

A Future Life of Binary Phase Diagrams

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Abstract

The article raises the question of what to do with one of the main achievements of metal science in recent years—binary phase diagrams. These diagrams play a key role in the science of alloys and therefore their reliability must be complete. However, the discovery of the “ordering-separation” phase transition, which showed that in binary alloys at certain temperatures the sign of the chemical interatomic interaction changes (and, consequently, the microstructure changes), forces us to reconsider our ideas about those areas. Currently, these areas are designated on diagrams as areas of a “disordered solid solution.” This article proposes, using transmission electron microscopy, to study all the so-called solid solution regions, and apply the results obtained to the studied regions of the phase diagram.

Keywords

Phase Transformation “Ordering-Separation”, Electronic Transition “Ionic Bond ↔ Covalent Bond”, Binary Phase Diagrams, Transmission Electron Microscopy

1. Introduction

Metallurgists and technologists working with alloys do not need to explain the exceptional importance of the reliability of binary phase diagrams. The information on phase diagrams is actually a guideline for any specialist who has to deal with a particular alloy, and therefore has no right to be unreliable. However, those specialists who constantly use such diagrams in their work are already accustomed to the fact that many of the lines separating certain areas on phase diagrams cannot be completely trusted. Researchers know well what these lines are. These are lines dividing regions with different microstructures, in particular, “solid solution regions”.

Phase transitions in alloys, depicted on binary phase diagrams, are divided into two types: massive (diffusion-free), in which at a certain temperature all

atoms of the matrix take part at once (melting, allotropy, magnetism) and diffusion, in which individual atoms of one type of alloy participate in chemical interaction with individual atoms of a different kind (tendency towards ordering) or when two atoms of the same kind are involved in chemical interaction with each other (tendency towards phase separation). Such a chemical interaction occurs when these two types of pairs of atoms, due to their diffusion, become nearest neighbors. It should be noted that this proximity does not arise by chance, but due to long-range forces of chemical attraction between two atoms A and B (ordering) or two atoms B (separation).

Phase diagrams began to be intensively constructed at the beginning of the last century, when X-ray phase analysis (XRD), which was used to detect both massive and diffusive phase transitions, became widespread throughout the world.

While massive transition lines could be determined by this method with a sufficient degree of accuracy, this method was not suitable for constructing diffusion transition lines. It was simply impossible to detect highly dispersed particles of new phases, much fewer clusters, using this method. This is due to the fact that the X-ray method cannot identify particles of new phases whose sizes are smaller than the sizes of the regions of coherent scattering of X-rays. Therefore, the absence of particles of highly dispersed phases in X-ray diffraction patterns has always been interpreted unambiguously by researchers: the observed microstructure is a disordered (*i.e.*, ideal) solid solution. This interpretation encounters an uncompromising objection from thermodynamics: as is known, ideal solid solutions do not exist in nature (let us recall, for example, Raoult's law, which is never satisfied for all pairs of elements).

In the 60s-70s of the last century, when the method of transmission electron microscopy (TEM) began to be widely used to study the microstructure of alloys, many authors were surprised to discover that the microstructure of the vast majority of binary alloys quenched in water from the solid solution region was two-phase and contained highly dispersed particles of chemical compounds [1] [2]. At that time, practically no metallurgist had any doubt that experiment, and not phase diagrams, was to blame for such a discrepancy. A version was even put forward that the decomposition of alloys, which occurs through the spinodal mechanism, occurs during the process of hardening itself, *i.e.*, in a very short time, comparable to the time of cooling the alloy in water. This behavior of the alloys was explained by the fact that during spinodal decomposition the stage of formation of critical nuclei is absent, and therefore the nucleation process is sharply accelerated.

That is why a collision arose already at that time when phase diagrams constructed according to X-ray diffraction data and allegedly containing regions of disordered solid solutions at high temperatures turned out to be two-phase when using the TEM method [3] [4].

Such "solid solution" regions can now be found in virtually all high-temperature parts of every binary phase diagram. This means that we don't actually know what the microstructure is in these regions of the phase diagram. It is unlikely

that such a situation in this field of knowledge can be called normal, when a TEM experiment reveals one type of structure, and an X-ray experiment reveals another type of structure.

The “ordering-separation” phase transition in various binary alloys has some characteristic features that manifest themselves at the level of changes in the microstructure: the sign of the energy of chemical interaction between dissimilar atoms changes for each system at a certain temperature (the “ordered separation” transition temperature). The microstructure that existed before the transition, for example, due to the tendency of the alloy to order (a solid solution with particles of chemical compounds), dissolves, and in its place, a microstructure is formed that arises due to the tendency of the alloy to stratify (a solid solution with clusters or particles of one particular type, or dissolved component). In some systems, such a change in sign (and microstructure) can occur at more than one temperature. When, during such a transition, the energy of chemical interatomic interaction passes through zero, it would be logical to assume that the microstructure of the alloy at this boundary will be a disordered solid solution. Indeed, such a situation is observed in the phase diagram in alloys of the Fe-Cr system [4].

