The ‘Ordering-Phase Separation’ Transition in Alloys
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By

Yuri Ustinovshikov
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ABSTRACT

This monograph represents a summary of completed, original work, embodying the results of extensive laboratory and theoretical investigations as well as new interpretations of existing problems in Materials Science. Using the examples of a number of binary Ni-base and Co-base alloys, the TEM method has shown that the main reason for the precipitation of particles of a new phase is the chemical interactions that always exist between all similar and dissimilar atoms of an alloy, both in the solid and in the liquid state. The magnitude and the sign of the energy of such interactions depend entirely on the temperature at which the precipitation process occurs. It has been found experimentally that the sign of the chemical interaction energy in many alloys changes with a temperature change (the ‘ordering-phase separation’ transition is observed). In each binary system, the temperature of such a transition is specific. In some systems, this transition can occur twice. It has been shown that the cause of the ‘ordering-phase separation’ transition is the electronic ‘ionic bond ↔ covalent bond’ transition. In an AB alloy, for example, which has a tendency to ordering, such a transition takes place when delocalization of a couple of the valence electrons occurs on the A and B atoms simultaneously with the hybridization of a couple of the valence electrons on the B atoms.

By the example of ternary ABC alloys of substitution, it has been shown experimentally (by TEM) that in a liquid state, there occurs separation into microscopic sites, in which the composition of each of site corresponds to the composition of either an A/B, A/C or B/C diffusion couple. The reason for such a separation is the existence in all alloys of ionic and covalent components of the chemical bond along with the metallic one. Such a heterogeneous structure consisting of different diffusion couples remains intact at all subsequent heat treatments of the alloy, while the microstructure within each diffusion couple (within each microscopic site) changes with the temperature of the heat treatment of the alloy and is a copy of the microstructure of the corresponding in composition binary alloy (at the same temperature). The obtained results show how a model of pairwise chemical interaction is realized in multi-component alloys and why multi-component chemical compounds and
Abstract

phases cannot be detected in multi-component alloys. These results also indicate exactly which microstructure is responsible for the remarkable properties of superalloys at high temperatures: it is the microstructure formed at high temperatures in diffusion couples because of the tendency to phase separation. Using the proposed approach in the design of new superalloys will help us to abandon the current empirical method of creating new alloys.

Since a disordered solid solution is formed in alloys in the temperature and/or concentration ranges where the energy of the chemical interaction is close to zero (but not at high temperatures, as it is believed nowadays), the principles of constructing phase diagrams consequently change completely. The work on the reform of binary phase diagrams should start with determining the temperature of the 'ordering-phase separation' transition. The elaboration of triple (and more) phase diagrams does generally not make sense, since a freshly melted alloy already consists of microscopic sites, within which only the pairwise chemical interaction that is characteristic of each diffusion couple is manifested. It is also pointless to carry out double heat treatment (quenching and tempering), since after any heat treatment, the alloy only acquires that structure which is typical for the temperature of this treatment. All these discoveries radically change the existing ideas about diffusion phase transformations in alloys and about the conditions of homogeneous solid solution formation.

Keywords: phase transitions; chemical interactions; ordering; phase separation; phase diagrams; heat treatment; ‘ordering-phase separation’ transition; ‘ionic bond ↔ covalent bond’ electronic transition; diffusion couples in multi-component alloys
CHAPTER ONE

INTRODUCTION

According to existing ideas in the literature [1], a solid solution in metal alloys is formed in those cases when, in a system consisting of atoms of different elements, a crystal lattice common for all elements is formed on the basis of the solvent lattice. It was assumed that, in all alloys, the magnitude of solubility of an element in the lattice of the solvent depends mainly on the difference in the sizes of the atoms of the solvent and the solute. If the difference in the sizes of dissimilar atoms that form the alloy exceeds about 14-15%, the solubility in the solid state is restricted (due to the 15% rule) and stable intermediate compounds form in the alloy [1]. The theoretical justification for this rule was obtained by considering the energy of elastic deformation that emerges during the formation of solid solutions. The difference in the sizes of A and B atoms predetermined the appearance of elastic stresses within the crystal lattice of the alloy. The magnitude of such elastic stresses, it was considered, determined the degree of solubility of the B atoms in the crystal lattice consisting of A atoms, and was that driving force which, when the temperature and, therefore, the solubility decreased, resulted in the precipitation of ‘excess’ phases from the solid solution. It was also believed that another important factor determining the magnitude of solubility in the solid state and the stability of intermediate phases was the magnitude of the electron concentration (e/a ratio) in the alloy [1].

