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Experimental investigation of the Mo–Ni–Re system

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ABSTRACT

Isothermal sections of the Mo–Ni–Re system have been investigated at 1200 °C and 1600 °C by characterization of the equilibrated arc melted alloys with the help of electron probe microanalysis (EPMA) and X-ray diffraction (XRD) techniques. The 1200 °C isothermal section proposed during the present study showed large extension of the Mo–Re σ phase and Mo–Ni δ phase in the ternary region. In addition, presence of two previously unknown ternary phases (a phase with structure prototype Mo_3CoSi and another having a modulated σ structure) was also observed. The isothermal section of the Mo–Ni–Re system at 1600 °C also showed large extension of σ phase in the ternary region whereas extension of Mo–Re χ phase in both isothermal sections was restricted to only few at.% Ni. The presence of the ternary phases observed in the 1200 °C isothermal was not evidenced in 1600 °C isothermal sections. In addition to the phase equilibria investigation in the ternary system, partial determination of the phase equilibria in the Mo–Ni and Mo–Re systems, and of the liquidus projection of the Mo–Ni–Re system was also carried out. The liquidus projection of the Mo–Ni–Re system proposed during present study showed extended primary crystallization fields of the σ and (Re) phases.

1. Introduction

Ni based superalloys are most commonly used for high temperature applications [1]. To further enhance their high temperature properties, several alloying additions are made. Molybdenum and rhenium are among the highly interesting elements for the development of Ni based superalloys. However, if their concentration is too large, topologically close packed phases also called as Frank–Kasper phases may form [2–5]. These are brittle intermetallic phases and have detrimental effect on the mechanical properties [6]. In order to avoid precipitation of Frank–Kasper phases and associated degradation in mechanical properties of Ni based superalloys, phase equilibria investigation of the Mo–Ni–Re system is necessary.

The Mo–Ni–Re system was previously investigated by Kodentsov et al. [2], Borisov et al. [3], Slyusarenko et al. [4] and Feng et al. [5]. Kodentsov et al. [2] studied the isothermal section of the Mo–Ni–Re system at 1152 °C by using the diffusion couple method. In addition to the large extension of the binary phases in the ternary region, the presence of two ternary intermetallic compounds was also observed. A more detailed investigation of the Mo–Ni–Re system was later carried out by Borisov et al. [3] and Slyusarenko et al. [4]. They determined the isothermal section at 1152 °C by using diffusion couples and equilibrated alloys. They studied homogeneity domains of different phases and reported the presence of only one ternary compound in the studied isothermal section. A more recent investigation of the Mo–Ni–Re system was carried out by Feng et al. [5]. They determined the isothermal section at 1200 °C by using diffusion triple. They did not observe presence of any ternary intermetallic compound in the studied system. For comparison, the previously reported isothermal sections of the Mo–Ni–Re system are presented in Fig. 1.

As illustrated in Fig. 1, the previous studies of the Mo–Ni–Re system contradict not only in terms of number and homogeneity domains of ternary phases but significant differences were also observed in the reported extension of the binary phases in the ternary region. In addition, crystal structure identification of the ternary intermetallic compounds was not carried out and these compounds were tentatively assigned as P [7,8] and R [9] phases only by the analysis of the literature information. The boundaries of three phase regions in the previous investigations [2,3] were not determined through the EPMA analysis of three phase samples and their positions were rather tentative. Moreover, reported ternary homogeneity domains show poor agreement with accepted binary data and are also not in compliance with Schreinemakers rule [10]. Therefore, in order to develop a better understanding of the phase equilibria in the Mo–Ni–Re system, a complete experimental redetermination of the Mo–Ni–Re system was necessary.

During the present study, isothermal sections of the Mo–Ni–Re ternary system have been investigated at 1200 °C and 1600 °C by characterization of equilibrated arc melted alloys with the help of electron probe microanalysis (EPMA) and X-ray diffraction (XRD) techniques. As the previously reported isothermal sections