The reasons for the attraction between dissimilar atoms, leading to the formation of chemical compounds in alloys (tendency to ordering), and the reasons for the attraction between like atoms, leading to the formation of clusters or particles of atoms of one of the dissolved components (tendency to phase separation), have now found an adequate explanation [5] within the framework of the existing electronic theory. Believing that a 100% metallic bond exists only in pure metals, and in alloys, a certain part of the valence electrons takes part in the formation of a strong chemical bond (ionic or covalent), the author [5] analyzed what bonds exist in alloys between the atoms of the components. He came to the conclusion that ionic bonding occurs in alloys when one or more pairs of valence electrons, which should have taken part in the formation of an electron gas, are localized on two or more (depending on the valence) nearby dissimilar atoms. This results in the formation of a common orbital and the formation of a chemical compound. A covalent bond is formed when one or more pairs of valence electrons participate in the formation of hybridized orbitals between atoms of the same name. In this case, either clusters or particles of atoms of one of the dissolved components (depending on the composition of the alloy) are formed in the structure of the alloy due to attraction between the nearest neighbors of the same name. This means that the property of alloys to change the sign of the chemical bond when the heating temperature changes follows from the very essence of the electronic structure of the alloys [5].

2. Experimental

We chose the binary alloy $\text{Co}_{75}\text{V}_{25}$ as the research object of this article. This was done to show what the ordering-separation transition is and how it can be displayed in modernized binary phase diagrams. The alloys under study were

quenched in water from various temperatures (including from the liquid state, when a small portion of liquid metal was poured from a crucible directly into water). After each low-temperature heat treatment, the alloys were also cooled in water to preserve the microstructure that forms in the alloy at the tempering temperature of interest to us. Foils were made from the castings and the microstructure was studied on an EM-125 transmission electron microscope using standard methods.

3. Results

Our studies have shown that quenching the $\text{Co}_{75}\text{V}_{25}$ alloy [6] from the liquid state fixes round-shaped particles of vanadium atoms in the solid solution, the bright-field image of which is shown in **Figure 1**. The electron diffraction pattern shows satellites near the main reflections of the matrix (**Figure 1**, inset). Obviously, these satellites arise due to the formation of particles of a more refractory element—vanadium, which crystallizes in a liquid solution due to the existence of a tendency for separation between the Co and V atoms, including in the liquid state of the alloy. This fact allows us to conclude for the first time that chemical bonds between atoms of components in alloys exist at all temperatures of both solid and liquid states; that in alloys, unlike pure metals, there are, in addition to metallic ones, ionic and covalent chemical bonds. Subsequently, all our studies confirmed these conclusions on other binary alloys. However, nothing like this can be found in existing phase diagrams.

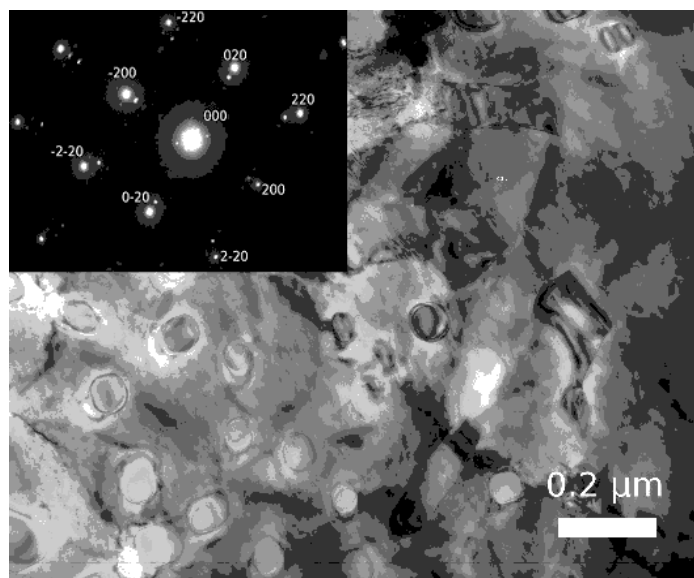


Figure 1. $\text{Co}_{75}\text{V}_{25}$ alloy. Quenching from a liquid state. Microstructure. Particles of V atoms are visible. Inset: electron diffraction pattern, [111] zone axis.

Figure 2 shows the microstructure and electron diffraction pattern (in the inset) of the same alloy, quenched from 1150°C . Particles of vanadium atoms in the form of clusters of arbitrary shape are observed in the figure.

