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Structure and corrosion resistance of $CoCrFeNiNb_xMo_y$ near-eutectic high entropy alloys

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Abstract: In this work, $CoCrFeNiNb_xMo_y$ high entropy alloys with variable niobium and molybdenum content (x = 0.35 or 0.4; y = 0.25 or 0.3) were prepared by using the induction melting in a form of ingots. The structure was investigated by the scanning electron microscopy method. Electrochemical measurements were performed in 5% NaCl solution at a temperature of 25 °C to assess the corrosion resistance. Mechanical properties were examined by the Vickers microhardness test. The $CoCrFeNiNb_{0.4}Mo_{0.3}$ alloy showed the best corrosion resistance in the 5% NaCl solution, showing the lowest values of the corrosion current density (114 nA/cm^2) and the highest polarization resistance (261 $k\Omega cm^2$). The highest hardness with a value of 457 HV_1 was obtained for the $CoCrFeNiNb_{0.4}Mo_{0.25}$ ingot.

Keywords: High entropy alloys, Eutectic composition, Corrosion resistance, Hardness

1. INTRODUCTION

The high entropy alloys represent a novel class of metallic materials which has been intensively developed in recent years. In order to achieve a high value of configurational entropy, their design involves use of five or more elements, with each in the content of 5 - 35 at.%. The increased configurational entropy favours the formation of solid solution phases, reducing their mixing free energy [1,2]. As a result of their exceptional properties, such as superior high-temperature strength [3], excellent corrosion resistance [4] and irradiation resistance [5], high entropy alloys characterize with wide range of possible applications in numerous fields, such as aerospace, chemical, and power generation sectors. Initially, the objective of the design of high entropy alloys was being to search for alloys characterized by single phase solid solution structures [2]. However, alloys exhibiting single phase face-centred cubic (FCC) structure generally characterized by rather low strength, whereas those with body-centred cubic (BCC) structure show limited ductility [3]. As a promising method to solve this issue, concept of eutectic high entropy eutectic alloys was proposed [6]. The dual-phase eutectic structure, combining solid FCC solution with the BCC solid solution or intermetallic phases, enables one to obtain an excellent strength-ductility balance, simultaneously allowing alleviation of common castability problems [6,7].

In previous work, high-entropy eutectic alloys were developed basing on the unitary alloying of the CoCrFeNi alloy by niobium and molybdenum [8,9]. In particular, $CoCrFeNiNb_{0.5}$ characterize with advantageous properties, including the compressive strength of 2200 MPa simultaneously at 17% plasticity [10]. Moreover, both niobium and molybdenum can positively affect the corrosion resistance of CoCrFeNi-based high entropy alloys, improving the stability of passivation layer by promoting the generation of Cr_2O_3 [11,12]. Furthermore, the method of eutectic high entropy eutectic alloys through synergistic alloying was recently proposed [13], based on the possibility of formation of infinite solid solutions between molybdenum, niobium, tantalum, and wolframium. Consequently, this work aims to investigate the structure and corrosion behaviour of near-eutectic $CoCrFeNiNb_xMo_y$ alloys (x = 0.35 or 0.4; y = 0.25 or 0.3) designed on the work [13].

2. MATERIALS AND METHODS

Alloys were prepared by the induction melting method, using elements with the 99.99 wt.% purity. The process was carried out using an NG-40 induction generator in an argon atmosphere. Ingots were solidified with a low cooling rate and ceramic crucibles from Al_2O_3 were used. The microstructure of ingots and plates was analysed using the Zeiss Supra 35 high-resolution scanning electron microscope (SEM). The hardness of the alloys was measured using a Future Tech FM-7000 Vickers hardness tester with a dwell time of load of 1000 g for a 15 s. To evaluate their corrosion resistance, the samples were subjected to potentiodynamic polarization measurements, conducted in the 5% NaCl solution. An Autolab 302N potentiostat equipped with a three-electrode measuring system was used for the study. A saturated calomel electrode (SCE) was used as the reference electrode, platinum wire was used as the counter electrode, and the material being tested was the working electrode. During electrochemical measurements, changes in open-circuit potential (E_{OCP}) were recorded in a stabilisation time of 3600 s, followed by polarization measurements in the range of – 400 mV to 400 mV, with a scan rate of 0.001 V/s. On the basis of the results obtained, the corrosion potential (E_{corr}), corrosion current density (jcorr), and polarization resistance (R_p) were determined with the use of the Tafel extrapolation method.

