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Ordering, phase separation, and phase transformations in Fe-*M* alloys

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Contents

Abstract. **Concepts of ordering, phase separation, and phase transformations in metallic solid solutions are discussed in the context of the latest experimental data on the microstructure of Fe-*M* alloys. It is shown that the type of chemical interaction between alloy component atoms depends on the degree of the localization of 3d-valence electrons on atoms rather than on the ratio of energies of ordering in different coordination shells. The morphology of the products of phase transformations in alloys with a tendency to ordering or phase separation is considered, and the known mechanisms of phase decomposition are analyzed. The decomposition of alloys having a tendency to ordering and to phase separation is described in thermodynamic terms. It is shown that solid-solution fields in phase diagrams are in fact regions where the alloys have a tendency to phase separation and where, at certain correlations between free-energy components, separation microstructures are formed. It is noted that phase transformations in alloys can occur at different levels of the structure of matter: the 'primary' occur at the level of changes (ordering – phase separation) in the electronic structure, and the 'secondary' are realized at the level of changes (order – disorder) in the microstructure.**

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1. Introduction

The theory of alloy phase transformations and the theory of alloy ordering were born at different times (the first sprang from Gibbs [1], and the second from Bein [2]) and are usually considered as two descriptions of two quite different ways of relaxation of a system from its nonequilibrium to the equilibrium state. It was assumed that the way in which the system would relax (i.e., either with the formation of a new phase or via ordering of the solid solution) depends on the concrete nature of the alloy [3]. It was recognized that a heterophase structure that is formed upon relaxation of the system can arise as a result of a redistribution of alloy component atoms over the sites of the crystal lattice. A redistribution that involves atomic displacements over large distances leads to either a change in only the composition of the phases (phase separation) or to changes in the composition and crystal lattices of the phases (phase transformation), whereas a redistribution related to atomic displacements over small distances leads to ordering [3]. When finding lines of a new phase in X-ray diffraction patterns of some alloys, conclusions were frequently made that a phase transition takes place; when finding diffuse X-ray scattering in X-ray diffraction patterns of other alloys, conclusions were made that an order – disorder transition, i.e., atomic ordering, occurred [4]. When in the second half of the twentieth century methods of transmission electron microscopy (TEM) obtained wide application and when it was found that the diffuse X-ray scattering can be a consequence of the formation of various highly dispersed clusters in the solid solution, which represent one of the initial stages of the formation of particles of a new phase and result in an increase in coherent elastic stresses [5, 6], it could have been expected that the phase transformations and ordering in alloys would be considered in terms of a single theory. However, this has not happened and, as before, the theory of alloy phase transformations and the theory of alloy

ordering have continued mainly developing separately and have different terminologies.

In this review we tried to analyze the existing concepts of phase transformations, ordering, and phase separation in light of experimental results obtained in recent years with the purpose of refining our views on the nature of transformations that occur in alloys during their relaxation and to reach a compromise between the theoretical concepts and experimental data.

2. Chemical interactions between the atoms of alloy components

The statistical theory of ordering is known to be based on the model of pairwise interactions. This model, also called the Bragg – Williams – Gorsky (BWG) model [7, 8], permits one to describe many effects observed in orderable alloys. Its further development, which made it possible to take into account the interaction of not only nearest but also next-nearest neighbors [9, 10], as well as the application of methods of computer simulation, should have helped in solving many problems related to the ordering processes in alloys. However, unfortunately, the results of such calculations cannot so far be recognized as adequate for real relaxation processes in alloys.

Let us consider one such work [11] devoted to numerical simulation (using the Monte Carlo method) of ordering processes in stoichiometric $Fe_{50}Cr_{50}$ and $Fe_{50}V_{50}$ alloys. It is known that measurements of partial vapor pressures of the alloy components at temperatures of 1100 – 1300 °C revealed positive deviations from Raoult's law in the Fe – Cr system [12], whereas the same method revealed negative deviations in the Fe – V system at temperatures $T = 1200 - 1400\,^{\circ}\mathrm{C}$ [13]. Based on these data, the authors of Ref. [11] selected $Fe_{50}Cr_{50}$ as an alloy that demonstrates a tendency to phase separation at all temperatures, and $Fe_{50}V_{50}$ as an alloy that demonstrates a tendency to ordering. The simulation was performed up to the seventh coordination shell (CS). In each CS (I – VII), the 'ground' state was chosen as follows: phase separation in CS I, B2 phase in CS II, B32 phase in CS III, B11 phase in CS IV, ..., and 'phase 7' in CS VII. Based on the results of simulation, the authors of Ref. [11] concluded that the energy of ordering can change sign upon going over from one coordination shell to another, and the atomic configuration that is formed in the alloys depends on whether the energy of ordering has a large positive value for at least one of the above seven ground states. Based on the extended method of perturbations, the authors of Ref. [11] showed that there arises a competition between the macroscopic tendency to phase separation and a local chemical tendency to ordering. Analogous inferences about the existence of a competition between the tendencies to ordering and phase separation at each point of the alloy were drawn in Refs [14, 15] whose authors also relied on the BWG model. It is obvious that the concept of competition between various tendencies existing in different coordination shells is absolutely beyond the framework of classical thermodynamics, according to which all directional diffusion processes in alloys are controlled by the difference in chemical potentials.

Neither is this concept confirmed experimentally. For example, the results of investigations of the $Fe_{50}Co_{50}$ alloy by the method of X-ray electron spectroscopy (XES) indicate that the sign of chemical interaction between the Fe and Co atoms is determined by some other factors rather than by their relative positions in the crystal lattice [16, 17]. By comparing the X-ray electron spectra of the valence band, obtained for $T < 730\,^{\circ}\mathrm{C}$ (the region where the tendency to ordering manifests itself) and for $T > 730\,^{\circ}\mathrm{C}$ (the region where the tendency to phase separation dominates), it was found that the shape of the spectrum, which for $T < 730\,^{\circ}\mathrm{C}$ has a two-band structure with an insignificant overlap of d bands, sharply changes for $T > 730\,^{\circ}\mathrm{C}$ and comes to resemble a superposition of the valence bands of pure Fe and Co. This means that at $T \approx 730\,^{\circ}\mathrm{C}$ there occurs a change in the degree of localization of the valence 3d electrons on iron atoms, which can be explained by the change from a tendency to ordering to a tendency to phase separation when the alloy temperature passes through the point $T = 730\,^{\circ}\mathrm{C}$ [16, 17].

Thus, the type of chemical interaction between the atoms of the alloy components depends on the structure of their d-electron bands and can change by varying temperature. The two types of chemical interactions that are described as the tendency to ordering (attraction between unlike atoms) and the tendency to phase separation (attraction between atoms of the same kind) predetermine two types of phase transformations. If the alloy exhibits a tendency to ordering, phase transformations with the formation of a chemical compound occur; on the other hand, in the presence of a tendency to phase separation, phase transformations with the precipitation of particles occur, with atoms of one component or another dominating in each of the phases. Therefore, the transition point from the tendency-to-ordering to tendency-to-phase-separation can be considered as a temperature of an ordering – phase-separation transformation occurring at the level of changes in the electronic structure.