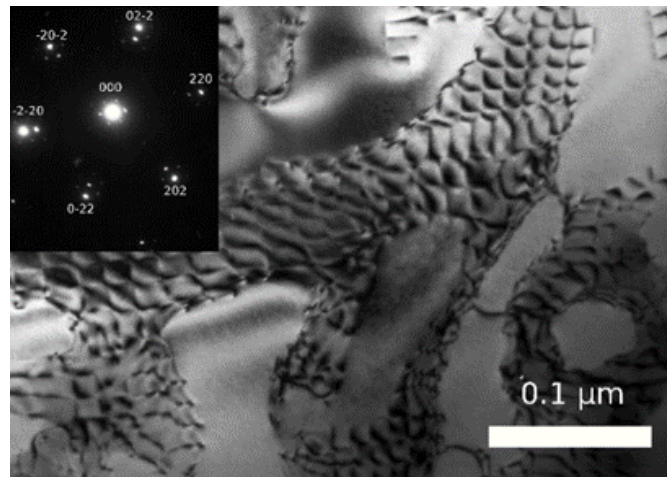


Figure 2. Alloy $\text{Co}_{75}\text{V}_{25}$. Hardening at a temperature of 1150°C . Bright-field image of colonies of vanadium atom particles. Insert: electron diffraction pattern, $[111]$ zone axis.

From these figures, it is clear that when the alloy quenching temperature decreases to 1150°C , the energy of chemical interaction between B atoms increases. This can be judged by comparing the number of particles of vanadium atoms released at 1550°C and 1150°C . In **Figure 2** it can be seen that the number of such particles is greater than after quenching from 1550°C . In the electron diffraction pattern obtained from such a colony, satellites from particles of vanadium atoms are also observed (**Figure 2**, inset).

When the heat treatment temperature is reduced to 800°C , a dissolving microstructure of phase separation is observed. This conclusion can be drawn from the fact that the microstructure of the alloy, is similar to the microstructure of the delamination in **Figure 2**, visible in **Figure 3**.

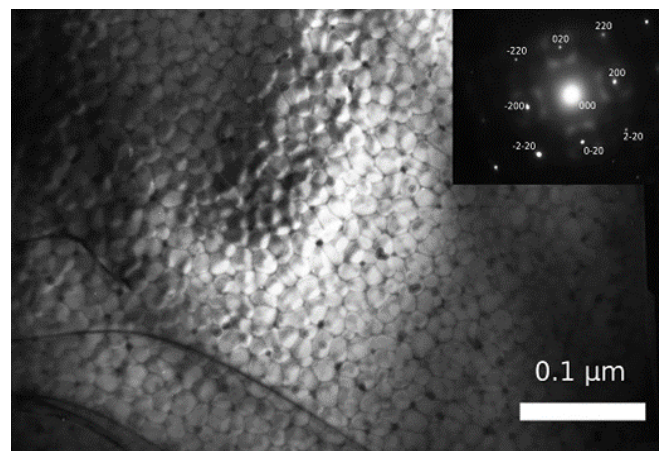


Figure 3. Alloy $\text{Co}_{75}\text{V}_{25}$. Quenching from 800°C . Microstructure of phase separation: bright-field image; microelectronogram (diffuse scattering is observed).

In another section (**Figure 4**) of the same foil, the structure of phase separation is no longer observed, and the electron diffraction pattern reveals a system of additional reflections belonging to the chemical compound Co_3V (type L_2).

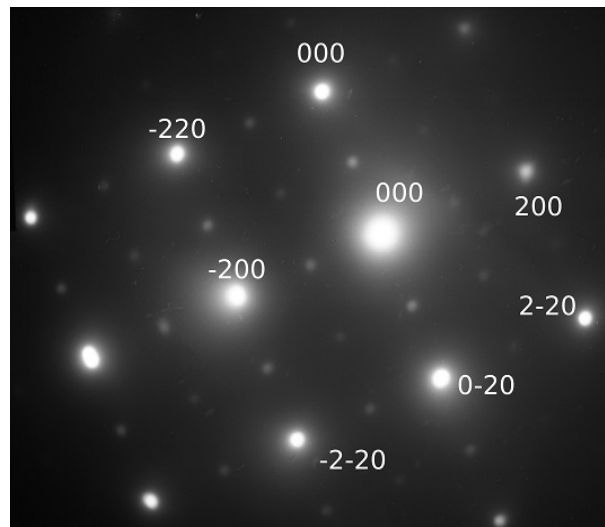


Figure 4. Alloy Co₇₅V₂₅. Quenching from 800°C. Micro-electronogram taken from another section of the same foil (weak reflections from phase particles are observed).

All this means that quenching from 800°C fixes the microstructure of the “ordering-separation” phase transition: in some areas of the alloy the microstructure dissolves, in other areas, an ordering microstructure is formed. We observed exactly the same picture earlier on alloys of the Ni-Co system [7]. At the same time, in alloys of a number of other systems (for example, Fe-Cr [3]), this transition goes through the stage of formation of electronic domains between the region in which separation occurs and the region in which ordering occurs.

