(REVIEW ARTICLE)

Fundamental changes in notions of the metallic alloy's nature

Yuri Ustinovshikov *

Udmurt Federal Research Center of Russian Academy of Sciences, Physical-Technical Institute, Russia, 426000 Izhevsk, 34 Baramzina St.

Abstract

The article "Fundamental changes in notions of the metallic alloys nature" is a collection of ideas and experimental results that unequivocally indicate that modern ideas about metallic alloys should become to history of alloys. Here we present to the reader the results of experiments obtained on two binary alloys $Ni_{75}Mo_{25}$ and $Ni_{88}Al_{12}$, as well as on one ternary alloy $Ni_{53}Mo_{35}Al_{12}$. These data are identical to the data we presented earlier obtained on alloys of 17 binary systems and seven ternary alloys. Briefly, the main conclusions of the experiments are as follows:

- Interatomic chemical interactions exist in all metal alloys at temperatures of both solid and liquid states.
- Chemical bonds in alloys have an amazing property to change their sign at a certain temperature (there is a phase transition "ordering - separation").
- The reason for this transition is the electronic transition "ionic bond ↔ covalent bond".
- The process of formation of new phases in alloys begins with the formation of diffusion micro-pairs formed during the melting of the alloy.

Such considerable differences between the existing notions about the nature of alloys and those revealed in this work should lead to changes in the technology of heat treatment of alloys, in the binary phase diagrams and to a change in the principles of creating new alloys.

Keywords: Alloys; Chemical bonds; Transmission electron microscopy; Microstructure; Phase transitions

---

1. Introduction

The development of human civilization is inconceivable without progress in the advancement of its material base, in which metals and metal alloys play one of the leading roles. In recent years, we have observed significant changes for the better in the elaboration of new alloys. However, unfortunately, they were achieved in a long, empirical way. This is because our ideas about the nature of alloys are still at the level of almost 100 years ago. This circumstance hinders progress in the development of new alloys and does not allow researching alloys in a necessary direction.

The source of the existing now theory of alloys dates back to when researchers, studying the solubility of a salt in water with decreasing temperature, found that in time, salt crystals precipitate from the solution. They suggested whether the process of nucleation of particles of a new phase during the tempering of quenched metal alloys does not occur in the same way as during the isolation of salt crystals from a supersaturated aqueous solution. The idea turned out to be tempting, and since then, metal science has been living with the illusions of the past: a solid solution disordered after quenching becomes to be supersaturated with a decrease in the heat treatment temperature, and particles of the excess phase precipitate from it. Only then, with such a separation, certain chemical bonds arise between the atoms of this

---

* Corresponding author: Yuri Ustinovshikov

phase. This means that not chemical interatomic bonds cause the formation of chemical compounds, but chemical compounds cause the occurrence of chemical interatomic bonds (!)

Obviously, the comparison of the process of formation of a new phase during the tempering of a metal alloy and the process of precipitation of salt crystals with a decrease in the temperature of the water-salt solution is highly incorrect. However, this idea is so ingrained in our heads that even the discussion on this topic, held by the journal Acta Metallurgica in 1960-80 [1, 2], ending in favor of existing ideas. This is not surprising, since in all universities of the world for many decades now, all professors have been presenting these ideas as an axiom that does not require proof.

The author of this article, starting his experimental work on the above topics, chose the direct method for studying the microstructure - TEM, and studied the microstructure of each alloy at all heat treatment temperatures (with an interval of about 200 - 300° C and, including in the liquid state).

We hope that the reader already knows some of our papers or monography [3], where it is described what the "ordering-separation" phase transition is in binary alloys. This is a phase transition that occurs at a well-defined temperature, when, in the A_xB_y alloy, atoms A and atoms B, instead of mutual attraction experience mutual repulsing. This is not surprising if we consider alloys from the point of view of the structure of their electronic structure.

