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The Structure of Guinier–Preston Zones. II. The Room-Temperature Ageing of the Al–Cu Alloy

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In a previous paper the diffuse intensity diffracted by a Guinier–Preston (G.–P.) zone was expressed as a trigonometrical series with the coefficients dependent on the structure of the zone. The present paper deals with the determination of these coefficients from the variation of the diffuse intensity in relrod (00*l*) by the method of least squares for the natural aged Al–Cu alloy. From these the concentration of copper atoms in various atomic planes of the G.–P. zone, as well as the displacements of these planes with respect to the matrix, were determined.

1. Introduction

In the first part of this paper (Toman, 1955) the diffuse intensity of X-rays diffracted by a Guinier–Preston (G.–P.) zone was expressed as a trigonometrical series with coefficients determined by the structure of the zone; the possibility of determining these coefficients from the measured diffuse intensity distribution in relrod (00*l*) was shown. The knowledge of these coefficients enables us to evaluate structural features of the zone, namely the coppper-atom fraction in the various atomic planes (001) of the G.–P. zone and the displacements of these planes with respect to the matrix.

This method is applied in this paper in a modified form to the determination of the structure of G.–P. zones of the natural aged Al–Cu alloy.

2. Experimental part

High-purity materials were used for the preparation of the Al–Cu alloy with 3·95% Cu, the impurity content (Si, Fe) being below 0·03%. The wires, made from cast ingots, were 1 mm. in diameter and were converted to monocrystals by means of the strain annealing method. The monocrystals were quenched at 520° C. and aged naturally for 10 days. The aged crystals were etched in sodium hydroxide solution at 30° C. The etched crystals, prismatic in shape with cross-section 0·2×0·2 mm., were used for X-ray diffraction.

The Weissenberg patterns were obtained by using monochromatized Cu $K\alpha$ radiation. The bent quartz crystal monochromator was employed.

3. Intensity measurements

The diffuse intensity (00*l*) was measured on the microphotometer for the values of the continuous variable l ranging from 1 to 5. A series of photographs was taken with different exposure times under controlled conditions on account of the considerable variation of darkening in the measured interval. The measured intensities were corrected for polarization and Lorentz factors as usual. The absorption factor was determined by means of graphical integration. The diffuse intensity shows considerable maxima in the neighbourhood of the relps of the matrix with the streaks going out from the diffuse maxima in the direction of increasing Bragg angle. This observation is in agreement with that of Gerold (1954). The diffuse intensity in relps (002) and (004) and in their close neighbourhood cannot be directly measured because it overlaps the Bragg reflexion of the matrix. The interpolation in this range involves a certain degree of arbitrariness.

4. The determination of the structure

The diffuse intensity of X-rays diffracted by a G.–P. zone can be expressed as a trigonometrical series

$$I(l)_{\text{diff.}} = K\left[\sum_{-\infty}^{+\infty} A_n \cos \pi ln - \pi l \sum_{-\infty}^{+\infty} B_n \sin \pi ln + \pi^2 l^2 \sum_{-\infty}^{+\infty} C_n \cos \pi ln - \pi^3 l^3 \sum_{-\infty}^{+\infty} D_n \sin \pi ln\right], \quad (1)$$

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where

$$\left.\begin{aligned} A_n &= \sum_{-\infty}^{+\infty} \alpha_r \alpha_{r-n}\,, \\ B_n &= \sum_{-\infty}^{+\infty} (f_r \varepsilon_r \alpha_{r-n} - f_{r-n}\varepsilon_{r-n}\alpha_r)\,, \\ C_n &= \sum_{-\infty}^{+\infty} (f_r \varepsilon_r f_{r-n}\varepsilon_{r-n} - f_r \alpha_{r-n}\varepsilon_r^2)\,, \\ D_n &= \sum_{-\infty}^{+\infty} (\varepsilon_r^2 \varepsilon_{r-n} f_r f_{r-n} - \tfrac{1}{3}\varepsilon_r^3 f_r \alpha_{r-n})\,. \end{aligned}\right\} \quad (2)$$