A further decrease in the heat treatment temperature to 550°C leads to the fact that reflections from the L₁₂ phase become more distinct and intense (Figure 5). In a bright-field image, it becomes possible to observe highly dispersed particles of the chemical compound L₁₂.

When the alloy is subjected to heat treatment at 350°C, another “ordering-stratification” transition is detected, which occurs in the alloy in the temperature range 400°C - 450°C.

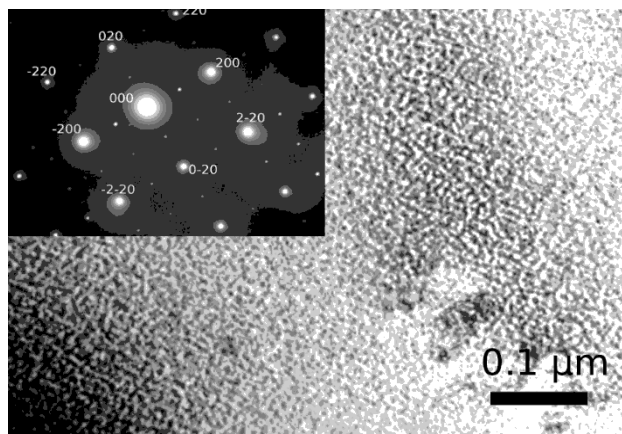


Figure 5. Alloy Co₇₅V₂₅. Quenching from 800°C. Micro-electronogram taken from another section of the same foil (weak reflections from phase particles are observed).

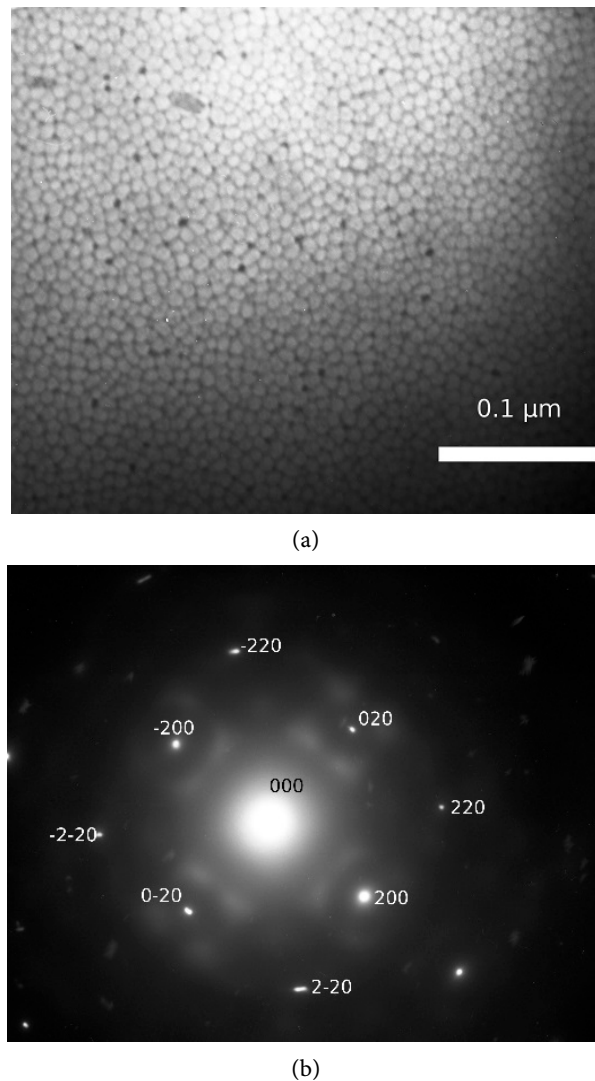


Figure 6. $\text{Co}_{75}\text{V}_{25}$ alloy. Quenching in water from 350°C . (a) Bright-field image of the phase separation microstructure; (b) electron diffraction pattern, $[001]$ zone axis; diffuse scattering is visible.

Figure 6 shows a cellular structure in which vanadium atoms accumulate within the boundaries of the cells, and cobalt atoms accumulate in the volume of the cells. The electron diffraction pattern again shows diffuse scattering, brighter than in **Figure 5** (inset). Thus, with a decrease in the heat treatment temperature, two “ordering-separation” phase transitions are observed in the alloy: at 800°C and at $400^\circ\text{C} - 450^\circ\text{C}$.

Figure 7 shows a section of the Co-V phase diagram, on which a line is drawn corresponding in composition to the $\text{Co}_{75}\text{V}_{25}$ alloy. This line shows the temperatures at which the above studies were carried out and the microstructures formed at these temperatures, which are shown in italics in the diagram. The graph shows that the agreement between the experimental results and what is shown in the diagram is minimal—only at one point (solidus). Graph in **Figure 7** gives a clear idea of what phase diagrams we use and how much we still have to

do to construct binary phase diagrams that meet the requirements for them.

