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Experimental Detection of Diffusion Micro-pairs in a Structure of the $Ni_{65}Mo_{20}Cr_{15}$ Alloy

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Abstract: The article raises the question of how diffusion pairs A/B, A/C, and B/C form in three-component alloys ABC. This issue solves experimentally using the TEM (transmission electron microscopy) method and $Ni_{65}Mo_{20}Cr_{15}$ alloy. The quenching of this alloy from a liquid showed that such pairs form in the liquid state of the alloy, and as the quenching temperature decreases, particles of the new phases form inside them. We concluded that not a disordered solid solution after high-temperature quenching "from a region of disordered solid solution at the phase diagrams" is the starting point for the formation of a low-temperature microstructure, but a liquid state, into which the alloy passes during its melting. The author hopes the results got will lead to a reorientation of our ideas about alloys and will change a lot both in the theory of alloys and in the technology of their manufacture.

Key words: TEM, superalloys, new phase formation, "ordering-phase separation" transition, transition "ionic bond ↔ covalent bond".

1. Introduction

Everyone has known for a long time that the solubility of a salt in water increases with increasing temperature, and vice versa. A long time ago, someone working with metal alloys "guessed" that the same thing can happen to alloys. Since then, the entire philosophy of Materials Science has been built on this postulate: with an increase in temperature, the solubility of atoms of alloying components in the solvent lattice increases, and vice versa. This means that chemical interactions between the atoms of the components in the alloy play a secondary role. In textbooks for students, atoms in a crystal lattice are depicted as chemically non-interacting balls. In all processes occurring in alloys, the main role is played by the difference in the sizes of atoms. All heat treatment and all phase diagrams are also based on the same postulate. It will soon be a hundred years since materials scientists live in this surreal world.

At the beginning of the twentieth century, the method of X-ray diffraction was used, turning out that it fully confirms the ideas mentioned above: In alloys quenched from high temperatures of the solid-state, the precipitates of the second phase were absent (disordered solid solution), and in those subjected to low-temperature heat treatment, particles of the second phase were precipitated. Apparently, many have forgotten that at one time A. Guinier warned us it is unnecessary to idealize X-ray phase analysis as a method for detecting highly dispersed particles of a new phase since its resolution is limited by the size of the regions of coherent scattering of X-rays. Indeed, starting in the 60s, when TEM (transmission electron microscopy) had become the subject of considerable use in materials science, many researchers were surprised that after quenching from the "solid solution region" they found highly dispersed particles of the second phase instead of a disordered solid solution. The journal *Acta Metallurgica*, together with other journals, held a discussion to find out how this contradiction between theory and experiment could be explained. However, none of the participants in this discussion could explain this phenomenon, and the discussion ended there.

The first work in which it was found why our ideas

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about alloys were too far from reality was published in 1996 [1]. The authors, studying the microstructure of Fe-Cr alloys by the TEM method, showed that at a certain temperature in these alloys, an amazing phenomenon for those times occurs: the sign of the chemical interaction between dissimilar atoms changes with temperature. As a result, the microstructure of the alloy also changes at this transition temperature. This phase transition was named “ordering-phase separation”. To date, 17 binary systems [2] have been investigated. Such a transition in these alloys was found at heating temperatures that are quite specific for each alloy. In various binary systems, there could be two or even three such transition temperatures. It was found that the reason for this phase transition is the electronic transition “ionic bond ↔ covalent bond” [3].

But the greatest interest is presented by studies of multi-component alloys. Under the conditions of the existence of pair interactions in metallic 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 three-component alloy, it is difficult to imagine how this can happen, unless we assume that particles of three-component phases form in them. Apparently, this is precisely why many researchers concluded that particles of three-component Laves phases should be precipitated in ternary alloys. However, this assumption about the existence of three-component phases contradicts the theory of pair interaction between two nearest neighbors, which follows from the electronic theory of alloys.