The expression (1) was derived in the first part of this paper (Toman, 1955; hereafter T(I)) and here it is written in a slightly more general form with a slight change in notation. α_r and ε_r are defined as in T(I). The evaluation of the coefficients a_n, b_n, c_n, d_n in T(I) was based on the Fourier transform of the measured diffuse intensity by the determination of the areas and moments in the neighbourhood of the integral values of the variable. When working on this problem it seemed more advantageous to start directly from the expression for the intensity (1) and, on the basis of the principle of the least squares, to require the expression

$$\int_0^\infty w(l)\,[I_{\text{obs.}}(l) - I(l)]^2 dl \quad (3)$$

to be a minimum. In (3) $w(l)$ is an appropriately chosen weighting function. The condition (3) leads to the normal equations. For $j = 0$ or 2, these take the form

$$\begin{aligned} 2T_j(k) = &\sum_{-\infty}^{+\infty} a_n [F_j(n+k) + F_j(n-k)] \\ &- \pi \sum_{-\infty}^{+\infty} b_n [F_{j+1}(n+k) + F_{j+1}(n-k)] \\ &+ \pi^2 \sum_{-\infty}^{+\infty} c_n [F_{j+2}(n+k) + F_{j+2}(n-k)] \\ &- \pi^3 \sum_{-\infty}^{+\infty} d_n [F_{j+3}(n+k) + F_{j+3}(n-k)]; \end{aligned} \quad (4a)$$

for $j = 1$ or 3, they are

$$\begin{aligned} 2T_j(k) = &\sum_{-\infty}^{+\infty} a_n [F_j(n+k) - F_j(n-k)] \\ &+ \pi \sum_{-\infty}^{+\infty} b_n [F_{j+1}(n+k) - F_{j+1}(n-k)] \\ &+ \pi^2 \sum_{-\infty}^{+\infty} c_n [F_{j+2}(n+k) - F_{j+2}(n-k)] \\ &+ \pi^3 \sum_{-\infty}^{+\infty} d_n [F_{j+3}(n+k) - F_{j+3}(n-k)]\,. \end{aligned} \quad (4b)$$

The functions T_j, F_j are defined for j even as follows:

$$T_j = \int_0^\infty w(l) f^2(l) l^j I_{\text{obs.}}(l) \cos \pi l k dl,$$

$$F_j = \int_0^\infty w(l) f^4(l) l^j \cos \pi l (n-k) dl;$$

and for j odd thus:

$$T_j = \int_0^\infty w(l) f^2(l) l^j I_{\text{obs.}}(l) \sin \pi l k dl,$$

$$F_j = \int_0^\infty w(l) f^4(l) l^j \sin \pi l (n-k) dl\,.$$

The coefficients a_n, b_n, c_n, d_n are given by the relations

$$A_n = a_n f^2(l),\ B_n = b_n f^2(l),\ C_n = c_n f^2(l),\ D_n = d_n f^2(l)\,,$$

where $f(l) = f_{\text{Al}}/z_{\text{Al}}$ is the unitary atomic factor. The functions F_0, F_1, F_2 convert into γ, χ, ψ, quoted in T(I), by choosing $w(l) = 1/f^2(l)$ for the weighting function. T_0 is the Fourier transform of the diffuse intensity. The functions F_j for j even have the main maximum at the zero value of the argument; they are even and decrease rapidly as the argument goes away from zero. For j odd the functions F_j are odd. In both cases the values of F_j are appreciable only in the close neighbourhood of the zero value of the argument. With respect to the properties of the functions F_j the equations (4) take the form

$$\left.\begin{aligned} T_0(k) &= a_k F_0(0) + \pi^2 c_k F_2(0)\,, \\ T_2(k) &= a_k F_2(0) + \pi^2 c_k F_4(0)\,, \\ -T_1(k) &= \pi b_k F_2(0) + \pi^3 d_k F_4(0)\,, \\ -T_3(k) &= \pi b_k F_4(0) + \pi^3 d_k F_6(0)\,. \end{aligned}\right\} \quad (5)$$

The following equations hold for T_j and F_j:

$$\frac{dT_j(x)}{dx} = (-1)^{j+1} T_{j+1} \pi(x),\quad \frac{dF_j(x)}{dx} = (-1)^{j+1} \pi F_{j+1}(x)\,.$$

The coefficients a_n, b_n, c_n, d_n, calculated from the measured diffuse intensity and equations (5), are given in Table 1. Their values are not placed on an absolute scale. The values of coefficients b_n and d_n, especially their higher orders, are considerably influenced by the manner of the interpolation of the measured intensity in the close neighbourhood of the Bragg reflexions.

