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Abstract

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A MODEL OF A THREE-DIMENSIONALLY MODULATED COMPLEX FOR EXPLAINING X-RAY PATTERNS WITH SATELLITES

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The models of a one-dimensionally modulated structure currently available ([1–3]) for explaining x-ray patterns with satellites contradict recently obtained new experimental data ([4,5]). For a more complete explanation of the experimental data, we propose a model of an equiaxed complex in which modulation of the interplanar spacing and of the scattering power occurs simultaneously in three ⟨100⟩ directions. We have carried out detailed calculations of x-ray scattering by such a complex and compared them with experimental data for the alloy Fe –Ni 9.5 at.%–Ti 9.3 at.%.

At the initial stages of aging of this alloy, in the initial supersaturated solid solution with an f.c.c. structure, a metastable CsCl-type (Fe, Ni)Ti phase is precipitated ([6]). In this case, diffuse scattering in the form of blurred satellites located along the ⟨100⟩ directions is observed near the fundamental reflections. For a more detailed study of this scattering, in the work proposed here we obtained several series of x-ray patterns, from which sections of isodiffuse surfaces were constructed (see Fig. 1) for specimens after two treatments: No. 1—rapid cooling (in an alkaline solution) from the heating temperature for quenching (1200°) followed by tempering at 500° for 16 h; and No. 2—slow cooling from 1200° in water with tempering at 500° for 10 h. Treatment No. 2 corresponds to a somewhat later stage of decomposition, since the decomposition process had already partially proceeded during cooling from 1200°.

Fig. 2. Model of a complex modulated simultaneously along three ⟨100⟩ directions

Figure 2: Fig. 2. Model of a complex modulated simultaneously along three ⟨100⟩ directions

Fig. 1. Sections of isodiffuse surfaces at reciprocal-lattice nodes 110 and 020 by the plane (001), passing through these nodes: **A**—treatment No. 1 (see text), node 110; **B**—treatment No. 2, node 110; **C**—treatment No. 1, node 020.

The intensity was estimated visually on a 5-point scale*. In Fig. 1 two isodiffuse lines are plotted: one corresponding to zero intensity (points at which the diffuse effect merges with the background on the x-ray pattern) and the second corresponding to an intensity of 2.5 points. The diffuse scattering near the 110 nodes has a number of characteristic features, one of which is the absence of scattering in the plane perpendicular to the vector $\mathbf{H}_{110}$. The scattering on both sides of the plane of zero intensity is elongated perpendicular to the vector $\mathbf{H}_{110}$. However, if after treatment

* The 5th point is at the points of maximum intensity of the diffuse scattering.

No. 2 (Fig. 1, B) it is distributed uniformly, then after treatment No. 1 (Fig. 1, A) a definite concentration of intensity is observed in the maxima along ⟨100⟩, although the intensity between the maxima remains quite substantial. In the 200 reflections (Fig. 1, C) maxima not only of the first but also of the second orders, located along [100], are visible; in addition, there is very weak diffuse scattering perpendicular to $\mathbf{H}_{020}$.

For an explanation of this scattering let us calculate the model of the complex shown in Fig. 2. It is analogous to the model given in ([5]) for Fe—Be, with the only difference that for Fe—Be we have a regular periodic arrangement of such complexes, whereas in our case there is a chaotic distribution. The latter assumption is not entirely accurate, but it makes it possible to simplify all the calculations considerably. As is seen from Fig. 2, the complex has the form of a cube bounded by the planes {100}. To simplify the calculations we shall neglect the modulation of the scattering power, which is of negligible importance for the case of the Fe—Ni—Ti alloy.

Fig. 2. Model of a complex modulated simultaneously along three ⟨100⟩ directions

The law of variation of the coordinates in the complex is described in general form by the equation:

$$\mathbf{r} = \mathbf{r}_k + \mathbf{u} = (x_k + u_x)\mathbf{i} + (y_k + u_y)\mathbf{j} + (z_k + u_z)\mathbf{k}; \tag{1}$$

