtained from the slope of the linear portion of the plot of $\ln[\rho_0 - \rho(t)]$ versus time for each ageing temperature. The values of $R(\beta)$ were plotted as a function of temperature for both alloys, as shown in Fig. 6. It is observed that the amplification factor, $R(\beta)$, is negative at temperatures higher than 800 K for Cu–46 at % Ni–4 at % Fe alloys, and then as temperature decreases, $R(\beta)$ becomes positive, presenting a maximum value at about 623 K. Cahn [8] has shown in his theory of spinodal decomposition, that phase decomposition takes place only for positive values of $R(\beta)$. This suggests that phase decomposition must have occurred in the Cu–46 at % Ni–4 at % Fe alloy aged at temperatures lower than 800 K. In addition, it is known that the value of $R(\beta)$ is equal to zero at the coherent spinodal temperature, thus the coherent spinodal temperature was estimated, from Fig. 6, to be at 790 ± 20 K in Cu–46 at % Ni–4 at % Fe alloy.

On the other hand, the plot of $R(\beta)$ versus temperature of Ni–30 at % Cu alloy, Fig. 6, showed the presence of a maximum of $R(\beta)$, located at about 500 K. The values of $R(\beta)$ determined at 623 and 673 K from Fig. 4, were still positive. These unexpected positive values were attributed to the decrease of electrical resistivity caused by the magnetic transformation of nickel, about 625 K [12]. The values of $R(\beta)$ at temperatures higher than 673 K were negative, and this suggests that phase decomposition did not take place. By following the decreasing tendency of $R(\beta)$, after this first maximum, the coherent spinodal temperature of Ni–30 at % Cu alloy was estimated to be at 590 ± 20 K.

4. Discussion

The decrease of electrical resistivity with ageing time for both alloys showed good agreement with that predicted by Equation 3. That is, because $R(\beta)$ is positive when spinodal decomposition occurs, the value of $\rho_0 - \rho(t)$ must be positive, and this means that electrical resistivity decreases with time.

The Cahn's theory of spinodal decomposition [8] defines the amplification factor $R(\beta)$ as follows

$$R(\beta) = -D[1 + (2\eta^2 Y/f'') + (2K/f'')\beta^2]\beta^2 \quad (4)$$

where D is the interdiffusion coefficient, f'' the second derivative of free energy, K the gradient energy coefficient, and $2\eta^2 Y$ represents the coherency-strain energy.

The $R(\beta)$ values, determined from Figs 4 and 5, were $0.5\text{–}5 \times 10^{-6}$ s^{-1}. Rundman and Hilliard [12] reported higher values of $R(\beta)$, $2\text{–}7 \times 10^{-5}$ s^{-1}, using small-angle X-ray scattering (SAXS) in an Al–22 at % Zn alloy aged at 338 K. This difference in magnitude could be attributed to the smaller atomic diffusivity in Ni–30 at % Cu and Cu–46 at % Ni–4 at % Fe alloys than in Al–22 at % Zn alloy [13], thus the smaller values of $R(\beta)$, obtained in this work, seem to be reasonable.

Likewise, the values of $R(\beta)$ determined from Ni–30 at % Cu alloy are close to those found for Cu–46 at % Ni–4 at % Fe alloy. This suggests that the contribution of f'' (driving force) to the value of $R(\beta)$ is greater than that of D (interdiffusivity) in the case of Ni–30 at % Cu alloy, and the contrary should occur in the case of Cu–46 at % Ni–4 at % Fe alloy. This is supported by the fact that the curve of $R(\beta)$ versus temperature in Cu–46 at % Ni–4 at % Fe alloy is located at temperatures higher than those in Ni–30 at % Cu alloy, and this should produce a faster diffusivity in the former.

The decrease of electrical resistivity in Cu–46 at % Ni–4 at % Fe alloy is larger than that in Ni–30 at % Cu alloy, and this could originate from a larger amplitude of concentration modulation in the former, which can be attributed to its higher diffusivity.

The coherent spinodal temperature of about 790 K determined for Cu–46 at % Ni–4 at % Fe alloy in the present work showed a good agreement with the value of 795 K determined by Poerschke *et al.* [6] using small-angle neutron scattering (SANS) in an alloy of the same composition. On the other hand, the coherent spinodal temperature of about 590 K agreed well with that of about 610 K calculated from thermodynamical data by Kim and Choo [2].

5. Conclusion

The spinodal decomposition in Ni–30 at % Cu and Cu–46 at % Ni–4 at % Fe alloys was studied using electrical resistivity measurements. The analysis of electrical resistivity results obtained by the modified Kolometz–Smirnov equation permitted the coherent spinodal temperature to be determined for each alloy. The coherent spinodal temperatures for Ni–30 at % Cu and Cu–46 at % Ni–4 at % Fe alloys were found at 590 and 790 K, respectively.

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References

1. L. ELFORD, F. MULLER and O. KUBACHEWSKY, *Ber.Busenges.* **73** (1969) 601.
2. D. G. KIM and W. K. CHOO, *Scripta Metall.* **19** (1985) 1415.
3. S. MEY, *Z. Metallkde* **78** (1987) 502.
4. W. WAGNER, R. POERSCHKE and W. WOLLENBERGER, *J. Phys. F Metal Phys.* **12** (1982) 405.
5. J. AALDERS, C. VAN DIJK and S. RADELAAR, in "Proceedings of the 2nd *Acta-Scripta Metall.* Conference On Early Stage Decompostion", Sonnenberg, Germany, edited by P. Haasen, V. Gerold, R. Wagner and M. F. Ashby (Pergamon Press, Oxford, 1983) p. 149.
6. R. POERSCHKE, W. WAGNER and H. WOLLENBERGER, *J. Phys. F Metal Phys.* **16** (1986) 421.
7. D. KOLOMETZ and A. SMIRNOV, *Fiz. Metal. Metalloved.* **14** (1969) 3.
8. J. W. CAHN, *Trans. Met. Soc. AIME* **242** (1968) 166.
9. D. T. SPRENG, J. E. HILLIARD and J. W. KAUFFMAN, *J. Appl. Phys.* **43** (1972) 2040.
10. W. SCHÜLE, P. SPINDLER and E. LANG, *Z. Metallkde* **66** (1975) 50.
11. P. L. ROSISTER, *J. Phys. F Metal Phys.* **11** (1981) 2105.
12. K. B. RUNDMAN and J. E. HILLIARD, *Acta Metall.* **15** (1967) 1025.
13. H. MEHRER, in "Diffusion in Metals and Alloys", Landolt-Bornstein New Series (Springer, Berlin, 1990) p. 291.

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