Microstructure, Mechanical Properties, and Corrosion Behavior of MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi High-Entropy Alloys

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Abstract

The development of high-entropy alloys (HEAs) has stimulated an ever-increasing interest from both academia and industries. In this work, three novel MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi HEAs containing low thermal neutron absorption cross section elements were prepared by vacuum arc melting. The microstructure, mechanical properties, and corrosion behaviors were investigated. A dominant body-centered cubic (BCC) phase was present in all these three HEAs. In addition, an ordered Laves phase was found to be another major phase in both MoNbFeCrV and MoNbFeCrTi alloys, whereas an ordered BCC (B2) phase was observed in the MoNbFeVTi alloy. The phase formation in these three alloys was discussed. It is found that the formation of the secondary phase in these alloys is mainly ascribed to the large atomic size difference and electronegativity difference. All the three HEAs show high hardness, high yield strength but limited plasticity. Moreover, the MoNbFeCrV, MoNbFeCrTi and MoNbFeVTi alloys exhibit excellent corrosion resistance in both deaerated 1 mol/L NaCl and 0.5 mol/L H₂SO₄ solutions at room temperature. However, further composition adjustment and/or thermomechanical processing is required to enhance the mechanical properties of the three alloys.

Keywords High-entropy alloy · Crystal structure · Microstructure · CALPHAD · Mechanical property · Corrosion

1 Introduction

The crystalline alloys and bulk metallic glasses (BMGs) are mainly composed of one or two principal metallic elements, such as steel, titanium alloys, aluminum alloys, Zr-based

BMGs [1, 2], and Cu-based BMGs [3, 4]. Meanwhile, other elements with minor concentrations are often purposely added to enhance the base alloy's performance. However, the limited number of the principal metallic elements in the periodic table hinders the development of new alloys. Recently, a new kind of emerging advanced materials termed as high-entropy alloys (HEAs) by Yeh et al. [5] has attracted an ever-increasing interest from both academia and industries for their unique microstructures and various attractive properties. Generally, HEAs are defined as those alloys containing at least five major elements with equimolar or near-equimolar concentrations between 5 and 35 at.% [5].

This innovative alloy design strategy enables researchers to design a vast number of alloys with desired properties such as unique microstructures [6–8], high strength [9–13], excellent corrosion resistance [14–16], good wear resistance [17–19], and high irradiation resistance [20–23]. Nevertheless, one has to keep in mind that the properties of HEAs vary substantially with different chemical compositions and concentrations. In practice, the selection of alloying elements for designing HEAs is highly dependent on specific purposes. For example, Co, Fe, and Ni are

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often chosen as alloying elements to design HEAs with attractive magnetic properties [24, 25]. Refractory metals such as Mo, Nb, Ta, and W are usually selected as alloying elements to design HEAs for high-temperature applications [9, 26–29]. Up to now, to the authors' knowledge, the work on the design of HEAs for application in the nuclear industry is scarce. Zhang et al. [30, 31] designed and prepared an AlCrMoNbZr HEA coating on N36 zirconium alloy (Zr–1Sn–1Nb–0.3Fe wt%) as cladding materials. The selected alloying elements (Al, Cr, Mo, Nb, and Zr) should have relatively low thermal neutron absorption cross sections (Zr, 0.18b; Al, 0.22b; Nb, 1.1b; Mo, 2.4b; and Cr, 3.05b) for nuclear power plant applications. Moreover, HEAs also exhibit excellent irradiation resistance according to recently published articles [23, 32–35]. The Fukushima Daiichi accident happened in 2011 underlined the inherent demerits of the currently used zirconium alloys. In the case of a loss-of-coolant accident (LOCA), zirconium alloys experienced severe strength loss and rapid high-temperature steam oxidation at temperature $T > 1200$ °C [36]. Therefore, the concept of accident tolerant fuel (ATF) was proposed to achieve higher safety margins under accident scenarios. The combinations of good corrosion resistance and excellent irradiation resistance make HEAs potential candidates for ATF cladding materials.