This very principle was used in the construction of equilibrium phase diagrams, in which, in the overwhelming majority of cases, regions of solid solutions were shown at high temperatures, and two-phase regions at low temperatures. All these ideas, which were formulated about 80 years ago when modern methods of investigating the crystal structure of the alloys were in their infancy, are still intact in Materials Science [1].

Experimental studies of the crystal structure of alloys conducted later with the help of X-ray diffraction (XRD) seemed to have fully confirm these views. Indeed, when this method was applied to alloys quenched
from high temperatures, no other phases besides the solid solution were found. Based on these data, they concluded, that at high temperatures, the microstructure of alloys was a disordered solid solution.

Thus, according to the ideas which have been described in sufficient detail elsewhere (for example, in monograph [2]), at high temperatures, an alloy is regarded as an equilibrium phase, i.e. as a homogeneous solid solution, in which the component atoms are randomly distributed over the sites of the lattice (substitution alloys) and interstices (interstitial alloys). In these cases, when the interaction potential $W$ is significantly lower than the thermal energy $kT$, the interaction potential can be neglected in favor of the thermal energy. Therefore, they believed that, at high temperatures, the alloy behaved like an ideal solid solution. Upon a decrease in temperature, when the interaction potential $W$ becomes substantially higher than the thermal energy $kT$, the relative positions of the component atoms in the solid solution is determined by the condition of minimum free energy and, as a result, a new phase precipitates. Thus, upon a decrease in temperature, the ‘order – disorder’ transition happens in the alloys. It has been considered that the physical reason for ordering was the interaction between the atoms of the components constituting the solid solution [2], though what this interaction consisted of was not specified.

However, in the 1960s-1970s, when the method of transmission electron microscopy (TEM) became widely used in the study of the microstructure of alloys, many authors were surprised to find that the microstructure of many alloys, quenched from the region of solid solutions, was two-phase. It contained either particles of a new phase in the solid solution or modulations of the composition. When such a two-phase microstructure was found in as-quenched alloys, almost no one doubted that the blame for the ongoing disagreements should be laid on the experiment, not on the phase diagrams. A new version was invented, according to which the diffusion of atoms in the alloy was sharply accelerated during the process of quenching itself, since the decomposition of the alloy proceeds via the spinodal mechanism (during spinodal decomposition, the stage of critical nuclei formation is absent).

As is known [3], the method of X-ray diffraction is severely limited concerning the possibility of identifying highly dispersed particles of the new phase, which are usually registered by a method of local analysis – the TEM method. This is precisely why a conflict arose, when, using XRD data, they built phase diagrams containing, it was asserted, regions of solid solutions at high temperatures, but when using the TEM method, a
completely different structure was discovered: a two-phase structure had been formed in these regions after quenching from these temperatures.

From an analysis of these data, it was concluded [4] that the regions of solid solutions in equilibrium phase diagrams were in fact two-phase regions. This conclusion agrees with the well-known axiom of thermodynamics, which states that in nature all solutions are non-ideal and have either positive or negative deviations from Raoult's law.
CHAPTER TWO

HISTORY OF THE DISCOVERY
OF THE ‘ORDERING-PHASE SEPARATION’
TRANSITION

2.1. Alloys of the Fe-Cr system

The sign of the ordering energy was usually determined by the method of measuring the partial pressure of the vapors of components at temperatures close to the melting point. Since this pressure abruptly drops with a decrease of the temperature and beginning at certain temperatures it is impossible to measure it, it was tacitly assumed that the sign of the ordering energy determined at very high temperatures remains the same at lower temperatures. This gave birth to the idea that each binary system is characterized by its own sign of ordering energy, which is constant for this system at any temperature.

