

The Short-Range Order and Ordering Energies in Gold–Copper Polycrystalline Alloys that Are Rich in Gold

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Abstract—The concentration dependence of the short-range order parameters in gold-rich polycrystalline disordered solid gold–copper solutions was investigated using the X-ray diffuse-scattering method. On the X-ray diffuse-scattering patterns of disordered alloys with 75, 83, and 90% gold, diffuse maximums that are typical of short-range order were absent in the region of the possible superstructure reflex (100), but in the region of the possible reflex (110), an intensity rise on the scattering patterns was revealed that noticeably depended on the gold concentration. The application of the method, taking the effects of static displacements on the considered coordination spheres into account, allowed the determination of short-range order parameters for nine coordination spheres. The spectra of short-range order parameters, which was calculated using the least-squares method, had the long-range sign-alternating representation that is inherent in the Cu_3Au superstructure. The absolute values of short-range order parameters were detected to decrease with an increase of the gold content in the alloys. The concentration dependence and small values of ordering energy of investigated polycrystalline alloys were revealed on the first coordination sphere using the Clapp–Moss method.

Keywords: X-ray diffuse scattering, short-range order, long-range order.

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INTRODUCTION

The short-range order in Cu–Au disordered solid solutions has been investigated repeatedly [1–5]. It has been studied in the most detail in copper–gold alloys that are rich in gold. The existence of short-range order in the Cu_3Au single-crystal alloy was noted in [4]. On the curves of the dependences of X-ray diffuse-scattering (XRDS) intensity on the grazing angle of disordered polycrystalline gold–copper alloys rich in gold [5], the diffuse maximums that are typical for short-range order were absent in the region of the possible superstructure reflex (100), while in the region of possible reflex (110), an XRDS intensity rise that noticeably depends on the gold concentration was revealed. The determination of short-range order parameters from the revealed complex scattering pattern was not performed in [5].

The goal of this work was to determine the spectrum of short-range order parameters in the gold-rich disordered solid solutions of gold–copper on the basis of the theory of M.A. Krivoglaz [6] allowing the effect of static displacements on the considered coordination spheres to be taken into account within the XRDS method.

INVESTIGATION TECHNIQUE

Gold–copper alloys containing 75, 83, and 90 at % gold were made from gold of special purity and elec-

trolytic copper in a shaft furnace in an argon atmosphere. The ingots were then homogenized at 760°C, after which the surface was ground and polished. The alloy of Cu_3Au composition was annealed at 700°C for 3 h and at 460°C for 8 h, while the alloy of CuAu_3 composition was used after annealing at 700°C for 3 h, at 500°C for 10 h, and at 300°C for 20 h in a vacuum no worse than 5×10^{-4} mmHg.

Diffusion scattering of X-rays was measured at the X-ray diffractometer on CoK_α radiation using a scintillation counter. The calculated values of scattering intensity were reduced to electron units by comparison with the intensity of scattering by fused quartz. After reduction to electron units, the contributions from air scattering, Compton scattering, thermal scattering, and double Bragg scattering were subtracted from the XRDS intensity.

Unlike [5], the effects of static displacements were taken into account on all coordination spheres on the basis of the theory that was developed by M.A. Krivoglaz [6]. According to this theory, the relationship of the XRDS intensity to the Fourier transform of interatomic correlation parameters ε has the form

$$I_D = N^2 \langle |C_\theta|^2 \rangle [\bar{f} \mathbf{q} \mathbf{A}_\theta - (f_A - f_B)]^2, \quad (1)$$

where

$$\langle |C_Q|^2 \rangle = \frac{1}{N} \left[c_A c_B + \sum_{\rho} \varepsilon(\rho) \cos \mathbf{q}\rho \right],$$

f_A and f_B are the atomic factors of X-ray scattering, c_A and c_B are the component concentrations, $\bar{f} = c_A f_A + c_B f_B$ is the concentration average atomic factor. The vector coefficients \mathbf{A}_Q were found from the system of algebraic equations in the Born–Begbie model [7]:

$$D_{Q_{ij}} \mathbf{A}_{Q_i} = \mathbf{P}_{Q_i}, \quad (i = 1, 2, 3),$$

where, for fcc lattices

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

$$D_{Q_{xy}} = D_{Q_{yx}} = a(C_{12} + C_{44}) \sin \frac{Q_x a}{2} \sin \frac{Q_y a}{2},$$

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

The remaining elements of the dynamic matrix D_Q and vector P_{Q_i} can be obtained by cyclic permutation of indices ($x \rightarrow y \rightarrow z$). The quantities C_{11} , C_{12} , and C_{44} that enter into the above expressions are the elastic constants of the matrix.

