

X-RAY DIFFRACTION STUDY OF DISCONTINUOUS PRECIPITATION IN Al-Cu ALLOYS

S. POPOVIC

Institute »Ruđer Bošković«, Zagreb

D. E. PASSOJA and P. BARRAND

Department of Metallurgy, University of Manchester, England

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Abstract: The discontinuous precipitation process of equilibrium Θ phase in Al-Cu alloys is studied by X-ray diffraction method using powdered samples. When the process takes place each matrix diffraction line splits into two components differing slightly in unit cell dimensions. The component with the smaller unit cell dimension corresponds to the as-quenched alloy, the other component corresponds to the slowly-cooled alloy. Proceeding the ageing time the former component gradually transforms into the latter. This transformation can be studied following the changes of the profiles of matrix diffraction lines at high Bragg angles. The ageing times, giving similar volume fractions having undergone the discontinuous precipitation process at two different temperatures, were determined. An activation energy for solute atom diffusion of 1.1 eV is obtained.

1. Introduction

Heterogeneous nucleation of the equilibrium Θ (Al₂Cu) phase at grain boundaries is a common occurrence in quenched and aged Al-Cu alloys¹. In its later stages growth of Θ into neighbouring grains proceeds by discontinuous precipitation, this is defined, for example, by Cahn². Similar phenomena have also been observed in Al-Ag alloys³ and in simultaneously aged and deformed Al-Cu alloys⁴. Cahn's model² was originally developed to explain the formation from solid solution of a lamellar two-phase structure, free from creep deformation. It was assumed that nucleation was easy and that

the main driving force was the overall free energy change accompanying the transformation.

The present work represents a part of a larger study of precipitation effects in binary and ternary Al alloys⁹. An X-ray diffraction method for the investigation of the discontinuous precipitation of Θ in the Al-Cu system is described.

2. Experimental

Bulk Al—3.9 wt % Cu material (1 mm thick sheets) was solution treated at 540 °C for 4 hours, quenched in water and then filed in order to prepare powder for X-ray samples. The 240—300 mesh fraction was selected and used in the investigation. Small amounts of powder (0.1 cm³) were wrapped in single thin Al foil and re-solution treated for 2 hours at 540 °C, quenched in water and aged immediately after quenching at 150 °C and 250 °C for various times. A slowly-cooled sample was also prepared after solution treatment at 540 °C; the cooling rate to room temperature was 2 °C/min. at 500 °C decreasing to 1 °C/min. at 200 °C and to 0.5 °C/min. at 100 °C.

Table

2Θ and $B_{1/2}$ values of the (422) $K\alpha_1$ diffraction line

S a m p l e		$2\Theta(^{\circ})$	$B_{1/2}(^{\circ}2\Theta)$
pure Al, annealed	a) slowly cooled	137.4 ₁	0.20
at 540 °C	b) water quenched	137.4 ₁	0.26
Al-Cu, solution treated	a) slowly cooled	137.5 ₁	0.34
at 540 °C	b) water quenched	138.1 ₁	0.28
Al-Cu, solution treated at 540 °C, quenched in water		137.5 ₁	0.35
and aged at 250 °C for 3 days		± 0.05	± 0.01
estimated error of measurements			

X-ray diffraction patterns were recorded by means of Siemens Kristalloflex IV diffractometer with a proportional counter and a single channel pulse-height analyser using Ni-filtered $\text{CuK}\alpha$ radiation. The profiles of the matrix diffraction lines at high Bragg angles (422), (420) and (311) were recorded as accurately as possible. The positions and profiles of the diffraction lines of the samples were compared with the diffraction lines of pure Al powder with the same granulation, annealed at 540°C for one hour and slowly cooled in the same manner as the Al-Cu sample. This sample was used to calibrate the angular scale of the diffractometer and for that reason its unit cell dimension was determined by the Debye-Scherrer film technique in a 114.6 mm diameter Philips camera. The asymmetric position of the film was used and the correction of the systematic errors was done by extrapolation method applying the $\cos^2\Theta/\Theta + \cos^2\Theta/\sin\Theta$ function⁹. The X-ray pattern was taken at $(20.0 \pm 0.5)^\circ\text{C}$ and the value of $(4.0492 + 0.0001)\text{ \AA}$ was obtained.

