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Nucleation of New Phases in Alloy: A Long Way to True

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Abstract

The article presents our generalization of electron microscopy results that got for binary and some ternary alloys based on Ni. These results are considered as the basis for the conclusion that chemical bonds between atoms are realized in binary alloys according to the principle of pair-wise chemical interaction. In ternary alloys, such a process begins with the separation of the liquid alloy into diffusion micro-pairs, inside which particles of a new phase are subsequently formed. The latter circumstance allows us to consider the liquid state of the alloy as the initial stage of the formation of a new phase. That formation of diffusion micro-pairs (and particles of a new phase inside them) occurs because of the presence of alloys, along with a metallic bond, of the ionic and covalent components of a strong chemical bond, which exist at all temperatures of the condensed state. The article shows what exactly needs to be done so that such a branch of science as the science of alloys can get rid of the empirical approach when creating new alloys.

Keywords

Alloys, Microstructure, Electronic Structure, Phase Transformation, Transmission Electron Microscopy

1. Introduction. Phenomenological Theories of Nucleation

The starting point for the development of theories of the emergence of new phases in condensed environments was the theory of the formation of drops of liquid from a supersaturate steam. Subsequently, the theory of nucleation and growth, developed from the ideas of Gibbs-Folmer-Weber-Becker-During [1], has been spread to metal alloys. It is now customary to call it a classic theory of nucleation. The alternative mechanism of decomposition—spinodal—is the same old concept as the theory of nucleation-growth. Both terms first appeared in the same work of Gibbs, who called spinodal, the limit of metastability. Spinodal decomposition was the dominant theory of decomposition at the beginning of the last century and only in 1926 Folmer and Weber [2] resurrected the theory of nucleation-growth. In the 60s, the heyday of the theory of spinodal decomposition began again thanks to the works of Cahn and Hilliard [3], which considered gradient and elastic energy in their works. Upon further consideration, the researchers concluded that the decomposition of alloys by the mechanism of the nucleation-growth occurs inside the metastaby region in phase diagram, and the decomposition by the spinodal mechanism is inside the unstable area. As we see, all these authors studied the mechanism of the nucleation of new phases in alloy, using only phenomenological research methods. It was believed that in a disordered solid solution obtained by water-quenching from high temperatures, interatomic chemical interactions “appear” at a lower heating temperature, which lead to its decomposition.

Numerous experimental works carried out by transmission electron microscopy (TEM) have been used only to determine by which mechanism—the nucleation-growth or spinodal—the nucleation of new phases occurs. It was believed that this can be determined by the morphology of the precipitates. However, the study of the microstructure of binary alloys by the TEM method was complicated because the particles of the new phase were found not only after the aging of alloys but also after water-quenching, when, according to both theories, them should not be (there should be a disordered solid solution). Such a contradiction between theory and the experiment caused a violent polemic in the scientific environment, and in the late 60s, the Acta Metallurgica journal, together with other journals, opened a discussion on this subject. Many explanations were proposed to this phenomenon [4] [5] [6], but not one of them could be called satisfactory. After a 20-year discussion, a satisfactory answer was never found why the theory does not coincide with the experiment, and the discussion was suspended “until better times.” Unfortunately, many have long forgotten about this discussion in the Materials Science. However, the problem itself has not gone away and is, in fact, a powerful brake in the development of alloy theory and in the development of new alloys, in creating plausible phase diagrams and in the improvement of heat treatment. If we follow the views that exist now in Materials Science, then everything that happens in alloys when the temperature of their heating changes remains at the same level that existed when Acta Metallurgica began its discussion.

But this does not mean that such a discussion was useless. It helped to understand that somewhere in our notions of diffusion phase transitions, an error crept in. Later, we discovered this error. It comprised the fact that when interpreting the X-ray phase analysis data, no one paid attention to the existing limitations of the X-ray method. This method does not allow registration of particles of a new phase, the sizes of which are smaller than the regions of coherent scattering of X-rays. A. Guinier warned about these restrictions [7]. However, despite this warning, all the compilers of the phase diagrams unconditionally used the method of X-ray phase analysis and, having not found any particles of the second phase in the alloy structure after quenching from the "solid solution region," asserted that the structure under study was a disordered solid solution. That is why, when using the method of transmission electron microscopy (TEM), the authors of [4] [5] [6] discovered particles of the second phase after quenching "from the solid solution region", the resolution of dispersed particles by the TEM method is several orders of magnitude higher than by the X-ray method.

