

SHORT-RANGE ORDER IN ALLOY Ni-14at.%Ir**Lkhamsuren Enkhtor**National University of Mongolia, <http://www.num.edu.nm>
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Abstract. The diffuse scattering of X-rays was used to study the short-range order in a polycrystalline solid solution of Ni-14at.%Ir. Its parameters are determined in the first five coordination spheres. It has been experimentally proved that there is a short-range order in type $L1_2$. In the Krivoglaz-Klapp-Moss approximation, the ordering energies for the considered coordination spheres are estimated. The stabilizing role of the short-range order in the formation of the crystal structure of the Ni-14 at.%Ir alloy was revealed.

Keywords: short-range order, size effect, diffuse X-ray scattering

UDC: 539.1

Bibliography - 18 references

Received 18.04.2018

RENSIT, 2018, 10(1):53-58

DOI: 10.17725/rensit.2018.10.53

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1. INTRODUCTION

Studies of the nickel-iridium system are discussed in [1-5]. The existence of short-range order in the *Ni-Ir* system was previously established experimentally by the method of diffusion scattering of X-ray (DSXR) in [3-5]. On the diffractogram of the *Ni-10at%Ir* alloy, diffuse scattering associated with short-range order was detected, and the values of the short-range order parameters in the first three coordination spheres were found using the technique [6]. In this case, the value of the short-range order parameter on the first coordination sphere turned out to be greater by modulus than

the maximum possible under homogeneous ordering. This fact was explained by the authors [3-5] as an implementation of the local short-range order in these alloys.

However, in the *Ni-Ir* system, a type of short-range order was not established in alloys rich in nickel [3-5].

Experimental studies of short-range order in disordered solid solutions make it possible to obtain information on the ordering energies

$$V_{ij} = \frac{1}{2} (V_{ij}^{AA} + V_{ij}^{BB} - 2V_{ij}^{AB}), \quad (1)$$

where $i \neq j$, V_{ij}^{AA} - corresponds to the interaction between atoms of type *A*, located at the sites of the Ising lattice *i* and *j*, etc. To do this, use, in particular, the Krivoglaz-Clapp-Moss (KCM) approximation [7, 8]

$$\alpha(k) = \frac{D}{1 + 2C_A C_B \beta V(k)}, \quad (2)$$

where $\alpha(k)$ is the DSXR intensity in Laue units, $\alpha(k)$ and $V(k)$ are the Fourier transforms of the short-range order parameters $\alpha(r)$ and ordering energies $V(r)$, C_A and C_B are the component concentrations, $\beta = 1/k_B T$, k_B is the

Boltzmann constant, and T is the temperature. The authenticity of this approximation has been verified repeatedly [9-11].

The purpose of this paper is to determine the short-range order parameters necessary for establishing its type in a solid solution of $Ni-14at.\%Ir$ (using the direct DSXR method), using these parameters to find ordering energies (using the KSM method), and estimating short-range energy for alloy $Ni-14at.\%Ir$.

2. TECHNIQUE OF EXPERIMENT AND CALCULATION OF SHORT-RANGE ORDER PARAMETERS

According to the state diagram of $Ni-Ir$ alloys [12], shown in Fig. 1, in alloys rich in nickel, in the temperature range from 1200°C to the solidus line, there is a region of solid solutions.