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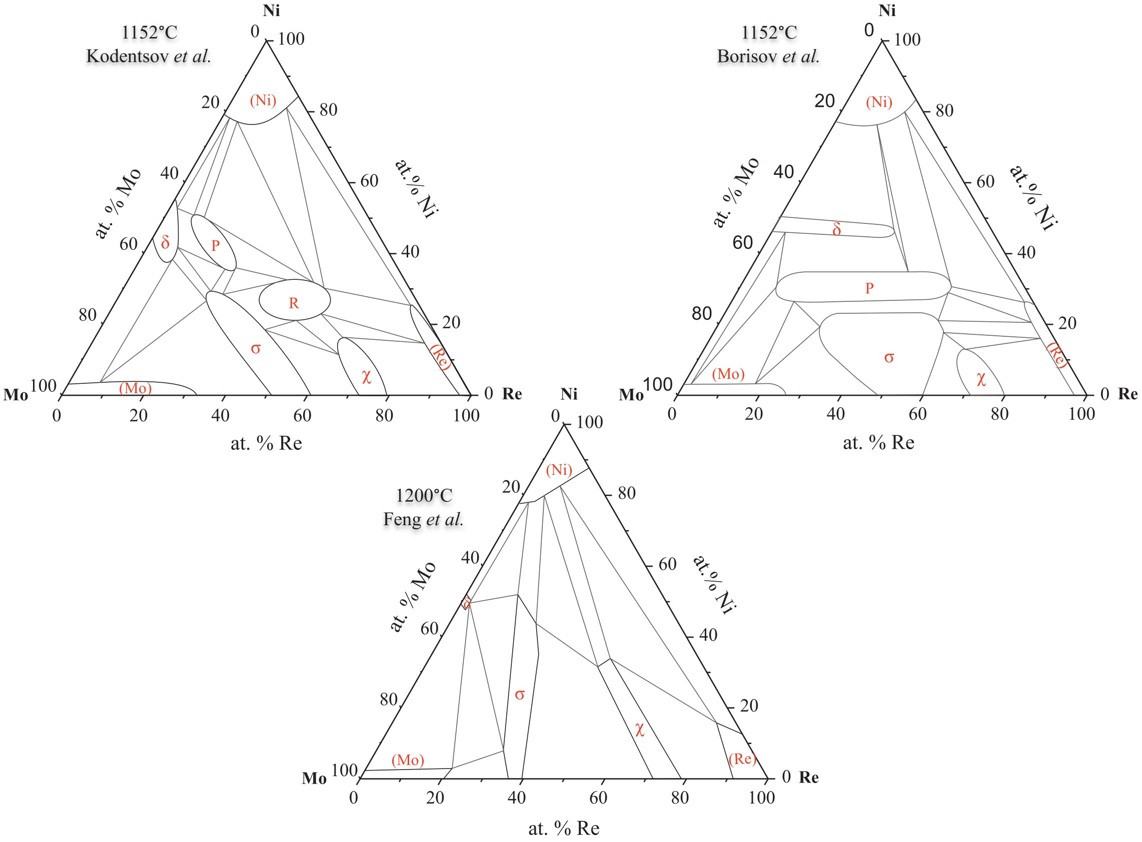

Fig. 1. Previous investigations of the Mo–Ni–Re system by Kodentsov et al. [2], Borisov et al. [3] and Feng et al. [5].

showed poor agreement with related binary systems, investigation of the phase boundaries in the Mo–Ni and Mo–Re binary systems was also carried out whereas phase boundaries data related to Ni–Re system was taken from our recent study [11]. By combining EPMA and XRD results of binary and ternary compositions investigated during the present study, isothermal sections of the Mo–Ni–Re system at 1200 °C and 1600 °C have been proposed. In addition to the phase equilibria determination, liquidus projection of the Mo–Ni–Re system was also studied and primary crystallization fields of different phases have been determined.

2. Experimental details

2.1. Sample preparation

The raw materials used for the present study consisted of pure metals powders (Mo: Sigma Aldrich, <150 μm, 99.99%; Ni: Alfa Aesar, <125 μm, 99.996%; Re: Alfa Aesar, <44 μm, 99.99%). These powders were mixed in the desired ratio in an agate mortar, compacted into pellets, and subjected to arc melting under argon atmosphere. The alloys were melted five times and flipped over after each melting to ensure the chemical homogeneity. Some of the Re rich compositions prepared during the present study showed higher weight losses during arc melting. The increase in weight loss for the Re rich samples was attributed to the evaporation of Ni because of its high vapor pressure at the extremely high melting temperature of the Re rich alloys (pure Re melts at 3186 °C [12]).

2.2. Annealing

To remove the concentration gradient appearing during solidification due to segregation and to attain thermodynamic equilibrium at the studied temperatures, annealing treatment was necessary. The refractory nature of the constituent elements required long annealing times and/or high temperatures. Therefore annealing of the samples at 1200 °C was carried out for 1680 h whereas 9 h of annealing were sufficient at 1600 °C.

For annealing at 1200 °C, as-cast samples were encapsulated in silica tubes under argon atmosphere and placed in a preheated resistance furnace for 1680 h. The insertion of argon inside the silica capsule was meant to avoid the evaporation of high vapor pressure metal i.e. Ni in the studied system, and collapsing of silica capsule at annealing temperature (1200 °C). The rapid cooling of the samples after annealing was carried out by quenching the silica tubes in water.

The annealing treatment of the as-cast samples at 1600 °C was carried out in a high frequency induction furnace in a water cooled copper crucible under an argon atmosphere. The temperature of the samples was measured with the help of an optical pyrometer. After annealing, induction heating was switched off and the rapid cooling of the annealed sample took place due to its contact with water cooled copper crucible.

2.3. Chemical characterization

In order to determine the composition of phases present in equilibrium, part of each sample was polished using standard polishing procedures and examined with the help of electron probe microanalysis (EPMA-CAMECA SX100) by using pure elements as standards. Large numbers of data points were measured on the grains of constituent phases. The chemical composition of each phase was determined by the average of the point measurements performed on that particular phase whereas the calculated standard deviation of these measurements indicated phase homogeneity.

2.4. Structural characterization

To determine the crystal structure and lattice parameters of the phases present in equilibrium, powder X-ray diffraction measurements were carried on a Bruker D8-Advance diffractometer (Bragg–Brentano geometry) equipped with copper Kα radiation and a rear graphite monochromator. Most of the samples by virtue of their high brittleness were easily reduced to fine powder. In case of ductile samples, XRD measurements were carried out on massive samples after cutting from the center and polishing. The XRD data was later refined by the Rietveld method with the help of the FULLPROF [13] program.

2.5. Scanning electron microscopy

For microstructural characterization of the alloys prepared for the determination of the liquidus projection, alloys in their as-cast state were polished using standard polishing procedures and analyzed with the help of scanning electron microscope (SEM-LEO 1530) in the back scattered electron (BSE) mode.