Process of New Phase Nucleation in Alloys

Yuri Ustinovshikov
Udmurt Federal Research Center of Russian Academy of Sciences, 34 Baramzina St., Izhevsk, Russia

Abstract: The article presents a generalization of our electron microscopic results got on some binary and ternary alloys based on Ni, Fe or Co. They are considered as the basis for the conclusion that chemical bonds between atoms are realized in alloys according to the principle of pair interaction. This process begins with the separation of the alloy into diffusion micro-pairs already in the liquid state, which makes it possible to consider the liquid state of the alloy as the initial stage of the new phase formation. With a subsequent decrease in temperature, particles of a new phase form inside a diffusion micro-pair. The formation of diffusion micro-pairs and phases within them occurs due to the existence in alloys, along with a metallic bond, of ionic and covalent components of a strong chemical bond at all temperatures of the condensed state. The article shows what exactly needs to be done so that such a branch of science as materials science could get rid of the empirical approach when creating new alloys.

Key words: “Ordering-phase separation” transition, chemical bonds in alloys, electronic structure of alloys, diffusional micro-pairs, TEM (transmission electron microscopy).

1. Introduction

It is believed that, present, everything is in order in the Material Science of alloys, theory coincides with practice. However, many researchers of the older generation have not yet erased from their memory the heated discussion that, together with other journals, was conducted by the journal Acta Metallurgica in the 70s and 80s. All researchers of the alloys [1-6] were extremely puzzled because after quenching the alloys in water “from the solid solution region on the phase diagram”, they all found not a “disordered” solid solution, but particles of the second phases. Nobody could explain this phenomenon, and the discussion simply had to be stopped “until better times”. Now, apparently, such a time has come now. The situation became clearer only when, in 1996, we discovered the “ordering-phase separation” transition in alloys of the Fe-Cr system [7]. The accepted phase diagram of this system [8] shows that, for example, in the Fe\sub{50}Cr\sub{50} alloy at temperatures up to 550 °C, phase separation occurs (i.e., clusters of chromium atoms are found), and in the temperature range 550-830 °C, ordering occurs (i.e. a chemical compound is formed-sigma-phase). Based on this diagram, already it is possible to conclude that in the iron-chromium system at a temperature of 550 °C, an ordering-phase separation transition occurs, i.e. the sign of the chemical interaction between the Fe and Cr atoms changes. However, the authors [9] went further and studied these alloys at higher temperatures when the structure of an alloy, by phase diagram, is a solid solution. Some results for the Fe\sub{50}Cr\sub{50} alloy are shown in Fig. 1.

It can be seen that, at temperatures above 1,150 °C, instead of a disordered solid solution, large particles of pure chromium were present in the microstructure of the alloy (high-temperature phase separation, Fig. 1a). It was found that in the temperature range 830-550 °C sigma—phase is formed, below 550 °C—again particles of chromium atoms, now as clusters (low-temperature phase separation). This could mean only one thing: at such temperatures in the Fe\sub{50}Cr\sub{50} alloy, the sign of the chemical interaction between Fe and Cr atoms changes [9].
2. The “Ordering-Phase Separation” Transition; “Ionic Bond ↔ Covalent Bond” Electronic Transition

The two transitions stated in the subtitle are, in fact, one transition, happening because with a change in temperature the sign of the chemical interaction between the atoms of the alloy changes to the opposite. The first transition (ordering-phase separation), which has been already mentioned, was discovered by us 25 years ago when studying the microstructure of Fe-Cr alloys, and shows what happens during such a transition with the microstructure [9]. This transition plays an extremely important role in the metallurgy of alloys and, being plotted on binary phase diagrams as a line of phase transition “ordering-phase separation”, will radically change many areas in these diagrams. The second transition was recently stated [10] using the electronic theory of alloys. This transition occurs at the level of the electronic structure and implies that ionic component of the chemical bond transforms into covalent one, and vice versa. All three components of the chemical bond exist at all temperatures at which the alloys are in a condensed state. These results radically change our understanding of phase transformations in alloys. Let us consider these transitions.

In various binary alloys, the “ordering-phase separation” transition has its own characteristic features, which are manifested at the level of a change
in the microstructure; in some systems, a change in sign of chemical interaction (and, therefore, a change in the microstructure) can occur at two and even three varied temperatures. At the transition temperature the energy of chemical interatomic interaction must be equal out to be zero, however at this temperature it can be found a microstructure both a disordered solid solution and a mixture of phases formed because of a tendency towards ordering or phase separation.