The only system that did not agree with these concepts and, therefore, gave rise to questions was the iron-chromium system. In the existing phase diagram of this system [5], three structural regions were observed (the temperatures indicated are for the Fe_{50}Cr_{50} alloy). A solid solution exists above 830°C. The \( \sigma \)-phase formed as a result of the tendency of alloys to ordering, located in the temperature range of 830-440°C. A microstructure, which consisted of clusters of chromium atoms in the solution and formed as a result of the tendency of the alloy to phase separation, is placed below 550°C. On the basis of these data, it could already be concluded that the phase diagram, in which a microstructure of ordering is formed at one temperature but microstructure of phase separation at the other, gives grounds for talking about a boundary between them, i.e. for talking about an 'ordering-phase separation' transition. On the contrary, some authors, for example Turchi et al. [6], suggested, because positive deviations from Raoult's law had been found in alloys of the iron-chromium system at high temperatures [7], suggested that the \( \sigma \)-phase was not a chemical compound at all. Although the \( \sigma \)-phase has all the attributes of a chemical compound, including a lattice of
its own, distinct from that of the matrix, but they thought that the $\sigma$-phase is a phenomenon, "pertaining to surfaces (reconstruction, segregation, etc.)" and that there are no contradictions here [6].

Fig. 1. Fe$_{50}$Cr$_{30}$ alloy. Water quenching from 1200°C. Bright-field micrographs. Inset: electron diffraction pattern taken from a coarse particle [11].

The situation turned out to be even more confusing when Ustinovshikov, Shirobokova and Pushkarev [8] discovered a microstructure which could not be attributed either to the structure of a disordered solid solution or the structure of a $\sigma$-phase in alloys of the same system, at high (1150°C and higher) temperatures, i.e. in the solid solution region. The authors [8] identified it as the structure of high-temperature phase separation (Fig. 1), as it was fixed after a heat treatment at the same temperatures, at which positive deviations from Raoult's law had previously been found [7]. In addition, a system of satellite reflections was observed in the electron diffraction pattern (Fig. 1, inset), which was obtained from these precipitates. The discovery of phase separation microstructures formed after quenching from high temperatures, i.e. from the region of solid solutions, was so unexpected that it led to the appearance of a number of critical works [9, 10].
The first experimental study to verify the existence of high-temperature phase separation in alloys of the iron-chromium system was undertaken using the Fe-45% Cr alloy as an example [9]. Using the TEM method, Kosythyna et al. [9] found that the microstructure of this alloy after quenching from 1150-1200°C was similar to that which had been obtained in Ref. [8]. However, they interpreted such precipitations as chromium nitrides, i.e. as a kind of ‘added’ phase formed by the chemical reaction of chromium atoms (from the alloy) with atoms of nitrogen (from the air) during a high temperature heat treatment for quenching. A second study was conducted using the Fe-51Cr49 alloy with the help of Mossbauer spectroscopy [10]. It is obvious that the choice of the method of research in Ref. [10] was poor, since it was hardly possible to judge a local phase separation of the alloy by the change of the partial gamma-resonance peaks of Mossbauer spectra. They were, therefore, unable to find the structure of the phase separation.

Fig. 2 shows the iron-rich part of an iron-chromium phase diagram, built on the results of electron microscopic studies of the microstructure of iron alloys with 20, 30, 40 and 50 wt.% of chromium [11]. From the diagram, it can be seen that two phase transitions occur in the Fe-Cr system, in which, for example, the microstructure that has formed as a consequence of the tendency to ordering is dissolving and a microstructure of phase separation is forming in its place (and vice versa). This occurs within the temperature ranges of 1100-850°C and 600-550°C (Fig. 2). Based on these data, it could be concluded that at the level of microstructures, such a phase transition is bound to pass through the stage of the existence of the solid solution in the alloy. The authors [11] gave this phase transition the name ‘ordering-phase separation’. The transition occurs at a temperature, specific for each system, at which the sign of the chemical interaction between atoms of A and B is reversed. It is obvious that the transformation of the microstructure formed as a result of the tendency to ordering into the microstructure formed as a result of the tendency to phase separation, and vice versa, is a consequence of the ‘ordering-phase separation’ transition. The transition itself, i.e. the process of changing the sign of the chemical interaction between dissimilar atoms, occurs at the level of changes in the electronic structure of the alloy.
Before considering the physical essence of this transition, we would like to decide on the issue of the use of such terms as ‘ordering energy’, ‘mixing energy’, ‘enthalpy of mixing’ and so on. Each of these terms refers to the same notion, but none of them is accurate enough in characterizing the chemical meaning of this energy. This energy emerges in any alloy due to the chemical interaction of the nearby dissimilar atoms.
that constitute the alloy. When the sign of the energy is negative, dissimilar atoms are attracted and a tendency to ordering takes place. When the sign is positive, a tendency to phase separation appears and clusters or grains consisting of atoms of the same kind are formed. Therefore, we should choose one term that best describes the chemical nature of this energy; from here on, we will therefore use the term ‘chemical interaction energy’.