3. Phase transformations in alloys showing a tendency to ordering

We now consider diffusion phase transformations that lead to the formation of a new phase in the form of chemical compounds. As was noted in Section 2, such transformations occur in the alloy as a result of its tendency to ordering [3, 18]. If the alloy has a stoichiometric composition, the formation of a new phase proceeds as a result of a redistribution of atoms (diffusion coefficient is positive) and a subsequent transformation of the lattice type or a subsequent change in the lattice parameter. In the theory of ordering, such a process is called long-range ordering [3, 18]. It is assumed that the new phase (superstructure, in terms of the theory of ordering) is formed simultaneously over the entire volume of the alloy [3, 18]. As follows from experiment, however, even in stoichiometric alloys this by no means always occurs. For example, the σ phase in $Fe_{50}V_{50}$ is indeed formed over the entire volume of the alloy for $T < 1200\,^{\circ}\mathrm{C}$ [19], whereas in the $Fe_{50}Cr_{50}$ alloy this phase is revealed after heat treatment at $T = 570 - 830\,^{\circ}\mathrm{C}$ only in a thin surface layer [20]. The cause is the development of high elastic stresses upon the precipitation of particles of the σ phase, which prevent a further transformation of the body-centered cubic (bcc) lattice of the Fe(Cr) solid solution into the tetragonal lattice of the σ phase [20]. Therefore, such a lattice transformation occurs only near the free surface of the sample. It is also worth noting that the σ phase in the $Fe_{50}Cr_{50}$ alloy is formed as a result of a gradual precipitation of individual particles inside the solid solution and subsequent 'collapse' of regions between them,

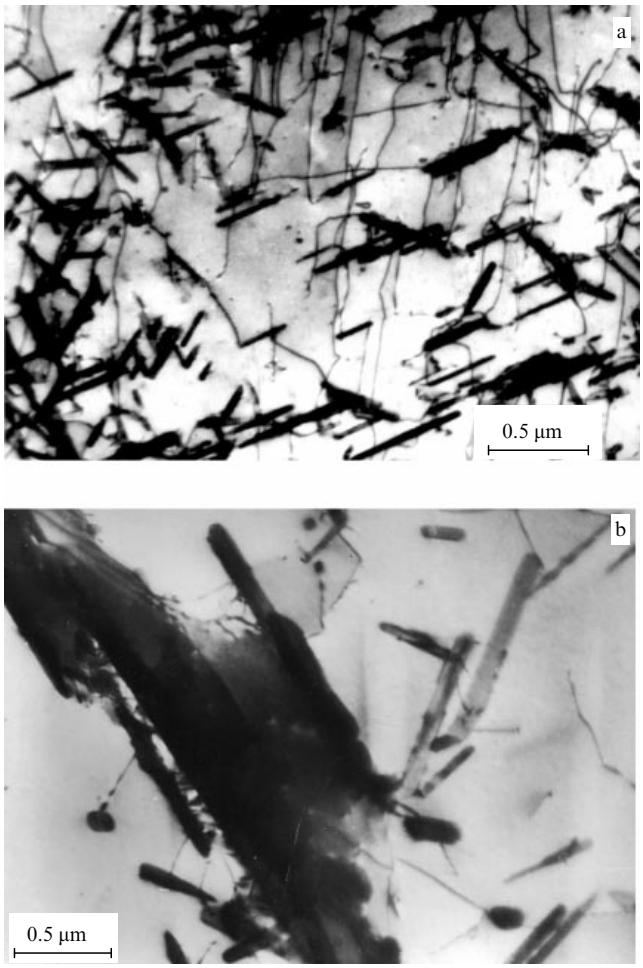

Figure 1. Microstructure of a subsurface layer in the $Fe_{50}Cr_{50}$ alloy quenched in water after holding at $T = 1200\,^{\circ}C$ for 1 h and subjected to a heat treatment at $T = 700\,^{\circ}C$ for 100 h: particles of the σ phase in a layer that is (a) more remote, and (b) less remote from the surface.

rather than by a simultaneous transformation of the lattice in the entire converted volume of the surface layer. This is well illustrated in Fig. 1.

In other stoichiometric alloys, the process can proceed in a different way, but again may not involve the entire volume of the alloy. As an example, we take the Fe_3Si ($D0_3$) phase which in contrast to the σ phase is considered in the theory of ordering as a 'superstructure' occupying the entire volume of the alloy even in the alloys of nonstoichiometric compositions [21, 22]. In the $Fe_{77}Si_{23}$ alloy, which is very close in composition to the stoichiometric composition of the $D0_3$ phase, the $D0_3$ phase occupies only 10% of the alloy volume irrespective of the duration of heat treatment [23, 24]. This result can be obtained by comparing intensities of both X-ray diffraction lines and reflections in electron diffraction patterns belonging to the solid solution and the $D0_3$ phase. Thus, it turns out in practice that the solid solution by no means transforms completely into the corresponding phase in all stoichiometric alloys, but in all such alloys the process of the formation of new phases proceeds in the same way — by normal diffusion.

If the composition of the alloy differs from the stoichiometry of the precipitating phase, then two cases should be considered [25, 26].

(1) The alloy composition is rather close to stoichiometric. In this case, the process starts from the formation of clusters of solute atoms, which is caused by uphill diffusion (negative diffusion coefficient) — that is, it goes on by the spinodal mechanism. As, with time, a composition corresponding to the stoichiometric composition of the precipitating phase is reached inside the clusters, there occurs a transformation of their lattices (via normal diffusion) into the lattice of the precipitating phase. A new structure is formed, which consists of particles of the new phase in the depleted solid solution. If we interrupt the aging process at the stage of cluster formation or conduct this process at a lower temperature, then a microstructure is fixed which, in terms of the theory of ordering, is called local short-range order (e.g., Guinier–Preston zones in aluminum alloys). These clusters still have a lattice type characteristic of the solid solution, but the lattice itself inside the clusters turns out to be somewhat distorted depending on the degree of their enrichment with the solute component.

(2) The alloy composition differs rather strongly from the stoichiometric composition of the precipitating phase. In this case, the relaxation process is restricted (because of the low atomic concentration of the solute component in the alloy) to only the formation of clusters in the solid solution. A structure is formed which, in the theory of ordering, is called local short-range order but differs from the analogous structure in the first case in that even prolonged aging of the alloy does not lead to a lattice transformation inside the clusters into the lattice of a new phase [25, 26]. The clusters are formed, as in the first case, via uphill diffusion, i.e., via the spinodal mechanism. As an example, we may take the so-called K state in Fe–Al alloys.