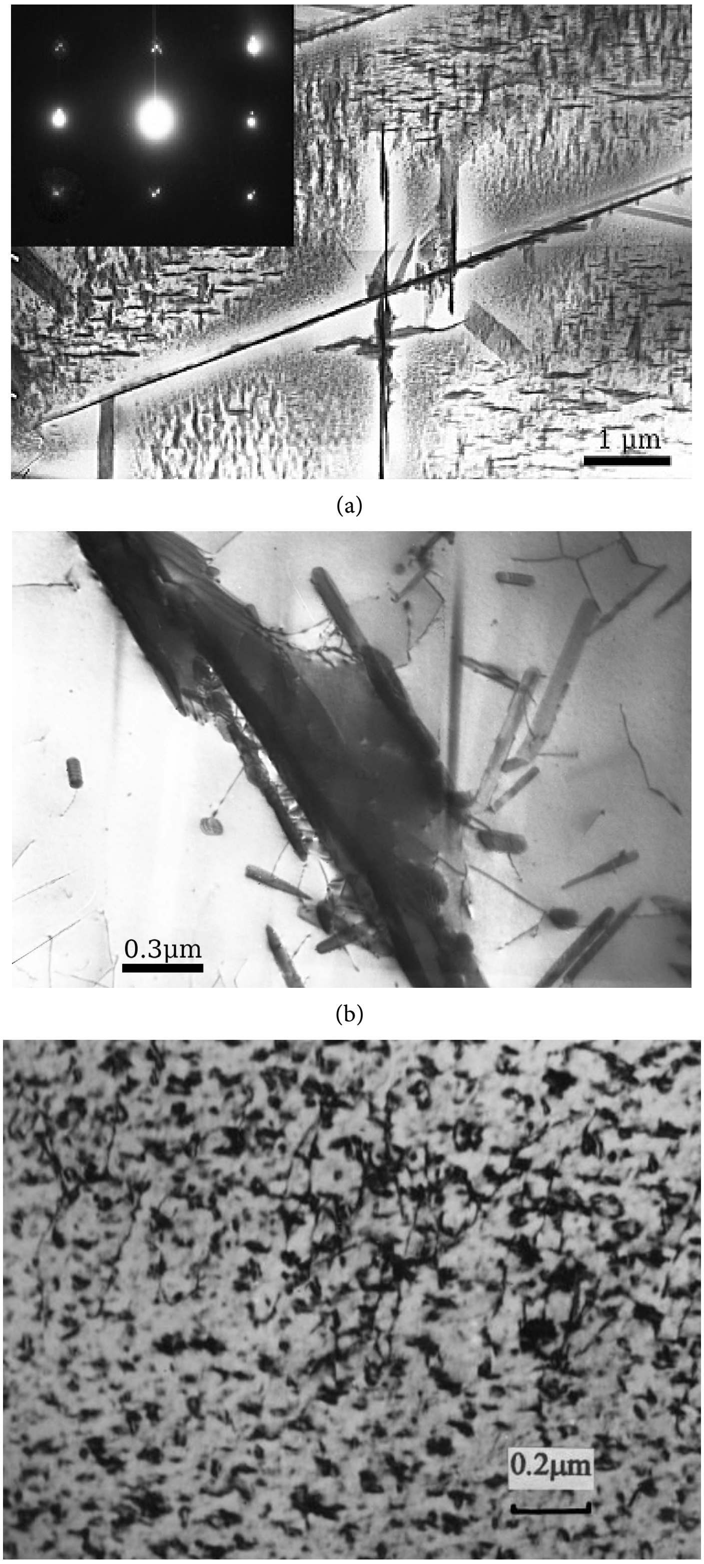
Unfortunately, many have long forgotten about this discussion in the Materials Science. However, the problem itself has not gone away and is, in fact, a powerful brake in the development of alloy theory and in the development of new alloys, in creating plausible phase diagrams and in the improvement of heat treatment. If we follow the views that exist now in Materials Science, then everything that happens in alloys when the temperature of their heating changes remains at the same level that existed when Acta Metallurgica began its discussion.

2. Discovery of the "Ordering-Phase Separation" Transition in Binary Alloys

2.1. Alloys of the Fe-Cr System

The first work in which it was discovered why existed ideas about alloys are so far from reality was published back in 1996 [8]. The authors, investigating the microstructure of alloys of the iron-chromium system by TEM, discovered a surprising phenomenon, which consists because at a quite definite heating temperature of these alloys, the sign of the chemical interaction between iron and chromium atoms changes. At high temperatures (above 1150˚C), phase separation is observed between Fe and Cr atoms (particles of atoms of pure chromium with the A12 lattice are formed **Figure 1(a)**). In the interval of temperatures 600˚C - 830˚C C, a σ-phase is forms (**Figure 1(b)**), *i.e.* phase separation is changed by ordering. Below 550˚C, again phase separation (clusters Cr-atoms) is observed (**Figure 1(c)**).

Already then it could be concluded that the presence on the same diagram at the same temperatures of a region in which there is a tendency to ordering, at other temperatures, a region in which a tendency to stratification occurs, should show that in the alloys of this system at the boundary of these two regions there should change the sign of the chemical interaction between the nearest neighbors should change. However, no one has come to this conclusion. On the contrary, some authors [9] considered that because positive deviations from the Raoult's law were found in alloys of the iron-chromium system at high temperatures, the σ-phase is not a chemical compound at all. The discovery of the Cr



(a)

(b)

(c)

Figure 1. $Fe_{50}Cr_{50}$ alloy: (a) Water-quenched from 1400˚C, high-temperature phase separation microstructure, inset: electron diffraction pattern, satellites near main reflections; (b) Water-quenched from 700˚C, microstructure with sigma-phase particles in the surface layer of the specimen; (c) 500˚C, low-temperature phase separation microstructure.

particles (**Figure 1(a)**) after quenching from high temperatures, corresponding to the region of solid solutions on the iron-chromium phase diagram, was so unexpected that it led to the appearance of several critical works and made us recall the explanation, fashionable in the 70 - 80 s, that these microstructures are formed in conducting the most quenching.

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 not only a microstructure of a disordered solid solution, but a mixture of phases formed because of a tendency towards ordering and phase separation.

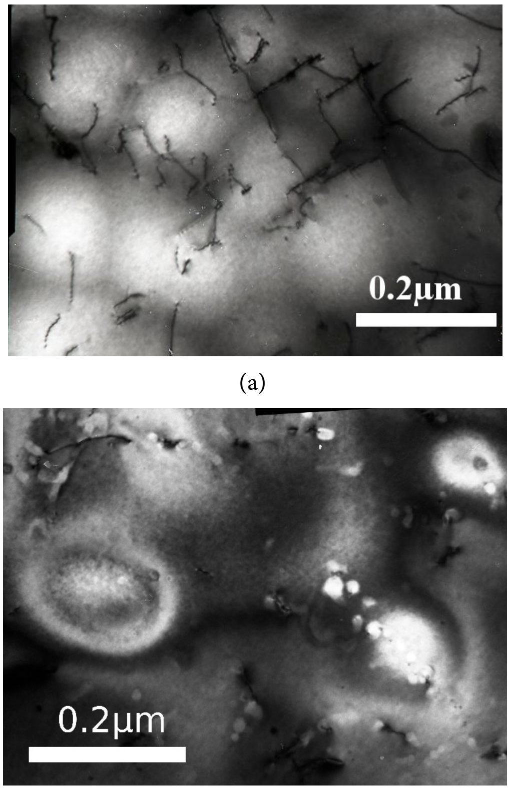
2.2. $Ni_{73}Co_{27}$ Alloy

The phase diagram of the Ni-Co system is characterized by great simplicity: for all compositions, at all temperatures, only the solid solution is shown in the diagram. No phase transformations except the allotropic α-Co → ε-Co (at 422˚C) occur in the system [10]. Apparently, this is why the literature on structural transformations in the alloys of this system is extremely scarce.

