Citation: Tsau, C.-H.; Chen, Y.-H.; Tsai, M.-C. The Effects of Niobium and Molybdenum on the Microstructures and Corrosion Properties of CrFeCoNiNbxMoyped alloys. Materials 2022, 15, 2262. https://doi.org/10.3390/ma15062262

Abstract: The present work systematically investigated the effects of niobium and molybdenum on the microstructures and corrosion properties of high-entropy CrFeCoNiNb_xMo_x alloys, the maximum content of (Nb + Mo) was 20 at.%. All of the alloys were prepared by arc melting under an argon atmosphere. In CrFeCoNiNb_xMo_x alloys (x = 0.15, 0.3 and 0.5), increasing Nb and Mo content would change the microstructure of the alloy from a hypoeutectic structure (x \leq 0.3) to a hypereutectic one (x = 0.5). All of the CrFeCoNiNbxMo1−x alloys (x = 0.25, 0.5 and 0.75) had a hypereutectic microstructure. Only two phases were analyzed in these alloys, which were face-centered cubic (FCC) and hexagonal close packing (HCP). Increasing the content of Nb and Mo increases the hardness of the alloys by the effects of the solid solution strengthening and formation of the HCP phase. The potentiodynamic polarization curves of these alloys were also measured in 1 M sulfuric acid and 1 M sodium chloride solutions to evaluate the corrosion resistance of these alloys. The CrFeCoNiNb0.3Mo0.3 alloy had the smallest corrosion rate (0.0732 mm/yr) in 1 M deaerated H_2SO_4 solution, and the CrFeCoNiNb0.15Mo0.15 alloy had the smallest corrosion rate (0.0425 mm/yr) in 1 M deaerated NaCl solution. However, the CrFeCoNiNb0.5Mo0.5 alloy still had the best combination of corrosion resistance and hardness in the present study.

Keywords: high-entropy alloy; CrFeCoNiNb_xMo_x; CrFeCoNiNbxMo1−x; microstructure; hardness; corrosion

1. Introduction

The alloys used in this study were prepared under the high-entropy alloy concept [1-3]. This high-entropy alloy concept provides researchers to develop new materials with suitable properties for applications. Researchers can smartly select the elements to prepare the materials, and many high-entropy alloys (HEAs) were thus produced with excellent mechanical, physical and chemical properties. Moreover, the shapes of high-entropy materials can be bulk alloys, thin films or coating alloys. For example, the casting, homogenization, cold rolling, recrystallization and deformation mechanism of equiatomic CoCrFeMnNi high-entropy alloy were well investigated [4,5]. The microstructures and compression properties of CoCrFeNiTiAl, high-entropy alloys were tested, and results indicated that the CoCrFeNiTiAl alloy had good compressive strength and elastic modulus [6]. The elements with a high melting point were selected to produce the refractory alloys, such as NbMoTaW, VNbMoTaW and HfTaTiNbZr-based alloys [7,8]. The high-entropy alloys can be prepared by mechanical alloying (MA) to obtain the alloys with nanocrystalline structures and enhance the properties [9,10].

Cobalt, chromium and nickel are wildly used to produce alloys with good corrosion resistance. Other elements are selected and added into CoCrNi alloy to change the microstructures and enhance the mechanical properties, such as CoCrFeMnNi alloy [11]. Co–CrFeNiSn has good passivation in sodium chloride solution compared with stainless
steels [12]. The AlCoCrFeNiTi₀.5 coating was fabricated by laser cladding coating and showed the optimal performance of corrosion and mechanical properties [13]. Minor additions of molybdenum could improve the corrosion resistance of the AlCrFe₂Ni₂ alloy by suppressing pit formation [14]. The addition of molybdenum could increase the corrosion resistance was observed in the (CoCrFeNi)₁₀₀−ₓMoₓ high-entropy alloys [15]. The study on the Al₀.₄CrFe₁.₅MnNi₀.₅Moₓ alloys indicated that adding molybdenum can effectively improve the impedance of passive film and reduce the corrosion current density and thus form a more stable passivation film [16]. The non-equimolar Cr₁₉Fe₂₂Co₂₁Ni₂₅Mo₁₃ alloy possessed better corrosion resistance compared with 304 stainless steel in both deaerated 1 M HNO₃ and 1 M HCl solutions [17]. The corrosion resistance of FeCuNbSiB and CrFeCoNiNbₓ alloys can be improved by adding niobium [18,19].

In our previous study on the corrosion properties of FeCoNi and CrFeCoNi alloys [20], the FeCoNi alloy had a better corrosion resistance by comparing with CrFeCoNi alloy. After adding molybdenum, the corrosion resistance of FeCoNiMo was not as good as that of the CrFeCoNiMo alloy [21]. This indicates that chromium is a very important element in developing a corrosion-resistant alloy. Therefore, the present work studied the effect of adding Nb and Mo on the CrFeCoNi alloy and evaluated the potential of the application.