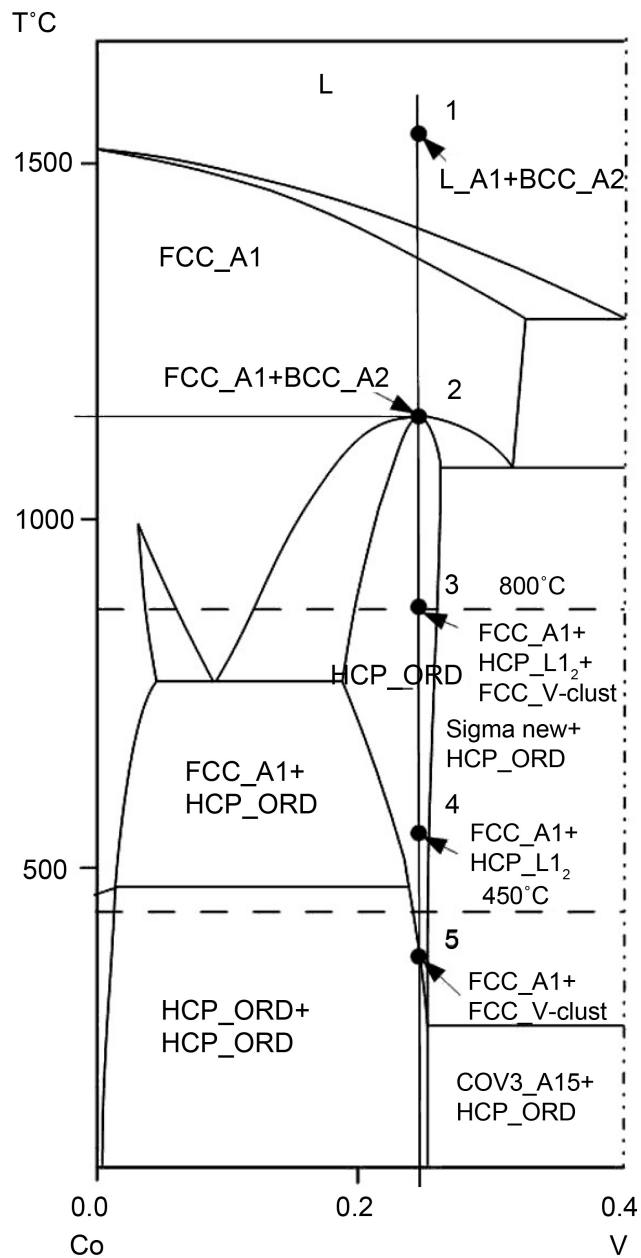
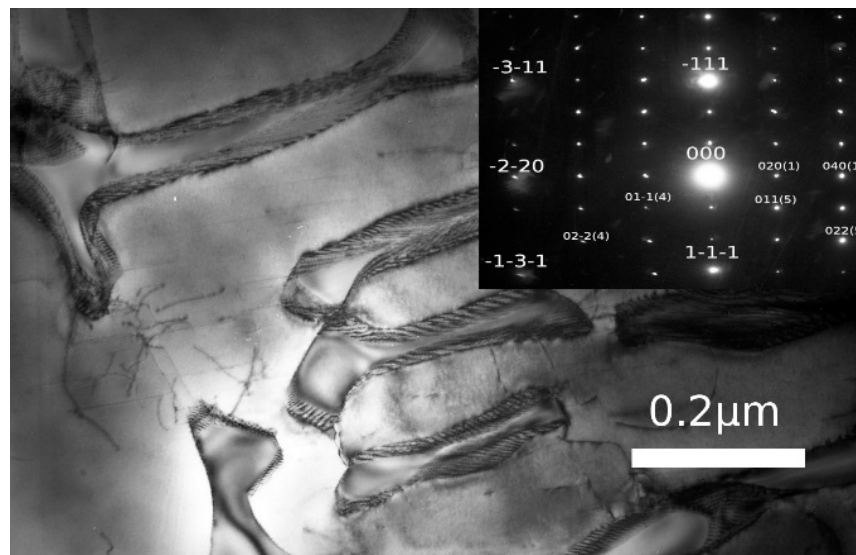


Figure 7. Co-V phase diagram provided by the National Physical Laboratory (USA). We have drawn dashed horizontal lines on this diagram, showing two temperatures of the “ordering-separation” phase transitions—at 800°C and 450°C. Microstructures in different areas of the diagram (points 1-5), indicated by the authors of the diagram, were obtained by X-ray diffraction.