So, it faced us with the question: how could two-component phases form from a disordered solution in a three-component alloy? When the binary alloy is in a liquid state, the atoms of each of the components, because of the very high diffusion rate, easily reach the equilibrium distribution of the chemical potential over the entire volume of the alloy. This means that the tendency to phase separation gives rise to AA and BB diffusion pairs but the tendency to ordering—gives to AB pairs. In a three-component ABC alloy, when it melts, the diffusion rate is also very high. This means that it can also form microscopic sites in which diffusion pairs A/B, A/C, or B/C (if there is a tendency to ordering in them) form. The diffusion pairs A/A, B/B, and C/C form when the tendency to phase separation takes place. Particles of chemical compounds and particles of atoms of dissolved components form in both solid and liquid states of the alloy. It shows that the aggregation state of the alloy is determined only by the metal bond [2].

Thus, the reason for the formation of diffusion pairs is precisely the chemical interatomic interactions, and it is these interactions that exist both in the solid and in the liquid state of the alloy. When the alloy melts, the ionic and covalent components of the interatomic chemical bond do not change, but only the metal component of the interatomic bond changes. The further the process of separation into diffusion pairs goes, the more difficult it is for any atom to create “its own” diffusion pair, since the number of unpaired atoms in alloy decreases. Therefore, the more components in the alloy, the more difficult it is to reach the equilibrium structure at any temperature. You can get a chaotic mixture of atoms with an incomprehensible structure. Now that the mechanism of microstructure formation in multi-component alloys has become known in one form or another, we can say that a miracle will not happen, no matter how many components we add to the high-entropy alloy.

All these explanations are like fantasy since we are used to believing that there are no chemical bonds in alloys at high temperatures. It is one thing to talk about the microstructure visible in the photographs and comment on it, and it is quite another thing to talk about a structure that no one has seen yet, but which, according to the logic of the phase formation process, must exist. This article is devoted to precisely experimental detection of such a structural formation as a diffusion pair in the alloy under study, $Ni_{65}Mo_{20}Cr_{15}$.

2. Experimental Procedure

In the presented article, an alloy of the composition $Ni_{65}Mo_{20}Cr_{15}$ was investigated. The alloy was chosen from considerations that simplify the interpretation of the results as much as possible: only diffusion pairs Ni/Mo and Ni/Cr can form in it, and a Mo/Cr pair can hardly be formed. To answer the question of what structure the alloy has in the liquid state, the studied alloys were quenched by pouring out a small amount of liquid metal directly from the ladle 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 precisely liquid state at the instant a liquid metal is in contact with the water. Blanks for thin foils were cut from the castings and foils were made using standard procedure. The study was carried out on an EM-125 transmission electron microscope at an accelerating voltage of 100 kV using standard procedure.

3. Results and Discussion

Since molybdenum is a fairly refractory metal, the formation of particles of Mo atoms in the alloy under study occurs at the maximum temperature that is reached in the melting zone of the furnace. That is why in Fig. 1, we observe a fully formed microstructure with molybdenum particles, which persist at temperatures down to 1,300 °C. This means that we cannot observe how the diffusion pair Ni/Mo forms. Electron microscopic analysis 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 pair, single-component particles of molybdenum atoms are observed, in the Ni/Cr diffusion pair—two-component clusters chromium atoms. In the Ni/Mo diffusion pair, below 1,250 °C, the tendency to phase separation is substituted for the tendency to ordering (the “Ordering-phase separation” transition), and the particles of Mo atoms dissolve. Obviously, only the Ni/Cr diffusion pair remains for study.

Before considering the formation of Ni/Cr diffusion pairs in the ternary alloy $Ni_{65}Mo_{20}Cr_{15}$, we present the results we got earlier on binary alloys of the nickel-chromium system. We must do this in order to compare the microstructures formed in the binary alloy Ni_2Cr and in the diffusion pair Ni/Cr of the ternary alloy ABC after the same heat treatment.

