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Diffusion phase transitions in alloys

Yu I Ustinovshchikov

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<u>Abstract.</u> We present a critical analysis of research on the thermodynamics, kinetics, and morphology of diffusion phase transitions in alloys. We show that diffusion phase transitions are mainly driven by the chemical potential difference due to a change in the sign of the chemical interaction among the component atoms. We explain how the sign of the chemical interaction energy can be obtained from experimental measurements. Examples are given to illustrate the kinetics and morphology of the ordering-separation phase transition in Ni- and Co-based alloys. We show how introducing the concept of the orderingseparation phase transition may affect our thinking in this area.

1. Introduction

Diffusion phase transformations occur in the majority of alloys upon a change in their heating temperature, and such transformations are always preceded by some redistribution of atoms of the components in the lattice of the alloys. These redistributions can be due to several reasons. In the early years of the formation of the views on such phase transformations, it was supposed that the precipitation of particles of the new phase from the solid solution is a consequence of the chaotic thermal motion of atoms in the lattice of alloys. As a result of this diffusion, a fluctuational overcoming of a certain energy barrier occurs with the formation of a critical nucleus of the new phase (the nucleation and growth, or classical nucleation theory). Later, however, a conclusion was made that the diffusion of atoms, which leads to the origin of a new phase, should appear as a consequence of the difference

Yu I Ustinovshchikov Physical-Technical Institute, Ural Branch of the Russian Academy of Sciences, ul. Kirova 132, 426000 Izhevsk, Russian Federation Tel. +7 (3412) 21 66 33. Fax +7 (3412) 72-25-39 E-mail: ust@ftiudm.ru

Received 18 October 2013, revised 2 December 2013 Uspekhi Fizicheskikh Nauk **184** (7) 723–737 (2014) DOI: 10.3367/UFNr.0184.201407b.0723 Translated by S N Gorin; edited by A M Semikhatov between the chemical potentials of the states of the alloy in the form of a nonequilibrium supersaturated solid solution and in the form of an equilibrium phase (the spinodal decomposition theory, e.g., the Cahn theory). Because the theory of nucleation and growth and the theory of spinodal decomposition do not overlap, they were regarded as alternatives that are applicable in different regions of the phase diagram: the classical theory working in the domain of compositions where the spinodal line is depicted in the phase diagram in the form of concave segments, and the spinodal decomposition theory in the domain of compositions where the spinodal curve is convex.

Modern concepts of the thermodynamics, kinetics, and morphology of diffusion phase transformations in alloys do not thus far completely correspond to the opportunities that have become available due to contemporary methods of study. The fact is that these concepts, just as the abovementioned theories, were formulated in the middle of the 20th century on the basis of the experimental data of those years, when many of the contemporary methods of study either did not exist or were at the initial stage of their development. Unfortunately, the ideas of those years have remained to date in an almost primordial form, whereas the methods for studying the structure of alloys and the equipment for such studies were constantly improving. Therefore, being based on the ideas that were predominant in the past and using the contemporary methods of study, in particular the method of transmission electron microscopy (TEM), we invariably come to a contradiction between these ideas and the results of experiments.

The use of the above-mentioned theories for explaining the experimental results obtained by the contemporary methods of studies, in particular TEM, leads us to an even larger gap between the ideas that are asserted by these theories and what is given by experiment. For example, already in the 1960s–1970s, in many alloys quenched in water from temperatures that correspond to regions of disordered solid solutions, either particles of precipitates of the new phase or a modulated structure were revealed by the TEM method. As the examples that are now classical, we can point to the alloys of systems such as Au-Ni [1], Ni-Mo [2], Fe-Be [3], Al-Zn [4], Cu-Be [5], and Nb-Zr [6], whose phase diagrams contain regions of solid solutions at high temperatures. The detection of such microstructures was sometimes explained by the fact that the regions of solid solutions in phase diagrams were determined insufficiently accurately [6], but in the majority of cases, the common opinion was that the decomposition of alloys by the spinodal mechanism occurs during the very process of quenching, i.e., in a very short time, comparable with the time of the alloy cooling in water. This was explained by the fact that upon spinodal decomposition, the stage of the formation of critical nuclei is absent [1-5]. This explanation contradicts both the Cahn theory of spinodal decomposition and the values of the experimentally determined diffusion coefficients, which are four orders of magnitude less than those required for diffusion in the process of formation of particles of the new phase to occur in the time of cooling of the alloy during its water quenching.

In order not to be enthralled by these 'strangenesses' of quenching, it is necessary to recall how phase diagrams, which are now conventional, were created in old times. The times when X-ray diffraction (XRD) was regarded as the only direct method that allows determining the phase composition of alloys at one point or another of a phase diagram are gone long ago; however, the phase diagrams that have been constructed using this method continue to be the main tool in the work of researchers. Back in his time, Guinier warned that the XRD method does not allow identifying particles of the second phase that have sizes less than the coherence domains [7]. This means that the highly dispersed phases that precipitate in the alloys of various systems cannot be fixed by the XRD method and are therefore absent from the conventional equilibrium phase diagrams. This fact, in turn, could be treated as follows: the regions of solid solutions in phase diagrams are not such regions, but are, rather, twophase regions that are fixed by water quenching. Therefore, the role of the basic tool that should be used to determine the phase composition of alloys in a phase diagram must belong to the local method of study-transmission electron microscopy. It was revealed in a number of studies performed using the TEM method that the phase composition of many alloys does not, in fact, correspond to the composition of the regions indicated in the conventional phase diagrams. These facts were considered in sufficient detail in our reviews [8, 9].

The conclusion that the regions of solid solutions in equilibrium phase diagrams are in reality two-phase regions agrees with the well-known axiom of thermodynamics that asserts that all solutions in nature are imperfect and have either positive or negative deviations from the Raoult law. In this case, the existence in conventional equilibrium phase diagrams of extensive regions of solid solutions, which are not equilibrium phases, raises certain questions that are due to the limited capabilities of the XRD method, which was used and is currently used for constructing phase diagrams.

The first mentions of the microstructures caused by phase separation, which are formed at high temperatures in the region of solid solutions of the Fe–Cr system, appeared in 1995–1996 [10, 11]. After water quenching from the temperature of 1200 °C, the Fe₅₀Cr₅₀ alloy exhibited a structure that in no way could be referred to as the structure of a disordered solid solution (Fig. 1) [11]. Based on the fact that positive deviations from the Raoult law had previously been revealed at high temperatures (1040–1400 °C) in the alloys of this system when measuring partial pressures of the vapors of



Figure 1. Fe₅₀Cr₅₀ alloy. Quenching in water from $1200 \,^{\circ}$ C after holding for 22 h.

the components [12], the authors of [10, 11] arrived at the conclusion that the structure presented in Fig. 1 should be referred to as phase separation. It is also known that in the alloys of this system at temperatures 440-830 °C, a chemical compound (a σ phase) is revealed that can be formed only in the case of negative deviations from the ideality. Based on these data, the authors of [10, 11] suggested that at the boundaries of the regions where the tendencies to both phase separation and ordering manifest themselves, an ordering-phase-separation phase transition should occur; moreover, this transition must occur at the level of changes in the electron structure because the atoms of the components reverse the sign of the chemical interaction under this transition. It is obvious that to experimentally detect this transition, it is necessary to use a method that could fix changes in the electron structure of the alloy upon a change in the temperature of heating the sample and therefore upon a change in the chemical interaction among the atoms of the components.