As you know, in a pure metal between its atoms, takes place a 100% metallic bond. However, when atoms of another metal are added to one metal (i.e., when creating a binary alloy), a certain part of the metal bonds in the alloy are replaced by chemical ones, ionic and/or covalent ones [4]. The ionic component of the chemical bond appears when, with a change in the alloy's temperature, the B atoms become the nearest neighbors of the A atoms. Because of this instantaneous proximity, their valence orbitals are localized, the chemical compound A_xB_y form. The covalent component of a chemical bond forms when two atoms of the dissolved component B become the nearest neighbors. Because of this instant proximity, their valence orbitals hybridize, i.e. a cluster forms comprising these two atoms B. Thus, we understand how an ionic bond forms and how a covalent bond forms. However, it does not understand why, at the temperature characteristic of each alloy, these bonds pass into one another, why an electronic transition occurs "ionic bond ↔ covalent bond". For the time being, we will perceive this transition as another mystery of nature, which at the microstructural level manifests itself as an "ordering-separation" phase transition.

2. Results

In this article, we will consider two binary alloys comprising the following components: $Ni_{75}Mo_{25}$ and $Ni_{88}Al_{12}$, as well as one ternary $Ni_{53}Mo_{35}Al_{12}$ alloy. In all these alloys, nickel is the solvent.

$Ni_{75}Mo_{25}$ alloy [5]. In the alloy after quenching from a liquid state, we can observe a microstructure where particles of Mo atoms are visible (Fig. 1a). The electron diffraction pattern got from the microstructure shows a system of diffraction maxima at the {1 ½ 0} positions (Fig. 1b).
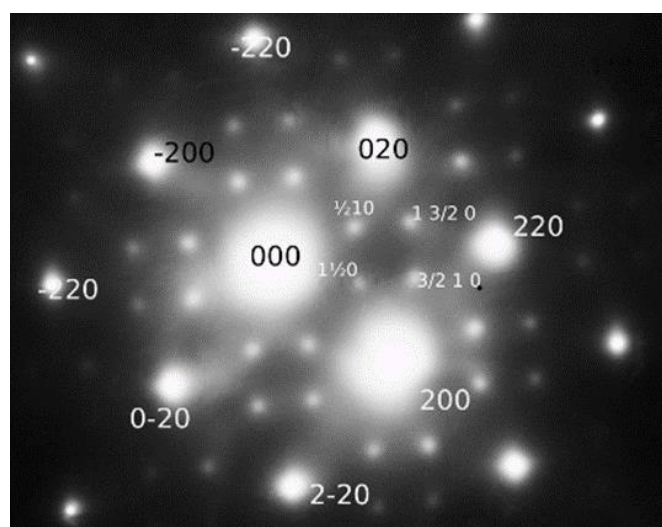

Figure 1 $Ni_{75}Mo_{25}$ alloy. Quenching from the liquid state. Electron diffraction pattern

We cannot interpret these reflections in terms of the formation of ordering structures resulting from quenching from high temperatures, since they do not coincide with the well-known reflections of the long-range order structures of the alloy under study

Reflections in positions {1 ½ 0} in Fig. 1 are interpreted as reflections formed near each of the main four symmetric pairs of {110} and {200} reflections from the BCC particles. This suggests that the liquid $Ni_{75}Mo_{25}$ alloy solidifies in such a way that the {110} and {200} planes of the BCC Mo particles that started the coherent lattice continue with the corresponding planes of the FCC solid solution $Ni_{75}Mo_{25}$ alloy. In the alloy after quenching from a liquid state, we can observe a microstructure where particles of Mo atoms are visible (Fig. 1). The electron diffraction pattern got from the microstructure shows a system of diffraction maxima at the {1 ½ 0} positions (Fig. 1).

