phys. stat. sol. (a) 5, 91 (1971)

Subject classification: 1.1; 21.1

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X-Ray Measurements on Spinodal Decomposition in Cu–Ni Alloys

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The influence of a spinodal decomposition on the half-width and position of diffraction profiles is treated theoretically and proved by X-ray measurements on Cu–Ni alloys with different thermal history. The decomposition ranges from 10 to 90 at% at 250 °C.

Der Einfluß einer spinodalen Entmischung auf die Halbwertsbreite und Lage von Beugungsprofilen wird theoretisch behandelt und durch Röntgenstrahlmessungen an Cu–Ni-Legierungen mit unterschiedlicher thermischer Vorgeschichte überprüft. Die Entmischung überstreicht 10 bis 90 At% bei 250 °C.

1. Introduction

In certain cases X-ray measurements of Cu–Ni alloys with different thermal history have shown a line-broadening. In order to find an explanation for this effect the following investigations were done.

The alloys of the binary system Cu–Ni show complete solubility in the liquid and the solid range [1]. The non-existence of long-range-ordered alloys of the types Cu_3Ni, CuNi, or $CuNi_3$ is proved by measurements of specific heats [2] and electrical resistivity [3]. During the last ten years numerous papers [4 to 15] have been published, showing a tendency to clustering for concentrations between 30 and 70 at% approximately. There is also evidence [9, 11, 16] for the occurrence of spinodal decomposition causing the short-range order. The course of the spinodal curve is assumed to be comparable with that of the Au–Ni system, with a position of its maximum at 300 °C and 50 at%. As a rough approximation the spinodal decomposition can be described by a sinusoidal distribution of the concentration [17, 18], but from a periodic fluctuation of the concentration a formation of side-bands in the diffraction patterns should be expected [19, 20]. A periodicity with long wavelengths is connected with a migration of the satellites against the main lines, thus causing a broadening. From Guinier's [21] treatment of possible diffraction effects the case of a disorder with correlation at large distances seems to be applicable to the present problem. Based on this model the shift and broadening of the X-ray diffraction profiles is discussed.

2. Theory

The concentration dependence of the lattice parameter $a(c)$ of Cu–Ni alloys can be approximated by a parabola:

$$a(c) = a_{Cu} - (a_{Cu} - a_{Ni})\, c - 4\, \Delta\, (1 - c)\, c\,. \qquad (1)$$

Δ is the deviation of $a(c)$ from Vegards law at $c = 0.5$. In the direction of the cube axes the variation of the concentration c is given by

$$c = c_0 + A \sin \frac{2\pi x}{B} . \qquad (2)$$

The maximum deviation A from the mean concentration c_0 of the alloy is found in equal distances B. From equations (1) and (2) the lattice parameter a_x at position x is

$$a_x = a_0 + [8\,\Delta\,c_0 - 4\,\Delta - (a_{Cu} - a_{Ni})]\,A \sin \frac{2\pi x}{B} + 4\,\Delta\,A^2 \sin^2 \frac{2\pi x}{B} . \qquad (3)$$

a_0 is the lattice parameter of the alloy of concentration c_0 without spinodal decomposition (see equation (1)). The mean deviation $\delta\bar{a}$ of $\delta a = a_x - a_0$ is found by integration:

$$\delta\bar{a} = \frac{1}{B}\int_0^B \delta a \, dx = 2\,\Delta\,A^2 . \qquad (4)$$

This result neglects the partial compensation of the lattice parameter fluctuations by elastic strains. In the system Cu–Ni a value of $\delta\bar{a} < 1 \times 10^{-4}$ Å is calculated for $A = 0.06$ (6 at%), that means a lattice parameter difference of at maximum 1×10^{-4} Å between the statistical arrangement and the spinodal decomposed state.