The discovery of transitions “ordering-phase separation” in many alloys helped to understand that it is the chemical interactions between the atoms of the components that determine all the diffusion processes occurring in the alloys, leading to the formation of certain phases. The question arises—what is the reason for this transition. Any changes in the type of microstructure, including the “ordering-phase separation” transition itself, cannot occur without corresponding changes in the electronic structure of the alloy. Using the method of XPS (X-ray photoelectron spectroscopy), we have shown that with a change in the electronic structure of alloys, the shape of the valence band changes with temperature. Based on the results got using the method of TEM (transmission electron microscopy), it was concluded that the change in the type of microstructure of the alloy occurs at approximately the same temperature at which the shape of the valence band of the alloy changes [11, 12].

Electronic domains detected by us [9] in the Fe-Cr alloys were considered earlier as some regions of the alloy, within which the sign of the ordering energy has already changed, compared with the surrounding matrix, where it remains the same [10]. Since the values of the chemical interaction energy have opposite signs on both sides of the domain wall, the electron beam passing through foil is deflected in opposite directions, which leads to a deficiency (light lines) or an excess (dark lines) of electrons during defocusing of the electron microscopic image. Thus, the formation of electronic domains, similar to the formation of magnetic and ferroelectric ones, is a consequence of changes in the electronic structure of alloys.

It is known that in alloys, as in pure metals, collectivization of valence electrons occurs. However, the presence in the alloy of two or more sorts of metal atoms, between which certain chemical interactions take place, leads to the appearance of other types of strong chemical bonds—ionic and covalent. The ionic component of the bond that arises in the AB alloy between the atoms of the dissolved component B and their nearest neighbors, the atoms of the solvent A, manifests itself if the atom B, diffusing in the lattice of the alloy AB, accidentally becomes the nearest neighbor of the atom A. Because of this instantaneous proximity, the pair of valence electrons localizes on these two dissimilar atoms with the formation of a common orbital. At the microstructure level, this process manifests itself as ordering atoms of alloy and formation of chemical compound $A_mB_n$ [10].

The covalent component of the chemical bond manifests itself when two atoms of the dissolved component B, diffusing in the alloy, accidentally become the nearest neighbors. Because of this instantaneous proximity, their valence orbitals hybridize and a cluster of these two B atoms forms. The cluster consists first of two B atoms, and then of a larger number of B atoms pairs. Thus, we can say that the “ordering-phase separation” transition, which at the microstructural level manifests itself as a change in the sign of the chemical interaction energy between atoms A and B, on the electronic level manifests itself in exactly the same way. This is a transition from a state when all pairs of valence electrons localized on atoms A and B and forming ionic bonds between them leave this state, and pairs of some valence electrons take part in the formation of hybrid orbitals, now between two atoms of the dissolved component B (which leads to phase separation). This allows us to call such a transition a transition from localization to hybridization of that part of the valence electrons that
are not involved in the formation of metallic bonds. Thus, the “ordering-phase separation” transition includes two elementary events: delocalization of valence electrons on atoms A and B and hybridization of valence electrons in pairs of atoms B. The existence of such an electronic transition may mean that upon heating to a certain temperature, the ionic component of the chemical bond between atoms is replaced by covalent [10].

3. Binary Alloys

If we consider the binary alloy AB, when it is in a liquid state, then because of the very high diffusion rate at this temperature, an equilibrium distribution of the chemical potential over the entire volume of the alloy is instantly achieved in it. This means that, in the AB binary alloy, a rearrangement occurs in the distribution of atoms of various types. When a tendency to phase separation takes place, diffusion pairs A/A and B/B form. When a tendency towards ordering takes place, diffusion pair A/B forms in solvent A. Later on, but sometimes concurrently, the corresponding chemical compound $A_mB_n$ forms in the diffusion pair according to the valence rule.

Prior to further consideration, it is necessary to say a few words about how we quenched alloys from the liquid state. To answer the question of what structure the alloy has in the liquid state, the studied alloy was quenched by pouring out a small amount of liquid metal directly from the crucible into the water. We supposed that pouring out the metal not into any intermediate container, but directly into the water, would cast aside any doubts that we are fixing the microstructure of the just liquid state at the instant a liquid metal is in contact with the water.