The microstructure of the $Ni_{73}Co_{27}$ alloy, exposed for 1 h at 1200˚C, is shown in **Figure 2(a)**. Round light spots with diffuse edges are observed on a dark background. It is obvious that formation of these clusters occurs without significant changes in the lattice's parameter, *i.e.* changes that could lead to the appearance of the diffraction contrast. A similar structure is observed after subsequent aging of the alloy at 800˚C and 600˚C [10].

2.3. Alloys of the Ni-Cr System

The phase transition "ordering-phase separation" in most of the binary systems studied by us occurs at a quite definite heating temperature of the alloys (transition temperature). However, in alloys of the nickel-chromium system, a somewhat unique picture is observed [11]. For example, in alloys with a chromium content of 32 wt.% and below at any heating temperature, there is only a tendency to phase separation since in the entire temperature range from 500˚C to 1500˚C, clusters of chromium atoms are noticed in the microstructure of this alloy (**Figure 3(a)** and **Figure 3(b)**). In alloys with a chromium content of 60 wt.% and above at all temperatures is observed only a tendency toward ordering, since particles of the Cr_2Ni compound are noticed in the microstructure (**Figure 3(c)** and **Figure 3(d)**). In alloy $Ni_{46}Cr_{54}$, the composition of which is between concentrations from 32% to 60% Cr, with a change in the heating temperature of the alloy, the usual transition "ordering-phase separation" is observed at 1200˚C (**Figure 3(e)** and **Figure 3(f)**).



(a)

(b)

Figure 2. $Ni_{73}Co_{27}$ alloy. Microstructure (a) after water-quenching from 1200˚C. (absorption contrast) and (b) after aging at 500˚C for 10 h (absorption and diffraction contrasts).

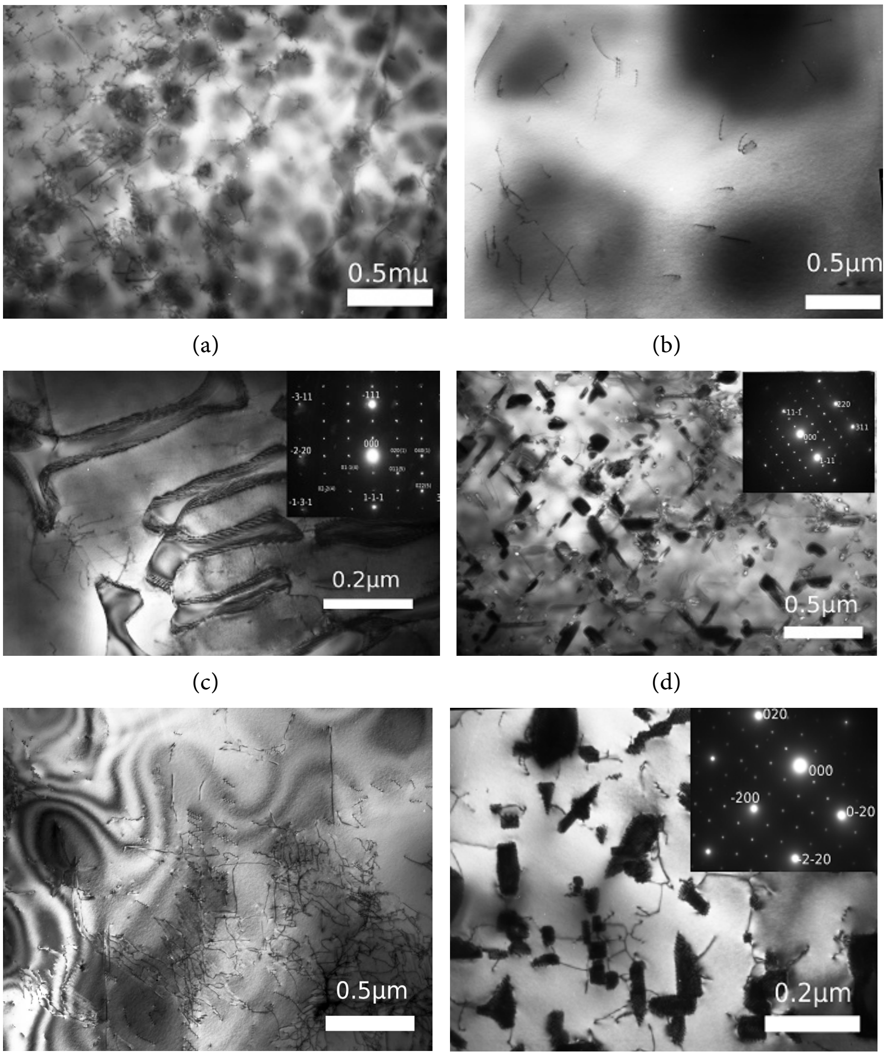
Many more features can be found in the alloys of each of 17 binary systems in the experimental study of the "ordering-phase separation" transition [12].

3. Electronic Transition "Ionic Bond ↔ Covalent Bond" in Binary Alloys

3.1. Alloys of the Fe-Cr System

The discovery of transition "ordering-phase separation" in various alloys helped to understand that it is precisely these chemical interactions between the atoms of the components determine all diffusion processes that occur of the alloys and lead to the formation of one or other phases. The question arises: what is the reason for this transition? That's clear 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 (**Figure 4**).

