Journal of Alloys and Compounds 714 (2017) 476–483

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Changes in electronic structure of metallic alloys at the transition 'ordering-phase separation'

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ARTICLE INFO

Article history:
Received 25 January 2017
Accepted 23 April 2017
Available online 24 April 2017

Keywords:
Electronic structure
Microstructure
'Ordering-phase separation' transition
Transmission electron microscopy

ABSTRACT

A brief review of works is given in which, using the method of transmission electron microscopy, the phase transition 'ordering-phase separation' has been found, which indicates that the sign of the energy of the chemical bond between the atoms of the components changes at a change in the temperature or composition of the alloy. It has been shown that in the case of the tendency to ordering, this sign is negative and chemical compounds are formed in the alloys, in the case of the tendency to phase separation, the sign is positive and formation of either clusters enriched with solute atoms or grains of solute atoms takes place in the alloys. Proofs are presented that the phase transition 'ordering-phase separation' begins with changes in the electronic structure of an A(B) alloy. It leads to delocalization of the valence electrons on the atoms of A and B and hybridization of the valence electrons on the atoms of B. Along with the metallic component, the covalent component of the chemical bond is formed. The transition 'phase separation-ordering' begins with dehybridization of the valence electrons on the atoms of B and localization of the valence electrons on the atoms of A and B. Along with the metallic component, the ionic component of the chemical bond is formed. Such changes in the electronic structure are the cause of subsequent changes in the microstructure of alloys.

1. Introduction

As is known, the fundamental properties of solids are determined by the nature of the chemical bond between the nearest neighbors. The chemical bond is usually understood as a combination of all forces acting on each atom in the solid and keeping it in the state of equilibrium. Three main types of a strong chemical bond exist between atoms – the metallic, ionic and covalent bonds. It is believed that the metallic bond occurs in metals and metallic alloys, when the valence electrons are collectivized and form an electron gas ("an array of positive ions in a sea of electrons"). The ionic bond forms between atoms of different species (usually, metals and non-metals), when atoms of one kind can transfer or share their valence electrons with atoms of another kind. This bond is characteristic for halides, alkalis, hydrides and other chemical compounds. The covalent bond forms between similar atoms of non-metals (nonpolar bond) and between dissimilar atoms of non-metals (polar bond) due to overlapping (collectivization) of a pair of valence electrons. These two electrons must, moreover, occupy two stable orbitals, one from each atom involved in the bond. These are, in brief, the current understandings of chemical bonds in solids.

For metallic alloys, these understandings are not entirely consistent with what we observe experimentally. There is no doubt that in metallic alloys, as well as in pure metals, there is a metallic bond, but in contrast to pure metals, where this bond is the only possible, in metal alloys, alongside with this bond, there must be other types of bonds, as well. Otherwise, it is impossible to explain the presence, in the microstructure of alloys, of second phase particles. It is obvious that the chemical bond inside these particles is different from the metallic bond existing in the rest of the matrix. In alloys, in which the microstructure is a eutectic or structures similar to it, clusters of atoms of the solute component, for example, inside these precipitations a covalent bond should take place; in alloys, in which chemical compounds precipitate- in such compounds there should exist an ionic bond.

A detailed study of the type of chemical bonds existing in alloys after various temperatures of heat treatment was conducted in a series of electron microscopic studies, the reviews of them published in Refs. [1,2]. It has been shown experimentally by the example of alloys of 17 binary systems that dissimilar atoms can participate in the formation of a chemical compound only if the

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http://dx.doi.org/10.1016/j.jallcom.2017.04.250
0925-8388/© 2017 Published by Elsevier B.V.

sign of the chemical interaction energy is negative, i.e. when they attract each other [1,2]. If the sign of the chemical interaction energy between the dissimilar atoms is positive, then a phase separation takes place in the alloy and enriched clusters or grains consisting of solute atoms are formed. It has been shown that the alloys have the ability to change the sign of the energy of the chemical interaction at a change in the temperature of their heat treatment or in the composition of the alloy [1,2]. Such a change of the sign the chemical interaction energy has been given the name phase transition ‘ordering-phase separation.’

The fact of the discovery of the phase transition ‘ordering-phase separation’ has shown that it is not the degree of supersaturation of the solid solution in alloying element that is the driving force of the process of new phase precipitation in alloys. Such a driving force is chemical interactions between atoms, which always exist in alloys, but manifest themselves differently at different temperatures. Two factors have a decisive influence -the sign and the absolute magnitude of the energy of the chemical interaction between dissimilar atoms [2]. The sign indicates which tendency is manifested in the alloy at this or that temperature - the tendency to ordering (minus), or the tendency to phase separation (plus). The absolute magnitude of this energy also plays a big role in whether there will or will not happen precipitation of these or those phases near the phase transition temperature [2]. It was believed that at the temperature of the phase transition ‘ordering-phase separation’, when the energy of the chemical interaction is close to zero, no other phases would form besides the solid solution. Therefore, it is precisely near the phase transition temperature that an alloy may have a disordered solid solution structure [1,2]. In more distant surroundings of the phase transition temperature, the absolute magnitude of the chemical interaction energy may be not high enough for precipitation of a new phase to start, and this fact can lead to expansion of the area in which the solid solution structure exists. Everything depends on the nature of the alloy. The latter may mean that near the phase transition line on the diagram there exists not a line but a range of temperatures within which a disordered solid solution structure is formed [2].