After quenching the alloys of the Ni-Cr system from 1,450 °C in water, we find two types of particles in the microstructure. In alloy $Ni_{40}Cr_{60}$, the composition

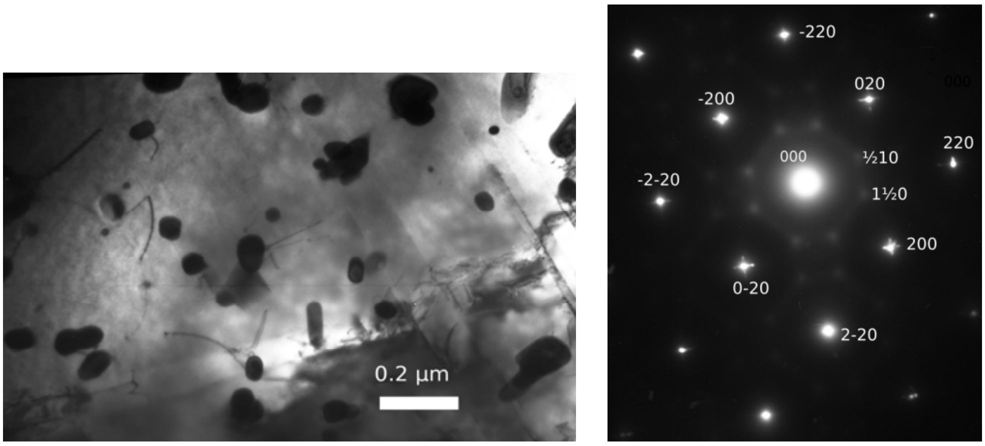
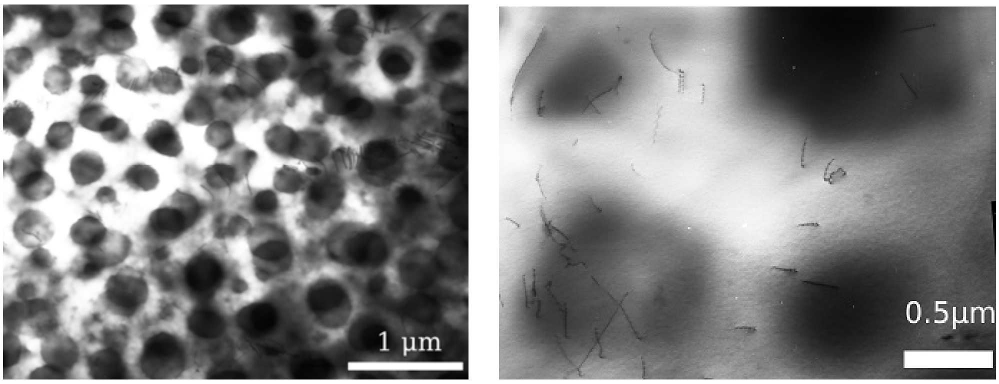
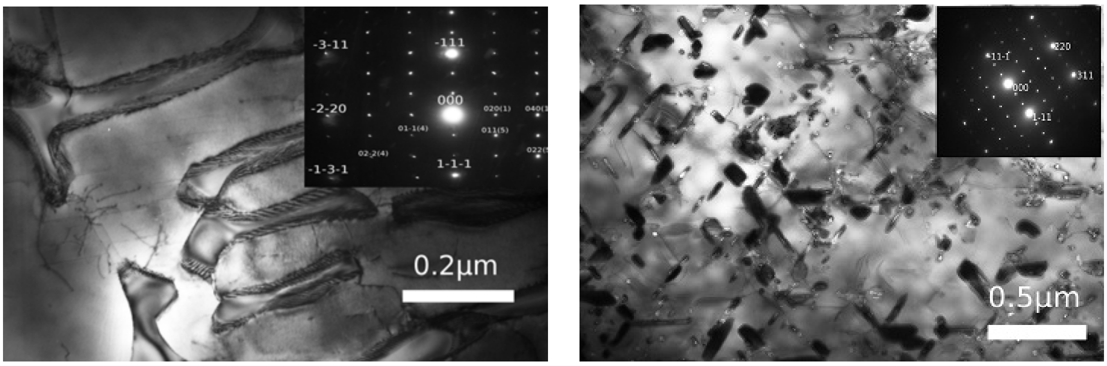


Fig. 1 Ni/Mo diffusion pair. (a) electron diffraction pattern, (b) water-quenching from 1,450 °C.



