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Mapping of the transition ‘ordering-phase separation’ into phase diagrams

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ABSTRACT

The article on the example of two alloys Co_2V and Co_3V discusses the principles of the modern phase diagram construction in connection with the discovery of the phase transition ‘ordering-phase separation’ in alloys. The results of electron microscopic studies of the Co_2V alloy after heat treatment at different temperatures are presented. Comparison of the obtained data with the existing Co-V phase diagram shows that these results do not coincide with those that follow from this diagram. An explanation of why this discrepancy exists is presented. It is concluded that the phase transition ‘ordering-phase separation’ must be considered when creating modern phase diagrams. Phase diagrams of Fe-Cr and Ni-Cr, taking into account the existence of such a transition were presented as examples. Methodical instructions on how to determine the temperature of the phase transition “ordering-phase separation” using the method of transmission electron microscopy are given. It is concluded that the introduction of such a concept as the phase transition ‘ordering-phase separation’ will change in future the principles that guide researchers in creating phase diagrams.

1. Introduction

As is known, phase diagrams were created in Materials Science with a view to allow researchers and engineers gaining an in-depth understanding of the relationship between heat treatment, structure and therefore properties of alloys at all length scales, including nanostructures. These diagrams, in fact, began to play the role of a guide in the world of alloys for engineers and researchers. They are designed to reflect the profound relationship between interatomic chemical interactions and phase transformations occurring in alloys with a change in the temperature. Therefore, they must contain all information about these transformations, i.e., each of them must be an encyclopedia of knowledge on alloys of the system. These diagrams have been built for binary systems of practically all pairs of metallic elements and published in a large number of reference books. Currently, adjusted phase diagrams, calculated using the CALPHAD method, are constantly being published on the Internet.

However, in the sixties-seventies, when the method of transmission electron microscopy (TEM) became widely used for studying the microstructure of alloys, many authors were surprised to find that the microstructures of many alloys, quenched from the solid solution regions, were not single-phase solid solutions but contained either particles of a chemical compound, or modulations of the composition [1–7]. Examples that have become classic are alloys of the systems of Ni-Mo [1], Fe-Be [2], Cu-Ti [3], Cu-Be [4], Nb-Zr [5], Fe-C [6,7] and many others, which, according to phase diagrams, at high temperatures, had regions of the solid solution.

When such results were published, almost no one doubted that the blame for such a disagreement with phase diagrams should be placed on the experimental procedure, not on the phase diagrams. A hypothesis was proposed, according to which, the decomposition of alloys proceeding by the spinodal mechanism, occurred during the very process of quenching, i.e., a very short period of time, comparable with the time of cooling the alloy in water. Such behavior of alloys was explained by the fact that at spinodal decomposition, the stage of critical nuclei formation is absent.

We have already discussed in detail [8] which is responsible for this situation: the method of X-ray diffraction (XRD) is integral and not able to detect highly dispersed particles of a new phase which are reliably registered by a local method – the method of TEM. The cause why the disagreements occurred was the fact that phase diagrams were built using XRD data; however, the microstructure was investigated using the method of TEM. Analysis of these data, allowed us to conclude [9] that the regions of the solid solution in

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equilibrium phase diagrams are in fact two-phase regions. In this case, the fact that in the generally accepted equilibrium phase diagrams there exist large regions of solid solution (which according to chemical thermodynamics is not an equilibrium phase) is quite explicable: the limited capabilities of the XRD method do not allow to use it for detecting highly dispersed phases.

The discovery of the phase transition ‘ordering-phase separation’ [10] has confirmed these suppositions. This transition occurs at a temperature, which is specific for each system, when the sign of the chemical interaction between atoms of A and B in the AB alloy is changed. The transition occurs at the level of changes in the electronic structure of the alloy (the shape of the valence band determined by X-ray photoelectron spectroscopy (XPS) is changed [11,12]). The change of the sign of the chemical interaction energy between component atoms reverses the direction of diffusion fluxes in the alloy, which affects changes in the type of microstructures. If a tendency to ordering is exhibited in the alloy, then chemical compounds are formed in the microstructure. If a tendency to phase separation is exhibited, then clusters (or grains) are formed, consisting mainly of atoms of one kind (is determined by TEM). As for the microstructures that existed before, they dissolve. Seventeen binary systems have been studied in more or less detail since the discovery (of the phase transition ‘ordering-phase separation’) and such a transition has been found in sixteen of them [9].

