Chemical Bond in Metallic Alloys: Electron Microscopic Study

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Abstract

A critical analysis of existing concepts of Materials Science – the nature of solid solutions and diffusion phase transitions, the energy of chemical interaction in alloys, the principles of phase diagram construction, the principles of conducting heat treatment of alloys is provided. It is shown that chemical interactions between dissimilar atoms always exist, in all alloys and at any temperature of heating the alloy. Experimental evidence is presented, showing that alloys have an amazing, not previously known property of changing the sign of chemical interaction between dissimilar atoms with a change of the heating temperature and sometimes with a change in the composition. It has been concluded that the discovery of the phase transition 'ordering-phase separation' radically changes the now existing ideas about diffusion phase transformations in alloys and about conditions of solid solution formation. Experimental data is presented, fully supporting the ideas expressed in the article. It has been shown that the transition 'phase separation-ordering' begins in an A(B) alloy with dehybridization of the valence electrons on the atoms of B and localization of some of the valence electrons on the atoms of A and B. As a result, along with the metallic component, the ionic component of the chemical bond is formed. It has been shown that a model of pair wise interaction is realized in multi-component alloys, according to which the chemical interaction within each of the diffusion couples of A-B occurs similar to the chemical interaction in a corresponding binary alloy. Using this approach, it has been found experimentally that the process of partitioning of a multi-component alloy into diffusion couples takes place in the liquid solution. It has been found that the remarkable properties of super alloys at high temperatures are manifested by the fact that a tendency to phase separation takes place in the majority of their diffusion couples at these temperatures. It is shown that formation of multi-component chemical compounds (including Laves phases) under conditions when there is a tendency to phase separation between species, is impossible in principle.

Keywords: Phase transitions; Chemical interactions; Ordering; Phase separation; Phase diagrams; Heat treatment

Introduction

According to the existing in the literature ideas a solid solution in metal alloys is formed in those cases, when in a system consisting of atoms of different elements, a common for all elements crystal lattice is formed on the basis of the solvent

lattice [1]. It is assumed, that in all alloys, the magnitude of solubility of some 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 forming the alloy exceeds about 14-15%, the solubility in the solid state is due to be restricted (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 emerging 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, as it was considered, determined one or another degree of solubility of atoms of B in the crystal lattice consisting of A atoms and was that driving force, which at a decrease of the temperature, and, therefore, a decrease in solubility resulted in 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 in the alloy (e/a) [1].

This very principle was used in the construction of equilibrium phase diagrams: in them, in overwhelming majority of cases, regions of solid solutions were shown at high temperatures, and two-phase regions at low temperatures. All these ideas formulated about 80 years ago, when modern methods of investigation of 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 confirmed these views. Indeed, when this method was applied to alloys quenched from high temperatures, no other phases besides the solid solution were found. On the basis of these data, they came to the conclusion, that at high temperatures, the microstructure of alloys was a disordered solid solution.

Thus, according to the ideas which have been in sufficient enough detail described, for example, in monograph, at high temperatures, an alloy is regarded as an equilibrium phase, i.e. as a homogeneous solid solution, in which component atoms are

randomly distributed over the sites of the lattice (substitution alloys) and interstices (interstitial alloys) [2]. In this case, when the interaction potential W is significantly lower than the thermal energy kT , the interaction energy can be neglected in comparison with the thermal energy. Therefore, they believed that, at high temperatures, the alloy behaved like an ideal solid solution. At a decrease of the temperature, when the interaction potential W becomes substantially higher than the thermal energy kT , the relative position of component atoms in the solid solution is determined from the condition of free energy minimum and, as a result, a new phase precipitates. Thus, at a decrease in the temperature, a phase transition of the “order - disorder” type happens in the alloys. It was considered that the physical reason for ordering was interaction between atoms of the components constituting the solid solution, though, what this interaction consisted in was not specified [2].

However in the sixties-seventies, 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 and contained either particles of a new phase in the solid solution or modulations of the composition [3-8]. When such a discovery was made, almost no one would doubt that the blame for such a disagreement should be laid on the experiment, not on the phase diagrams. A version was invented, according to which the diffusion of atoms in the alloy was sharply accelerated during the process of quenching itself, since decomposition of the alloy proceeds via the spinodal mechanism (during spinodal decomposition, the stage of critical nuclei formation is absent).

As is known, the method of X-ray diffraction is severely limited in the possibility of identifying highly-dispersed particles of the new phase, which are usually registered by a local method of analysis – the method of TEM [9]. This is precisely why a conflict arose, when, using XRD data, they built phase diagrams containing, as it was asserted, regions of solid solutions at high temperatures, and using the method of TEM, discovered that a completely different structure - a two-phase one was formed in these regions after quenching from these temperatures.

From an analysis of these data, it was concluded that the regions of solid solutions in equilibrium phase diagrams are in fact two-phase regions [10]. This conclusion agrees with the well-known axiom of thermodynamics stating that in nature all solutions are non-ideal and have either positive or negative deviations from Raoult's law.

History of the discovery of the transition ‘ordering-phase separation’

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 at a decrease of the temperature this pressure abruptly drops, and, beginning with certain temperatures, it is impossible to measure

it, then it was tacitly assumed that the sign of the ordering energy determined at very high temperatures remains the same at lower temperatures, as well. This gave birth to the idea that each binary system is characterized by its own sign of the 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, three structural regions were observed (the temperatures are indicated for the $\text{Fe}_{50}\text{Cr}_{50}$ alloy): 1) above 830°C - a solid solution, 2) in the temperature range of $830 - 440^\circ\text{C}$ - a σ -phase formed as a result of the tendency of alloys to ordering, and 3) below 550°C - a microstructure, which is clusters of chromium atoms in the solid solution and forms as a result of the tendency of the alloy to phase separation [11]. Already on the basis of these data, it could be concluded that the existence in the phase diagram of two regions, in one of which a microstructure of ordering is formed and in the other - a microstructure of phase separation, gives grounds for saying that, at a transition from one region to the other (i.e. a change in the temperature or concentration), a phase transition should occur in alloys of this system. Still, no one made such a conclusion. On the contrary, some authors, basing on the fact that at high temperatures, positive deviations from Raoult's law had been found in alloys of the iron-chromium system, suggested that the σ -phase was not a chemical compound at all (although it has all attributes of a chemical compound, including a lattice of its own, distinct from that of the matrix), but was a “the phenomena pertaining to surfaces (reconstruction, segregation, etc.)” and, therefore, there were no contradictions there [12,13].

The situation turned out to be even more confusing when in alloys of the same system, at high (1150°C and higher) temperatures, i.e. in the solid solution region, the authors discovered a microstructure which could not be attributed either to the structure of a disordered solid solution or the structure of a σ -phase [14]. The authors identified it as the structure of high-temperature phase separation (Figure 1), as it was fixed after a heat treatment at the same temperatures, at which positive deviations from Raoult's law had been previously found [13,14]. In addition, a system of satellite reflections was observed in the electron diffraction pattern (Figure 1, inset) obtained from such 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 appearance of a number of critical works [15,16].

Figure 1: $\text{Fe}_{50}\text{Cr}_{50}$ alloy. Water-quenching from 1200°C : Bright-field micrographs. Electron diffraction pattern taken from a coarse particle (inset).

The first experimental study to verify the existence of the high-temperature phase separation in alloys of the iron-chromium system was undertaken by the example of the Fe-45% Cr alloy [15]. Using the method of TEM, it was found that the microstructure of this alloy after quenching from 1150 - 1200°C was similar to that which had been obtained in Reference [14]. However, they interpreted such precipitations as chromium nitrides, i.e., as a kind of an “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 Fe₅₁Cr₄₉ alloy, with the help of Mossbauer spectroscopy [16]. It is obvious that the choice of the method of research in Reference 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 corresponding to pure iron. Therefore, they did not manage to find the structure of phase separation [16].

Figure 2 shows the iron-rich part of an iron-chromium phase diagram, built on the results of electron microscopic studies of the microstructure of alloys of iron with 20, 30, 40 and 50 wt. % of chromium [17]. From the diagram, it can be seen that in the Fe-Cr system, there occur two phase transitions, in the result of 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 (Figure 2)

Figure 2: The Fe-rich portion of the Fe-Cr phase diagram. Dashed lines show the temperatures of phase transition ‘ordering-phase separation’. Designations: ■ – solid solution microstructure; Δ – phase separation microstructure; Δ-6-phase at the surface (tendency to ordering).

On the basis of 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 have given this phase transition the name “ordering-phase separation” [17]. Since the discovery of this transition, 17 binary systems have so far been studied and in 16 of them the transition has been experimentally found. 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 phase transition ordering –phase separation. The transition itself, that is, 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 the above terms refers to basically the same notion, but each of them is not accurate enough in characterizing the physical meaning of this energy. This energy emerges in any alloy due to the chemical interaction of nearby dissimilar atoms constituting 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, then a tendency to phase separation appears and clusters or grains consisting of atoms of the same kind are formed. Therefore, we think that we should choose one term that best describes the physical nature of this energy and call this energy “chemical interaction energy”. From this point on, in this article, we will use exactly this term.

When in the process of heating or cooling the alloy, the temperature passes through the phase transition point, the energy of the chemical interaction between component atoms passes through zero, in connection with which, the microstructure, which has formed in a certain temperature range near this point, is bound to be a disordered solid solution [18]. It was believed that the transition temperature was the same for all alloys of a given system, but specific for each system [18].

The discovery of the phase transition ‘ordering-phase separation’ in alloys has shown that it is not the degree of super saturation of the solid solution in alloying element that is the driving force of the process of new phase precipitation. The factor having a decisive influence in this process, is which sign the chemical interaction energy has at one or another 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 there will or will not occur precipitation of these or those phases [19]. It was agreed that at the temperature of the phase transition ‘ordering-phase separation’, when the chemical interaction energy is close to zero, no other phases can form, except the solid solution [19]. In a more distant neighborhood of the phase transition temperature, the absolute magnitude of the chemical interaction energy can also be insufficiently high for the precipitation of a corresponding new phase to begin, and this circumstance can lead to expansion of the region in which there exists the structure of the solid solution. Everything depends on the nature of the alloy. The latter means that in a certain temperature range, in the vicinity of the phase transition line in the diagram, there may exist a stripe, within which a disordered solid solution structure is formed

Figure 3 presents a scheme showing the dependence of the chemical interaction energy of the Fe₅₀Cr₅₀ alloy on the temperature [19,20]. This scheme shows experimentally determined points (1 and 2) of the phase transition ‘ordering-phase separation’. The intersection points of the chemical interaction energy curve E with lines (3,4,5).

Figure 3: The energy of the chemical interaction (E) vs. temperature for $\text{Fe}_{50}\text{Cr}_{50}$ alloy. Designations: 1 and 2 – points of high-temperature (1) and low-temperature (2) phase transitions ‘ordering-phase separation’ ($E=0$); 3 and 5 – E levels above of which the phase separation microstructure is formed in the alloy; 4 – E level above of which the σ -phase is formed.

show energy levels, above which (in absolute value) there begins formation of the second phase. They were determined along the temperature axis in figure 2 as points separating the one- and two-phase regions in the phase diagram of Fe-Cr. The distances on the scale of temperature between the positive and negative thresholds in the case of high-temperature and low-temperature phase transitions ‘ordering-phase separation’ are very different. In the first case, this distance is approximately 300°C, in the second - about 50°C. Based on this scheme, the following conclusions have been made [20]:

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

b. Precipitation of this or that phase and formation of a solid solution depend not on the degree of solubility of 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 phase transition ‘ordering-phase separation’, because it is the region where the chemical interaction energy between dissimilar atoms is close to zero.

d. For every heating temperature of the alloy a quite definite microstructure corresponds, 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 latter means that there is absolutely no point in quenching alloys before their tempering (aging), in order to obtain a structure of the solid solution, the more so, because the temperatures, from which such quenching is usually carried out, in most cases do not correspond to the regions of the solid solution.

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

It is absolutely obvious that the observed changes in the microstructure of the alloys at the phase transition ‘ordering-phase separation’ occur not by themselves, but due to definite changes in the electronic structure of the alloys, at temperatures quite specific for each system. For example, Figure 4 shows specific formations which were previously found in alloys of the Fe-Cr system and named “electron domains”, later on called “chemical domains” [17,18]. Such domains appearing at high-temperature (Figure 4a) and low-temperature (Figure 4b).

Figure 4: $\text{Fe}_{50}\text{Cr}_{50}$ alloy. Chemical domains formed at high-temperature transition ‘ordering-phase separation’ (water-quenched from 1200°C for 1 h and then from 700°C for 4 h) (a) and at low-temperature transition (water-quenched from 700°C for 1 h and then from 550°C for 4 h) (b).

phase transitions ‘ordering-phase separation’ is best observed at defocusing electron microscopic images of specimens that have undergone a double heat treatment. For example, at a high-temperature transition in the $\text{Fe}_{50}\text{Cr}_{50}$ alloy - after 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). At a low-temperature transition, these domains (Figure 4b) are observed after quenching in water from the region of ordering (700 - 800°C) and a subsequent aging in the phase-separation region (500 - 550°C).

Chemical domains are considered as microscopic portions, inside of which the sign of the chemical interaction energy has already changed for the opposite relative to other surrounding portions, in which the sign would remain as before. An electron beam passing through the foil, in which chemical domains have formed, should deviate in opposite directions on both sides of the domain boundary and it leads to a deficiency (bright lines) or an excess (dark lines) of electrons at defocusing the electron microscopic image [17]. It should be noted here, that similar domains are observed in electron micrographs of the alloys at their transition both in the ferromagnetic state (when the domains differ in the magnetization vector orientation), and in the ferroelectric state, (when the difference is in the direction of spontaneous polarization). It means that the nature of the contrast from all the above-mentioned domains is the same and the contrast is formed due to the difference in the electronic structure of neighboring domains.

Earlier, 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) [17]. However, later it was 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 [21]. Existence of such a metastable state (incomplete phase transition 'ordering-phase separation') in the bulk of the alloy prevents the formation of the σ -phase in the entire volume of the alloy; the latter forms only in a thin surface layer, where, apparently, the surface plays a role of some catalyst for the process of transition from ordering to phase separation [21].

The discovery of such formations as chemical domains in the microstructure of alloys of the Fe-Cr system and stainless Ni-Cr steel indicates that the phase transition 'ordering phase separation' begins in these alloys at the level of changes in the electronic structure [17,22]. Therefore, it would be interesting to find out what exactly changes occur in the electronic structure, which may lead to a change in the sign of chemical bonds between dissimilar atoms. In our opinion, the most appropriate method, which would allow doing this, is the method of X-ray Photoelectron Spectroscopy (XPS). This method was for the first time used to determine the sign of the chemical interaction energy at heating and cooling specimens of binary alloys of a number of systems in reference 23.