Exactly the same picture is observed after quenching this alloy from 1300° C. This means that the type of microstructure of the alloy is determined not by its state of aggregation at such temperatures, but by completely different parameters. A further decrease in the alloy's temperature by only 100°C dramatically changes the type of microstructure: instead of the structure formed because of a tendency to delamination, a chemical compound Ni_3Mo forms as long square-section laths (Fig. 2 a, b). This shows that in the temperature range of 1250°C, the "ordering-separation" phase transition occurs in the alloy under study.
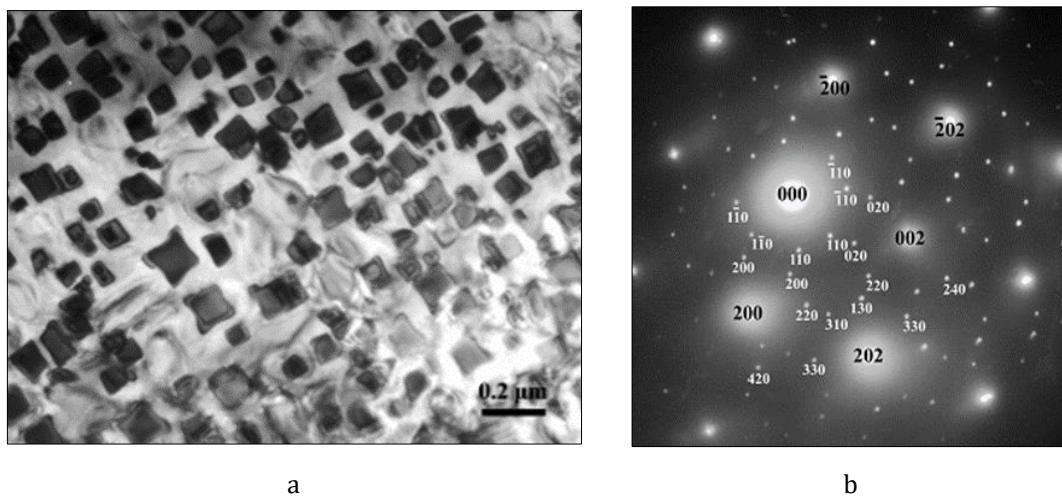

a   b

Figure 2 $Ni_{75}Mo_{25}$ alloy. Quenching from 1000°C. Bright-field image of the microstructure (a); electron diffraction pattern (b)
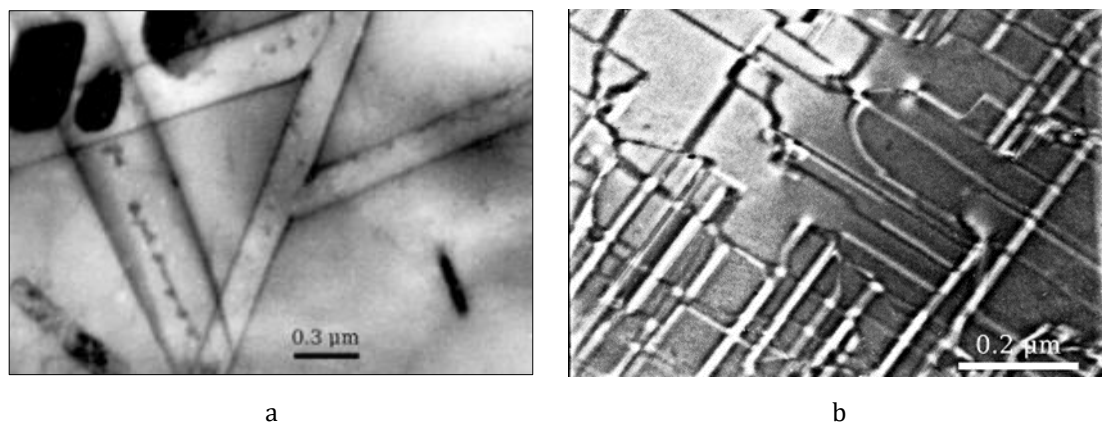

a   b

Figure 3 Electronic domains formed in the microstructure of the Fe-50 % Cr alloy at high-temperature (a) and low-temperature (b) "ordering-separation" phase transition

For the first time, information about the experimental detection of such a phase transition appeared in our work [3]. It investigated Fe-20; 30; 40 and 50 atomic percent of Cr. In all these alloys, the "ordering-separation" transition was found at two temperatures - 550 and 1150°C. It would seem that the transition from plus to minus must pass through zero, and therefore we must obtain a disordered solid solution. However, this does not apply to our phase transition,

the nature of which is electronic. Even the microstructure testifies to this: Figure 3 shows the electronic domains, which we consider being sections of the alloy, within which the sign of the chemical interaction has already changed to the opposite in comparison with neighboring sections, where it remains the same. In this transition, there can be no question of any disordered solid solution as an intermediate phase.*Ni$_{88}$Al$_{12}$ alloy*. Fig. 4a shows the electron diffraction pattern (a) and the dark-field image of the microstructure (b) got from a satellite near the (020) reflection [6]. Such formation of clusters usually shows the ordering of a binary alloy at 1300°C into particles comprising one component each, i.e. about the positive deviation of the investigated alloy from Raoult's law. With a further decrease in temperature (1200, 1000 and 700°C), the sign of the ordering energy changes to the opposite and the chemical compound Ni$_3$Mo (L1$_2$) forms in the alloy (Fig. 5). Thus, we can conclude that in the Ni$_{88}$Al$_{12}$ alloy the "ordering-separation" phase transition occurs in the temperature range of 1200—1300°C.

