

STRUCTURE AND PHASE TRANSITIONS

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ROLE OF METALLIC ALLOY INTERATOMIC CHEMICAL REACTIONS WITH STRUCTURE FORMATION DURING HEAT TREATMENT

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A new approach to explaining structure formation processes in alloys during heat treatment is suggested, which differs essentially from the traditional one. Experimental proof of the hypothesis that processes occurring in alloys during heat treatment develop due to interatomic chemical bonds (ionic and covalent) existing at condensed state temperatures is provided. This means that at each heating temperature alloy acquires a microstructure differing from that formed at other temperatures with respect to composition or size of precipitating particles. This makes quenching from the range of disordered solid solutions a superfluous operation, especially in the light of the fact that such solutions do not exist in nature. It is recommended to exclude quenching from the production process, which should be limited solely to tempering.

Key words: alloys, heat treatment, transmission electron microscopy, microstructure.

INTRODUCTION

Quenching and tempering (ageing) heat treatment of alloys has been known for a long time and it is currently performed in almost all engineering plants of the world. According to ideas conclusively formulated at the start of the last century in alloys after quenching from high temperature there is formation of a disordered solid solution microstructure. Subsequent tempering, performed at a lower temperature, leads to a situation that solid solution obtained as a result of quenching appears to be “supersaturated,” and from it there is precipitation of “excess” phases (by a spinodal mechanism” or a generation-growth mechanism). However, in the 1960 – 80s many researchers, for example [1, 2], using a transmission electron microscopy method (TEM), revealed that a quenched binary alloy microstructure is a not entirely disordered solid solution: within it after this quenching new phase particles are observed. This in no way fitted the then existing and now current ideas about metal alloy micro-

structure. Discussion at that time on this theme could not explain this phenomenon.

Only in 1996 when the authors of [3] observed within Fe – Cr alloy after quenching from a temperature above 1150°C particles of chromium atoms did it become clear that this is a reason for divergence between theory and experiment. In fact, existing ideas about alloys were formulated on the basis of x-ray phase analysis data, by means of which it is impossible to detect new phase particles having a size smaller than an x-ray beam coherent scattering region. At the same time, the TEM method, based upon other principles, free from this disadvantage, makes it possible to reveal very fine new phase particles (and also clusters) formed during at alloy heating temperatures for hardening. By comparing the microstructure formed in alloys of the Fe – Cr system at temperatures above 1150°C (chromium atom particles), at 600 – 830°C (α -phase) and below 550°C (chromium atom clusters), in [13] the authors concluded that within Fe – Cr alloys there is interatomic chemical interaction. With a change in temperature there is a change in the sign of this interaction from plus (tendency towards layering) to minus (tendency towards ordering), and then again to layering. Authors in [4]

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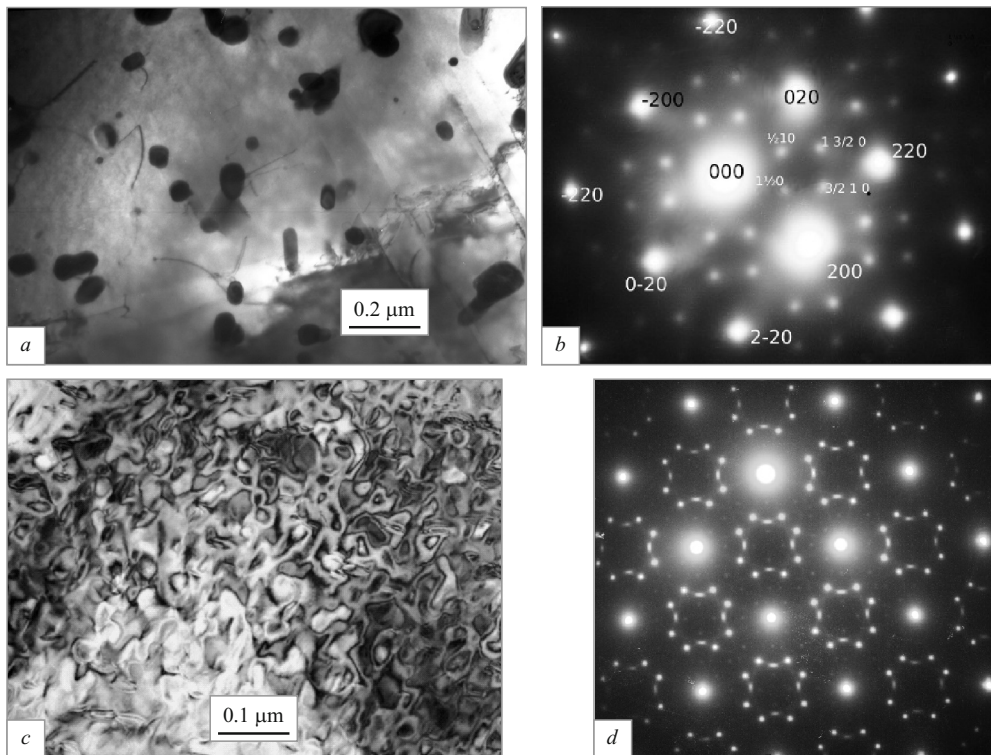