The sign of the chemical interaction energy of an AB alloy, at some temperature of study, can be judged upon by the shape of the valence bands, obtained by the method of XPS, at heating the alloy to this temperature [23]. 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 as a result of a stronger spatial localization of the electron density of the solvent in the vicinity of its own atoms, then it means that in the immediate environment of A atoms there are A atoms, and so we can say, that AA and BB bonds form in the alloy, i.e., 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 means, that in the alloy, at this temperature, there are no AA bonds between the atoms of the solvent and, therefore, each atom of the A solvent is involved in a bond with atoms of the dissolved B component, that is, there is a tendency to ordering and formation of a corresponding AmBn chemical compound.

X-ray photoelectron spectra of the valence band were obtained on the $\text{Co}_{50}\text{Ni}_{50}$ alloy at the following temperatures of specimen heating: 200, 500, 800 and 1100°C [23].

Figure 5 shows the valence band spectra obtained at these temperatures, as well as 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 Co and Ni atoms, which are characteristic of the ordered state, when unlike atoms are in the immediate environment.

Figure 5: $\text{Fe}_{68}\text{Ni}_{32}$ alloy. Photoelectron spectra of the valence band. Reference spectra: (a) Fe, (b) Ni. Experimental spectra obtained at 200 (c), 500 (d), 800 (e) and 1100°C (f).

At temperatures of 800 and 1100°C, the spectra of the valence bands have the form of a superposition of the valence bands of the components, where the form of the valence band of the solvent atoms, i.e., Co is predominant. This allowed authors to say that at these temperatures, in the studied alloy, a tendency to phase separation is displayed [23]. Therefore, in the temperature range between 500 and 800°C, a phase transition 'ordering-phase separation' takes place in the alloy, during which the sign of the chemical interaction energy is reversed.

Alloys of the Fe-C system

As is well-known from the accepted phase diagram of Fe-C, in alloys of this system, there are two types of microstructures: microstructures formed as a result of the tendency to phase separation (solid solution of carbon in iron + graphite), and microstructures formed as a result of the tendency to ordering (solid solution of carbon in iron + cementite). Assuming that graphite is the stable phase and cementite is metastable, they came to the conclusion that in this system there are two types of equilibrium - stable (Fe-C) and metastable (Fe- Fe_3C). Which of these types of precipitates will form depends, as it is believed, not so much on the temperature of heating, as on the scenario, according to which the decomposition of Fe-C alloys will occur - towards achieving the phase equilibrium "austenite (ferrite) - cementite " or towards the equilibrium "austenite (ferrite) - graphite." However, absolutely unclear remains the question of how the Fe-C system itself chooses the way to decompose.

In the sixties-eighties of the XX century, many researchers using the method of TEM, found that after quenching in water from the single phase region of austenite (950 - 1223°C), in the structure 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 enriched and depleted in carbon modulations of the composition. The authors called such a structure abnormal, even though precisely this structure could explain the facts of hypereutectoid steel graphitization at temperatures above A_{cm} [24-28]. An electron microscopic study of the microstructure of tool carbon steel quenched in water from 1150 and 900°C, also showed that clusters of carbon atoms are present in the structure of this steel (Figure 6)[29].

Figure 6: Fe-1.31%C alloy water-quenched from 1150°C: bright-field image.

The author has placed the experimental data (obtained by them and the authors of [24-28]) indicating the existence of carbon atom clusters in the structure of martensite at appropriate points of the generally accepted Fe-Fe₃C phase diagram (Figure 7) [29]. Previously they removed from this diagram the austenite + cementite region disposed above the eutectoid line. The existence of such a region is an obvious mistake of the authors of the Fe-Fe₃C phase diagram. Indeed, the fact that cementite dissolves upon heating steel above the eutectoid line was discovered as early as 1938 and repeatedly confirmed later [30]. On the basis of these data, it was concluded that graphitization of iron-carbon alloys occurs practically throughout the entire range of compositions, at temperatures above the eutectoid. As noted by Kusunoki and Nagakura, in steels, clusters of carbon atoms are found after quenching from high temperatures over the entire range of compositions containing from 0.2 to 1.67 wt. % C. Therefore, the more carbon there is in the alloy, the larger are the sizes of graphite particles (compare, for example, the sizes of clusters in figure 6 and the sizes of graphite particles in cast iron) [26].

Electron microscopic results also show that quenching of the carbon steel from a temperature of 790°C in water does not lead to formation of carbon clusters (indicated by a blank box in the phase diagram, (Figure 7) [29]. Since cementite in the structure 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 at the same time the line of the phase transition ordering-phase separation. This means that above it, there takes place a tendency to phase separation, and graphitization occurs in alloys (and 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 phase transition ordering-phase separation) is quite explicable: the very large sizes of graphite particles formed mainly in the liquid solution, do not give them an opportunity to dissolve while cooling the casting or during isothermal aging of the alloy below the eutectoid temperature. All these data allow us to consider the phase diagram of Fe-C in a somewhat different light than it is presented in reference literature.

In it, the austenite (A) + cementite region is absent, as above the line of the phase transition ordering-phase separation cementite cannot exist.

Figure 7: Fe-6.67%C phase diagram. Carbon clusters revealed by Izotov (1968) are designated as •, Nagakura et al. (1975 and 1979) and Kusunoki et al. (1981) as *, Tyapkin et al. (1975) as Δ, Sandvik (1983) as x; 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).

It is difficult to imagine, how the structure in the L + A region transforms into A + C at lowering the temperature. Therefore, instead of the field L + A in Figure 7, should be the L + C region (as in hypereutectic compositions), because carbon, as a more refractory element, under the conditions of the tendency toward phase separation, should always be the first to precipitate from the liquid. But then, 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 quenching of steel, usually performed for obtaining the structure of martensite is a totally useless and perhaps even harmful (quenching cracks) operation, as the necessary microstructure can be obtained by simple isothermal tempering at an appropriate temperature. If it is necessary to get a purely martensitic microstructure (without carbon clusters), then quenching should be carried out from the temperature region adjacent to the line of the phase transition ordering-phase separation, i.e. above the line Acm at 20 - 30°C (which, by the way, is done, when quenching tool carbon steels). This is precisely the range of temperatures from 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 phase transition ordering-phase separation is very close to the eutectoid line and, most likely, coincides with it.

Survey of recent advances in the study of the transition 'ordering-phase separation'

Alloys of the Ni-Mo system

Most interesting structural changes are observed in alloys whose composition corresponds to the left part of the Mo-Ni phase diagram (compositions from Ni₂Mo to Ni₄Mo) [11]. Structural changes taking place in these alloys during heat treatment have remained unexplained for almost 50 years. In many works it was found that quenching of such alloys from high temperatures (above 1000°C) led to appearance of a system of diffraction maxima at {1 ½ 0} positions in electron diffraction

patterns. The diffraction maxima at $\{1 \frac{1}{2} 0\}$ positions do not correspond to the superlattice reflections of any of the three chemical compounds (Ni_2Mo , Ni_3Mo and Ni_4Mo) precipitating at lower temperatures. It means that the appearance of such maxima cannot be considered as a certain initial stage of the formation of such compounds. It seems obvious that if quenching is conducted from the solid solution region, then, in the Ni-25 at.% Mo and Ni-20 at.% Mo alloys, the solid solution structure should be fixed. It would mean that no additional reflections could be observed in electron diffraction patterns except for the fundamental reflections from the solid solution. In some studies they have already expressed doubts about the fact that the diffraction maxima at $\{1 \frac{1}{2} 0\}$ positions not matching the D1_a and D0_{22} reflections of the long-range order can hardly be considered as being related to with the short-range ordering stage of these structures [31-34]. To explain the situation, some authors have suggested, that at the stage, when the diffraction maxima at $\{1 \frac{1}{2} 0\}$ positions appear, certain clusters are formed, which do not possess all the symmetry elements of the corresponding long range order structures, and therefore, these clusters cannot be considered as nuclei of long range order phases [33].

Comparison of the results obtained in References [31-34] allowed the authors to suggest that in the discussed Mo-Ni alloy system, they most likely deal not with two kinds of order differing in the completeness of the ordered arrangement of atoms in the lattice (i.e. with a long-range or a short-range order) but with two kinds of order differing in the sign of the chemical interaction between the component atoms (i.e. with ordering or phase separation) [35]. Therefore, the authors supposed, that the diffraction maxima at $\{1 \frac{1}{2} 0\}$ positions, found in the electron diffraction patterns of Ni-Mo alloys after their high-temperature quenching as a result of the short-range order formation, in reality appear as the consequence of the process of phase separation taking place in the alloys at high temperatures [35].

Such an explanation of the reasons for the appearance of the system of diffraction maxima at $\{1 \frac{1}{2} 0\}$ positions in electron diffraction patterns eliminates many contradictions characteristic of the former approach. If the reflections of the "short-range" order $\{1 \frac{1}{2} 0\}$ occur as the result of phase separation which takes place while the alloy is being heated for quenching, it means that quenching only fixes the structure formed during exposure at high temperatures. In this case, it becomes clear why the "long-range" and "short-range" orders are formed in different temperature ranges (they are two types of ordering, which differ in the sign); why the diffraction maxima at $\{1 \frac{1}{2} 0\}$ is the same for the Ni-20 at.% Mo and Ni-25 at.% Mo alloys; what "miracles" happen to the Ni and Mo atoms when their diffusion rate at water-quenching (according to References [31-34]) becomes so high that it exceeds (by 4 orders of magnitude) the experimentally obtained diffusion rates of Mo atoms in the Ni lattice; etc.

Researchers who encountered the problem of casting liquid Ni-20 at.% Mo and Ni-25 at.% Mo alloys into molds, found the very low castability of these alloys (even at temperatures

exceeding the liquidus temperature by 200°C) to be very surprising. This suggested that a precipitation of solid particles consisting of atoms of the much more high-melting Mo takes place at a temperature above the liquidus line indicated in the Mo-Ni phase diagram. To check this suggestion, the Ni_4Mo alloy was quenched from the liquid state (1600 °C) directly into ice water [35]. The obtained electron diffraction pattern was absolutely similar to the one shown in figure 8.

Figure 8: Ni-25 at.% Mo alloy as-quenched from 1300°C. Electron diffraction pattern. [001] zone axis. The accepted indexing is shown in the top right corner of the electron diffraction pattern.

Such coincidence was explained by the fact that the suggestion concerning the formation of solid Mo particles in the liquid solution at temperatures above the liquidus line is confirmed [35]. In this case, the system of diffraction maxima at $\{1 \frac{1}{2} 0\}$ positions on the electron diffraction pattern of quenched alloys should not be considered as the result of "short-range order" but as the consequence of the precipitation of highly-dispersed solid particles of Mo atoms in the liquid solution. Such precipitation, according to the authors, can take place due to the existence of the tendency to phase separation in alloys of the Mo-Ni system at high temperatures including the liquid state [35].

As was shown, subsequent heat treatment of the Ni-20 at.% Mo and Ni-25 at.% Mo alloys at 700-900°C leads to disappearance of the system of diffraction maxima at $\{1 \frac{1}{2} 0\}$ positions [35]. In the Ni-20 at.% Mo alloy, a system of superlattice reflections (Figure 9a) is observed. This system is characteristic of the Ni_4Mo chemical compound with the D1_a structure. An electron micrograph of the microstructure is shown in figure 9b. It has been concluded that the D1_a phase particles are rods, whose cross section is close to square [35].

Heat treatment of the Ni-25 at.% Mo alloy at 700 – 900°C also leads to disappearance of the system of diffraction maxima at $\{1 \frac{1}{2} 0\}$ positions and appearance of a system of additional reflections [35]. This system of reflections was not characteristic of the D0_{22} structure, which is usually considered as inherent in the Ni_3Mo phase [35].

The authors have discovered an electron diffraction pattern consisting of two systems of reflections, namely, 1) reflections from the D1_a structure and 2) .

Diffusion arcs which were found to belong to the orthorhombic bcc Ni_2Mo phase (the Pt_2Mo -type) [35]. Thus, the discovery of a phase transition 'ordering –

Figure 9: Ni-20 at.% Mo alloy heat treated at 800°C for 24 h: (a) Electron diffraction pattern, [001] zone axis: The set of two systems of superlattice reflections is observed on the pattern. The first numeral under reflection indexed corresponds to the first system, the second numeral – the second system; (b) bright-field micrograph at (010) orientation of the foil.

-phase separation' in the Ni-20 at.% Mo and Ni-25 at.% Mo alloys and determination of the temperature of the transition allowed to find out why after a heat treatment at high temperatures, the diffraction maxima at $\{1 \frac{1}{2} 0\}$ positions appear in the electron diffraction patterns of these alloys, why these maxima do not coincide with the superlattice reflections of the Ni_3Mo ($\text{D}_{0,22}$) and Ni_4Mo ($\text{D}_{1,4}$) phases, and why in the Ni-25 at.% Mo alloy, instead of Ni_3Mo ($\text{D}_{0,22}$) phase precipitates we find a mixture of particles of two phases - Ni_4Mo ($\text{D}_{1,4}$) and Ni_2Mo (Pt_2Mo) [35].

Ni₈₈Al₁₂ alloy

The decomposition of alloys of the Ni-Al system has been widely studied experimentally for a long time [36,37]. Excellent mechanical and anticorrosion properties of these alloys becoming apparent at high temperatures appear due to coherent microstructures formed in the nickel-base solid solution because of the precipitation of geometrically close-packed intermetallic compounds [38]. The microstructures show high phase and structural stability up to the temperatures of melting since they have low diffusion coefficients even at high temperatures [38,39].

A detailed structural study based on the example of the Ni-12 at.% Al alloy was carried out in Reference [40]. Figure 10 shows an electron diffraction pattern of the alloy, water-quenched from 1300°C. To a certain extent, the intensity and sharpness of the satellite reflections in the electron diffraction pattern, depend on the deflection of foil orientation from the [001] zone axis. When the deflection is considerable, the intensity of fundamental and satellite reflections is almost the same (Figure 10). The presence of such satellites in the electron diffraction pattern of a binary alloy, the component atoms of which crystallize in the same lattice type, usually indicates the formation of two solid solutions with different lattice parameters, namely, enriched and depleted in the alloying element, i.e. it means that a phase separation occurs in the solid solution.

It is known that at the temperature, from which the alloy was water-quenched (1300°C), pure aluminum is in the liquid state. So, the author assumed that when the alloy solidifies, clusters enriched in Al atoms are the last to solidify in the Ni₈₈Al₁₂ alloy

as the result of the tendency to phase separation, and therefore, when the alloy is water-quenched from 1300 °C.

