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DIRECT DETECTION OF INHOMOGENEOUS SHORT-RANGE ORDER IN THE Al–Cu (0.5 at.%) ALLOY

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It has been shown by the technique of X-ray diffuse scattering that in the Al–Cu (0.5 at.%) alloy immediately after its preparation there is inhomogeneous short-range order.

INTRODUCTION

The Al–Cu alloys are characterized by a rather narrow range of solid solutions: the copper concentration attains a value of about 2 at.% at 800°C and then decreases sharply with decreasing copper content [1, 2]. The structure and properties of the Al–Cu precipitation-hardening alloys were studied in [3–9]. It was found that, in addition to the Θ phase, there also occur Guinier–Preston phases. In [3], when interpreting changes in the electroconductivity in the Al–Cu alloys, clusters with short-range order were assumed to exist. However, no direct evidence for the short-range order in the Al–Cu solid solutions had been found earlier [2, 8–11]. Moreover, it was thought until recently [6, 10, 12] that short-range ordering in such systems cannot be detected by X-ray analysis.

This work is focused on the detection of short-range order in diluted Al–Cu solid solutions.

EXPERIMENTAL

The Al–Cu (0.5 at.%) alloy was prepared from pure raw materials in a corundum crucible of a resistor furnace under a KCl–NaCl flux with subsequent cooling of the crucible (together with the furnace) down to room temperature. A cylindrical sample cut out from an ingot was then ground and polished until glittering. The alloy was annealed in a vacuum oven. The intensity of X-ray diffuse scattering (the FeK_α radiation) was measured with a diffractometer of scintillation counting. The measured data of diffuse X-ray scattering was converted to the electron units using the procedure described in [11].

The Cowley parameters of short-range order (α_i) were obtained on a BESM-6 computer by the least-squares technique using the following expressions:

$$J(q_j) = nc_A c_B (f_A - f_B)^2 \sum_i \alpha_i \left[C_i \frac{\sin q_j R_i}{q_j R_i} + L_{ij} + Q_{ij} \right], \tag{1}$$

where $J(q_j)$ are the experimentally obtained intensities of X-ray scattering; $q_j = 4\pi \sin\theta/\lambda$ (λ is the wavelength of the X-ray radiation, θ is the angle of scattering); n is the number of atoms in a unit cell; c_A and c_B are the atomic concentrations of the components; f_A and f_B are the atomic factors of X-ray scattering; C_i is the coordination number for the ith coordination sphere; R_i are the radii of coordination spheres; i are the numbers of coordination spheres; j are the numbers of points in the diffraction pattern; L_{ij} and Q_{ij} are, respectively, the modulating functions of the linear and quadratic size effects averaged over a sphere of radius q. These functions depend on the alloy parameters as follows:

$$L_{ij} = -2(f_A - f_B)^2 \langle f \rangle nc_A c_B \frac{1}{v} \frac{\partial v}{\partial c} \frac{\langle \mathbf{q}\mathbf{A}_\mathbf{Q} \cos \mathbf{q}\mathbf{R}_m \rangle^{ij}_{\varphi\gamma}}{J_1}, \tag{2}$$

$$Q_{ij} = \langle f \rangle^2 nc_A c_B \left(\frac{1}{v} \frac{\partial v}{\partial c} \right)^2 \frac{\langle (\mathbf{q}\mathbf{A}_\mathbf{Q})^2 \cos \mathbf{q}\mathbf{R}_m \rangle^{ij}_{\varphi\gamma}}{J_1}, \tag{3}$$

$$J_1 = nc_A c_B (f_A - f_B)^2, \tag{4}$$

$$\langle f \rangle = c_A f_A + c_B f_B, \tag{5}$$

where J_1 is the intensity of the Laue scattering; v is the volume of the unit cell; $\partial v/\partial c$ is the derivative of the volume v with respect to the concentration c; $\langle\ldots\rangle^{ij}_{\varphi\gamma}$ denotes averaging over the angles φ and γ at fixed values of $\mathbf{q}$, i, and j; Q is the scattering vector reduced to the first Brillouin band; $\mathbf{A_Q}$ is the proportionality factor between the Fourier amplitudes of the waves of statistical displacements $\mathbf{U_Q}$ and concentration waves $\mathbf{C_Q}$: $\mathbf{U_Q} = \mathbf{A_Q C_Q}$; and $\mathbf{R}_m$ is the radius vector of the mth atom.