2. Materials and Methods

The CrFeCoNiNbₓMoₓ and CrFeCoNiNbₓMo₁₋ₓ alloys were prepared by arc-melting under argon atmosphere after accurate weighting. Each melt was about 100 g. Table 1 lists the nominal compositions of the alloys. The microstructures of the alloys were examined by a scanning electron microscope (SEM, JEOL JSM-6335, JEOL Ltd., Tokyo, Japan) after regular metallurgical processes. The compositions of the alloys and the phases existing in the alloys were analyzed by an energy dispersive spectrometer (EDS). An X-ray diffractometer (XRD, Rigaku ME510-FM2, Rigaku Ltd., Tokyo, Japan) was used to identify the phases in the alloys, and the scanning rate was fixed at 0.04 degrees per second. A Vicker’s hardness tester (Matsuzawa Seiki MV1, Matsuzawa Ltd., Akita, Japan) was used to measure the hardness of the alloys, and the loading force was 19.61 N (2000 gf).

Table 1. The nominal compositions of the as-cast alloys.

| Alloys           | Cr  | Fe  | Co  | Ni  | Nb  | Mo  |
|------------------|-----|-----|-----|-----|-----|-----|
| CrFeCoNiNb₀.₁₅Mo₀.₁₅ | 20.49 | 22.00 | 23.22 | 23.13 | 5.49 | 5.67 |
| CrFeCoNiNb₀.₃Mo₀.₇₅ | 18.43 | 19.79 | 20.89 | 20.81 | 9.88 | 10.20 |
| CrFeCoNiNb₀.₅Mo₀.₅ | 16.25 | 17.46 | 18.42 | 18.35 | 14.52 | 14.99 |
| CrFeCoNiNb₀.₇₅Mo₀.₂₅ | 16.22 | 17.42 | 18.38 | 18.31 | 7.24 | 22.44 |
| CrFeCoNiNb₀.₇₅Mo₀.₂₅ | 16.29 | 17.50 | 18.46 | 18.40 | 21.83 | 7.52 |

The potentiodynamic polarization curves of the alloys were tested by a three-electrode electrochemical device (Autolab PGSTAT302N, Metrohm Autolab B.V., Utrecht, The Netherlands). One electrode was the specimens mounted in epoxy resin with an exposed area of 0.196 cm² (0.5 cm in diameter). The second electrode was a counter (a platinum wire). The third electrode was a reference one, which was a saturated silver chloride electrode (Ag/AgCl, SSE). This potential of the reference Ag/AgCl electrode was 0.197 V higher than the standard hydrogen electrode (SHE) at 25 °C [22]. All of the potentiodynamic polarization curves were tested at 30 °C, and the scanning rate of the potentiodynamic polarization test was 1 mV per second. Nitrogen bubbled through the process to degas the oxygen in the solutions. The solutions of 1 M sulfuric acid and 1 M sodium chloric solutions were prepared by reagent-grade acids and deionized water.
3. Results and Discussion

This work was divided into two parts to investigate the effect of Nb and Mo content on the effects of CrFeCoNiNb$_x$Mo$_y$ alloys. Part 1 was the CrFeCoNiNb$_x$Mo$_x$ alloys, and $x$ was 0.15, 0.3 and 0.5. The same amount of Nb and Mo was added to the CrFeCoNi alloy. The relationships between the properties and the microstructures were also investigated. Part 2 studied the properties of CrFeCoNiNb$_1$Mo$_{1-x}$ alloys, where $x$ was 0.25, 0.5 and 0.75. This part studied the effect of different ratios of Nb and Mo on the microstructures and properties of the alloys. The total amount of Nb and Mo was fixed at one part (20 at.%). This work would easily crack during solidification if an excess amount of Nb and Mo was added.