During the process of heating or cooling the alloy, when the temperature passes through the phase transition point, the energy of the chemical interaction between component atoms passes through zero. It therefore follows that the microstructure, which has formed in a certain temperature range near this point, is bound to be a disordered solid solution [12]. It was believed that the transition temperature was the same for all alloys of a given system [12].

The discovery of the ‘ordering-phase separation’ transition in alloys has shown that the degree of the supersaturating of the solid solution by the alloying element is not the driving force of the new phase precipitation process. The factor that has a decisive influence in this process is the sign that the chemical interaction energy has at a given temperature: negative (a tendency to ordering), or positive (a tendency to phase separation). The absolute magnitude of this energy also plays a big role in whether precipitation of these phases will or will not occur [13]. It was believed that at the temperature of the ‘ordering-phase separation’ transition, when the chemical interaction energy is close to zero, no other phases could form, except the solid solution [13]. In a more distant neighborhood of the phase transition temperature, the absolute magnitude of the chemical interaction energy can be insufficiently high for the precipitation of a corresponding new phase to begin; this circumstance can lead to the expansion of the region in which the structure of the solid solution exists. Everything depends on the nature of the alloy. The latter means that in a certain temperature range, near the phase transition line in the diagram, there may be a stripe within which a disordered solid solution structure is formed.
Fig. 3. The energy of the chemical interaction (E) vs. temperature for Fe_{50}Cr_{50} alloy. Designations: 1 and 2 – points of high-temperature (1) and low-temperature (2) ‘ordering-phase separation’ transitions (E=0); 3 and 5 – E levels above which the phase separation microstructure is formed in the alloy; 4 – E level above which the σ-phase is formed [4].

Fig. 3 presents a scheme showing the dependence of the chemical interaction energy of the Fe_{50}Cr_{50} alloy on temperature [13]. This scheme shows the experimentally determined points (1 and 2) of the ‘ordering-phase separation’ transition. The intersection points of the chemical interaction energy E curve with lines (3), (4), and (5) show energy levels, above which (in their absolute value) the formation of the second phase begins. They were determined along the temperature axis in Fig. 2 as points separating the one- and two-phase regions in the phase diagram of Fe-Cr. The distances between the positive and negative thresholds on a temperature axis in the case of high-temperature and low-temperature ‘ordering-phase separation’ transitions are very different (Fig. 2). In the first case, this distance is approximately 300°C and about 50°C
in the second. Based on this, the following conclusions have been made [13]:

a. The sign of the energy of the chemical interaction between dissimilar atoms is not constant for the majority of metallic systems but varies according to the change of the temperature of the alloy (sometimes more than once).

b. The precipitation of this or that phase and the formation of a solid solution depend not on the degree of solubility of the atoms of one component in the lattice of the other, but on the sign and the absolute magnitude of the energy of the chemical interaction between dissimilar atoms (Fe and Cr).

c. The microstructure of a disordered solid solution is formed over the entire bulk of the alloy only in the temperature region adjacent to the temperature of the ‘ordering-phase separation’ transition, because this is the region where the chemical interaction energy between dissimilar atoms is close to zero.

d. Every heating temperature of the alloy corresponds with a quite definite microstructure, which is formed during the exposure of the alloy at this temperature and does not depend on what the structure of the alloy was prior to the given heat treatment.

The final remark means that there is absolutely no point in quenching alloys before their tempering (aging), in order to obtain a structure of the homogeneous solid solution. What is more, in most cases the temperatures from which such quenching is usually carried out do not correspond with the regions of the solid solution.

