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TEM study of structural and phase transformations in the $Ni_{75}Mo_{20}Al_5$ alloy

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ABSTRACT

Using the method of transmission electron microscopy, we studied the microstructure evolution of the $Ni_{75}Mo_{20}Al_5$ alloy at temperatures ranging from 600 to 1600 °C. It has been shown that above the temperature of the transition "ordering-phase separation" (1200–1300 °C) a phase separation process occurs in the Ni/Mo and Ni/Al diffusion pairs. Below the transition temperature the Mo_3Al and Ni_3Al phases are formed. At temperatures of 800 °C and below, high-dispersion particles of the Ni_3Mo phase precipitate. The role of Al in the heat resistance of Ni–Mo system superalloys is discussed.

1. Introduction

Phase transformations occurring during heat treatment of binary Ni–Mo alloys and ternary Ni–Mo–Al alloys are characterized by the presence of interesting and sometimes difficult to explain peculiarities of the precipitation of coherent phases, which to some extent are the cause of fine mechanical properties of these alloys at high temperatures. It is for that reason that such alloys have been the subject of numerous experimental and theoretical studies over the past few years [1–8]. The foundation of all the works on this subject has been the concept, that in such alloys, short-range order in the arrangement of atoms of different elements evolves into long-range order. Using the terminology of electron microscopy, this meant that short-range order which is characterized by appearance of diffraction maxima in electron diffraction patterns at positions {1 1/2 0}, transforms into long-range order [i.e., in Ni–Mo alloys, for example, Ni_4Mo ($D1_a$), Ni_3Mo ($D0_{22}$) or Ni_2Mo (Pt_2Mo) "superstructures" are formed]. Yet, the system of diffraction maxima of the short-range order {1 1/2 0} has almost no coincidences with the systems of reflections from the above-mentioned superstructures. From this, it follows, that the diffraction maxima at positions {1 1/2 0} cannot be regarded as a consequence of the fact that some short-range order appears in the alloys, which later transforms into long-range order. However, in the majority of published works, for example, in Refs. [1–8], regardless of experimental facts, the diffraction maxima at positions {1 1/2 0} in the electron diffraction patterns are interpreted as a structural state of short-range order.

Comparing the results obtained by the method of X-ray photoelectron spectroscopy (XPS) with the results obtained by transmission electron microscopy (TEM) [9], we came to the conclusion that in alloys of the Ni–Mo system, after quenching from 1600 °C (i.e., from the liquid state), the diffraction maxima at positions {1 1/2 0} in the electron diffraction patterns appear only when, according to XPS, a tendency to phase separation takes place [9]. At lowering the temperature of the heat treatment below 1200 °C, when in alloys of the Ni–Mo system (according to XPS data) the tendency to phase separation is replaced by the tendency to ordering, the diffraction maxima at positions {1 1/2 0} in the electron diffraction patterns received from most areas of the alloy, disappear. Instead of them, a system of reflections is formed, which may be identified as the result of the formation of these or those Ni_xMo_y chemical compounds. Such abrupt changes detected simultaneously by the methods of XPS and TEM indicate that in Ni–Mo alloys, in the temperature range of 1200–1300 °C, there occurs phase transition "ordering-phase separation" [9].

A similar phase transition "ordering-phase separation" has been discovered at the same temperature in the $Ni_{88}Al_{12}$ alloy [10], as well. After heat treatment at 1300 °C, diffuse satellites were observed in the electron diffraction patterns, in the vicinity of the fundamental reflections of the matrix, indicating the formation of two solid solutions – enriched and depleted in aluminum, that is, indicating that in the alloy there exists a tendency to phase separation. At the same time, the diffraction maxima at positions {1 1/2 0} were also observed in the electron diffraction patterns (actually, they are less intense than in the $Ni_{88}Al_{12}$ alloy), which, as

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already noted, points to a tendency to phase separation. Heat treatment at 1200 °C resulted in the disappearance of all indications of phase separation in the electron diffraction patterns and appearance of reflections from the Ni_3Al ($L1_2$) phase [10].

