DIFFUSE SCATTERING AND STRUCTURE OF SUPERSATURATED IONIC SOLID SOLUTION NaCl-AgCl

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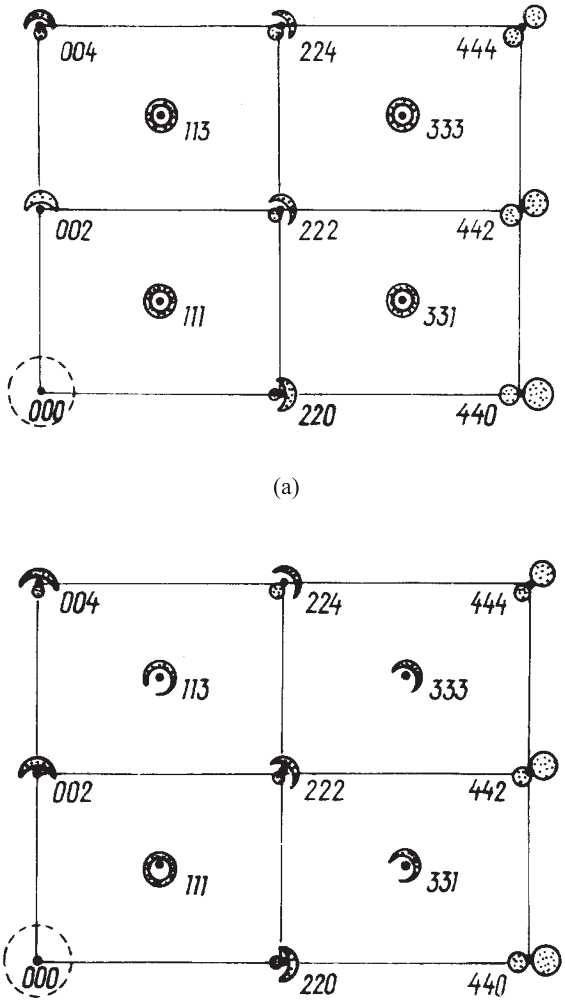
Many papers have been devoted to the study of the decomposition mechanism of the of supersaturated metallic solid solution. The main results of these investigation can be summarized as follows. The sequence of structure transformations during the decomposition of supersaturated solid solution is characterized by the emergence of metastable phases before the equilibrium phase. In the general case this basic precipitation sequence is identified as supersaturated solid solution → Guinier-Preston zones → metastable phases → stable phase.

Unfortunately, the number of papers devoted to the study of the decomposition of supersaturated non-metallic systems is rather limited. Hence, it is unclear whether there is a common decomposition mechanism for metallic and non-metallic systems. The present investigation has been carried out with the purpose of establishing the general regularities of the decomposition of supersaturated non-metallic solid solutions.

The polycrystalline and single-crystal samples of a NaCl – AgCl alloys with AgCl content equal to 10, 17, and 30 mol.% in different stages of decomposition were studied by X-ray diffuse scattering method. The specimens were homogenized at 500 °C for 1 hour and then quenched in streaming air. The X-ray photographs were obtained both by the methods of taking a series of stationary-crystal photographs with step-by-step rotation of specimen, and the methods of rotation and oscillation. X-ray photographs were taking on a cylindrical film by using non-filtered Cu radiation.

At the early stages of decomposition diffuse effects in the form of rings (halos) and crescents are observed on the X-ray photographs of these alloys. Fig.1 presents the schematic distribution of the diffuse effects in the (110) plane of the reciprocal lattice of the matrix. Formerly such types of diffuse effects were observed in X-ray patterns of quenched and naturally aged alloys Al – Ag, Al - Zn, Al - Ag - Zn, and Al - Zn – Mg [1-3]. For the NaCl - 17 mol.% AgCl alloys we found diffuse effects of halo-type around the reciprocal lattice points of matrix with odd (*hkl*), while around the points with even (*hkl*) diffuse effects were of crescents-type. With Σh_i^2 exceeding 20 the diffuse effects around points having even Miller indices are transformed into type II satellites. The diffuse effects around the points with odd *hkl* are considerably weaker and remain unchanged for all reflection orders. The occurrence of type II satellites is associated with the presence of distortion regions in the vicinity of the coherent particles. As the lattice parameter of AgCl is smaller than the lattice parameter of NaCl, dilatation distortions should arise in the vicinity of AgCl particles. The interpretation of the observed diffraction effects at this stage of decomposition is dealt with in detail in [4].