3. Results and Discussion

The Bragg angles, 2Θ , and the half maximum peak breadths $B_{1/2}$, of the (422) $\text{K}\alpha_1$ line of pure Al and Al-Cu as-quenched and slowly-cooled sam-

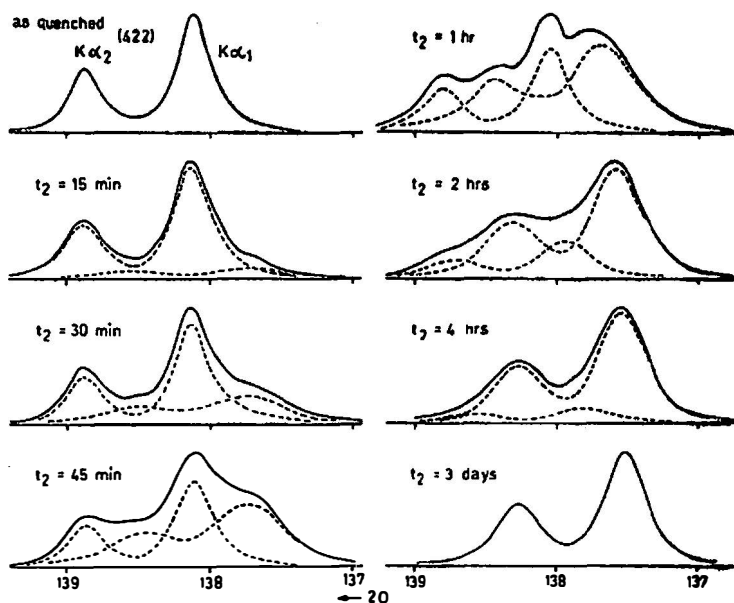


Figure 1. The profiles of the (422) $\text{K}\alpha$ diffraction line of the Al-3.9 wt % Cu alloy, aged at 250°C for various times.

ples are shown in the Table. The unit cell dimension of the as-quenched Al-Cu sample is 0.22 % smaller than the unit cell dimension of pure Al; this is in good agreement with previous results for Al-rich Al-Cu solid solution with similar compositions^{7, 9}).

The Al-Cu slowly-cooled sample showed the Θ equilibrium precipitate diffraction lines corresponding to a tetragonal structure with unit cell dimensions $a = 6.066 \text{ \AA}$ and $c = 4.874 \text{ \AA}$, as has already been reported⁹).

Diffraction lines of pure Al powder quenched in water were somewhat broader than the lines of the slowly cooled sample. This was probably due to some amount of defects introduced into the crystal lattice by quenching. On the other hand, slowly cooled Al-Cu sample had broader lines than the quenched sample; this may be explained in terms of a distortion of the matrix around the Θ precipitates.

The matrix diffraction lines of the Al-Cu samples, aged at 250 °C up to 5 hours and at 150 °C up to 60 days, showed composite features. They consisted of the two components: the high-angle component, corresponding to the as-quenched Al-Cu sample, and the low-angle component, corresponding to the slowly-cooled Al-Cu sample. As the ageing proceeded a gradual transformation of the high-angle component into the low-angle component, with a little larger unit cell dimension, took place. Profiles of the (422) $K\alpha$ diffraction line for several samples aged at 250 °C for various times are shown in Fig. 1. It was not possible to resolve graphically the composite profile into its components with great accuracy, especially in cases where the two components were of similar size. One can, however, follow the approximate angular positions of the components during ageing and make rough estimates of the ratio of their integrated intensities. This value corresponds to the volume fraction of the matrix which has undergone the discontinuous precipitation. Fig. 2 shows $2\Theta K\alpha$ values for the two components of the (422) diffraction line for samples aged at 250 °C and the volume fraction of the low-angle component (the shown error bars indicate the estimated accuracies). The high-angle component did not change its position at short ageing times, but having prolonged it moved slowly toward lower angles and at the same time it became broader. It was difficult to fix the position of the low-angle component at short ageing time, but it seemed that it also moved, though only slightly, toward lower angles as ageing proceeded, becoming sharper when it approached the position of the slowly cooled sample.

Similar changes in angular positions and shapes of diffraction lines were observed for foil samples treated in the same way. Since the foil samples consisted of large grains which were not randomly oriented, the positions and profiles of their diffraction lines could not be defined as accurately as those of the powder specimens.

As the ageing proceeded weak diffraction lines of Θ phase appeared, becoming more visible for those samples approaching the slowly cooled condition. Two or three very weak additional peaks were observed during ageing, which could be interpreted in terms of the intermediate tetragonal Θ' precipitate with unit cell dimensions $a = 4.05 \text{ \AA}$, $c = 5.8 \text{ \AA}$.