2.2. Changes in the electronic structure of alloys at the ‘ordering-phase separation’ transition (experimental data)

It is obvious that the observed changes in the microstructure of the alloys at the ‘ordering-phase separation’ transition do not occur by themselves, but are due to definite changes in the electronic structure of the alloys at quite specific temperatures for each system. For example, Fig. 4 shows specific formations which were previously found in alloys of the Fe-Cr system and named ‘electron domains’ [14], later called ‘chemical domains’ [12]. Such domains appearing at high-temperature (Fig. 4a) and low-temperature (Fig. 4b) ‘ordering-phase separation’ transitions are best
observed when defocusing the electron microscopic images. For example, a high-temperature transition in the Fe\textsubscript{50}Cr\textsubscript{50} alloy should be observed after a quenching in water from the phase separation region (1200-1400°C) and a subsequent aging for some time in the region of ordering (700-800°C). For a low-temperature transition, these domains (Fig. 4b) are observed after a quenching in water from the region of ordering (700-800°C) and a subsequent aging in the phase-separation region (500-550°C).

Electron domains are considered as microscopic portions, inside which the sign of the chemical interaction energy has already changed to the opposite of the other surrounding portions, in which the sign remains as before. An electron beam passing through the foil, in which electron domains have formed, should deviate in opposite directions on both sides of the domain boundary, and leads to a deficiency (bright lines) or an excess (dark lines) of electrons when defocusing the electron microscopic image [11]. It should be noted here, that similar domains are observed in electron micrographs of the alloys at their transitions both in a ferromagnetic state (when the domains differ in the magnetization vector orientation) and in a ferroelectric state (when the difference is in the direction of spontaneous polarization). This means that the nature of the contrast from all the above-mentioned domains is the same and that the contrast is formed due to the difference in the electronic structure of the neighboring domains.

Previously, the formation of chemical domains was considered as a temporary, unstable state of the alloy (the state of transition from the tendency to phase separation to the tendency to ordering) [11]. However, it was later found that domains in the alloys of the Fe-Cr system might
testify that a certain metastable state of the alloy is characteristic for the given temperature [15]. The existence of such a metastable state (an incomplete ‘ordering-phase separation’ transition) in the bulk of the alloy prevents the formation of the σ-phase in the entire volume of the alloy. The σ-phase forms only in a thin surface layer, where, apparently, the surface plays some form of catalytic role for the process of the transition from ordering to phase separation [15].

The discovery of such formations as electron domains in the microstructure of alloys of the Fe-Cr system [11] and stainless Ni-Cr steel [16] indicates that the ‘ordering-phase separation’ transition begins at the level of changes in the electronic structure of these alloys. Therefore, it would be interesting to find out exactly what changes occur in the electronic structure that may lead to a change in the sign of chemical bonds between dissimilar atoms.

In our opinion, the most appropriate method for this study is X-ray photoelectron spectroscopy (XPS). This method was first used to determine the temperature at which the sign of the chemical interaction energy is changed [17]. The use of the method of XPS for determining the sign of the ordering energy of alloys is based on the fact that in high vacuums, at increasing the temperature of heating the specimen, a rapid evaporation of atoms from the specimen surface begins. The information obtained under such experimental conditions already concerns the entire volume of the specimen, not only its surface layer. The shape of the valence bands, obtained at this temperature, allowed the determination of the sign of the ordering energy at a definite temperature of the study. In this case, if the shape of the valence band of the alloy is similar to the shape of the valence band of the pure A solvent, then it means that in the immediate environment of A atoms there are A atoms. It can suppose that A-A and B-B bonds form in the alloy (there is a tendency to phase separation). If the distribution of the density of 3d-states in the alloy is similar to the distribution of the electron density in the valence band of the dissolved component, then it can suppose that in the alloy, at this temperature, there are no A-A bonds between the atoms of the solvent. It means that each atom of the A solvent is involved in a bond with atoms of the dissolved B component, i.e. there is a tendency to ordering and AₐBₙ chemical compounds precipitate in the solid solution.
Fig. 5. Co$_3$Ni alloy. Photoelectron spectra of the valence band. Reference spectra:
(a) Ni, (b) Co. Experimental spectra obtained at 200 (c), 500 (d), 800 (e) and
1100°C (f) [17].
For example, X-ray photoelectron spectra of the valence band were obtained for the Co$_3$Ni alloy at the following temperatures of specimen heating: 200, 500, 800 and 1100°C [17]. Fig. 5 shows the valence band spectra obtained at these temperatures, as well as the reference spectra of pure Co and Ni (at room temperature). At temperatures of 200 and 500°C, the valence band spectra of the alloy have a double band structure due to a small overlap of the d-bands of the Co and Ni atoms. At temperatures of 800 and 1100°C, the spectra of the valence bands have the form of a superposition of the valence bands, where the form of the valence band of the solvent atoms, i.e. Co, is predominant. This allowed the authors [17] to say that at these temperatures, in the studied alloy, a tendency to phase separation is displayed. Therefore, in the temperature range between 500 and 800°C, an ‘ordering-phase separation’ transition takes place in the alloy, during which the sign of the chemical interaction energy is reversed.