Figure 10: Ni-12 at.% Al alloy. Water-quenching from 1300°C for 1 h: electron diffraction pattern; the foil orientation is some deflected from [001] zone axis.

they are observed in electron diffraction patterns as very fuzzy satellite reflections [40]. After quenching from 1200°C, no satellites are observed in the electron diffraction patterns and the microstructure is a solid solution [40].

Figure 11: The same alloy. Water-quenching from 700°C, electron diffraction pattern (inset), dark-field micrograph using a (-100) super lattice spot from inset

Figure 11 shows a dark-field image of the microstructure (after aging at 700°C for 24 h) taken from the superlattice reflection in the electron diffraction pattern. Disk-like particles are clearly seen in the dark-field image using the most bright satellite spot near the (200) fundamental reflection [40]. This pattern was interpreted as belonging to the Ni_3Al phase [40]. It means that at 700°C, the tendency to ordering exists in the alloy.

It is known that at the temperature, from which the alloy was water-quenched (1300°C), pure aluminum is in the liquid state. Perhaps, when the alloy is heated to 1300°C prior to water-quenching, clusters of Al-atoms formed in the Ni₈₈Al₁₂ alloy are in some quasi-liquid state. After quenching from 1200°C, no satellites are observed in the electron diffraction patterns. The authors came to the conclusion that the transition 'phase separation-ordering' takes place at temperature somewhat above 1200°C.

Alloys of the Ni-Cr system

It is considered that the atomic arrangement in these ordered alloys is isomorphous with the Pt_2Mo type. The formation of the Pt_2Mo type superstructure was revealed by an electron diffraction method in the Ni-33.3at. %Cr alloy annealed

at 500°C for 1600h [41]. Marucco, studying the electrical resistivity of various Nimonic and Inconel alloys, tried to explain some changes in their properties by the precipitation of such a phase, but found no diffraction evidence of its existence [42]. Apparently, not without reason, some researchers engaged in construction of phase diagrams ignore this phase. For example, the Ni-Cr phase diagram at the site www.Calphad.com.2006 is depicted only above the temperature of 600°C, at which, according to Reference, the Ni₂Cr phase should not form two alloys were studied: the Ni₄₀Cr₆₀ and Ni₆₈Cr₃₂ alloy [11,43]. According to the conventional phase diagram of Ni-Cr, at compositions close to the Ni₄₀Cr₆₀ alloy, a eutectic is formed in the Ni-Cr system [11]. This could mean that in alloys of such a composition there becomes apparent a tendency to phase separation. However, over the entire temperature range of the study, from the liquid state of this alloy to 550°C, only structures corresponding to the tendency to ordering were found experimentally.

This conclusion follows from which presents a bright-field image and an electron diffraction pattern obtained from a specimen as-quenched from the liquid (1450°C) state (figure 12).

Figure 12: Ni₄₀Cr₆₀ alloy. Quenching from the liquid state (1450°C). Bright-field image of the microstructure. Inset: electron diffraction pattern, [1-12] zone axis; orientation relationship: {112} M // {102}Cr₂Ni; super lattice reflections from variants (1), (4), (5) are given in orthorhombic indices; fundamental reflections are given in cubic indices.

The microstructure consists of relatively large grains of an elongated shape, randomly arranged in the solid solution. A dislocation network is visible along the boundaries of the grains. An electron diffraction pattern, obtained from these grains (Figure 12, inset), indicates that they have an orthorhombic lattice of the Pt₂Mo type, characteristic of the Ni₂Cr chemical compound. However, according to the conventional phase diagram of Ni-Cr, such a compound is formed only at temperatures below 590°C.

Figure 13: Ni₆₈Cr₃₂ alloy. Bright-field image of the microstructure after water-quenching from liquid state. Absorption contrast.

A similar structure of chromium atom clusters was observed in electron microscope images also after quenching the alloy from 1200, 1000°C and below. However, it was noticed that with a decrease in the temperature of heat treatment the number of clusters reduces and their contours become still more blurred [43]. At the same time, the Ni₂Cr phase in this alloy was not found at all.

Thus, experimental results have been obtained, indicating that the signs of the chemical interaction between component atoms in the Ni₄₀Cr₆₀ and Ni₆₈Cr₃₂ alloys are constant over the entire temperature range of their heating, only in the Ni₄₀Cr₆₀ alloy, this sign is negative and in the Ni₆₈Cr₃₂ alloy, it is positive [43]. This means that the boundary between the areas of ordering and phase separation in the phase diagram of Ni-Cr should be located between these two compositions and should to a greater extent depend on the change in the concentration than on the change in the temperature.

Figures 12-14 show the TEM results which allow to conclude that the signs of the chemical interaction between component atoms in the Ni₄₀Cr₆₀ and Ni₆₈Cr₃₂ alloys remain constant over the entire temperature range of their heating, only in the Ni₄₀Cr₆₀ alloy, this sign is negative (Figures 12,14) and in the Ni₆₈Cr₃₂ alloy, it is positive

Figure 14: Ni₄₀Cr₆₀ alloy. Aging at 550°C. Bright-field image of the microstructure; inset: electron diffraction pattern, [1-12] zone axis.

This means that the boundary between the Areas of ordering and phase separation in the phase diagram of Ni-Cr should be located between these two compositions, i.e. the position of the transition line in the Ni-Cr phase diagram to a greater extent depends on the change in the concentration than on the change in the temperature.

An electron microscopic study of the microstructure of the Ni₄₆Cr₅₄ (3), Ni₅₆Cr₄₄ (4) and Ni₆₂Cr₃₈ (5) alloys after heat treatment at different temperatures has been carried out in order to determine the line of the phase transition 'ordering-phase separation' in the Ni-Cr system [44]. The results have been compared with the data obtained previously for the Ni₄₀Cr₆₀ and Ni₆₈Cr₃₂ alloys. It has been found that, for example, in the Ni₆₂Cr₃₈ alloy- (Figure 16), the tendencies to ordering or phase separation are already manifested not in the whole temperature range of its heating. If, after quenching from the liquid state, clusters of chromium atoms are observed in the structure of the alloy (Figure 15), indicating the tendency to phase separation, then, at lowering the temperature of heat treatment to 1000°C, a

microstructure characteristic of the tendency to ordering (Figure 17) is already observed and, after aging at 550°C, again – the structure of phase separation.

Figure 15: $\text{Ni}_{62}\text{Cr}_{38}$ alloy. Bright-field image of the microstructure after water-quenching from liquid state. Absorption contrast.

Figure 16: $\text{Ni}_{62}\text{Cr}_{38}$ alloy. Bright-field image of the microstructure after heat treatment at 1000°C. Inset: electron diffraction pattern

Figure 17: Ni-Cr phase diagram. Compositions of alloys studied are pointed out in the diagram by the vertical lines and numerous. Symbols: $\square$ = ordering microstructure; $\circ$ = phase separation one.

A dashed line separating the points in the phase diagram, in which ordering structures and structures of phase separation had formed, was constructed in the diagram.

Such a dashed line can be regarded as the line of the phase transition 'ordering-phase separation'. As can be seen, its position in the diagram in a greater degree depends on the concentration of the alloy than on the heat-treatment temperature.

Ni_3V alloy

At present, few authors dispute the generally accepted opinion, that at 1045°C, the disordered Ni-V solid solution undergoes an ordering transformation to form a stoichiometric ordered Ni_3V phase [45-48]. The crystal structure of the ordered

Ni_3V phase consists of tetragonal D0_{22} unit cells. The correlation of the fcc and D0_{22} lattices allows the formation of three variants of unit cell packing, and in each of the variants, the c' axis of the phase lattice should be oriented along one of the three a -axes of the lattice of the disordered fcc solution [45]. It is believed that in the process of water quenching (the rate of cooling can reach about 10^5 °C/s) from high temperatures, this very three-variant long-range order forms in the Ni-25 at% V alloy. As it was shown in references [45,46], the kinetics of the ordering reaction in the stoichiometric $\text{Ni}_{75}\text{V}_{25}$ alloy is very fast and cannot be fully suppressed by brine quenching even in the "as-melt-spun" condition when quenching rates can achieve 10^5 °C/s. At the same time, many authors think that the long-range order D0_{22} structure is formed during the straight phase transition $\text{A1} \rightarrow \text{D0}_{22}$ which takes place during quenching the alloy in water when the alloy temperature passes through the point of 1045°C [45-48]. How such phase transition occurs and how the three-variant structure of the D0_{22} phase is formed within the crystal lattice of the A1 solid solution during such a short period is not explained in detail. During the phase transition $\text{A1} \rightarrow \text{D0}_{22}$, which is believed to take place at 1045 °C, the redistribution of V atoms on the lattice sites (from statistical to ordered state) can occur only by diffusion, which requires quite a definite time. Even more time is necessary to orient the unit cells of the D0_{22} phase so

that the χ^3 axes of the D0_{22} phase were located along each of the three mutually perpendicular axes of the disordered fcc solid solution. It is precisely this arrangement of the unit cells of the D0_{22} phase in the alloy that provides the formation of the three-variant ordered structure with a characteristic arrangement of extra reflections in the electron diffraction patterns. In this case, it should be noted that if the formation of the D0_{22} phase with the three-variant packing of unit cells occurred in the solid solution, it would necessarily lead to a growth of elastic stresses both inside the D0_{22} phase and inside the solid solution, which, in its turn, would be reflected in the electron diffraction pattern in the form of various distortions in the shape and arrangement of the reflections. As it is shown in References, no distortions of the kind are observed in the electron diffraction patterns [45-48].

As it has already been mentioned, it is believed that the $\text{A1} \rightarrow \text{D0}_{22}$ phase transition taking place at 1045°C cannot be suppressed by any of the quenching methods [45-48] although the cooling rate of, for example, thin specimens, even at conventional water quenching is very high and can approach to 10^5 °C /s. It is obvious, that at such a cooling rate, no diffusional phase transitions in $\text{Ni}_{75}\text{V}_{25}$ alloy have time to happen. This raises the question as to how during quenching from high temperatures (e.g., from 1200°C) atoms of vanadium manage to occupy the sites in the lattice, which lead to the transformation from fcc to D0_{22} at temperatures below 1045°C.

A reasonable answer to this question can only be obtained if one assumes that the formation of the three-variant D0_{22} structure takes place during slow cooling of the casting from the liquid state. It is in the liquid solution and at a temperature no lower than the solidus, that all conditions are present for unimpeded formation of the three-variant D0_{22} structure: in

Further prolonged aging, at 800°C for 180 h, leads to full disappearance of Ni_4V (D_{1a}) particles and, in some places, disappearance of the A1 solid solution. The electron diffraction pattern (Figure 21) demonstrates only a system of fundamental reflections from the $\text{D}_{0_{22}}$ phase. Thus, separation of the structure into the solid solution and the $\text{D}_{0_{22}}$ phase with the three-variant packing of cells, which takes place during solidification, leads to the fact, that in the process of relaxation, for example at 800°C, each of these structures evolves according to its own scenario: the three-variant microstructure of the $\text{D}_{0_{22}}$ phase gradually transforms into the one-variant structure, while the solid solution transforms into the equilibrium $\text{D}_{0_{22}}$ phase through precipitation of the metastable intermediate Ni_4V (D_{1a}) phase. As the end result, the Ni_3V ($\text{D}_{0_{22}}$) microstructure will be formed in the whole volume of the alloy [49].

Figure 21: $\text{Ni}_{75}\text{V}_{25}$ alloy water-quenched from 800°C for 180 h; electron diffraction pattern. $\text{D}_{0_{22}}$ phase.

Thus, the phase transition ordering-phase separation in the $\text{Ni}_{75}\text{V}_{25}$ alloy, at a change in its temperature, was not detected. Does this mean that in the Ni-V system, such a transition is absent? Apparently it does not, because in this system, there might appear the same situation as in the Ni-Cr system (if a component prevails in the composition of the alloy, then, in this alloy, at all heating temperatures there exists, for example, a tendency to ordering, if the other component dominates, then a tendency to phase separation takes place). Therefore, in this case it is necessary to conduct an additional study of an alloy, in the composition of which vanadium would prevail.

Fe-Ni system

Alloys of the Fe-Ni system play a very important role in modern engineering: iron dominated alloys (invar) have very low values of the linear expansion temperature coefficient; nickel dominated alloys (permalloys) are soft magnetic materials with a very high magnetic permeability. The vast majority of authors, who studied these alloys, explained the emergence of such properties in the Fe-Ni alloys by their structural features, in particular, the formation of a short-range and / or a long-range order, ordering, formation of a modulated structure, etc [50-52]. These conclusions were based on integral methods of microstructure research (X-ray diffraction, neutron diffraction, Mossbauer spectroscopy, study of changes in the physical properties of the alloys and the like). Direct local electron microscopic methods for studying the microstructure were used rather infrequently and the interpretation of the results, especially in terms of the short- and long-range order did not clarify the general picture of

the processes forming such structures, which, in its turn, made it impossible to link specific changes in the properties of alloys with specific changes in their microstructure.

The $\text{Fe}_{68}\text{Ni}_{32}$ and $\text{Fe}_{23}\text{Ni}_{77}$ alloys were investigated in [53]. Let us consider the results obtained for the first of them. After quenching in water from a temperature of 1300°C the microstructure shown in figure 22 is formed in many microscopic portions of the $\text{Fe}_{68}\text{Ni}_{32}$ alloy. Round dark spots with diffuse edges and sizes of the order of 0.1-0.2 μm are observed, as a result of the electron-microscopic absorption contrast from certain clusters. It is obvious that the formation of these clusters occurs without any significant elastic changes in the lattice, that is, changes that could lead to the appearance of the diffraction contrast. The cause for the formation of such clusters of nickel atoms becomes clear if the electron microscopic data is compared with the results obtained by the method of XPS [53]. Such a comparison leads to the conclusion that the formation of the microstructure shown in figure 22

Figure 22: $\text{Fe}_{68}\text{Ni}_{32}$ alloy. Water-quenching from 1300°C. Bright-field image of a microstructure

is a consequence of the fact that a tendency to phase separation exists in the alloy at 1300°C.

At lowering the heat treatment temperature to 740°C, the morphology of clusters in electron microscopic images changes. This seems to be associated with an increase of nickel concentration in nickel-enriched clusters.

Figure 23: $\text{Fe}_{68}\text{Ni}_{32}$ alloy aged at 800°C. Bright-field images of a microstructure.