Electronic domains detected [12] in the Fe-Cr alloys were considered by us earlier as some regions of the alloy, within which the sign of the ordering energy has already changed, compared to the surrounding matrix, where it remains the same [13]. 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



(a) (b)

(c) (d)

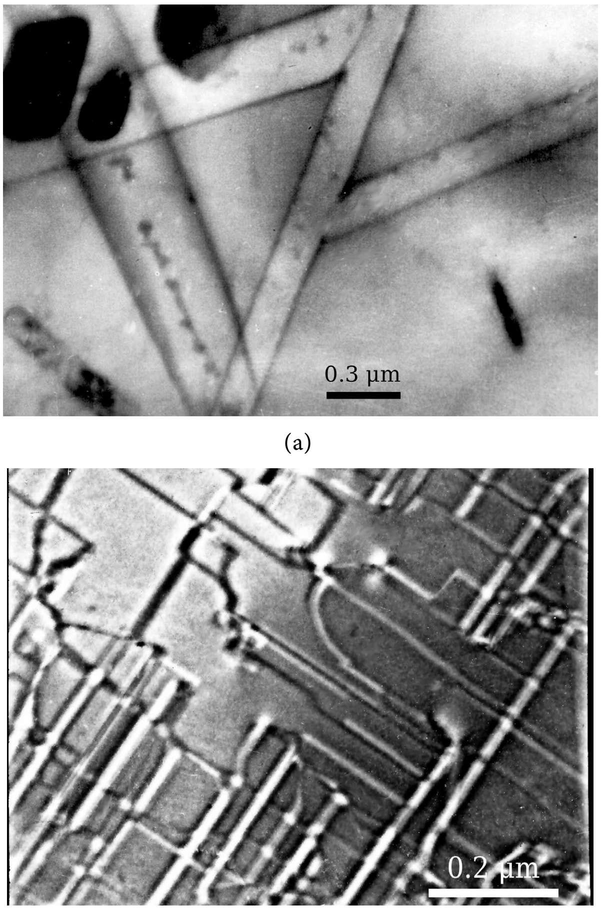
(e) (f)

Figure 3. Alloys of the Ni-Cr system. (a) $Ni_{68}Cr_{32}$, water-quenching from a liquid state. Absorption contrast. Cr-clusters; (b) $Ni_{68}Cr_{32}$, water-quenching from 500˚C; Absorption contrast. Cr-clusters; (c) $Ni_{40}Cr_{60}$ [9], water-quenching from a liquid state. Ni_2Cr particles. (d) $Ni_{40}Cr_{60}$, water-quenching from 550˚C. Ni_2Cr particles. (e) $Ni_{46}Cr_{54}$, water-quenching from a liquid state. Absorption contrast. Cr-clusters; (f) $Ni_{46}Cr_{54}$, water-quenching from 1000˚C. Ni_2Cr particles [11].

deflected in opposite directions. This 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 is like the formation of magnetic and ferroelectric ones.

3.2. Ni_3Co Alloy

A sign of the ordering energy in the Ni_3Co alloy was determined also by the method of XPS, at the following temperatures of specimen heating: 200˚C, 500˚C, 800˚C and 1100˚C [10]. **Figure 5** shows these results. Temperature of the transition ordering-phase separation was determined by XPS as being between



(a)

(b)

Figure 4. $Fe_{50}Cr_{50}$ alloy: (a) Water-quenched from 1400˚C, then water-quenched 900˚C, 1 h. Electron domains; (b) Water-quenched from 700˚C, then water-quenched from 500˚C, 1 h. Electron domains.

500˚C - 800˚C [10].

At temperatures of 200˚C and 500˚C, the valence band spectra of the alloy have a double band structure because of a small overlap of the d-bands of Co and Ni atoms, which is characteristic of the ordered state, when unlike atoms are in the immediate environment. At temperatures of 800˚C and 1100˚C, the spectra of the valence band have the form of a superposition of the valence band of the components. This happens when the form of the valence band of the solvent atoms, *i.e.*, Co, is predominant. This allows us to say that at the temperatures in the studied alloys, a tendency to phase separation is displayed. Therefore, in the temperature range between 500˚C and 800˚C "ordering-phase separation" transition takes place in the alloy, during which sign of the ordering energy is reversed.

Thus, the electronic transition "ionic bond ↔ covalent bond" can be interpreted as follows:

The covalent component of the chemical bond is caused when two atoms of

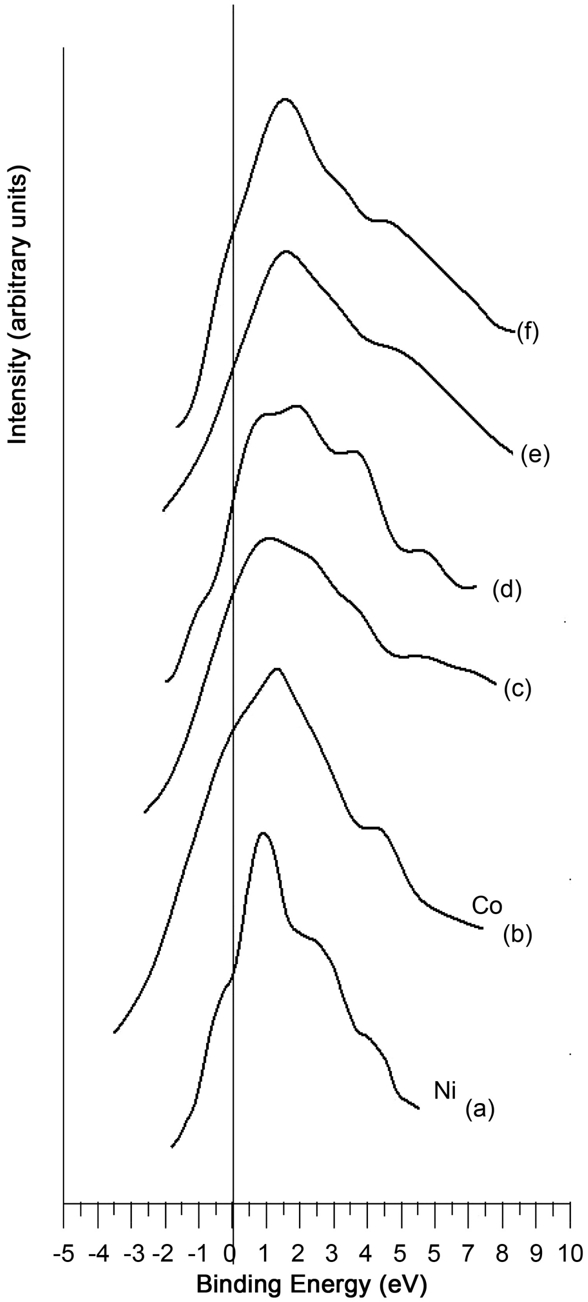


Figure 5. Ni_3Co alloy. Photoelectron spectra of the valence band. Reference spectra: (a) Ni, (b) Co. Experimental spectra obtained at 200 (c), 500 (d), 800 (e), 1100˚C (f).

the dissolved component B, because of their diffusion, become the nearest neighbors. Because of this instantaneous proximity, their valence orbitals hybridize and a cluster comprising 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 manifest itself as a change in the sign interaction energy between atoms A and B, on the electronic level present 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 [13].

