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The effect of cooling rate on α-phase ordering in Cu–12.4 wt% Al alloy

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The formation of a superlattice in the α-phase of Cu–12.4 wt% Al alloy was studied during cooling. Specimens cooled at different rates were examined using electron microscopy and differential thermal analysis. The superlattice structure formed was described by means of the *D*-parameter which determines the position of superspots in the reciprocal lattice. Variation of the *D*-parameter with cooling rate has a linear form, hence it may be concluded that the superlattice in the α-phase is formed as a transitional structure. The relationship between the *D*-parameter and enthalpy suggests that the latter can be taken as a measure of superstructure development.

1. Introduction

Since Jewett and Mack [1] delineated the range of the α_2-superlattice in the α-phase for the Cu–Al diagram (Fig. 1), numerous studies have been carried out to obtain information on the structure and to analyse the kinetics of the ordering process. Gaudig and Warlimont [2], using electron microscopy, investigated the α_2-phase which precipitates coherently at 340° C in a supersaturated α-phase. Further studies by these authors [3] have shown that prolonged annealing at 250° C causes precipitation of α_3-phase. These α_2 and α_3 phases have one-dimensional antiphase shift structures based on $L1_2$ superlattice and can be constructed by assuming a uniform and regular arrangement of shift planes with a step length of $M = 1/2D$, where D describes the position of superspots in the reciprocal lattice as shown in Fig. 2. For α_2 the parameter $D = 3/8$ and for α_3, $D = 5/14$ [2, 3].

The kinetics of the ordering process were also studied by differential thermal analysis [3, 4] and the results obtained were in agreement with those from electron microscopy investigations. The thermal effect connected with the formation of ordering in α-phase depends on the chemical composition of the studied alloy and varies from 0.4 to 2 J g^{-1} [5–7].

The aim of the present work was to determine the effect of linear cooling rate on formation of the superlattice in the α-phase by measuring the *D*-parameter and correlating its value with the enthalpy of this process measured by means of differential thermal analysis and differential scanning calorimetry.

2. Experimental procedure

The Cu–12.4 wt % Al alloy was melted in an induction furnace, the copper was of 99.97% and the aluminium of 99.95% purity. After casting and hammering, rods of 6 mm diameter were obtained and used for the studies.

The samples were heated to 700° C for 30 min and cooled at a rate of 0.5° C min^{-1} to 500° C. At this temperature the specimens were annealed for 2 h to obtain the $\alpha + \gamma_2$ eutectoid. From this state the samples were quenched in ice water to obtain the disordered α-phase or cooled at different rates from 25 to 0.2° C min^{-1} to obtain a various degrees of ordering.

Order–disorder processes in the α-phase were studied using differential thermal analysis (DTA), differential scanning calorimetry (DSC) and electron microscopy.

DTA curves were obtained during heating of the samples in the temperature range 25 to 600° C using a type TA1 thermoanalyser

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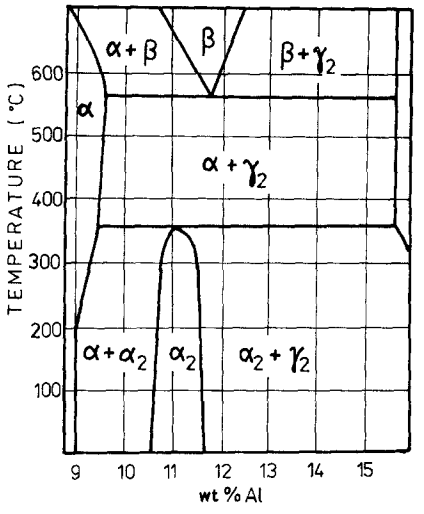

Figure 1 Part of the phase diagram for the Cu–Al system [1].

produced by the firm Mettler. For measurements a macro-DTA NiCr–Ni thermoelement was used. Copper of 99.99% purity was used as a standard sample. To determine the temperatures of phase transitions, the cylindrical samples of 5 mm diameter and 5 mm height with a drilled hole were put directly on the terminals of the thermoelement. To determine the thermal effects of the transitions, the samples studied were placed in Al_2O_3 crucibles in order to obtain measurement conditions approximating to those in which the calorimetric calibration curve of the thermoelement was determined. Tests were carried out in a helium protective atmosphere.