In our previous work [37], eight elements (i.e., Zr, Nb, Mo, Cr, Fe, Ni, V, and Ti) were first chosen as alloying elements to design equiatomic quinary HEAs for nuclear power plant applications due to their relatively low thermal neutron absorption cross sections. Empirical parameter calculations and CALPHAD (acronym of calculation of phase diagrams) modeling were performed for the 56 alternative alloys to accelerate the design process. Finally, a single-phase MoNbCrVTi HEA was successfully designed and prepared. The empirical parameters include the enthalpy of mixing (ΔS_{mix}), the entropy of mixing (ΔH_{mix}), the atomic size difference (δ), and Ω ($\Omega = T_m \Delta S_{\text{mix}} / |\Delta H_{\text{mix}}|$) parameter, etc. Though the high entropy values can stabilize the solid solution phase in HEAs, it is not the decisive factor as indicated in Refs. [38, 39]. The ΔH_{mix} and δ also have a considerable impact on the formation of solid solution phases in HEAs. Therefore, the Ω parameter seems to be more reliable than the individual ΔS_{mix} or ΔH_{mix} . Zhang et al. [40] proposed that solid solution phases are likely to form when $\Omega \geq 1.1$ and $\delta \leq 6.6\%$. Except the single-phase MoNbCrVTi alloy, another three HEAs (MoNbFeCrV, MoNbFeCrTi and MoNbFeVTi) also have higher Ω values and relatively lower δ values. These HEAs were prepared by vacuum arc melting, and the microstructure, mechanical properties, and corrosion resistance at room temperature were preliminarily investigated.

2 Experimental

Three novel MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi HEAs were prepared by vacuum arc melting in a water-cooled copper crucible under a Ti-gettered argon atmosphere. The corresponding pure metals with purity higher than 99.5 wt% were weighed to obtain the nominal composition. Each alloy ingot was flipped over and then re-melted at least five times in order to achieve chemical homogeneity. The prepared button-shaped ingots were about 44 mm in diameter and 10 mm in thickness.

The crystal structure was identified using an X-ray diffractometer (XRD, X'PERT PRO) using $\text{CuK}\alpha$ ($\lambda = 1.5406$ Å) radiation, operated at a voltage of 40 kV and a current of 40 mA. The scanning range is from 20° to 100° with a scanning speed of 4°/min. The microstructure was characterized using a scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS). The volume fractions of different phases in an alloy were calculated using Image-Pro Plus software. The CALPHAD modeling was performed using ThermoCalc™ software with the TTNI8 thermodynamic database. Vickers hardness was measured on polished cross-sectional surfaces using a 136° Vickers diamond pyramid with a load of 500 g for 15 s. The reported hardness values were the average of seven random measurements. Compression testing was performed on cylindrical specimens with a diameter of 3 mm and a height of 6 mm using an Instron 5582 machine with an initial strain rate of 10^{-3} s^{-1} .

The samples for electrochemical tests with a dimension of 10 mm × 10 mm × 1 mm were cut from the bulk material by electric discharge machine. Each test specimen was welded with a copper line on the back and then cold-mounted with epoxy resin. The exposed surface area was about 1 mm². The electrochemical measurements were conducted in both 1 mol/L NaCl and 0.5 mol/L H₂SO₄ solutions using a typical three-electrode system which consists of a test specimen as the working electrode, a platinum sheet as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrochemical measurements were performed at room temperature. The test solution was deaerated by bubbling high-purity nitrogen gas for 30 min before the electrochemical measurements to eliminate the effect of dissolved oxygen. Potentiodynamic polarization measurements were carried out at a scan rate of 1 mV/s from an initial potential of −0.5 V to a final potential of 1.5 V versus the open-circuit potential (OCP). Before the polarization measurement, the OCP was recorded for 30 min to reach a steady-state potential. Then, the specimen was cathodically polarized at −0.5 V versus the OCP for 5 min to remove the existing surface oxides. The potential was

controlled, and the current was measured using a potentiostat (Gamry Reference 600). At least three specimens were prepared to ensure the reproducibility. After the potentiodynamic polarization measurement, the specimen was removed from the test solution, rinsed with distilled water, and dried in air. Then, the corroded surfaces were observed by SEM.

3 Results and Discussion

3.1 Crystal Structure

XRD patterns of the MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi HEAs are shown in Fig. 1a–c, respectively. The diffraction peaks of the MoNbFeCrV alloy are indexed as belonging to two different phases. One is a disordered BCC (A2) phase with the lattice parameter $a = 307.66$ pm. Another is an ordered Laves (C15) phase with an FCC crystal structure and the lattice parameter $a = 654.64$ pm. For the

MoNbFeCrTi alloy, one BCC phase with the lattice parameter $a = 314.49$ pm and another ordered Laves (C15) phase with the lattice parameter $a = 696.06$ pm are observed. The large lattice parameter differences between the Laves phases in the MoNbFeCrV and MoNbFeCrTi alloys result from the different chemical compositions. It is noted that an ordered BCC (B2) phase instead of an ordered Laves phase is identified in the MoNbFeVTi alloy. Also, another BCC phase is identified. The lattice parameter for the BCC phase and the B2 phase is $a = 315.43$ pm and $a = 284.74$ pm, respectively.