2. Use of the X-ray electron spectroscopy method for determining the sign of the ordering energy

The ordering energy sign is usually determined by measuring partial pressures of the vapors of the components at temperatures close to the melting point of the alloy. With decreasing the temperature, these pressures decrease sharply and, beginning from certain temperatures, cannot be measured, and therefore it was usually assumed that the sign of the ordering energy determined at very high temperatures is also retained at lower temperatures. Thus, it was considered that each binary system has its own ordering energy sign, which is constant for this system at any temperature. Other methods were also used, e.g., the measurement of molar volume by the method of an immobile droplet. Recently, owing to experiments carried out by X-ray electron spectroscopy (XPS) at different temperatures of sample heating, the existing concept (that the sign of deviations from the ideality is the same for all temperatures of heating) had to be rejected. It was shown that in the alloys of many systems at a temperature that is specific for each system, the sign of the ordering energy can change [13-15]. This change means that a transition should occur in the alloys in which the tendency

toward ordering is changed by the opposite tendency, i.e., a tendency toward phase separation appears in the alloy [13–15]. It is obvious that this transition can occur only at the level of changes in the electron structure.

The use of the XPS method (which, as is usually assumed, is the method for studying thin surface layers of a material) for determining the sign of the ordering energy of alloys at different temperatures is based on the fact that in a high vacuum, an increase in the temperature of the sample causes an accelerated evaporation of atoms from its surface. Therefore, the information obtained under such conditions of the experiment refers to all atoms that are located both on the surface and in the bulk of the sample.

The sign of the ordering energy, which depends on the temperature of the study, was decided from the shape of the valence bands obtained by the XPS method at this temperature. It was assumed that if the peak of the valence band of the alloy overlaps with the peak of the valence band of a pure component A that has a stronger spatial localization of the electron density in the environment of its own atoms (as a result of either its greater atomic weight or the fact that it is the solvent), then the nearest vicinity of A atoms contains A atoms, and therefore it is possible to speak about the formation of A-A bonds in the alloy and, consequently, also of the B-B bonds; hence, in the AB alloy, the tendency toward phase separation is observed. If the distribution of the density of 3d states in the alloy had a two-band structure because of an insignificant overlap of the d bands of atoms A and B, then it would be assumed that no A-A bonds existed in the alloy at a given temperature and therefore each atom A was involved in bonds with the atoms of component B; hence, the tendency toward ordering was assumed.

As an example, we examine the results obtained by the XPS method on the alloy Co₃Ni [16]. The XPS spectra were obtained at sample temperatures of 200, 500, 800, and 1100 °C. The spectra of the valence band, as well as the standard spectra of pure Co and Ni (at room temperature) are shown in Fig. 2. At temperatures of 200 and 500 °C, the spectra of the valence bands of the alloy have a two-band structure because of an insignificant overlap of the d bands of Co and Ni atoms, which is characteristic of an ordered state, when unlike atoms are located in the nearest neighborhood. At temperatures of 800 and 1100 °C, the spectra of the valence bands take the form of a superposition of the valence bands of the components, in which the shape of the valence band of the Ni atoms, which have a greater atomic weight, predominates. This suggests that at such temperatures in the alloy under consideration, a tendency toward phase separation is observed. Consequently, in the temperature range 500-800 °C an ordering-phase-separation transition occurs in the alloy, in which the sign of the ordering energy is reversed.

It is obvious that the changes that occur in the 3d valence band of the alloy upon the ordering-phase-separation transition must also lead to changes in the inner levels, in particular, to changes in the parameters of the multiplet splitting of the 3s spectra of Co and Ni in the Co₃Ni alloy. From the table that contains the results obtained, we see that the distance Δ between the maxima of the multiplets, which gives information about the exchange interaction between 3s and 3d shells, i.e., about the change in the spin state for the atoms of Co and Ni in the alloy, decreases upon ordering in comparison with that in the case of Co and Ni, both pure and in the alloy, when the tendency toward phase separation is manifested in it. This means that upon ordering, the



Figure 2. X-ray photoelectron spectra of the valence band of the alloy Co_3Ni obtained at different temperatures: (1) 200 °C; (2) 500 °C; (3) 800 °C; (4) 1100 °C. The spectra of the pure metals (5) Co and (6) Ni are given as standards.

interatomic distance between Co and Ni decreases, which, as can be assumed, is a consequence of enhancing the attraction between them. The atomic magnetic moments μ_{Co} and μ_{Ni} then increase, in contrast to the atomic magnetic moments of both pure Co and Ni and Co and Ni atoms in the alloy with the tendency toward phase separation manifested in it. This indicates that the number of uncompensated d electrons in the atoms of the components increases. Upon heating to 1100 °C, the distances between the multiplets of Ni and Co increase, which indicates a strengthening of the localization of d electrons in the vicinity of their own atoms.

Thus, in an ordering-phase-separation transition, a radical reconstruction of the electron structure of the alloy occurs, which reverses the sign of the chemical interaction between the atoms of the alloy components. Such a transition, which, in the existing classification can be referred to as a second-order transition, changes the direction of the diffusion flux of atoms, which leads to the dissolution of the existing microstructure and the formation of a new microstructure,

Samples	3s-spectra	$T, ^{\circ}\mathrm{C}$	I_2/I_1	⊿, eV	$\mu_{ m Co}/\mu_{ m B}$	$\mu_{ m Ni}/\mu_{ m B}$
Co ₃ Ni	Со	500	0.5	3.2	3.2	
Co ₃ Ni	Ni	500	0.4	2.7		2.2
Co ₃ Ni	Со	1100	0.3	3.4	1.7	
Co ₃ Ni	Ni	1100	0.3	3.3		1.7
Со	Со	20	0.3	4.6	1.7	
Ni	Ni	20	0.1	4.3		0.5

Table. Parameters of the multiplet splitting* of the 3s spectra of the Co₃Ni alloy.

* I_2/I_1 is the ratio of the intensities of multiplet splitting lines; Δ is the energy distance between the maxima of the multiplet splitting in 3s spectra; μ_{Co} and μ_{Ni} are the magnetic moments of Co and Ni atoms, and μ_B is the Bohr magneton.

corresponding to the opposite sign of chemical interaction. This means that the ordering-phase-separation transition occurs consecutively on two levels of the structure of the material: first, at the level of changes in the electron structure of the alloy (second-order transition) and then at the level of changes in the microstructure (first-order transition).

3. Examples of the ordering–separation phase transition in some binary alloys

3.1. Alloys of the Ni-Mo system

The equilibrium Ni₄Mo (D1_{*a*}), metastable Ni₃Mo (D0₂₂), and metastable Ni₂Mo (Pt₂Mo type) phases are considered in the literature as superstructures that are formed in the disordered solid solution Ni(Mo) with a face-centered cubic (fcc) lattice at temperatures of 700–900 °C [17–21]. It is assumed in [17–21] that before the formation of such phases in the Ni–(8–33)% Mo alloys, a short-range order is formed, which is detected in the electron diffraction patterns by diffraction peaks in the positions {1 1/2 0} (Fig. 3) [22]. In this case, the short-range diffraction peaks do not coincide with the reflections of the Ni₄Mo (D1_{*a*}) or Ni₃Mo (D0₂₂) phase. This noncoincidence forced the authors of [22, 23] to ask the question whether the diffraction patterns are formed as a consequence of the formation of short-range order in these alloys.