(Figure 23) [53]. A microstructure very similar to a modulated structure is formed instead of round dark spots. The obtained structural results allow concluding that it is precisely such a fcc structure consisting of nickel-enriched and depleted modulations that is responsible for the high invar properties of

the alloy, when at a change of the temperature, lattice expansion in modulations of one kind occurs due to lattice compression in modulations of another kind [53].

At lowering the heat treatment temperature to 450°C, a system of additional reflections appears in the electron diffraction patterns (Figure 24),

Figure 24: Fe₂₃Ni₇₇ alloy. Electron diffraction pattern; zone axis is near $[001]_{A1'} (100)_{A1} // (100)_{L12}; [010]_{A1'} // [110]_{L12}$.

Evidencing the nucleation of highly-dispersed particles of a new L₁₂ phase (usually called the γ' -phase) on the {110} planes of the disordered matrix. This appearance of reflections alongside with almost complete absence of contrast from these particles made the authors assume that this occurs due to the fact that the crystal lattice of the particles of this phase is fully coherent with the lattice of the surrounding fcc solid solution [53]. So, it may be concluded that at temperatures below 500°C, highly-dispersed particles of the L₁₂ phase precipitate as a consequence of the tendency of these alloys to ordering.

Co₇₀Mo₃₀ alloy

The Co-Mo phase diagram has been created by the work of many researches. In the recent years a critical evaluation of the experimental data has been carried out and calculated phase diagrams using various thermodynamic models have been constructed [54, 55]. As was detected, the Co₇₀Mo₃₀ alloy has a sufficiently high hardness after any heat treatment. For example, hardness of the alloy after quenching from liquid state is about 850 HV, after quenching from 1200°C — 790 HV. Following 800°C aging up to 50 h gradually decreases hardness from 790 to 700 HV. It was considered that the high level of hardness after any heat treatment is attributable to the fact that the Co₃Mo (A3) chemical compound forming at temperatures below 1045°C strengthens the alloy either at the cost of its own high hardness (when most part of the matrix is transformed into Co₃Mo), or through distortion of the matrix structure due to precipitation of coherent fine-dispersed Co₃Mo phase particles on the slip planes [54,55].

The tendency toward phase separation revealed with the help of the XPS method allowed authors to conclude that at temperatures below the solidus, phase separation into Mo-enriched and Mo-depleted clusters takes place in the Co₇₀Mo₃₀ alloy [56]. Electron-microscopic study of the alloy in quenched state from temperatures 800, 1200 and 1300°C showed that in all of the cases, the microstructure of the alloy is the same and represents a uninterrupted periodic alternation of isolated

rounded light-color clusters (about 10-15 nm in diameter), separated by dark diffuse boundaries (Figure 25) [56].

Figure 25: Co₇₀Mo₃₀ alloy water-quenched from 1300°C. Bright-field micrograph.

This microstructure resembles an “unfinished” (lacking sharpness) cellular structure, and therefore, for short, it can be called a “quasi-cellular structure” [56]. The ratio of the total areas occupied by light rounded clusters and dark boundaries in the micrographs, which we estimate as 3:7, allowed authors to assume that the first are clusters enriched in Mo and the second are clusters enriched in Co [56]. This quasi-cellular structure is often superposed by strain contrast usually arising at allotropic and martensitic phase transitions. In the selected area electron-diffraction patterns obtained from such a structure, only the fundamental reflections are observed.

At quenching from the liquid state (1450°C) a solid solution structure without any trace of strain contrast is observed, with only stacking faults present [56]. The hardness of the alloy has high values (about 850 HV). This can mean that the phase transition α -Co $\rightarrow$ ϵ -Co is not the reason for the high hardness of the Co₇₀Mo₃₀ alloy. The reason seems to lie in the fact, that taking part in the formation of Mo-enriched clusters inside the α -Co lattice, the atoms of Mo, whose size is 7% larger than those of Co, significantly distort the lattice in the whole volume of the alloy. Such distortion of the lattice is also preserved at all temperatures below the solidus temperature. Apparently, it is the true cause of the high hardness of the investigated alloy. Thus, in alloys similar in composition to the investigated alloy, at lowering the temperature from the solidus, there occurs decomposition of the liquid solution into clusters strongly enriched in Mo and Co (a quasi-cellular structure is formed)[56].

Conclusions to paragraph 3

1. Since, according to thermodynamics, all solutions existing in nature are not ideal, then, for metal alloys, this postulate of thermodynamics can mean that a chemical interaction must always take place between dissimilar atoms constituting an alloy. Experimental results presented in the article have shown that such a chemical interaction in alloys exists at all temperatures studied, including the cases when the alloy is in the liquid state. The energy of such a chemical interaction depends on the alloy heating temperature in a complicated way, changing from positive to negative values, and for each binary system there exists such a dependence of its own.

2. Using the methods of TEM and XPS, it has been

discovered that metal alloys in binary systems have a surprising and still unexplained property of changing the sign of the energy of the chemical interaction between dissimilar atoms. Such a change of the sign, given the name “phase transition ordering-phase separation” occurs at a specific for each system temperature, and sometimes, at a change of the alloy composition. It has been experimentally shown that this transition occurs at the level of changes in the electronic structure of the alloy. The change of the sign of the chemical interaction energy subsequently leads to a change in the type of microstructures: if the alloy has a tendency to ordering, chemical compounds are formed in the microstructure, if it has a tendency to phase separation, then, clusters (or grains), are formed consisting mostly of atoms of one kind. At the phase transition point, the magnitude of the chemical interaction energy of the alloy passes through zero and, therefore, at temperatures neighboring this point, a structural state close to the disordered solid solution may be form.

3. The existence in the nature of such a phase transition means that all previous ideas about the decomposition of solid solutions (occurring due to a decrease in solubility with a decrease in the temperature), do not correspond to reality, and hence the phase diagrams constructed on the basis of such principles do not reflect the real picture of the processes of microstructure formation taking place in alloys. Therefore, the introduction of such a concept as the phase transition ‘ordering-phase separation’ is to completely change the principles that guide researchers in constructing phase diagrams. The method of TEM should become the main method for the study of the micro- and crystalline structure. It is necessary to begin such a reconstruction of phase diagrams with an experimental detection of the lines of phase transition ‘ordering-phase separation’ for each of the binary systems and plotting of these lines in corresponding phase diagrams. Taking into consideration the number of binary systems in nature, it is easy to guess how long such work can last.

4. It has been found that, in the result of holding the alloy at any temperature studied, there forms a microstructure specific for every of these temperatures, while the preceding microstructure is not inherited and disappears. This implies a very important conclusion, which allows significantly simplifying the technology of heat treatment and, therefore, reducing its cost. In fact, any quenching of any alloy, especially as performed from the so-called solid solution region in currently existing phase diagrams is absolutely useless, since the same structure, after the same tempering, is obtained without any preceding heat treatment including quenching.

Systems with a “blurred” phase transition ‘ordering-phase separation’

Ni-Co system

The results of the study of alloys of the Ni-Co system by the method of XPS have already been discussed in paragraph 2.2. It has been found that the temperature of the phase transition ordering –phase separation lies in the temperature range of 500-800°C [23]. For a more accurate determination of the transition

temperature the authors used the method of TEM [23].

Determination of the sign of the ordering energy was usually performed by the method of measuring the partial pressure of the vapors of components at temperatures close to the melting point of the alloy under study. Since at a decrease of the temperature this pressure abruptly drops, and, beginning with certain temperatures, it is impossible to measure it, then it was tacitly assumed that the sign of the ordering energy determined at very high temperatures remains the same at lower temperatures, as well. Thus, it was assumed that each binary system is characterized by its own sign of the ordering energy, which is constant for this system at any temperature. Other methods were also used, for example, measurement of the molar volume by the stationary droplet method. With the help of the latter method, for example, it was determined, that in the Ni_3Co liquid alloy, negative deviations of the partial molar volume from ideal mixing take place [57]. In another study, using the method of Knudsen cell mass spectrometry, they came to the conclusion that Ni-Co alloys are a regular solution with a slightly positive enthalpy of mixing [58].

It should be stressed that not in all systems the phase transition ‘ordering-phase separation’ leads to a clear division of the phase diagram into regions, in which microstructures of ordering, phase separation or a disordered solid solution are formed. For example, in the system of Ni-Co, after quenching from a temperature of 1200°C, a microstructure was detected which consists of circular light-color spots with diffuse edges and dimensions of the order of 0.1-0.2 μm located on a dark background (Figure 26) [23].

Figure 26: $\text{Ni}_{73}\text{Co}_{27}$ alloy. Microstructure after water-quenching from 1200°C. (Absorption contrast).

Such spots are observed due to electron microscopic Absorption contrast from clusters of atoms of the solute component, i.e. cobalt, which has a smaller “mass thickness” in comparison with the surrounding nickel-enriched solid solution. A similar structure is observed after exposure of the alloy at 1000 - 600°C [23]. After aging of the alloy at 500°C, one can observe certain microscopic sites of the foil, where both microstructures of ordering (bright particles of small size) and phase separation (dissolving round Co clusters) coexist at the same time (Figure 27), while the region of the disordered solid solution is completely absent [23].

Existence in one and the same image (Figure 27)

Figure 27: $\text{Ni}_{73}\text{Co}_{27}$ alloy. Microstructure after aging at 500°C for 10 h (absorption and diffraction contrasts).

of two different types of precipitates in which the signs of the chemical interaction energy are opposite, indicates that the phase transition 'ordering-phase separation' in alloys of this system does not occur simultaneously at all points of the alloy. Therefore, based on the obtained experimental results of TEM and XPS, in such alloys, one can evaluate not the temperature, but the range of the temperatures, in which the energy of chemical interaction changes its sign: such a range of temperatures in the system of Ni-Co is slightly above 600°C [23].

Co-V system

Another example, demonstrating a direct dependence of the microstructure upon the sign and the absolute magnitude of the chemical interaction energy (Figure 3) is the Co-V system. A structural study of the Co-18, 2% V alloy, heat-treated at 800°C for 168 and 553 hours, was conducted in [59]. The authors came to the conclusion that after both the periods of heat treatment, the crystal structure of the alloy was $\text{Co}_3\text{V}_{(112)}$.

Author has conducted a more detailed study on the example of Co_3V alloy [60]. Quenching of the alloy from the liquid state fixes the vanadium particles, the bright-field image of which is presented in figure 28.

Figure 28: Co_3V alloy. Water-quenching from liquid state. Bright-field image of the microstructure; inset: electron diffraction pattern, [111] zone axis.

It testifies to this the electron diffraction pattern, near the fundamental reflections, which correspond to the fcc lattice of Co, satellites appearing from these bcc of particles are visible (Figure 28, inset). Obviously, these precipitates are particles of a more refractory element - vanadium, which crystallize in the liquid solution due to the tendency to phase separation, which exists in the alloy at high temperatures [60].

At lowering the temperature of the alloy from 1550

to 1150°C, the absolute magnitude of the chemical interaction energy increases. This can be judged by an increase in the sizes or number of vanadium atom particles, formed at 1550 and at 1150°C. Figure 29 shows a colony of such particles after quenching from 1150°C. Its size is larger than the sizes of the particles formed at 1550°C. In the electron diffraction pattern obtained from such a colony, one can observe satellites belonging to the bcc lattice of vanadium (Figure 29, inset).

Figure 29: Co_3V alloy. Water-quenching from 1150°C. Bright-field images of the colonies of the particles; inset: electron diffraction pattern, [111] zone axis.

Further lowering of the heat treatment temperature to 800 °C leads to the fact that in various areas of the foil, it becomes possible to observe two different types of structures - formed as a result of the tendency to phase separation and formed as a result of the tendency to ordering. Precisely the same picture was demonstrated by alloys of the Ni-Co system after heat treatment at temperatures, at which the phase transition 'ordering-phase separation' took place in them (Figure 27) [23].

The bright-field image, obtained from one of the microscopic sites of the foil after heat treatment of the Co_3V alloy at 800 °C shows a microstructure consisting of very fine grains (Figure 30)

Figure 30: Co_3V alloy. Water-quenching from 800°C. Bright-field image of the phase separation microstructure and electron diffraction pattern, [001] zone axis (inset).

In the electron diffraction pattern obtained from such a structure, one can observe diffuse scattering (Figure 30, inset). Apparently, the dissolution stage of the phase-separation microstructure (i.e. dissolution of particles of vanadium atoms in the lattice of cobalt) is fixed in this microscopic site. Elsewhere in the microscopic sites of the foil, areas are observed where the microstructure of ordering is forming or has already formed. For example, Figure 31.

Figure 31: Co₃V alloy. Another microscopic site of the foil: Electron diffraction pattern, [001] zone axis.

shows an electron diffraction pattern, in which a system of extra-reflections, indicating precipitation of the L_{12} phase, is visible. However, in the bright-field image, particles of the new phase are not detected. It indicates that precipitates producing such reflections are fully coherent with the matrix.

It is obvious that the process of the phase transition 'ordering-phase separation' in the Co₃V alloy at 800°C does not occur simultaneously throughout the whole volume: in some microscopic sites of the foil, quenching has fixed a moment, when the microstructure of phase separation still remains in the alloy; in others, the moment when particles of bcc vanadium are still dissolving and the moment when particles of the Co₃V chemical compound with an L_{12} structure have already precipitated. This allows assuming that 800°C is the temperature close to the temperature of the phase transition 'ordering-phase separation'. Unlike the alloy, the regions of ordering and phase separation in many other systems are clearly demarcated, and, therefore, in them, quenching from the transition region, where the chemical interaction energy is close to zero, may lead to formation of the microstructure of a disordered solid solution. Further lowering of the heat treatment temperature to 500°C leads to the fact that the reflections from the L_{12} phase become more clear and intense, and in the bright-field image, it becomes possible to observe particles of the L_{12} phase.

If the alloy is subjected to heat treatment at 350°C, then, according to structural data, it becomes possible to detect one more phase transition ordering-phase separation taking place in the alloy at temperatures of about 450°C. Figure 32a shows a cellular structure, which has formed after heat treatment at 350°C. The sizes of the cells are substantially smaller than those after heat treatment at 800°C (Figure 30).

Figure 32: Co₃V alloy. Aging at 350°C. Bright-field image of the microstructure (a) and electron diffraction pattern, [001] zone axis (b).

A diffuse scattering is again observed in the electron diffraction pattern (Figure 32b), which is somewhat brighter than that in figure 30. Thus, at lowering the heat treatment temperature, two phase transitions are observed in the alloy: at 800°C, there occurs a transition phase separation-ordering; at 450°C - a transition ordering-phase separation.