Expression (1) can be written as

$$I_D(q) = \Phi_0^{AB}(q) - \frac{1}{2} \sum_i C_i [\varepsilon^{AA}(r_i) \Phi_i^{AB}(q)], \quad (2)$$

where the short-range order-modulating functions, which are connected with static displacements, have the following form for the zeroth and other coordination spheres:

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

$$\Phi_i^{AB}(q) = (\sum_{R_i} [(f^A - f^B) + f \mathbf{q} \mathbf{A}_Q^{AB} \cos \mathbf{q} \mathbf{R}_i \sin \varphi, \gamma],$$

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

Table 1. Values of the short-range order parameters for disordered solid solutions Au–10 at % Cu, Au–17 at % Cu, and Au–25 at % Cu

at % Cu	25	CuAu ₃	17	10	Cu ₃ Au
	α_i	α_i	α_i	α_i	α_i
1	−0.12	−0.10	−0.06	−0.04	−1/3
2	0.60	0.24	0.34	0.26	1
3	−0.12	−0.09	−0.04	−0.02	−1/3
4	0.14	0.11	−0.01	0.00	1
5	−0.07	0.00	−0.04	−0.03	−1/3
6	0.77	0.05	0.55	0.51	1
7	−0.19	−0.02	−0.13	−0.12	−1/3
8	1.03	0.05	0.61	0.69	1
9	−0.02	−	−0.01	−0.03	−1/3
$a, \text{Å}$	3.99	−	4.02	4.04	−
β	0.28	−	0.22	0.20	−

Table 2. Calculated V_1/k_B values of the first three coordination spheres for gold–copper alloys that are rich in gold

i	Au–10 at % Cu	Au–17 at % Cu	Au–25 at % Cu
1	7	7	79
2	−440	−234	−130
3	14	9	98

$Y = 0$, and $Y - Z = 0$, while the integration can be conducted using the expressions

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

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

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

The parameters of interatomic correlations are connected with the Cowley short-range order parameters by the relationship $\varepsilon_i^{AA} = \mathbf{C}_A \mathbf{C}_B \alpha_i$. The parameters used in the calculations are given in Tables 1 and 2. Values of the lattice parameter a for the alloys under study were found from the reflexes of diffractograms located at large scattering angles. As the elastic constants, those of gold [8] were taken. The distortion parameters $\beta = \frac{1}{v} \frac{\partial v}{\partial c}$, where v is the unit cell volume, were calculated from experimental dependences of crystal-lattice parameters on the concentration $a(c)$

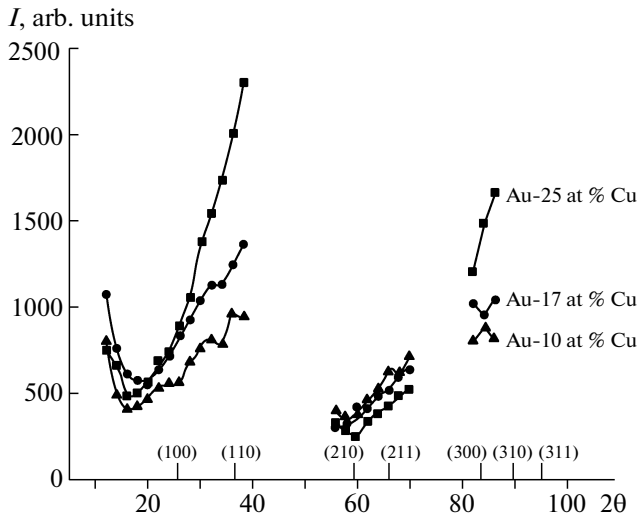


Fig. 1. The calculated values of the XRDS intensity of disordered polycrystalline solid solutions on the basis of gold containing 10, 17, and 25 at % copper. The vertical lines denote the positions of the possible superstructure reflexes of the CuAu_3 ordered phase.

using the relationship $\beta = \frac{3a_1 - a_2}{ac_1 - c_2}$. Atomic factors and dispersion corrections of copper and gold were borrowed from [9] and [10], respectively.