The superstructure of the α-phase was studied using a JEM-200B electron microscope. Thin foils from the samples were obtained by electrochemical polishing in a solution of chromic acid anhydride (50 g) in concentrated orthophosphoric acid (400 ml).

3. Results

Electron microscopy examination showed a lamellar $\alpha + \gamma_2$ eutectoid microstructure with a different degree of α-phase ordering in all samples studied after the described heat treatment.

Fig. 3 shows an [0 0 1] electron diffraction pattern of a sample quenched in ice water. Beside the strong spots belonging to the f c c α-phase, streaks can be seen lying at the half distance between the fundamental 0 0 2 spots, which is evidence of short range order.

Before the influence of cooling rate was studied it was necessary to prove the superlattice for the equilibrium α_2 and α_3-phases.

Fig. 4 shows the electron diffraction patterns of α-phase for specimens heated isothermally for 300 h at 240° C (Fig. 4a) and at 300° C (Fig. 4b). From measurement of distances between spots on the diffraction patterns, the D parameter was calculated. For samples heated isothermally at 240° C the D parameter has an approximate value of $D = 0.357 \pm 0.002$ (5/14) corresponding to α_3 superstructure (Fig. 4a). For samples heated isothermally at 300° C the parameter D has an approximate value of $D =$

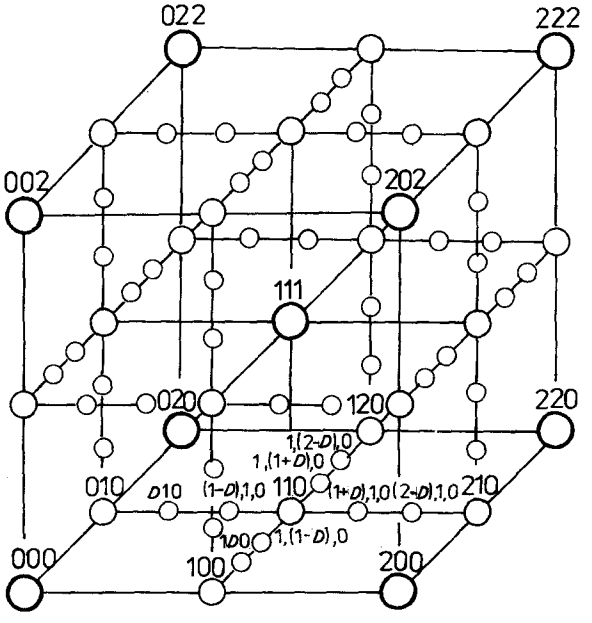

Figure 2 Reciprocal lattice of the α_2 superstructure $D = 3/8$ and the α_3 superstructure $D = 5/14$ in the Cu–Al alloy [2]. O, f c c fundamental reflections; o, Cu_3Au-type superlattice reflection positions; ∘, long period superlattice reflection positions.