A comparison of the structural changes that occur in the alloys of the Ni–Mo system [17–21] at certain temperatures



Figure 3. Ni₄Mo alloy. Quenching from the liquid state (1600 °C) into water. SAED pattern.

with thermodynamic data for this system at the same temperatures indicates that there is a certain correlation between these sets of data. For example, it was shown that the enthalpy of the formation of a chemical compound in the Ni_{0.48}Mo_{0.52} alloy is a temperature-dependent factor, which changes from negative values at 700 °C to positive values at 1300 °C [24]. Meshkov et al. [25] and Katayama et al. [26], who investigated Ni-Mo alloys in a wide range of compositions ($0.3 \le x_{Mo} \le 0.75$), came to the same conclusions. The data in [27] also indicate a very strong temperature dependence of the enthalpy of the formation of chemical compounds in the Ni_{0 775}Mo_{0 225} alloy and positive values of the enthalpy at high temperatures. The use of the XPS method for determining the sign of the ordering energy, which depends on the temperature of the sample, showed that at temperatures near 1200 °C, an ordering-phaseseparation transition occurs in the Ni₄Mo and Ni₃Mo alloys. This means that in the alloys of the Ni-Mo system at high temperatures, a tendency should exist toward the phase separation of the solid solution.

Therefore, it is quite possible that the maxima in the positions $\{11/20\}$ detected in the electron diffraction patterns of Ni–Mo alloys after their high-temperature quenching and identified as being due to a short-range order that precedes the long-range order (see Fig. 3) are, in reality, a consequence of the formation of a structure of phase separation in the alloys at high temperatures. This phase separation already begins in the liquid state, when crystalline particles consisting of Mo atoms precipitate from the liquid solution [22, 23].

In this case, the set of maxima in the positions $\{1 \ 1/2 \ 0\}$ in the electron diffraction patterns of quenched alloys should be considered not as the result of 'short-range order' but as a consequence of the precipitation from the liquid solution of highly dispersed solid particles, which consist of Mo atoms and, apparently, have a body-centered cubic (bcc) structure. Such precipitation can occur because of the existence of a tendency to phase separation in the Ni–Mo system at high temperatures [22, 23]. The authors of [21] came to similar conclusions; they consider that the solid particles of Mo atoms are formed in Ni–Mo alloys at high temperatures as a consequence of a 'morphological instability' during the liquid–crystal phase transition.

The heat treatment of the Ni₄Mo alloy at 700–900 °C leads to the disappearance of the maxima in the positions $\{1 \ 1/2 \ 0\}$. A system of additional reflections is formed in their place, which indicates the precipitation of particles of the chemical compound Ni₄Mo with the Dl_a structure (Fig. 4). The morphology of these precipitates represents a set of rods oriented in the (100) directions, with a nearly quadratic shape of the cross section.

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Figure 4. Ni₄Mo alloy quenched from $1200 \,^{\circ}$ C and then heat treated at 800 $^{\circ}$ C for 24 h. SAED pattern. The inset shows a bright-field image in the plane (010).

The heat treatment of the alloy Ni₃Mo at the same temperatures also leads to the disappearance of the system of maxima in the positions $\{11/20\}$, which were formed earlier at high temperatures. Another system of additional reflections shown in Fig. 5 appears in their place. This system of reflections is not characteristic of the $D0_{22}$ structure, which, as is assumed in almost all literature sources [17-21], precipitates in the Ni₃Mo alloy. The electron diffraction pattern was identified as consisting of two systems of reflections: a system of reflections from the $D1_a$ structure (see Fig. 4) and a system of diffuse arcs that belong to an orthorhombic (distorted bcc) Ni₂Mo phase (Pt₂Mo type) [19]. It was shown that this situation occurs because a decrease in the temperature to below that of the ordering-phase-separation transition leads to the beginning of the dissolution of the crystalline particles of Mo atoms formed above the liquidus line. At those local points where these particles were located previously, at the beginning of the process of their dissolution, the concentration reaches a value that corresponds to Ni₂Mo, and therefore particles of the Ni₂Mo phase with a Pt₂Mo structure are formed at these locations. In the alloy regions depleted of Mo, when the concentration reaches a value that corresponds to the Ni₄Mo composition, particles with the Dl_a structure are formed. These intermediate metastable phases are formed in the alloy because direct reconstruction of the $A1 \rightarrow D0_{22}$ lattice in the alloys is crystallographically impossible [28]. During prolonged aging of the Ni₃Mo alloy at a temperature of 800 °C, the $Ni_4Mo(D1_a)$ and $Ni_2Mo(Pt_2Mo$ type) phases are transformed into the stable Ni₃Mo(D0₂₂) phase in the bulk of the alloy [22, 23].

Thus, the detection of an ordering-phase-separation transition put an end to the long dispute concerning the interpretation of the electron diffraction pattern presented in Fig. 3: this arrangement of maxima in the positions $\{1 \ 1/2 \ 0\}$ in the electron diffraction pattern appears when the liquid phase begins to be separated, with precipitation of crystalline particles of Mo atoms from the liquid solution. The subse-



Figure 5. Ni₃Mo alloy quenched from 1300 $^\circ$ C and then heat treated at 800 $^\circ$ C for 24 h. SAED pattern.

quent dissolution of these particles in the temperature range of ordering leads to the simultaneous precipitation of particles of two chemical compounds: Ni_4Mo with a $D1_a$ structure (in the alloy regions depleted of Mo) and Ni_2Mo with the Pt₂Mo structure (in the regions enriched in Mo), which during subsequent aging are transformed into the $D0_{22}$ phase over the entire volume of the alloy.

3.2 Ni₈₈Al₁₂ alloy

The decomposition of Ni–Al alloys has been examined for a long time in many experimental studies. It was revealed that the special mechanical and anticorrosive properties of such alloys detected at high temperatures are caused by the presence of coherent microstructures that are formed in a nickel-based solid solution due to the precipitation in it of the topologically close-packed intermetallic compounds $Ni_3Al(L1_2)$ [29–31].

Figure 6 shows the electron diffraction pattern of an alloy obtained after its quenching into water from 1300 °C. At a significant deviation of the orientation of the foil from the [100] zone axis, the intensities of the fundamental and satellite reflections are approximately identical. The detection of such satellites in the electron diffraction pattern of a binary alloy whose component atoms form the same type of crystal lattice (face-centered cubic in the case of Ni–Al alloys), usually indicates the formation in the matrix solid solution of clusters enriched in or depleted of the alloying element, i.e., having a lattice parameter that differs from that of the matrix solution. The formation of such clusters should be regarded as a phase separation of the solid solution, which usually occurs in the case of a positive interaction energy between the atoms of the alloy components.

We see in Fig. 6 that besides the satellite reflections previously revealed in Ni–Mo alloys, the electron diffraction pattern contains a system of maxima in the positions $\{11/20\}$, which was identified as being formed as a result of the phase separation of the liquid solution with the formation of crystalline particles consisting of Mo atoms. Therefore, the presence in the electron diffraction pattern (see Fig. 6) of the



Figure 6. Ni₈₈Al₁₂ alloy. Quenching in water from $1300 \,^{\circ}$ C (1 h). The SAED pattern was obtained at the orientation of the foil somewhat differing from the [100] zone axis.

system of maxima in the positions $\{11/20\}$ can also be considered a sign of the existence of a tendency toward phase separation rather than of the formation of a shortrange order in the alloy.