3.1. CrFeCoNiNb$_x$Mo$_x$ Alloys

The microstructures of as-cast CrFeCoNiNb$_x$Mo$_x$ alloys, $x = 0.15, 0.3$ and 0.5, are shown in Figure 1. In our previous study, the CrFeCoNi alloy had an FCC-structured granular microstructure and some Cr-rich precipitates with HCP structure [20]. After adding Nb and Mo, the microstructures of as-cast CrFeCoNiNb$_x$Mo$_x$ alloys became dendritic ones. The dendrites of CrFeCoNiNb$_x$Mo$_x$ alloys showed a single phase, and the interdendrites of CrFeCoNiNb$_x$Mo$_x$ alloys showed a eutectic structure. Table 2 shows the chemical compositions of the alloys and the phases existing in the alloys. According to our previous study [23], the HCP phase had higher Nb and Mo content, and FCC had higher Cr-Fe and Ni content. Therefore, the FCC and HCP phases were easy to identify by detecting the compositions. The dendrites of CrFeCoNiNb$_{0.15}$Mo$_{0.15}$ and CrFeCoNiNb$_{0.3}$Mo$_{0.3}$ alloys were an FCC phase and the dendrites of CrFeCoNiNb$_{0.5}$Mo$_{0.5}$ alloy were an HCP-structured laves phase. All of the interdendrites of CrFeCoNiNb$_x$Mo$_x$ alloys were a eutectic structure with two phases which were FCC and HCP phases (laves phase). This indicated that the alloy changed from a hypoeutectic alloy to a hypereutectic one. That is, CrFeCoNiNb$_{0.15}$Mo$_{0.15}$ and CrFeCoNiNb$_{0.5}$Mo$_{0.5}$ alloys were hypoeutectic alloys, and CrFeCoNiNb$_{0.5}$Mo$_{0.5}$ alloy was a hypereutectic alloy.

![Figure 1. Cont.](image-url)
Figure 1. SEM micrographs of as-cast CrFeCoNiNb xMo x alloys: (a) CrFeCoNiNb0.15Mo0.15 alloy; (b) CrFeCoNiNb0.3Mo0.3 alloy; (c) CrFeCoNiNb0.5Mo0.5 alloy.

Table 2. The chemical compositions of the as-cast CrFeCoNiNb xMo x alloys and the phases in each alloy analyzed by SEM/EDS.

| Alloys          | Weight Percent |
|-----------------|----------------|
|                 | Cr  | Fe  | Co  | Ni  | Nb  | Mo  |
| CrFeCoNiNb0.15Mo0.15 overall | 23.9 ± 0.9 | 24.2 ± 4.9 | 25.6 ± 0.4 | 17.2 ± 4.8 | 5.0 ± 0.2 | 4.1 ± 0.2 |
|                 |     |     |     |     |     |     |
| FCC             | 24.9 ± 1.3 | 25.3 ± 0.3 | 22.3 ± 1.1 | 20.5 ± 1.2 | 3.1 ± 0.7 | 3.9 ± 0.6 |
| HCP             | 19.8 ± 0.5 | 16.0 ± 1.4 | 26.6 ± 1.3 | 16.6 ± 0.5 | 10.4 ± 0.3 | 10.6 ± 0.2 |
| CrFeCoNiNb0.3Mo0.3 overall | 23.1 ± 1.3 | 20.4 ± 1.5 | 18.1 ± 2.1 | 21.7 ± 1.6 | 9.2 ± 0.5 | 7.5 ± 0.8 |
|                 |     |     |     |     |     |     |
| FCC             | 23.6 ± 2.0 | 23.3 ± 2.2 | 20.4 ± 2.8 | 25.8 ± 3.0 | 2.0 ± 0.4 | 5.1 ± 0.6 |

Figure 2 shows the XRD patterns of the CrFeCoNiNb xMo x alloys. Two phases of FCC and laves phases (HCP structure) were identified in these alloys. The FCC phase was the main phase in the CrFeCoNiNb0.15Mo0.15 alloy. Only a small amount of laves phase was in this alloy. Increasing the Nb and Mo content resulted in increasing the amount of laves phase. The laves phase became the major phase in the CrFeCoNiNb0.5Mo0.5 alloy. This result quite matches with the SEM observation.

Figure 3 plots the hardness of CrFeCoNiNb xMo x alloys as a function of Nb and Mo content. Increasing Nb and Mo content would almost linearly increase the hardness of the CrFeCoNiNb xMo x alloys. The hardness of CrFeCoNiNb0.15Mo0.15 alloy was only 215 HV, and the hardness of CrFeCoNiNb0.5Mo0.5 reached 553 HV. Adding Nb and Mo into CrFeCoNi alloy increases the hardness because the atomic radiuses of niobium and molybdenum are larger than those of the other elements. The atomic radiuses of niobium
Table 2. The chemical compositions of the as-cast CrFeCoNiNb$_{x}$Mo$_{x}$ alloys and the phases in each alloy analyzed by SEM/EDS.