3.2 Microstructure Analysis

3.2.1 MoNbFeCrV

The MoNbFeCrV alloy shows a typical dendritic microstructure (Fig. 2a), and at least three distinct phases are recognized from Fig. 2b. Additionally, a transition layer (TL) of about 1 μm in thickness is present at the outside surface of the dendrites. The chemical compositions of

Fig. 1 X-ray diffraction patterns of **a** MoNbFeCrV, **b** MoNbFeCrTi, **c** MoNbFeVTi high-entropy alloys

Fig. 2 **a–c** SEM backscatter electron images of the as-cast MoNbFeCrV alloy, **d–h** elemental mappings of Mo, Nb, Fe, Cr, and V

Table 1 Chemical compositions (at.%) of the as-cast MoNbFeCrV alloy determined by EDS

Region (phase)	Mo	Nb	Fe	Cr	V
Overall	19.9	21.0	20.5	18.7	19.9
BCC	31.0	21.3	11.0	16.0	20.7
Laves	11.2	24.1	30.2	19.8	14.7
Transition layer	26.1	17.8	13.7	18.8	23.6
Sigma	17.5	8.7	21.8	21.7	30.3

these individual phases are listed in Table 1. Furthermore, EDS mappings (Fig. 2d–h) show that the dendrite is rich in Mo, and the continuously distributed phase in the interdendritic region is rich in Nb, Fe, and Cr. One BCC phase and the other Laves phase had been identified from the XRD analysis (Fig. 1a) of this alloy. The lattice parameter of the BCC phase is 307.66 pm which is slightly lower than that of pure Mo with the lattice parameter of 314.60 pm [41]; thus, the Mo-rich phase is recognized as the BCC phase and the (Nb, Fe, Cr)-rich phase is the Laves phase. The Laves phase may have a stoichiometry close to $(\text{Cr, Fe})_2\text{Nb}$ based on the data given in Table 1. The TL is enriched with Mo and V. Finally, the discretely distributed phase (denoted as V-rich phase in Fig. 2b) in the interdendritic region is rich in V, Cr, and Fe, but heavily depleted of Nb. The volume fractions of the BCC phase together with the

TL, Laves phase, and V-rich phase are 37.0%, 60.6%, and 2.4%, respectively.

In order to further elucidate the microstructural complexity in the MoNbFeCrV alloy, the CALPHAD modeling was carried out. The calculated equilibrium phase diagram and non-equilibrium (NE) solidification curves of MoNbFeCrV alloy are presented in Fig. 3. The equilibrium phase diagram predicts the formed phases under low cooling rate which cannot be reached in actual solidification process, while the NE solidification simulates the process with a large cooling rate which is close to the experimental condition. The NE solidification was performed using Scheil–Gulliver models [42, 43] which assume that no diffusion occurs in the solid phases, while the diffusion in the liquid phase is infinite. Figure 3a presents the calculated equilibrium phase diagram, and it predicts the liquidus temperature of 1926 °C from which a primary BCC starts to form. The solidus temperature is 1350 °C. The Laves phase forms when the temperature is lower than 1387 °C. The primary BCC phase decomposes into BCC#1 and Laves phase when the temperature is lower than 1350 °C. Then a Sigma phase appears at 1247 °C and a BCC#2 phase starts to form at 996 °C. The predicted compositions at 800 and 1000 °C using TTNI8 database are listed in Table 2, and the results show that the BCC#1 phase is rich in Mo and Nb. The predicted composition at 1000 °C is very close to the experimental data as shown in Table 1. The Laves phase is enriched with Nb, Fe, and Cr.