As is known, at the quenching temperature employed (1300 °C), aluminum is in the liquid state. When the Ni₈₈Al₁₂ alloy solidifies, the clusters that are enriched in aluminum solidify last because of the low melting point of aluminum. After quenching from a lower temperature (1200 °C), no maxima are observed in the positions $\{11/20\}$ in the electron diffraction patterns, but the microstructure represents a solid solution. As is known [8], in those alloys in which an ordering-phase-separation transition is observed, the structure of the solid solution can be formed at a temperature close to the temperature of this phase transition. Therefore, we assumed in [32] that the ordering-phase-separation transition occurs in this alloy at temperatures slightly greater than 1200 °C, and hence a microstructure characteristic of the tendency toward ordering should be formed in the alloy at lower temperatures.

Indeed, subsequent aging at 700 °C of the alloy that was previously subjected to quenching from 1300 °C sharply changes the electron-microscopic picture shown in Fig. 6. The microstructure and the electron diffraction pattern obtained from the alloy after aging at T = 700 °C are shown in Fig. 7. The electron diffraction pattern indicates that the precipitates in the micrograph are particles of the Ni₃Al phase. This can mean that a tendency toward ordering is observed in the alloy at T = 700 °C, which leads to the formation of the chemical compound Ni₃Al [32].

Thus, in the alloy $Ni_{88}Al_{12}$ at a temperature slightly exceeding 1200 °C, an ordering–phase-separation transition occurs at the level of changes in the electron structure. As a result of this transition, the microstructure in which aluminum is in the state not connected chemically with nickel (in the form of enriched clusters, with a tendency toward phase separation) is dissolved, and in place of clusters of Al atoms, particles of the chemical compound Ni₃Al are formed, which have the L1₂ crystal structure (tendency toward ordering).



Figure 7. Ni $_{88}$ Al₁₂ alloy. Aging of the quenched alloy Ni $_{88}$ Al₁₂ at 700 °C (24 h): SAED pattern, [001] zone axis.

3.3 Ni-Co alloys

The phase diagram of the Ni–Co system is very simple; at all compositions at any temperatures, only a solid solution is indicated in the diagram. No phase transformations occur in alloys with a high content of cobalt [33] except the allotropic α -Co $\leftrightarrow \epsilon$ -Co transition (at 422 °C). Apparently, it is for this very reason that the literature on the structural transformations in alloys of the Ni–Co system is extremely scant (there are only some structural data obtained by optical and scanning microscopy). At the same time, as was repeatedly noted in [8, 9], the presence in some equilibrium phase diagram of a solid-solution region that is not an equilibrium phase indicates gaps in our knowledge rather than the real structural state of one alloy or another at some temperature.

As was noted in Section 2, the XPS spectra for the alloys of Co_3Ni and Ni_3Co were obtained at temperatures of 200, 500, 800, and 1100 °C. The spectra of the valence band obtained for the Co_3Ni alloy at the above temperatures are given in Fig. 2. Based on the XPS data, a conclusion was made that the ordering-phase-separation transition occurs in the temperature range 500–800 °C [16].

A study of changes in the microstructure under the ordering-phase-separation transition was conducted on the Ni₃Co alloy with a low content of Co. In the Ni₃Co alloy, after holding for 1 h at a temperature of 1200 °C, the structure shown in Fig. 8 is formed. Round bright spots approximately 0.1–0.2 μ m in size with diffuse edges are observed against a dark background, apparently as a consequence of electron-microscopic absorption contrast caused by aggregates of cobalt atoms, which have a smaller 'mass thickness' than the surrounding solid solution enriched in nickel. It is obvious that such aggregates are formed without any changes in the lattice that could lead to the appearance of diffraction contrast. A similar structure is observed after aging of the alloy at 800 °C for 3 h [16].

As the aging temperature is decreased to $600 \,^{\circ}$ C, clusters of Co atoms, similar to those shown in Fig. 8, begin dissolving. Simultaneously with their dissolution, smaller bright particles, which can be seen with an electron microscope (also because of the absorption contrast) are formed along the contours of dislocations and the boundaries of subgrains (Fig. 9).

The authors of [16] reach the conclusion that the transition from clusters of a larger size to precipitates smaller



Figure 8. Ni₃Co alloy water quenched from 1200 °C. Absorption contrast.



Figure 9. Ni₃Co alloy, quenching from 1200 °C into water + aging (500 °C, 10 h). Bright-field image.

in size occurs gradually by means of the simultaneous dissolution of large clusters and the formation of small bright particles both at the defects of the crystal structure and in the defect-free regions of the matrix, including places where the dissolved large clusters were located previously (see Fig. 9). The authors of [16] note that the process of the dissolution of coarse clusters occurs as a result of the motion of concentric waves of dark contrast, which propagate from the periphery of the cluster to its center (see Fig. 9). Since the contrast from the dispersed particles is absorptive, the type of their lattice cannot be determined with the aid of TEM. Nevertheless, the authors of [16] conclude that the structure of these particles corresponds to the chemical compound Ni₃Co₂.

3.4 Ni-Cr alloys

In accordance with the commonly adopted phase diagram of Ni–Cr alloys [33], it can be assumed that in compositions close to Ni₄₀Cr₆₀, where the eutectic is observed in the diagram, a tendency toward phase separation is manifested in the alloys of this composition. At compositions close to Ni₆₈Cr₃₂, a tendency toward ordering appears; at temperatures below 590 °C, this tendency leads to the formation of the chemical compound Ni₂Cr with an orthorhombic lattice. The



Figure 10. Ni₄₀Cr₆₀ alloy. Quenching from the liquid state (1450 °C), bright-field image. In the inset, a SAED pattern is given; $[1\bar{2}]$ is the zone axis, the orientation relation is $\{112\}_{M} || \{102\}_{Cr_2Ni}$; the additional reflections from the variants 1, 4, and 5 are given in terms of the orthorhombic indices; the fundamental reflections are given in cubic indices.

precipitation of the Ni₂Cr compound has been mentioned by many authors [35–37], but none of them could fix this phase experimentally.

In [34], we attempted to determine whether there can be a situation where a change in the component concentration in the Ni–Cr system leads to a change in the sign of the chemical interaction between the Ni and Cr atoms. For this, we performed an electron-microscopic examination of the structure of the Ni₄₀Cr₆₀ alloy formed after heat treatment at different temperatures, which, according to the Ni–Cr phase diagram, is formed as a consequence of the tendency toward phase separation, and of the Ni₆₈Cr₃₂ alloy at temperatures below 60 °C, which manifests a tendency toward ordering. We assumed that determining this is fundamentally important not only for those phase diagrams in which a similar situation appears but also in general for the theory of chemical bonding in alloys.

3.4.1 Ni₄₀Cr₆₀ alloy. The microstructure of the alloy after quenching from the liquid state (from $T = 1450 \,^{\circ}\text{C}$) consists of relatively coarse grains of an elongated shape randomly located in a solid solution; near their boundaries, a dislocation network can be seen (Fig. 10). The selected-area electron diffraction (SAED) pattern obtained from these grains (see the inset in Fig. 10) indicates that they have a Pt₂Mo orthorhombic structure, i.e., the structure of the chemical compound Ni₂Cr, which, according to the Ni-Cr phase diagram, is formed in alloys close in composition to Ni₂Cr at temperatures below 590 °C. The formation of the chemical compound Cr₂Ni in a liquid solution means that the alloy at 1450 °C has a very strong tendency toward ordering, which leads to the formation of grains of the chemical compound with the Pt₂Mo structure even at temperatures above the liquidus line in the phase diagram [34].

As the temperature from which the quenching of the alloy is performed decreases from 1450 to 1200 °C, these grains increase in size; upon a further decrease in the temperature of the heat treatment of the alloy, their fragmentation begins.