| Alloys          | Weight Percent |
|-----------------|----------------|
|                 | Cr  | Fe  | Co  | Ni  | Nb  | Mo  |
| CrFeCoNiNb$_{0.15}$Mo$_{0.15}$ overall | 23.9 ± 0.9 | 24.2 ± 4.9 | 25.6 ± 0.4 | 17.2 ± 4.8 | 5.0 ± 0.2 | 4.1 ± 0.2 |
|                 | FCC | 24.9 ± 1.3 | 25.3 ± 0.3 | 22.3 ± 1.1 | 20.5 ± 1.2 | 3.1 ± 0.7 | 3.9 ± 0.6 |
|                 | HCP | 19.8 ± 0.5 | 16.0 ± 1.4 | 26.6 ± 1.3 | 16.6 ± 0.5 | 10.4 ± 0.3 | 10.6 ± 0.2 |
| CrFeCoNiNb$_{0.3}$Mo$_{0.3}$ overall | 23.1 ± 1.3 | 20.4 ± 1.5 | 18.1 ± 2.1 | 21.7 ± 1.6 | 9.2 ± 0.5 | 7.5 ± 0.8 |
|                 | FCC | 23.6 ± 2.0 | 23.3 ± 2.2 | 20.4 ± 2.8 | 25.8 ± 3.0 | 2.0 ± 0.4 | 5.1 ± 0.6 |
|                 | HCP | 18.7 ± 0.6 | 14.6 ± 0.2 | 17.9 ± 2.6 | 17.8 ± 0.2 | 19.2 ± 0.2 | 11.8 ± 2.5 |
| CrFeCoNiNb$_{0.3}$Mo$_{0.5}$ overall | 21.4 ± 0.4 | 19.4 ± 1.6 | 19.8 ± 0.3 | 17.6 ± 2.1 | 11.0 ± 0.2 | 10.8 ± 0.7 |
|                 | FCC | 22.1 ± 0.9 | 20.4 ± 1.4 | 18.4 ± 0.3 | 22.8 ± 0.4 | 7.1 ± 1.2 | 9.2 ± 0.5 |
|                 | HCP | 17.3 ± 0.3 | 23.6 ± 5.2 | 19.1 ± 0.8 | 14.2 ± 0.8 | 16.9 ± 0.1 | 15.6 ± 0.9 |

Figure 2. XRD patterns of as-cast CrFeCoNiNb$_{x}$Mo$_{x}$ alloys.
Thus, the CrFeCoNiNb$_{0.3}$ passivation regions of these alloys were breakdown at a potential ($E_b$) of about 1.2 V (SHE) due to oxygen evolution reaction [26].

Figure 3 shows the potentiodynamic polarization curves of the as-cast CrFeCoNiNb$_{x}$Mo$_x$ alloys in 1 M deaerated H$_2$SO$_4$ solution at 30 °C. The potentiodynamic polarization data of these polarization curves are listed in Table 3. The potentiodynamic polarization curves of the alloys with potential negative than corrosion potential ($E_{corr}$) was the cathode. The potentiodynamic polarization curves of the alloys with potential positive than corrosion potential was the anode. The corrosion potential ($E_{corr}$) of CrFeCoNiNb$_{x}$Mo$_x$ alloys was very close. The standard electrode potential of the elements used in present work is listed in Table 4 [25]. The niobium is more active than the other elements because the standard electrode potential of niobium is more negative. Therefore, the corrosion potential of CrFeCoNiNb$_{0.5}$Mo$_{0.5}$ alloy had the most negative corrosion potential ($E_{corr}$). The corrosion current densities ($i_{corr}$) of CrFeCoNiNb$_{x}$Mo$_x$ alloys were all around 10 µA/cm$^2$. The potentiodynamic polarization curve of CrFeCoNiNb$_{0.15}$Mo$_{0.15}$ alloy had an apparent anodic peak, and the other alloys had no anodic peak. The passivation potential ($E_{pp}$) and critical current density ($i_{crit}$) of the anodic peak of CrFeCoNiNb$_{0.15}$Mo$_{0.15}$ alloy is listed in Table 3. Thus, the CrFeCoNiNb$_{0.3}$Mo$_{0.3}$ and CrFeCoNiNb$_{0.5}$Mo$_{0.5}$ alloys easily entered into the passivation regions and formed the passive films during corrosion in H$_2$SO$_4$ solution. The lowest passivation current densities ($i_{pass}$) of these alloys were about 12 A/cm$^2$. All the passivation regions of these alloys were breakdown at a potential ($E_b$) of about 1.2 V (SHE) due to oxygen evolution reaction [26].