2.3. Alloys of the Fe-C system

As is well known from the accepted phase diagram of Fe-C, there are two types of microstructures in alloys of this system: microstructures formed as a result of the tendency to phase separation (iron+graphite), and microstructures formed as a result of the tendency to ordering (iron+cementite). Assuming that graphite is the stable phase and cementite is metastable, a lot of authors came to the conclusion that in this system, there are two types of equilibrium – stable (Fe-C) and metastable (Fe-Fe$_3$C). Which of these precipitates forms depends, it is believed, not so much on the temperature of the heating as the scenario according to which the decomposition of the Fe-C alloys occurs – either towards the achievement of the ‘austenite (ferrite)-cementite’ phase equilibrium or the ‘austenite (ferrite)-graphite’ equilibrium. However, the question of how the Fe-C system itself chooses the way to decompose remains unclear.

Between the 1960s-1980s, many researchers [18-22], using the TEM method, found that after water-quenching from the single phase region of austenite (950-1223°C), in the austenite regions of many hypereutectoid steels (1.1-1.67% C), there formed a two-phase microstructure, containing, as the second phase, either clusters of carbon atoms or highly carbon enriched and carbon depleted modulations of the composition. The authors [18] called such a structure abnormal, even though precisely this structure could explain hypereutectoid steel graphitization at temperatures above $A_{cm}$. An electron microscopic study of the microstructure of tool carbon
steel quenched in water from 1150 and 900°C also showed the presence of clusters of carbon atoms in the structure of this steel (Fig. 6) [23].

Ustinovshikov [23] placed the experimental data (obtained by him and the authors of [18-22]) that indicated the existence of carbon clusters in the microstructure of austenite at appropriate points of the generally accepted Fe-Fe₃C phase diagram (Fig. 7). Based on these data, it was concluded that the graphitization of iron-carbon alloys occurs throughout practically the entire range of compositions, at temperatures above the eutectoid. As noted by Kusunoki and Nagakura [20], clusters of carbon atoms are found in steels after quenching from high temperatures over the entire range of compositions that contain from 0.2 to 1.67 wt.% C. The more carbon there is in the alloy, the larger the sizes of the carbon clusters in steel and graphite in cast iron. The fact that cementite dissolves above the eutectoid line was discovered by Wells back in 1938 and has been repeatedly confirmed since.

Electron microscopic results [23] also show that quenching of carbon steel from a temperature of 790°C in water does not lead to the formation of carbon clusters (Fig. 7, indicated by a blank box in the phase diagram). Since cementite in the microstructure of steels is found only
after heat treatment at temperatures below the eutectoid and never above it, it can be assumed that the eutectoid line is also the line of the ‘ordering-phase separation’ transition. This means that above it, a tendency to phase separation takes place, and graphitization occurs in alloys (steels and cast irons). The presence of graphite in the structure of cast irons below the eutectoid line in the diagram (below the line of the ‘ordering-phase separation’ transition) is quite explicable: the very large sizes of graphite particles formed mainly in the liquid solution do not allow them to dissolve. All these data allow us to consider the phase diagram of Fe-C in a somewhat different light than that which is presented in the literature (Fig. 7).