The aging of an alloy at a temperature of 550 °C leads to the formation of two types of structures with the approximately identical morphology but with different dispersiveness. Some of these particles are formed during the fragmen-



Figure 11. Ni₄₀Cr₆₀ alloy, aging at a temperature of 550 $^\circ C$ for 300 h: dark-field image of precipitates.

tation of the chemical compound Cr_2Ni , which precipitates from the liquid solution (see Fig. 10). Other particles precipitate from the solid solution, which is formed at the temperature of the solidus line. Figure 11 shows a dark-field image of the microstructure formed in the regions of the alloy that solidified at the solidus temperature. Particles of the Ni₂Cr₃ phase can be seen. Thus, with a decrease in the temperature of heat treatment and an increase in its duration, each of these structures is developed according to its own scenario (grains of the Cr_2Ni phase are gradually fragmented, and particles of the Ni₂Cr₃ phase are coarsened) and the structure of the alloy approaches the equilibrium [34].

3.4.2 Ni₆₈Cr₃₂ alloy. Quenching the Ni₆₈Cr₃₂ alloy from the liquid state (T = 1450 °C) leads to the formation in it of the structure shown in Fig. 12. Round dark spots with diffuse edges are observed in the micrograph. Such diffuse spots can be regarded as aggregates of atoms of the dissolved component in the lattice of the solvent. It is obvious that these are aggregates of chromium atoms and that they cannot be referred to as 'embryos' of the Ni₂Cr phase, because they are formed at high temperatures and are destroyed with a reduction in the temperature, while the Ni₂Cr phase was



Figure 12. $Ni_{68}Cr_{32}$ alloy. Bright-field image of the microstructure after quenching from the liquid state.

previously observed in alloys of this composition only after prolonged aging at temperatures less than 590 °C [35–38]. The structure of the clusters of chromium atoms similar to that shown in Fig. 12 is also observed in electron-microscopic micrographs after quenching the alloy from temperatures of 1200 and 1000 °C; however, it was noticed that with a decrease in the heat treatment temperature, the number of clusters decreases and their contours become eroded.

In the Ni₆₈Cr₃₂ alloy, the Ni₂Cr phase was not observed at the above temperatures, including the range 500–550 °C, i.e., the temperatures at which, according to the phase diagram, it must precipitate. We note that the diffraction data concerning the detection of the Ni₂Cr phase in Ni–Cr alloys with a high content of nickel are given in only one study [36]; in others, the precipitation of this phase was judged only from indirect data [35, 37, 38].

Thus, heat treatment at 700 °C and lower temperatures leads to the formation of neither clusters nor particles of any new phases in the structure of the Ni₆₈Cr₃₂ alloy [32, 39]; in other words, based only on microstructural data, it is impossible to decide which of the tendencies is manifested in this alloy at aging temperatures. However, it is completely obvious that at high temperatures, the change in the sign of the chemical interaction between the atoms of the components in the nickel–chromium system occurs with a change in the concentration of alloy components [32, 39]. Hence, the Ni–Cr system is the first of those systems for which the possibility of a change in the sign of chemical interaction was confirmed experimentally to depend on a change in the concentration of the alloy components [32, 39].

3.5 Ni₃V alloy

Phase transformations in the Ni₃V alloy have been investigated in a large number of experimental studies, which is due to the extremely interesting and sometimes difficult to explain structural changes observed in the alloy after different heat treatments. At present, almost no one doubts the commonly adopted idea that in the disordered fcc solid solution of the Ni-25% at.% V alloy, an ordering occurs at 1045 °C with the formation of the Ni₃V phase (D0₂₂) that has a tetragonal distortion of 1.8% [40-43]. The relationship between the lattices of the fcc solid solution and the ordered D0₂₂ allows three variations of the stacking of unit cells in the ordered phase $D0_{22}$ to be formed [43]. It is assumed that in the process of water quenching from high temperatures in a Ni-25 at.% V alloy, a three-variant long-range order is formed. As was shown in [43], the formation of a three-variant long-range order during quenching cannot be suppressed even upon spinning, when the cooling rate is much higher than in the case of water quenching. The authors of [40–43] assume that the long-range $D0_{22}$ structure is formed as a result of the phase transition A1 \rightarrow D0₂₂, which occurs when the temperature of the alloy passes through the point 1045 °C. How such a phase transition occurs and how a multivariant D022 structure is formed inside the crystal lattice of the A1 solid solution (without a lattice distortion) in such a short time have not been explained in detail.

As regards the electron diffraction pattern obtained from the multivariant system of packing of the unit cells of the $D0_{22}$ phase, during subsequent aging of the quenched ordered Ni–25 at.% V alloy at lower temperatures, first the reflections of the variant II gradually begin disappearing, and then those of variant III, and only the reflections of variant I are retained [28]. The authors of [28] assumed that the reason for the decrease in the variance of the tetragonal $D0_{22}$ phase is the decrease in the fields of anisotropic internal stresses in the alloy as a result of the decrease and increase in the *a* and *c* axes of the cubic matrix. On the other hand, they considered that the process of decreasing the variance of the structure is simply the process of its roughening, similar to Ostwald ripening [43].

During the A1 \rightarrow D0₂₂ phase transition, which, as is assumed, occurs at 1045 °C, a redistribution of the V atoms over the lattice sites from the statistical distribution to an ordered distribution can occur only as a result of diffusion, which requires a certain time to be realized. An even longer time is required for the c' axis of the unit cells of the D0₂₂ phase to become oriented such that the *a* axes of the $D0_{22}$ phase are located along each of the three mutually perpendicular a axes of the disordered A1 solid solution. Specifically, it is precisely at such an arrangement of the unit cells of the $D0_{22}$ phase in the alloy that a three-variant ordered structure is formed with a characteristic arrangement of additional reflections in the electron diffraction pattern. We note that if the formation of the $D0_{22}$ phase with the three-variant array of unit cells occurs inside the A1 solid solution, it would necessarily lead to the growth of elastic stresses inside both the $D0_{22}$ phase and the solid solution, which would in turn be reflected in the electron diffraction pattern in the form of various distortions of the shape and arrangement of reflections. As was shown in [40-43], no such distortions in the electron diffraction patterns are observed.

In [44, 45], we assumed that the process of the formation of the multivariant $D0_{22}$ structure occurs in the liquid solution rather than in the solid state. The argument was based on the fact that it is precisely in the liquid solution that all the conditions for the free formation of the multivariant $D0_{22}$ structure are satisfied: the rate of diffusion of the alloy components in the liquid state is significantly higher than in the solid solution, and the formation of the $D0_{22}$ phase and the arrangement of its unit cells into a three-variant structure is not accompanied by the growth of elastic stresses. It then becomes clear why, in the electron diffraction patterns, any distortions are absent that usually occur upon the appearance in the crystal lattice of elastic stresses that can be connected with phase transitions occuring in it.

To verify the assumption that the $D0_{22}$ phase is formed from the liquid solution, the alloy was quenched from the liquid (1600 °C) state [44, 45]. In the SAED pattern, a characteristic system of additional reflections from the three-variant $D0_{22}$ structure and a system of fundamental reflections from the A1 solid solution are observed (Fig. 13). But if the quenching was performed from the solid state (from the temperature of 1200 °C), then the reflections in the electron diffraction pattern, which correspond to the second variation of the array of unit cells, were sometimes merely absent (Fig. 14). This means that with a decrease in the quenching temperature, the degree of the variance of the packing of the $D0_{22}$ unit cells decreases up to the formation of a single-variant structure in the alloy at 1000 °C.