Table 1. *The experimental values of coefficients* a_n, b_n, c_n, d_n

n	a_n	πb_n	$\pi^2 c_n$	$\pi^3 d_n$
0	15·1	—	0·30	—
1	13·8	−1·66	0·10	0·03
2	11·8	−1·28	0·35	0·02
3	10·1	−0·87	−0·20	0·02
4	8·6	−0·62	−0·13	0·02
5	7·2	−0·45	−0·10	0·01
6	6·1	−0·38	−0·08	0·01
7	4·7	—	−0·07	—
8	3·6	—	−0·06	—
9	2·6	—	−0·05	—
10	2·0	—	−0·04	—

The quantities m_r and ε_r were determined by successive approximations from equations (6):

Table 2. *Occupations and displacements of various atomic planes* (001) *of the G.–P. zone calculated for different scale factors*

	Scale factor = 1		Scale factor = 7·8		Scale factor = 25·0	
r	m_r (%)	ε_r (Å)	m_r (%)	ε_r (Å)	m_r (%)	ε_r (Å)
0	19·6	$-0{\cdot}00$	54·9	0·00	98·0	0·00
1	10·0	$-2{\cdot}06\times10^{-2}$	28·0	$-5{\cdot}05\times10^{-2}$	50·0	$-7{\cdot}88\times10^{-2}$
2	7·8	$-0{\cdot}83\times10^{-2}$	21·8	$-2{\cdot}06\times10^{-2}$	39·0	$-3{\cdot}11\times10^{-2}$
3	6·0	$-0{\cdot}16\times10^{-2}$	16·8	$-0{\cdot}42\times10^{-2}$	30·0	$-0{\cdot}69\times10^{-2}$
4	4·6	$-0{\cdot}02\times10^{-2}$	12·9	$-0{\cdot}04\times10^{-2}$	23·0	$-0{\cdot}06\times10^{-2}$
5	3·5	—	9·8	—	17·5	—
6	2·6	—	7·3	—	13·0	—
7	1·8	—	5·0	—	9·0	—
8	1·2	—	3·4	—	6·0	—
9	0·8	—	2·2	—	4·0	—
10	0·5	—	1·4	—	2·5	—

Table 3. *The experimental and calculated values of* a_n, b_n, c_n, d_n

		Scale factor = 1				Scale factor = 7·8				Scale factor = 25·0			
n		a_n	πb_n	$\pi^2 c_n$	$\pi^3 d_n$	a_n	πb_n	$\pi^2 c_n$	$\pi^3 d_n$	a_n	πb_n	$\pi^2 c_n$	$\pi^3 d_n$
0	Obs.	15·1	—	0·30	—	118	—	2·34	—	378	—	7·50	—
	Calc.	14·8	—	0·45	—	115·2	—	3·10	—	370	—	8·60	—
1	Obs.	13·8	−1·66	−0·10	0·03	108	−12·9	−0·78	0·23	345	−41·5	−2·50	0·75
	Calc.	13·2	−1·53	−0·12	0·002	102·3	−12·9	−0·33	0·04	330	−42·0	−1·12	0·28
2	Obs.	11·8	−1·28	−0·35	0·02	92	−10·0	−2·73	0·19	295	−32·0	−8·70	0·60
	Calc.	11·6	−1·17	−0·21	0·008	90·9	− 9·82	−2·14	0·15	290	−31·2	−8·60	0·78
3	Obs.	10·1	−0·87	−0·20	0·02	79	− 6·80	−1·56	0·11	253	−21·8	−5·00	0·35
	Calc.	10·2	−0·80	−0·17	0·003	79·5	− 6·71	−1·64	0·08	255	−21·4	−6·25	0·45
4	Obs.	8·6	−0·62	−0·13	0·02	67	− 4·84	−1·00	0·10	215	−15·5	−3·20	0·30
	Calc.	8·7	−0·59	−0·09	0·001	67·9	− 5·02	−0·94	0·02	217	−15·9	−3·70	0·12
5	Obs.	7·2	−0·45	−0·10	0·01	56	− 3·50	−0·78	0·08	180	−11·3	−2·50	0·25
	Calc.	7·3	−0·47	−0·04	—	56·7	− 4·01	−0·51	—	183	−12·7	−2·13	—
6	Obs.	6·1	−0·38	−0·08	0·01	48	− 2·90	−0·63	—	153	− 9·5	−2·00	—
	Calc.	5·9	−0·40	−0·01	—	46·2	− 3·30	−0·23	—	147	−10·5	−1·17	—
7	Obs.	4·7	—	−0·07	—	37	—	−0·55	—	118	—	−1·75	—
	Calc.	4·7	−0·33	—	—	36·4	− 2·67	−0·14	—	118	− 8·5	0·88	—
8	Obs.	3·6	—	−0·06	—	28	—	−0·47	—	90	—	−1·50	—
	Calc.	3·6	−0·24	—	—	28·4	− 2·00	−0·11	—	90	− 6·3	−0·57	—
9	Obs.	2·6	—	−0·05	—	20	—	−0·39	—	65	—	−1·25	—
	Calc.	2·5	−0·18	—	—	19·8	− 1·49	—	—	62	− 4·3	0·50	—
10	Obs.	2·0	—	−0·04	—	16	—	−0·31	—	50	—	−1·00	—
	Calc.	2·1	−0·13	—	—	16·5	− 1·03	—	—	53	− 2·4	−0·40	—