The phase transition ‘ordering-phase separation’ occurs at a temperature, which is quite definite for each binary system. With the help of the XPS method, it has been shown that this transition occurs at the level of changes in the electronic structure of alloys (the shape of the valence band at such a transition changes [3,4]). Using the results obtained by the TEM method, it has been concluded that the change of the type of the alloy microstructure occurs at approximately the same temperature, at which the shape of the alloy valence band changes.

Such an interpretation of chemical bonds existing in alloys [1,2], gave rise to the following question: what is the energy of the chemical interaction and how does it correlate with the above mentioned views of chemistry on the types of chemical bonds. To answer this question, this article discusses the previously presented results of experimental studies of some alloys of transition metals, in which there occurs the phase transition ordering-phase separation. In light of these results, we also discuss the existing ideas about the types of chemical bonds in relation to metal alloys.

2. Survey of recent advances in the study of the transition 'ordering-phase separation'

2.1. Fe-Cr alloys

The phase transition 'ordering-phase separation' was first detected in the Fe-Cr alloys [5]. The Fe-rich part of the Fe-Cr phase diagram was constructed taking into account the existence of two such transitions [6]. In a modernized form, this diagram is shown in Fig. 1. From the diagram it follows that at temperatures of 1200–1400 °C, as well as 550 °C and below, a phase separation microstructure is formed in the $Fe_{50}Cr_{50}$ alloy (Fig. 2). The sigma-phase is formed in the temperature range of 600–830 °C. (Although this phase is formed only in the surface layer of the specimen up to 0.4 mm thick, nevertheless, its presence indicates that this layer of the alloy has a tendency to ordering). In the rest of the volume of the alloy, a metastable structure of chemical (electron) domains is formed, which consists of alternating microscopic sites of the solid solution, in some of which, there is a tendency to phase separation while in others, a tendency to ordering (Fig. 3). The presence of the chemical domains prevents formation of the sigma-phase in those microscopic sites of the volume where these domains have formed [7].

The width of this temperature range in which only the solid solution is formed may be different for every transition. As can be seen from Fig. 1, in the Fe-Cr system, where two phase transitions 'ordering-phase separation' occur, at the high-temperature transition, the width of the range is about 850–1150 C°C. At low-temperature transition, this range is equal to 550–600 °C [5]. Outside these temperature ranges, the absolute magnitude of the chemical interaction energy is sufficient for the second phase to form in the alloy: the sigma-phase (at the surface of the specimen) when the sign is negative, or clusters enriched in Cr atoms when the sign is positive.

Using all these experimental data, a scheme (Fig. 4) was built, which explains how in the $Fe_{50}Cr_{50}$ alloy, the sign and the absolute value of the chemical interaction energy change at changing the temperature in the vicinity of the point of the phase transition

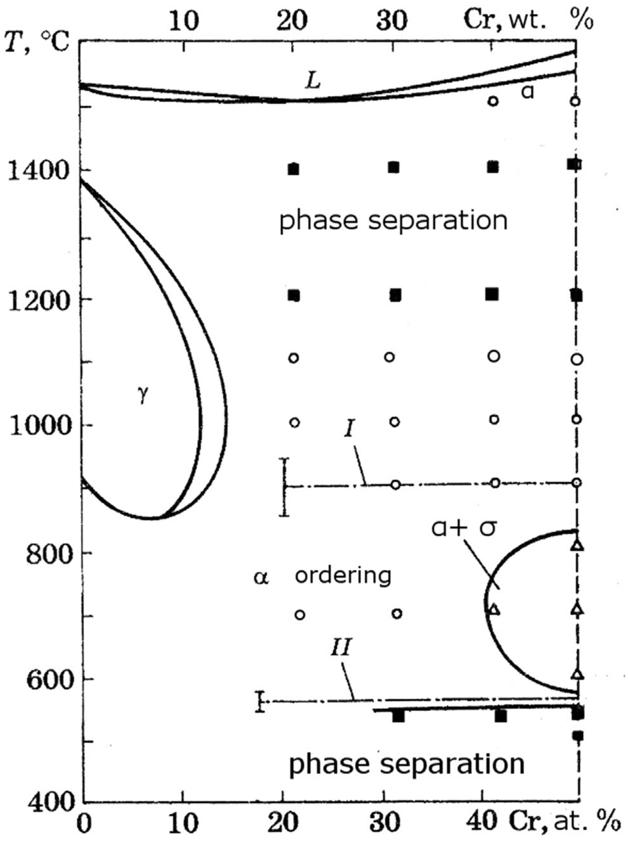

Fig. 1. The Fe-rich portion of the Fe-Cr phase diagram. Dashed lines show the temperatures of phase transition ‘ordering-phase separation’. Designations: o – solid solution microstructure; □ – phase separation microstructure; Δ -σ-phase at the surface (tendency to ordering).