Following from this, it becomes clear that it is not the degree of supersaturation of solid solution that is the driving force of new phase formation. Two factors have a decisive influence on this process: the sign of the chemical interaction energy (otherwise known as ordering energy) and the absolute magnitude of this energy [9]. The sign indicates the trend which appears in the alloy at a given temperature – a tendency to ordering (minus) or a tendency to phase separation (plus). The absolute magnitude of this energy also plays a big role in whether there will or will not occur precipitation of new phases [9]. It is clear that at the temperature of the phase transition ‘ordering-phase separation’, when the chemical interaction energy is zero, no new phase can precipitate. We would like to emphasize that at some distance from the transition point, the absolute magnitude of the chemical interaction energy may be insufficient for precipitation of a new phase and it also can lead to formation of a solid solution. This means that not only at the exact temperature of the transition but also in a certain range of temperatures near the phase transition point, there can be formed the microstructure of a disordered solid solution [9].

It becomes obvious that the existence of such a phase transition in alloys can not be further ignored; it is necessary to display this transition in phase diagrams because it is precisely this transition that directly determines changes in the microstructure of alloys. The next question is how to do it, if the principles on the basis of which the currently existing phase diagrams were created (precipitation of new phases occurs due to an increase in the degree of supersaturation of the solid solution occurring at lowering the temperature of the solution) and the principles that underlie the phase transition “ordering -phase separation” (precipitation of new phases occurs as a result of a change in the sign and/or the absolute value of the chemical interaction energy depending on the heat treatment temperature of the alloy) are completely incompatible.

Briefly, the principles that underlie the phase transition ‘ordering-phase separation’ can be formulated as follows: 1. Chemical interaction between dissimilar atoms exists always, in all alloys and at any temperature of heating. 2. Precipitation of this or that phase and formation of a solid solution depends not on the degree of solubility of solutes in the lattice of the solvent, but on the sign and the absolute magnitude of the energy of the chemical interaction between dissimilar atoms. 3. The sign of the energy of the chemical interaction between dissimilar atoms is not a constant for the majority of metallic systems but varies with the change of the temperature of the alloy (sometimes more than once). Of course, if the basic principles of these two approaches differ fundamentally, it is unlikely to be expected that the interpretation of microstructures will be the same.

In the literature on Co-V alloys, we have discovered only two articles in which microstructure studies of the Co-V alloys were conducted with the help of the TEM method. One of these studies was the work of Aoki and Echigoya [13]. They investigated the Co –18.2% V alloy. After a heat treatment at 800° C during 553 h, the alloy showed sharp satellite spots appearing near the fundamental reflections. The authors [13] concluded that particles giving these satellites are the Co_3V ($L1_2$) phase. The first attempt to verify this was the work which was carried out on the Co_3V alloy, the composition of which corresponded to the stoichiometric composition of the Co_3V phase [14]. It was found that in the Co_3V alloy, the phase transition ‘ordering-phase separation’ occurs two times – at a temperature of about 800 and about 450 °C. Above 800 °C, including the liquid state, a tendency to phase separation takes place in the alloy, which leads to formation of bcc particles of vanadium atoms in the solution. In the temperature range of 450–800° C, a tendency to ordering takes place in the alloy, which results in precipitation of particles of the Co_3V chemical compound of the $L1_2$ type. At temperatures below 450 °C, a honeycomb microstructure is formed in the alloy, as a consequence of the emergence of the tendency to phase separation. By comparing the obtained results with the existing phase diagram of Co-V, it has been shown that these data coincide [14] only in the point of the solidus temperature.

Of course, on the grounds of the structural study of only one alloy [14] it is rather risky to draw a far-reaching and important conclusion that the existing phase diagram of Co-V gives a distorted view of what processes occur in the Co-V system. Precisely this was the reason to study another alloy of the said system - the Co_2V alloy. According to the phase diagram, the Co_2V alloy has a two-phase region (Co_3V + CoV (σ)) at temperatures up to 1026 °C and a eutectic - at temperatures of 1026–1242 °C [15].

2. Experimental

The Co_2V alloy was melted from pure components (99.7% Co and 99.8% V) in a vacuum induction furnace. Castings were forged to rods (4 × 4 mm section). Specimens for TEM investigation (discs, 3 mm in diameter x 0.2 mm thickness) were cut from forged pieces and further heat-treated in quartz ampoules. The heat treatment of the alloy under study was conducted in the same manner as the alloy Co_3V [14]: at 1150, 800, 500 and 350° C. This was done in order to facilitate the interpretation of results. Quenching from the liquid state was performed by simply pouring the molten metal from the crucible into water. Thin foils were obtained by electropolishing in a 15% solution of sulfuric acid in methanol. The foils were examined in an electron microscope EM -125 at an accelerating voltage of 100 kV.

3. Results

Quenching of the alloy from the liquid state fixes the microstructure, similar to that previously found in the Co_3V alloy at the same heat treatment. The bright-field image of the microstructure is presented in Fig. 1. In the electron diffraction pattern, near the fundamental reflections, which correspond to the fcc lattice of Co, satellites appearing from these bcc of V-particles are visible (Fig. 1, inset). These particles of a more refractory element - vanadium crystallize in the liquid solution due to the tendency to phase separation, which exists in the alloy at high temperatures [14].