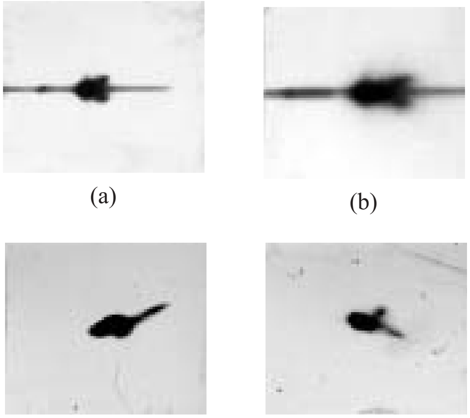


(a)

(b)

Fig. 1. Schematic distribution of the diffuse effects in the (110) plane of the reciprocal lattice for the NaCl-17 mol.% AgCl (a) and NaCl-30 mol.% AgCl (b) alloys [1]

A prolonged natural ageing brings about a transformation of diffuse effects. The X-ray photographs taking from quenched and aged for 6 years single crystal of NaCl - 10 mol.% AgCl alloy show diffuse streaks shifted slightly from the matrix spots in the <111> directions of increasing diffraction angles. Similar diffuse streaks were observed on the X-ray photographs of the quenched and aged Al - Zn alloys [3, 5, 6]. Fig.2 shows the X-ray photographs for oscillating crystals. The number of streaks near each matrix spot varies depending on the reflex indices from 2 to 4 - for type (n00) reflections; for (nnn) reflections it is equal to 4;



(a) (b)

(c) (d)

Fig.2. Diffuse effects on X-ray photographs for quenched and naturally aged for 6 years NaCl-10 mol.%AgCl alloy: (a) (420); (b) (600); (c) (531); (d) (620); oscillation crystal; θ increases from left to right

for (nn0) reflections it is equal to 2; for (nn2n) reflections it is equal to 3. The distribution of these streaks in the reciprocal lattice space is shown schematically in Fig.3. The length of the streaks grows with increasing Σh_i^2. The distribution of the diffuse streaks intensity exhibits the same regularity as that of the diffuse effects intensity at the early stages of decomposition. The diffuse streaks near matrix spots having odd indices *hkl* are considerably weaker in intensity than diffuse streaks near matrix spots having even indices *hkl*.

The existence at the early stages of decomposition of ring diffuse effects may be explained by the emergence in the solid solution of spherical particles, predominantly enriched with silver ions (Guinier-Preston zones). The average size of Guinier-Preston zones (G.P.zones), determined from the slope of the intensity distribution curve, is 3,45 nm, while the spacing between G.P.zones, determined from the position of the intensity maximum, is 16,9 nm. The average size of G.P.zones increases with the growth of the time of ageing . This leads to the growth of coherent strains near the G.P.zones. The shape of G.P.zones changes from spherical to ellipsoidal as a result of anisotropy of elastic constants.. The emergence at this stage of decomposition of diffuse streaks oriented in the <111> direction and shifted relative the matrix reflections in the directions of large diffraction angles can be explained by two different factors: the emergence of reflections due to a new phase or modulation of crystal lattice parameter in the <111> direction. In this paper the diffuse streaks are considered as reflections from the transition rhombohedral phase precipitating in the form of discs in the crystal {111} planes. For the determination of the new phase parameters reflections (600) and (620) with the highest value of Σh_i^2 were used. Parameters of the transition rhombohedral phase, which we shall designate as $AgCl_R$, have been found to be: a = 0.5564 nm and $\alpha = 91°13'$. A thorough check has revealed the absence of ordering. This shows that silver and sodium ions are distributed chaotically in the lattice of this phase in crystallographically equivalent positions. The characteristic feature of the rhombohedral phase is the equality of d_{110} interplanar spacing of $AgCl_R$ to the d_{110} interplanar spacing of matrix, this being the result of conservation of the average spacing between ions in (111) planes. The conservation of the average spacing between (110) planes in the course of the emergence of the rhombohedral phase leads to that the numbers of streaks (rhombohedral phase reflections) around the reciprocal lattice points have been found to be unequal. Since in the NaCl - AgCl alloys are platelets of four orientations, two diffuse reflections must be observed near type (nn0) points, and three near type (nn2n) points. In the vicinity of the other matrix reflections there should be visible four reflections of the rhombohedral phase. Thus, the second stage of decomposition of NaCl - AgCl ionic solid solution is characterized by the emergence of the metastable rhombohedral phase $AgCl_R$ precipitating as platelets or discs in {111} planes. In the case of metallic system transition metastable precipitates also are observed at this stage of decomposition. Their habit coincides either with {111} planes (as in the case of Al - Ag, Al - Zn alloys) or {100} (as in the case of Al - Cu alloy). Thus, the correspondence between all the decomposition stages to one another also reflects the common features in the decomposition of solid solutions with different types of binding.

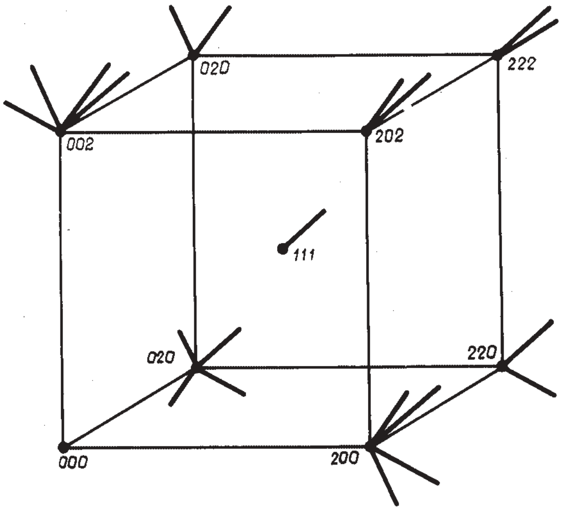


Fig.3. Schematic distribution of the diffuse streaks in the space of the reciprocal lattice for quenched and naturally aged for 6 years NaCl-10 mol.% AgCl alloy

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