3. RESULTS AND DISCUSSION

The microstructures of the alloys investigated are shown in Figure 1. The results suggest the dual-phase structure of the alloys. According to the publication of Tsau et al. [14] the darker phase can be identified as a face-centred cubic solid solution of CoCrFeNi that is characterized with low solid solubility of niobium and molybdenum, while the brighter phase is an intermetallic Laves phase, exhibiting a hexagonal closed-packed structure. In the case of the $CoCrFeNiNb_{0.35}Mo_{0.25}$ alloy, the microstructure is composed of FCC solid solution dendrites between the lamellar eutectic. Similarly, precipitates of the Laves phase can also be observed. The $CoCrFeNiNb_{0.35}Mo_{0.3}$ and $CoCrFeNiNb_{0.4}Mo_{0.25}$ alloys characterise with more homogenous structure – resulting from an increased volume content of the eutectic structures, although the presence of the bulk Laves phase can still be observed. In turn, for the

CoCrFeNiNb$_{0.4}$Mo$_{0.3}$ alloy, numerous dendrites constituted of the Laves phase can be observed, suggesting its hypereutectic composition.

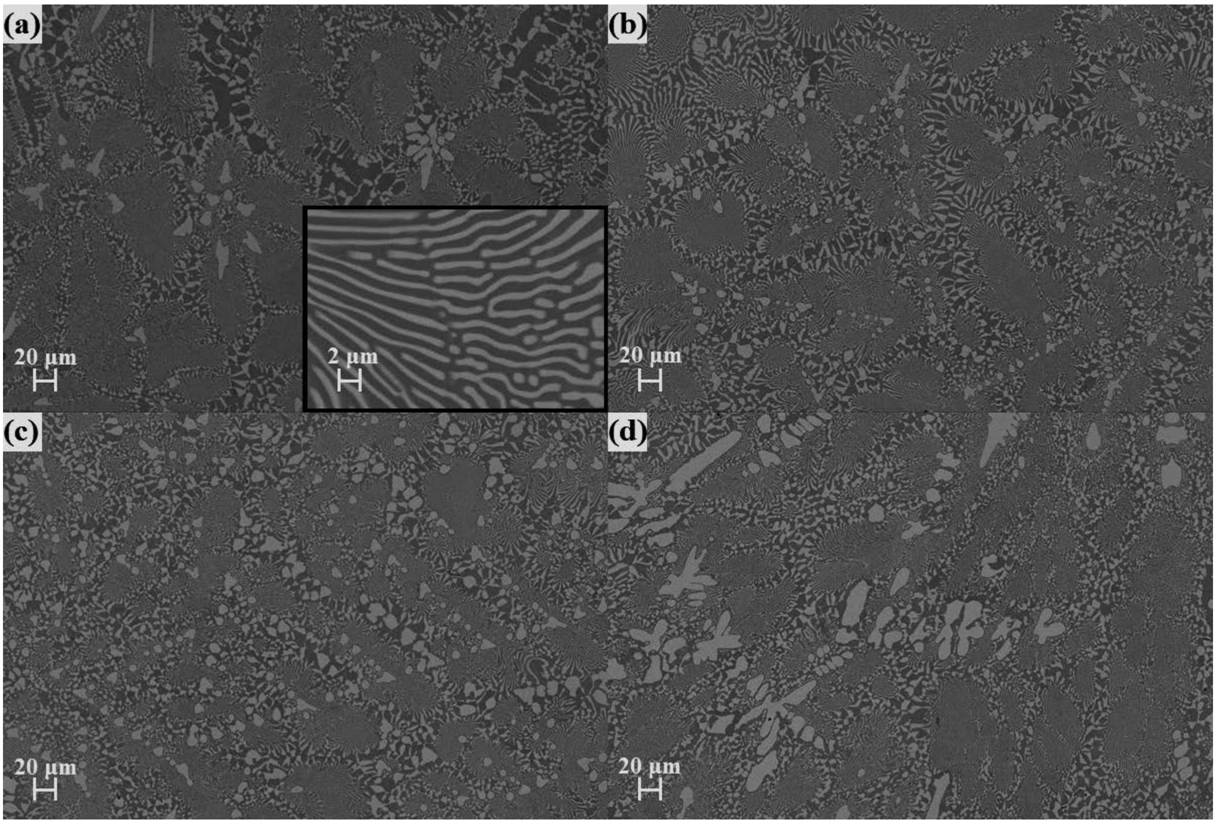

Figure 1. Microstructures of the CoCrFeNiNb$_{0.35}$Mo$_{0.25}$ (a), CoCrFeNiNb$_{0.35}$Mo$_{0.3}$ (b), CoCrFeNiNb$_{0.4}$Mo$_{0.25}$ (c), CoCrFeNiNb$_{0.4}$Mo$_{0.4}$ (d) alloys in the as-cast state

The results of the hardness tests of the CoCrFeNiNb$_x$Mo$_y$ alloys in the as-cast state are presented in Figure 2. All of the alloys investigated are characterised with comparable values of hardness, varying in a relatively narrow range of 448 to 457 HV$_1$. However, a noticeably lower standard deviation can be observed for CoCrFeNiNb$_{0.35}$Mo$_{0.3}$, which can be attributed