Fig. 1. Structure of alloy $Ni_{75}Mo_{25}$ after water quenching from a liquid condition (*a, b*) and from $800^{\circ}C$ (*c, d*); *a, c*) light field image; *b, d*) electron diffraction pattern.

have called this transition “ordering – layering”. Subsequently by using the TEM method this transition was revealed within alloys of 17 binary systems.

Based upon experimental results obtained by means of x-ray analysis the currently existing heat treatment theory for alloys has been constructed on the basis of proposals that chemical interatomic interaction within alloys quenched from high temperature is entirely absent. It is considered that they only develop at hardening temperatures, the reason is not understood, whereas chemical compound particles have been detected within alloys by experiment. However, our experimental studies of alloys quenched from a liquid condition have demonstrated that chemical bonds exist within alloys, and particles of chemical compounds form when alloys are still in a liquid condition [5, 6]. This fact contradicts the main positions of both new phase generation theory and also heat treatment theory.

In the present article we have attempted to show on the example of one binary and one ternary alloy that “ordering – layering” phase transition proceeding in these alloys at certain heating temperatures and having signs of chemical interaction between two neighboring atoms. Each pair of neighboring atoms is capable of transition, i.e., it is one of the main factors forming an alloy microstructure and therefore it is necessary to consider its role in selecting alloy heat treatment.

The aim of the present work is to analyze from the proposed theoretical ideas that in fact it proceeds in metal alloys

at heat treatment temperatures, and why it is not possible to perform alloy hardening “from a solid solution region.”

METHODS OF STUDY

Alloys $Ni_{75}Mo_{25}$ and $Ni_{50}Mo_{25}Co_{25}$ were studied after quenching from $1300^{\circ}C$, which is normally used in order to obtain a disordered solid solution. These alloys were quenched from a liquid condition, i.e., a small portion of molten metal was poured from a crucible directly into water.

Microstructural analysis of alloys was performed using an EM-125 transmission electron microscope. Foils for study were prepared by a standard procedure.

RESULTS

Alloy $Ni_{75}Mo_{25}$. For those who have encountered the problem of pouring liquid Ni – Mo-alloys its very low fluidity even on heating by $200^{\circ}C$ above the liquidus line has been surprising. Analysis of the alloy structure after water quenching from a liquid condition (Fig. 1*a* and *b*) makes it possible to explain the reason for this. Dark rounded molybdenum particles are seen in Fig. 1*a* that form simultaneously on charge melting. This signifies that at liquid state temperatures within the alloys studied there is a tendency towards phase layering. In fact, in electron diffraction patterns an ad-

