Check for updates

(RESEARCH ARTICLE)

A cardinal change in heat treatment of metallic alloys

Yuri Ustinovshikov *

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

Abstract

This article shows that the current heat treatment, based on the misconceptions of the last century, should be. Here we present to the reader the results of experiments obtained on two binary alloys Ni75Mo25 and Ni75Co25, as well as on one ternary alloy Ni50Mo25Co25. These data can be considered similar to the data we presented earlier obtained on alloys of 17 binary systems and 7 ternary alloys. The article gives the experimental evidence that all processes occurring in the metallic alloys during heat treatment owe their origin to interatomic chemical bonds (ionic and covalent) that exist at all temperatures of the condensed state. This means that at each heating temperature of the alloy, its own microstructure forms, which differs from microstructures at other temperatures in the composition or dispersity of the precipitated particles. Here, alloy quenching "from the region of solid solutions" turns out to be an unnecessary operation. The article proposes to exclude it from the technological process, limiting itself only to tempering. This will bring large savings to all machine-building plants around the world.

Keywords: Alloys; Heat Treatment; Transmission Electron Microscopy; Microstructure.

1. Introduction

Heat treatment of metal alloys "quenching + tempering (aging)" has been known for a long time and is currently carried out at almost all machine-building plants in the world. According to the ideas that were finally advertisement the beginning of the last century, in alloys, after quenching from high temperatures, a microstructure of a disordered solid solution forms. Subsequent tempering, carried out at a lower temperature, leads to the fact that the solid solution got after quenching is "supersaturated" and "excess" phases are deposited from it (either by the spinodal mechanism or by the nucleation-growth mechanism). However, in the 60-80s, many authors, for example [1, 2], who used the method of transmission electron microscopy (TEM), found out that the microstructure of quenched binary alloys is not a disordered solution at all, because particles of new phases are found in it after such quenching. This did not fit with the ideas that existed then and now exist about the microstructure of metal alloys. The discussion on this topic, held by many journals, could not explain this phenomenon.

Only in 1996, when we [3] discovered particles of chromium atoms in alloys of the Fe-Cr system after quenching from temperatures 1200 - 1450°C, it became clear what was the reason for this a discrepancy between theory and experiment. The existing ideas formed based on X-ray phase analysis data, which could not detect particles of new phases that had dimensions smaller than the regions of coherent X-ray scattering. While the TEM method does not have such a drawback, and therefore detects dispersed particles of new phases (as well as clusters) formed at the heating temperatures of the alloy for quenching. Comparing the microstructures formed at temperatures above 1150°C (particles of chromium atoms), 600 - 830°C (σ-phase) and below 550°C (clusters of chromium atoms), the authors [3] concluded that the interatomic chemical interaction changes its sign from the tendency to ordering (-) to the tendency

* Corresponding author: Yuri Ustinovshikov

to phase separation (+), and vice versa when the heating temperature of the alloy is changes. The authors [3] called this phase transition "ordering-separation".

Based on the experimental results got with the help of X-ray analysis, the now existing theory of heat treatment of alloys uses the thesis that chemical interatomic interactions in alloys quenched from high temperatures are absent. They "appear" only at tempering temperatures, moreover is not clear for what reason. However, our experimental studies of alloys quenched from the liquid state have shown that chemical bonds exist in the liquid state of an alloy [5, 6]. This leaves no chance for the further existence of both the theories of the nucleation of new phases and the theory of heat treatment of alloys.

In this article, we will use two examples to show what the "ordering-phase separation" phase transition presents, which occurs in binary and ternary alloys at any well-defined heating temperature and changes the sign of the chemical interaction between two neighboring atoms.

Since such a transition is characteristic of each pair of neighboring atoms, this means that it presents one of the key factors that form the microstructure of alloys, and therefore we must consider its role in the heat treatment of alloys. This article shows what happens in alloys during their heat treatment and, therefore, why there need to quench the alloy from the high-temperature region of the so-called "disordered" solid solution.