The D0₂₂ phase is formed at the liquidus temperature; the remaining part of the liquid solution solidifies at the solidus temperature, forming an A1 lattice. A further decrease in the heat treatment temperature to 800 °C leads to the decomposition of the solid solution. However, the decomposition occurs not by the direct transformation A1 \rightarrow D0₂₂ but via the formation of the metastable intermediate phase Ni₄V(D1_a), which has the same lattice as Ni₄Mo (see Fig. 4) and is



Figure 13. Ni_3V alloy. Quenching from the liquid state. SAED pattern, zone axis [001].



Figure 14. $\rm Ni_3V$ alloy. Aging (800 $^\circ C,$ 84 h). Solid solution + a $\rm D0_{22}$ structure.

formed because the forward reaction $A1 \rightarrow D0_{22}$ in the alloys of Ni–Mo and Ni–V systems is impossible crystallographically [28]. After being held at 800 °C for 180 h, the entire alloy is transformed into the D0₂₂ phase (Fig. 15).

Thus, in [44, 45], we could not detect the ordering–phaseseparation transition in the Ni₃V alloy. In the entire temperature range, this alloy exhibits a tendency toward ordering, and all diffusion structural transformations in it are caused by the occurrence of two processes: the transformation of the unstable three-variant D0₂₂ structure, which was formed in the liquidus–solidus temperature range, into the stable single-variant structure; and the reconstruction of the lattice of the nonequilibrium Al solid solution, which solidified at the solidus temperature, into the D0₂₂ phase via the formation of the intermediate metastable D1_{*a*} phase.



Figure 15. Ni₃V alloy. Aging (800 °C, 180 h). A D0₂₂ structure.

3.6 Alloys of the Fe–Ni system

Alloys of the Fe-Ni system play a very important role in modern engineering: alloys with a predominant concentration of iron (Invars) have very low values of the thermal coefficient of linear expansion, while those with the predominant concentration of nickel (Permalloys) are softmagnetic materials with a very high magnetic permeability. The overwhelming majority of authors who have investigated Fe-Ni alloys explain the appearance of such properties by specific structural features of these alloys, in particular, by the formation in them of short-range and/or long-range order, by ordering, by the formation of a modulated structure, etc. [46, 47]. Such conclusions were reached based on the results of microstructure studies by integral methods (XRD, neutron diffraction, Mössbauer spectroscopy, the study of changes in the physical properties of alloys, etc.). Local electron-microscopic methods for the study of microstructure were used relatively rarely, and the interpretation of their results, especially in terms of shortrange and long-range order, did not explain the general picture of the processes of the formation of such structures, which did not allow relating a concrete change in the properties of alloys to a concrete change in their structure. As regards the commonly adopted Fe-Ni phase diagram, two temperature ranges are observed fairly well in it: one above and one below the temperature interval 500-600 °C. At temperatures below 500 °C, real (or presumed) chemical compounds are formed [33]; at temperatures above 600 °C, there are regions of solid solutions in the system. The presence of a solid-solution field in the equilibrium phase diagram, which, as is known from thermodynamics, is not an equilibrium phase, indicates the existence of gaps in our knowledge rather than the real structural state of the alloy at these temperatures.

3.6.1 Fe₆₈Ni₃₂ alloy. After water quenching from the temperature of 1300 °C (after holding for 1 h), the structure shown in Fig. 16 was revealed in many regions of the Fe₆₈Ni₃₂ alloy. Round dark spots 0.1-0.2 µm in size with diffuse edges are observed against a bright background, apparently as a consequence of electron-microscopic absorption contrast from some aggregates of atoms of the dissolved component, i.e., nickel, which, because of its heavier atomic weight, has a greater 'mass thickness' than the surrounding solid solution, which is depleted of nickel [15]. It is obvious that such accumulations of atoms are formed without any significant elastic changes in the lattice, which could lead to the appearance of diffraction contrast. We also note that the remaining components of the contrast visible in Fig. 16 (extinction contours, dislocations) are formed as a result of diffraction contrast. The reason for the formation of such clusters of nickel atoms becomes clear if we compare the electron-microscopic data with those obtained by the XPS method, which show that in the temperature range 500-800 °C, an ordering-phase-separation transition occurs in the alloy, with the sign of the ordering energy reversed. This comparison led the authors of [15] to the unambiguous conclusion that the formation of the structure presented in Fig. 16 is a consequence of the existence of a tendency toward phase separation in the alloy at a temperature of 1300 °C.

As the heat treatment temperature decreases to 740 °C, changes in the morphology of clusters in the electronmicroscopic micrographs and in the type of contrast from the clusters are observed; as the authors of [15] assume, these changes are connected with an increase in the nickel concentration in clusters enriched in nickel (Fig. 17). Instead of the structure containing rounded dark spots with diffuse edges, one that is very similar to a modulated structure is formed. It can be supposed that this structure is observed because of the diffraction contrast, since the boundaries between composition modulations are much more pronounced than those in the case of absorption contrast (cf. Figs 16 and 17). However, no satellites are observed in the electron diffraction patterns, apparently because the difference between the lattice parameters values in the depleted and enriched modulated regions is small and, moreover, the fcc lattice is preserved in the modulated regions depleted of nickel. The authors of [15] supposed that precisely the fcc



Figure 16. Fe₆₈Ni₃₂ alloy. Water quenching from $1300 \,^{\circ}$ C. Bright-field image of the microstructure.



Figure 17. Fe₆₈Ni₃₂ alloy. Water quenching from 740 $^{\circ}$ C. Bright-field image of the microstructure.

structure consisting of modulated regions enriched in and depleted of nickel is responsible for the high Invar properties of the alloy: as the temperature increases, the lattice expansion in modulations of one type is compensated by the lattice contraction in modulations of the other type.

A decrease in the aging temperature to $500 \,^{\circ}$ C, at which, according to the XPS results, the tendency toward ordering in the alloy is manifested, does not result in detecting particles of any chemical compounds in the structure of the alloy. In the bright-field image of the structure, only dislocations are visible. In the electron diffraction patterns, no features that could be indicative of the precipitation of particles of some new phase are observed either [15].

As is known, alloys of the Invar composition acquire their remarkable physical properties after heat treatment at temperatures of approximately 750 °C, i.e., when their structure, according to the phase diagram, represents a solid solution and according to the experimental results in [15], is a modulated structure formed as a result of the tendency toward phase separation. Apparently, it is precisely the modulated structure, whose existence allows reasonably explaining the mechanism of the appearance of such a surprising phenomenon as the Invar effect, that is the reason for this effect in Fe–Ni alloys.

3.6.2 Fe₂₃Ni₇₇ alloy. The quenching of this alloy from the liquid state (from 1600 °C) also fixes a microstructure corresponding to phase separation in it, albeit of a somewhat different morphology than that shown in Fig. 16. Quite a similar pattern is observed in the microstructure of the Fe₂₃Ni₇₇ alloy after its quenching from 1000 °C. In this case, with the temperature decrease, the size of the dark spots increases, and the degree of their darkening decreases [15]. Heat treatment at a temperature of 740 °C leads to a change in the morphology of the alloy. The structure of a solid solution with long narrow laths unevenly located in it is observed. Between such laths and the solid solution, clear boundaries can be seen quite well, which indicates a change in the type of contrast to the diffraction contrast. However, no satellites in electron diffraction patterns are observed, apparently because the elastic lattice distortions at the boundaries between the impoverished and enriched regions of the alloy are small. It is obvious that this structure is



Figure 18. Fe₂₃Ni₇₇ alloy. Water quenching from 740 $^{\circ}$ C. SAED pattern, the [001] zone axis. In the inset, bright-field image of the microstructure.

formed as a consequence of the tendency toward phase separation [15].