The broadening of the lines due to a periodic concentration profile can be found as follows: A Cauchy intensity distribution of the undistorted line profile with a half-width b_0 is assumed:

$$i(\theta) = \frac{i_{max}}{1 + \frac{4}{b^2}(\theta - \theta_0)^2} . \qquad (5)$$

The resulting profile $I(\theta)$ is the sum of profiles located at different angles θ_0 and with different values of i_{max}:

$$I(\theta) = \frac{1}{B}\int_0^B \frac{i_{max}}{1 + \frac{4}{b_0^2}\left(\theta - \arcsin \frac{\lambda \sqrt{h_i h_i}}{2\,a_x}\right)} dx . \qquad (6)$$

For the used experimental arrangement (X-ray diffractometer, filtered CuK radiation) the half-width b_0 of the undistorted (111) CuKα profiles has been

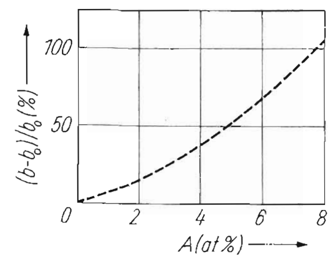

Fig. 1. Dependence of line-width b of the (111) CuK diffraction profiles on decomposition A

found to be 0.065 (°θ). An evaluation of b (half-width according to the decomposed state) from equation (6) can be done by the use of a computer. In Fig. 1 the increase $(b - b_0)/b_0$ in dependence of A is presented. The effect of line-broadening is, as compared with the lattice parameter variation, much higher.

3. Experimental Results and Discussion

The above-mentioned results have been experimentally verified. In an induction furnace different alloys from high-purity copper and nickel (99.99%) were molten under argon atmosphere in alumina crucibles. After homogenization at 1000 °C (one week) the alloys were heated up for 24 h 50 °C below their solidifying temperature in order to produce a sufficient number of thermal vacancies. By a rapid quench ($\approx 10^4$ deg s^{-1}) these vacancies were frozen-in at room temperature. The following heat treatment at 250 °C for 50 h caused migration of the vacancies and spinodal decomposition of the alloys. From the quenched state the reference values a_0 and b_0 were obtained, and after decomposition the a- and b-values. The results can be seen from Table 1 and Fig. 2.

Table 1

Lattice parameter of a 50 at% Cu–50 at% Ni alloy in the quenched and decomposed state

lattice parameter a (Å)	
quenched	decomposed
3.570_2	3.570_4
3.570_2	3.570_4
3.569_9	3.570_2
3.569_9	3.570_3
3.570_0	3.570_4
3.570_0	3.570_2

Table 1 contains results of six independent measurements of the lattice parameters of an alloy with 50 at% of both copper and nickel. In spite of the limited accuracy of $\pm 1 \times 10^{-4}$ Å the predicted increase of a after spinodal decomposition can be recognized. The line-broadening is, as mentioned before, much better observable. From Fig. 1 and 2 the values of $A(c)$ can be deduced, as shown in

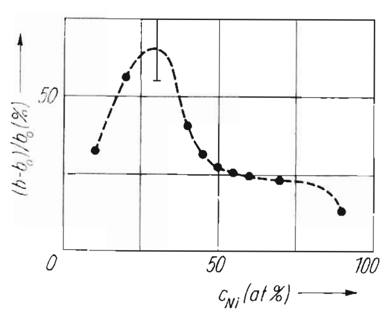

Fig. 2. Measured line-width b after decomposition as a function of concentration c_{Ni}

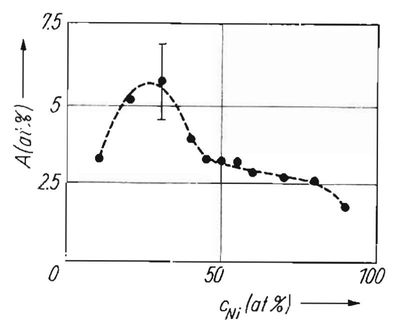

Fig. 3. Decomposition A depending on concentration c_{Ni}

Fig. 3. It is interesting to see that the decomposition ranges from 10 to 90 at% with its maximum value of A at 30 at% Ni. Perhaps this is an explanation for earlier works [5, 22], assuming a long-range order of the type Cu_3Ni. Also the dependence of the magnetic moment at low temperatures, as discussed by Robbins et al. [10], can be understood much better. A formation of short-range order for alloys with comparable low copper contents has also been suggested by Roberts and Barrand [15] from measurements of magnetomechanical damping. A further description of the spinodal range is impossible, since at temperatures higher than 300 °C no decomposition occurs and at temperatures lower than 200 °C the vacancy migration is insufficient to cause decomposition.

Acknowledgement

I am indebted to Prof. Dr. F. Lihl for supposing this research work.

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(Received January 7, 1971)