Fig. 2 shows such structures formed in the liquid state of alloys of the Ni-Cr system—Ni$_{60}$Cr$_{32}$ (a tendency to ordering, Ni$_2$Cr is a chemical compound with an orthorhombic lattice of the Pt$_2$Mo type [13]) and Ni$_{40}$Cr$_{60}$ (tendency to phase separation, clusters of chromium atoms).

Now that the author of this article has discovered the “ordering-phase separation” transition in alloys of 17 binary systems, we will show out how pair interaction will occur in binary alloys of one from systems we studied earlier.

Let us consider in more detail how the microstructure of one of binary alloys researched by us changes with a change in its heating temperature. Let us choose Co$_3$V alloy in which the “ordering-phase separation” transition is observed at two temperatures [14]. Quenching the alloy from the liquid state fixes the vanadium particles, the bright-field image of which is presented in Fig. 3. The electron diffraction pattern shows satellites appear near main reflections of these particles (Fig. 3, inset). Obviously these satellites in

![Fig. 2 Ni$_{60}$Cr$_{32}$ (a); Ni$_{40}$Cr$_{60}$ (b) alloys. Water quenching from liquid state. Bright field image of the microstructure. Inset: electron diffraction pattern (a); absorption contrast (b) [13].](image)
the electron diffraction pattern result from vanadium particles formation, which crystallize in the liquid solution thanks both to the tendency to phase separation in the Ni/V diffusion pair and high melting point of vanadium.

By lowering the temperature of the alloy from 1,550 to 1,150 °C, the sizes and number of vanadium atom particles formed at 1,150 °C are increased. Fig. 3 shows a colony of such particles after quenching from 1,150 °C. In the electron diffraction pattern got from such a colony, one can observe satellites belonging to the BCC lattice of vanadium (Fig. 4, inset). At lowering the heat treatment temperature to 800 °C it becomes possible to observe two original structures in
various areas of the same foil (Fig. 5). One type formed because of the tendency to phase separation, and another type formed because of the tendency to ordering. Such a transition proceeded via a simultaneous dissolution of cobalt-rich clusters and formation of particles of the chemical compound.

The bright-field image, obtained from one of the microscopic sites of the foil after heat treatment of the Co$_3$V alloy at 800 °C, shows a microstructure comprising very fine grains (Fig. 5a) [14]. It can be assumed that this microstructure is a mixture of clusters enriched and depleted in vanadium, which are detected at the stage of the dissolution of the phase separation structure. Indeed, in the electron diffraction pattern obtained from this structure, instead of satellites, one can observe diffuse scattering (Fig. 5a, inset). This may be why the dissolution stage of the phase separation microstructure, i.e. the dissolution of particles of vanadium atoms in the cobalt lattice, is fixed in this microscopic site.

![Co$_3$V alloy. Water quenching from 800 °C. (a) Bright field image of the phase separation microstructure. Electron diffraction pattern, (001) zone axis. Diffusion scattering (inset). (b) Another microscopic site of the same foil: electron diffraction pattern, (001) zone axis; L1$_2$ phase [14].]
In other microscopic sites of the same foil, areas are observed where the microstructure of ordering is formed or has already formed. For example, Fig. 5b shows an electron diffraction pattern in which the system of additional reflections, showing a precipitation of the L12 phase, is visible. However, in the bright-field image, particles from the new phase are not detected. This shows that precipitates producing such reflections are fully coherent with the matrix. This allows the assumption that 800 °C is the temperature close to the temperature of the “ordering-phase separation” transition. Unlike Fe-Cr alloys in which the regions of ordering and phase separation are divided by the disordered solid solution region, in the Co3V alloy the region is absent. The process of the “ordering-phase separation” transition in the Co3V alloy occurs at 800 °C non-simultaneously throughout the volume: in some microscopic sites of the thin foil, the microstructures of phase separation are still dissolving and in another microscopic sites the particles of the Co3V chemical compound with an L12 structure have already been formed. This confirms our assumption that 800 °C is the temperature close to the temperature of the “ordering-phase separation” transition. Unlike the Co3V alloy, the regions of ordering and phase separation in many other systems are clearly demarcated.

