Materials Chemistry and Physics 165 (2015) 14–18

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Phase transition 'ordering-phase separation' in alloys of Ni–Cr system

Y. Ustinovshikov

Physical-Technical Institute, 132 Kirov St., Izhevsk, 426000, Russia

HIGHLIGHTS

- Transition line 'ordering-phase separation' was constructed for Ni–Cr system.
- The chemical interaction energy sign changes with changes in Ni–Cr alloys composition.
- Method of determination of the 'ordering-phase separation' line is offered.

ARTICLE INFO

Article history:
Received 25 December 2014
Received in revised form
21 April 2015
Accepted 9 May 2015
Available online 26 September 2015

Keywords:
Alloys
Phase transitions
Electron microscopy (TEM)
Microstructure

ABSTRACT

An electron microscopic study of the microstructure of the $Ni_{46}Cr_{54}$, $Ni_{56}Cr_{44}$ and $Ni_{62}Cr_{38}$ alloys after heat treatment at different temperatures has been carried out in order to determine the line of the phase transition 'ordering-phase separation' in the Ni–Cr system. The results have been compared with the data obtained previously for the $Ni_{40}Cr_{60}$ and $Ni_{68}Cr_{32}$ alloys. It has been shown that in the $Ni_{46}Cr_{54}$ alloy as in the $Ni_{40}Cr_{60}$ one, particles of the Ni_2Cr chemical compound are formed in the entire temperature range, as a result of the tendency to ordering. Heating of the $Ni_{56}Cr_{44}$ and $Ni_{62}Cr_{38}$ alloys to certain temperatures leads to formation of phase separation microstructures, heating to others leads to the appearance of ordering microstructures. The obtained experimental results indicate that the position of the line separating the regions of ordering and phase separation in the phase diagram of Ni–Cr, in a greater degree depends upon changes in concentration than changes in temperature.

1. Introduction

The phase transition 'ordering-phase separation', which consists in the fact that at certain temperatures, the sign of the energy of the chemical interaction between the component atoms constituting the alloy is reversed, has been found in many systems, a review of which is given in Ref. [1]. It was believed that such a phase transition occurs at a quite definite for each binary system temperature for each binary system, which was named the temperature of the phase transition 'ordering-phase separation'. When in the process of heating or cooling an alloy the temperature passes through the phase transition point, the sign of the energy of the chemical interaction between component atoms passes through zero changes. In this connection, the microstructure, which has formed in a certain temperature range near this point, is a disordered solid solution. It was believed that each system had its own transition temperature, which was the same for all alloys of this system. Therefore, they believed that to determine the temperature of such a phase transition it was sufficient to take only one of any alloys of this system and to investigate it. The temperature of the phase transition 'ordering-phase separation' can be determined either by carrying out a study of changes in the microstructure formed in the alloy after its heat treatment at different temperatures by the method of transmission electron microscopy (TEM), or the study of changes in the electronic structure at heating and cooling the specimen to different temperatures by the method of X-ray photoelectron spectroscopy (XPS). Indeed, for a number of systems in which two or more compositions were studied (for example, $Fe_{80}Cr_{20}$, $Fe_{70}Cr_{30}$, $Fe_{60}Cr_{40}$, $Fe_{50}Cr_{50}$ [1]; $Fe_{68}Ni_{32}$, $Fe_{23}Ni_{77}$ [2]; Ni_3Mo, Ni_4Mo [3]), the temperature of the phase transition 'ordering-phase separation', for all compositions studied, was the same.

There also are systems, in the alloys of which, at temperatures close to the temperature of the phase transition 'ordering-phase separation', a disordered solid solution is not formed. In this range of temperatures, for example, at transition from phase separation to ordering, there occurs 1)a simultaneous dissolution of clusters enriched in alloying component which formed earlier as a consequence of the tendency to phase separation, and 2) precipitation of

E-mail address: ust@ftiudm.ru.

http://dx.doi.org/10.1016/j.matchemphys.2015.05.027
0254-0584/

particles of chemical compounds forming as a result of the tendency to ordering. This can be found in the results of the study of alloys of the Ni-Co [4] and Co–V [5] systems. In the Ni_3Co and Co_3V alloys of these systems, in the vicinity of the phase transition point, there exists a strip of a microstructure consisting of two types of alternating sites. In some of these sites, the dissolution of the microstructure of phase separation is not yet over, and in the others - the microstructure of phase separation has already dissolved and an ordering microstructure has formed in its place.

However, there exists one more system which differs from other systems in the fact that in it, the phase transition {ordering-phase separation} occurs as a result of a change in concentration, not a change in the temperature of the alloy. Only one system of this kind is known so far - the Ni–Cr system [6]. It was found that in this system, the sign of the ordering energy of the $Ni_{40}Cr_{60}$ and $Ni_{68}Cr_{32}$ alloys was different in the entire temperature range of their heating, although the author [6] interpreted his results somewhat differently. Such a change in the type of the chemical bonding between dissimilar atoms, which occurs in dependence upon the change of the concentration of alloys, does not yet have any reasonable explanation.