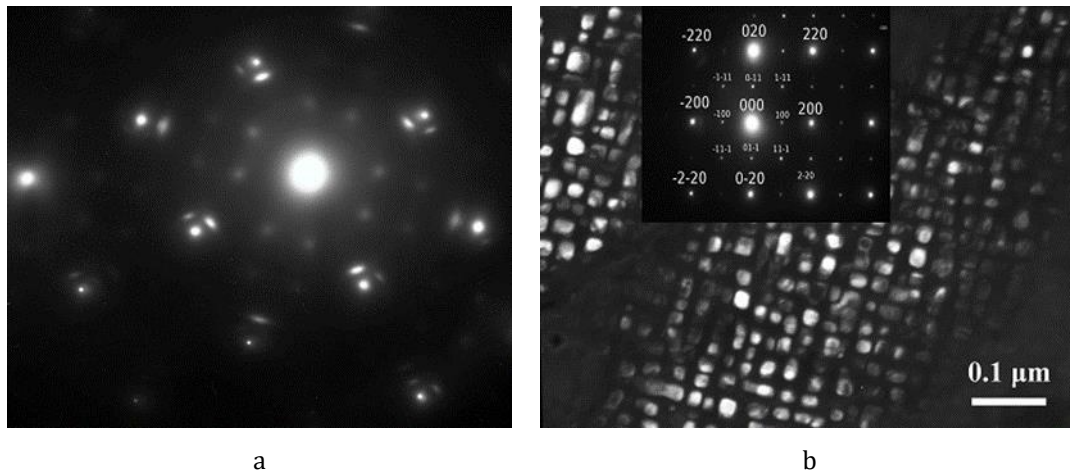a   b

Figure 4 Ni$_{88}$Al$_{12}$ alloy. Quenching from a liquid state (tendency to separation) (a); and quenching from 1000°C: chemical compound Ni$_3$Mo (L1$_2$). The electron diffraction pattern is in the Inset (b)

Ternary Ni$_{53}$Mo$_{35}$Al$_{12}$ alloy. As is known from the electronic theory, in ternary alloys, as in binary ones, the chemical interatomic interaction is pair-wise [7]. Therefore, ternary Laves phases cannot form in a ternary alloy. We have shown that the ABC ternary alloy, while still in the liquid state divided into diffusion micro-pairs A/B, A/C, and B/C. Each diffusion micro-pair occupies its own microscopic area. All phases formed in ternary alloys comprised atoms of no more than two components [8].
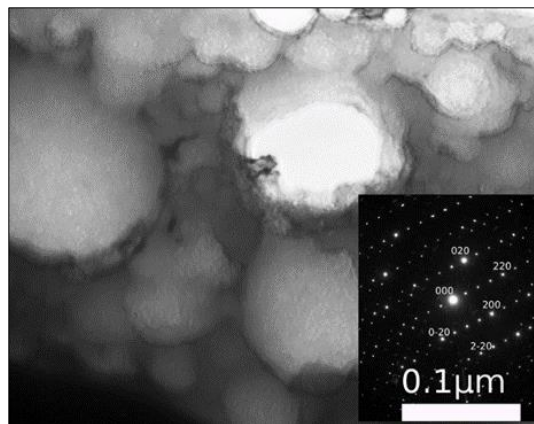

Figure 5 *Ni$_{53}$Mo$_{35}$Al$_{12}$* alloy. Quenching from the liquid state. Light-field image. Accumulations of particles of the Mo3Al phase. Inset: Electron diffraction pattern (the zone axis is close to the direction <001>)

In the Ni$_{53}$Mo$_{35}$Al$_{12}$ alloy, this process has its own characteristics, since the aluminum and Molybdenum atoms form the Mo$_3$Al chemical compound, the melting point of which is about 2600°C. This means that the chemical bond between the Al and Mo atoms is very strong. Therefore, in Fig. 6 we see the microstructure of solid Mo$_3$Al particles in the investigated liquid alloy. This compound forms instantly in the process of melting the charge. The same microstructure as in Fig. 1 is

retained in the alloy under study after its quenching from 1300°C. As was shown above, at a temperature of about 1200°C, the "ordering–separation" transition occurs in binary alloys of the Ni–Mo system [4].