Fig. 7. Fe-6.67% C phase diagram. Carbon clusters designation: •-revealed by Izotov and Utevsky (1968); ⋆-Nagakura et al. (1975; 1979) and Kusunoki et al. (1981); ▲-Tyapkin et al. (1975); x-Sandvik (1983). Data obtained in the present work are designated as ▪ (if carbon clusters are found in the martensite structure) and as □ (if they are not found) [23].
Here the austenite (A) + cementite region is absent, as cementite cannot exist above the line of the ‘ordering-phase separation’ transition. It is difficult to imagine how the structure in the L+A region transforms into A+C by lowering the temperature. Therefore, instead of the L+A field in Fig. 7, there should be an L+C region (as in hypereutectic compositions) because carbon, as a more refractory element, should always be the first to precipitate from the liquid under the conditions of the tendency toward phase separation. In this case, the whole high-temperature part of the diagram must change, to both the right and left of the location of the experimental points. This means that a full-scale study of the Fe-Fe₃C diagram is necessary.

Based on the corrected phase diagram of Fe-Fe₃C, it can be concluded that the quenching of steel, usually performed to obtain the structure of martensite is a totally useless and perhaps even harmful operation (resulting in quenching cracks), as the necessary microstructure can be obtained by simple isothermal tempering at an appropriate temperature. If it is necessary to get a purely martensite microstructure (without carbon clusters), then quenching should be carried out from the temperature region adjacent to the line of the ‘ordering-phase separation’ transition, i.e. above the line $A_{cs}$ at 20-30°C (which, incidentally, is done when quenching carbon tool steels). This is precisely the range of temperatures at which it is usually recommended to water-quench carbon steels in order to avoid their graphitization. Hence, it can be concluded that the line of the ‘ordering-phase separation’ transition is very close to the eutectoid line and, most likely, coincides with it.

2.4. Alloys of the Fe-Mo system

The phase separation in Fe-Mo alloys containing up to 20% Mo has been the subject of a lot of research conducted since the 1960s. Hornbogen (1961), Higgins and Wilkes (1972), Erickson and Cohen (1971), and Marcus et al. (1967), using the methods of electron microscopy, diffuse X-ray scattering and Mössbauer spectroscopy, found that at 550°C (the beginning of the aging of such alloys), zones of molybdenum atoms were formed before the formation of particles of the Fe₂Mo equilibrium phase. During a more detailed investigation of Fe- (13-20) at.% Mo alloys, carried out later by Miyazaki et al. [24], it was found that the aging of such alloys at 600°C led to the formation of particles of the Fe₂Mo phase. By lowering the aging temperature to 550 or 500°C, a tweed, and then a modulated structure along the <100> directions of the matrix, were formed.
in the Fe-15 % Mo alloy. With an increase of the duration of the aging at 550ºC, particles of the Fe₂Mo phase were formed inside the modulated structure and then, when the modulated structure dissolved, the sizes of Fe₂Mo particles increased. Miyazaki believed that these two types of microstructures were formed inside (modulated structures) and outside (particles of the Fe₂Mo phase) the region limited by the spinodal curve. The alloys inside the spinodal region were considered to decompose according to the spinodal mechanism and outside it according to the nucleation-growth mechanism.

Later, using structural data, the authors [24], adjusted the position of the spinodal curve. It was believed [24] that, if the alloy was aged slightly above the coherent spinodal temperature, a mixed structure formed, consisting of a modulated structure and particles of the Fe₂Mo phase distributed inside it. The presence of such a mixed structure indicated, in the opinion of the authors [24], that the transition from the spinodal mechanism of decomposition (inside the spinodal region) to the mechanism of nucleation-growth (outside the spinodal region) occurred gradually; that is, the spinodal curve was not a line in the phase diagram, but a sufficiently wide band.

The microstructure of the Fe-20 at. % Mo alloy, formed after aging at 500ºC, was investigated by Isheim [25], using the methods of field-ion microscopy and atom probe. It was determined that dark modulations inside the modulated structure can contain up to 90% of Mo atoms after aging for 20 hours and up to 95.7% after 45 hours.