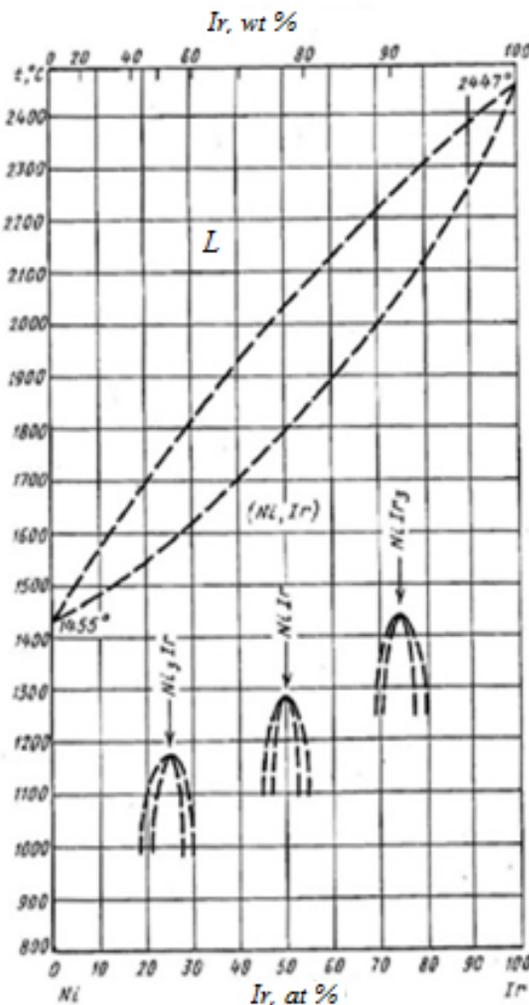


Fig. 1. The state diagram of $Ni-Ir$.

Considering the existence of a solid solution region, $Ni-14at.\%Ir$ alloy was chosen to study short-range order in nickel-iridium solid solutions.

The alloy was smelted in an arc furnace in a medium of pure helium. The starting materials were 99.9% pure iridium powder and 99.99% electrolytic nickel. The sample was annealed at 1400°C for 10 hours and quenched in water. The sample was then polished on skins and diamond paste up to a mirror surface.

Diffuse X-ray scattering was measured on an X-ray diffractometer on $CuK\alpha$ radiation using a scintillation counter. The measured values of the scattering intensity were reduced to electronic units by comparison with the scattering intensity by fused quartz. After reduction to electronic units, the contributions of air scattering, Compton, thermal, double Bragg and Laue scattering were subtracted from the intensity of DSXR.

The effects of static displacements were taken into account on the basis of the MA Krivoglaz theory [7]. According to this theory, the relationship between the intensity of the DSXR of a single-crystal alloy and the Fourier-image of the short-range order parameters has the form

$$I_D = N^2 \langle |C_q|^2 \rangle [\bar{f} \mathbf{q} \mathbf{A}_Q - (f_A - f_B)]^2, \quad (3)$$

where

$$\langle |C_q|^2 \rangle = \frac{1}{N} C_A C_B \left[1 + \sum_m \alpha(\mathbf{p}_m) e^{i\mathbf{k}\mathbf{p}_m} \right], \quad (4)$$

I_D is the scattering intensity, N is the number of atoms, C_A, C_B is the concentration of the components, \mathbf{q} is the scattering vector, \mathbf{p}_m is the radius vector of the m th atom, Q is the scattering vector reduced to the first Brillouin zone, f_A, f_B are the atomic scattering factors of the X-ray rays, $\bar{f} = C_A f_A + C_B f_B$ is the average concentration of the atomic factor.

Vector coefficients \mathbf{A}_Q were from the system of algebraic equations in the Born-Begby model:

$$\hat{\mathbf{D}}_Q \mathbf{A}_Q = \mathbf{P}_{Q_j}, \quad (i, j = 1, 2, 3), \quad (5)$$

where for FCC gratings:

$$D_{Q_x} = aC_{11} \left[2 - \cos \frac{Q_x}{2} \left(\cos \frac{Q_y}{2} + \cos \frac{Q_z}{2} \right) \right] + a(2C_{44} - C_{11}) \left(1 - \cos \frac{Q_y}{2} \cos \frac{Q_z}{2} \right),$$

$$D_{Q_y} = D_{Q_x} = a(C_{12} + C_{12}) \sin \frac{Q_x}{2} \sin \frac{Q_y}{2},$$

$$P_{Q_x} = \frac{a^2}{12} (C_{11} + 2C_{12}) \sin \frac{Q_x}{2} \left(\cos \frac{Q_y}{2} + \cos \frac{Q_z}{2} \right) \frac{1}{v} \frac{\partial v}{\partial c}.$$

The remaining terms of the dynamical matrix $\hat{\mathbf{D}}_{\mathbf{Q}}$ and the vector $\mathbf{P}_{\mathbf{Q}_i}$ can be obtained by cyclic permutation of the indices ($x \rightarrow y \rightarrow z$).