This means that the chemical orientation of the Ni and Mo atoms relative to each other changes sharply from separation to ordering.
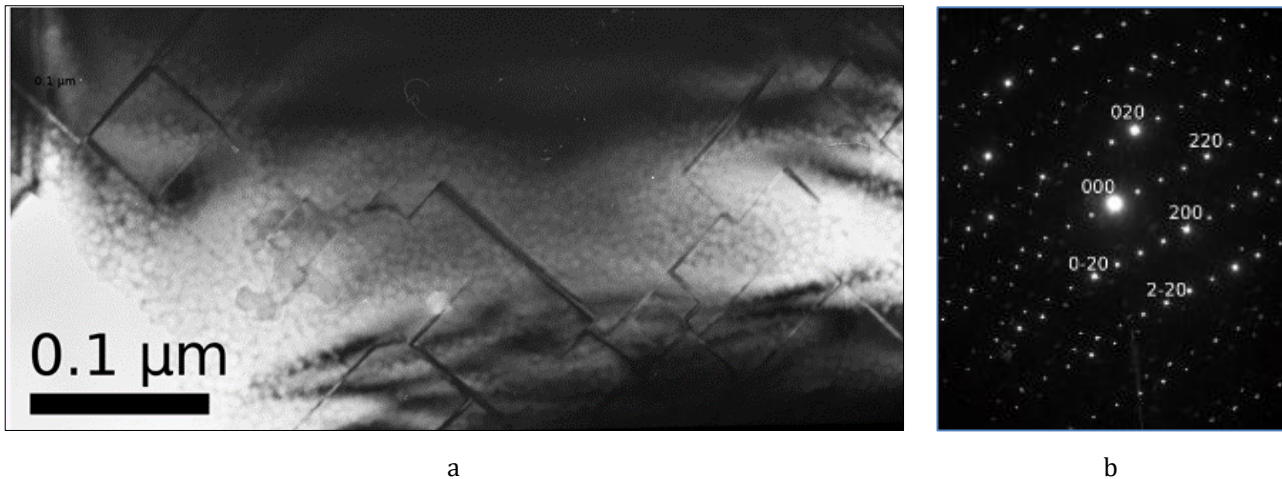

a   b

Figure 6 Ni$_{53}$Mo$_{35}$Al_{12} alloy. Quenching from the liquid state. Another bright-field image of the internal structure of a large Mo$_3$Al particle (a). Electron diffraction pattern (b)

Fig. 6 shows the internal microstructure of a large solid particle Mo$_3$Al in the investigated liquid alloy. When the charge is melted, this compound is formed instantly. Therefore, the matrix cannot form Mo/Ni and Al/Ni diffusion pairs. The alloy under study forms the same microstructure as in Figs. 5 and 6 after being quenched from 1300°C. However, at a temperature of about 1200°C, when the "ordering-separation" phase transition occurs in the Ni-Mo system, the microstructure of the alloy studied changes totally (Fig. 7).

The "ordering-separation" transition, which should occur at 1200-1300°C in Ni/Mo diffusion micro-pair. However, at this moment of heat treatment, such pairs in the ternary alloy studied have not yet formed. Almost all molybdenum is bound as a chemical compound Mo$_3$Al. Therefore, the "ordering-separation" phase transition causes the chemical compound Mo$_3$Al formation. This means that the chemical orientation of the Ni and Mo atoms in the Ni/Mo pair relative to each other sharply changes from separation to ordering. The same thing happens with the atoms in Ni and Al in the micro-pair of the same name (Fig. 7).
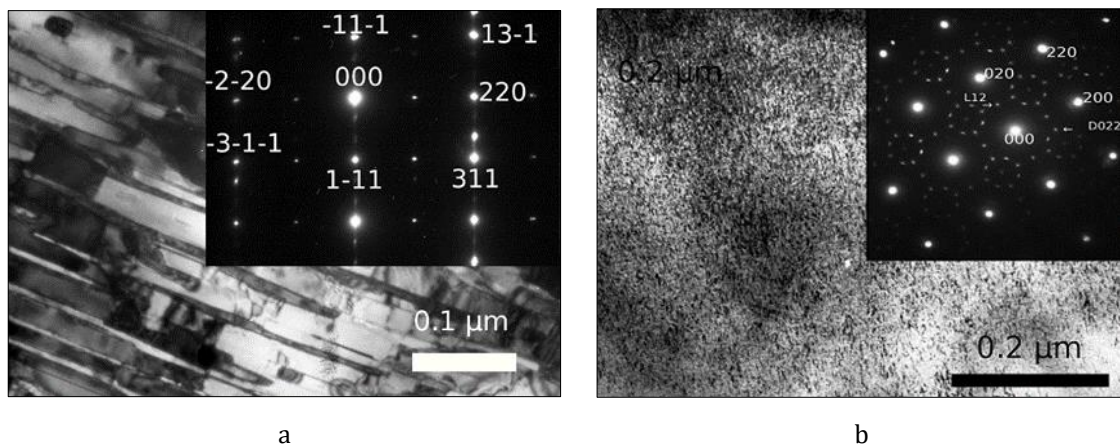