With a decrease in the heat treatment temperature to $450 \,^{\circ}$ C, i.e., below the temperature of the ordering-phaseseparation transition, a system of additional reflections (Fig. 18) appears in the electron-diffraction patterns, which indicates the nucleation of highly dispersed particles of the new phase L1₂ (which is usually called the γ' phase) on the {110} planes of the disordered matrix. The reflections are fairly weak, but are nevertheless well distinguished. The formation of the system of reflections from particles of the L1₂ phase in a virtually complete absence of contrast from these particles forced the authors of [15] to assume that the crystal lattice of the new-phase particles is completely coherent to the lattice of the ambient fcc solid solution.

A prolonged heat treatment of the alloy at 450 °C leads, as is known, to a sharp increase in the initial and maximum magnetic permeability in alloys with compositions close to that under investigation. Therefore, the authors of [15] arrived at the conclusion that the permalloy properties of the alloy were due to the formation of highly dispersed completely coherent particles of the ordered L1₂ phase in the γ solid solution.

4. Ternary Ni–X–Al alloys

In Ni–X–Al nickel-based superalloys, two types of phases are usually formed: Ni₃Al (L1₂) and Ni₃X (D0₂₂). In some studies [31], the authors assumed that the combination of such phases in the structure occurs due to a eutectoid reaction during low-temperature aging. However, this opinion is not in complete agreement with practice. Indeed, if the formation of the microstructure that ensures the high heat resistance of nickel superalloys occurred during the low-temperature eutectoid decomposition, then the heating of turbine blades under operating conditions to temperatures exceeding the eutectoid decomposition temperature would lead to the loss of the superalloy properties of these alloys much earlier than this occurs in practice.

4.1 Ni₇₀Mo₂₅Al₅ alloy

Ternary Ni–Mo–Al alloys were studied in [30], where 15 compositions of the alloys of Ni with 5–20 at.% Mo and 5–22 at.% Al were investigated. Apart from the stable Ni₃Al (L1₂) and Ni₃Mo (D0₂₂) phases, several metastable phases, such as Ni₄Mo (D1_a), Ni₂Mo (Pt₂Mo type), and a short-range-order state, have been revealed. The authors of [30] assumed that the metastable phases play an important role in the strengthening of these alloys. In the Ni–25 at.% Mo– 5 at.% Al alloy, a topologically close-packed σ -Ni–Mo phase was detected and described in sufficient detail; between grains of this phase, plates of an H phase were located in the form of wedge-shaped domains [31]. It was assumed that the σ phase is responsible for the degradation of the mechanical properties of Ni–Mo-based alloys.

In [48], we considered the diffusion processes in the $Ni_{70}Mo_{25}Al_5$ alloy as taking place in three diffusion pairs: Ni/Mo, Ni/Cr, and Mo/Cr. We assumed that the phase transitions in these diffusion pairs occur analogously to those in the appropriate binary alloys of the Ni–Mo, Ni–Cr, and Mo–Cr systems. It is obvious that the sequence and the completeness of these phase transitions depend on the temperature at which the heat treatment of the alloys is conducted and on the relations among the values of the chemical affinities between the elements in these diffusion pairs at each temperature of study [48].

In the electron diffraction pattern of the alloy after its water quenching from the liquid state (1600 °C), a system of diffraction maxima in the positions $\{1 \ 1/2 \ 0\}$ can be seen, which is similar to that shown in Fig. 3. The diffraction maxima, which are relatively weak in intensity, are visible only near the zero reflections. As was shown in [22], these maxima appear in the electron diffraction patterns of Ni₄Mo and Ni₃Mo only if phase separation occurs in the alloys, such that one of the separated phases is in the liquid state.

The investigation of a water-quenched alloy after its heat treatment at 1300 °C for 1 h shows that besides the diffraction maxima at the positions $\{11/20\}$ in the electron diffraction pattern, weak satellites appear near the fundamental reflections, which are similar to those revealed in the binary alloy $Ni_{88}Al_{12}$ (see Fig. 6) but have a low intensity. The presence of such satellites in the electron diffraction pattern permitted us [32] to conclude that phase separation into clusters enriched in and depleted of aluminum occur in this alloy at high temperatures (1300 °C). Therefore, the presence of such satellites in the electron diffraction pattern of this alloy can also be treated as phase separation in the Ni-Al diffusion pair leading to the formation of clusters enriched in Al. It is obvious that the aggregates of Al atoms at 1300 °C cannot exist in the solid state and, apparently, this is one of the reasons for the appearance of diffraction maxima in the electron diffraction patterns in the positions $\{11/20\}$.

Because the Mo₃Al phase starts to form in the Mo–Al system, according to the Al–Mo phase diagram [33], at temperatures of about 2400 °C, i.e., in the liquid state, we can expect the Ni₇₅Mo₂₀Al₅ alloy at temperatures above the liquidus line to contain both crystalline particles of Mo atoms formed as the result of the tendency toward phase separation



Figure 19. $Ni_{70}Mo_{25}Al_5$ alloy. Quenching from $1200\,^\circ C$ after holding at the temperature for 1 h. Bright-field image of the microstructure.

in the Ni/Mo diffusion pair, and quasi-liquid aggregates of Mo and Al atoms that correspond to the Mo_3Al phase in chemical composition and which were formed as the consequence of the tendency toward ordering in the Al/Mo diffusion pair.

As soon as the alloy temperature decreases to that of the ordering-phase-separation transition $(1200-1300 \,^\circ\text{C})$, signs of the chemical interactions between the atoms of Ni and Mo and between the atoms of Ni and Al become opposite, and the atoms of Ni and Mo and Nii and Al tend to form the corresponding chemical compounds between themselves. The Mo and Al atoms form colonies of fairly large disk-shaped precipitates of the Mo₃Al phase (Fig. 19), which has an A15 cubic lattice. Such colonies were observed (although in smaller numbers) after quenching the alloy from the temperature of $1200 \,^\circ\text{C}$ (after holding for 1 h) and after subsequent heat treatments at lower temperatures (1000 and 800 $^\circ\text{C}$).

The atoms of aluminum in other regions of the alloy, which are free of disk-shaped particles of the Mo₃Al phase, form particles of the chemical compound with nickel (Ni₃Al (L1₂)). A decrease in the heat treatment temperature increases the dispersiveness of such precipitates. After the heat treatment of the alloy in the range 600–700 °C, a mixture of particles of the two phases is observed: Ni₃Mo (D0₂₂) and Ni₃Al (L1₂) [48].

4.2 Ni₇₅V₂₀Al₅ alloy

At present, two opposite tendencies can be observed in the development of new superalloys and the improvement of existing alloys: the tendency toward an increase in the number and/or amount of 'refractory' elements X in the composition of Ni–X-Al superalloys, and the tendency toward simplification of the composition of superalloys. On the one hand, it is usually assumed that the addition to the binary alloys Ni–M (where M is Mo, V, Al, and other similar elements) of some amounts of other 'refractory' elements X (Ti, Nb, etc.) leads to an increase in the number of intermetallic phases in the alloys, which must lead to an even greater increase in the heat resistance of superalloys. On the other hand, the complication of the chemical and hence phase composition is known to lead to an increase in the imperfection of the structure and therefore to a reduction in the heat resistance of the alloy.