$$\left.\begin{aligned} a_n &= (Z_{\mathrm{Cu}}-Z_{\mathrm{Al}})^2 \sum_{-\infty}^{+\infty} m_r m_{r-n}\,, \\ b_n &= 2Z_{\mathrm{Al}}^2 \sum_{1}^{\infty} (1+m_r)(m_{r-n}-m_{r+n})\varepsilon_r\,. \end{aligned}\right\} \qquad (6)$$

These were given in T(I) in a somewhat different notation. Here m_r is the copper atom fraction in the rth plane of the G.–P. zone and ε_r is the displacement of the rth atomic plane (001) of the G.–P. zone from its position in the matrix. The values of m_r and ε_r are evaluated for various scale factors in Table 2.

The coefficients a_n and b_n were used for the determination of m_r and ε_r. Furthermore, the values of the coefficients c_n and d_n, which also depend on m_r and ε_r, are available.

For these we have

$$c_n = Z_{\mathrm{Al}}^2 \sum_{-\infty}^{+\infty} (\varepsilon_r \varepsilon_{r-n} f_r f_{r-n} - \varepsilon_r^2 f_r m_{r-n})\,,$$

$$d_n = Z_{\mathrm{Al}}^2 \sum_{-\infty}^{+\infty} (\varepsilon_r^2 \varepsilon_{r-n} f_r f_{r-n} - \tfrac{1}{3}\varepsilon_r^3 f_r m_{r-n})\,.$$

The scale factor can be determined, at least in principle, from the agreement between c_n and d_n calculated on the basis of m_r and ε_r, obtained for different scale factors and those observed. The linear dependence of the coefficients a_n, b_n, c_n, d_n on the scale factor, together with the linear dependence of m_r on its square-root and a more complicated kind of dependence of ε_r on the scale factor enables us to determine it. The calculated coefficients a_n, b_n, c_n, d_n for m_r and ε_r, compared with the observed values, are given in Table 3 for different scale factors.

The table shows the best agreement of experimental and calculated values c_n and d_n for the greatest scale factor $K = 25$. Thus the structure of the G.–P. zone is given in the last column of Table 2.

To carry out an objective analysis of these results it seems essential to recapitulate the leading ideas of the present structure determination. On the basis of a certain general model we have deduced the possibility of expressing the diffuse intensity diffracted by a G.–P. zone as a trigonometrical series with coef-

ficients dependent on the structure of the G.–P. zone. These were determined by applying the method of least squares. If we assume the correctness of the proposed model of the G.–P. zone, then the series (1) with these coefficients should give the best agreement with the measured intensity distribution in the relrod (00l). The coefficients a_n served for the determination of the concentration of copper atoms in various atomic planes of the G.–P. zone, and similarly b_n gave the displacements of these planes with respect to their positions in the matrix. The coefficients c_n and d_n can be calculated from these quantities, using the relations following from the properties of the model. A comparison of the calculated values of c_n and d_n with that given by experiment enables us on the one hand to determine the scale factor and on the other hand to make us sure of the self-consistency of the model. This is summarized in Table 3, which shows a satisfactory agreement: the course of the calculated coefficients c_n and d_n is identical with that of those measured. The calculated and measured coefficients agree even better than in the order of magnitude.