a   b

Figure 7 Alloy Ni$_{53}$Mo$_{35}$Al_{12}. Quenching from 1000°C. Bright-field images of the microstructure of diffusion micro-pairs Ni$_3$Mo (a) and Ni$_3$Al (L1$_2$) (b). Insets show corresponding electron diffraction patterns

When studying the Ni$_{53}$Mo$_{35}$Al_{12} alloy by TEM, we again encountered by the same fact that we discovered earlier in some other ternary alloys: in one region of the foil, we find one binary (or one-component) phase, in another region of the

same foil, a completely different one. This immediately indicates that the alloy is divided into certain sections that differ from each other in composition, i.e. into two different diffusion micro-pairs: Ni/Mo and Ni/Al.

Fig. 7(a, b) shows that a Ni/Mo diffusion micro-pair was formed. Electron diffraction pattern (Inset) shows that the particles seen in this figure are the Ni$_3$Mo phase. These results show that the formation of diffusion micro-pairs can occur not only in the liquid state of the alloy, but also at lower temperatures, when the "ordering-separation" transition has already occurred in the alloy.

In another section of the same foil, we observed a completely different microstructure with the participation of aluminum. Fig. 7b shows the microstructure inside a Ni/Al diffusion micro-pair. The electron diffraction pattern shows that the particles seen in this figure are the Ni$_3$Al (L1$_2$) phase [. Thus, aluminum, freed from the "guardianship" of molybdenum in the chemical compound Mo$_3$Al, forms a new Ni/Al diffusion micro-pair. As we can see, the formation of diffusion micro-pairs can occur not only between a solvent and a dissolved component, but also between two dissolved components; not only in the liquid state of the alloy but also at lower temperatures, when the "ordering-separation" transition occurs in the alloy.

3. Discussion

We have found that, in binary and ternary alloys, there is a chemical interaction between similar and dissimilar atoms. Such interaction occurs both in the liquid and in the solid state of the alloy. This means that we can never receive a disordered solid solution after quenching the alloy from high temperatures, even if we are quenching from the liquid state. This also means that at each temperature, its own microstructure formed, which differs from any other microstructure in the type or fineness of precipitates. It turned out that the final microstructure of the alloy is determined by the temperature of the final heat treatment, i.e. tempering. Heat treatment, such as quenching from the region of "disordered solid solutions", does not affect the final microstructure of the alloy. The electronic transition "ionic bond ↔ covalent bond" and the transition "ordering - phase separation" occurring at the level of the microstructure can be interpreted as the ionic component of the chemical bond which is activated when, with an increase the temperature of the alloy nearest neighbors form. Because of instantaneous proximity, their valence orbitals localize, i.e. the chemical compound A$_x$B$_y$ form. The covalent component of the chemical bond, which is activated for the same reason, causes the two atoms of the dissolved component B to become the nearest neighbors. Because instant proximity, their valence orbitals hybridize, i.e., a cluster forms comprised these two B atoms.

However, our experimental detection of such transitions and their publication in the literature for over 20 years did not lead to any progress in the worldview of metallurgists, and, as a result, to the appearance of works by other authors on this topic. Although, thanks to our experiments, these changes simply suggested themselves, since their introduction would significantly improve the technological properties of all heat-treated parts and products made of metal alloys and more than halve the cost of their heat treatment [9]. It could happen in all the engineering plants in the world. Perhaps the complete lack of interest of metallurgists in these two transitions is explained because, in this case, they would have to change their ideas about alloys and change your attitude towards binary phase diagrams [10]. However, it is difficult to make this step when the entire community of metallurgists thinks alternatively and university professors teach of students alternatively.