4. Ternary Alloys. Diffusion Micro-Pairs as Origin Structure of Nucleation Process

Under the conditions of the existence of paired inter-atomic 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 three-component alloy, it is hard to imagine how this can happen, if not to assume that particles of the three-component phases form in them. Apparently, this is precisely the reason many researchers concluded that in ternary alloys, there is a possibility of a precipitation of three-component Laves phases, even though the electronic theory of alloys does not allow this possibility (there can be only pair's interaction between metallic atoms).

This circumstance prompted the author of this review 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 would correspond to the compositions of the binary alloys he had already studied. This was necessary to do this to compare the microstructure of a binary alloy and approximately the same in composition diffusion micro-pair in ternary alloys. All alloys were quenched in water from various temperatures, including from the liquid state.

The experimental TEM results got by us earlier on three-component alloys showed that only two-component chemical compounds (when a tendency to ordering), and two-component clusters or one-component particles of a dissolved element (when a tendency to phase separation) can be detected in them. Since covalent and ionic bonds arise in alloys only because the interaction between the nearest neighbors is paired, three-component phases cannot form in them in principle. The question immediately arises: how should the redistribution of the atoms of each of the three components occur so that when there is a pair chemical interaction between the atoms of a three-component alloy, two-component phases are formed in it? As noted above, when a binary alloy is in a liquid state, the atoms of each of its components, because of a very high diffusion rate, quickly reach an equilibrium state throughout the entire volume of the alloy. This means that at such a diffusion rate in the ABC alloy, the alloy regions close in composition to the A/B, A/C, or B/C pairs rather easy to form, if at the quenching temperature between the atoms in each of these pairs there is a tendency to ordering. A/A, B/B, and C/C pairs are formed when there is a tendency for phase separation between atoms. This process is also facilitated by the very high temperature during alloy smelting. If such a liquid alloy is quenched in water, then it is possible to fix the microstructure of the equilibrium state at the temperature from which the quenching was carried out, and to be able to study it.

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

The composition of the $Ni_{50}Co_{25}Mo_{25}$ alloy [14] was chosen from those considerations that the binary alloys of the Ni-Mo [15], Ni-Co [10], Co-Mo [16] systems have already been investigated by us earlier and the transition temperatures "ordering-phase separation" in these systems were already known. We begin our discussion of experimental results got at the temperatures at which the $Ni_{50}Co_{25}Mo_{25}$ alloy is in the liquid state. After quenching from the liquid state, in different microscopic sites of the same thin foil, we can observe different microstructure. For example, **Figure 5** shows round, light precipitates observed thanks to electron microscopic absorption contrast. The conclusion that they are clusters of precisely cobalt atoms was made here because absolutely the same structure was observed in the Ni_3Co binary alloy after heat treatment at 1200˚C (**Figure 6**, inset) [10].

At the second microscopic site of the same thin foil, we observe a microstructure where particles of Mo atoms are visible (**Figure 7**). An electron diffraction

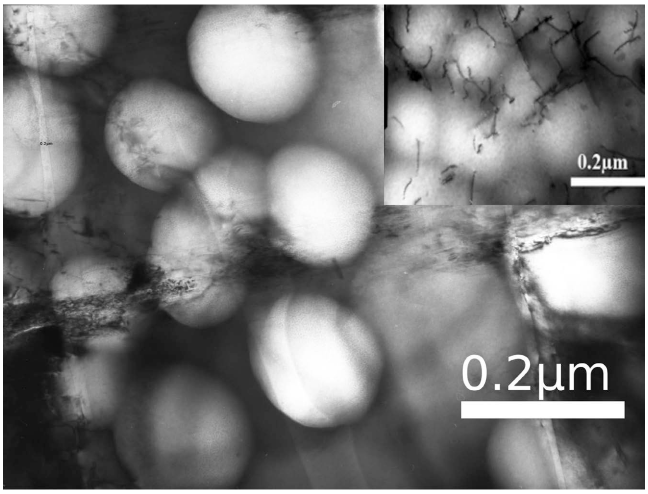


Figure 6. $Ni_{50}Co_{25}Mo_{25}$ alloy. Water-quenching from the liquid state. Microstructure. Inset: Ni_3Co alloy. Water-quenching from 1250˚C.

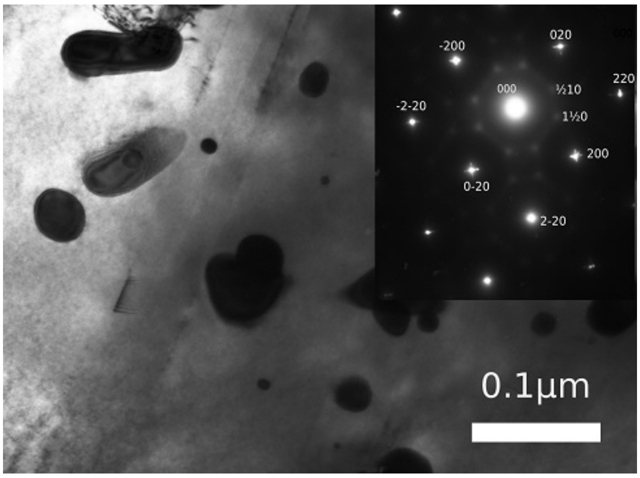


Figure 7. $Ni_{50}Co_{25}Mo_{25}$ alloy. The second microscopic site of the same thin foil. Water-quenching from the liquid state: Microstructure. Inset: Electron diffraction pattern; zone axis [211].