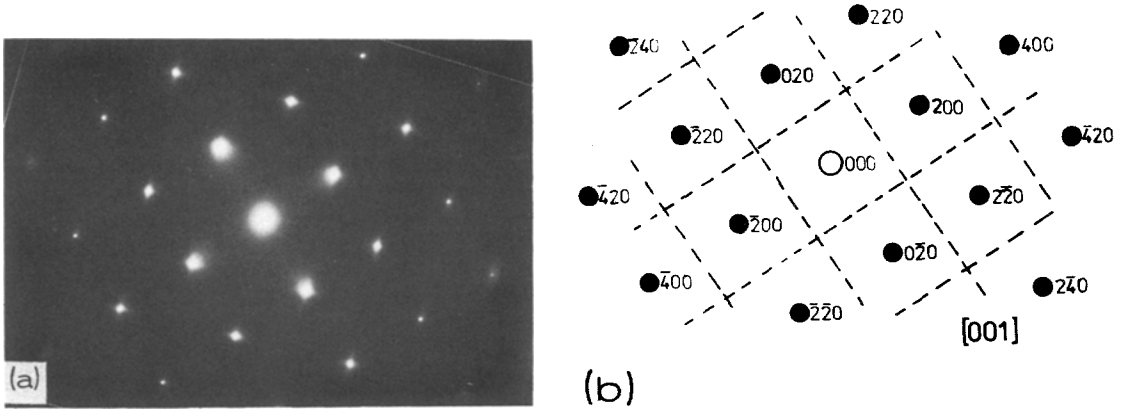

Figure 3 (a) Diffraction pattern and (b) schematic diagram for the [0 0 1] zone axis from the α-phase obtained after quenching.

0.375 ± 0.002 (3/8) corresponding to α_2 superstructure (Fig. 4b). This confirms data reported in the papers of Gaudig and Warlimont [2, 3].

On the basis of these data, the influence of the cooling rate on superlattice formation could be studied. Decrease in cooling rate from 25 to 0.2° C min^{-1} causes an increase in superlattice spots intensity and also in the value of the *D*-parameter.

This effect can be seen in Fig. 5, which shows the electron diffraction pattern for three samples cooled at different rates. The *D*-parameter measured as a function of cooling rate in Fig. 6 shows a linear form.

Fig. 7 shows the microstructure (a) and dark-field image (b) formed by a superlattice reflection and reveals the microdomains of α_2-superstructure.

In order to study the formation of ordering and disordering processes, differential thermal analysis (DTA) has been used. Fig. 8 shows the DTA curve for heating a previously quenched sample. The two exothermic reactions (stages 1 and 2) and one endothermic (stage 3) can be related to the following processes occurring in the α-phase.

Stage 1: annihilation of the frozen vacancies and short range order development.

Stage 2: superlattice formation.

Stage 3: disordering.

The thermal effect of the superlattice formation calculated from the areas of the DTA and DSC peaks has a value of 2.1 ± 0.4 J g^{-1}.

During heating of samples previously slowly cooled and heated to 300° C, thermal effects were found in the temperature range 260 to 460° C (Fig. 9). This may be interpreted as the heat absorbed in the process of disappearance of the α_2-superlattice. The thermal effect of this process, determined from the area under the peaks, was 2.5 ± 0.5 J g^{-1}.

The magnitude of the thermal effect due to

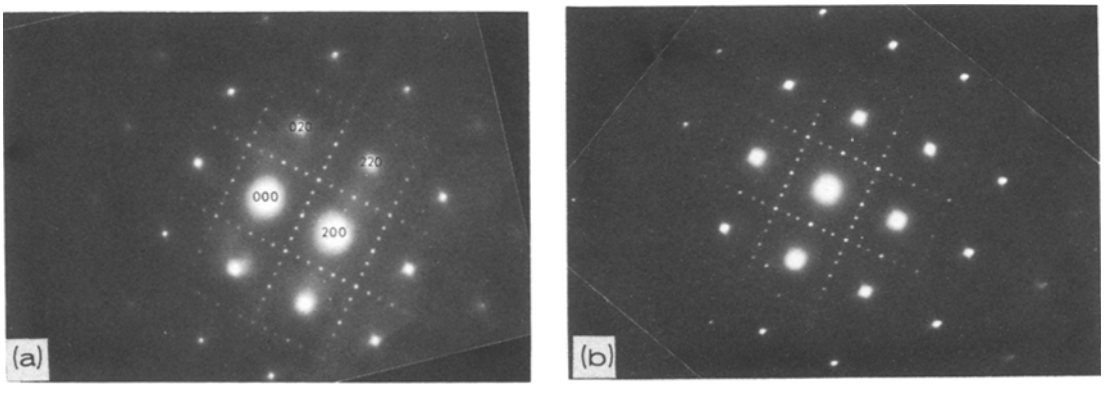

Figure 4 Diffraction patterns from the α-phase for samples quenched in ice water and then heated isothermally at (a) 240° C for 300 h and (b) 300° C for 300 h.