Table 3. Potentiodynamic polarization data of the as-cast CrFeCoNiNb$_{x}$Mo$_x$ alloys in 1 M deaerated H$_2$SO$_4$ solution at 30 °C.

|       | CrFeCoNiNb$_{0.15}$Mo$_{0.15}$ | CrFeCoNiNb$_{0.3}$Mo$_{0.3}$ | CrFeCoNiNb$_{0.5}$Mo$_{0.5}$ |
|-------|-------------------------------|-------------------------------|-------------------------------|
| $E_{corr}$ (V vs. SHE) | −0.03 | −0.05 | −0.06 |
| $i_{corr}$ (µA/cm$^2$) | 11.9 | 7.0 | 10.0 |
| $E_{pp}$ (V vs. SHE) | 0.18 | N/A | N/A |
| $i_{crit}$ (µA/cm$^2$) | 67.5 | N/A | N/A |
| $i_{pass}$ (µA/cm$^2$) | 12.5 | 13.1 | 12.2 |
| $E_b$ (V vs. SHE) | 1.21 | 1.19 | 1.19 |

Figure 3. Hardness of as-cast CrFeCoNiNbxMox alloys. Each value is the average hardness of the alloy.
Figure 4. Potentiodynamic polarization curves of as-cast CrFeCoNiNb_xMox alloys tested in the 1 M deaerated sulfuric acid solution at 30 °C.

Table 4. Standard electrode potential at 25 °C [25].

| Reaction          | Electrode Potential (E° vs. SSE) |
|-------------------|---------------------------------|
| Cr, Cr^{3+}       | −0.74                           |
| Fe, Fe^{2+}       | −0.44                           |
| Co, Co^{2+}       | −0.227                          |
| Ni, Ni^{2+}       | −0.25                           |
| Nb, Nb^{3+}       | −1.10                           |
| Mo, Mo^{3+}       | −0.20                           |

Figure 5 displays the potentiodynamic polarization curves of the as-cast CrFeCoNiNb_xMox alloys in 1 M deaerated NaCl solution at 30 °C. The potentiodynamic polarization data of these polarization curves are listed in Table 5. The corrosion potential (E_{corr}) of CrFeCoNiNb_{0.15}M-o_{0.15} alloy was more negative than the other alloys, and CrFeCoNiNb_{0.15}M-o_{0.15} alloy also had the smallest corrosion current density (i_{corr}). All of the potentiodynamic polarization curves of CrFeCoNiNb_{x}Mox alloys in 1 M deaerated NaCl solution had apparent anodic peaks. Additionally, the potentiodynamic polarization curves of CrFeCoNiNb_{0.15}M-o_{0.15} and CrFeCoNiNb_{0.3}M-o_{0.3} alloys had small secondary anodic peaks. The CrFeCoNiNb_{0.15}M-o_{0.15} alloy had the lowest passivation current density. The passivation current densities (i_{pass}) of these alloys were about 9–15 μA/cm².

3.2. CrFeCoNiNb_{x}M_{1−x} Alloys

The microstructures and properties of CrFeCoNiNb_{x}M_{1−x} alloys were studied in this part. The total amount of Nb and Mo of these alloys was kept as one part; the amount of Nb and Mo thus equaled 20 at.%. The microstructures of as-cast CrFeCoNiNb_{x}M_{1−x} alloys, x = 0.25 and 0.75, are shown in Figure 6. All of the CrFeCoNiNb_{x}M_{1−x} alloys, x = 0.25, 0.5 and 0.75, had a hypereutectic microstructure because a large amount of Nb and Mo were added into these alloys. The dendrites of CrFeCoNiNb_{x}M_{1−x} alloys were an HCP phase (laves phase), and the interdendrites of CrFeCoNiNb_{x}M_{1−x} alloys were a eutectic structure with FCC and HCP phases (laves phase). Table 6 lists the chemical compositions of the alloys and the phases existing in the alloys. As described above, the Nb and Mo content in the HCP phase of the alloys is higher than that in the FCC phase.
The chemical compositions of the as-cast CrFeCoNiNb alloys, x = 0.25 and 0.75, are shown in Figure 6. All of the CrFeCoNiNb \(x\)Mo were added into these alloys. The dendrites of CrFeCoNiNbxMo1 had a hypereutectic microstructure because a large amount of Nb and phase (laves phase), and the interdendrites of CrFeCoNiNbxMo1 0.25, 0.5 and 0.75, had a hypereutectic microstructure because a large amount of Nb and Mo thus equaled 20 at.%. The microstructures of as-cast CrFeCoNiNb xMo1 parts. The total amount of Nb and Mo of these alloys was kept as one part; the amount of content in the HCP phase of the alloys is higher than that in the FCC phase.