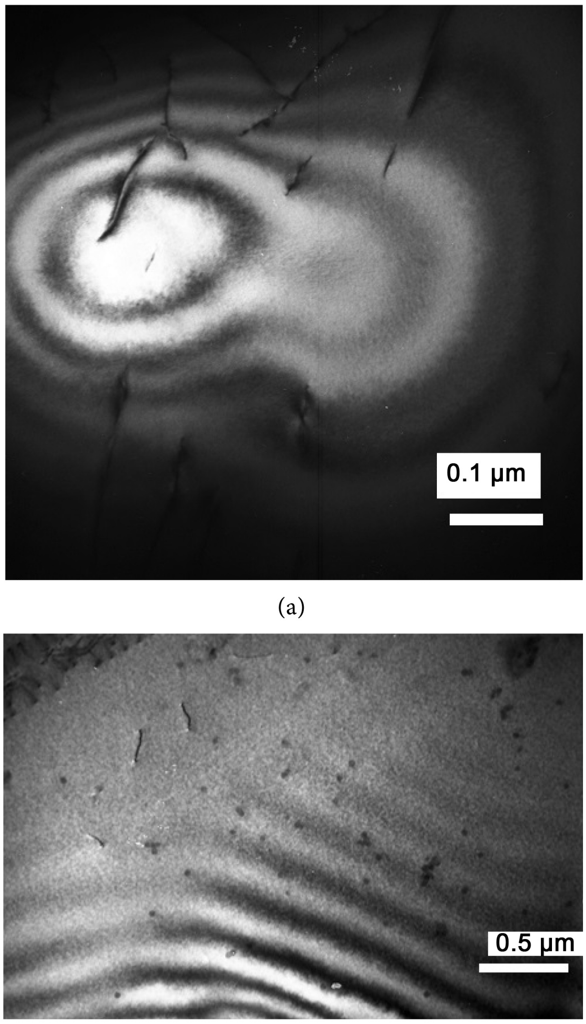
pattern got from the microstructure (inset) show satellites near the fundamental reflections and a system of the weak diffraction maxima at positions {1 1/2 0} Therefore, because of the tendency to phase separation in a diffusion pairs Ni/Mo, particles of Mo atoms form when the Ni-Mo matrix is still in a liquid state. Since molybdenum is a rather refractory metal, the formation of particles of Mo atoms in the alloy under study occurs at the maximum temperature, which is reached in the melting zone of the furnace. Therefore, in Figure 7, we observe an already fully formed microstructure of phase separation as accumulations of particles of molybdenum. This structure is preserved and at a temperature of 1300˚C.

The detection of the different microstructure in different microscopic sites of the same foil, which differ in chemical composition and the type of precipitates shows that the chemical composition at each site corresponds to a chemical composition in one or other diffusion pair (in the first case, Ni/Co, in the second Ni/Mo). This convinces us that the diffusion pairs are formed really in a liquid state and represent areas with an increased concentration of one of solute component. It should be noted that those microscopic sites of the foil, in which the Mo-particles are detected (Figure 7), do not contain Co-clusters (Figure 6).

4.2. $Ni_{65}Mo_{20}Cr_{15}$ Alloy

The $Ni_{65}Mo_{20}Cr_{15}$ [17] alloy was chosen for this study because, at liquid state temperatures, there is a tendency for all three of its components to phase separation. But the main role in the alloy's choice was played because in binary Ni-Cr alloys with a low chromium content, clusters of chromium atoms look like absorption contrast waves that can stretch without interruption from one border of the chromium-rich diffusion micro-pair to the opposite border. It is this arrangement of clusters that helped us get information about the size of the chromium-rich micro-pair. We discovered such a morphology of chromium atom clusters earlier when studying the Ni62Cr_{38} binary alloy after its quenching from the liquid state (**Figure 8**) [11].

When such a binary alloy is in a liquid state, because of the very high diffusion rate at this temperature, equilibrium is quickly reached in it throughout the volume of the alloy. Such an equilibrium does not correspond to a random distribution of atoms in the $Ni_{62}Cr_{38}$ binary alloy, but to the formation of an inhomogeneous microstructure comprising chromium-rich regions in a chromium-depleted matrix. The driving force behind such a process is the covalent chemical bond that occurs within each pair of chromium atoms when these two atoms, by diffusing, become dearest neighbors. This bond is responsible for the tendency to phase separation observed in the Ni/Cr diffusion pair.



(a)

(b)

Figure 8. $Ni_{65}Mo_{20}Cr_{15}$ alloy. Ni/Cr diffusion pair. Microstructure. Quenching from 1550˚C (a) and from 1500˚C (b). Absorption contrast.

Investigating the $Ni_{65}Mo_{20}Cr_{15}$ alloy by TEM, we again encountered the same fact: in some areas of the foil, we find some phases, in other areas of the same foil, others. This immediately suggests that in the alloy, already in the liquid state, there is a separation into certain sections that differ from each other in composition. Since the solvent in the alloy under study occupies almost 2/3 of the volume of the alloy, such a composition can decompose into only two types of micro-pairs, enriched in Mo and enriched in Cr. After quenching from 1550˚C, clusters of chromium atoms are observed as concentration waves of the absorption contrast, which emanate from a certain light colored centers in a thin foil (**Figure 8(a)**).

When the quenching temperature is lowered to 1500˚C (**Figure 8(b)**), the entire surface area of the foil in the Ni/Cr diffusion pair turns out to be dissected by such contrast waves as in **Figure 8(b)**. Such concentration in homogeneities can form only because of the tendency to phase separation. The size of the region occupied by the Ni/Cr diffusion pair can be estimated from the number of such contrast waves that fit into such a region. This value approximately reaches several tens of microns. Now that we have seen that diffusion pairs exist in alloys and that it is with their formation in a liquid alloy that the entire process of alloy microstructure formation begins, it is time to pay attention to the terminology that we use when designating this new microstructure element. It is known that the term "diffusion pairs" already exists and is used to study the diffusion parameters of various atoms in alloys at various temperatures. Therefore, in our case, we propose to use the term "diffusion micro-pairs", which is the best suited for such an element of the microstructure.

Unfortunately, the concept of the "diffusion micro-pair" has not yet been included in the everyday life of alloys scientists, since there was no conclusive experimental evidence of its actual existence. All my explanations were like fantasy, since everybody used to believing that there are no chemical bonds in alloys at high temperatures that the mutual arrangement of atoms of different sorts is completely chaotic in the liquid state of an alloy, and that chemical bond "appears" as the temperature drops.