Further lowering the heat treatment temperature to 500 °C leads to the reflections from the L12 phase becoming clearer and more intense (Fig. 6), and it becomes possible to observe particles of the L12 phase in the bright-field image. If the alloy is subjected to heat treatment at 350 °C, then, according to structural data, it becomes possible to detect one more “ordering-phase separation” transition taking place in the alloy at temperatures of about 450 °C. Fig. 7a shows a cellular structure which was found after heat treatment at 350 °C. We again observed a diffuse scattering in the electron diffraction pattern, which is brighter than that in Fig. 5a (inset). Thus, by lowering the heat treatment temperature, two phase transitions “ordering-phase separation” are observed in the alloy: at 800 °C and at 450 °C.

Thus, using the example of a binary alloy Co3V, we show how the temperature of the “ordering-phase separation” transition should be determined for any binary alloy. For the Co3V alloy, there are two such transition temperatures: 450 and 800 °C. How accurately you determined the temperature of such a transition for the alloy under study, so accurately you can draw a line separating two regions with different phase composition on the binary phase diagram AB you constructed.

---

**Fig. 6** Co3V alloy. Water quenching from 500 °C. (a) Electron diffraction pattern; (b) bright-field image of the microstructure [14].
Under the conditions of existence of paired chemical interactions between the nearest neighbors in alloys, it is easy for us to understand the process of formation of chemical compounds (during ordering) or clusters (during phase separation) in binary alloys. When such a process occurs in a multi-component alloy, it is difficult to imagine how this can happen, unless it is assumed that, for example, particles of multi-component phases form in a multi-component alloy. Apparently, therefore many researchers concluded that particles of three-component Laves phases precipitate in ternary alloys. However, the assumption of the existence of such three-component chemical compounds contradicts the theory of pair interaction, which states that chemical interaction in alloys is possible only between two nearest neighbors. Therefore, the theory of pair interaction logically flows from the electronic theory of alloys [10].

4. Multi-component Alloys

It is believed that in multi-component alloys, addition of each component brings its own distinguishing features to the alloy, which improves one or another property. This approach encourages the addition to the alloy of those elements that have previously proven themselves on the positive side in other alloys as “improving” certain of their properties. So there is a desire to create multi-component alloys, including the so-called high-entropy, increasing the number of “useful” components in the alloy. However, an increase in the number of components in the alloy can hardly change the nature of the interatomic interaction itself. Most likely the opposite is true. Such an increase can interfere with implementing the normal course of interaction between atoms of certain components. As is known, in all metal alloys there is a pair chemical interaction, which manifests itself during diffusion only between two nearest neighbors in line with the sign of a chemical potential. Therefore, let us consider what the pair interaction leads to in such a complex ensemble as a multi-component metal alloy.

Under the conditions of the existence of pair interatomic interactions in alloys, it is easy for us to understand the process of the formation of chemical compounds (during ordering) or clusters (during phase separation) in binary alloys. When such a process occurs in a multi-component alloy, even in a three-component alloy, it is difficult to imagine how this can happen. Many researchers assume that particles of three-component phases form in the alloys to corresponding in composition to the alloy.

Fig. 7 Co<sub>3</sub>V alloy. Water quenching from 350 °C. (a) Bright-field image of the phase-separation microstructure; (b) electron diffraction pattern, (001) zone axis, diffuse scattering [14].
Therefore, they concluded that in ternary alloys there is a possibility of precipitating three-component Laves phases, although the electronic theory of alloys does not allow such a possibility (only pair chemical interaction takes place between the nearest neighbors). This circumstance prompted the author of the article to carry out TEM studies of some ternary alloys, the compositions of which were selected in such a way that at least two diffusion pairs in these alloys corresponded to the compositions of the binary alloys he had already studied. This was necessary in order to compare the microstructure of a binary alloy with approximately the same in composition diffusion pair in ternary alloys. All these alloys (binary and ternary) were quenched in the water at various temperatures, including when they were in the liquid state.

The author [15], introducing the concept of a diffusion pair, suggested that the very process of the formation of such pairs occurs precisely in the molten metal, when the diffusion rate is extremely high. The reason for the formation of diffusion pairs is the same chemical bonds (ionic and covalent), which, with decreasing temperature, lead to the formation of chemical compounds or particles (clusters) comprising atoms of the dissolved component. This means that chemical bonds, like the electronic structure, during melting of the alloy continue to exist, like the alloy itself.