The tables of averaged values $\langle\ldots\rangle^{ij}_{\varphi\gamma}$ from [13] were used in the calculations. The elastic constants for the Al–Cu (0.5 at.%) alloys were taken equal to those of pure aluminum; their ratios c_{12}/c_{11} and c_{44}/c_{11} are required to calculate the averaged values $\langle\ldots\rangle^{ij}_{\varphi\gamma}$ [13].

RESULTS AND DISCUSSION

The experimentally measured intensities of X-ray diffuse scattering for the Al–Cu (0.5 at.%) alloy just after its preparation are presented in Fig. 1. A strong diffuse maximum typical of short-range order is seen in the region of 2θ scattering angles of 14–38°. The calculations of the short-range order parameters from the X-ray scattering values shown in Fig. 1, carried out under the assumption that the copper content in the alloy was 0.5 at.% (as weighed), gave no satisfactory results. This led us to a suggestion that the Al–Cu (0.5 at.%) alloy just after its preparation is in an inhomogeneous state, so that there are regions enriched in copper up to $C \approx 3$ at.% which are surrounded with a matrix depleted of copper.

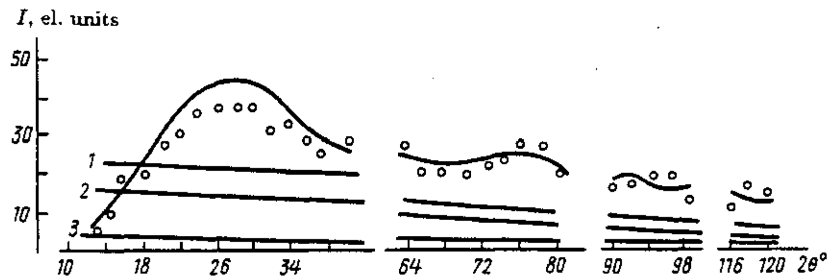

Fig. 1

Intensity of X-ray diffuse scattering (in electron units) by the Al–Cu (0.5 at.%) alloy versus angle 2θ. The experimental data are indicated by open circles. The solid curve represents calculated data. Curves 1, 2, and 3 are the Laue scattering curves calculated for copper contents of 3, 2, and 0.5 at.%, respectively.

Figure 1 also gives calculated curves of the intensity of the Laue scattering for the copper contents 0.5, 2, and 3 at.%. The measured intensities at angles $2\theta = 12$–38° are seen to fit better to the Laue scattering curve calculated for the copper content 3 at.%. It implies that the observed intensity distribution from the Al–Cu (0.5 at.%) alloy is related to the scattering by regions enriched in copper atoms ($c \approx 3$ at.%). For this reason, the parameters of the short-range order were calculated for the compositions 0.5, 2, and 3 at.% Cu. It was found that in all the cases the sign of the short-range order parameter in the first coordination sphere (α_1) was negative. For the composition $c = 3$ at.% Cu, the calculated value of α_1 was −0.06. It corresponds to the existence of inhomogeneous short-range order in the Al–Cu (0.5 at.%) alloy with unlike atoms as predominant neighbors.

Further measurements of the X-ray scattering intensity for the Al–Cu (0.5 at.%) alloy were carried out after six-month ageing of the sample at room temperature. The data obtained for angles $2\theta = 10$–40° are presented in Fig. 2. The blurred diffuse maximum caused by the inhomogeneous short-range order is seen to disappear after the ageing, and instead a much more narrow intensity maximum appeared in the range of angles $2\theta = 10$–15°. It is also seen that the scattering intensity diminishes in the range of angles $2\theta = 18$–38°. A maximum of intensity similar to that observed at the angles 10–15° was earlier found in [9] in the diffraction patterns of ageing Al–Ag alloys. It was related to the formation of Guinier–Preston bands I. Apparently, the marked changes in the scattering intensity observed after the ageing are also related to the formation of Guinier–Preston bands I in the Al–Cu (0.5 at.%) alloy. The appearance of Guinier–Preston