Figure 9 shows the microstructure of the clusters, which are found inside the Ni/Cr diffusion micro-pair after the alloy has been quenched from 1300˚C. It can be seen that both in the liquid (**Figure 8(b)**) and in the solid state (**Figure 9**), the microstructure has almost the same morphology. With a further decrease in the quenching temperature of the alloy, the "ordering-phase separation" phase transition occurs in diffusion micro-pairs, accompanied by a corresponding change in the microstructure.

In other areas of the same foil of the $Ni_{65}Mo_{20}Cr_{15}$ alloy, accumulation of rounded particles are observed (**Figure 10(a)**), similar to those found in the $Ni_{50}Co_{25}Mo_{25}$ alloy (**Figure 6**). The electron diffraction pattern in **Figure 10(b)** shows that these are particles of Mo atoms, *i.e.*, it is a microstructure of the diffusion micro-pair Ni/Mo. At 1200˚C, when the "ordering-phase separation"

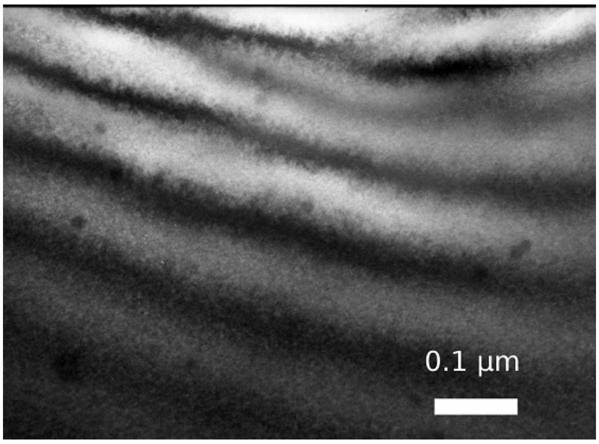
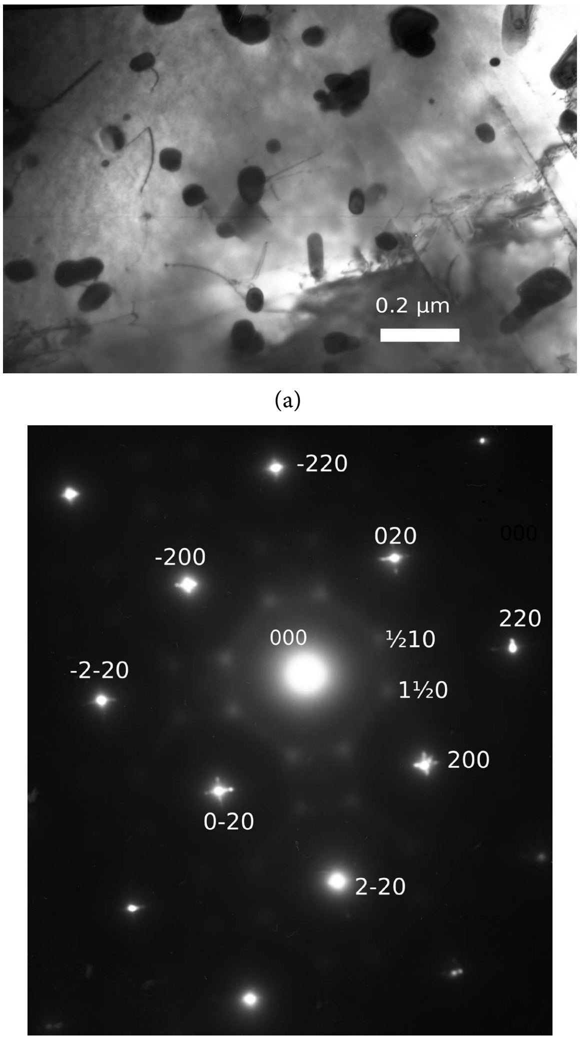


Figure 9. $Ni_{65}Mo_{20}Cr_{15}$ alloy. Quenching in water from 1300˚C. Absorption contrast. Diffusion micro-pair Ni/Cr.



(a)

(a)

Figure 10. $Ni_{65}Mo_{20}Cr_{15}$ alloy. Ni/Mo diffusion micro-pair. Quenching in water from 1500˚C: (a) Microstructure (Mo-particles); (b) microelectron diffraction pattern.

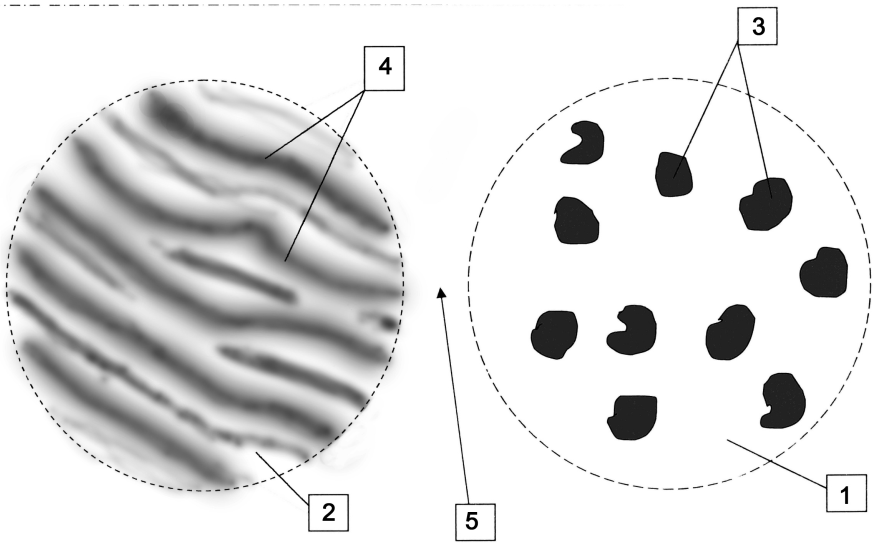


Figure 11. Hypothetic image of diffusion micro-pairs in $Ni_{65}Mo_{20}Cr_{15}$ alloy. Explanatory captions: 1. Ni/Mo diffusion pair; 2. Ni/Cr diffusion pair; 3. Mo-particles; 4. Cr-clusters in the Ni lattice; 5. A space dividing Ni/Mo and Ni/Cr diffusion micro-pairs.

transition occurs in Ni/Mo diffusion micro-pairs, Mo atom particles dissolve and take part in the formation of $Ni_3Mo(D0_{22})$ and $Ni_4Mo(D1_a)$ phases.