Two alloys were studied in Ref. [6]: the $Ni_{40}Cr_{60}$ and $Ni_{68}Cr_{32}$ alloy. According to the existing phase diagram of Ni–Cr [7], at compositions close to the $Ni_{40}Cr_{60}$ alloy, a eutectic is formed in the Ni–Cr system. This could mean that in alloys of such a composition there becomes apparent a tendency to phase separation. However, over the entire temperature range of the study, from the liquid state of this alloy to 550 °C, only structures corresponding to the tendency to ordering were found experimentally. The microstructure after quenching from the liquid (1450 °C) state consists of relatively large grains of an elongated shape, randomly arranged in the matrix. An electron diffraction pattern, obtained from these grains, indicates that they have an orthorhombic lattice of the Pt_2Mo type, characteristic of the Ni_2Cr chemical compound [6]. However, according to the existing phase diagram of Ni–Cr, such a compound is formed only at temperatures below 590 °C.

On the other hand, when the existing binary phase diagrams were constructed, it was not considered reprehensible to depict the diagrams in such a way that from the positions of the lines in the diagram one could conclude that the sign of the ordering energy might change with a change in the composition of the alloy. However, the possibility of a change of the type of chemical bonding between components atoms at a change of their concentration in alloys is defined a further puzzle of nature.

It was believed that atomic ordering is isomorphic to the lattice of the Pt_2Mo phase. Electron diffraction patterns were provided, indicating that after prolonged aging (1600 h) at 500 °C, a Ni_2Cr orthorhombic phase of the Pt_2Mo type precipitates in some alloys of the Inconel and Nimonic type [8]. Marucco [9], exploring some physical properties of different Nimonic and Inconel type alloys, explained a decrease in the electrical resistivity and an increase in hardness at prolonged (more than 1000 h) aging at 500 °C by precipitation of such a phase, however he failed to find any diffraction evidence of its existence.

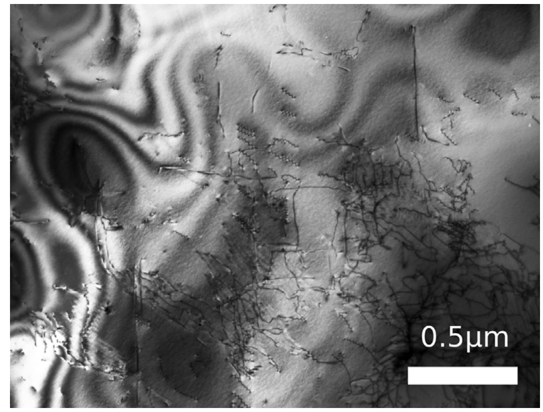

Fig. 2. $Ni_{56}Cr_{44}$ alloy (№4). Quenching from the liquid state (1450°C). Bright-field image of the microstructure.

Formation of the Ni_2Cr chemical compound in the liquid solution means that the $Ni_{40}Cr_{60}$ alloy, at 1450 °C, has a very strong tendency to ordering. Thus, the process of solidification of the $Ni_{40}Cr_{60}$ alloy begins not with the formation of an eutectic consisting of nickel and chromium grains (as it follows from the diagram), but with a formation of grains of the Ni_2Cr chemical compound with an orthorhombic lattice of the Pt_2Mo type from the liquid solution.

As it was shown [6], at lowering the temperature (from which the quenching of the alloy was carried out) of 1200 °C, the grains of the Ni_2Cr phase grow in sizes. At further lowering of the alloy heat treatment temperature, fragmentation of Ni_2Cr grains begins. For example, after heat treatment at 1000 °C, the grains have substantially smaller sizes and are more randomly distributed than after quenching from 1200 °C. Lowering the heat treatment temperature to 800 °C leads to an even greater fragmentation of the grains and reduction of their sizes, and after prolonged aging at 550 °C, a highly dispersed structure is observed, in which particles of the Ni_2Cr chemical compound are arranged along the crystallographic planes of the matrix [6].

Quenching of the $Ni_{68}Cr_{32}$ alloy from the liquid state (1450 °C) leads to the formation of the round dark spots with diffuse edges. The author [6] considered them as clusters of chromium atoms in the nickel matrix. Apparently, the high level of the energy of the

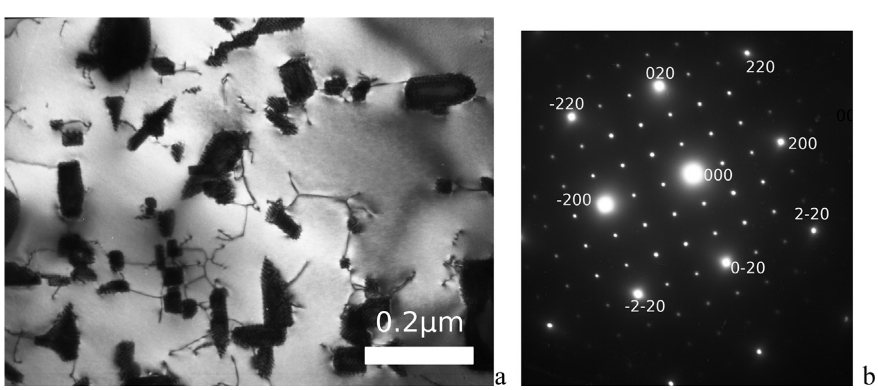

Fig. 1. $Ni_{46}Cr_{54}$ alloy (№3). Quenching from 1000 °C: (a) Bright-field image of the microstructure; (b) electron diffraction pattern, [001] zone axis.