2. Experimental Method

I quenched two binary ($Ni_{75}Mo_{25}$ and $Ni_{75}Co_{25}$) and one a ternary ($Ni_{50}Mo_{25}Co_{25}$) alloys under study from the liquid state. Here, a small portion of liquid metal was poured from the crucible directly into water. We quenched also these alloys in water from a high temperature (1300°C) of solid state, which is usually used to get a "disordered solid solution" microstructure. After each heat treatment at more low temperature, I also cooled the alloys in water in order to preserve the microstructure of the alloy at the temperature of tempering. The foils were made from the castings and then the microstructure was studied on an EM-125 transmission electron microscope according to the standard method.

3. Results

3.1. Alloy Ni₇₅Mo₂₅

For those who had to deal with the problem of pouring liquid Ni-Mo alloys, it seemed surprising that its very low fluidity of that alloy even when it was overheated by 200°C above the solidus line. Now it becomes clear what we connect this with the phenomenon. The Fig. 1a shows dark rounded particles of molybdenum, which formed at the melting of the charge. This means that even at temperatures of the liquid state, the alloy under study has the tendency to phase separation. Indeed, we observe on the electron diffraction pattern a system of additional reflections {1 1½ 0} as four symmetrical pairs (Fig. 1b). These reflections formed near each of the fundamental reflections {110} and {200}. Quenching of the same alloy from 1300°C, i.e. temperature, at which "a disordered solid solution" takes place, gives the same picture.
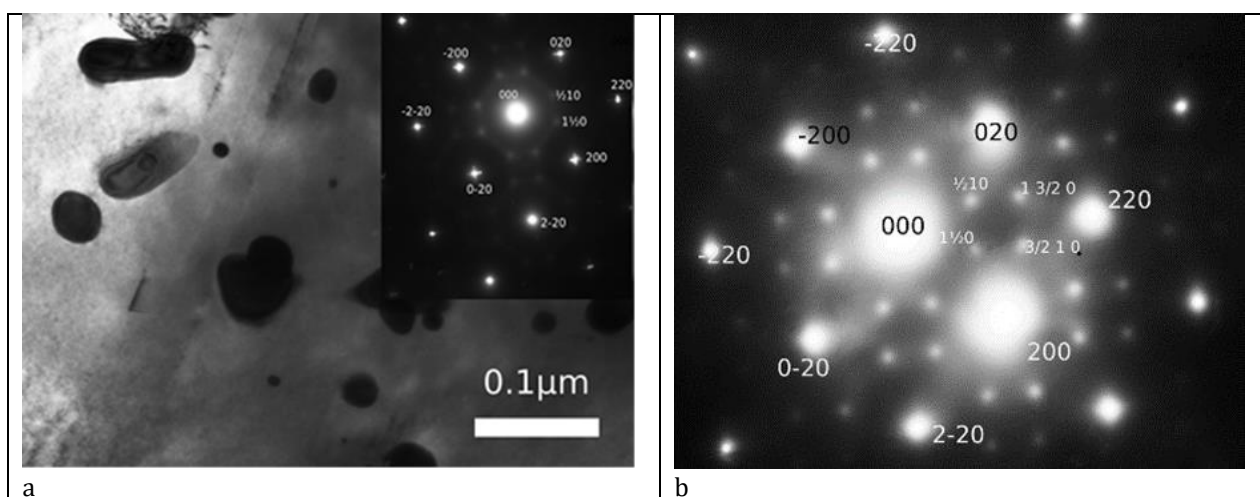