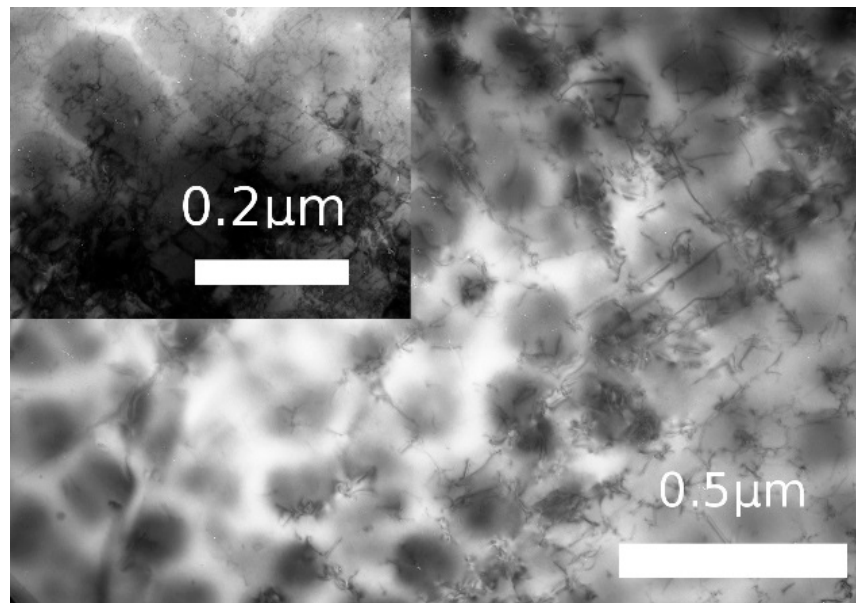
So, in the $\text{Co}_{75}\text{V}_{25}$ alloy, the “ordering-phase separation” transition occurs twice—at temperatures of 800 and 400°C - 450°C. Above 800°C, the alloy tends to undergo phase separation, which leads to the precipitation of bcc particles of vanadium atoms. In the temperature range 450°C - 800°C, the alloy tends to or-

der, which leads to the dissolution of particles of the chemical compound Co_3V type L1_2 . Below 400°C , a transition to phase separation is observed again.

Let us give a few more alloys as examples of what kind of microstructure exists in the regions that are now referred to in phase diagrams as regions of solid or liquid solutions. For example, **Figure 8(a)** shows that in the alloy $\text{Ni}_{40}\text{Cr}_{60}$.



(a)



(b)

Figure 8. (a), (b) Microstructure of the alloys $\text{Ni}_{40}\text{Cr}_{60}$ (a) and $\text{Ni}_{68}\text{Cr}_{32}$ (b) at 1455°C . Inset (a) is an electron diffraction pattern, inset (b) is the microstructure after heat treatment at 1000°C .

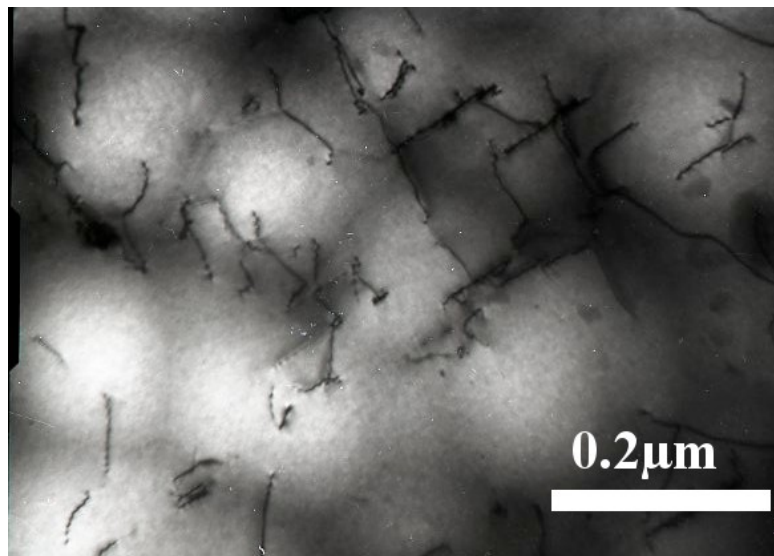
And $\text{Ni}_{68}\text{Cr}_{32}$ at 1455°C , that is, above the liquidus line, particles of the Ni_2Cr phase (Pt_2Cr type) are formed on the generally accepted Ni-Cr phase diagram, formed as a consequence of the tendency towards ordering. **Figure 8(b)** shows

that in the $\text{Ni}_{68}\text{Cr}_{32}$ alloy at 1455°C clusters of Cr atoms of round shape are formed as a consequence of the tendency to phase separation.