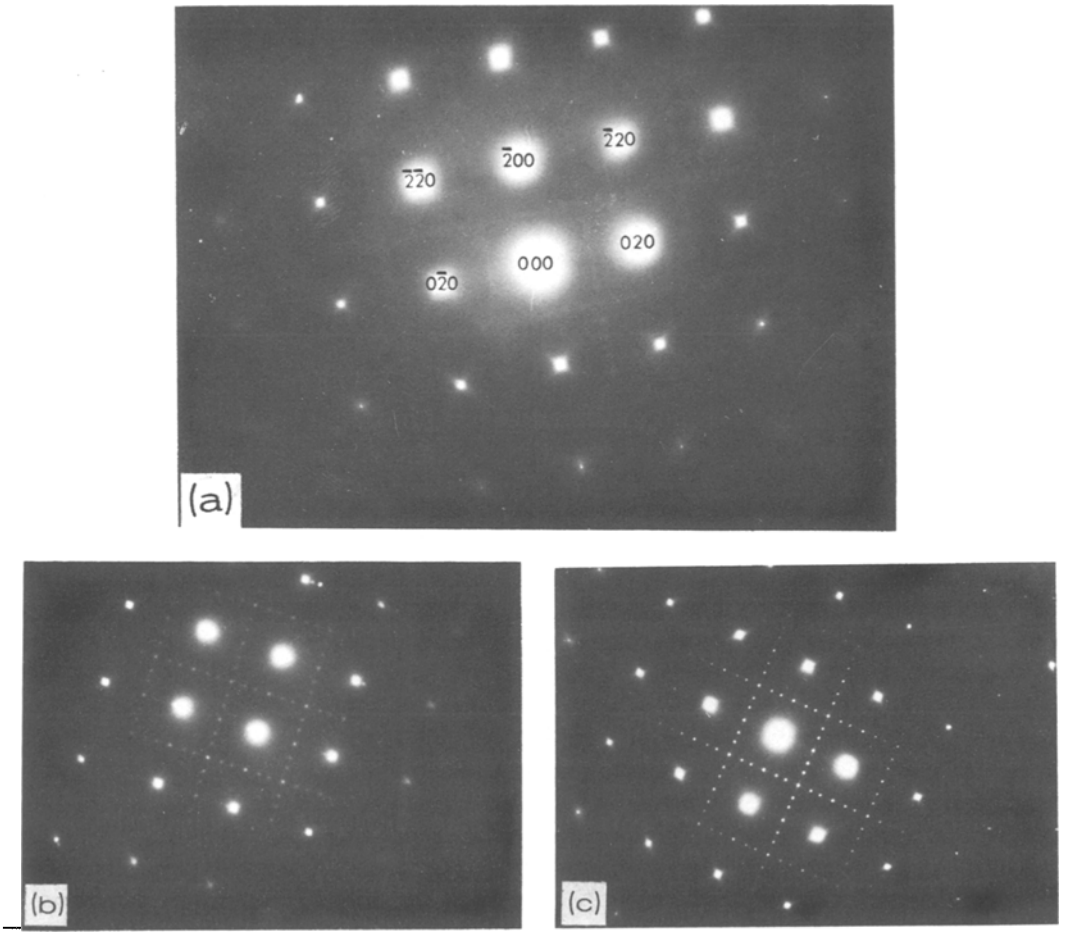

Figure 5 Electron diffraction patterns from the α-phase in sample cooled from 500° C at a rate of (a) 25° C min^{-1}, (b) 8° C min^{-1}, and (c) 0.2° C min^{-1}.

order–disorder transformations is, however, dependent on the degree of ordering of the phase undergoing transformation. Based on microscope examination it was shown that the type of superlattice formed in the α-phase depends on the rate at which the eutectoid was previously cooled. The magnitude of this thermal effect due to the disorder process during heating of the samples shows the linear dependence between enthalpy and cooling rate (Fig. 10). Since both the *D*-parameter and the thermal effect of the process of order disappearance during heating of the superstructure are dependent on the rate of prior cooling of the eutectoid, a correlation between these two values may be anticipated.