Figure 1 Alloy Ni75Mo25. Quenching into water from a liquid state. (a) bright-field image; (b) electron diffraction pattern
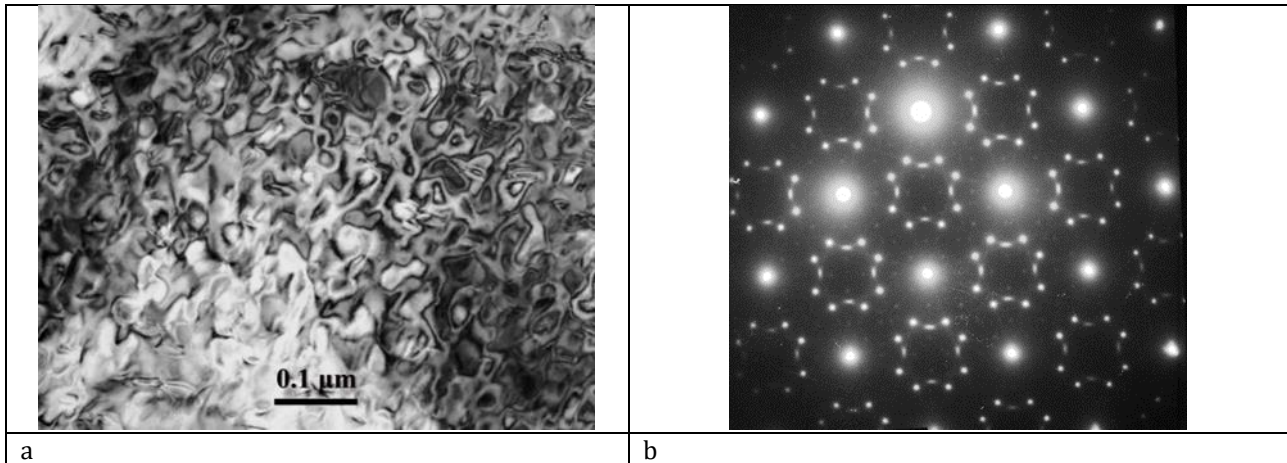
Figure 2 Alloy $Ni_{75}Mo_{25}$. Quenching from 800° C. (a) bright-field image; (b) electron diffraction pattern**.**

Quenching of the alloy from 800°C leads to the disappearance of the system of additional reflections {1 1½ 0}. Fig. 2 shows the microstructure and electron diffraction pattern of the $Ni_{75}Mo_{25}$ alloy, which differs from the previous one. The electron diffraction pattern was deciphered by us as comprising a combination of two systems of reflections: a system of reflections from particles of a chemical compound with a structure of the $D1_{\alpha}$ type and a system of diffuse arcs that belong to the orthorhombic body-centered Ni_2Mo phase (of the Pt_2Mo type). From a comparison of structural data on Figs. 1 and 2, below 1200°C, the phase transition "separation - ordering" occurs in the alloy, i.e. the sign of the chemical interaction between Ni and Mo atoms changes from plus to minus [7].

The detection of particles of molybdenum atoms in the liquid state of the alloy and the existence of the "ordering - separation" phase transition at lower temperatures allows us to conclude that chemical bonds take place at both solid and liquid state of the alloys. This means that no amount of quenching will allow us to get a disordered (i.e., ideal) solid solution. This also means that, finally, materials science will have to agree with thermodynamics and recognize the indisputable fact that ideal solid solutions do not exist in nature. In addition, to abandon the rudiment of past years - double heat treatment "quenching + tempering". Leave yourself, please, only tempering at the same temperature at which you carried it out earlier after quenching for "solid solution", and you will get the same microstructure.

3.2. $Ni_{75}Co_{25}$ alloy

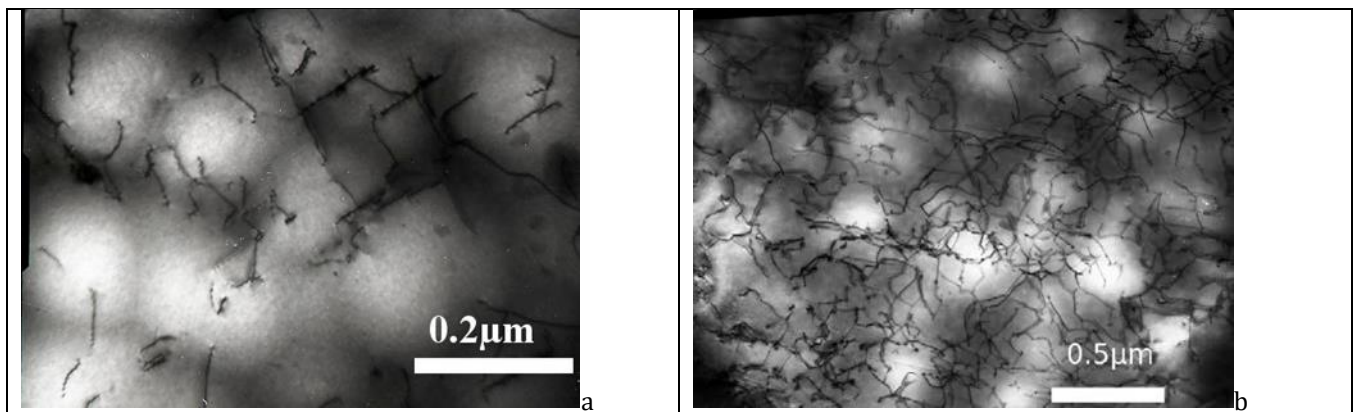**Figure 3** $Ni_{75}Co_{25}$ alloy. Microstructure (a) after water quenching from liquid state and (b) at 800°C (absorption contrast).