A source of possible error lies in a certain inaccuracy connected with the interpolation of the diffuse intensity in the close neighbourhood of the Bragg reflexions. Especially the higher orders of b_n and d_n are extremely sensitive to the kind of interpolation selected.

The agreement between the observed intensity and that calculated from the proposed structure is here the final criterion, as in all cases of the X-ray structure analysis. This agreement is satisfactory in the whole range (see Table 4).

Table 4. *Comparison of the observed and calculated diffuse intensity in the neighbourhood of relps* (001), (002), (004)

l	$I_{obs.}$	$I_{calc.}$	l	$I_{obs.}$	$I_{calc.}$	l	$I_{obs.}$	$I_{calc.}$
0	185*	164	1·80	2	1	3·75	—	—
0·10	35	46	1·85	7	4	3·80	—	—
0·20	9	7	1·90	17	14	3·85	1	1
0·30	7	4	1·95	51	44	3·90	4	2
0·40	5	3	2·00	69*	65	3·95	9	9
0·50	5	2	2·05	49	51	4·00	14*	15
0·60	3	2	2·10	26	25	4·05	8	12
0·70	2	1	2·15	12	16	4·10	4	6
0·80	1	1	2·20	7	8	4·15	3	4
			2·25	6	7	4·20	2	3
			2·30	5	6	4·25	1	2
			2·40	4	5	4·30	1	2
			2·50	4	5	4·40	1	2
			2·60	3	4	4·50	1	2
			2·70	2	2	4·60	—	1
			2·80	1	1	4·70	—	—
						4·80	—	—

* Obtained by interpolation.

5. Discussion of the results

The characteristic feature of the G.–P. zone, as derived from the calculations of this paper, is its disc shape. The G.–P. zone is not represented by one single copper-rich plane only, but consists of a few atomic planes in which the concentration of copper atoms decreases in both directions from the central atomic plane. The decrease is quite rapid, as follows from the copper-atom content: for the fifth atomic plane it amounts to 17 atomic% compared with 98 atomic% in the central plane.

The structure of the G.–P. zone is further characterized by the displacements of the atomic planes from their positions in the matrix. These are limited to the innermost atomic planes in the centre of the zone and do not reach the magnitude expected from the known atomic radii of Cu and Al. This can be explained by the strains produced by the coherency of the zone with the Al matrix.

The data about the structure of G.–P. zones found in the literature are those of Guinier (1952) and Gerold (1954). Since Guinier's work has a rather qualitative character, it does not contain definite conclusions about the concentrations of copper atoms in various atomic planes and their displacements with respect to the matrix, though the disc shape of the zone is assumed. Guinier's conception of the G.–P. zone is further based on the intensity measurements which do not show the diffuse maxima found by Gerold (1954) and present author.

Gerold starts from very careful measurements of the diffuse intensity, but his calculations are not sufficiently general. He assumes *a priori* that the copper atoms segregate only into the central atomic plane of the G.–P. zone and then tries to arrive at agreement between the observed and calculated intensities by a suitable choice of the displacements of the neighbouring atomic planes. This agreement cannot be reached with Gerold's model in the whole range of the relrod in the interval $1 < l < 5$, as shown by him. The agreement in the neighbourhood of (002) maximum is good, but that round the (004) maximum is unsatisfactory.

The structure of the G.–P. zone resulting from our calculations differs appreciably from that proposed by Guinier and Gerold, but it gives a satisfactory agreement between the measured and the calculated intensities of the X-ray diffuse intensity. The objective reality of the proposed structure depends on the correctness of our primary assumptions. These are on the one hand the conception of the G.–P. zones as approximately two-dimensional independently diffracting structures, and on the other hand that all the diffuse intensity, including the diffuse maxima, is due to the diffraction by the G.–P. zones alone. If both these assumptions are correct, then the structure now proposed gives the best agreement between the observed and the calculated diffuse intensity.

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