Fig. 11 shows the relationship between results

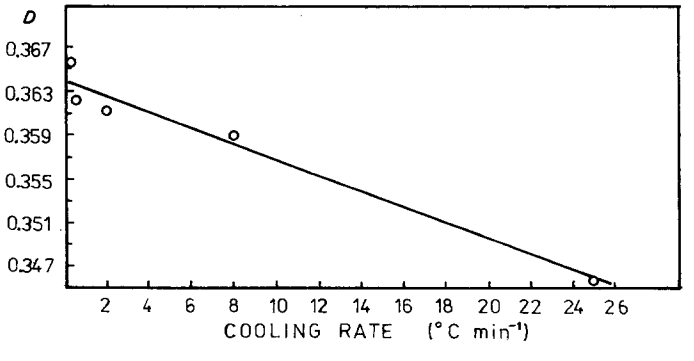

Figure 6 The *D*-parameter as a function of cooling rate for the α-phase.

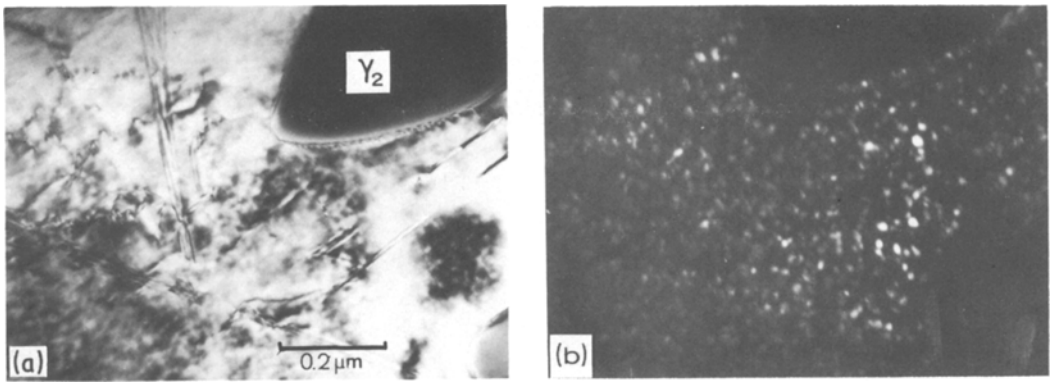

Figure 7 (a) Microstructure and (b) dark-field image of α_2-microdomains.

of examinations of α-phase ordering obtained by electron microscopy and from thermal analysis. From this it may be concluded that both the *D*-parameter and the heat of transformation may be used for quantitative assessment of degree of α-phase ordering.

4. Conclusion

The quenched α-phase exhibits short range order which after prolonged annealing causes the formation of a superlattice described as α_2- or α_3-phase [3]. These results were confirmed in this work and on that basis the influence of cooling rate on superlattice formation could be studied. The decrease in cooling rate from 25 to 0.2° C min^{-1} causes an increase in superlattice spot intensity and in the value of the *D*-parameter. The value of the *D*-parameter obtained for higher cooling rates corresponds rather with the α_3-phase, and for the lowest cooling rate approaches the α_2-phase. From the linear variation of the *D*-parameter with cooling rate it may be concluded that the superlattice in the α-phase is developed by transitional structures. It is obvious that even for the slowest cooling rate the ordering state obtained deviates from the equilibrium state. Hence in practical heat treatment conditions, the transitional superlattice will appear. The linear relation holding between the *D*-parameter and enthalpy suggests that the latter can be taken as a measure of development of the transitional superstructures in the α-phase.