In another work [26], it was found that after quenching the Fe-15% Mo alloy from 1350ºC, the microstructure was a solid solution. Aging the alloy at 600ºC resulted in the precipitation of particles of the Fe₂Mo phase. If aging was carried out at 550ºC for 1 hour, then a modulated structure, the electron diffraction pattern of which showed satellites near matrix reflections, was first formed in the alloy.
Further aging of the Fe-15% Mo alloy at 550°C for 3 hours leads to the fact that the modulations formed at the beginning of aging lose their original shape and begin to dissolve. Against the background of the modulated structure, it is possible to observe highly dispersed particles located mainly along the elastic-soft directions of the matrix (Fig. 8a).

Exposure of the alloy at 550°C for 5 hours leads to a significant increase in the dimensions of these particles by dissolving the modulated structure (Fig. 8b). An electron diffraction pattern taken from such a particle indicates that this is the Fe$_2$Mo phase. We can therefore say that the temperature of the ‘ordering-phase separation’ transition is somewhere in the range of 550-600°C.

2.5. Alloys of the Fe-W system

According to the existing Fe-W phase diagram, the region of solid solutions in this system starts from temperatures above 800°C and extends to all compositions only before the solidus temperature. The maximum content of tungsten in the solid solution is achieved at 1300°C and is 6.6 at. %. In order to study the microstructure corresponding to the high-temperature state of the alloy, Ustinovshikov and Sapegina [27] quenched specimens of the Fe-15% W alloy in water from temperatures of 1100, 1200, 1300 and 1400°C. After quenching from 1100°C, massive particles of the Fe$_7$W$_6$ phase were observed in electron microscopic images, but the microstructure was already a homogeneous solid solution by the quenching from 1200°C. It would seem that with a further increase in the temperature of heating, the alloy would also have a solid solution structure. However, after the quenching from 1300°C, precipitates are observed in the electron microscopic images in the form of modulations.
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In the electron diffraction patterns obtained from such a microstructure, satellites are observed close to the main reflections of the matrix. Analysis shows that these satellites appear from particles with a crystal lattice of tungsten. Such particles of tungsten atoms form as a result of the existence in the Fe-15% W alloy of a tendency to phase separation at 1300°C. With an increase in the heat-treatment time of the alloy at 1300°C or with an increase in the heat-treatment temperature to 1400°C, the particles of tungsten atoms become larger and exist in the form of accumulations of particles.

Because the tendencies towards ordering and phase separation are alternative, it would be logical to assume that the transition from the ordering structure to the phase separation structure will occur by dissolving one structure and forming another in its place. In order to find out how such a process proceeds at 600°C aging, the lattice parameter of the solid solution was measured after quenching the alloy from 1300°C and subsequent aging at 600°C.

The results obtained on the same specimen are presented in Fig. 10. With an aging time of up to 20 minutes, the lattice parameter measured after quenching from 1300°C decreases. This indicates that at the very beginning of the aging process, tungsten atoms continue to precipitate from the solid solution. According to the generally accepted Fe-W phase diagram, the temperature of 600°C corresponds to the existence of the two-phase region $\alpha$+Fe$_3$W, i.e. a region of ordering. However, as shown in

![Image](image_url)
Fig. 10, the process of phase separation continues at the beginning of aging in the alloy. After 30 minutes of aging, the lattice parameter increases dramatically (Fig. 10), and the microstructure is a solid solution. Aging at 600°C for 1 hour leads to a sharp decrease in the lattice parameter (Fig. 10) and changes in the morphology of the precipitates. Further aging at 600°C leads to the complete dissolution of this intermediate chemical compound (Fig. 10, second peak on the lattice parameter curve) and the subsequent precipitation of the stable Fe$_2$W phase (Fig. 11). Particles of this phase have an irregular shape, are first located at dislocations and defects, and then coagulate into accumulations.

Thus, the ‘ordering-phase separation’ transition occurs twice in the Fe-15W alloy at the temperatures of about 1300 and about 600°C [27]. If, at 1200°C, a narrow region of the solid solution is the boundary between the regions where only ordering or only phase separation takes place, then, in the second case, such a separation is not observed in the diagram. In this case, the mixed region of phase separation and ordering exist at the same temperature (600°C) in the form of alternating microscopic sites, between which microscopic sites of the solid solution are located.