However, it was still unclear what a diffusion pair is and whether it is an element of the microstructure of the alloy. It was assumed [15] that during the solidification of the alloy the structure comprising such diffusion pairs is kept until the next remelting. With decreasing temperature (and sometimes at the same time), phase particles inside such pairs form that correspond to the temperature under study. All these explanations were like fantasy, since everyone was accustomed to believing that the higher the temperature, the weaker the chemical interactions between the atoms of the alloy, and at the melting temperature they are equal to zero. Even now, everyone continues to believe that the mutual arrangement of atoms of different kind in the liquid state is completely chaotic and that chemical bonds “arise” only at relatively low heating temperatures, when the thermal energy of the alloy becomes lower than the energy of the chemical bond between the atoms. Let us give some examples.

The composition of the Ni₅₀Co₂₅Mo₂₅ alloy [16] was chosen because the diffusion pairs Ni/Mo, Ni/Co, Co/Mo, from which this alloy consists, was previously investigated by us as binary alloys of the Ni-Mo systems [17], Ni-Co [11], Co-Mo [12]. Therefore, all their microstructures are known. The transition temperatures “ordering-phase separation” in these systems were known only for Ni/Mo pairs—about 1,200 and Ni/Co—600 °C. In this ternary alloy, the number of Ni/Mo and Ni/Co pairs is equal, so we would expect that the amount of Mo/Co pairs will be negligible. We discuss some experimental results obtained by us at temperatures at which the Ni₅₀Co₂₅Mo₂₅ alloy is in a liquid state.

After quenching from a liquid state, we can observe a different microstructure in different microscopic areas of an ordinary thin foil. For example, in one of the microscopic areas of the thin foil, we observe a microstructure where particles of Mo atoms are visible (Fig. 8a). The electron diffraction pattern obtained from the microstructure (inset) shows satellites near the main reflections and a system of weak diffraction maxima at the \{1 ½ 0\} positions. Because of the tendency towards phase separation in the Ni/Mo diffusion pair and high temperature of Mo melting, particles of Mo atoms form when Ni atoms are still in the liquid state.

In Fig. 9, we have given the mutual arrangement of diffusion micro-pairs and particles of new phases formed inside them in a three-component alloy, as we imagine today.

Clusters containing isolated stacking faults (Fig. 10a) have a composition that is apparently close to that of Ni₅₀Co alloy (when the stacking fault energy is
minimal [16]), and the rest of the matrix is depleted in cobalt. Fig. 10b shows that these two types of structures (Co-clusters and stacking faults) can be arranged in alternating layers, thin enough so that the electron beam can form a joint image of the layers lying on top of each other.

The detection of different microstructures in different microscopic areas of the same foil, which differ in the chemical composition and type of precipitates, shows that the chemical composition in each area corresponds to the chemical composition of a particular diffusion micro-pair (in the first case, Ni/Mo, in the second, Ni/Co). This once again convinces us that diffusion pairs indeed form in a liquid state and represent sites with a predominant concentration of one of the dissolved components.

Many authors believe that among the components making up the super alloy of the Tribaloy type, chromium increases corrosion resistance and hardens the solid solution [18], molybdenum and silicon are

![Image](image-url)
used to impart wear resistance to the alloy because of their participation in the formation of the Laves phase [19]. However, nobody gives information as to under what temperature-time conditions Laves phases in alloys of the Tribaloy type form and decompose. All these conflicting views appeared while interpreting the same experimental results.

Thus, we can say that in all three diffusion pairs of the alloy at temperatures below the solidus line, there is a tendency to phase separation and, therefore, a
phase separation microstructure should form. The experimental detection of any chemical compound, including the Laves phase, in Co-Mo-Cr alloys can only be explained because such a phase is a Co\(_3\)Mo phase since it precipitates in a Co/Mo diffusion micro-pair at a temperature above the solidus line when the pair takes place tendency towards ordering [15]. When the ingot is cooled below the solidus line, this phase can persist, since the particle size is such that there is not always enough time for them to dissolve during the cooling of the ingot. Indeed, in many works, for example Ref. [19], Laves phases were found after studying alloys in the as-cast state.