Thus, the precipitation of new phases in alloys and the process of ordering in alloys is, in essence, one and the same phenomenon which can be described in terms of both phase formation and ordering. Certainly, the terminology of phase formation is preferable, since it permits one to describe all manifestations of the process of the formation of new phases in solid solutions. Under these conditions, the term 'ordering', in our opinion, should be used only for the designation of such a chemical interaction between unlike atoms, in which the attraction between these atoms reveals itself. In this case, the sign of the deviation of the solid solution from Raoult's law is negative, the energy of ordering is negative, and, as a result of relaxation of any such system exhibiting a tendency to ordering, the new phase precipitates in the form of chemical compounds either in the entire alloy volume (this may occur only in alloys of stoichiometric composition) or in the form of particles that are formed in the solid solution of nonstoichiometric composition. It is obvious that the term 'phase separation' has an opposite meaning: the sign of the deviation of the solid solution from Raoult's law is positive, the energy of ordering is also positive, and the relaxation of such systems leads to the formation of phase-separation microstructural modes.

4. Phase transformations in alloys showing a tendency to phase separation

In the theory of ordering, phase separation of alloys is usually considered as one of the types of ordering for which the ordering energy has the opposite (positive) sign. Since in the phase diagrams of Fe-*M* alloys [27] no regions are found in which phase-separation structures could be formed (except for the Fe–Cr system at temperatures $T < 570\,^{\circ}C$ [27]), phase

separation was usually considered as a kind of ordering that is encountered in Fe-*M* alloys only rarely [28]. At the same time, the phase-separation structures are seen relatively frequently in other types of phase diagrams — these are eutectics, where the process of phase separation begins during the solidification of the liquid solution, and eutectoids, where phase separation proceeds in a solid solution. Such structures can easily be revealed using optical microscopy [29].

In the 1960s – 1970s, modulated structures were revealed in many alloys quenched from temperatures corresponding to the solid-solution field. The assumption that these structures could have belonged to phase-separation structures had not even been considered, since many researchers did not believe in the possibility of solid-solution separation at high temperatures (by the way, many do not believe this even at present [30]). Such examples, which have now become classical, are alloys of the systems Au – Ni [31], Ni – Mo [32], Fe – Be [33], Al – Zn [34], Cu – Be [35, Nb – Zr [36], and some other systems which exhibit solid-solution fields in their phase diagrams at high temperatures. The occurrence of such microstructures was sometimes explained as a result of the insufficiently accurate determination of the boundaries of the solid-solution fields in the phase diagrams [36], although in most cases it was assumed that the alloy decomposition via a spinodal mechanism proceeds in a very short time comparable with the time of cooling of the alloy in water, since there is no stage of nucleation in the case of spinodal decomposition [30 – 35]. The latter conclusion contradicts both the Cahn theory of spinodal decomposition (Cahn solved the conventional equation of diffusion) [37] and the experimentally determined values of diffusion coefficients. A simple calculation with the use of these diffusion coefficients shows that the time required for the formation of relatively course modulated structures found in Refs [31 – 36] is quite insufficient in the case of water quenching of alloys [38].

Phase-separation microstructures were recently revealed using TEM in quenched alloys of the systems such as Fe – Cr [39 – 42], Fe – Ti [43, 44], Fe – Co [16, 17], Fe – W [45], Fe – V [46, 47], and Fe – Mn [48]. The first mention of phase-separation microstructures formed in high-temperature regions of solid solutions of the Fe – Cr system appeared in 1995 – 1996 [39, 40]. After quenching in water from 1200 °C, the Fe – 47 wt.% Cr alloy exhibited an $\alpha_1 + \alpha_2$ structure consisting of Cr-enriched fine-dispersed dark particles of the α_2 phase, located randomly in the Cr-depleted α_1 solid solution. Along with the $\alpha_1 + \alpha_2$ structure, coarse particles of a J phase (formed as a result of phase separation) were present, inside which periodically distributed dark layers strongly enriched in chromium were observed against a bright background (chromium-depleted solid solution) (Fig. 2a). In the electron diffraction pattern of particles of the J phase, satellites are seen near the fundamental reflections of the solid solution (Fig. 2b). With increasing holding time at $T = 1200$ °C or increasing temperature to 1400 °C, regions become apparent inside the J-phase particles whose electron diffraction patterns yield a set of reflections that

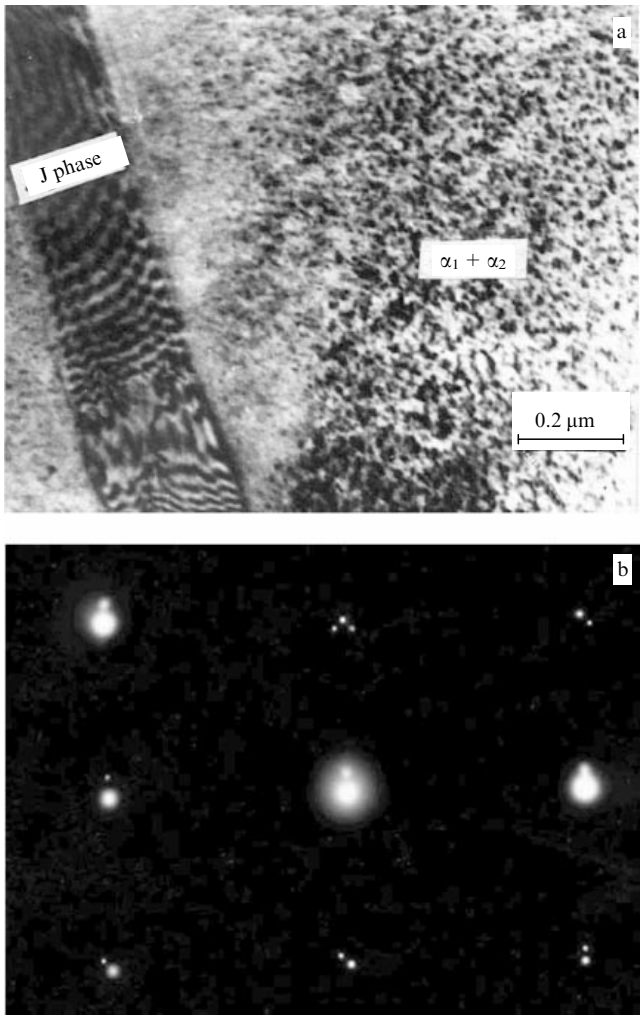

Figure 2. (a) Microstructure and (b) electron diffraction pattern of the J phase formed in the $Fe_{50}Cr_{50}$ alloy after holding at $T = 1200$ °C for 1 h and fixed by quenching in water.