Therefore, in the Co₃V alloy, the phase transition 'ordering-phase separation' occurs two times - at temperatures of about 800 and about 450°C. Above 800°C, a tendency to phase separation takes place in the alloy, which leads to the precipitation of bcc particles of vanadium atoms from the fcc solution. In the temperature range of 450 - 800°C, a tendency to ordering is displayed in the alloy, which results in precipitation of particles of the Co₃V chemical compound of the L_{12} type. At temperatures below 450°C, a honeycomb structure is formed in the alloy, as a consequence of the emergence of the tendency to phase separation [60].

Since the heat treatment temperatures at which the microstructure of alloys was studied in [23,35,40,53,56,60] were chosen using the existing phase diagrams, this choice was not systemic: in some cases it fell on states corresponding to well-formed microstructures of ordering or phase separation, while in some other cases we had to investigate the microstructure forming during the phase transition 'ordering-phase separation'. Therefore, now it is too early to draw general conclusions on whether the transition 'ordering-phase separation' occurs simultaneously over the whole volume of the alloy through the stage of formation of the disordered solid solution microstructure, as it was previously thought [23,40,53,56]. Or, such a transition does not occur simultaneously over the entire volume of the alloy and, at the moment of quenching the alloy, microstructures of one type are fixed in some microscopic sites of the foil, while in other sites microstructures of another type are fixed [23,60].

Chemical bond between atoms in terms of the electron theory of alloys

As is known, the fundamental properties of solids are determined by the nature of the chemical bond between the nearest neighbors.

The chemical bond is usually understood as a combination of all forces acting on each atom in the solid and keeping it in the state of equilibrium. Three main types of a strong chemical bond exist between atoms – the metallic, ionic and covalent bonds. It is believed that the metallic bond occurs in metals and metallic alloys, when the valence electrons are collectivized and form an electron gas ("an array of positive ions in a sea of electrons"). The ionic bond forms between atoms of species (usually, metals and non-metals), when atoms of one kind can transfer or share their valence electrons with atoms of another kind. This bond is characteristic for halides, alkalis, hydrides and other chemical compounds. The covalent bond forms between similar atoms of non-metals (no polar bond) and between dissimilar atoms of non-metals (polar bond) due to overlapping (collectivization) of a pair of valence electrons. These two electrons must, moreover, occupy two stable orbitals, one from each atom involved in the

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For metallic alloys, these understandings are not entirely consistent with what we observe experimentally. There is no doubt that in metallic alloys, as well as in pure metals, there is a metallic bond, but in contrast to pure metals, where this bond is the only possible, in metal alloys, alongside with this bond, there must be other types of bonds, as well. Otherwise, it is impossible to explain the presence, in the microstructure of alloys, of second phase particles. It is obvious that the chemical bond inside these particles is different from the metallic bond existing in the rest of the matrix. In alloys, in which the microstructure is a eutectic or structures similar to it, clusters of atoms of the solute component, for example, inside these precipitations a covalent bond should take place; in alloys, in which chemical compounds precipitate- in such compounds there should exist an ionic bond.

A detailed study of the type of chemical bonds existing in alloys at various temperatures of heat treatment was conducted in a series of electron microscopic studies, the reviews of them published in References [10,20]. It has been shown experimentally by the example of alloys of 17 binary systems that dissimilar atoms can participate in the formation of a chemical compound only if the sign of the chemical interaction energy is negative, i.e. when they attract each other [10,20]. If the sign of the chemical interaction energy between the dissimilar atoms is positive, then a phase separation takes place in the alloy and enriched clusters or grains consisting of solute atoms are formed. It has been shown that the alloys have the ability to change the sign of the energy of the chemical interaction at a change in the temperature of their heat treatment or in the composition of the alloy [10,20]. Such a change of the sign the chemical interaction energy has been given the name phase transition ‘ordering-phase separation.’

The fact of the discovery of the phase transition ‘ordering-phase separation’ has shown that it is not the degree of super saturation of the solid solution in alloying element that is the

driving force of the process of new phase precipitation in alloys. Such a driving force is chemical interactions between atoms, which always exist in alloys, but manifest themselves.

Differently at different temperatures. Two factors have a decisive influence -the sign and the absolute magnitude of the energy of the chemical interaction between dissimilar atoms [20]. The sign indicates which tendency is manifested in the alloy at this or that temperature - the tendency to ordering (minus), or the tendency to phase separation (plus). The absolute magnitude of this energy also plays a big role in whether there will or will not happen precipitation of these or those phases near the phase transition temperature [20]. It was believed that at the temperature of the phase transition ordering-phase separation, when the energy of the chemical interaction is close to zero, no other phases would form besides the solid solution. Therefore, it is precisely near the phase transition temperature that an alloy may have a disordered solid solution structure [10,20]. In more distant surroundings of the phase transition temperature, the absolute magnitude of the chemical interaction energy may be not high enough for precipitation of a new phase to start, and this fact can lead to expansion of the area in which the solid solution structure exists. Everything depends on the nature of the alloy. The latter may mean that near the phase transition line on the diagram there exists not a line but a range of temperatures within which a disordered solid solution structure is formed [20]. The latter may mean that near the phase transition does not exist in the graph line, but the temperature range in which the formed structure is a disordered solid solution [20].

The phase transition ‘ordering-phase separation’ occurs at a temperature, which is quite definite for each binary system. With the help of the method of X-ray photoelectron spectroscopy, it has been shown that this transition occurs at the level of changes in the electronic structure of alloys (the shape of the valence band at such a transition changes [23,35]). Using the results obtained by the method of transmission electron microscopy, it has been concluded that the change of the type of the alloy microstructure occurs at approximately the same temperature, at which the shape of the alloy valence band changes.

Such an interpretation of chemical bonds existing in alloys [10,20], gave rise to the following question: what is the energy of the chemical interaction and how does it correlate with the above mentioned views of chemistry on the types of chemical bonds. To answer this question, this article discusses the previously presented results of experimental studies of some alloys of transition metals, in which there occurs the phase transition ‘ordering-phase separation’. In light of these results, we also discuss the existing ideas about the types of chemical bonds in relation to metal alloys.

Analysis of the experimental data obtained from the microstructure study of alloys suggests that for alloys, the existing ideas about the chemical bond are not quite adequate to the experiment. If in pure metals, there actually exists only one type of the chemical bond – the metallic bond, then, adding to the metallic atoms of another component (including pure metal)

leads to appearance in such an alloy also of other types of the chemical bond - ionic and covalent. This can be concluded from the experimental results obtained by an electron microscopic study of the microstructure of various metallic alloys. According to these results, at certain temperatures, intermetallic compounds precipitate in the microstructure of such alloys. Formation of intermetallic compounds indicates that such a bond occurs when one or more pairs of valence electrons, which were to have taken part in formation of the electron gas, are found to be localized on two adjacent, dissimilar atoms, leading to formation of their common orbitals. At changing the heating temperature, in the microstructure of the same alloys, it is possible to observe dissolution of chemical compounds and precipitation of clusters or grains of atoms of the solute component. Such a formation of clusters or grains consisting of solute atoms which occurs in the place where there previously existed chemical compounds can only be due to the fact that in the alloys, the ionic component of the bond that existed between dissimilar atoms disappears and the covalent component is formed which occurs between the atoms of the solute element.

If we compare the understandings of the nature of the chemical bond in metallic alloys existing today in Physics and Chemistry, with the considered in this article results of a microstructure study, there arises a feeling that the subject of the discussion both in the first and in the second case is one and the same phenomenon, described with the help of different terminology. Indeed, the ionic component of the bond that takes place in an A(B) alloy between atoms of the solute component B and their nearest neighbors – atoms of the solvent A, manifests itself when (as it is believed in Materials Science) in the alloy, there comes into existence a tendency to ordering and the chemical compound $AmBn$ is formed.

The covalent component of the chemical bond manifests itself if two atoms of the solute component B, diffusing in the alloy, at some point in time, happen to be the nearest neighbors and, as a result of this momentary neighborhood, in them there occurs hybridization of the valence orbitals, that is, clusters are formed first of two atoms of B and then - from a greater number of pairs of atoms of B. Such a process of clustering is considered in Materials Science as occurring in alloys due to the tendency to phase separation. Therefore, it becomes clear that the tendency to ordering occurs due to the fact that in a metallic alloy, along with the metallic component, there exists the ionic component of the chemical bond between atoms of A and B, and the tendency to phase separation manifests itself due to the existence of the covalent component of the chemical bond between atoms of B along with the metallic component. It should be noted that the ionic and the covalent components can simultaneously co-exist only during the transition 'ordering - phase separation', that is, the transition « the ionic component of the bond ↔ the covalent component of the bond ». Thus, the phase transition 'ordering phase separation' includes two elementary acts: delocalization of the valence electrons on atoms of A and B, and hybridization of the valence electrons on atoms of B. This transition occurs due to the electron-phonon interaction: the collapse of a pair of

metallic atoms, between which for example, there has been an ionic bond, leads to emission of a phonon while the formation of a pair of metallic atoms with a covalent bond leads to absorption of a phonon. As for the transition 'phase separation-ordering' – it includes de-hybridization of the valence electrons on atoms of B and localization of the valence electrons on atoms of A and B. The existence of such an electronic transition may indicate that in the alloy, at a change in the temperature or concentration, the ionic component of the chemical bond between the atoms is replaced by the covalent component, and vice versa.

Conclusions to paragraph 5

1. Formation of chemical compounds in alloys occurs when there takes place a tendency to ordering determined as coexistence of the metallic and ionic components of the chemical bond.

2. Formation of phase separation microstructures (clusters, grains of the solute in the solid solution, or eutectics) occurs when there takes place a tendency to phase separation, determined as coexistence of the metallic and covalent components of the chemical bond.

3. The phase transition 'ordering-phase separation' that occurs at a change in the temperature of the alloy heat treatment or at a change in the concentration of the alloy is such a transition, in the process of which, the ionic component of the chemical bond between the atoms, due to the electron-phonon interaction, is replaced by the covalent component, or vice versa.

4. The attraction between dissimilar atoms, leading to formation of chemical compounds in alloys (tendency to ordering) and the attraction between similar atoms, which leads to formation of clusters of solute atoms (tendency to phase separation), can be adequately explained in terms of the electron theory of alloys. They can be considered as a result of, respectively, localization and hybridization some of the valence electrons in those local points of the alloy, where such particles are formed.

Practical Insights

Phase Diagrams

Creation of binary phase diagrams of a new generation should be guided by two principles which have already been mentioned above:

1. Chemical interactions between dissimilar atoms exist in the alloys at any temperature of heating. This is evidenced by at least the following facts: chemical compounds (formed as a result of the tendency towards ordering) and clusters (grains), consisting mainly of atoms of one component and formed as a result of the tendency towards phase separation are found in the microstructure after water-quenching not only from the solid state, but from liquid one as well.

2. A disordered solid solution is formed in alloys only in the temperature range where the energy of the chemical interaction is close to zero (i.e., at that temperature at which

phase transition 'ordering-phase separation' occurs).

The work on the reform of phase diagrams should start with determining the temperature of the phase transition 'ordering-phase separation'. In order to determine the temperature of transition in a binary system AB it is necessary to conduct a study on at least two alloys, whose compositions correspond approximately to the A_2B and AB_2 compositions in the A-B phase diagram. This temperature can be determined by two methods - TEM and XPS. The first of these is more affordable. The second requires that an XPS spectrometer should be provided with a furnace to heat the samples. Prior to the study by TEM, the samples are heat-treated at various temperatures (at the discretion of the researcher).

If in an alloy heat-treated at any two temperatures, dramatically different types of the microstructure are found, it means that the temperature of the transition 'ordering-phase separation' may be located between these two temperatures. Subsequently, this transition temperature can be refined by additional experiments conducted at temperatures lying within the test interval. The same procedure for the detection of the transition temperature should be held with the second alloy, as well. If in both the alloys, these two temperatures vary in the range of $\pm 50^\circ\text{C}$, then this is the temperature of the phase transition "ordering-phase separation" for the whole system. If the transition temperatures of these two alloys are found to be located outside this range, then the task of determining the transition temperature for the entire system is substantially complicated. In this case, we can assume that the phase transition 'ordering-phase separation' occurs in such a system not only with a change of the temperature but also with a change in the composition of alloys. In this case, the research should be continued by the procedure proposed for the Ni-Cr system, which has been discussed above (3.3) [43,44]. From the above discussion, it follows that introduction of such a concept as the phase transition 'ordering-phase separation' into common use changes our previous understanding of the driving forces of the process of new phase formation. It becomes apparent that in order to change this situation, more work is needed to modernize the existing phase diagrams. Such modernization should take into account the existence of the phase transition 'ordering-phase separation' in alloys and it should be carried out using a local analysis method - the method of TEM [61].

Chemical interactions between dissimilar atoms, existing in alloys at all temperatures of heating and also the property of alloys to change the sign of the chemical interaction with a change in the temperature and / or concentration have led to a revision of our understanding of the principles of phase diagram construction and the conditions of formation of these or those microstructures. In this article, we have given strong evidence of the fact that the actual microstructure of alloys rarely coincides with that indicated in the existing phase diagrams. Absolutely trustworthy are only those lines in the phase diagrams that separate the regions where massive phase transitions (polymorphic, magnetic, ferroelectric, and others) occur. The lines in the phase diagrams, separating regions of different

microstructures formed as a result of diffusion are correct only in some cases, where such structures (eutectics, eutectoids, and particles of chemical compounds) are fairly coarse, so that they can be reliably detected by the XRD method. In other cases, especially when in the phase diagrams the regions of "solid solutions" are indicated, it is necessary to use the TEM method to identify the actual microstructure in these regions.

Heat treatment

Heat treatment of alloys came into usage long before the scientific foundations had been laid, explaining the nature of thermal effects on the structure and properties of alloys. The theory of heat treatment was developed in the early twentieth century with regard to steel and then to all other alloys. It was based on one simple thesis borrowed from the theory of water solutions: the higher is the heating temperature of the alloy, the higher is the solubility of the alloying component in the lattice of the solvent. Therefore, they thought that it was necessary to first transfer the alloy into the equilibrium state by heating it to a temperature at which atoms of the alloying component would have been statistically unevenly dissolved in the lattice of the solvent and then to fix this state by quenching. Such a solution, after quenching, became "supersaturated" by the alloying component. Exposure at tempering temperatures, by analogy with water solutions, led to precipitation of particles of an "excess" phase, determining these or those properties of alloys. On the basis of these ideas, they believed that performing quenching before tempering was obligatory, as it was precisely the operation that led to formation of a solid solution supersaturated by the alloying element and it was precisely such a super saturation that was the main driving force of the decomposition of alloys during tempering.