For a polycrystalline alloy, expression (1) can be rewritten in the form

$$I_D(q) = C_A C_B \Phi_0^{AB}(q) + C_A C_B \sum_i C_i \alpha_i(r_i) \Phi_i^{AB}(q) \quad (7)$$

where the modulating functions of the short-range order associated with static displacements for the zero and other coordination spheres have the form

$$\Phi_0^{AB}(q) = \left\langle \left[(f^A - f^B) + \langle f \rangle (\mathbf{qA}_Q^{AB}) \right]^2 \right\rangle_{\varphi, \gamma}, \quad (8)$$

$$\Phi_i^{AB}(q) = \left\langle \sum_{\mathbf{R}_i} \left[(f^A - f^B) + \langle f \rangle (\mathbf{qA}_Q^{AB}) \right]^2 \cos(\mathbf{qR}_i) \right\rangle_{\varphi, \gamma}, \quad (9)$$

where i is the number of the coordination sphere, C_i is the coordination number, α_i is the short-range order parameter for the i -th coordination sphere, $|\mathbf{q}| = 4\pi \sin\theta/\lambda$, $\mathbf{Q} = \mathbf{q} - \mathbf{G}$, \mathbf{G} is the reciprocal lattice vector of the solid solution, λ is the wavelength of the X-ray radiation used, $\langle \dots \rangle_{\varphi, \gamma}$ – averaging over all orientations of the scattering vector (in spherical coordinates with respect to φ, γ). In the case of crystals of cubic syngony, the calculation can be reduced by a factor of 48 with averaging over the solid angle bounded by the planes $Z = 0, X - Y = 0, Y - Z = 0$, and integration using expressions

$$\langle \mathbf{qA}_Q \rangle_{\varphi, \gamma} = \frac{12}{\pi} \int_0^{\pi/4} d\varphi \int_{\pi/2}^{\gamma_0} (\mathbf{qA}_Q) \cos \gamma d\gamma,$$

$$\langle (\mathbf{qA}_Q)^2 \rangle_{\varphi, \gamma} = \frac{12}{\pi} \int_0^{\pi/4} d\varphi \int_{\pi/2}^{\gamma_0} (\mathbf{qA}_Q)^2 \cos \gamma d\gamma, \quad (10)$$

$$\gamma_0 = \frac{\pi}{2} - \arcsin \left(\frac{\sin \varphi}{\sqrt{1 + \sin^2 \varphi}} \right).$$

The values of the lattice parameter a for the alloys studied were found from the rear reflections of the diffractograms. The elastic constants Ni were taken from [13] and Ir from [14]. The distortion parameters $\beta = \frac{1}{v} \frac{\partial v}{\partial \tilde{N}}$ were calculated from the experimental dependence of the parameters of crystal lattices on the concentration $a(c)$ [1] using the relation $\beta = \frac{3}{a} \frac{a_1 - a_2}{c_1 - c_2}$. Thermal diffuse scattering was calculated according to [15]. In this case, the value of the Debye temperature of the alloy from [1] was used.

Atomic factors and dispersion corrections for nickel and iridium were taken from [16] and [17], respectively.

3. RESULTS OF THE EXPERIMENT AND THEIR DISCUSSION

The results of measurements of the intensity of diffuse X-ray scattering, minus the side components, by the *Ni-14at.%Ir* alloy are shown in **Fig. 2**.

It can be seen that in the first interval of angles a sharp increase in intensity is observed with increasing slip angle 2Θ . In this case, the DSXR curve passes through a maximum at 2° equal to 30° . In subsequent intervals, the intensity values turned out to be small in magnitude and weakly oscillating. The maximum determined lies between the possible superstructural maxima (100) and

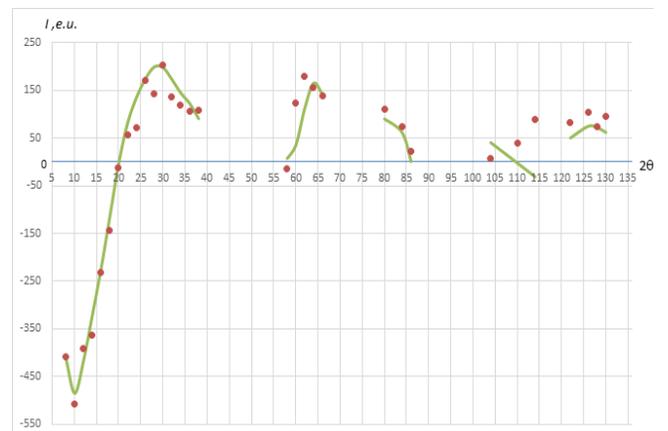


Fig. 2. Dependence of the diffuse scattering intensity I on the angle 2Θ by the alloy *Ni-14at%Ir*, ● - experiment, — - synthesis.