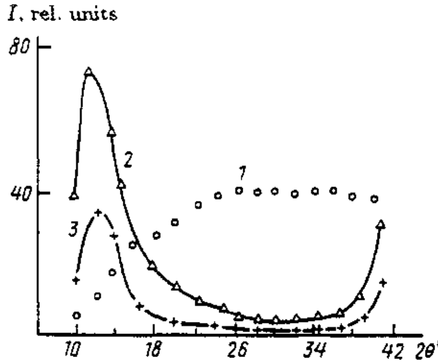

Fig. 2

Intensity of X-ray scattering by the Al–Cu (0.5 at.%) alloy versus the angle 2θ: (1) just after the alloy preparation; (2) after six-month ageing; (3) after additional annealing at 550°C for two hours.

bands I also resulted in the disappearance of copper-rich regions with the inhomogeneous short-range order, which manifested itself in the disappearance of the diffuse maximum.

The results of intensity measurements carried out after subsequent (after the ageing) annealing at 550°C are also given in Fig. 2 The annealing resulted in a further decrease in the maximum intensity at angles $2\theta = 10$–$15°$. This decrease is caused by a partial desorption of the regions containing the Guinier–Preston bands I.

The presence of inhomogeneous short-range order in the Al–Cu (0.5 at.%) alloy established in this work is in line with the data on the activity coefficient [14]. According to [15], the activity coefficients γ_A are related to the parameter of short-range order α_1 by the following expression:

$$\ln \gamma_A = \frac{C_1}{2} \ln\left(1 + \frac{c_B}{c_A}\alpha_1\right). \tag{6}$$

The estimates obtained by Eq. (6) showed that for the Al–Cu solid solutions α_1 is negative. This finding is in qualitative agreement with our results. However, the application of the X-ray diffuse scattering method also revealed that ageing of the alloy at room temperature brings about a transformation of the short-range order into Guinier–Preston bands.

CONCLUSIONS

In freshly prepared Al–Cu solid solutions, there exists the inhomogeneous short-range order in the arrangement of the constituent atoms. Ageing at room temperature results in dramatic changes in the intensity of X-ray diffuse scattering: the diffuse maximum attributed to the short-range order disappears and a scattering pattern specific to the Guinier–Preston bands I appears.

REFERENCES

1. M. Hansen and K. Anderko, *Constitution of Binary Alloys,* McGraw-Hill, New York, 1958.
2. L. F. Mondolfo, *Aluminum Alloys: Structure and Properties,* Butterworth, London, 1976.
3. T. Kanadi and A. Sakakibara, *Phys. Status Solidi A,* vol. 114, no. 4, p. K17, 1989.
4. T. Kanadi and A. Sakakibara, *Phys. Status Solidi A,* vol. 117, no. 2, p. K97, 1990.
5. P. Mueller and B. Schofeld, *Acta Metall.,* vol. 37, no. 8, p. 2125, 1989.
6. A. N. Bekrenev and L. I. Mirkin, *Low-Angle X-Ray Analysis of Material Deformation and Rupture* (in Russian), Moscow, 1991.
7. G. Dlubek, R. Krause, and G. Wendrock, *Acta Univ. Wratisl., Mat., Fis., Astron.,* vol. 46, p. 96, 1989.
8. Yu. A. Bagaryatskii, *Dokl. Akad. Nauk SSSR,* vol. 77, p. 261, 1951.

9. A. Guinier, *Heterogeneities in Solid Solutions* (*Solid State Physics*, vol. 9), Academic Press, New York, 1959.
10. M. I. Zakharova, *Atomic Crystal Structure and Properties of Metals and Alloys* (in Russian), Moscow, 1972.
11. V. I. Iveronova and A. A. Katsnel'son, *Short-Range Order in Solid Solutions* (in Russian), Moscow, 1977.
12. V. M. Silonov and Saleh Hamami, *Fiz. Met. Metalloved.*, no. 4, p. 124, 1990.
13. A. A. Katsnel'son, O. V. Kris'ko, V. M. Silonov, and T. V. Skorobogatova, *Allowance for Atomic Displacement in Diffuse Scattering by Polycrystalline FCC and BCC Alloys* (in Russian), VINITI Typescript no. 4751, Moscow, 1983.
14. R. Haltgren, P. Desal, P. Hawkins, et al., *Selected Values of the Thermodynamic Properties of Binary Alloys,* ASFM, Ohio, 1973.
15. G. Vasilev, A. A. Katsnel'son, and V.M. Silonov, *Fiz. Met. Metalloved.*, vol. 45, p. 584, 1978.

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