to its more homogeneous microstructure. Compared to the CoCrFeNi base alloy, which exhibits a hardness of approximately 135 HV [15], a substantial increase in hardness can be observed. That effect can be assigned mainly to the secondary phase strengthening, which results from the precipitation of the Laves phase, and, to a lesser extent, also to the strengthening of the solid solution of the FCC phase by solute niobium [16].

The corrosion resistance of the alloys investigated was evaluated on the basis of electrochemical measurements, performed in the 5% NaCl solution at a temperature of 25 °C. Changes in open-circuit potential as a function of time (a) and potentiodynamic polarization curves (b) for the as-cast alloys are shown in Figure 3. The parameters obtained as a result of the measurements conducted are summarized in the Table 1. Based on the tests conducted, it can be stated that the best corrosion resistance characterizes the CoCrFeNiNb$_{0.4}$Mo$_{0.3}$ alloy. It is confirmed by the lowest corrosion current density (114 nA/cm^2) and the highest polarisation resistance (261 kΩcm^2). However, in terms of polarization resistance, also CoCrFeNiNb$_{0.35}$Mo$_{0.25}$ and CoCrFeNiNb$_{0.4}$Mo$_{0.25}$ alloys are also characterized with similar values of R_p, in both cases exceeding 250 kΩcm^2. In turn, the higher corrosion potential recorded for $CoCrFeNiNb_{0.35}Mo_{0.3}$ and $CoCrFeNiNb_{0.4}Mo_{0.3}$ alloys can be attributed to a higher concentration of molybdenum with a more positive standard potential (Mo/Mo^{2+} – 0.2 V vs. standard hydrogen electrode) [17].

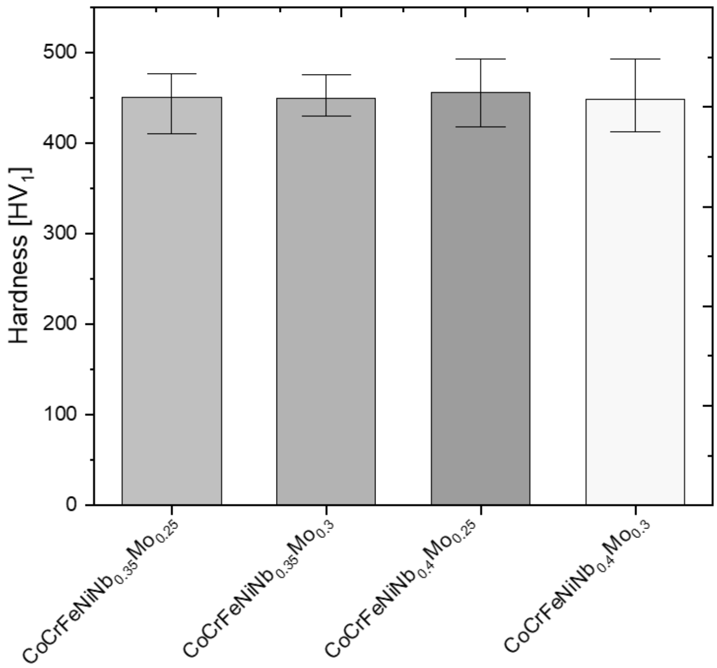

Figure 2. Variation of Vickers hardness of the $CoCrFeNiNb_xMo_y$ alloys in as-cast state