When aluminum is added to Ni-V alloys, which is considered to improve the high-temperature (high-strength) properties of these alloys, it is assumed that the combination of Ni₃Al and Ni₃V alloys, which are formed in the structure of the A1 solid solution as a result of low-temperature eutectoid decomposition, can improve the heat resistance of the alloy [29]. In this case, it is assumed that the structure of eutectoid decomposition formed at 1045 °C and lower temperatures must be preserved at temperatures that exceed 1045 °C, in view of the 'low diffusion mobility of atoms in the fcc structure' [29]. However, this opinion clearly runs counter to practice. In reality, as was noted above, if the formation of the microstructure that is responsible for the high heat resistance of Ni-V-Al superalloys occurred during the lowtemperature eutectoid decomposition, then the heating of turbine blades under service conditions at temperatures that exceed the eutectoid decomposition temperature would inevitably lead to the dissolution of the eutectoid structure and therefore to the loss of the superalloy properties of such alloys much earlier than this is observed in practice.

Assuming that the A1 \rightarrow D0₂₂ phase transition occurs in ternary Ni–V–Al alloys at 1045 °C, the heat treatment of such alloys in [29] was performed according to the following scheme: water quenching from 1100 °C (solid-solution treatment) and subsequent aging at 1000 °C of different durations, up to 840 h (after this treatment, the eutectoid decomposition structure is formed, as the authors of [29] assumed). It was supposed that such heat treatment of different durations would allow investigating the evolution of the microstructure in the A1 \rightarrow D0₂₂ phase transition, and the conclusion was made that the process of the decomposition of alloys is inevitably associated with the ordering of two different phases: Ni₃Al (L1₂) and Ni₃V (D0₂₂); the mechanism of this transition is not pearlitic and remains unexplained thus far.

Upon the addition of aluminum to Ni–V alloys, chemical interactions in the new emergent diffusion pairs (Ni–Al and V–Al) occur, besides the chemical interaction between atoms of nickel and vanadium. Because the concentration of aluminum in the $Ni_{75}V_{20}Al_5$ alloy is not very large, the formation of the microstructure occurs mainly in the Ni–V diffusion pair. The nature of this process can be judged from the results of the investigation of the binary alloy Ni_3V [45] (see Section 3.5).

Figure 20 shows a bright-field image of the microstructure after quenching of the Ni₇₅V₂₀Al₅ alloy from the liquid state (1500 °C) into water [44]. Particles of precipitates are visible in the micrograph. In the electron diffraction pattern obtained from such particles, additional reflections are observed. Because the precipitates visible in Fig. 20 are fixed by quenching from the liquid state, they must already exist in the liquid state, i.e., at a temperature of 1500 °C. If we consider sharp water quenching as a heat treatment that should fix the structure formed by diffusion when holding the alloy at the temperature from which the quenching is performed, then it is completely reasonable to regard these particles as aggregates of pure aluminum atoms that are already formed in the liquid state of the alloy. This, by the way, is confirmed by the presence of bright features in the form of arcs (see Fig. 20) fixed at the moment of solidification of the liquid alloy upon its pouring into water. There can be only one reason for the formation of such clusters: the tendency toward phase separation in the Ni/Al diffusion pair, which was previously revealed in the binary alloy



Figure 20. Ni₇₀Mo₂₅Al₅ alloy. Quenching from the liquid state. Bright-field image of the microstructure.

 $Ni_{88}A1_{12}$ at temperatures above 1200 °C [32]. At higher temperatures, aluminum exists in the alloy in a state chemically nonbound with nickel, i.e., it forms clusters that are in the liquid state (see Fig. 20).

In other regions of the foil, whose orientation is close to [001], after quenching of the alloy from the liquid state, a system of additional reflections from the three-variant $D0_{22}$ structure and a system of fundamental reflections from the solid solution are observed. Because the ordering-phaseseparation transition has not been revealed in binary Ni-V alloys (at any temperature, only a tendency toward ordering is observed in this system [44]), the chemical compound Ni₃V $(D0_{22})$ can exist in the Ni/V diffusion pair of this alloy at any temperature below the liquidus line, at which it begins forming. Therefore, particles of the Ni₃V (D0₂₂) phase after heat treatment at different temperatures differ only in the degree of their dispersiveness and in the variance [44]. Indeed, after quenching of the Ni₇₅V₂₀Al₅ alloy from 1200 °C, according to electron diffraction patterns, a two-variant structure of the $D0_{22}$ phase is revealed, which indicates the transformation of the three-variant structure into the twovariant one with a decrease in the heat treatment temperature. Aging at 800 °C for 80 h leads to an even larger reduction in the degree of the variance-to the formation of a singlevariant structure of the D0₂₂ phase. In bright-field micrographs, a structure is observed that consists of a mixture of small grains of the $Ni_3V(D0_{22})$ and $Ni_3Al(L1_2)$ phases [44]. Therefore, it is not surprising that the detection of this structure led the authors of [29], who investigated alloys of the Ni–V–Al system, to the conclusion on the eutectoid nature of the decomposition of the solid solution in these alloys.

The results in [44] showed that the addition of an element such as aluminum to Ni–V alloys can limit the maximum working temperature of the Ni₇₅V₂₀Al₅ alloy to values lower than the temperature of the ordering–phase-separation transition in the Ni–Al diffusion pain. At the same time, if aluminum is not added to Ni–V alloys, the maximum working temperature of the Ni–V alloys can be approximately estimated as the solidus temperature, at which the Ni–V alloy solidifies, rather than the temperature of the ordering–phase-separation transition, above which the aluminum clusters are in the liquid (or quasi-liquid) state.

5. Conclusions

The experimental detection of the ordering-phase-separation transition, which occurs at a specific temperature at the level of changes in the electron structure, has allowed revealing and explaining the nature of diffusion phase transformations in alloys. Methods have been suggested to determine the temperature of the ordering-phase-separation transition for different alloys with sufficient accuracy and thereby to control the direction of diffusion fluxes by changing the heat treatment temperature. Hence, the usual practice of heat treatment of alloys that includes obligatory quenching from the 'solid solution' field before aging seems to be useless, and the 'solid solution' fields in phase diagrams can be regarded as regions with an unknown structure. The structure in these regions should be verified by the TEM method in order to determine their real structure. The phase diagrams, especially those with 'solid solution fields', must be refined by drawing lines that correspond to the temperature of the orderingphase-separation transition. Simultaneously, it is necessary to abandon the commonly adopted stereotype that a nonideal solid solution can exist in alloys as an equilibrium phase and that the 'solid solution fields' can be depicted in equilibrium phase diagrams.

From the examples given in this review, we can conclude that the direction of the diffusion flux in an alloy is determined by the sign of the chemical interaction between the atoms of the components. Besides the ordering-phaseseparation transition, the direction of the diffusion flux can be affected by other factors, which in the Ni-V system, for example, has long been hindering a reasonable explanation of the formation of a three-variant $D0_{22}$ structure in the alloys of this system.

We also note that the separation of phase transitions into first- and second-order ones does not reflect the real picture. Any phase transitions occur depending on a change in some external factor (temperature, pressure) on the level of changes in the electron structure. In turn, the changes in the electron structure under such transitions lead to a change in the properties (magnetic, ferroelectric, superconducting, etc.so-called second-order transitions) either directly or through a change in the aggregate state, crystal lattice type, or microstructure (first-order transitions).

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