Usually, diffusion micro-pairs in multi-component alloys form during their smelting [11]. However, if a chemical compound's melting point is higher than the alloy, we cannot fix these micro-pairs, and compounds will found first (for example, Mo$_3$Al). If lower, then we will find the formation of chemical compounds takes place inside the diffusion micro-pairs.

When a ternary alloy forms three diffusion micro-pairs at once, the uphill diffusion of atoms of each component will be on coming. As a result, the rate of formation of one or another diffusion pair will slow down significantly, and perhaps even drop to zero. Most likely, these streams are separated either in time or in temperature. However, at many number of antiparallel streams, they are completely suppressed. Therefore, the more components an alloy contains, the slower one or other diffusion micro-pairs will form in it.

That is why in high-entropy alloys (HEA), which contain five or more components, diffusion micro-pairs do not form. By performing a straightforward calculation, it becomes apparent that forming 10 diffusion micro-pairs is theoretically possible. Such an amount of pairs determines the identical to number of directions for the diffusion of atoms of each of the components. The absence of diffusion of atoms over long distances means that there are also no chemical interatomic interactions in them. All properties of such alloys change. Apparently, materials with such properties cannot longer be called alloys. In their properties and structure, they are more similar to metal ore. It turns out interesting with

HEA. A person has invested considerable effort and money to receive pure metals from natural metal ore, only to produce synthetic metal ore from these metals later.

4. Conclusion

This article shows metallurgists should come to terms with the existence in nature of such a type of microstructure as diffusion micro-pairs and say goodbye to such a type of microstructure as a disordered solid solution. And the sooner they do this, the less effort and money will be spent all over the world on heat treatment of alloys (water-quenching "to get a disordered solid solution" will disappear), on the design of new and improvement of existing alloys. The phase diagrams of binary alloys will become more informative and truthful (because of the regions of non-existent disordered solid solutions will disappear). We will understand many of the mysteries of nature regarding metallic alloys that nature has hidden from us for many years. However, for this, all of us, alloy specialists, will need to contribute to this work.

The author hopes this article will open the door for everyone to a new era in the science's development of metal alloys, where interatomic chemical interactions are the driving force of all processes occurring in the alloy.

References

[1]   LA Nesbit, DE Laughlin. Solid-state morphological instability of Ni_4Mo precipitates. J Crystal Growth 1981; 51:273-278.

[2]   G Van Tendeloo, S Amelinkx, D De Fontaine. On the nature of the "short-range order" in 1 ½ 0 alloys. Acta Crystallogr. 1985; B41: 281-292.

[3]   Yuri Ustinovshikov. The 'Ordering-Phase Separation' Transition in Alloys. Cambridge Scholars Publishing. Newcastle upon Tyne. UK 2019.

[4]   Y. Ustinovshikov. Changes in electronic structure of metallic alloys at the transition 'ordering-phase-separation'. J Alloys & Compounds 2017; 714: 476-483.

[5]   Y. Ustinovshikov, I. Shabanova. Phase transitions in alloys of the Ni-Mo system. Mat Chemic Phys 2011; 129: 975-980.

[6]   Y. Ustinovshikov. Phase transition 'ordering-phase separation' in the Ni-12 at %Al alloy. J Alloys & Compounds 2012; 528: 141-145.

[7]   Y. Ustinovshikov. Multi-component alloys: Regularities in the formation of microstructures. J Alloys & Compounds 2018; 735: 2298-2302.

[8]   Y. Ustinovshikov. Formation of microstructures responsible for remarkable properties of the Ni- and Co-based superalloys. Acta Mater 2016; 111: 66-74.

[9]   Y. Ustinovshikov. A new paradigm for heat treatment of alloys. J Alloys & Compounds. 2014; 614: 258-263

[10]   Y. Ustinovshikov. Mapping of the transition 'ordering-phase separation' into phase diagrams. J Alloys & Compounds 2017; 691: 713-720.

[11]   Y. Ustinovshikov. Experimental detection of a structure of diffusion micro-pairs in the $Ni_{65}Mo_{20}Cr_{15}$ alloy. J of Mater Science & Engineering A. 2021; 11: 63-70.