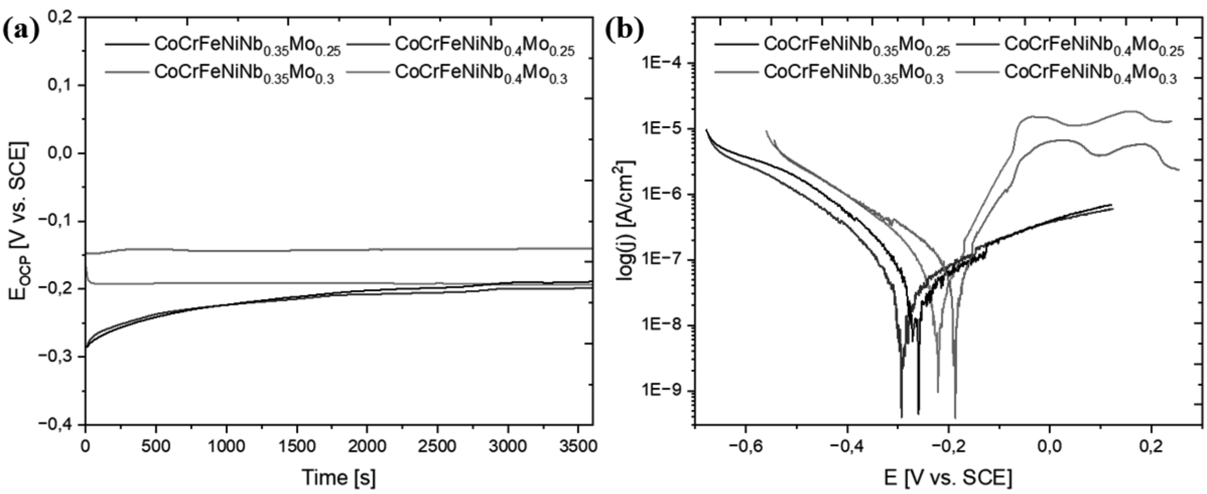

Figure 3. Changes of open-circuit potential (a) and potentiodynamic polarization curves (b) of $CoCrFeNiNb_xMo_y$ alloys in 3.5% NaCl solution at 25 °C

Table 1. Results of the electrochemical tests conducted in the 5% NaCl solution at 25°C

Alloy	E_{corr} [mV]	j_{corr} [nA/cm^2]	R_p [kΩcm^2]
$CoCrFeNiNb_{0.35}Mo_{0.25}$	−273	892	252
$CoCrFeNiNb_{0.35}Mo_{0.3}$	−191	588	112
$CoCrFeNiNb_{0.4}Mo_{0.25}$	−292	632	252
$CoCrFeNiNb_{0.4}Mo_{0.3}$	−223	114	261

4. CONCLUSIONS

The significant volume content of the eutectic structure was confirmed for all of the alloys tested, indicating their near-eutectic composition. However, for the $CoCrFeNiNb_{0.35}Mo_{0.25}$ alloy, the presence of FCC solid solution FCC dendrites can be observed, indicative of its hypoeutectic composition, while, in the case of the $CoCrFeNiNb_{0.4}Mo_{0.3}$ dendrites composed of the Laves phase, can be observed, which allows us to describe that alloy as hypereutectic. A slight influence of variation in the concentration of niobium and molybdenum was found, simultaneously all alloys characterise with high values of hardness with the maximum value of 457 HV_1 obtained for $CoCrFeNiNb_{0.4}Mo_{0.25}$ ingot. The $CoCrFeNiNb_{0.4}Mo_{0.3}$ alloy showed the best corrosion resistance in the 5% NaCl solution, showing the lowest values of the corrosion current density (114 nA/cm^2) and the highest polarization resistance (261 $k\Omega cm^2$).

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