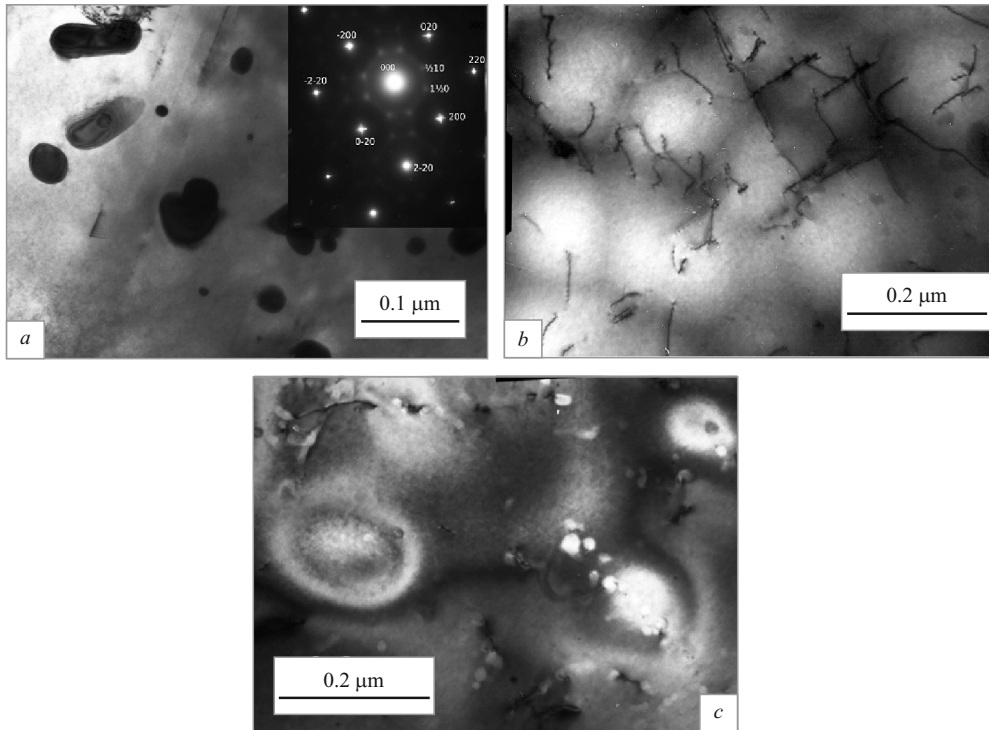


Fig. 2. Structure of alloy $\text{Ni}_{50}\text{Mo}_{25}\text{Co}_{25}$ after water quenching from liquid condition (*a, b*) and from 600°C (*c*): *a*) Ni/Mo diffusion micropore; *b*) Ni/Co diffusion micropores; *c*) phase transition “layering – ordering” in Ni/Co diffusion micropore.

ditional reflection $\{1 \frac{1}{2} 0\}$ system is observed in the form of four symmetrical pairs (Fig. 1*b*), which form within the vicinity of each of fundamental reflections $\{110\}$ and $\{200\}$. Alloy quenching from 1300°C , i.e., from a temperature that is in the range normally used for preparing a “disordered solid solution” gives precisely the same result.

However after alloy quenching from 800°C a system of supplementary reflections $\{1 \frac{1}{2} 0\}$ in an electron diffraction pattern disappears. The microstructure and electron diffraction pattern of alloy $\text{Ni}_{75}\text{Mo}_{25}$ after quenching from 800°C differs fundamentally from preceding examples (Fig. 1*a* and *b*). An electron diffraction pattern in Fig. 1*d* is interpreted as consisting of a collection of two reflection systems: a reflection system from particles of a chemical compound with structure type D1_a and a set of diffusion arcs which concern orthorhombic BCC-phase Ni_2Mo (type Pt_2MO). From comparison of these data it follows that at temperatures below 1200°C within $\text{Ni}_{75}\text{Mo}_{25}$ alloy there “layering – ordering” phase transition, i.e., the chemical interaction sign between atoms of Ni and Mo changes from plus to minus [7].

Detection of molybdenum atom particles within a melt and existence “ordering – phase layering” transition proceeding at lower temperatures, make it possible to conclude that the chemical bond occurs in both alloy solid and liquid states. From this it also follows that such quenching does not

lead to formation of a disordered (i.e., ideal) solid solution since alloy is not in a liquid state. This also signifies that it is necessary to consider thermodynamic rules and to acknowledge the indisputable fact ideal solid solutions do not exist in nature. Consequently, refraining from the rudiment of past years, i.e., double heat treatment (quenching + tempering or ageing), only tempering remains at the same temperature with which it was conducted previously after quenching “for a solid solution.”

Alloy $\text{Ni}_{50}\text{Mo}_{25}\text{Co}_{25}$. When we are talking about a diffusion micropair within ternary alloys and why it forms, it is possible to provide the example of alloy $\text{Ni}_{50}\text{Mo}_{25}\text{Co}_{25}$ whose composition was selected in order that the sum of dissolved component atoms equaled the number of solvent atoms. Water quenching this alloy from a liquid state leads to the situation that within it there may be formation of solely two diffusion pairs Ni/Mo and Ni/Co. The microstructure is provided in Fig. 2 obtained after quenching $\text{Ni}_{50}\text{Mo}_{25}\text{Co}_{25}$ alloy in water from a liquid state. Particles of molybdenum are seen in Fig. 2*a* in one of the foil sections, and in the inset is an electron diffraction pattern strands are observed close to the main reflections. These strands point to lattice distortion within an Ni – Mo-micropair separated by Mo particles. It should be noted that in this electron diffraction pattern some additional reflections $\{1 \frac{1}{2} 0\}$ still remain, also contained in

an electron diffraction pattern for binary alloy $\text{Ni}_{75}\text{Mo}_{25}$ after quenching from a melt (Fig. 1*b*).