(a) (b)

Fig. 2 Alloy $Ni_{40}Cr_{60}$ in the nickel-chromium system. Quenching in water from a liquid state (a) and from 550 °C (b). Clusters (particles) of chromium atoms (the tendency to phase separation) [4].



(a) (b)

Fig. 3 Alloy $Ni_{68}Cr_{32}$. Quenching in water from a liquid state (a) and from 550 °C (b). Insets: Electron diffraction pattern shows that the Cr_2Ni phase particles were formed [4].

of which is quite close to the composition of the Ni/Cr diffusion pair of the alloy under study (especially in the liquid state, when molybdenum is present as the form of particles in Fig. 1) there are round dark clusters of chromium atoms (with blurred edges), because of the tendency to phase separation (Fig. 2). In the alloy $Ni_{68}Cr_{32}$, large elongated particles of the chemical compound Ni_2Cr with boundaries comprising a dense network of dislocations (Fig. 3) form, because of the tendency towards ordering. These results allowed the author [4] to conclude that the "ordering–phase separation" transition occurs not only when the temperature of the alloy changes, but also when its composition changes.

In Ni/Cr diffusion pair with chromium content, close to the $Ni_{40}Cr_{60}$ alloy under study, the tendency to phase separation takes place at all heating temperatures.

Figs. 2 and 3 show that in the entire temperature range of alloys $Ni_{40}Cr_{60}$ and $Ni_{68}Cr_{32}$ no transitions "ordering-phase separation" occur. This means that the line of such a transition will be between these compositions. Such a line was constructed using alloys of three intermediate compositions [4].

In alloy $Ni_{46}Cr_{54}$, we could fix the boundary between the two types of microstructures—the cluster structure formed because of the tendency to phase separation (Fig. 2) and particles of the chemical compound Ni_2Cr formed because of the tendency to ordering (Fig. 3). In contrast to alloys of the Fe-Cr system, where regions of disordered solid solution are between these types of microstructures [5], in the Ni-Cr system, microstructures of the ordering and phase separation regions are in contact (Fig. 4). Apparently, at temperatures of the liquid state, the boundary between the Ni-Cr alloy compositions in which there is a tendency to ordering and in which there is a tendency to phase separation passes somewhere between the intermediate compositions [4].

Detection of a microstructure that is not a disordered solid solution after quenching from a liquid state (Figs. 1-4) may show that chemical interactions exist in both crystalline and liquid states. This does not contradict the electronic theory of alloys. The invoking of the electronic theory of alloys in explaining this transition (the "ordering-phase separation" transition [2], the electronic transition "ionic bond-covalent bond" [3]), apparently, should have completely changed the existing scientific concepts in Materials Science. However, so far this has not happened.

It is easy for us to understand how, under the conditions of the existence of pair chemical interactions, the process of the formation of the chemical compounds Ni_2Cr (at the tendency to ordering) or clusters of atoms Cr (at the tendency to phase separation) in binary alloys. When such a process occurs in a three-component alloy, it is to recognize hard enough, unless one assumes that a three-component chemical compound forms. Apparently, this is precisely the reason many researchers concluded that in ternary alloys there is a possibility of precipitation of three-component Laves phases, although the electronic theory of alloys does not allow this possibility.

Let us consider what processes occur in the studied alloy in those micro-volumes that are occupied by Ni/Cr diffusion pairs. After quenching the alloy from 1,550 ° C, clusters of chromium atoms are observed in diffusion pairs Ni/Cr as concentration waves of absorption contrast, which emanate from a certain light-colored center in a thin foil, forming apparently, in the moment of contact of the liquid alloy with water (Fig. 5).