The conclusion that the solid-solution regions in equilibrium phase diagrams are in fact two-phase regions agrees with the well-known axiom of thermodynamics that in nature all solutions are no ideal and have either positive or negative deviations from Raoult's law. This can lead to decomposition of such solutions and the higher is the temperature of heating (i.e., the higher is the diffusion mobility of atoms), the faster is the decomposition. If the regions in the phase diagram, which are now referred to as regions of solid solutions are in fact two-phase regions, then quenching in water from such a region will also lead to fixation of a two-phase structure, not a solid solution at all. This means that the purpose of quenching from high temperatures - receiving a structure of a disordered solid solution - will not be achieved. On the basis of the experimental data above (paragraphs 3 and 4) it can be concluded that particles of the new phase formed during aging, are formed precisely at the temperature of aging and have no connection with particles fixed by quenching. Thus, there is no point in quenching to obtain a microstructure, which disappears leaving no traces after carrying out a subsequent aging and hence has no any effect on aging microstructure.

A completely different approach to the heat treatment of alloys is proposed, which became possible after the experimental

discovery of the phase transition 'ordering-phase separation' in alloys. This approach is based on the following postulates [19]:

1. The sign of the energy of the chemical interaction between dissimilar atoms is not a constant for most of systems but varies with the change of the temperature of heat treatment (sometimes more than once).
2. Each temperature of heat treatment leads to formation of its own characteristic microstructure that is formed after, or at the same time with the dissolution of the preceding microstructure.
3. The structure of a disordered solid solution can be obtained by quenching in water from the temperature region adjacent to the temperature of the phase transition 'ordering-phase separation', because it is in this region that the chemical interaction energy is close to zero.
4. Quenching of alloys from the so-called region of the solid solution, which is usually performed before tempering (aging) is a totally unnecessary and useless operation that does not in any way affect the final structure of the alloy forming later at the temperature of tempering (aging).

Phase transition 'ordering-phase separation' in multi-component alloys

All of the above in sections 1-4 about the phase transition 'ordering-phase separation' refers to binary alloys. An increase in the number of alloy components leads to a corresponding increase in the number of possible couples of dissimilar atoms (which in Reference 61 were called 'diffusion couples'). In the framework of the pair wise interaction model, it seems reasonable to consider the diffusion processes in the ternary alloy ABC as occurring in three diffusion couples A/B, A/C and B/C. As will be seen from the following experimental results, such an approach was quite justified [61]. It should also be assumed that phase transitions of the 'ordering-phase separation' type, taking place in the respective binary alloys of the systems A-B, A-C and B-C, in the ternary alloy ABC manifest themselves similarly in each of its diffusion couples A/B, A/C and B/C [61]. It is obvious, that the probability of occurrence of these or those structural transformations depends not only on the sign of the chemical interaction energy in each diffusion couple of the ternary alloy, but also on the absolute magnitudes of this energy between the dissimilar atoms at different temperatures[61].

Ni₇₅Mo₂₀Al₅ alloy

Comparing the results obtained by the method of X-ray photoelectron spectroscopy with the results obtained by transmission electron microscopy, authors came to the conclusion that in alloys of the Ni-Mo system, after quenching from the liquid state, the diffraction maxima at positions $\{1 \frac{1}{2} 0\}$ in the electron diffraction patterns (Figure 8) appear only when, according to XPS, a tendency to phase separation takes place [35]. At lowering the temperature of the heat treatment below 1200°C, when in alloys of the Ni-Mo system (according to XPS data) the tendency to phase separation is replaced by the tendency to ordering, the

diffraction maxima at positions $\{1 \frac{1}{2} 0\}$ in the electron diffraction patterns received from most areas of the alloy, disappear. Instead of them, a system of reflections is formed, which may be identified as the result of the formation of these or those Ni_xMo_y chemical compounds. Such abrupt changes detected simultaneously by the methods of XPS and TEM indicate that in Ni-Mo alloys, in the temperature range of 1200 -1300 °C, there occurs phase transition 'ordering-phase separation' [35].

A similar phase transition "ordering-phase separation" has been discovered at the same temperature in the Ni₈₈Al₁₂ alloy, as well [40]. After heat treatment at 1300°C, diffuse satellites were observed in the electron diffraction patterns, in the vicinity of the fundamental reflections of the matrix (Figure 10), indicating the formation of two solid solutions - enriched and depleted in aluminum, that is, indicating that in the alloy there exists a tendency to phase separation. At the same time, the diffraction maxima at positions $\{1 \frac{1}{2} 0\}$ were also observed in the electron diffraction patterns (actually, they are less intense than in the Ni₈₈Al₁₂ alloy), which, as already noted, points to a tendency to phase separation. Heat treatment at 1200°C resulted in the disappearance of all indications of phase separation in the electron diffraction patterns and appearance of reflections from the Ni₃Al (L₁₂) phase [40].

Phase transformations occurring during heat treatment of ternary Ni-Mo-Al alloys are characterized by the presence of interesting and sometimes difficult to explain peculiarities of the precipitation of coherent phases, which to some extent are the cause of fine mechanical properties of these alloys at high temperatures. It is for that reason that such alloys have been the subject of numerous experimental and theoretical studies over the past few years. The foundation of all the works on this subject has been the concept, that in such alloys, short-range order in the arrangement of atoms of different elements evolves into long-range order. Using the terminology of electron microscopy, this meant that short-range order which is characterized by appearance of diffraction maxima in electron diffraction patterns at positions $\{1 \frac{1}{2} 0\}$, transforms into long-range order (i.e., in Ni-Mo alloys, for example, Ni₄Mo (D1₄), Ni₃Mo (D0₂₂) or Ni₂Mo (Pt₂Mo) "superstructures" are formed[35]). Yet, the system of diffraction maxima of the short-range order $\{1 \frac{1}{2} 0\}$ has almost no coincidences with the systems of reflections from the above-mentioned superstructures. From this it follows, that the diffraction maxima at positions $\{1 \frac{1}{2} 0\}$ cannot be regarded as a consequence of the fact that some short-range order appears in the alloys, which later transforms into long-range order. However, in the majority of published works, for example, in references 4,31-34,62-64, regardless of experimental facts, the diffraction maxima at positions $\{1 \frac{1}{2} 0\}$ in the electron diffraction patterns are interpreted as a structural state of short-range order.

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Ternary alloys of Ni-Mo-Al have also been studied by some authors. For example, Sano and Nemoto have studied 15 compositions of alloys of the Ni - Mo - Al system [65]. In addition to stable Ni_3Al (L_{12}) and Ni_3Mo ($\text{D}_{0_{22}}$) phases, several metastable phases, such as Ni_4Mo (D_{1_3}), Ni_2Mo (Pt_2Mo) and a short-range order state have been found. The authors assumed that the metastable phases play an important role in strengthening these alloys [65]. In the Ni-25 at% Mo-5 at.% Al alloy, Kulkarni and Dey have discovered and described in sufficient detail the coherent σ -Ni-Mo phase with H-phase plates in the form of wedge-shaped domains located between the grains of the phase [66]. It was believed that the σ -phase is the cause of degradation of mechanical properties of Ni-Al based alloys.

Currently, two opposing tendencies have taken shape in the development of new superalloys and improvement of existing ones: a tendency to increase the number of “refractory” elements X in Ni-M-X superalloys, and a tendency to simplify the composition of superalloys. On the one hand, they believe that when you add a certain number of “refractory” elements X (Ti, Nb, etc.) to binary Ni-M alloys (where M - Mo, V, Al and other similar elements), the number of coherent intermetallic phases in the alloy increases, which should lead to an even greater increase of the heat resistance of alloys. On the other hand, complication of the chemical and, consequently, the phase composition is known to lead to an increase in the imperfection of the microstructure, which may cause an opposite effect - a lowering of the high temperature strength of superalloys.

Diffusion processes in the $\text{Ni}_{75}\text{Mo}_{20}\text{Al}_5$ alloy were considered as occurring in three diffusion couples - Ni/Mo, Ni/Al and Mo/Al [61]. It was supposed that the phase transitions taking place in the Ni/Mo and Ni/Al diffusion couples are similar to phase transitions in Ni-Mo and Ni-Al binary alloys, which have already been investigated in references 35 and 40, respectively.

The electron diffraction pattern obtained from the $\text{Ni}_{75}\text{Mo}_{20}\text{Al}_5$ alloy after quenching it in water from the liquid state (1500°C) is shown in figure 33.

In the electron diffraction pattern one can see a system of diffraction maxima at positions $\{1 \frac{1}{2} 0\}$. These diffraction maxima are quite weak in intensity and are visible only near the zero reflection. A similar system of diffraction maxima of higher intensity and in the whole area of the electron diffraction pattern was already discussed earlier. This fact, in combination with the results of X-ray photoelectron spectroscopy, allowed the authors to come to the conclusion that in these alloys, phase separation takes place already in the liquid state and crystalline particles

consisting mainly of Mo atoms are formed in the liquid solution [35].

Figure 33: [18] $\text{Ni}_{75}\text{Mo}_{20}\text{Al}_5$ alloy. Quenching from liquid state: electron diffraction pattern.

In the electron diffraction pattern one can see a system of diffraction maxima at positions $\{1 \frac{1}{2} 0\}$. These diffraction maxima are quite weak in intensity and are visible only near the zero reflection. A similar system of diffraction maxima of higher intensity and in the whole area of the electron diffraction pattern was already discussed earlier. This fact, in combination with the results of X-ray photoelectron spectroscopy, allowed the authors to come to the conclusion that in these alloys, phase separation takes place already in the liquid state and crystalline particles consisting mainly of Mo atoms are formed in the liquid solution [35].

Figure 34: $\text{Ni}_{75}\text{Mo}_{20}\text{Al}_5$ alloy. Quenching from 1300°C for 1 h: bright-field image of microstructure; inset: electron diffraction pattern.

Quenching of the alloy after heat treatment at 1300°C shows that in addition to the diffraction maxima in positions $\{1 \frac{1}{2} 0\}$, weak satellites appear near the fundamental reflections $\{200\}$ in the electron diffraction pattern. Similar satellites, but of a higher intensity, have been found in the Ni-12% Al binary alloy after a similar heat treatment (Figure 10) [40].

The presence of the satellites in the electron diffraction pattern gave the authors [40] an opportunity to suppose that in the Ni-12% Al binary alloy, at high (1300°C) temperatures, there occurs a phase separation of the solid solution into clusters enriched and depleted in aluminum. Therefore, satellites in the electron diffraction pattern of the alloy may also be interpreted as the result of phase separation in the Ni-Al diffusion couple.

It is worthy of note that diffraction maxima at positions $\{1 \frac{1}{2} 0\}$, observed in alloys of the Ni-Mo and Ni-Al systems after high-temperature quenching, are formed only when a tendency to phase separation takes place in these alloys [35, 40]. Here, the

authors noted one more condition of no small importance, under which the occurrence of such maxima at positions $\{1 \frac{1}{2} 0\}$ is possible - phase separation should occur at such a temperature when one of the separating phases is in the liquid (or quasi-liquid) state [61]. For example, if in the alloys of the Ni-Mo system such a phase is the liquid solution, in which, at a decrease of the temperature, crystalline particles of molybdenum precipitate as a consequence of the existence in the alloy of the tendency to phase separation, then, in the alloys of the Ni-Al system, in which at temperatures of about 1300°C, clusters of aluminum atoms are formed due to the same reason, these clusters, as it can be assumed, should be in some kind of quasi-liquid state in view of the low melting point of aluminum [35,40].

The Mo/Al concentration ratio in the $\text{Ni}_{75}\text{Mo}_{20}\text{Al}_5$ alloy is 4:1, which is quite close to the 3:1 ratio of these elements in the Mo_3Al chemical compound. Therefore, it can be assumed that the composition of the alloy allows the formation of particles of such phases at certain temperatures. In the Mo-Al system, the Mo_3Al phase begins to form at temperatures of about 2150 °C [66]. So, it is possible to expect that in the $\text{Ni}_{75}\text{Mo}_{20}\text{Al}_5$ alloy, at temperatures above the liquidus, not only crystalline clusters of Mo atoms (formed as a result of the tendency to phase separation in the Ni / Mo diffusion couple), but also Mo_3Al phase particles (formed as a result of the tendency to ordering in the Mo / Al diffusion couple) are present [61]. As soon as the temperature of the alloy lowers to the temperature of the phase transition 'ordering-phase separation' (1200 - 1300°C), the Mo enriched and Al enriched clusters in the Ni / Mo and Ni / Al diffusion couples begin to dissolve.

Diffusing from these clusters into the solid solution, atoms of Mo and Al form colonies of rather large disk-shaped precipitates of the Mo_3Al phase (Figure 34). An electron diffraction pattern, obtained from such colonies, is shown in figure 34 (inset).

When measuring the lattice parameter of this phase ($a = 0.495 \text{ nm}$) from the electron diffraction pattern, it was found that it is identical to the lattice parameter of the Mo_3Al phase which has a cubic lattice of the Al_5 type. It should be emphasized that after quenching the alloy from 1300°C and above, such colonies were not found [61].

Since in the couple Mo/Al the tendency to ordering exists at very high temperatures and particles with the crystal lattice of the Mo_3Al phase are not found after quenching from 1300°C, it can be assumed that the formation of the lattice of this phase is hindered not so much by the high diffusion mobility of atoms at such temperatures as by the tendency to phase separation in the Ni / Mo and Ni / Al diffusion couples.

The internal structure of such a Mo_3Al crystal particle is shown in figure 35, the electron diffraction pattern - in figure 35 (inset).

Figure 35: $\text{Ni}_{75}\text{Mo}_{20}\text{Al}_5$ alloy. Internal structure of α massive particle of the Mo_3Al phase: bright-field image. Inset: electron diffraction pattern, $[001]\text{Al} // [112]\text{Al}_5$.

Figure 36: $\text{Ni}_{75}\text{Mo}_{20}\text{Al}_5$ alloy. Phase Ni_3Al (L_{12}) formed at 800°C for 24 h. Inset: electron diffraction pattern; $[112]\text{Al} // [001]\text{Ni}_3\text{Al}$.

Interpretation of the electron diffraction pattern allowed coming to the conclusion, that they are precipitates of the Ni_3Al (L_{12}) phase. It is surprising, that, after a heat treatment at same temperatures, it becomes possible to find chemical compounds of aluminum and molybdenum in some microscopic sites of the foil alongside with formation of aluminum/nickel compounds in other microscopic sites. This phenomenon can only be explained if it is assumed that the crystalline particles of molybdenum are irregularly distributed in the liquid solution over the volume of the alloy.

After the heat treatment of the alloy in the temperature range of 600 - 800°C, in some microscopic sites of the foil one can observe a microstructure consisting of highly dispersed particles (Figure 37); the electron diffraction pattern taken from the micrograph is shown in figure 37 (inset).