EXPERIMENTAL RESULTS

Figure 1 presents the measured values of XRDS intensity of gold-based disordered polycrystalline solid solutions containing 10, 17, and 25 at % copper and annealed at the lowest temperature after the obtained data were reduced to electron units and the thermal, Compton, and dual Bragg scatterings were excluded. The vertical lines denote positions of possible superstructure reflexes of the ordered CuAu_3 phase with $a = 3.99 \text{ \AA}$. It can be seen that for all three solid solutions in the domain of existence of possible superstructure reflexes (100)–(110) and (210)–(211), modulated diffusion scattering is present, which is typical for alloys with short-range stratification. It is also seen that in diffractograms in the region of the possible superstructure reflex (100) with a growth in the grazing angle 2θ , a weak increase in the diffusion scattering intensity is observed, which grows noticeably with approach to the reflex (100). The interpretation of this curve is ambiguous and was not given in [5].

DISCUSSION OF THE RESULTS

In this work, the short-range order parameters of disordered solid solutions of Au–10 at % Cu, Au–17 at % Cu, and Au–25 at % Cu were found using the least-squares method from the XRDS curves given in Fig. 1 and, in contrast to [5], following the technique

described above, which takes into account the static displacements in an arbitrary coordination sphere with the use of expression (2). The results of calculations of short-range order parameters for the polycrystalline alloy Au–25 at % Cu and literature data for the single-crystal alloy of the same composition [4] are presented in the second and third columns of Table 1. In the fourth and fifth columns of Table 1, the short-range order parameters for the Au–17 at % Cu and Au–10 at % Cu alloys are presented. In the last column of Table 1, the short-range order parameters for the Cu_3Au superstructure are given. Values of the parameters of crystal lattices a and the parameter β , which were used in this work, are presented in two lower rows of Table 1. A peculiarity of this technique is the use of the static displacement parameter β to choose a value that is important. This parameter was found from the concentration dependences of the crystal lattice parameters. From Table 1 it can be seen that for all three investigated alloys, Au–10 at % Cu, Au–17 at % Cu, and Au–25 at % Cu, the short-range order parameters appeared to be negative for odd coordination spheres, while for even coordination spheres they were positive. A similar distribution of signs is also typical of both the Cu_3Au superstructure and the single-crystal Cu_3Au [4]. These results show that short-range order, which is characteristic of the Cu_3Au superstructure, is set in gold-rich polycrystalline disordered solid solutions of gold–copper. It should be noted that the short-range order parameters appeared to be substantial in magnitude and in some cases close to the maximum possible values. The significant magnitude of the parameters α_i on the far coordination spheres indicates the existence of long-range interatomic interactions in the alloys.

In [11], an expression was suggested that connects the Fourier transform of the spectrum of short-range order parameters $\alpha(\mathbf{k})$ with the Fourier transform of the spectrum of ordering energies $V(\mathbf{k})$:

$$\alpha(\mathbf{k}) = \frac{1}{[1 - (T_C/T)V(\mathbf{k})/V(\mathbf{k}_m)]}, \quad (3)$$

where T_C is the temperature of the order–disorder phase transition and T is the temperature of hardening,

$$V(\mathbf{k}_m) = \frac{1}{2c_A c_B (1/k_B T)} \quad (4)$$

is the Fourier transform of the ordering energy at the point of reciprocal space \mathbf{k}_m , and c_A and c_B are the concentrations of components. From these expressions it is seen that knowing the T_C value, it is possible to calculate $V(\mathbf{k}_m)$ and $\alpha(\mathbf{k})$ for all values \mathbf{k} from the first Brillouin zone, and then the spectrum of short-range order parameters $\alpha(R_i)$. The Fourier transform of energies $V(\mathbf{k})$ entering in (3) can be also calculated on the basis of model values of ordering energies $V(R_i)$. When expressions (3) and (4) are used, it becomes