Simplicity characterizes the phase diagram of the Ni-Co system: for all compositions, at any temperature, only the disordered solid solution is shown in the diagram. No phase transformations besides the allotropic α-Co$\leftrightarrow$ ϵ-Co occur in the system. Clearly, that is why the literature on structural transformations occurring in alloys of this system is scarce. 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 only the disordered solid solution form. For example, in the $Ni_{75}Co_{25}$ alloy, after quenching from a liquid state, a microstructure was detected

which comprised round bright spots with diffuse edges and dimensions of the order of 0.1-0.2 micron located on a dark background (Fig.3)[8].
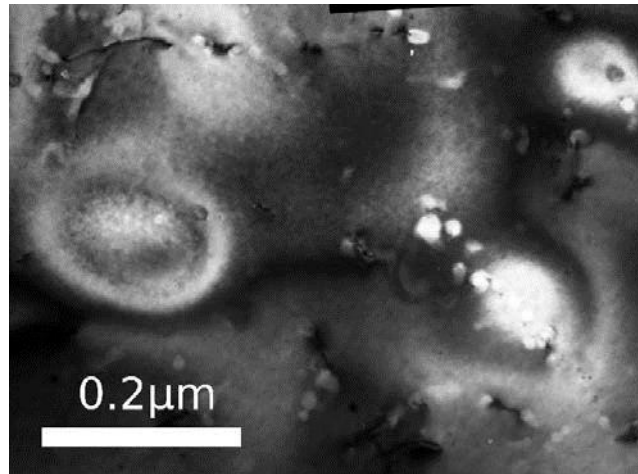

Figure 4. $Ni_{75}Co_{25}$ alloy after aging at 500°C. Bright-field image of the microstructure: Co clusters (absorption contrast); particles of a second phase (diffraction contrast).

Such spots are observed due to electron microscopic absorption contrast (not diffraction contrast) arising 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) and, therefore, more bright contrast in the electron microscopic image. A similar microstructure is observed after a heat treatment of the alloy at 1000 - 600°C [8]. After aging the alloy at 500°C, one can observe certain microscopic sites of the foil, where both microstructures of ordering (bright particles of a small size) and phase separation (dissolving round Co clusters) coexist at the same time (Fig. 4).

Existence on common image 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 the Ni-Co system does not occur simultaneously at all points of the alloy. Therefore, based on the obtained experimental results of TEM, in such alloys, one can evaluate not the temperature, but the range of the temperatures, in which the energy of the chemical interaction changes its sign: such a range of transition temperatures in the system of Ni-Co is between 500 - 550°C.

3.3. Alloy $Ni_{50}Mo_{25}Co_{25}$.

When asked what diffusion micro-pairs is in ternary alloys and why they form, it has been cited as an example the $Ni_{50}Mo_{25}Co_{25}$ alloy, the composition of which was chosen so that the sum of atoms of the dissolved components was equal to the number of solvent atoms. The quenching of such an alloy from a liquid state into water leads to the fact that only two diffusion micro-pairs, Ni/Mo and Ni/Co, can form in this alloy. Figure 5 (a, b) shows the microstructures got after quenching the alloy under study from the liquid state. On one section of the foil (Fig. 5a), we see particles of Mo atoms, and on the inset, we see an electron diffraction pattern with streaks issues from the fundamental reflections. Such streaks indicate the distortion of the lattice inside the Ni/Mo diffusion micro-pair by precipitating Mo particles. It should be noted that some additional reflections {1 1½ 0} still remain on the electron diffraction pattern, which we observed in the electron diffraction pattern of the $Ni_{75}Mo_{25}$ binary alloy (Fig. 1b).