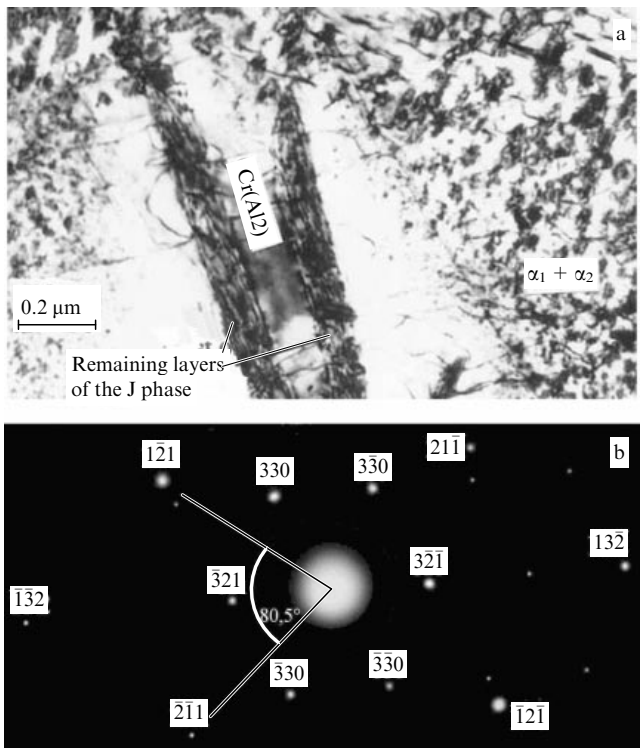

Figure 3. (a) Microstructure and (b) electron diffraction pattern of the bright layer inside the J phase. The $Fe_{50}Cr_{50}$ alloy after holding at $T = 1400$ °C for 1 h and quenching in water.

correspond to the A12 lattice of metastable chromium (Fig. 3). Thus, the micrographs presented in Figs 2 and 3 permit one to reveal the sequence in which phase separation occurs. The fine chromium-enriched clusters that were the first to form coalesce into coarse particles even more enriched in chromium, which were called the J phase in Ref. [40]; the subsequent further enrichment of the particles with chromium leads to the formation inside them of metastable chromium with the A12 lattice.

Microstructural modes characteristic of phase separation were observed in Fe–Co alloys quenched in water from temperatures corresponding to the solid-solution field with the A2 type structure. While in the surface layer of up to 70 μm in thickness the phase separation into the bcc Fe(Co) phase and face-centered cubic (fcc) Co(Fe) phase occurred in the entire volume of the layer, in the remaining volume of the alloy the particles of the fcc Co(Fe) phase constituted only 10% [16, 17, 49]. Clusters strongly enriched in tungsten were also revealed in Fe–W alloys with 15 and 18 wt.% W after their quenching from the solid-solution field temperature (1200 °C) [45]. A phase-separation field was revealed in the Fe–V system for $T \leqslant 600$ °C, with the field of existence of the σ phase closing at $T = 650$ °C [46, 47]. It was also shown that in the Fe–Mn alloys with 20–40 wt.% Mn in the temperature range of 600–1200 °C there proceeds a process of phase separation of the solid solution into regions enriched in and depleted of manganese as a consequence of the tendency to phase separation, existing in this system [48].

In the Fe–Ti system, a modulated microstructure was revealed by TEM and field-ion microscopy (Fig. 4) in the entire field of solid solutions up to very low concentrations of titanium (0.3%) after quenching in water from $T = 1200$ °C. The field-ion micrograph shown in Fig. 4b displays a plane perpendicular to the direction of modulations. Bright features in the figure are treated as iron atoms [43, 44]. The composition of these modulations was determined in the Fe–5 wt. % Ti alloy with the aid of free-ion atom-probe to be as follows: modulations enriched in Ti (dark in Fig. 4a, and bright in Fig. 4b) contained about 15% Ti; the modulations depleted of Ti contained 2% Ti. The aging of the quenched Fe–5 wt.% Ti alloy at 600 °C led to the complete dissolution of the modulated structure and subsequent formation of particles of an Fe_2Ti phase. On those grounds, the authors of Refs [43, 44] concluded that the modulated structure fixed

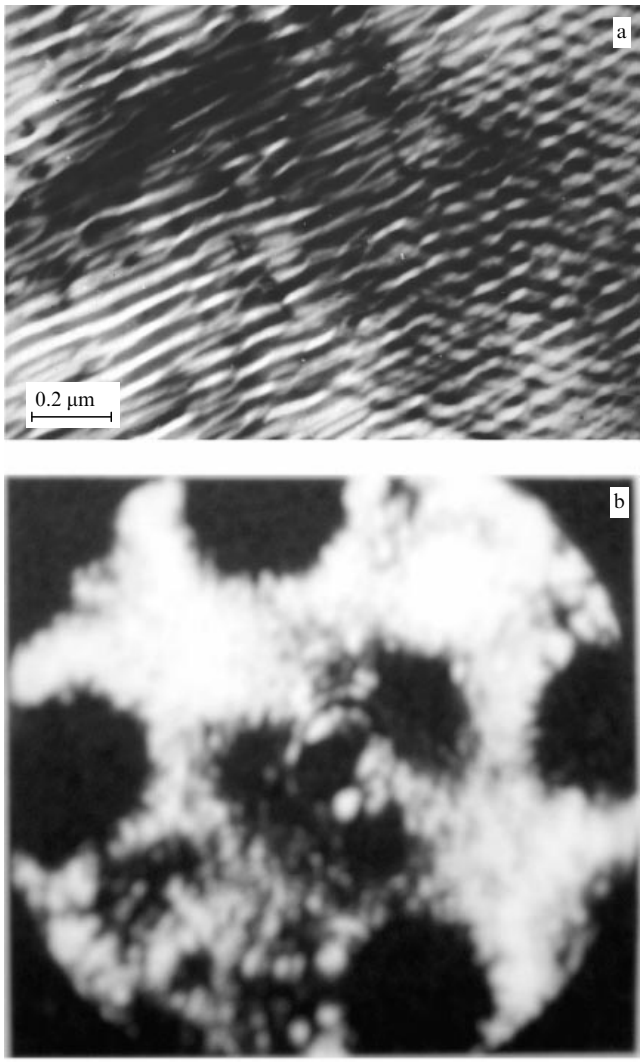

Figure 4. (a) Electron microscope and (b) field-ion microscope images of a modulated structure of the $Fe_{95}Ti_5$ alloy quenched in water from $T = 1200$ °C after holding for 1 h.