Fig. 11a shows a bright-field image of the microstructure of the Co\(_{53}\)Mo\(_{35}\)Cr\(_{12}\) alloy after water-quenching from a liquid state (1,550 °C) [18]. We can observe alternating dark and light elongated grains of the Co\(_3\)Mo phase as slightly flexed arcs. Inside light arcs, we observe narrow transverse dark bands, which occur in the crystal lattice during quenching. It is apparent that these particles of the Co\(_3\)Mo phase are located inside the Co/Mo diffusion micro-pair. Fig. 11b shows the electron diffraction pattern takes from the microstructure in Fig. 11a. The pattern shows that such particles have the hexagonal structure D\(_{019}\), which is characteristic of the Co\(_3\)Mo phase. These grains form during 1,340 °C, i.e. when the Co\(_3\)Mo phase solidifies. Along with reflections from a chemical compound, we observe randomly scattered reflections, apparently from particles of molybdenum atoms. It can be assumed that inside the diffusion pair enriched in molybdenum, in the liquid state of the alloy, the transition “ordering-phase separation” occurs and the chemical compound Co\(_3\)Mo decomposes, forming particles of molybdenum atoms. However, because of the low chromium content in the alloy, we could not detect Cr clusters in Cr-enriched diffusion pairs.

Electron microscopic analysis of the Ni\(_{65}\)Mo\(_{20}\)Cr\(_{15}\) [20] alloy shows that in different sites of the same foil quenched from the liquid state (1,450 and 1,550 °C), and from 1,300 °C, accumulations of only two types of precipitates of the second phase are found: in the Ni/Mo diffusion micro-pair the particles of molybdenum atoms are observed, in the Ni/Cr diffusion micro-pair—two-component clusters of the chromium atoms [20]. The microstructure containing Mo particles in the Mo-enriched diffusion micro-pairs in Ni\(_{65}\)Mo\(_{20}\)Cr\(_{15}\) alloy shows that shape and sizes of Mo-particles fully coincide with Fig. 8a (Ni\(_{60}\)Co\(_{25}\)Mo\(_{25}\) alloy) and therefore are not given here.

Processes occur in the alloy, in those micro-volumes that are occupied by Ni/Cr diffusion micro-pairs were considered in our work [20]. After quenching the alloy...
Fig. 12  Ni₆₅Mo₂₀Cr₁₅ alloy. Water-quenching into the water from a liquid state (1,550 °C). Microstructure. Absorption contrast. Ni/Cr diffusion micro-pair (a). Water-quenching from 1,450 °C (b) [20].

The mere fact of detection in the structure of a liquid ternary alloy of binary or single-component precipitates of the second phase of different composition at different points of the same foil could force a reader to conclude that this alloy in a liquid state is at the stage of decomposition. It turns out to be divided into two types of diffusion micro-pairs in which either only the particles of molybdenum atoms are observed (Fig. 8a), or clusters of chromium atoms (Fig. 12). Obviously, there is simply no other explanation for this. We emphasize that in Ni/Cr diffusion micro-pair with low chromium content, close to the alloy under study, the tendency to phase separation takes place at all heating temperatures.

from 1,550 °C, clusters of chromium atoms are observed in diffusion micro-pairs Ni/Cr as concentration waves of the absorption contrast, which emanate from a certain light coloured center in a thin foil, forming apparently, in the moment of contact of the liquid alloy with water (Fig. 12a).

With a further decrease in the quenching temperature to 1,450 °C, the entire surface area of the foil in each Ni/Cr diffusion micro-pair turns out to be scarred by such waves of the contrast (Fig. 12b). Such concentration in homogeneity forms because of the existence of a tendency to phase separation. It is possible to estimate the diffusion micro-pair volume by the number of contrast waves that fit into the Ni/Cr diffusion micro-pair in Fig. 12b. This value can reach several tens of micron.

5. Discussion

The detection of diffusion micro-pairs in multi-component alloys, as well as the “ordering-phase separation” transition, radically changes the existing ideas about how new phases form in alloys and how the heat treatment of alloys should be carried out. Let us start with heat treatment.

(1) Due to the fact that disordered solid solutions are not found in nature (this is evidenced at least because Raoult’s law is never fulfilled), then there is no sense in such “quenching on a solid solution”. As we have shown [22], such quenching is a completely useless operation, the abandonment of which on a global scale will save many millions of dollars.

(2) When prescribing heat treatment, it is necessary to proceed from the principles that each temperature of heat treatment has its own microstructure (i) and that the equilibrium state of the microstructure is achieved at each temperature after holding for a certain duration (if an alloy is in the liquid state, this time is close to zero).