Table

The values of the short-range order parameters α_i and the ordering energies V_i for the Ni-14at.%Ir alloy and the short-range order parameters α_i for the $L1_2$ superstructure.

	α_i	V_i , meV	$\alpha_i(L1_2)$
1	-0.039	14.7	-0.333
2	0.092	-39.0	1
3	-0.018	7.5	-0.333
4	0.052	-20.5	1
5	-0.026	12.8	-0.333

(110), located respectively at the angles of 25.1 and 35.8 degrees by 2 degrees. Similar changes in the intensity of DSXR indicate the existence of a short-range order in the Ni-14at.%Ir alloy. The values of the short-range order parameters α_i for the Ni-14at.%Ir alloy were found from the experimental dependence of the diffuse scattering intensity on the angle 2Θ (Fig. 2) and are given in the **Table**. It is seen that the value of the parameter α_i is negative and, in contrast to [3-5], does not exceed the maximum possible value of the short-range order parameter with homogeneous ordering. On the third and fifth coordination spheres, the values of α_i also turned out to be negative, and on the second and fourth spheres positive. Those. for the alloy Ni-14at.%Ir experimentally established for the first five coordination spheres alternation of signs of the parameters of short-range order.

The reliability of the found values of the short-range order parameters α_i was verified by the reverse recalculation, i.e. restoration of the values of the initial intensity as a function of the slip angle (synthesized curve). This dependence is also shown in Fig. 2. It can be seen that the synthesized curve is close to the experimental curve, which is one of the criteria for the reliability of the values of the short-range order parameters α_i found.

The last column of the table shows the values of the short-range order parameters for the $L1_2$ superstructure.

It can be seen that this superstructure is characterized by the alternation of the

signs of the short-range order parameters α_i . Comparing the found signs of the short-range order parameters for the Ni-14at.%Ir alloy and the $L1_2$ superstructure, it can be asserted that it implements the short-range order in the $L1_2$ superstructure type. The parameters of short-range order and ordering energy for the first five coordination spheres, given in the table, can be used to estimate the value of the short-range energy of the E_{SRO} alloy using the expression [18]:

$$E_{SRO} = C_A C_B \sum_i C_i V_i \alpha_i. \quad (11)$$

The values of the ordering energies V_i included in this expression were calculated according to the following scheme. First, using the experimental values of the short-range order parameters α_i , the function values were found. Then, using the expression (2), the values of the function for the values belonging to the irreducible part of the Brillouin zone were determined. After that, the ordering energy values were found for the first five coordination spheres, also given in the Table. It turned out that they, like the short-range order parameters α_i , are of an alternating nature. Using the found values of the ordering energies for the first five coordination spheres and using expression (11), the short-range energy of Ni-14at.%Ir was estimated. It turned out to be negative and equal to -6.3 meV. The obtained value of short-range energy for the Ni-14at.%Ir alloy indicates that the short-range order introduces an appreciable stabilizing contribution to the energy of its crystal structure.

4. CONCLUSION

Allowance for static displacements of atoms by the DSXR Krivoglaz MA method allowed to determine the parameters of short-range order in a solid solution of Ni-14at.%Ir in five coordination spheres. Depending on the number of the coordination sphere, their alternating character is revealed, which

indicates the existence of a short-range order in the alloy of the $L1_2$ type. It is shown that in the alloy Ni-14at.%Ir, short-range order plays a stabilizing role in the formation of its crystal structure.

ACKNOWLEDGMENT

The work was carried out with the financial support of the project P2016-1127 of the advanced studies of the Mongolian State University on the theme "Study of phase transitions and static displacements in solid solutions" and the project of the Science and Technology Fund of the Ministry of Science, Education and Culture of Mongolia on the theme "Study of lattice dynamics and ordering in intermetallic solid solutions".

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