Figure 37: $\text{Ni}_{75}\text{Mo}_{20}\text{Al}_5$ alloy. Prolonged (300 h) aging at 600°C: bright-field image of microstructure. Inset: electron diffraction pattern; zone axis is near to $[001]\text{Al}$.

The author [61] identified this system of extra-reflections as appearing from particles of two phases - Ni_3Mo (D0_{22}) and Ni_3Al (L_{12}).

Reasoning from general concepts of the influence of the dispersity of precipitating phases on the strength properties of alloys, one could suppose that massive particles of such phases as Mo_3Al and Ni_3Al , precipitating at high temperatures, have a negative effect on the high-temperature strength of the alloy. It is possible; however, that these precipitates do not affect the high-temperature strength of the alloy, because their lattices are coherent to the lattice of Ni-Mo-Al superalloys' matrix. However, in any case, one should not be tempted by the development of new superalloys by means of adding still more various "refractory" elements until it is experimentally proved that the high-temperature strength and durability of superalloys with such additives do not deteriorate due to precipitation of, for example, colonies of Mo Al phase particles and massive particles of the Ni_3Al phase at high temperatures.

The presented experimental data and their interpretation lead to the conclusion that introduction of Al into superalloys of the Ni-Mo system has a negative effect on the heat resistance of the alloy at high temperatures, since at a temperature of 1200°C and somewhat below, aluminum takes part in the formation of coarse Ni_3Al phase particles and colonies consisting of disk-shaped particles of the Mo_3Al chemical compound.

$\text{Ni}_{75}\text{V}_{20}\text{Al}_5$ alloy

It is considered that aluminum, when it added to the alloys of the Ni-V system, like in the case with alloys of the Ni-Mo system, improves the heat-resistant properties of these alloys. They believe that it is precisely the combination of the Ni_3Al and Ni_3V phases formed in the structure of the A1 solid solution as a result of a low-temperature eutectoid decomposition that can improve the heat resistance of alloys [67-70]. In this case they think that the low-temperature eutectoid decomposition structure will remain at high temperatures as well, because of "low atomic diffusivity owing to its close packed structure" [69]. However, this point of view does not fully agree with practice. In fact, if the formation of the microstructure which provides the high heat resistance of Ni-V-Al superalloys occurred during low-temperature eutectoid decomposition, then, heating of turbine blades under operating conditions to temperatures higher than the temperature of the eutectoid decomposition would lead to a back reaction, and, as a consequence, to loss of high-temperature properties of superalloys, much earlier than it usually happens in practice.

Assuming that in ternary alloys of the Ni-V-Al system the phase transition $\text{A1} \rightarrow \text{D0}_{22}$ happens at 1045 °C, the heat treatment of such alloys in reference 68,69 was performed by the following scheme: quenching from 1100°C into water (the structure after such a heat treatment was considered to be a solid solution) and subsequent aging at 1000°C of various durations up to 840 h (the authors believed it to be the structure of the eutectoid decomposition). It was expected that such a heat treatment will allow exploring the evolution of the microstructure during the phase

transition $\text{A1} \rightarrow \text{D0}_{22}$. They came to the conclusion that the process of alloy decomposition is invariably associated with ordering of two different phases - Ni_3Al (L_{12}) and Ni_3V (D0_{22}) and the mechanism of such decomposition is not a pearlitic type [67]. It is obvious, that introduction of aluminum into Ni-V alloys should lead to the fact that chemical interactions in the newly emerging Ni-Al and V-Al diffusion couples are added to the chemical interaction between the atoms of nickel and vanadium in the Ni/V pair.

To determine what influence on the structure and hence the heat-resistance of superalloys of the Ni-V system is produced by addition of aluminum to their composition, a structural study of the $\text{Ni}_{75}\text{V}_{20}\text{Al}_5$ alloy was carried out using the method of TEM [49]. Since in this alloy the concentration of aluminum is not very high, the main process of microstructure formation proceeding in it at temperature changes occurs in the Ni-V diffusion couple. However, the Ni-Al diffusion couple also introduces significant corrections.

Figure 38 presents the microstructure after quenching the $\text{Ni}_{75}\text{V}_{20}\text{Al}_5$ alloy from the liquid state (1500°C). In the micrograph one can observe particles of precipitates, which have a light contrast. The electron diffraction pattern obtained from these particles exhibits extra-reflections in the vicinity of the fundamental ones (Figure 38, inset).

Figure 38: $\text{Ni}_{75}\text{V}_{20}\text{Al}_5$ alloy. Quenching from liquid state (1500°C): bright-field micrograph. Inset: electron diffraction pattern

Since the precipitates presented in Figure 38 are fixed by quenching the alloy from the liquid state, it follows that they exist already in the liquid state, i.e. at 1500°C. It is quite reasonable to consider these particles as clusters of atoms of pure aluminum, forming already in the liquid state of the alloy. The cause of the formation of such clusters may be only a tendency of Ni and Al atoms to phase separation, which was previously found in the binary $\text{Ni}_{88}\text{Al}_{12}$ alloy at high temperatures (above 1200°C) [40]. Apparently, a similar chemical interaction takes place in the Ni/Al diffusion couple of the $\text{Ni}_{75}\text{V}_{20}\text{Al}_5$ alloy, as well. Above this temperature, the aluminum in the alloy is in the form of aluminum-rich liquid or quasi-liquid clusters [40].

At the same time, if aluminum is not introduced into alloys of the Ni-V system, then, evaluation of the maximum working temperature of Ni-V superalloys can be oriented not on the temperature of the phase transition 'ordering-phase separation' in the Ni-Al diffusion couple, but on the solidus temperature. Figure 39 shows a lamellar-like microstructure consisting of dark and light fine grains. The specimen was aged at 800°C for 180 h. The microstructure is rather similar to the microstructure forming as a result of eutectoid decomposition of various alloys. Therefore, it

is not surprising, that the discovery of such a microstructure led the authors studying Ni-V-Al alloys to the conclusion about the eutectoid decomposition of the solid solution in these alloys and the leading role of the eutectoid decomposition at temperatures below 1045°C in increasing heat resistance of alloys [69,70]. Now that we have shown that grains of the Ni_3V (D_{022}) phase (dark contrast in figure 39) and grains of the Ni_3Al (L_{12}) phase (bright contrast in figure 39)

Figure 39: $\text{Ni}_{75}\text{V}_{20}\text{Al}_5$ alloy. 800°C aging for 180 h: bright-field micrograph

are formed in different temperature ranges (the first - during the solidification of the alloy, the second - as a consequence of the phase transition 'ordering-phase separation' in the Ni-Al diffusion couple), the hypothesis of the eutectoid decomposition of the Ni-V-Al solid solution should be abandoned.

So, introduction of low-melt aluminum into Ni-V superalloys lowers the heat resistance of such alloys, because above 1200°C, in the Ni-Al diffusion couple, a phase transition ordering-phase separation takes place which leads to the formation of aluminum clusters existing at these temperatures in the quasi-liquid state [49].

Model $\text{Ni}_{50}\text{Co}_{25}\text{Mo}_{25}$ alloy

As already mentioned in paragraph 7.1, investigating the ternary $\text{Ni}_{75}\text{Mo}_{20}\text{Al}_5$ alloy by the method of TEM, the author had found a very interesting fact: In various microscopic sites of the foil, differing chemical compounds (or clusters of atoms of the components) are registered, which can be considered as the result of a chemical interaction between the atoms within this or that couple of Ni/Mo, Ni/Al and Mo/Al [61]. Perhaps such peculiarities of phase formation in multicomponent alloys were previously observed and published by other researchers; however, we failed to find such information in the literature. On the contrary, in the literature there prevail ideas that in multi-component alloys, superalloys in particular, multi-component chemical compounds are formed. As mentioned above, the authors [23,35,56] considered phase transitions taking place in these diffusion couples as occurring similarly to phase transitions in the corresponding binary alloys of the Ni-Mo, Ni-Co and Mo-Co systems [71]. Phase transitions in the binary alloys of the Ni-Mo, Ni-Co and Mo-Co systems have already been discussed in paragraphs 3.1, 3.6 and 4.1.

Although the phase transition 'ordering-phase separation' was found in alloys of all three binary systems (Ni-Mo, Ni-Co

and Co-Mo), however, the temperature of the transition in these systems was different and this fact should be taken into account in the analysis of the structural changes in the alloy. In the Ni/Mo diffusion couple, this temperature is close to 1250°C, in the Ni/Co couple - to 600°C [23,35] (in both cases, ordering is observed below these temperatures), whereas in the couple of Co/Mo, such a transition occurs at a temperature close to the solidus, below which a tendency to phase separation takes place [56]. The scheme shown in figure 40.

Figure 40: $\text{Ni}_{50}\text{Co}_{25}\text{Mo}_{25}$ alloy. Scheme illustrating the signs of the chemical interaction and temperatures of phase transition 'ordering-phase separation' in each of the diffusion couples.

provides a visual representation of the changes occurring with the signs of the chemical interaction energy and temperatures of the phase transition 'ordering-phase separation' in all three diffusion couples existing in the $\text{Ni}_{50}\text{Co}_{25}\text{Mo}_{25}$ alloy [71].

After quenching from the liquid state, in different microscopic sites of the foil, different microstructures can be observed. For example, figure 41 shows round light-color spots observed due to electron microscopic absorption contrast from clusters of cobalt atoms. The conclusion, that they are clusters of precisely cobalt atoms was made here on the basis of the fact that absolutely the same structure was observed in the Ni_3Co binary alloy after heat treatment at 1200°C (Figure 41, inset) [23].

Figure 41: $\text{Ni}_{50}\text{Co}_{25}\text{Mo}_{25}$ alloy. Water-quenching from the liquid state. Microstructure. Inset: Ni_3Co alloy [23]. Water-quenching from 1250°C

As indicated above, the formation of such clusters occurs without any drastic differences in the lattice parameter of the clusters and the matrix, which could lead to the appearance of diffraction contrast in the bright-field image.

At other microscopic sites of the same foil, a microstructure was observed, where stacking faults alternated with defect-free microscopic sites of the matrix (the so-called "isolated" stacking faults [72]) (Figure 42a). Such alternation can be regarded as phase separation of the solid solution into clusters

Ni₆₅Mo₂₀Cr₁₅ alloy

The group of nickel-based alloys having high corrosion resistance and containing in its composition molybdenum and chromium has long been known under the common name of "Hastelloy". These alloys have different compositions but almost always contain Mo and Cr as alloying elements. The main advantage of these alloys is their effective work in the condition of contact with aggressive media at high pressures and temperatures. All properties of these Hastelloy alloys have been sufficiently well studied, but the microstructural aspects of the formation of these properties are still not fully cleared up. It is believed that particles of the ordered L_{12} phase (γ' - phase) formed in the temperature range of 600 - 700°C, are the primary strengthening phase in these alloys and the chemical composition of this phase corresponds to $Ni_3(Mo, Cr)$ [73]. In other works, for example in reference 74 it is supposed that the main strengthening effect in these alloys occurs when the ordered $Ni_2(Mo, Cr)$ phase of the Pt_2Mo type, with average particle size of about 10 nm, precipitates.

The diffusion processes in the $Ni_{65}Mo_{20}Cr_{15}$ alloy were considered as occurring in three diffusion couples - Ni/Mo, Ni/Cr and Mo/Cr. It was believed that phase transitions taking place in these diffusion couples occur similarly to phase transitions in the corresponding binary alloys of the Ni-Mo, Ni-Cr and Mo-Cr systems [75]. The question as to what diffusion processes occur in binary alloys of the Ni-Mo system was considered in the previous sections.

To estimate what the interatomic chemical interactions in the diffusion couple of Cr/Mo are, one can use the results, on the basis of which the Cr-Mo phase diagram has been constructed [11]. This diagram shows a continuous series of solid solutions at temperatures above 890°C, and a region of phase separation - below this temperature [11]. However, a thermodynamic study of the alloys of this system at high temperatures showed that a tendency to phase separation also appears at temperatures significantly above 890°C. For example, positive deviations from Raoult's law were detected in the alloys of this system, in the liquid (1600°C) state, by measuring the partial vapor pressure above the sample surface [76]. A comparison of the data obtained in the study of alloys of this system leads to the conclusion that in this system, at all temperatures, there is a tendency to phase separation, i.e. the atoms of Mo and Cr tend to diffuse not to each other to form a chemical compound, but on the contrary, from each other and, therefore, they, in principle, cannot participate in the formation of any chemical compounds, as it is supposed in references [73,74,75].

As was shown in reference, in the part of the diagram of Ni-Cr, where concentration of nickel atoms prevails (for instance, the $Ni_{68}Cr_{32}$ alloy), heat treatment at any temperature leads to formation of clusters of chromium atoms (after quenching from the liquid state, as well) [43]. Therefore, the tendency to phase separation takes place in the diffusion couple Ni/Cr at any heating temperature of the alloy studied.

The microstructure of the $Ni_{65}Mo_{20}Cr_{15}$ alloy after quenching from the liquid state (1600°C) is shown in figure 45.

Figure 45: $Ni_{65}Mo_{20}Cr_{15}$ alloy. Quenching from the liquid state. Microstructure.

Rounded dark precipitates are observed. They are particles of Mo atoms, which are formed in the liquid solution due to the existence of a tendency to phase separation in the Ni-Mo diffusion couple at high temperatures and due to the high solidification temperature of molybdenum.

After exposure of the alloy at 1300°C (with subsequent quenching in water), dark particles of Mo atoms are still observed in the microstructure (Figure 46) but their dimensions are considerably reduced. In the diffusion couple of Ni/Mo, below 1250°C, the tendency to phase separation is substituted on the tendency to ordering. Along with dissolving particles of Mo atoms, one can observe periodic waves of contrast, which can be regarded as concentration inhomogeneities in the distribution of chromium within the Ni-Cr diffusion couple (Figure 46).

Figure 46: $Ni_{65}Mo_{20}Cr_{15}$ alloy. Quenching from 1300°C. Bright-field image.

It is obvious that such inhomogeneities are formed as a result of the existence of a tendency to phase separation in the Ni-Cr diffusion couple [43]. They have become visible due to absorption contrast.

These inhomogeneities are observed at lower temperatures, as well, for example at 800 °C, but now in the form of alternating dark and bright rounded spots with diffuse edges, i.e. in the form of conventional clusters (Figure 47, clusters are visible due to absorption contrast). A similar structure of clusters of chromium atoms was observed in the electron microscopic image of the $Ni_{68}Cr_{32}$ binary alloy after quenching the alloy from 1200 and 1000°C [43].