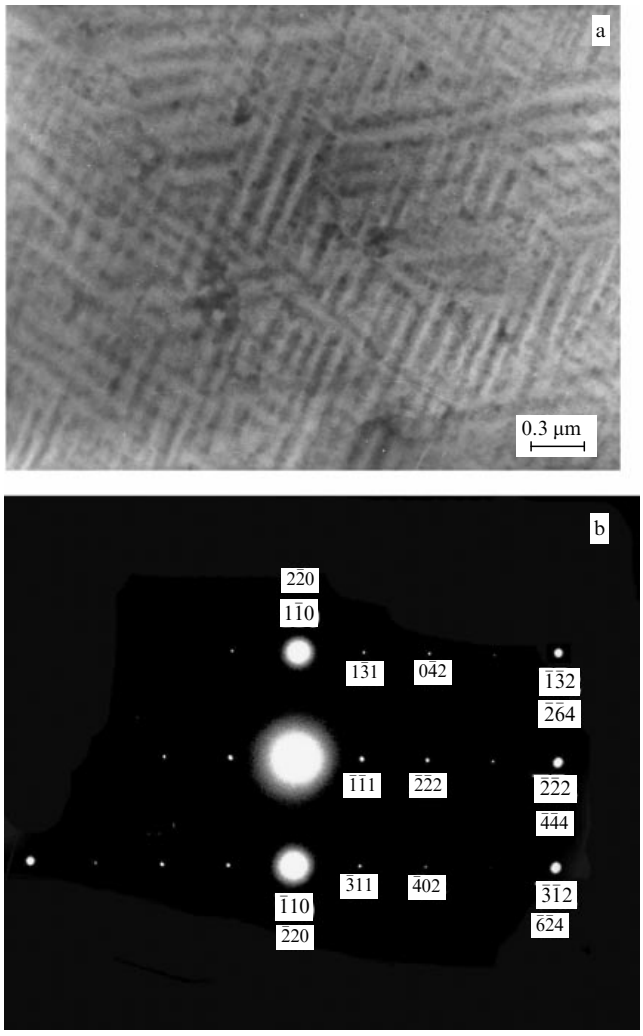

Figure 5. Fe–15.5 at.% Si alloy aged at $T = 650$ °C for 120 h: (a) bright-field image of a modulated structure, and (b) related electron diffraction pattern. Foil orientation (112).

by quenching from $T = 1200\,^{\circ}\mathrm{C}$ is formed as a consequence of the alloy tendency to phase separation.

Many authors believe [31 – 36] that the occurrence of a modulated structure can be considered as proof of the existence in the alloy of a tendency to phase separation. However, in reality a modulated structure is formed for quite different reasons. For example, as was shown in Refs [23, 24], the Fe – Si system, in which it is by no means possible to suspect the existence of a tendency to phase separation, also exhibits a modulated structure. Such a microstructure and the related electron diffraction pattern are shown in Fig. 5. A dark-field analysis indicates that the bright modulations in Fig. 5a represent a $D0_3$ phase enriched in silicon, while the dark modulations represent a silicon-depleted solid solution. Thus, the facts of revealing the modulated structures cannot be considered as proof of the existence of a tendency to phase separation in one alloy or another. The formation of such a structure is rather a result of specific crystallographic features of a concrete alloy, due to which the formation of enriched clusters and phases leading to an increase in elastic stresses in the process of precipitation proves to be most probable in the form of modulations along elastically soft directions of the matrix. It should be emphasized that in the case of a tendency to phase separation the electron diffraction patterns of the modulated structure contain satellites indicating the existence of two solid solutions in the alloy (in the Fe – Cr system, this refers to the J phase) [31 – 36, 40 – 42], or no satellites are observed if the concentration of the second component in the alloy is small, e.g., in Fe – 5 wt.% Ti [43, 44]. In the case of a tendency to ordering, a modulated structure can be formed only in nonstoichiometric alloys, and their electron diffraction patterns contain a system of additional reflections from enriched modulations inside which the lattice of a new phase was formed (e.g., in the Fe – Si system) [23, 24].

Some authors, for example, Cahn [50], considered the modulated structure as being characteristic of only those alloys that decompose via a spinodal mechanism. Indeed, the formation of a periodic concentration distribution that arises upon alloy decomposition always followed from the Cahn theory [37], but a modulated structure in alloys that were assumed to decompose by the spinodal mechanism was by no means always revealed [18, 51]. As will be shown in Section 6, the spinodal mechanism of decomposition in nonstoichiometric alloys is the single actually existing mechanism. Therefore, the revealing of a modulated structure in some alloys cannot be considered as proof of the spinodal character of their decomposition and, as was shown above, cannot be considered as evidence of the existence of a tendency to phase separation in the alloy.

5. Thermodynamic concept of alloy decomposition

Following Cahn's theory [37], we can suppose that the formation of a different morphology differing from modulated one is a consequence of the fact that the alloy decomposition proceeds by the nucleation-and-growth mechanism rather than by the spinodal mechanism. Although the theory of nucleation and growth as applied to alloys was formulated at the beginning of the twentieth century on the basis of speculative concepts of the nucleation of liquid droplets from a supersaturated vapor [49], it has been up to now considered as one of the fundamental theories in the explanation of nucleation of new phases in solid solutions. However, this theory does not take into account the fact that chemical interactions should necessarily exist between the atoms of the components constituting the solid solution. The theory introduces a concept of the existence of a certain energy barrier which, notwithstanding the second law of thermodynamics, is overcome by the system in the process of its relaxation, which permits the critical nucleus, which was formed by a fluctuational mechanism, to grow further [52, 53]. At the same time, a fluctuation-induced increase in the free energy at local points, which is necessary to overcome this barrier, requires, according to calculations [25], such large waiting times that this process becomes quite unlikely. Its realization proves to be practically impossible even in the presence of numerous defects in the alloy, which facilitate, according to Ref. [54], the formation of critical nuclei. All the above permitted the authors of Refs [55, 56] to conclude that alloy decomposition cannot proceed by the mechanism of nucleation and growth and that a new phase, which is revealed by TEM in the form of incoherent irregular-shaped particles and is usually assumed to be an argument in favor of decomposition by the nucleation-and-growth mechanism, should be considered as being fixed at the stage of its roughening rather than nucleation. For example, a decrease in the aging time or a decrease in the heat-treatment temperature always permitted one to reveal, using TEM, clusters preceding the formation of particles of a new phase [56].

The impossibility of finding any signs that would confirm the real existence of the nucleation-and-growth mechanism in alloys forced us to pay greater attention to the commonly accepted thermodynamic concept of correlations between the concentration dependence of free energy, which has the form of a curve with one maximum and two minima, and the phase diagram [57]. According to this concept, the spinodal curve in the phase diagram separates two regions in one of which the decomposition proceeds by the spinodal mechanism, and in the other by the nucleation-and-growth mechanism. It is obvious that the absence of evidence for the existence of the nucleation-and-growth mechanism equally means the absence of the spinodal as a separating line. Indeed, no one of the available phase diagrams constructed for both the Fe-M alloys [27] and other alloys [58] contains a spinodal curve, although there have been undertaken numerous attempts to construct this curve both theoretically (see, e.g., Ref. [59]) and experimentally (see, e.g., Ref. [60]).