$\mathbf{r}_k$ is the vector characterizing the position of the k-th node of the average lattice; $\mathbf{u}$ is the displacement of an atom from the k-th node of the average

lattice; u_x, u_y, u_z are the components of this displacement along the axes [100], [010], and [001]. We assume that $u_x = u_x(x)$; $u_y = u_y(y)$; $u_z = u_z(z)$. If the scattering volume contains N independently scattering complexes, then for the amplitude of diffuse scattering, following Bagaryatskii ([8]), one may write:

$$A_{\mathrm{d}}(s) = N\bar{F}\left(\sum_x\sum_y\sum_z \exp\{-2\pi i[s_x(x_k+u_x)+s_y(y_k+u_y)+s_z(z_k+u_z)]\}-\right.$$

$$\left.-\sum_x\sum_y\sum_z \exp[-2\pi i(s_{xx}k+s_{yy}k+s_{zz}k)]\right). \qquad (2)$$

We have sums of two types:

$$\varphi_{1,x} = \sum_x \exp(-2\pi i s_{xx}k), \qquad \varphi_{2,x} = \sum_x \exp[-2\pi i s_x(x_k+u_x)]. \qquad (3)$$

Let us calculate these sums for our complex, denoting the number of interplanar spacings in the core of the complex by $2m$, and in the entire complex by $2M$. $\bar{a}$ is the mean lattice parameter, a_1 the minimum and a_2 the maximum distance between the planes {100}, corresponding to titanium-depleted and titanium-enriched regions, respectively. These distances (see Fig. 2) are constant along the corresponding ⟨100⟩ directions within the core of the complex (a_2) and outside the core (a_1); $\Delta a_1 = \bar{a} - a_1$ and $\Delta a_2 = \bar{a} - a_2$.

Calculation of the sums gives

$$\varphi_{1,x} = 2\operatorname{cosec}\pi s_x \cdot \cos M\pi s_x \cdot \sin(M+1)\pi s_x - 1; \qquad (4)$$

$$\varphi_{2,x} = 2\operatorname{cosec}\left(1-\frac{\Delta a_1}{\bar{a}}\right)\pi s_x \cdot \cos\left[\frac{\Delta a_1}{\bar{a}}(M-m)+(M+m)\right]\pi s_x\times$$

Fig. 3. Calculated, under the assumption of a three-dimensionally modulated complex, isodiffuse curves $|A_{\mathrm{d},\mathbf{k}}|^2 = \text{const}$ at reciprocal-lattice nodes 110 and 020 in the (001) plane passing through these nodes. *A*–for the parameters $2M = 40,\ 2m = 20$, node 110; *B*–for the parameters $2M = 80,\ 2m = 40$, node 110; *V*–for the parameters $2M = 40,\ 2m = 20$, node 020.
a–$I = 0$; *b*–$5\%I_{\max}$; *v*–$25\%I_{\max}$; *g*–$50\%I_{\max}$; *d*–$80\%I_{\max}$.

$$\times\sin(M-m+1)\left(1-\frac{\Delta a_1}{a}\right)\pi s_x + 2\operatorname{cosec}\left(1+\frac{\Delta a_2}{a}\right)\pi s_x\times$$

$$\times\cos(m-1)\left(1+\frac{\Delta a_2}{a}\right)\pi s_x \cdot \sin m\left(1+\frac{\Delta a_2}{a}\right)\pi s_x - 1. \qquad (5)$$

Figure 3. Calculated, under the assumption of a three-dimensionally modulated complex, isodiffuse curves $|A_{\mathrm{d},\mathbf{k}}|^2 = \mathrm{const}$ at reciprocal-lattice nodes 110 and 020 in the (001) plane passing through these nodes. A–for the parameters $2M = 40,\ 2m = 20$, node 110; B–for the parameters $2M = 80,\ 2m = 40$, node 110; V–for the parameters $2M = 40,\ 2m = 20$, node 020. a–$I = 0$; b–$5\%I_{\max}$; v–$25\%I_{\max}$; g–$50\%I_{\max}$; d–$80\%I_{\max}$.

Figure 3: Figure 3. Calculated, under the assumption of a three-dimensionally modulated complex, isodiffuse curves $|A_{\mathrm{d},\mathbf{k}}|^2 = \mathrm{const}$ at reciprocal-lattice nodes 110 and 020 in the (001) plane passing through these nodes. A–for the parameters $2M = 40,\ 2m = 20$, node 110; B–for the parameters $2M = 80,\ 2m = 40$, node 110; V–for the parameters $2M = 40,\ 2m = 20$, node 020. a–$I = 0$; b–$5\%I_{\max}$; v–$25\%I_{\max}$; g–$50\%I_{\max}$; d–$80\%I_{\max}$.