Fig. 3 **a** Equilibrium phase diagram for MoNbFeCrV alloy, **b** non-equilibrium solidification curve for MoNbFeCrV alloy using Scheil–Gulliver models, **c** composition of liquid phase, **d** composition of BCC phase, **e** composition of Laves phase, **f** composition of Sigma phase

Table 2 Predicted composition for MoNbFeCrV alloy at 800 °C and 1000 °C using TTNI8 database

Temperature (°C)	Phase	Mo	Nb	Fe	Cr	V
800	BCC#1	43.6	29.8	1.1	7.6	17.8
	Laves	5.9	27.4	39.5	27.2	0
	Sigma	6.5	0	33.6	15.8	44.1
	BCC#2	6.7	2.3	5.5	44.3	41.2
1000	BCC#1	31.0	21.9	5.0	16.7	25.4
	Laves	6.5	26.8	39.8	26.9	0
	Sigma	7.2	0	34.7	18.2	39.8

The Sigma phase is rich in Fe and V, and Sigma phase tends to be formed when atomic percent of V is about 32–67% at lower temperatures as shown in the binary phase diagram [44]. It is seen that the BCC#2 phase is heavily enriched with Cr and V. The predicted NE curves shown in Fig. 3b indicate that a BCC phase starts to form at 1926 °C. The Laves phase, Sigma phase, and an ordered BCC (B2) phase successively form at 1375, 1314, and 1198 °C, respectively. When the solidification is completed, the dominant BCC phase has a mole fraction of 65.6%, followed by Sigma phase of 17.9% and Laves phase of 15.8%. The mole fraction of the B2 phase is only about 0.6%. The B2 phase is unlikely to form in the as-cast alloy due to its lowest formation temperature and the smallest mole fraction. Figure 3c–f shows the compositions of the liquid phase, BCC phase, Laves phase, and Sigma phase formed during the NE solidification. The formation of new phases from the liquid with decreasing temperatures significantly alters the curve shape of the liquid phase composition. The liquid phase is firstly depleted of Mo and Nb, whereas Fe and V are continuously enriched. It indicates that the primary BCC phase is rich in Mo and Nb, which is consistent with the simulated result shown in Fig. 3d as well as the experimental result (Fig. 2

and Table 1). The Laves phase is rich in Fe, Nb, and Cr. The Sigma phase is heavily enriched with V and Fe, but depleted of Nb and Mo. Three phases including a BCC phase, a Laves phase, and a Sigma phase are predicted to form from both the calculated equilibrium phase diagram and the NE solidification simulation. Compared to the experimental results, it is thereby deduced that the Mo-rich dendrite is the BCC phase, the (Nb, Fe, Cr)-rich phase is the Laves phase, and the V-rich phase is the Sigma phase. The TL may have a BCC structure for the richness of Mo and V which are usually BCC phase stabilizer. Furthermore, this kind of TL was also observed in the NbCrMo_{0.5}Ta_{0.5}TiZr alloy [26] and it is suggested that the TL may retain the same crystal structure with the primary dendritic phase.

3.2.2 MoNbFeCrTi

Figure 4a–c presents the microstructure of the MoNbFeCrTi alloy. This alloy also displays a dendritic microstructure (Fig. 4a). Three distinct microstructural constituents including the bright dendrites, the gray phase, and the dark phase can be recognized from Fig. 4b. The chemical composition of these different phases is listed in Table 3. EDS mappings

Fig. 4 a–c SEM backscatter electron images of the as-cast MoNbFeCrTi alloy, d–h elemental mappings of Mo, Nb, Fe, Cr, and Ti

Table 3 Chemical compositions (at.%) of the as-cast MoNbFeCrTi alloy determined by EDS

Region (phase)	Mo	Nb	Fe	Cr	Ti
Overall	19.9	20.7	20.1	19.3	20.0
White regions (BCC)	34.9	26.2	8.5	14.4	16.0
Gray regions (Laves)	8.6	18.1	29.6	28.0	15.7
Dark regions (B2)	3.8	6.2	28.8	11.7	49.5

given in Fig. 4d–h clearly show that the dendrite is rich in Mo and Nb, depleted by Fe, Cr, and Ti. The gray phase is enriched with Fe, Cr, and Nb. It is noted that the dark phase (denoted as Ti-rich phase in Fig. 4b) in the interdendritic regions is heavily enriched with Ti and Fe. It implies that the bright dendrite solidifies first during cooling, followed by the gray phase and the Ti-rich dark phase which solidifies at the end of the solidification. The volume fraction of the dendrites, the gray phase, and the Ti-rich phase is 49.4%, 49.5%, and 1.1%, respectively. XRD analysis (Fig. 1b) shows that one BCC phase and one Laves phase are identified in the MoNbFeCrTi alloy. Therefore, combined with the XRD result and EDS analysis, the bright dendrite is deduced to be the BCC phase, while the gray phase is the Laves phase.