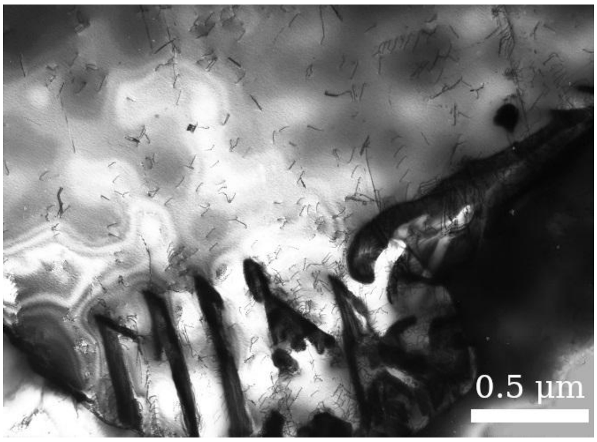


Fig. 4 Alloy $Ni_{46}Cr_{54}$. Quenching in water from a liquid state (1,450 °C).

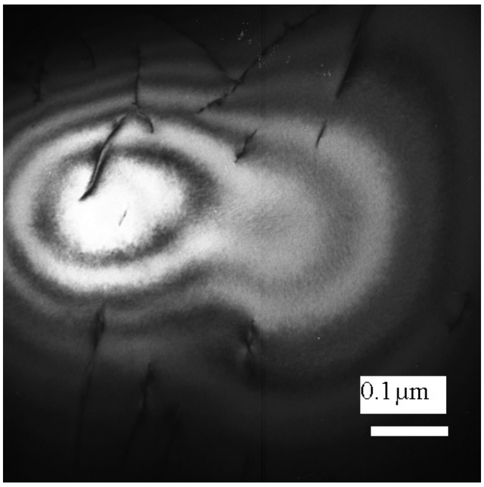


Fig. 5 Ni/Cr diffusion pair. Water-quenching from 1,550 °C.

With a decrease in the quenching temperature to 1,450 ° C, the entire surface area of the foil in the Ni/Cr diffusion pair turns out to be scarred by such waves of contrast, as in Fig. 6. Such concentration inhomogeneity forms because of the existence of a tendency to phase separation. It is possible to estimate the diffusion pair volume by the number of contrast waves that fit into the Ni/Cr diffusion pair in Fig. 3. This value reaches several tens of microns.

Now that we have made sure that diffusion pairs really exist in alloys and that it is with their formation in a liquid alloy that the entire process of forming the microstructure of the alloy begins, it is time to deal with the terminology of this new element of the microstructure. It has been known that the term "diffusion pairs" already exists in Materials Science and is used to study the parameters of interdiffusion of