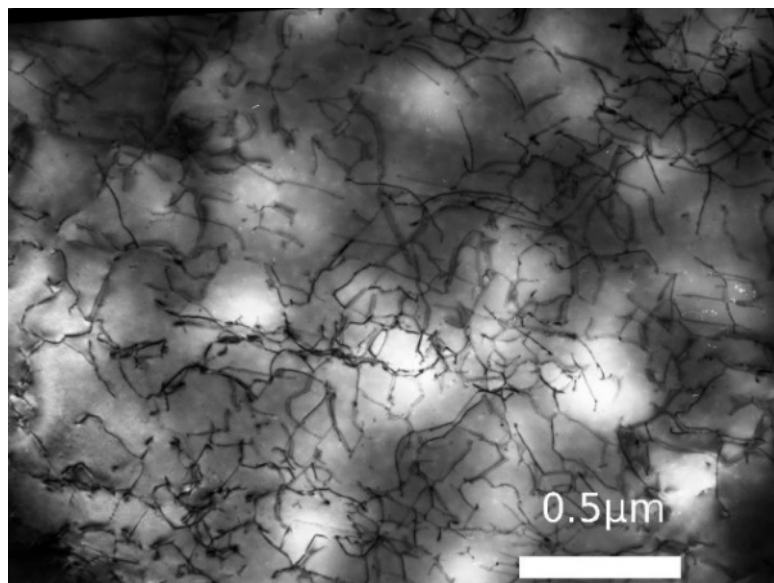
Figure 9 shows the microstructure (in the form of light blurry spots) in the Ni_3Co alloy, obtained after quenching from the liquid state (b) and after quenching from 800°C (a).

One can guess that this is the microstructure of clusters of Co atoms, which is formed due to the existing tendency in the Ni_3Co alloy to delamination at temperatures of the liquid state 800°C (and lower). Now look at the existing phase.

N-Co diagram. You will see that in all these areas of the diagram, there are no chemical interatomic interactions between the nickel and cobalt atoms.



(a)



(b)

Figure 9. Ni_3Co alloy. Water quenching from the liquid state (a) and 800°C (b). Absorbance contrast.

Figure 10 shows the microstructure that forms in the $\text{Co}_{70}\text{Mo}_{30}$ alloy due to the tendency to phase separation at heating clear to solidus temperatures. This microstructure consists of a molybdenum framework filled with cobalt atoms. This is why the alloy has such high hardness at pre-melting temperatures. At 1045°C in the alloy a phase transition occurs “ordering-separation” takes place, the chemical compound Co_3Mo forms and the hardness decreases.

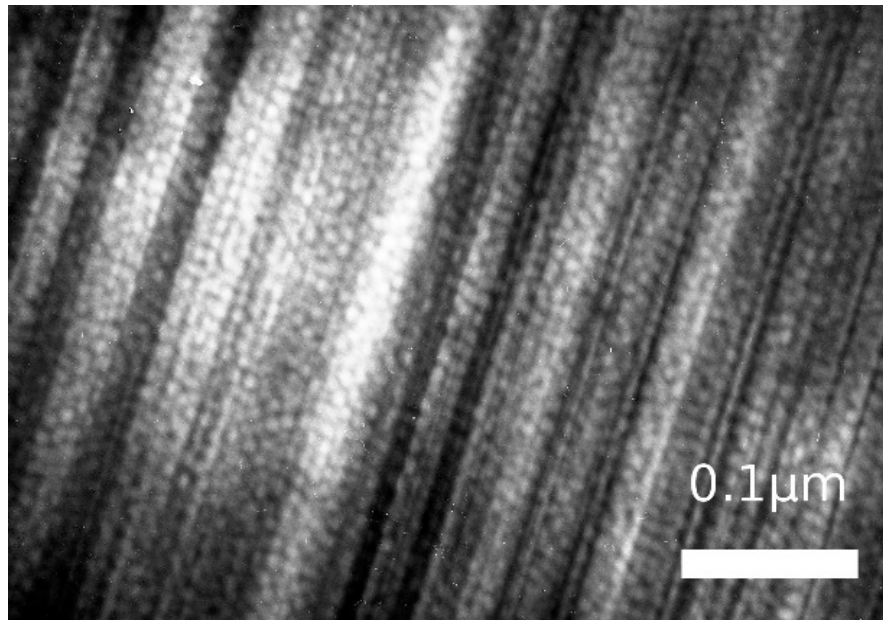


Figure 10. $\text{Co}_{70}\text{Mo}_{30}$ alloy. Queching from 1300°C . Cellular microstructure.