possible to find $\alpha(\mathbf{k})$ by means of varying the $V(R_i)$ and then to determine theoretical values of $\alpha(R_i)$. As the sought values $V(R_i)$, the values are assumed that correspond to theoretical values $\alpha(R_i)$ that are closest to the experimental values, $\alpha(R_i)$. An analogous scheme was previously used in [11] for estimating the values of the ratios V_2/V_1 and V_3/V_1 for the single-crystal alloy CuAu₃ using values of short-range order parameters from [4]. It was found that the ratios of ordering energies V_2/V_1 and V_3/V_1 for the single-crystal alloy CuAu₃ equal -1.2 and 0.9 , respectively. Similar calculations for the polycrystalline alloys gold–copper have not been performed previously. In this work, the above-described scheme was implemented for the polycrystalline disordered solid solutions of Au–10 at % Cu, Au–17 at % Cu, and Au–25 at % Cu. According to the values of the short-range order parameters given in Table 1, the values of the ordering energies for the first three coordination spheres were selected and are presented in Table 2. It can be seen that for all three polycrystalline disordered solid solutions, the values of the ordering energies on the first and third coordination spheres are positive, while those on the second coordination sphere are negative. This distribution of signs of ordering energies is typical of the Cu₃Au superstructure. However, the values of the parameters V_1/k_B proved to be lower in magnitude than the V_2/k_B values, although in disordered solid solutions the inverse situation has been observed [11]. The concentration dependence of the parameter V_2/k_B is also seen, which consists of a sharp reduction in its absolute values with the growth in the copper content. For the Au–25 at % Cu alloy, the V_2/k_B value is almost three times lower in magnitude than the V_2/k_B value for the Au–10 at % Cu alloy.

CONCLUSIONS

It was found that diffusion scattering connected with short-range order is present on diffractograms of polycrystalline disordered solid gold–copper solutions containing 25, 17, and 10 at % copper. For all three

alloys, the spectra of short-range α_i order parameters (which have the long-range sign-alternating behavior inherent in the superstructure Cu₃) were calculated from the XRDS intensity using the least-squares method. Their noticeable concentration dependence is revealed. When the copper content increases, a growth in absolute values of the α_i parameters is observed. Using the Clapp–Moss method [11], the ordering energy values were estimated for the first three coordination spheres; a peculiarity of these spheres consisted of small values for the first coordination spheres in comparison with the analogous values for solid solutions that are rich in copper. These data are evidence that there are no anti-phase domains in the alloys under study.

REFERENCES

1. V. I. Iveronova and A. A. Katsnel'son, *Short Range Order in Solid Solutions* (Moscow, 1977) [in Russian].
2. V. M. Silonov, *Introduction to Microscopic Theory of Solid Solutions* (Moscow, 2005) [in Russian].
3. V. M. Silonov, Radiotekhn. Nanosistemy. Inform. Tekhnol. **3**, 34 (2011).
4. B. N. Batterman, Appl. Phys. **28**, 556 (1957).
5. A. A. Katsnel'son, P. P. Safronov, V. G. Moiseenko, and V. M. Silonov, Fiz. Met. Metalloved. **43**, 111 (1977).
6. M. A. Krivoglaz, *Theory of X-ray and Heat Neutron Dispersion by Real Crystals* (Moscow, 1967) [in Russian].
7. G. H. Begbie and M. Born, Proc. Roy. Soc. A **188**, 179 (1947).
8. I. N. Frantsevich, F. F. Voronov, and S. A. Bakuta, *Elastic Constants and Coefficients of Elasticity of Metals and Nonmetals* (Kiev, 1982) [in Russian].
9. J. H. Hubbell, W. H. Veigele, E. A. Briggs, R. T. Brown, D. T. Cromer, and R. J. Howerton, J. Phys. Chem. Data **4**, 471 (1975).
10. M. J. Cooper, Acta Crystallogr. **16**, 1067 (1963).
11. S. C. Moss and P. C. Clapp, Phys. Rev. **171**, 764 (1968).

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