On Figure 11 shows a hypothetical image of diffusion micro-pairs formed in the liquid state of the alloy under study. Within these micro-pairs, corresponding new phases (particles of Mo atoms and clusters of chromium atoms) form. Since the melting points of Mo and Cr are higher than those of Ni, the formation of phases inside of the micro-pairs occurs almost simultaneously with the formation of the diffusion micro-pairs.

5. Discussion

In the $Ni_{50}Co_{25}Mo_{25}$ and $Ni_{65}Mo_{20}Cr_{15}$ ternary alloys given as examples, in which only one type of diffusion micro-pairs is formed: solute/solvent. Diffusion micro-pair solute/solute is not formed. For the formation of each of these micro-pairs, an uphill diffusion of solute atoms is necessary in the direction where these micro-pairs will be located. The diffusion of atoms of the first and second solutes cannot proceed simultaneously, since their directions are different. Therefore, as soon as the diffusion into the first micro-pair finishes, the diffusion into the second will begin. Naturally, the diffusion of those atoms proceeds first, the chemical bond of which with the atoms of the solvent is higher. Unfortunately, it is now difficult to say whether the formation of a third diffusion micro-pair will occur in a ternary alloy, if its composition is equi-atomic, or in a four-component alloy. It all depends on the magnitude of the chemical bond of specific pairs. We would like to note that in the literature there have not yet been any mentions of multi-component alloys in which three types of new phases precipitated would have been simultaneously found.

Diffusion micro-pairs in the ternary alloy are formed during its melting when the diffusion mobility is very high. If the melting point of a chemical compound formed in such an alloy is higher than the melting point of the alloy itself, then particles of chemical compounds are formed simultaneously with these micro-pairs and inside them. If lower, then the process of formation of chemical compounds can be represented as two stages: the formation of the enriched micro-pairs themselves and then of formation of a chemical compound inside them at the temperature of its formation.

Diffusion micro-pairs are not formed in multi-component alloys in two cases: when the amount of the added component is small (up to 2% - 3%) and when the alloy comprises 5 or more components (for example, high entropy alloys—HEAs). When the concentration of alloying atoms in the ternary alloy does not exceed 2% - 3%, such additives can lead only to a little solid-solution hardening at the expense of a distortion of the crystal lattice. Diffusion micro-pairs do not form because of a low solutes content. This conclusion follows from numerous examples of existing grades of multi-component alloys, where such additives lead to nothing. Such small additions in three-component alloys most likely play the role of unnecessary and, perhaps, even harmful impurities.

A lot of work on the creation, study and use of high-entropy alloys (HEAs) has been carried out over the past two decades. The authors of these works are confident that, compared to typical metal alloys, they have unique properties because of high hardness, thermal and corrosion resistance, thermal stability at elevated temperatures, etc. Although researchers have been working on such alloys for over 20 years and have got many experimental results, none of the alloys is yet in demand for industrial use. The discovery of the phase transition “ordering-separation of phases”, it would seem, should have interested the scientific audience and attracted it to work in this direction. However, as far as we know, nothing of the kind happened, perhaps because most alloy researchers were busy studying high-entropy alloys, which attracted them with their unpredictability and “intriguing” properties [18] [19].

They get a high-entropy alloy, in which the diffusion of atoms over long distances is completely suppressed, diffusion micro-pairs are completely absent, and chemical interactions between metal atoms cannot manifest themselves. In such alloys, the nucleation of new phases is completely excluded, and lattice distortions cannot be removed using conventional heat treatment. It is quite possible that the exclusive attention currently given to these alloys will not justify itself in the future.

Thus, the formation of diffusion micro-pairs in ternary alloys lets us consider chemical interatomic bonds as the key participant in the process of microstructure formation. An increase in the number of components in the alloy to over three sharply reduces the possibility of the formation of diffusion pairs and, by doing so, suppresses up-hill diffusion in the alloy. It is easy to calculate that when melting four-component alloys, there can be maximum 6 such diffusion pairs. This means that the diffusion of atoms, which is an obligatory attribute of the manifestation of chemical interactions in alloys, can be practically completely suppressed even at temperatures in the liquid state. Here, diffusion micro-pair solute/solute is not always formed. The diffusion of atoms of the first and second solutes cannot proceed simultaneously, since directions of their uphill diffusion are different. Therefore, as soon as the diffusion with the first micro-pair formation is finished, the diffusion with the second will begin. Naturally, the diffusion of those atoms proceeds first, whose energy of the chemical bond with the atoms of the solvent is higher.

6. Conclusions

In this article, we showed how the process of nucleation of new phases in binary and ternary alloys occurs under conditions of the existence of a pair chemical interaction between atoms. It turned out that the processes occurring in alloys differ essentially from those described in textbooks that we should come to terms with the existence in nature of a further type of microstructure as diffusion micro-pairs. Although this type of microstructure is an intermediate link on the way to the formation of new phases in alloys, its presence says that all processes occurring in alloys with temperature take place thanks to chemical bonds (ionic and covalent) existing both in the liquid and solid states of an alloy.

The article presents experimental showing how the microstructure of metal alloys is formed during thermal exposure. The results got show that the existing ideas about alloys are too far from reality. It is shown that all interactions between the atoms that make up the alloy obey two laws: the law of pair-wise chemical interaction between similar and dissimilar atoms and the law that allows these interactions to change their sign of the chemical interaction with temperature. These two laws are the laws of nature, and man is powerless to change them, except to use them in his daily activities to create new alloys and develop new technologies for processing alloys. Our discoveries of the "ordering-phase separation" transition and the "ionic bond ↔ covalent bond" electronic transition, the experimental detection of "diffusion micro-pairs" in the smelting of alloys will change with time our idea of what metal alloys are and how particles of new phases are nucleated in them.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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