It is natural that under these conditions the representation of the concentration dependence of free energy in the form of a curve with one maximum and two minima [57], as is assumed at present, is unjustified, since the mechanism of nucleation and growth corresponding to the concave part of the curve of the concentration dependence of free energy is never realized upon the decomposition of solid solutions [55, 56]. The first attempt to present a thermodynamic description of the process of alloy decomposition occurring solely through the spinodal mechanism in the entire range of compositions for the cases where the tendency to both ordering and phase separation is dominating was undertaken in Refs [61 – 63]. Figure 6 displays the concentration dependences of free energy at a temperature T_1 for the $A - B$ system in the initial (nonequilibrium) and final (equilibrium) states for the cases of the dominating tendency to phase separation (Fig. 6a) and ordering (Fig. 6b). The final result of the system relaxation for the case of phase separation in alloys of the composition fg at a temperature T_1 is a mixture of grains

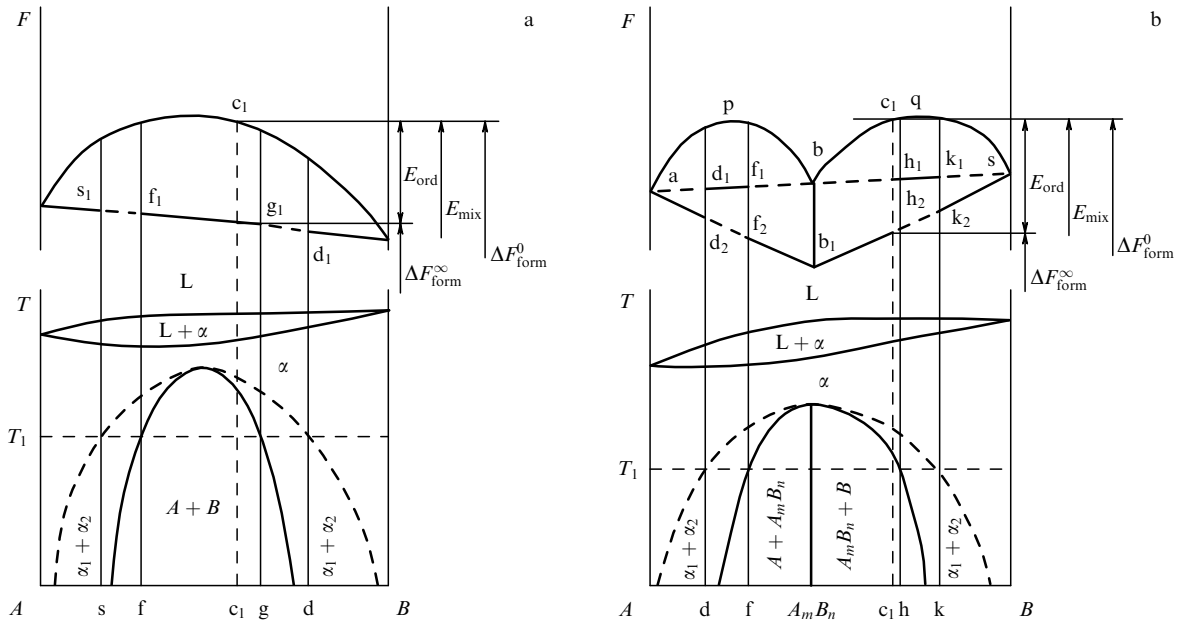

Figure 6. Schematic of a dependence of the free energy on the composition of an $A-B$ alloy in disordered and stable states at the temperature T_1: (a) a tendency to phase separation, and (b) a tendency to ordering. All energy levels are given for an alloy of composition c_1.

consisting of atoms A and B. The free energy of these compositions decreases to a level of the f_1g_1 section (Fig. 6a). As the concentration of the solute component decreases (compositions sf and gd in the diagram), the final microstructure is developed in the form of clusters enriched in and depleted of the solute. With the formation of such a structure, the minimum level of free energy corresponding to a mixture of grains of the components A and B (composition sections s_1f_1 and g_1d_1) cannot be reached (dashed lines). With a further decrease in the concentration of the alloying component, the compositions As and dB can be considered as infinitely diluted solid solutions.

Similar considerations are also possible in the case where the $A-B$ alloy has a tendency to ordering (Fig. 6b). In this conditions, the decrease in free energy upon the relaxation of nonstoichiometric alloys occurs in two stages.

(i) Stage of formation of enriched clusters in which the concentration tends to the stoichiometric composition of the precipitating phase. This is shown in Fig. 6b by the line $ad_1f_1bh_1k_1s$.

(ii) The process of the transformation of the lattice characteristic of a given solid solution into a lattice corresponding to the structure of the new phase A_mB_n, which occurs inside the clusters. In stoichiometric alloys, the relaxation process starts directly from the formation of the lattice of the new phase in the entire volume.

The free energy of a disordered solid solution, shown by the lines apb and bqs, decreases upon the formation of the lattice of the new phase A_mB_n inside the clusters (alloys of nonstoichiometric composition) to the line $f_2b_1h_2$, and in the entire volume of the alloy of stoichiometric composition the free energy is lowered to the point b_1 (Fig. 6b). In alloys with a lower concentration of the alloying component (compositions df and hk), the alloy decomposition process stops at the stage of cluster formation, since the composition inside the clusters does not reach the stoichiometric one and, therefore, the minimum level of free energy (composition sections d_2f_2 and h_2k_2) cannot be reached (dashed lines).

6. Solid-solution fields in phase diagrams

According to thermodynamics, virtually all solid solutions are not ideal. This means that they should display a tendency to either ordering or phase separation, which under conditions of large diffusion mobility of the alloy component atoms can lead to the formation of decomposition microstructures corresponding to this or that tendency. In this connection, a nonideal solid solution cannot be considered as an equilibrium phase; so, equilibrium phase diagrams, especially at elevated and high temperatures, should not contain fields corresponding to such nonequilibrium phases as a nonideal solid solution. However, solid-solution fields are present in virtually each phase diagram and, most frequently, just at high temperatures, when the diffusion mobility of atoms is sufficiently high to ensure the decomposition of the solid solution.

The formation of microstructures consisting of chromium-enriched and chromium-depleted particles, which were found in the solid-solution field of the Fe–Cr system [39–42], and the occurrence of positive deviations from the ideality in the same field [12] can be considered as direct proof for the existence of a tendency to phase separation in the solid-solution field. In this case, the question arises as to why the tendency to phase separation leads to the formation of microstructural modes characteristic of phase separation only in the temperature range from 1100 to 1450 °C, while in the ranges of 830–1100 °C and 1450–1550 °C the solid solution remains undecomposed (Fig. 7). To answer this question, we should consider correlations between all the components of free energy in the $A-B$ system. The mixing energy E_{mix} (i.e., the energy of formation of a disordered state which is nothing but the solid solution under consideration) is usually defined as the difference between the energy of the disordered solid solution and the sum of concentration-weighted energies of the alloy components. The ordering energy E_{ord} (i.e., the difference between the energy of a chemically disordered state and the energy of a special