Round white spots with diffuse edges and sizes of about 0.1–0.2 microns are observed against a dark background forming because of absorption contrast from clusters of atoms of the other dissolved component, i.e. cobalt (Fig. 3a). Other elements of the microstructure, such as dislocations, are observed in the micrograph because of the diffraction contrast. With a decrease in the heat treatment temperature to 600° C, the "separation-ordering" phase transition begins ithe alloy [8]. Fig. 3b shows this transition. Clusters of Co atoms dissolve (absorption contrast) and small light particles of the chemical compound Ni_3Co form in their place (diffraction contrast).
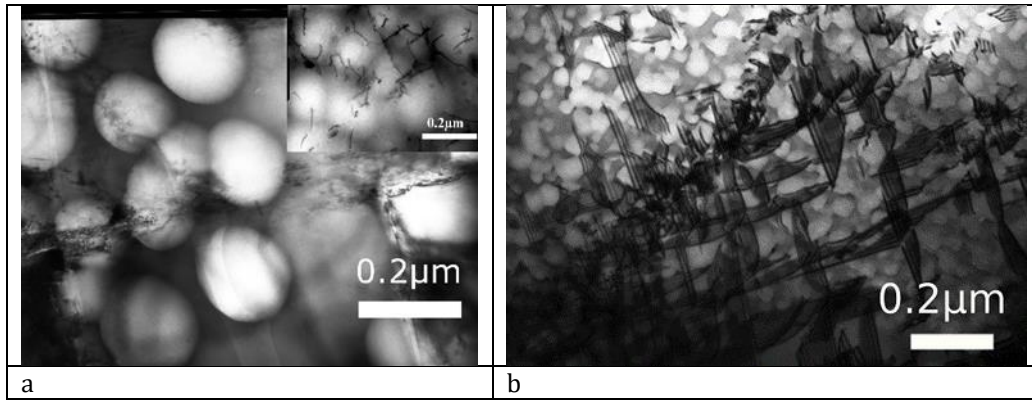
Figure 5 (a) Ni₅₀Mo₂₅Co₂₅ alloy. Ni/Co diffusion micro-pair. Quenching from 1300°C. Absorption contrast. Inset: The same microstructure in the binary Ni₃Co alloy after the same heat treatment (b) Ni₅₀Mo₂₅Co₂₅ alloy. Diffusion micro-pair Ni/Co. Heat treatment temperature - 500°C. Two-lower microstructure. Low layer - clusters of cobalt atoms. Absorption contrast. Top layer- stacking faults.

4. Discussion

At the beginning of this article, we provided experimental evidence using the example of two binary and one ternary alloy, what the "ordering-separation" phase transition is, the electronic transition "ionic bond-covalent bond", what diffusion micro-pairs are. I made it to be done in order to show readers that my words about these physical and chemical processes and these structures are not "the absurd work of a people's scientist," as the reviewers of my articles write about me. I invite readers, without going into my above-stated theory of alloys, to check in practice heat treatment which of us is right, and to conduct a small experiment in factory and/or laboratory conditions.

Heat treatment of metal alloys "quenching + tempering (aging)" has been known for a very long time and is currently carried out at almost all machine-building plants in the world. According to existing concepts, after quenching at high temperatures, a microstructure of a disordered solid solution forms in alloys. Subsequent tempering, carried out at a lower temperature, leads to the fact that the solid solution comprising quenching becomes "supersaturated" and "excess" phases are released from it (either by the spinodal mechanism or by the nucleation-growth mechanism).