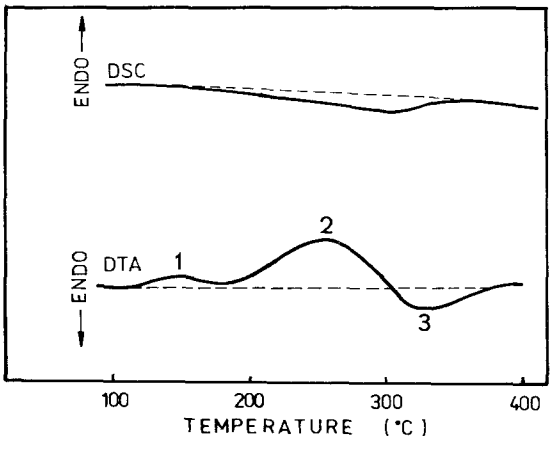

Figure 8 DTA and DSC curves obtained during heating the studied alloy previously quenched from 500° C in ice-water.

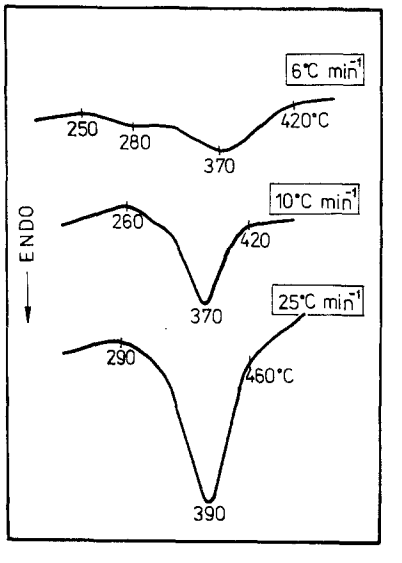

Figure 9 DTA curves obtained during heating of ordered samples at 300° C for 300 h. Heating rate: 6, 10 and 25° C min^{-1}.

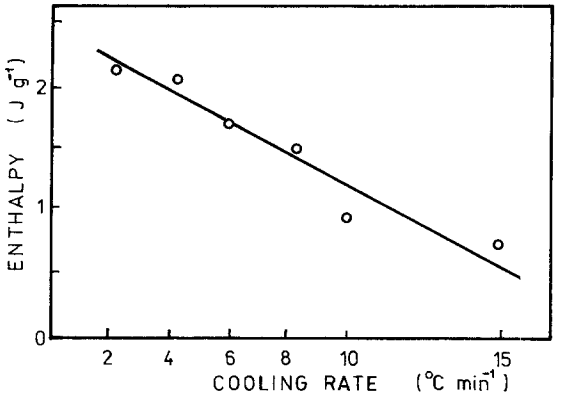

Figure 10 Enthalpy of the disorder as a function of cooling rate.

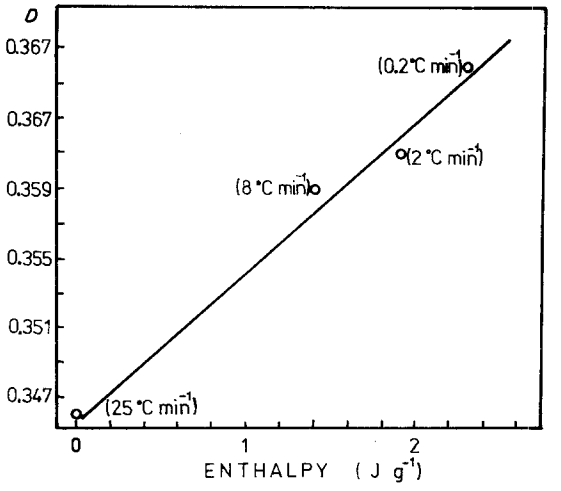

Figure 11 Relationship between the *D*-parameter of the superlattice and enthalpy.

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