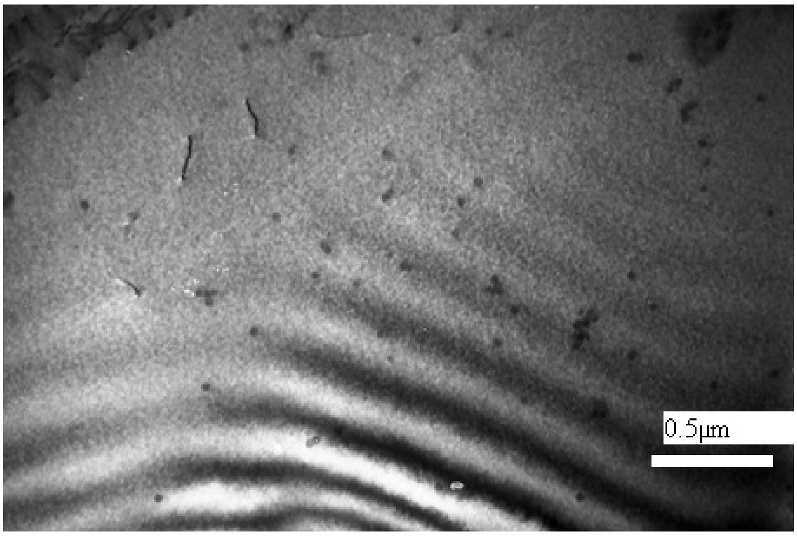
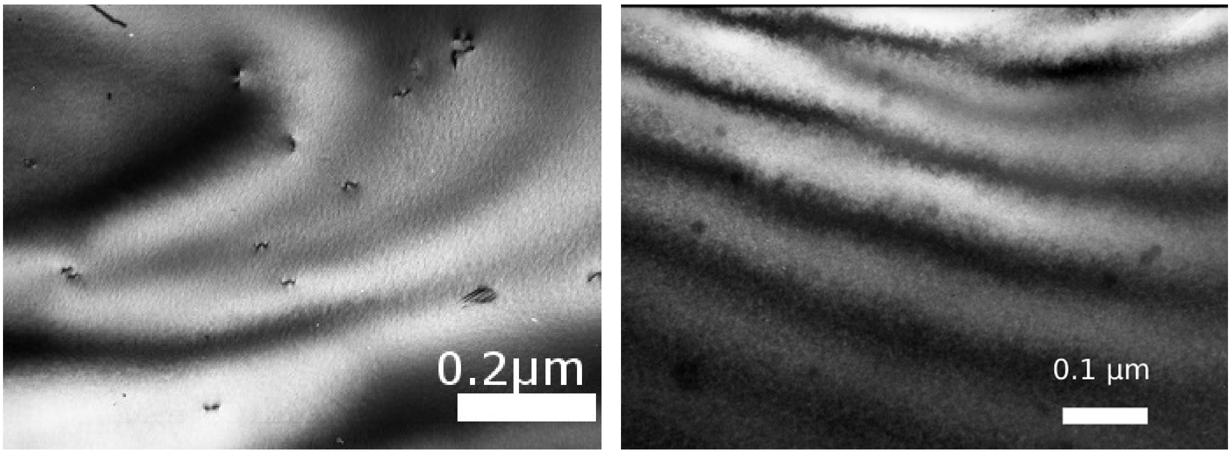


Fig. 6 Ni/Cr diffusion micro-pair. Water-quenching from 1,450 °C.



(a) (b)

Fig. 7 (a) Ni/Cr diffusion micro-pair, (b) water-quenching from 1,300 °C.

different atoms at different temperatures. Therefore, in our case, we propose to use the term "diffusion micro-pairs", which is the best fit for this element of the microstructure.

Fig. 7 shows the microstructure of Ni/Cr diffusion micro-pair after alloy quenching from 1,300 °C. Comparing the microstructure in Figs. 2-4, it can be concluded that with a decrease in the quenching temperature the Cr-clusters microstructure spreads over the volume of the diffusion micro-pair.

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 is divided into microscopic regions in which either only the particles of molybdenum atoms are observed (Fig. 1), or only clusters of chromium atoms (Figs. 5-7). Obviously, there is simply no other explanation for this. 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.

Fig. 8 shows a hypothetical image of diffusion pairs and corresponding phases in a three-component alloy studied at temperatures of the liquid state. Such a distribution of the chemical composition, corresponding to the arrangement of diffusion pairs in