Table 5. Potentiodynamic polarization data of the as-cast CrFeCoNiNb \(x\)Mo in 1 M deaerated NaCl solution at 30 °C.

| Weight Percent | Cr | Fe | Co | Ni | Nb | Mo |
|----------------|----|----|----|----|----|----|
| CrFeCoNiNb0.15Mo0.15 | 16.3 ± 3.4 | 17.6 ± 1.6 | 18.5 ± 1.0 | 18.1 ± 1.6 | 7.8 ± 1.3 | 21.7 ± 2.5 |
| CrFeCoNiNb0.3Mo0.3 | 14.8 ± 2.3 | 15.2 ± 2.8 | 20.2 ± 1.5 | 15.4 ± 1.3 | 8.7 ± 0.2 | 25.7 ± 0.6 |
| CrFeCoNiNb0.5Mo0.5 | 16.9 ± 0.6 | 17.5 ± 2.6 | 18.8 ± 2.0 | 18.9 ± 1.2 | 20.2 ± 0.2 | 7.7 ± 0.2 |

Figure 7 shows the XRD patterns of the CrFeCoNiNb \(x\)Mo1 alloys. Two phases existing in these alloys were FCC and HCP-structured laves phases. The HCP phase was the main phase in these CrFeCoNiNb \(x\)Mo1 alloys, and the FCC phase became the minor phase in these alloys. Figure 8 displays the hardness of CrFeCoNiNb \(x\)Mo1 alloys, some of the data were from our previous study [23]. According to our previous study, the overall hardness of the alloy was contributed by the hard HCP dendrites and the soft interdendrites (HCP + HCC). The hardness of both HCP and FCC phases increased with increasing the content of Nb and Mo due to solid solution strengthening. However, the hardness of
the FCC phase was still softer than that of the HCP phase. Because the hardness of interdendrites was softer than that of dendrites, increasing the volume fraction of interdendrite would decrease the overall hardness of the alloy. The CrFeCoNiNb0.25Mo0.75 alloy had the lowest hardness among these alloys because of the largest ratio of interdendrites in this alloy. The CrFeCoNiNb0.75Mo0.25 alloy had the highest hardness of 625 HV among the alloys in the present study.

Figure 6. SEM micrographs of as-cast CrFeCoNiNb\(_x\)Mo\(_{1-x}\) alloys: (a) CrFeCoNiNb\(_{0.25}\)Mo\(_{0.75}\) alloy and (b) CrFeCoNiNb\(_{0.75}\)Mo\(_{0.25}\) alloy.
Figure 7. XRD patterns of as-cast CrFeCoNiNbxMo1−x alloys.

Figure 8. Hardness of as-cast CrFeCoNiNbxMo1−x alloys. Each value is the average hardness of the alloy. Some of the data are from our previous study [23].

Figure 9 shows the potentiodynamic polarization curves of the as-cast CrFeCoNiNbxMo1−x alloys in 1 M deaerated H2SO4 solution at 30 °C. The potentiodynamic polarization data of these polarization curves are listed in Table 7. The corrosion potential (Ecorr) and the corrosion current densities (i_corr) of CrFeCoNiNbxMo1−x alloys were very close; the CrFeCoNiNb0.75Mo0.25 alloy had the lowest i_corr of about 5 μA/cm2. The potentiodynamic polarization curve of CrFeCoNiNb0.25Mo0.75 and CrFeCoNiNb0.75Mo0.25 alloys had apparent anodic peaks, but the CrFeCoNiNb0.5Mo0.5 alloy had no anodic peak. The passivation potential (Epp) and critical current density (i_crit) of the anodic peaks of the alloys are listed in Table 7. This indicated that the CrFeCoNiNb0.5Mo0.5 alloys easily entered the passivation regions and formed the passive films during corrosion in H2SO4 solution among these alloys. The current densities of the passivation regions (i_pass) of CrFeCoNiNb0.5Mo0.5
and CrFeCoNiNb_{0.75}Mo_{0.25} alloys were about 12 A/cm^2, but the CrFeCoNiNb_{0.25}Mo_{0.75} alloy had a larger passivation current density (i_{pass}). The passivation regions of these alloys were all breakdown at a potential (E_{b}) of about 1.2 V (SHE) because of oxygen evolution reaction [26]. In order to compare the properties of corrosion potential, corrosion current density, anodic peak and passivation region of each alloy in the present study, the CrFeCoNiNb_{0.5}Mo_{0.5} alloy had the best corrosion resistance among the alloys in H_2SO_4 solution.

![Potentiodynamic polarization curves of as-cast CrFeCoNiNb_{x}Mo_{1-x} alloys tested in 1 M deaerated sulfuric acid solution at 30 °C.](image)

**Figure 9.** Potentiodynamic polarization curves of as-cast CrFeCoNiNb_{x}Mo_{1-x} alloys tested in the 1 M deaerated sulfuric acid solution at 30 °C.

|                | CrFeCoNiNb_{0.25}Mo_{0.75} | CrFeCoNiNb_{0.5}Mo_{0.5} | CrFeCoNiNb_{0.75}Mo_{0.25} |
|----------------|----------------------------|--------------------------|-----------------------------|
| E_{corr} (V vs. SHE) | -0.06                     | -0.06                    | -0.06                       |
| i_{corr} (µA/cm^2)  | 10.2                       | 10.0                     | 4.9                         |
| E_{pp} (V vs. SHE)  | 0.17                       | N/A                      | 0.11                        |
| i_{crit} (µA/cm^2)  | 58.3                       | N/A                      | 35.7                        |
| i_{pass} (µA/cm^2)  | 44.1                       | 12.2                     | 11.9                        |
| E_{b} (V vs. SHE)   | 1.21                       | 1.19                     | 1.19                        |

Table 7. Potentiodynamic polarization data of the as-cast CrFeCoNiNb_{x}Mo_{1-x} alloys in 1 M deaerated H_2SO_4 solution at 30 °C.