(3) On the binary phase diagrams that currently exist, only lines that show massive phase transitions
Process of New Phase Nucleation in Alloys

(liquidus, solidus, allotropic, magnetic, etc.) are credible. The lines that separate the different regions at the phase diagrams, diverged by the type of the second phase, almost all are erroneous [23]. Therefore, it will be necessary to rebuild almost all binary phase diagrams that currently exist using the TEM method. If you count how many binary systems exist, you can imagine how many years such a job can last.

It will be necessary to restructure our ideas about the conditions for the existence of a homogeneous solid solution and finally agree with chemical thermodynamics that there are no ideal solid solutions in nature—Raoult’s law does not hold.

(4) It will need to understand that chemical interatomic interactions exist in alloys at not only the solid state, and when the alloy is in liquid state.

(5) To determine the transition temperature “ordering-phase separation” for each binary system, it will be necessary to do a lot of experimental work using the TEM method. I am sure that many new experimental discoveries await us along the way.

(6) It is well to remember the existing attempts to achieve higher properties of alloys (high-multi-component superalloys, high-entropy alloys, etc.) by complicating their chemical composition are unlikely to lead to such an improvement under conditions of pair interatomic interaction. Therefore, I would like to warn the future authors of such works from disappointment. Simplifying the composition of, for example, superalloys will make it possible to full use the heat-resistant capabilities of the main pair of components of a particular alloy.

6. Conclusion

It has been experimentally established that the formation of a microstructure in alloys begins with the formation of diffusion micro-pairs—areas of a liquid alloy several tens of microns in size, with an increased concentration of a certain component dissolved in the solvent lattice. The driving force behind the formation of diffusion micro-pairs is the natural tendency of each specific system to achieve an equilibrium state at each specific temperature of its heating. The driving force behind the formation of diffusion micro-pairs is the natural tendency of each specific system to achieve an equilibrium state at each specific temperature of its heating. This driving force is ionic and covalent interatomic bonds, which always manifest themselves between the nearest neighbors in alloys. Diffusion micro-pairs form only in the liquid state of the alloy, when the diffusion mobility of atoms is several orders of magnitude higher than in the solid state. After the alloy has solidified, the size and shape of diffusion micro-pairs remain unchanged at further temperature lowering, and inside these pairs, corresponding chemical compounds or clusters can be formed.

Introducing such a concept as “diffusion micro-pairs” completely changes our understanding of how the process of nucleation of new phases in alloys, including multi-component ones, occurs, and why the precipitated phases in them can only be two-component (tendency to ordering) or particles (clusters) of a dissolved component (a tendency to phase separation).

Theoretically, a multi-component alloy should separate into as many diffusion micro-pairs as its composition allows, but in practice such a complete separation is hardly possible. It all depends on the concentration of a particular component in the alloy and on the number of components in the alloy. The further the process of separation of the alloy into diffusion micro-pairs goes, the more difficult it is for any single atom to find its “own” diffusion pair, even despite the very high diffusion rate of atoms in the liquid state of the alloy. With many components in the alloy, the possibility of forming micro-pairs can be quickly exhausted, and as a result, the remaining areas of the alloy will be a chaotic mixture of atoms, it is not clear what structure. Therefore, hopes for the use of high-entropy alloys in the industry are unlikely to have bright prospects in the future.
For each family of multi-component alloys of interest to us, I propose to create a structural data bank, which would include all the experimental results got by the TEM method for binary alloys, the composition of which would correspond to the composition of the phases precipitated inside diffusion micro-pairs. In addition, it is necessary to take into account that in each type of the diffusion micro-pairs, with a decrease (or increase) in temperature, an “ordering-phase separation” transition will occur, and therefore it is necessary to know the temperature of such a transition (according to the results of studies of the corresponding binary alloys). Having such data for each binary alloy, it becomes possible to predict all structural changes that will occur in the investigated multi-component alloy with a change in temperature, and, thus, to predict the properties that your future alloy will have after any heat treatment. This makes it much easier to find composition options that will improve the properties of your alloy.

Acknowledgement

I would like to thank the engineer Nikolay Kostenkov (Udmurt University) for preparing the electron microscope for operation and making thin foils.

Conflict of Interest

Because in this area of material science I work alone, without assistants and like-minded people, I cannot have a conflict of interest with anyone.