In contrast to the existing theory of heat treatment, in alloys at all temperatures, there is a chemical interaction between similar (covalent bond) and dissimilar (ionic bond) atoms. Such an interaction exists both in the liquid and in the solid state of the alloy. This means that we can never get a disordered solid solution after quenching the alloy from high temperatures, even if we will quench from the liquid state. This also means that at each temperature forms own microstructure, which distinguished from any other microstructure by type or dispersity of precipitates. The final microstructure of an alloy is determined by the temperature of the final heat treatment, i.e. tempering. The heat treatment, such as quenching from region "disordered solid solutions", does not affect the final microstructure of the alloy. In parallel with these recommendations, the article discuss a process of nucleation of new phases by the example of one of binary and one of ternary alloys occurs under conditions of the existence in alloys of a pair chemical interaction between atoms. This discussion shows that the processes occurring in alloys differ essentially from those described in textbooks. Thus, the electronic transition "ionic bond ↔ covalent bond" and the occurring at the microstructure level transition "ordering—phase separation" can be interpreted by proceeding as follows: The ionic component of the chemical bond is activated when, with an increase in the alloy's temperature, and, therefore, with an acceleration of diffusion, A and B atoms become the nearest neighbors.

Because of this instantaneous proximity, their valence orbitals are localized, i.e. the chemical compound A_xB_y forms. 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 of this instantaneous proximity, their valence orbitals hybridize, i.e. a cluster forms comprising these two atoms B.

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. In addition, 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. 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 very many ideas about alloys. Moreover, it is difficult to take this step when the entire community of metallurgists thinks differently and university professors teach of students differently.

In the experimental part of the article, we presented the reader with the results of our studies of binary and ternary substitution alloys. The cardinal difference between our research (TEM) and those works (XRD) on the basis of which the current theory of alloys was built is immediately striking. Now that it has become clear to us that the X-ray method is not suitable for these purposes, and that those authors who used the TEM method in the discussion of 1960-80 were right, there is no doubt that our ideas about the existence of some disordered solid solution in alloys should go down in the history of alloy science. If this is really the case, then any quenching in water from any heating temperature of the alloy should lead to formation of the microstructure that formed in the alloy at this temperature. It has been known that almost every machine-building plant in the world uses "double" heat treatment of alloys - quenching from the region of a "disordered" solid solution + tempering at low temperatures. Select a few parts from the batch intended for quenching and simply do not make it. Compare their microstructure and properties with those parts that have been as-quenched. I should note that for the purity of the experiment, samples (or parts) that have been quenched should be cooled in water to fix the microstructure characteristic of your tempering temperature. Even if you are not strong in alloy theory, you will be able to deduce whether you need that quenching to get a "disordered solid solution" before tempering.

5. 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, metallurgical scientists, 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. They are the cause for both the nucleation of new phases and structures in the liquid state of an alloy and changing phases and structures during the "ordering- separation" phase transition.

References

[1]   J Higgins, RB Nicholson, P. Wilkes, Precipitation in iron-beryllium system, Acta metallurgica 1974; 22: 201-217.

[2]   DE Laughlin, JW Cahn, Spinodal decomposition in age-hardening Cu-Ti alloys, Acta metallurgica 1975; 23: 329-339.

[3]   Y. Ustinovshikov, M. Shirobokova, B. Pushkarev. A structural study of the Fe-Cr system alloys. Acta Materialia 1996; 44: 5021-5032.

[4]   Y. Ustinovshikov. The "Ordering – Phase Separation" Transition in Alloys, Monograph 2019, Cambridge Scholar Publishing, Great Britain.

[5]   Y. Ustinovshikov. Nucleation of new phases in alloy: a long way to true, Adv. Mater. Phys. Chem. 2022; 12: 10, 1-20.

[6]   Y. Ustinovshikov. Formation of diffusion micro-pairs in the $Ni_{68}Mo_{20}Al_{12}$ alloy, Materials Letters 2022; Vol. 326; 1 Nov 2022; 132936.

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

[8]   Y. Ustinovshikov, I. Shabanova, N. Lomova. TEM study of the 'ordering-phase separation' transition in Ni-Co alloys. Journal Advanced Microscopy Researches 2013; 8: 276-282.

[9]   Y. Ustinovshikov. Phase transformations in alloys of the Ni-Cr system, Mater. Chem Phys 2015; 165: 14-18.

[10]   Y. Ustinovshikov. Phase and structural transformations in the $Ni_{65}Mo_{20}Cr_{15}$ alloys at changing the temperature of heat treatment. J. Alloys & Compounds. 2014; 588: 470-473.