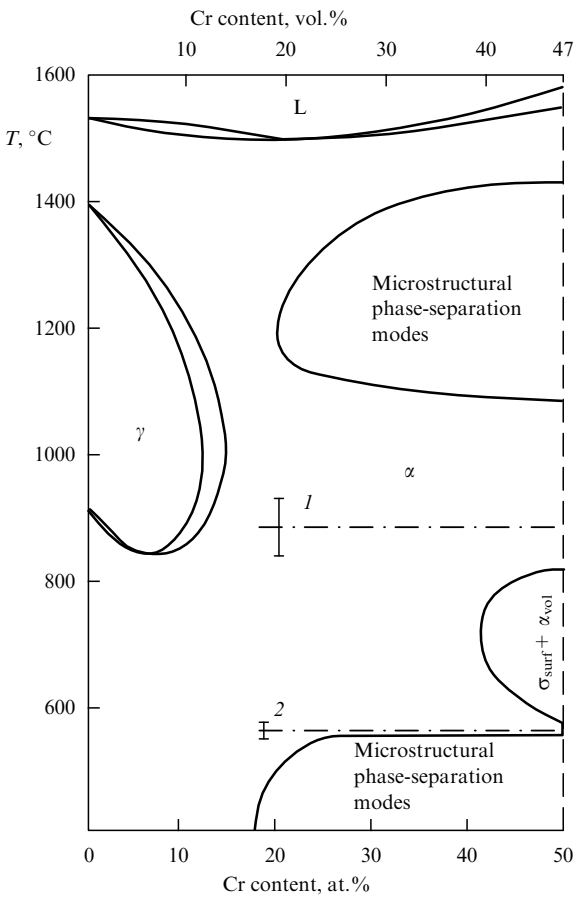

Figure 7. Part of the Fe – Cr phase diagram. Dot-and-dash lines *1* and *2* are the lines of the ordering – separation phase transitions. The field of existence of the σ phase is designated as the α solid solution in the volume of the alloys (α_{vol}) and the layer of the σ phase at the surface (σ_{surf}).

atomic configuration that is formed as the final result of the solid-solution decomposition) is usually given in terms of the effective pairwise interaction. The sign of the ordering energy (positive for the case of a tendency to phase separation, and negative for the tendency to ordering) should be considered only as determining the occurrence of this or that ordering configuration rather than as affecting the magnitude of the free energy of the alloy. It is for this reason that in the expression for the free energy F_{form} we should take into account the absolute value of the ordering energy E_{ord} [64, 65].

The free energy of the completely disordered solid solution of composition c_1 (see Fig. 6) can be written down as

$$\Delta F^0_{form}(c,T) = \Delta E_{mix}(c) + k_B T\big[c\ln c + (1-c)\ln(1-c)\big], \tag{1}$$

while the free energy after the complete phase separation of the solid solution into grains of pure components (or upon the formation of a chemical compound in the entire volume of the alloy of stoichiometric composition) as

$$\Delta F^{\infty}_{form} = \Delta E_{mix}(c) - \big|\Delta E_{ord}(c,T)\big| + k_B T\big[c\ln c + (1-c)\ln(1-c)\big]. \tag{2}$$

The free energy of formation of the alloy, according to Fig. 6, is defined as the difference between the energies of mixing and ordering. This means that the free energy of alloy formation is maximum in the case of a disordered solid solution rather than after its decomposition or the formation of a chemical compound, as follows from Refs [11, 66], in which the free energy of an alloy is considered as the sum of the energies of mixing and ordering.

It follows from Eqns (1) and (2) that the system with a nonzero interaction between the atoms of the alloy components (i.e., $E_{ord} \neq 0$) approaches a statistical distribution of unlike atoms in two cases: either when the temperature is high and, therefore, the thermal component of free energy is greater than the energy of ordering, or when the absolute value of the ordering energy decreases and becomes lower than the sum of the thermal and elastic components of free energy for a given temperature. The latter is possible when the system approaches a temperature at which a phase transition 'phase separation – ordering' occurs, i.e., the sign of the ordering energy changes [41, 42]. Such a transition in Fe – Cr alloys was for the first time observed in Ref. [20] due to the appearance of so-called electron domains (e-domains) in electron microscope images; these features will be discussed in detail in Section 7. The electron domains were considered as some regions of the alloy inside which the energy of ordering has already changed its sign to the opposite one, while in the remaining regions of the matrix the sign of the ordering energy remained unaltered [20].

Based on the above reasoning and taking into account Eqns (1) and (2), the condition of the existence of a disordered solid solution in a system with interaction between the components can be written as follows:

$$k_B T\big[c\ln c + (1-c)\ln(1-c)\big] \geqslant \big|\Delta E_{ord}(c,T)\big|, \tag{3}$$

and with allowance for elastic stresses arising upon decomposition, as

$$\varphi^2 Y + k_B T\big[c\ln c + (1-c)\ln(1-c)\big] \geqslant \big|\Delta E_{ord}(c,T)\big|. \tag{4}$$

Here, $Y = E(1-\nu)$ is a function of the crystallographic direction, φ is the linear deformation per unit composition difference, E is Young's modulus, and ν is Poisson's ratio.

According to relationships (3) and (4), a statistical distribution of atoms that is established experimentally at various points of the solid-solution field by no means implies that the energy of alloy ordering at these points is zero. Relationships (3) and (4) show under which conditions disordered solid solutions can exist in systems with interaction, including high temperatures, when the disordered distribution of the component atoms is favored by entropy. For example, the structure of the Fe – Cr solid solution [41, 42], fixed by quenching from 1450 – 1550 °C (exceeding the field of high-temperature phase separation, see Fig. 7), is formed as a consequence of the fulfillment of condition (4) due to the high values of the entropy component of the alloy free energy. The structure of the solid solution formed at temperatures of 830 – 1100 °C, i.e., below the high-temperature phase-separation field in the Fe – Cr phase diagram (see Fig. 7), develops because of the decrease in the absolute value of the ordering energy with approaching the alloy temperature equal to 830 °C. At this temperature there occurs a separation – ordering phase transition and, consequently, the sign of the ordering energy changes to the opposite one, i.e., the energy of ordering passes through zero.

7. Classification of phase transformations

Distinguishing two types of diffusional phase transformations in alloys, as caused by either a tendency to ordering or a tendency to phase separation, does not affect the existing thermodynamic theory of phase transitions, which divides them into first-order and second-order transitions [67, 68]. It was shown in our previous works [69, 70] using microstructural methods of investigations that the processes of ordering and formation of new phases in solid solutions, which previously were considered as different, represent one and the same phenomenon which is an alternative to phase separation. Later on, we concluded [69] that the ordering – phase-separation and order – disorder phase transitions are the transitions that occur on various levels of the structure of matter, namely, the first at a level of changes in the electronic structure, and the second at a level of changes in the microstructure. The assumption that structural phase transitions in alloys are caused by changes in the electronic structure is by no means something new. However, the conclusion that the ordering – separation electronic phase transition predetermines the possibility of subsequent order – disorder structural phase transitions was made for the first time in Ref. [70]. We will show this using the Fe – Cr system as an example, since it is precisely in this system that the phase transformations occurring on the microstructural level and on the electronic level have been fixed utilizing one and the same experimental method, namely, TEM.