For one complex we may write

$$A_{\mathrm{d},\mathbf{k}}(s) = F(\varphi_2, x\varphi_2, y\varphi_2, z - \varphi_1, x\varphi_1, y\varphi_1, z). \tag{6}$$

Using the notation we have adopted for the Guinier complex model, which assumes modulation of the interplanar spacing only along one direction [100], we write

$$A_{\mathrm{d},\mathbf{k}}(s) = F(\varphi_{2,x} - \varphi_{1,x})\varphi_{1,y}\varphi_{1,z}. \tag{7}$$

As is known, from the distance of the satellites from the main maxima in the [100] direction, we can estimate the size of the complex in this direction.

Thus, for a numerical calculation of the quantity A_{d}, we must know the parameters $2M,\ 2m,\ a_1,\ a_2$, and $\bar{a}$. We determine $2M$ from the distance of the satellites; $2m$, from the broadening of the superstructure reflections. From the position of the main reflections characterizing the mean lattice for the alloy, we determine $\bar{a}$; from the position of the superstructure reflections, a_2. The quantity a_1 is determined from the relation $ma_2 + (M - m)a_1 = M\bar{a}$. The value a_2 was determined more accurately for treatment No. 2, where the broadening of the superstructure reflections is smaller; $a_2 = 2.91$ Å. We assume that this value is also valid for the earlier stage–for treatment No. 1.

For treatment No. 2 the quantities $2M$ and $2m$ are estimated by us respectively as 80 and 40, and for treatment No. 1 as 40 and 20; $\bar{a} = 2.89$ Å.

Let us compare the results of the calculation (Fig. 3) with the experimental data (Fig. 1). First of all, attention is drawn to the presence of a plane of zero intensity at the 110 reciprocal-lattice node for the calculated (Figs. 3A and 3B) and experimental (Figs. 1A and 1B) data, perpendicular to $\mathbf{H}_{110}$. The character of the isodiffuse lines is also the same: they describe regions elongated perpendicular to $\mathbf{H}_{110}$. Some difference is observed when comparing the data

Fig. 4

Figure 4: Fig. 4

for treatment No. 1 (Figs. 1A and 3A). On the calculated curves, maxima along the ⟨100⟩ directions appear very weakly, whereas experimentally they appear more clearly. More complete agreement is found for treatment No. 2 (Figs. 1B and 3B). When comparing the data for the 020 reflection, satisfactory agreement between the experimental and calculated data is also observed. A certain difference, readily explained by the neglect in the calculations of modulation of the scattering power, consists in the fact that experimentally for the 020 reflection weak scattering is observed perpendicular to the vector $\mathbf{H}_{020}$.

Fig. 4. Isodiffuse curves calculated on the assumption of Guinier complexes, $|A_{d,\mathbf{k}}|^2 = \text{const}$, at the reciprocal-lattice node 110 in the plane (001) passing through this node, for the parameters $2M = 40$ and $2m = 20$. The designations are the same as in Fig. 3.

In Fig. 4 a calculation of the quantity $|A_d|^2$ is given for the 110 reflection for the case of a model of a one-dimensionally modulated Guinier complex, taking into account unequal scattering by these complexes and an equal probability of the presence of complexes of all three possible orientations along ⟨100⟩. The calculation was made for the parameters $2M = 40$; $2m = 20$; $\bar{a} = 2.89$ Å; $a_1 = 2.87$ Å; $a_2 = 2.91$ Å. As is seen from a comparison of Figs. 1A and 4, the experimental data are in substantial contradiction with the calculated ones.

A qualitative comparison of the results of the calculation carried out by us with experimental data for other alloys (Ni–Si [9], alni [4]) also confirms the correctness of describing the alloy structure by means of a model of a three-dimensionally modulated complex. The chosen model is also in agreement with theoretical investigations on the thermodynamics of decomposition [10].

Here we have assumed a chaotic distribution of nuclei of the new phase. In reality, however, there is a certain correlation in their positions relative to one another, which should lead to the maxima in diffuse scattering becoming increasingly distinct in the ⟨100⟩ directions, as we also observed for treatment No. 1.

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Note: Figure translations are in progress. See original paper for figures.