Figure 10 shows the potentiodynamic polarization curves of the as-cast CrFeCoNiNb_{x}Mo_{1-x} alloys in 1 M deaerated NaCl solution at 30 °C. The potentiodynamic polarization data of these polarization curves are listed in Table 8. The cathodic limit current density (i_{L}) was found in these CrFeCoNiNb_{x}Mo_{1-x} alloys. The cathodic limit current density meant that the maximum reaction rate was limited because of the diffusion rate of hydroxyl ions (OH^-) in the solution [26]. The corrosion potential (E_{corr}) of CrFeCoNiNb_{0.25}Mo_{0.75} alloy was more positive than the other alloys; the corrosion potential (E_{corr}) of CrFeCoNiNb_{0.5}Mo_{0.5} and CrFeCoNiNb_{0.75}Mo_{0.25} alloy was very close. Moreover, the corrosion current density (i_{corr}) of CrFeCoNiNb_{0.25}Mo_{0.75} alloy was larger than the other alloys. The corrosion current density (i_{corr}) of CrFeCoNiNb_{0.5}Mo_{0.5} and CrFeCoNiNb_{0.75}Mo_{0.25} alloys were about 10 µA/cm^2. All of the CrFeCoNiNb_{x}Mo_{1-x} alloys had apparent anodic peaks in 1 M deaerated NaCl solution. The passivation regions of CrFeCoNiNb_{0.5}Mo_{0.5} and CrFeCoNiNb_{0.75}Mo_{0.25} alloys were better than that of CrFeCoNiNb_{0.25}Mo_{0.75} alloy. The minimum passivation current densities (i_{pass}) of CrFeCoNiNb_{0.5}Mo_{0.5} and CrFeCoNiNb_{0.75}Mo_{0.25}
alloys were about 15 μA/cm². When comparing the properties of corrosion potential, corrosion current density, anodic peak and passivation region of each alloy in the present study, the CrFeCoNiNb₀.₅Mo₀.₅ alloy had the best corrosion resistance among the alloys in NaCl solution.

Figure 10. Potentiodynamic polarization curves of as-cast CrFeCoNiNb₀.₁₅Mo₀.₁₅ alloys tested in the 1 M deaerated sodium chloric solution at 30 °C.

Table 8. Potentiodynamic polarization data of the as-cast CrFeCoNiNb₀.₁₅Mo₁₋ₓ alloys in 1 M deaerated NaCl solution at 30 °C.

| CrFeCoNiNb₀.₂₅Mo₀.₇₅ | CrFeCoNiNb₀.₅Mo₀.₅ | CrFeCoNiNb₀.₇₅Mo₀.₂₅ |
|-----------------------|---------------------|-----------------------|
| E_{corr} (V vs. SHE)  | -0.20               | -0.28                 | -0.30                 |
| i_{corr} (μA/cm²)     | 31.0                | 10.7                  | 10.8                  |
| E_{pp} (V vs. SHE)    | -0.04               | 0.03                  | 0.03                  |
| i_{crit} (μA/cm²)     | 43.2                | 47.0                  | 36.0                  |
| i_{pass} (μA/cm²)     | 34.4                | 15.0                  | 15.6                  |
| E_b (V vs. SHE)       | 1.32                | 1.19                  | 1.26                  |

The corrosion rate of the alloys in deaerated 1 M H₂SO₄ and 1 M NaCl solutions can be calculated by assuming that all of the corrosion types of the alloys in these solutions are a type of uniform corrosion. Therefore, the relationship between corrosion depth of one year and corrosion current density is listed as the following Equation [27]:

\[
\text{corrosion depth} = \frac{M \cdot i_{corr} \cdot t}{\rho \cdot n \cdot F}
\]