One part of this investigation was to determine the ageing times t_1 , at 150°C , and t_2 , at 250°C , which gave similar complex shapes of diffraction lines, i.e. similar volume fractions having undergone the discontinuous precipi-

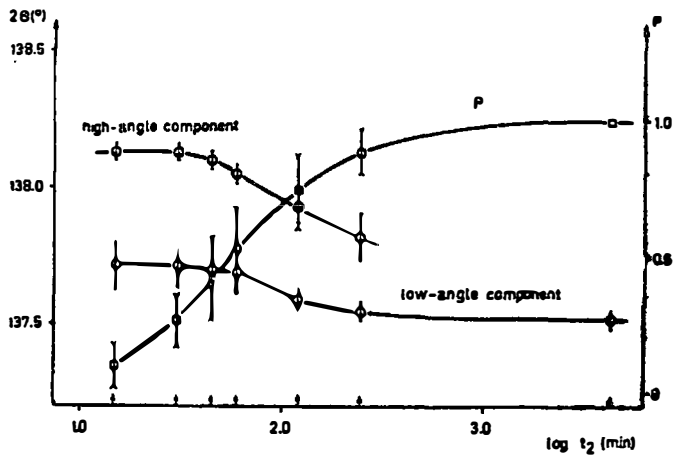


Figure 2. Bragg angles, 2θ , of high and low angle components of the $(422) \text{CuK}\alpha_1$ diffraction line and the volume fraction of the low angle component, P , as a function of the ageing time, t_2 , at 250°C (estimated accuracy shown in figure).

tation process. At the beginning of ageing, t_1/t_2 was < 100 , but as ageing proceeded, t_1/t_2 increased, tending to a value ~ 300 . It was found that $t_2 = 2$ hours was equivalent to $t_1 = 650$ hours, while $t_2 = 4$ hours corresponded to $t_1 = 1320$ hours. The complex shapes of high-angle diffraction lines were compared in order to determine the corresponding times t_1 and t_2 , rather than the integrated intensities of either component.

The activation energy for solute atom diffusion, E_D , can be calculated using the equation for the number of jumps, n , made by solute atoms during the ageing time t :

$$n = At \exp\left(-\frac{E_D}{kT}\right),$$

where A is a constant for a given material, k Boltzmann's constant and T is the absolute ageing temperature. Using the value $t_1/t_2 = 330$, obtained in this investigation, it follows:

$$E_D = \frac{k \ln \left(\frac{t_1}{t_2} \right)}{\frac{1}{T_1} - \frac{1}{T_2}} = 1.1 \text{ eV} .$$

E_D here is a very slowly varying function of t_1/t_2 for the temperatures chosen in these experiments, and an error of ± 10 in t_1/t_2 corresponds to an error of ± 0.01 eV in E_D .

4. Conclusion

It has been shown that discontinuous precipitation of equilibrium Θ , in an Al — 3.9 wt % Cu alloy, can be studied using X-ray diffraction methods. The matrix diffraction lines split into two components, having slightly different unit cell dimensions, corresponding to the as-quenched alloy and the slowly cooled alloy, respectively. As ageing proceeds the former component gradually diminishes while the latter becomes stronger. An approximate activation energy, for solute atom diffusion during this process, of 1.1 eV is obtained.

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**ISTRAŽIVANJE DISKONTINUIRANE PRECIPITACIJE U SLITINI
Al-Cu POMOĆU RENDGENSKIH DIFRAKCIJSKIH METODA**

S. POPOVIĆ

Institut »Ruđer Bošković«, Zagreb

D. E. PASSOJA i P. BARRAND

Department of Metallurgy, University of Manchester, England

S a d r Ź a j

Proces diskontinuirane precipitacije ravnotežne faze θ u slitini Al-Cu istraživan je pomoću rendgenske difrakcijske metode praška. Kad proces počne, difrakcijske linije matrice cijepaju se u dvije komponente, koje se malo razlikuju u dimenzijama elementarne ćelije. Komponenta s manjom ćelijom odgovara kaljenoj slitini, dok druga komponenta odgovara slitini sporo hlađenoj s temperature krute otopine.

Tokom starenja prva komponenta postepeno prelazi u drugu. Ova transformacija može se pratiti promatranjem promjena profila difrakcijskih linija matrice kod velikih Braggovih kutova. Kod dvije temperature starenja određena su vremena koja daju jednake omjere komponenata. Za aktivacionu energiju difuzije atoma Cu dobivena je vrijednost 1.1 eV.