Both the equilibrium phase diagram (Fig. 5a) and NE simulation (Fig. 5b) predict the formation of three phases, i.e., one BCC phase, one Laves phase, and an ordered BCC (B2) phase during the solidification. The BCC phase solidifies first from the liquid, followed by the Laves phase and B2 phase. The predicted mole fraction of the B2 phase according to the equilibrium phase diagram at 400 and 600 °C is 16.4% and 16.3%, respectively. Nevertheless, the mole fraction of the B2 phase calculated by the NE simulation is merely 2.7% which is close to the experimental value of 1.1%. The experimental results agree well with the NE simulation calculations. Moreover, the composition of the B2 phase predicted by the equilibrium phase diagram and NE simulation (Fig. 5c) is heavily enriched with Ti and Fe with

a stoichiometry close to 1:1. Hence, it is suggested that the Ti-rich phase, which solidifies at the end of the solidification with a small volume fraction of 1.1%, should have an ordered BCC (B2) structure.

3.2.3 MoNbFeVTi

The MoNbFeVTi alloy (Fig. 6a–c) consists of three distinct phases with the chemical composition given in Table 4. This alloy also exhibits a dendritic microstructure. Elemental mappings, as shown in Fig. 6d–h, indicate that the bright dendrites are enriched with Mo and Nb, but depleted of Fe, V, and Ti. The gray phase in the interdendritic regions is rich in Fe, V, and Ti. Then it is seen that the minor dark phase (denoted as Ti-rich phase in Fig. 6b) is heavily enriched with Fe and Ti. The volume fractions of the dominant bright dendrites, the (Fe, V, Ti)-rich gray phase, and the minority dark (Fe, Ti)-rich phase are about 60.6%, 38.1%, and 1.3%, respectively.

It is noted that two phases are identified through the XRD pattern of the MoNbFeVTi alloy (Fig. 1c), and the lattice parameter of the BCC phase is calculated to be 315.43 pm which is close to the lattice parameter of Mo (314.70 pm) [44], whereas the lattice parameter of the B2 phase is 284.74 pm that is close to the lattice parameter of Fe (288.65 pm) [44]. Moreover, chemical compositions as shown in Table 4 show that the bright dendrite is enriched with Mo and Nb, while the gray phase is densely rich in Fe. Furthermore, both the calculated equilibrium phase diagram (Fig. 7a) and the NE solidification simulation (Fig. 7b) results demonstrate that the dominant phases formed in the MoNbFeVTi alloy are the A2 and B2 phase. The equilibrium phase diagram predicts that the A2 phase starts to form at 1966 °C and the B2 phase forms at $T \leq 1194$ °C, as indicated in Fig. 7a. The solidus temperature is predicted to be 1163 °C. The fractions of the A2 phase and the B2 phase almost remain constant at $T \leq 1000$ °C. The specific mole fractions at 600 °C are

Fig. 5 **a** Equilibrium phase diagram for MoNbFeCrTi alloy, **b** non-equilibrium solidification curve for MoNbFeCrTi alloy using Scheil–Gulliver models, **c** composition of BCC (B2) phase

Fig. 6 a–c SEM backscatter electron images of the as-cast MoNbFeVTi alloy, d–h elemental

Table 4 Chemical compositions (at.%) of the as-cast MoNbFeVTi alloy determined by EDS

Region (phase)	Mo	Nb	Fe	V	Ti
Overall	19.3	19.3	21.4	19.4	20.6
White regions (BCC)	31.3	24.5	9.0	18.9	16.3
Gray regions (B2)	4.8	16.8	39.9	18.6	19.9
Dark regions (B2)	2.7	6.7	36.5	12.0	42.1

59.5% and 40.5% for the A2 phase and B2 phase, respectively. The values are very close to the experimental results. Figure 7b presents the NE solidification simulation and the solidification begins at $T = 1966^\circ\text{C}$ from which the A2 phase forms. Only the A2 phase solidifies from

the liquid until another B2 phase forms at $T \leq 1172^\circ\text{C}$. Also, one Laves phase and one Sigma phase start to form at $T = 1078^\circ\text{C}$ that is very close to the solidus temperature (1068°C) at which the solidification is complete. After the solidification process, the mole fractions of the A2 phase and the B2 phase are predicted to be 62.4% and 30.8%, respectively. Therefore, based on the experimental results and the CALPHAD modeling, it is concluded that the bright dendrite is the A2 phase and the gray phase is the B2 phase. It is unlikely to identify the crystal structure of the dark Ti-rich phase by XRD since the volume fraction is less than 5%. The Fe–Ti binary phase diagram [44] shows that the B2 phase is likely to form when the ratio between Fe and Ti is close to 1:1. The chemical composition analysis (Table 4) reveals that the ratio between Fe

Fig. 7 a Equilibrium phase diagram for MoNbFeVTi alloy, b non-equilibrium solidification curve for MoNbFeVTi alloy using Scheil–Gulliver models

and Ti in the Ti-rich phase is very close to 1:1, which indicates that the Ti-rich phase in this alloy may also have an ordered BCC (B2) structure.