where \(M\) is the average atomic mass (g/mol), \(i_{corr}\) is the corrosion current density (A/cm²), \(t\) is the corrosion time (31,536,000 s, 1 yr), \(\rho\) is the average density (g/cm³), \(n\) is the number of average valence electron and \(F\) is the Faraday constant (96,500 C/mol). This study assumes that the average density of an alloy is \(\rho = \sum X_i \rho_i\), where \(X_i\) and \(\rho_i\) are the molar fraction and density of element i. The corrosion rates (mm per year) of the alloys in deaerated 1 M H₂SO₄ and 1 M NaCl solutions are listed in Table 9. The CrFeCoNiNb₀.₃Mo₀.₃ alloy had the smallest corrosion rate (0.0732 mm/yr) in 1 M deaerated H₂SO₄ solution, and alloy CrFeCoNiNb₀.₇₅Mo₀.₂₅ had the largest corrosion rate (0.3315 mm/yr) in this solution. The CrFeCoNiNb₀.₁₅Mo₀.₁₅ alloy had the smallest corrosion rate (0.0425 mm/yr) in 1 M
deaerated NaCl solution, and CrFeCoNiNb_{0.5}Mo_{0.5} and CrFeCoNiNb_{0.75}Mo_{0.25} alloys had larger corrosion rate in this solution. The corrosion rate of CrFeCoNiNb_{0.5}Mo_{0.5} alloy (0.1152 mm/yr) in 1 M deaerated NaCl solution was higher than that of CrFeCoNiNb_{0.15}Mo_{0.15} alloy in the same solution. However, the CrFeCoNiNb_{0.5}Mo_{0.5} alloy still possessed the best combination of corrosion resistance and hardness among these alloys.

Table 9. Corrosion rates of the as-cast alloys in deaerated 1 M H\textsubscript{2}SO\textsubscript{4} and 1 M NaCl solutions at 30 °C.

| Alloys                | 1 M H\textsubscript{2}SO\textsubscript{4} (mm/yr) | 1 M NaCl (mm/yr) |
|-----------------------|-----------------------------------------------|-----------------|
| CrFeCoNiNb\textsubscript{0.15}Mo\textsubscript{0.15} | 0.1204                                        | 0.0425          |
| CrFeCoNiNb\textsubscript{0.3}Mo\textsubscript{0.3}  | 0.0732                                        | 0.1043          |
| CrFeCoNiNb\textsubscript{0.25}Mo\textsubscript{0.75}| 0.1091                                        | 0.0532          |
| CrFeCoNiNb\textsubscript{0.5}Mo\textsubscript{0.5}  | 0.1077                                        | 0.1152          |
| CrFeCoNiNb\textsubscript{0.75}Mo\textsubscript{0.25}| 0.3315                                        | 0.1172          |

4. Conclusions

The microstructures, hardness and corrosion properties of hypoeutectic CrFeCoNiNb\textsubscript{x}Mo\textsubscript{x} alloys (x = 0.15 and 0.3) and hypereutectic CrFeCoNiNb\textsubscript{x}Mo\textsubscript{1-x} alloys (x = 0.25, 0.5 and 0.75) were studied. There were two phases (FCC and HCP) in these alloys. The dendrites of hypoeutectic CrFeCoNiNb\textsubscript{y}Mo\textsubscript{x} alloys (x = 0.15 and 0.3) were an FCC phase; the interdendrities of these alloys was a eutectic structure which the phases were HCP and FCC phases. The dendrites of hypereutectic CrFeCoNiNb\textsubscript{x}Mo\textsubscript{1-x} alloys (x = 0.25, 0.5 and 0.75) were an HCP-structured laves phase, and the interdendrities of these alloys were a eutectic structure with HCP and FCC phases. Increasing the content of Nb and Mo would increase the hardness of the alloys because of the formation of the hard HCP phase and the effect of solid solution strengthening. The CrFeCoNiNb_{0.75}Mo_{0.25} alloy had the highest hardness of 625 HV among the alloys in present study. After potentiodynamic polarization test in deaerated 1 M H\textsubscript{2}SO\textsubscript{4} and 1 M NaCl solutions at 30 °C, the CrFeCoNiNb_{0.5}Mo_{0.5} alloy had the best corrosion resistance among these alloys by comparing the properties of corrosion potential, corrosion current density, anodic peak and passivation region of the alloys. Therefore, CrFeCoNiNb_{0.5}Mo_{0.5} alloy was the best alloy among these alloys by comparing the corrosion properties and hardness.

Author Contributions: Conceptualization, C.-H.T.; methodology, C.-H.T., Y.-H.C. and M.-C.T.; formal analysis, C.-H.T., Y.-H.C. and M.-C.T.; investigation, C.-H.T., Y.-H.C. and M.-C.T.; data curation, C.-H.T., Y.-H.C. and M.-C.T.; writing—original draft preparation, C.-H.T.; writing—review and editing, C.-H.T.; supervision, C.-H.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors are grateful to the Ministry of Science and Technology of the Republic of China for its financial support under the project MOST 110-2221-E-034-007.

Conflicts of Interest: The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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