References

[1] Woodilla, J. E., and Averbach, B. L. 1968. “Modulated Structures in Au-Ni Alloys.” Acta Metallurgica 16: 255-63.
[2] Chevalier, J. P., and Stobbs, W. M. 1976. “An Electron Diffraction Study of Short-Range Order in Quenched Ni$_3$Mo Alloys.” Acta Metallurgica 24: 535-42.
[3] Higgins, J., Nicholson, R. B., and Wilkes, P. 1974. “Precipitation in Iron-Beryllium System.” Acta Metallurgica 22: 201-17.
[4] Laughlin, D. E., and Cahn, J. W. 1975. “Spinodal Decomposition in Age-Hardening Cu-Ti Alloys.” Acta Metallurgica 23: 329-39.
[5] Phillips, L. A., and Tanner, L. E. 1973. “High-Resolution Electron Microscopy Observations on GP Zones in an Aged Cu-2 wt.% Be Crystal.” Acta Metallurgica 21: 441-8.
[6] Flewitt, P. E. 1974. “Phase Transformations in Nb 16 to 40% Zr Alloys above the Monotectoid Temperature.” Acta Metallurgica 22: 47-63.
[7] Ustinovshikov, Y., Shirobokova, M., and Pushkarev, B. 1996. “A Structural Study of the Fe-Cr System Alloys.” Acta Metallurgica 44: 5021.
[8] ASM Handbook, Alloy Phase Diagrams, ASM International, 1992.
[9] Ustinovshikov, Y., Pushkarev, B., and Igunnov, I. 2002. “Fe-Rich Portion of the Fe-Cr Phase Diagram: Electron Microscopy Study.” J. Mater. Sci. 37: 2031.
[10] Ustinovshikov, Y. 2017. “Changes in Electronic Structure of Metallic Alloys at the Transition ‘Ordering-Phase Separation’.” J Alloys & Compds. 714: 476-83.
[11] Ustinovshikov, Y., Shabanova, L., and Lomova, N. 2011. “TEM study of the ‘Ordering-Phase Separation’ Transition in Ni-Co Alloys.” JAdv Microscopy Res 8: 276.
[12] Ustinovshikov, Y., and Shabanova, I. 2012. “Nature of High Hardness in the Co$_{50}$Mo$_{30}$ Alloy.” Mat Chem Phys 129: 975.
[13] Ustinovshikov, Y. 2012. “Phase Transformations in Alloys of the Ni-Cr System.” J Alloys & Compds 543: 227-32.
[14] Ustinovshikov, Y. 2015. “Phase Transitions Ordering-Phase Separation in the Co$_3$V Alloy.” J Alloys & Compds 639: 669-74.
[15] Ustinovshikov, Y. 2019. “Ordering-Phase Separation” Transition in Alloys. Monograph: Manchester Scholars Publishing.
[16] Ustinovshikov, Y. 2014. “Structural-Thermodynamic Method of Phase Analysis of Multi-component Alloys Based on the Example of the Ni$_5$Co$_2$Mo$_{25}$ Alloy.” J Alloys & Compds 614: 113-7.
[17] Ustinovshikov, Y., and Shabanova, I. 2011. “Phase Transition in Alloys of the Ni-Mo System.” Mat Chem Phys 129: 975-80.
[18] Shibuya, S., Kaneno, Y., Tsuda, H., and Takasugi, T. 2007. “Microstructural Evolution of Dual Multiphase Intermetallic Alloys.” Intermetallics 15: 338.
[19] Soga, W., Kaneno, Y., and Takasugi, T. 2006. “Phase Relation and Microstructure of Intermenallic Alloys.” Intermetallics 14:170.
[20] Ustinovshikov, Y. 2014. “Structural Transformations in the Co$_{50}$Mo$_{15}$Cr$_{12}$ Alloy at Different Temperatures.” J Alloys & Compds 602: 135-9.
[21] Ustinovshikov, Y. 2021. “Experimental Detection of Diffusion Micro-pairs in a Structure of the Ni_{65}Mo_{20}Cr_{15} Alloy.” Journal of Mater Sci & Eng A 11 (4-6): 63-70. doi: 10.17265/2161-6213/2021.4-6.005.

[22] Ustinovshikov, Y. 2012. “A New Paradigm for Heat Treatment in Alloys.” J Alloys & Compds 543C: 227-32.

[23] Ustinovshikov, Y. 2017. “Mapping of the Transition ‘Ordering-Phase Separation’ into Phase Diagrams.” J Alloys & Compds 691: 713-20.