However, in another section of the foil an entirely different picture is revealed. Round light spots with size of the order of 0.1 – 0.2 μm with diffused edges are observed in Fig. 2*b* due to absorption contrast for clusters of dissolved component atoms, i.e., cobalt. Other elements of the microstructure, for example dislocations, are revealed within a micro-picture due to diffraction contrast. Therefore it follows from Fig. 2*a* and *b* that the alloy microstructure in a liquid state is a mixture of areas within which accumulation of molybdenum atom particles or clusters of cobalt atoms are located. We have called these areas diffusion micropairs. The size of diffusion micropairs could be evaluated by studying alloy $\text{Ni}_{65}\text{Mo}_{20}\text{Co}_{15}$ [8]. In this alloy apart from Ni/Mo diffusion micropairs there is formation of a second NiCr diffusion micropair whose structure is periodic waves of contrast from chromium atom clusters spreading from one micropair boundary to an opposite boundary. This situation also makes it possible to evaluate the size of micropairs as equal to some tens of microns [9].

With quenching temperatures lower than 1200°C in binary $\text{Ni}_{75}\text{Mo}_{25}$ alloy a “layering – ordering” transition commences [7]. The same transition at this temperature is observed in an Ni/Mo ternary alloy diffusion micropair. The alloy microstructure formed at 800°C is shown in Fig. 1*c* and *d*. It is seen that after an “ordering – layering” phase transition, proceeding at 1100 – 1200°C there are no Ni/Mo diffusion micropairs formed previously in an alloy liquid state.

With a further reduction in quenching temperature to 600°C a “layering – ordering” transition commences within an Ni/Co diffusion pair. The alloy structure at the instant of this transition is shown in Fig. 2*c*: clusters of cobalt atoms (absorption contrast) are dissolved and within their vicinity there is formation of fine light particles of Ni_3Co chemical compound (diffraction contrast). Therefore, in ternary alloy within diffusion micropairs of each type “ordering – phase layering” transition proceeds at the same temperature as also in binary alloys corresponding to them with respect to composition.

DISCUSSION OF RESEARCH RESULTS

The results of experimental studies obtained indicate that in contrast to currently existing ideas about heat treatment, within metal alloys at all temperatures there is chemical interaction between similar (covalent bond) and differing (ionic bond) atoms. These reactions exist in both alloy liquid and solid states. The latter signifies that we sometimes cannot obtain disordered solid solution after alloy quenching from the “solid solution region” even if quenching is conducted from a liquid state. This also indicates that at each temperature within a alloy there is formation of a microstructure layer differing from the microstructure at other temperature with respect to type or dispersion. The final alloy

microstructure is determined by final heat treatment temperature, i.e., tempering (ageing). Preliminary heat treatment, such as quenching from a “disordered solid solution region,” cannot affect the alloy final microstructure if after it some other heat treatment is performed.

The experimental results obtained make it possible to draw the following conclusions: “ordering – layering” phase transition, including changes in chemical reaction sign between atoms *A* and *B* and proceeding at the level of changes within the microstructure of binary alloy *AB*, is a consequence of “ionic bond \leftrightarrow covalent bond” electron transfer. This transition may be interpreted as follows.

1. The ionic component of a chemical bond is activated when with an increase in alloy temperature, and consequently acceleration of diffusion, atoms *A* and *B* become close neighbors. Due to this approach their valent orbitals are localized, i.e., chemical bond A_xB_y forms.

2. A covalent component of a chemical bond is activated for the same reason: two atoms of dissolved component *B* become close neighbors when with this approach their valent orbitals are hybridized, i.e., a cluster forms consisting of these two *B* atoms.

It should be noted that transitions detected experimentally by us and our publications on the same problem so far have not led to any changes in the world view of metallurgists. At the same time, development and practical use these proposed approach to explaining process proceeding within alloys during heat treatment provide new possibilities for increasing production and operating properties components and objects, and also significantly reduce expenditure for their heat treatment.

CONCLUSIONS

The experimental results obtained and their analysis make it possible to consider reliably existence of this type of microstructure as diffusion micropairs, and conversely negate presence of this type of microstructure as a disordered solid solution. Confirmation and acknowledgment of these ideas will make it possible to make significant changes in metal alloy heat treatment technology, and to correct binary alloy phase diagrams, including regions of existing disordered solid solutions. Possibly, one of the directions for future development of metal alloy science becomes an approach within which the moving force of all processes occurring with an alloy will be acknowledged as interatomic chemical interactions. They are a reason for generation of new phases and structures within an alloy liquid state and changes in the type of structure during “ordering – layering” phase transition

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