As is known from reference books, the optimum combination of corrosion resistance and ductility of most Hastelloy-type alloys is observed after a heat treatment at 1150 - 1175°C (cooling in water or air). As it follows from reference75, it is at

these temperatures that in the solid solution occurs complete dissolution of particles of Mo atoms, formed when the alloy was in the liquid state. And it is precisely in the range of these temperatures the extended Cr- cluster microstructure forming in the Ni-Cr diffusion couple are observed (Figure 46). Hence, it can be concluded that the high level of corrosion resistance, forming in Hastelloy-type alloys in the result of their heat treatment at 1150 -1175°C, owes its origin both to the phase separation microstructure forming in the diffusion couple of Ni/Cr, and to dissolution of Mo particles due to change of the sign of the chemical interaction energy in the diffusion couple of Ni/Mo at about 1250°C.

At lowering the heat treatment temperature to 650°C, the morphology of the $\text{Ni}_{65}\text{Mo}_{20}\text{Cr}_{15}$ alloy changes. Electron diffraction pattern (Figure 48).

Figure 47: $\text{Ni}_{65}\text{Mo}_{20}\text{Cr}_{15}$ alloy. Microstructure after quenching from 800°C.

Figure 48: $\text{Ni}_{65}\text{Mo}_{20}\text{Cr}_{15}$ alloy. Microstructure after quenching from 650°C. Electron diffraction pattern. Inset: Dark-field image in the reflection pointed by the arrow.

shows that the precipitates are chemical compounds of Ni_2Mo with a structure of the Pt_2Mo type (arrow points out the reflection from which the dark-field image was obtained - inset). Since such a compound in the Ni-20 at.% Mo binary alloy is not a stable phase, the authors supposed that in the Ni-Mo-Cr alloys, the Ni_2Mo compound has the chemical composition of $\text{Ni}_2(\text{Mo}, \text{Cr})$, in which atoms of chromium may replace some of the atoms of molybdenum, to "strengthen the stability of this compound" [35,77]. However, this supposition is in conflict with the results [43,44], from which it becomes clear that in alloys of the Ni-Cr system (where the Cr concentration prevails), the tendency to phase separation takes place at all temperatures. This means that between the atoms of Cr and Mo, there takes place a repulsive interaction but not attraction. This type of interaction excludes the possibility of the $\text{Ni}_2(\text{Mo}, \text{Cr})$ phase formation in the alloy. Actually, the attempt of the authors to electrolytically extract particles of $\text{Ni}_2(\text{Mo},$

Cr) from the solid solution of the Hastelloy C-22HS alloy, and then to determine their chemical composition did not lead to the desired results: the amount of chromium in the anodic deposit was much lower than expected [77].

$\text{Co}_{53}\text{Mo}_{35}\text{Cr}_{12}$ superalloy

The alloy belongs to a group of wear-resistant alloys, which, as it is considered [78], obtain high strength and hardness due to formation of coarsely dispersed intermetallic Laves phase particles. Its composition is similar to that of known Cobalt-based Triballoy alloys — T-400C and T-800, containing approximately the same amount of Mo and Cr, plus about 2.5% Si and 0.1-0.2 % C [78]. Alloys of this composition are generally regarded as hypereutectic alloys, containing 30-70 % of a solid intermetallic component distributed in a relatively soft solid solution [78]. The solid primary phase is a triple Laves phase having a melting point of about 1560 °C and a composition approximately corresponding to compositions $\text{Co}_3\text{Mo}_2\text{Si}$ or CoMoSi [78,79]. It is formed in the process of cooling the alloy after melting [79]. It is also believed that among the components constituting the alloy, chromium increases corrosion resistance and hardens the solid solution (as it increases the probability of occurrence of high-temperature fcc → hcp phase transition at room temperature), molybdenum and silicon are used to impart wear resistance to the alloy due to their participation in the formation of the Laves phase; in addition to that, molybdenum strengthens the solid solution and cobalt tends to increase the viscosity of the matrix [78,79]. However, none of the above-mentioned References [79-80] provides information as to under what time-temperature conditions Laves phases in alloys of the Triballoy type are formed and decomposed. All these conflicting views appeared while interpreting the same experimental results due to the fact that in the phase analysis in references 79-80, the sign of the chemical interaction energy between the atoms of the components constituting the alloy was not taken into consideration.

An attempt was made to experimentally determine due to what kind of chemical interactions, and under what thermal conditions Laves phases are formed in the system of Co-Mo-Cr [81]. The fact is that, as seen from generally accepted binary phase diagrams of Co-Cr and Cr-Mo, at approximately the same proportions of components as in the corresponding diffusion couples of the $\text{Co}_{53}\text{Mo}_{35}\text{Cr}_{12}$ alloy, only a phase separation takes place at high temperatures between the atoms of Cr and Co, Cr and Mo [58,76,81]. It is suggested that it occurs in the entire heating temperature range [76]. In the $\text{Co}_{70}\text{Mo}_{30}$ alloy, the tendency to phase separation also takes place; moreover it remains in the range of temperatures from ambient to the solidus ones. Such a sign of the chemical interaction was discovered experimentally, using the methods of X-ray photoelectron spectroscopy and transmission electron microscopy [56]. At a temperature close to the solidus temperature, a phase transition 'ordering-phase separation' takes place in the $\text{Co}_{70}\text{Mo}_{30}$ alloy, which means that only above this temperature chemical compounds may be formed in the alloy [56].

The diffusion processes in the $\text{Co}_{53}\text{Mo}_{35}\text{Cr}_{12}$ alloy were considered as occurring in three diffusion couples - Co/Mo, Co/Cr and Mo/Cr [81]. It was believed that phase transitions occurring in these diffusion couples, proceed similarly to phase changes in the corresponding binary alloy systems of Co-Mo, Co-Cr and Mo-Cr. What diffusion processes occur, for example, in the diffusion couple of Cr/Mo, was already discussed in the previous section.

As mentioned above, in the $\text{Co}_{70}\text{Mo}_{30}$ binary alloy, the phase transition 'ordering-phase separation' occurs at temperatures close to the solidus temperature [56]. Since the composition of the alloy studied in reference 56 is close to the composition of the Co_3Mo phase, then it was natural to expect that this very phase would precipitate when the alloy solidified like that.

The atomic ratio of Co and Cr in the Co/Cr diffusion couple of the $\text{Co}_{53}\text{Mo}_{35}\text{Cr}_{12}$ alloy is approximately 4:1. At the same ratio of atoms in the binary alloy, according to the known phase diagram of Co-Cr [11, 58], the solid solution A1 begins to separate when its temperature drops below 900°C. Above 900°C, according to the diagram, its structure is a solid solution, but in reality it is unknown. It can be assumed, that at temperatures above 900°C, this alloy has a tendency to phase separation as well, since in this system, at compositions close to equiatomic, a phase separation of the alloy starts directly in the liquid state [58].

Thus, it is possible to say that in all the three diffusion couples of the alloy, at temperatures below the solidus line, there takes place a tendency to phase separation and, therefore, phase separation microstructures should form. In this case, experimental detection of the Laves phase in Co-Mo-Cr alloys can be explained only by the fact, that such a phase is a Co_3Mo phase and it precipitates in the Co/Mo diffusion couple at a temperature above the solidus line, when the tendency to ordering takes place in the couple [58]. When the ingot is cooled below the solidus line, this phase is preserved because the sizes of its particles are such that it is insufficient time for their dissolving during the cooling of the ingot. Indeed, in all the mentioned References [78-80]. Laves phases were found when studying alloys in the as-cast condition (without a subsequent heat treatment at temperatures below solidus).

Figure 49: $\text{Co}_{53}\text{Mo}_{35}\text{Cr}_{12}$ alloy. Water-quenching from the liquidus-solidus region. (a) Bright-field image of the Co_3Mo phase; Inset: Electron-diffraction pattern. (b) Another distribution of Co_3Mo phase particles.

Figure 49 shows a fairly large particle precipitating in the liquidus-solidus temperature range. Its outer contours allow saying that it was formed in the absence of elastic resistance of

the environment, i.e. in the liquid solution. The electron diffraction pattern in figure 49 (inset) shows that this particle has a hexagonal D0_{19} structure, which is peculiar for the Co_3Mo phase. Figure 49b shows Co_3Mo phase particles distribution (dark precipitates) at the moment of solidification of the alloy during water-quenching. Heat treatment at 1250°C results in complete dissolution of the Co_3Mo phase particles formed in the liquid state of the alloy. One can observe an fcc solid solution with a large number of stacking faults (Figure 50), indicative of low stacking fault energy in this microstructure.

Lowering the heat treatment temperature to 1000°C leads to some changes of the microstructure in the bright-field image (Figure 51). On most microscopic sites of the foil, the stacking faults structure disappears and a well-developed dislocation structure is observed in its place. Dark particles of a rounded form appear which can be interpreted as particles consisting of chromium atoms. In the inset in figure 51,

Figure 50: $\text{Co}_{53}\text{Mo}_{35}\text{Cr}_{12}$ alloy. Water-quenching from 1250°C. Stacking faults on the bright-field images of the microstructure

Figure 51: $\text{Co}_{53}\text{Mo}_{35}\text{Cr}_{12}$ alloy. Water-quenching from 1000°C. Microstructure: Cr-enriched clusters are formed in the Co/Cr diffusion couple.

near the fundamental reflections, satellites are visible, which arise due to the formation of these particles. In other microscopic sites of the foil, stacking faults still exist, although the contrast from these faults noticeably dims.

Alloys of the binary Co-Mo system, the $\text{Co}_{70}\text{Mo}_{30}$ alloy in particular, after heat treatment at any temperature below the solidus have a very high hardness (about 790-850 HV) and a cellular microstructure, formed as a result of the tendency to phase separation [56]. This means that the $\text{Co}_{53}\text{Mo}_{35}\text{Cr}_{12}$ alloy, in the composition of which the Co/Mo diffusion couple occupies the dominant position, must have the same hardness and microstructure.

Thus, the author of investigating the $\text{Co}_{53}\text{Mo}_{35}\text{Cr}_{12}$ alloy, did not find in it any phases, close to Laves phases in the structure and morphology [81]. Therefore, explaining the high hardness and wear resistance of the alloy by precipitation of particles of Laves phases in it [79,80,82], seems to us premature for the

following reasons:

1. The alloy matrix, consisting mainly of the Co/Mo diffusion couple, is an exceptionally stable construction at all heating temperatures due to the formation of a cellular microstructure in it and due to the existence of the tendency to phase separation in all three diffusion couples.

2. Coarse particles of a Laves phase cannot be considered as hardening the matrix.

3. Such methods of chemical analysis as Energy-Dispersive X-ray Spectroscopy (EDXS) and Electron Energy Loss Spectroscopy (EELS) cannot guarantee that information obtained with their help about the chemical composition of any particle in a foil concerns only with the volume of the particle. Therefore, there are no sufficient grounds to consider Laves phases as multi-component chemical compounds.

Some recommendations for creation of new multicomponent alloys [83].

1. Chemical interactions between dissimilar atoms in superalloys and apparently in other multi-component alloys are realized on the basis of the principle of pairwise interaction. The process of partitioning of a multi-component alloy ABC into diffusion couples A/B, A/C, B/C occurs in the liquid solution, when the diffusion mobility of atoms is very high, and the resistance of the environment is relatively small. The driving force of such a process of partitioning are the chemical interactions between dissimilar atoms i.e. the tendency to phase separation or the tendency to ordering. Because of this, quenching of the liquid alloy into water fixes a microstructure consisting of microscopic sites, corresponding in their composition to this or that diffusion couple.

2. If a multi-component alloy is being designed, the identification of chemical interactions occurring in each of diffusion couples of such an alloy becomes much more complicated. In this case, there appears a necessity to first assess whether these or those small additives should be introduced to the alloy and how these additives can change the overall pattern of chemical interactions in the alloy. This is precisely why, in designing multi-component alloys, it is so important to know the temperature of the phase transition 'ordering-phase separation' of that binary alloy, which corresponds to the given diffusion couple of a multi-component alloy.

3. For each family of multi-component alloys it is proposed to create a database, which would include all experimental results obtained by the method of TEM for binary alloys, whose composition would correspond to each, similar in concentration, diffusion couple of the designed multi-component alloy. With such data, it becomes possible to predict essentially all structural changes which will occur in a multi-component alloy at a change in the temperature. This, in its turn, will substantially facilitate the search of variants of composition, which would lead to improvement of the designed alloy properties.

4. The high level of corrosion resistance in the Hastelloy alloy is achieved when the highly-dispersed microstructure of phase separation is formed in the Ni/Cr diffusion couple, and si-

multaneously with this process, the Mo-particles formed in liquid state are dissolved in the Ni/Mo diffusion couple.

5. The Tribaloy type alloys gain high hardness and wear resistance through the formation of a cellular microstructure, formed in consequence of the tendency towards phase separation in the Co/Mo diffusion couple. In alloys of this composition, at temperatures below the solidus, only a tendency to phase separation is realized between all the dissimilar atoms in each diffusion couple.

Conclusion

Our understanding of this or that physical phenomenon always changes with time and usually corresponds to the level of experimental technique at the given period. Recall the once fashionable classical theory of "nucleation & growth" of a new phase, the theory of "in-situ" nucleation of special carbides in alloyed steels, and so on. Where are they now? They are being gradually forgotten because their description of processes occurring in nature differs from reality. At the same time, there are other theories and ideas which have come to us from the past century, but have so deeply rooted into our minds, that even now, when the experiment does not verify them, we believe that they are the unquestionable truth. For example, we cannot imagine equilibrium phase diagrams without regions of solid solutions at high temperatures, although the latter, from the point of view of thermodynamics, are not an equilibrium phase at any temperature. We cannot imagine the probability of decomposition of a quenched solid solution without its "supersaturation" in the solutes, which occurs at a decrease of the solution temperature. We cannot imagine a heat treatment, carried out to obtain a highly dispersed two-phase structure, which would not include a preliminary high-temperature quenching from the solid solution region.

The discovery of the phase transition 'ordering -phase separation' in alloys puts an end to these ideas. It becomes clear that the ideas about the nature of alloys that we acquired in our universities turn out to be largely outdated, as they are based on experimental data obtained as far back as the mid-twentieth century and without the use of the method of TEM. From the above discussion, it follows that introduction of such a concept as the phase transition 'ordering-phase separation' into common use changes our previous understanding of the driving forces of the process of new phase formation. Also it becomes apparent that in order to change this situation a great number of experimental studies is to be carried out to upgrade existing phase diagrams. The phase transition 'ordering-phase separation', regarded as a consequence of changes in the chemical interaction sign is such a transition, in the process of which, the ionic component of the chemical bond between the atoms, due to the electron-phonon interaction, is replaced by the covalent component, or vice versa.

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