Ternary alloys of Ni–Mo–Al have also been studied by some authors. For example, Sano and Nemoto [11] have studied 15 compositions of alloys of the Ni–Mo–Al system. In addition to stable Ni_3Al ($L1_2$) and Ni_3Mo ($D0_{22}$) phases they have found several metastable phases, such as Ni_4Mo ($D1_a$), Ni_2Mo (Pt_2Mo) and a short-range order state. The authors [11] assumed that the metastable phases play an important role in strengthening these alloys. In the Ni–25 at.% Mo–5 at.% Al alloy, Kulkarni and Dey [12] have discovered and described in sufficient detail the coherent σ-Ni–Mo phase with H-phase plates in the form of wedge-shaped domains located between the grains of the phase. It was believed that the σ-phase is the cause of degradation of mechanical properties of Ni–Al based alloys. The authors [12] came to the conclusion that such a phase is formed during the solidification of the alloy and it retains its size and shape at all other temperatures of aging.

Currently, two opposing tendencies have taken shape in the development of new superalloys and improvement of existing ones: a tendency to increase the number and/or quantity of refractory elements X in Ni–M–X superalloys, and a tendency to simplify the composition of superalloys. On the one hand, they believe that when you add a certain number of refractory elements X (Ti, Nb, etc.) to binary Ni–M alloys (where M–Mo, V, Al and other similar elements), the number of coherent intermetallic phases in the alloy increases, which should lead to an even greater increase of the heat resistance of alloys. On the other hand, complication of the chemical and, consequently, the phase composition is known to lead to an increase in the imperfection of the microstructure, which may cause an opposite effect – a lowering of the high temperature strength of superalloys.

In this paper, we investigated structural and phase transformations that occur when changing the temperature of heat treatment of the $Ni_{75}Mo_{20}Al_5$ ternary alloy and made an attempt to determine what impact on the heat resistance of the Ni–Mo system alloys is provided by the introduction of aluminum into their composition.

2. Experimental

The Ni–20 at.% Mo–5 at.% Al alloy was melted from pure components [Mond-nickel (99.9 wt.% Ni), 99.8 wt.% Mo and electrolytic Al (99.99 wt.% Al)] in an induction vacuum furnace. The melting was repeated under a slag layer in order to ensure homogeneity of the alloy. From the castings weighing about 1 kg, blanks were prepared. The blanks (4 × 4 mm square bars) were quenched into ice water from the temperature range of the solid solution (mainly, from 1200 °C). Quenching from the liquid state (1600 °C) was performed by simply pouring the molten alloy from the crucible into ice water. Specimens for TEM (disks of 3 mm in diameter and 0.2 mm in thickness) were prepared from the quenched blanks. Part of the specimens was further heat treated in evacuated quartz ampoules at temperatures of 600–1300 °C, after which they were cooled in ice water. Thin foils were prepared by electrolytic polishing in a solution consisting of 20 parts of perchloric acid and 80 parts of ethanol by volume. Electron microscopy studies were carried out at an accelerating voltage of 100 kV.

Diffusion processes in the investigated alloy were considered as occurring in three diffusion couples – Ni/Mo, Ni/Al and Mo/A1. We supposed that the phase transitions taking place in the Ni/Mo and Ni/Al diffusion couples are similar to phase transitions in Ni–Mo and Ni–Al binary alloys, which have already been investigated by us in Refs. [9,10] respectively.