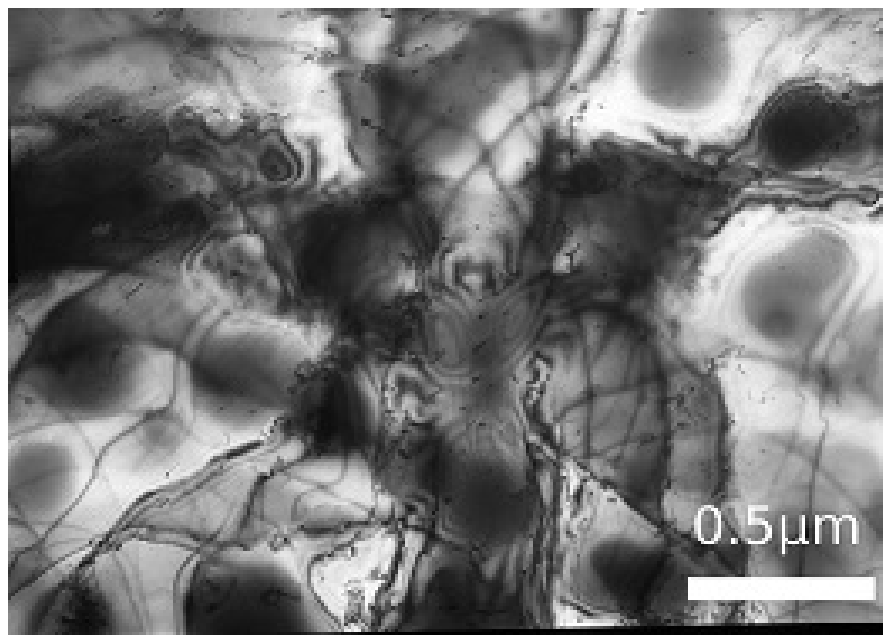


Figure 11. $\text{Fe}_{68}\text{Ni}_{32}$ alloy. Queching from 1300°C .

As shown in **Figure 11**, clusters of nickel atoms in γ -iron. Round clusters of

nickel atoms are observed due to absorption contrast.

Thus, all regions of solid solutions in existing phase diagrams and some other regions should currently be considered as “white spots” that are waiting for their researchers. Collections of binary phase diagrams published in many countries present readers with the high-temperature microstructure of alloys in these diagrams in the form of vast regions of disordered (*i.e.*, ideal) solid solution. At the same time, all researchers understand perfectly well that there cannot be ideal solid solutions in nature, and that the X-ray method for detecting microstructures in alloys has a low resolution. Why this happens is unclear. Therefore, our task of rearranging binary phase diagrams is to, using the method of transmission electron microscopy, determine what microstructure exists in regions of a supposedly disordered solid solution.

4. Discussion

A deep misconception is the idea existing in metallurgy that as the heating temperature of alloys increases, the diffusion of atoms accelerates and becomes chaotic, and at the same time, the chemical interatomic interactions that existed at lower temperatures disappear. Chemical bonds in alloys exist as long as the alloys themselves exist with their electronic structure, *i.e.*, during the entire time of their condensed state. These bonds cannot disappear, just as the electronic structure in metal alloys cannot disappear.

As is known, all the basic properties of alloys are determined by the chemical bond between nearest neighbors. This idea, first expressed by A. F. Ioffe, was subsequently repeatedly confirmed by experimental and theoretical works of other authors. The participation of a pair of nearby atoms in a chemical bond is described by the model of pair chemical interaction. It is believed that such a model is quite correct for binary alloys.

The “ordering-separation” transition we described in this article using the example of the $\text{Co}_{75}\text{V}_{25}$ alloy, as well as other examples, indicates that all diffusion structural-phase transformations that take place in binary alloys with temperature changes owe their origin to the chemical interatomic interactions that exist in alloys at all temperatures of the condensed state. What does this mean for existing phase diagrams constructed from experimental data and obtained using X-ray diffraction analysis? This means that such sections of phase diagrams must be constructed using the TEM method. One person cannot do such a job. This work must be done by the entire metallurgical community. It is necessary that all “white spots” on the phase diagrams disappear.

The “ordering-separation” phase transition that we discovered in alloys of 17 binary systems allowed us to conclude that all structural changes in metal alloys occur due to chemical interatomic interactions. The discovery of such chemical bonds in the liquid state of alloys led to the conclusion that chemical bonds exist in alloys at temperatures not only of the solid, but also of the liquid condensed state. These two discoveries mean that binary phase diagrams based on the idea

that at high temperatures the chemical interactions in alloys disappear and the structure is a disordered solid solution are incorrect. In the current situation, materials science has two options:

1) Leave binary phase diagrams unchanged, informing users that only the lines of massive phase transformations in these diagrams are correct. Regions of solid solutions, conclusions about the existence of which were obtained by the X-ray method, should be considered not to inspire confidence.

2) Draw the lines of the “ordering-separation” phase transition on the phase diagrams using the method of transmission electron microscopy. Before this, it is necessary to remove all areas of the solid solution, as well as those areas whose microstructure was obtained using X-ray phase analysis.

5. Conclusion

The article raises the question of what to do with one of the main achievements of materials science in previous years, which is the phase diagram of binary alloys. It is well known that phase diagrams play a key role in the creation of any metal machines and structures and therefore their reliability must be complete. However, the discovery of the “ordering-separation” phase transition, showing that chemical interatomic interactions are realized throughout the entire temperature range of the condensed state of alloys, forces us to reconsider all ideas about metal alloys.

Conflicts of Interest

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

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