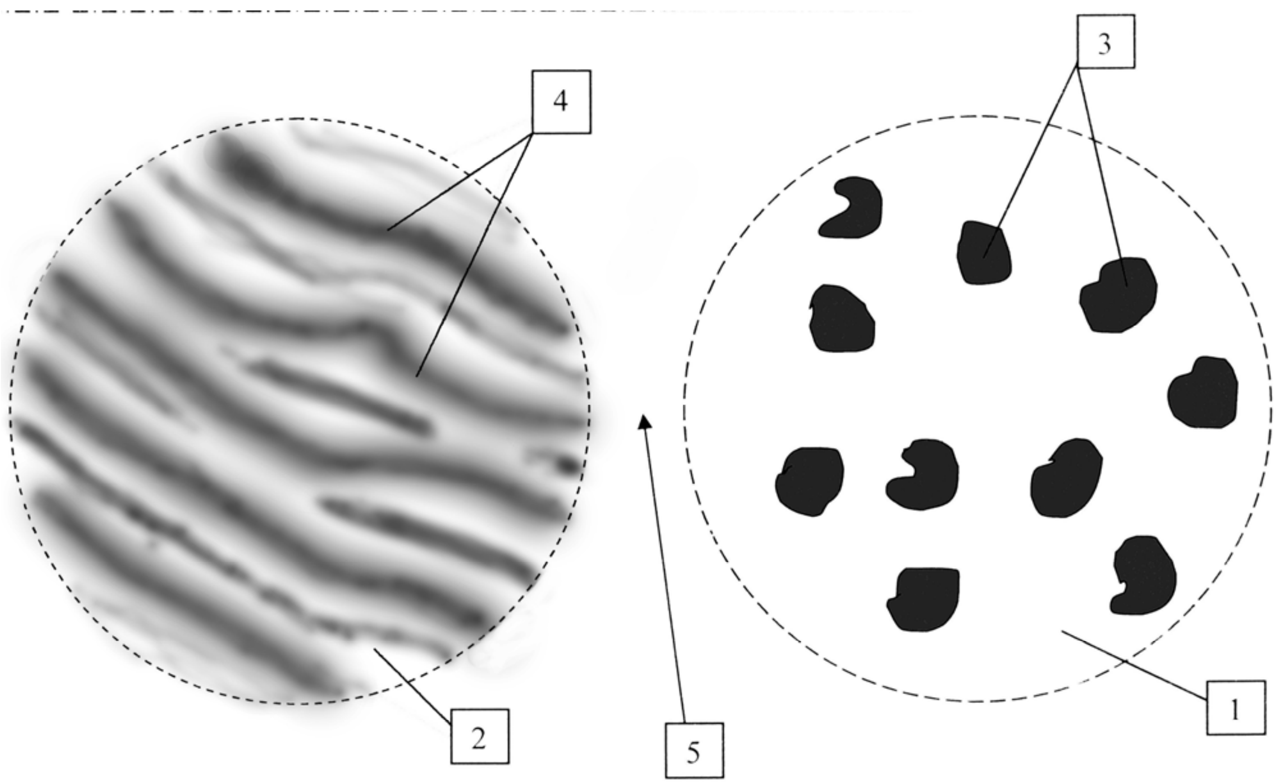


Fig. 8 Hypothetic image of diffusion micro-pairs in $Ni_{65}Mo_{20}Cr_{15}$ alloy.
1. Ni/Mo diffusion pair; 2. Ni/Cr diffusion pair; 3. Mo-particles; 4. Cr-clusters in the Ni lattice; 5. A space dividing Ni/Mo and Ni/Cr diffusion micro-pairs.

Fig. 8, is retained during the entire time of their existence, i.e. until the next re-melting. The presence of phases inside diffusion pairs, their structure, and dispersion, completely depends on the heat treatment temperature of the alloy.

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 one or two components. It was experimentally established that the starting point of the new phase formation is not a disordered solid solution formed after quenching from a solid-state at high temperatures, but a liquid state into which the alloy passes during its melting in a furnace. Diffusion micro-pairs form in a liquid alloy because of the existence of ionic or covalent components of chemical bonds between the nearest neighbors. The microstructure of these diffusion micro-pairs can be fixed after quenching the liquid alloy in the water. The ionic and covalent chemical bonds are the reason for the formation of both particles of the corresponding phases within the diffusion micro-pairs and the diffusion micro-pairs themselves.

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Conflict of Interests

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.

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