3. Results and discussion

We shall start the consideration of the results of the structural changes occurring in the alloy with the high-temperature heat treatment. First of all, we shall consider the electron diffraction pattern obtained from the investigated alloy after quenching it in water from the liquid state (1600 °C) (Fig. 1a). [It can be assumed that the liquidus temperature of the studied alloy ranges from

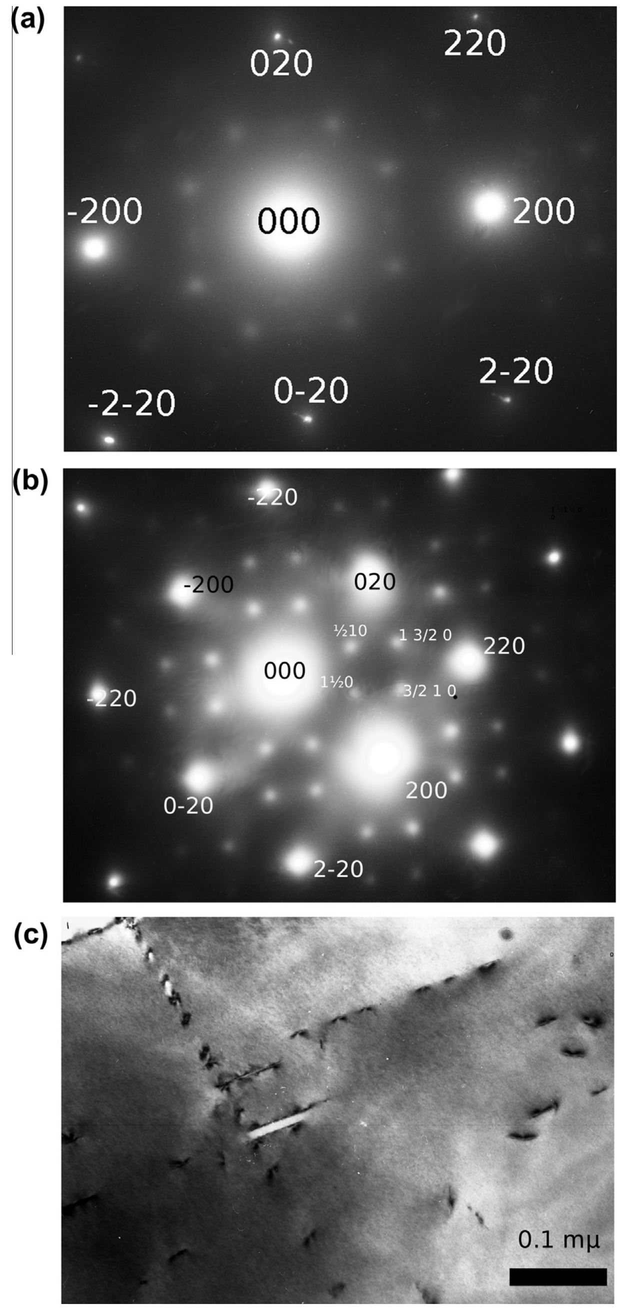

Fig. 1. Quenching from liquid state; electron diffraction pattern; zone axis is near $[001]_{A1}$: (a) $Ni_{75}Mo_{20}Al_5$ alloy; (b) Ni_4Mo alloy; (c) bright-field image of microstructure in $Ni_{75}Mo_{20}Al_5$ alloy.

1450 ($Ni_{95}Al_5$ alloy) to 1460 °C (Ni_{80} Mo_{20} alloy)]. In the electron diffraction pattern one can see a system of diffraction maxima at positions {1 1/2 0}. These diffraction maxima are quite weak in intensity and are visible only near the zero reflection. A similar system of diffraction maxima of higher intensity and in the whole area of the electron diffraction pattern was observed earlier in binary Ni–Mo alloys (Fig. 1b). This fact, in combination with the results of X-ray photoelectron spectroscopy, allowed the authors [9] to come to the conclusion that in these alloys, phase separation takes place already in the liquid state and crystalline particles consisting mainly of Mo atoms are formed in the liquid solution.

Fig. 1c shows that precipitates in the bright-field image of the microstructure of the studied alloy, quenched from the liquid state, are practically not resolved. At the same time, when the diffraction