As was noted in Section 6, various microstructural modes of phase separation were revealed in Fe – Cr alloys in different temperature ranges, namely, coarse structures of high-temperature phase separation within 1100 – 1450 °C; the σ phase in the surface layer and a solid solution in the bulk of samples for $T = 570 - 830$ °C, and a low-temperature phase separation for $T \leqslant 550$ °C. Between the regions of the above structural states in the Fe – Cr phase diagram (Fig. 7), narrow regions of the α solid solution and lines of separation – ordering phase transitions (dashed lines *1* and *2* in Fig. 7) were positioned. These lines were constructed based on the TEM data, which revealed specific microstructures (Fig. 8) in the temperature ranges between the fields of phase separation and ordering. Such microstructures were for the first time found in Refs [20, 41, 42] in Fe – Cr alloys with 30 – 47 wt. % Cr after they were heat-treated for the formation of microstructures of phase separation (or ordering) and were later subjected to heat treatment in the temperature range of formation of microstructures of ordering (or phase separation). As a result of such heat treatment, the initial phase-separation microstructure became dissolved (sometimes not completely) and a phase transition occurred in the alloy at a level of changes in its electronic structure (note that this transition did not occur simultaneously in the entire volume of the alloy). As a result, the energy of ordering changed its sign to the opposite one in some regions of the alloy, while in other regions no such changes occurred, so that precipitates in the form of coarse laths were observed in the micrographs. Such precipitates, shown in Fig. 8, were called electron domains since they, as magnetic and ferroelectric domains, were observed in the regime of a defocusing of the electron microscope image. Since on different sides of the domain boundary (wall) the values of the ordering energy E_{ord} have opposite signs, the electron beam, when passing through the foil, is deflected in opposite directions, which leads to a lack (bright lines) or excess (dark lines) of electrons upon image defocusing. Thus, the electron domains, just as magnetic and ferroelectric domains, in fact represent conventional photographic imagery of a phase transition that occurs at a level of changes in the electronic structure of the alloy.

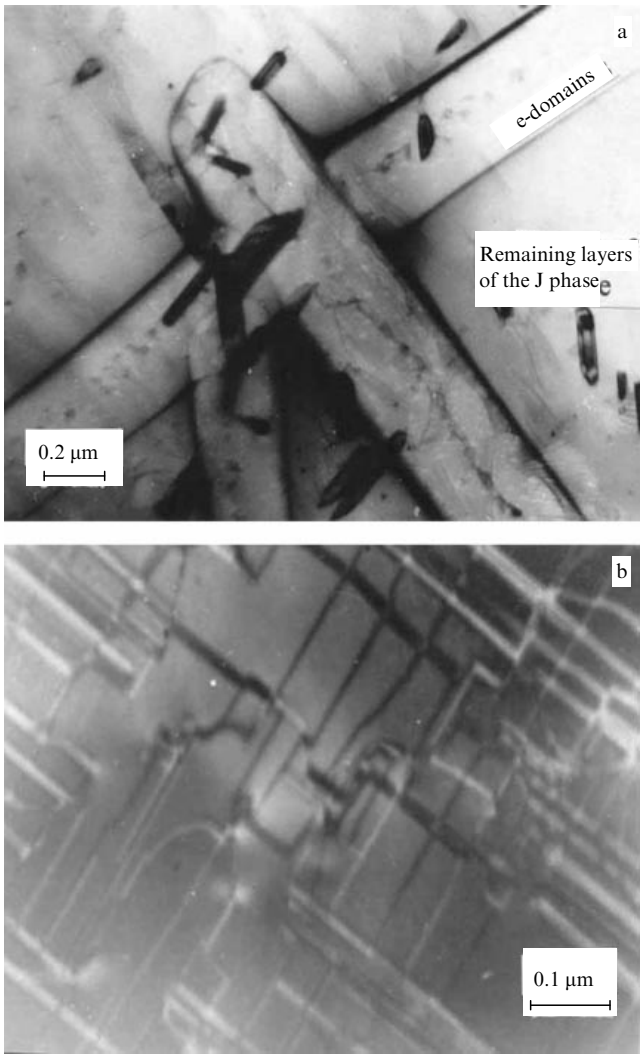

Figure 8. (a) $Fe_{50}Cr_{50}$ alloy quenched in water starting from $T = 1200$ °C after holding for 1 h (phase-separation microstructure) and then heat-treated at $T = 700$ °C for 1 h. Debris of the J phase are seen. (b) $Fe_{50}Cr_{50}$ alloy subjected first to a heat treatment at $T = 700$ °C for 8 h, and then at $T = 550$ °C for 4 h. In all the cases, cooling in water.

The microstructural data obtained using TEM indicate that the microstructure of high-temperature phase separation, for example, in the $Fe_{50}Co_{50}$ alloy, is formed only when the shape of the valence-band spectra of Fe and Co atoms, revealed by the XES method, resembles a superposition of the valence bands of pure Fe and Co [16, 17], i.e., for $E_{ord} > 0$. This means that the phase transitions occuring at a level of changes in the electronic structure are the original source of phase transitions that happen later at the microstructural level. In other words, we may conclude that this is one and the same phase transition which is made at two different steps of a hierarchical staircase of the structure of matter and, therefore, is separated in time and space.

8. Conclusions

The theories of phase transitions, ordering, and nucleation and growth were developed in the distant past when the experimental level of investigations of alloy structure was relatively low. In recent decades, with the advent of new methods, especially, transmission electron microscopy (TEM) and X-ray electron spectroscopy (XES), this level increased significantly and the results of experimental investigations stopped fitting into the narrow framework of the above-mentioned theories. It is just this conflict between theory and experiment that has served as a cause for the representation of a given review. The experimental results that were considered here permit us to formulate some theses that do not agree with the existing theories of phase formation and ordering.

(1) The type of chemical interaction in the alloy, which manifests itself as specific tendencies to ordering or phase separation, is determined by the degree of localization of 3d valence electrons on the alloy-component atoms and can change with varying temperature. The temperature at which the chemical interaction changes its sign can be considered as the point of a phase transition of the ordering – phase-separation type that occurs at a level of changes in the electronic structure. This conclusion does not agree with the results of computer simulation that employs the model of pairwise interaction, according to which this or that type of interatomic interactions manifests itself in an alloy as a result of competition between a macroscopic tendency to phase separation and a local chemical tendency to ordering.

(2) All phase transitions can be divided into 'primary', occurring at a level of changes in the electronic structure, and 'secondary', occurring as a consequence of 'primary' ones at a level of changes in the alloy microstructure.

(3) The type of microstructural phase transitions is determined by the sign of the ordering energy: a negative sign leads to the manifestation of a tendency to ordering in the alloy, which results in the formation of chemical compounds, while a positive sign results in a tendency to phase separation, which leads to the formation of a mixture of particles in each of which atoms of one of the components dominate.

(4) In all alloys which display a tendency to phase separation and in nonstoichiometric alloys which show a tendency to ordering the decomposition starts from the formation of clusters, i.e., these alloys decompose only via a spinodal mechanism.

(5) Since for solid solutions the decomposition by the nucleation-and-growth mechanism has not been confirmed either theoretically or experimentally, the spinodal curve that separates the regions of existence of the spinodal mechanism and the nucleation-and-growth mechanism cannot be considered as really taking place in phase diagrams. Therefore, the concentration dependence of the free energy of solid solutions should be represented only as a convex curve in the entire range of compositions both in the case of ordering and in the case of phase separation.

(6) The solid-solution fields in phase diagrams are actually regions in which a tendency to phase separation has been revealed experimentally. Whether this tendency will lead to the formation of phase-separation microstructures depends on the relationship between the entropy, elastic, and chemical components of free energy at this or that point of the phase diagram.

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