The results of the present work indicate that these three HEAs all show complex microstructures. At least three phases are presented in each of the MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys. The BCC phase is the dominant phase in all three alloys. The Laves phase is presented in the MoNbFeCrV and MoNbFeCrTi alloys. However, the MoNbFeVTi alloy has another B2 phase. In addition, a small amount of Sigma phase or B2 phase is still formed at the end of the solidification process in these alloys. It is seen that the different alloying elements substantially affect the phase formation in the three alloys. Recently, various semi-empirical parameters have been proposed to differentiate solid solutions or intermetallic phases in HEAs. The majority of these parameters are based on atomic size difference (δ) and enthalpy of mixing (ΔH_{mix}) [45]. In addition, several parameters are based on the entropy of mixing (ΔS_{mix}) and electronegativity (χ). For example, Zhang et al. [46] suggested that solid solution phases would form when $-15 \leq \Delta H_{\text{mix}} \leq 5$ kJ/mol, $12 \leq \Delta S_{\text{mix}} \leq 17.5$ J/(mol K), and $\delta \leq 6.5\%$. However, Guo et al. [47] suggested that the solid solution phases would form if $-22 \leq \Delta H_{\text{mix}} \leq 7$ kJ/mol, $11 \leq \Delta S_{\text{mix}} \leq 19.5$ J/(mol K), and $\delta \leq 8.5\%$. Meanwhile, another two different criteria have also been proposed by Jiang et al. [48] and Ren et al. [49]. Indeed, the ΔH_{mix} , ΔS_{mix} , and δ are related to the phase formation of HEAs. However, the suggested values are mainly obtained from analysis of different numbers and types of reported alloys in the literature. The criteria suggested by Zhang et al. [46] were widely accepted in the HEA community. As numerous new HEAs have been explored continuously, Zhang et al. [50] proposed a new parameter $\Omega = T_m \Delta S_{\text{mix}} / |\Delta H_{\text{mix}}|$ to replace ΔH_{mix} . It is suggested that solid solutions tend to form when $\Omega \geq 1.1$ and $\delta \leq 6.6\%$. More specific values have been proposed by Senkov et al. [51] to differentiate solid solution or intermetallic phases; only solid solution phases will form when $\Omega \geq 1.1$ and $\delta \leq 3.6\%$ or $\Omega \geq 10$; both solid solution phases and intermetallic phases are present if $1.1 \leq \Omega \leq 10$ and $\delta \geq 3.6\%$. The values of ΔH_{mix} , ΔS_{mix} , δ , and Ω for the MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys are listed in Table 5. Only ΔH_{mix} , ΔS_{mix} , and δ values failed to predict the phase formation in the MoNbFeCrV and

MoNbFeVTi alloys. The intermetallic phase may be formed in the MoNbFeCrTi alloy due to the large δ value. The more strict criteria suggested by Senkov et al. [51] can approximately predict the formation of intermetallic phases in the three alloys. Wang et al. [52] proposed a geometrical parameter γ by considering the atomic packing misfitting to investigate the solid solubility in multi-component alloys. The results indicated that if only solid solutions formed, the γ value should be less than 1.175. Another purely geometrical parameter $\Lambda = \Delta S_{\text{mix}} / \delta^2$ was proposed by Singh et al. [53] to predict the formation of disordered solid solutions in multi-component alloys. The results showed that the Λ values are prescribed for the formation of single-phase DSS ($\Lambda > 0.96$) and two-phase mixtures ($0.24 < \Lambda < 0.96$) involving compounds ($\Lambda < 0.24$) [53]. Table 5 gives the γ and Λ values of the three alloys, and only the γ value for the MoNbFeCrV alloy is failed to predict the phase selection. However, as pointed out in Ref. [52], the proposed criteria are necessary conditions but not sufficient conditions to predict the phase selection in HEAs. The experimental results show that both MoNbFeCrV and MoNbFeCrTi alloys mainly consist of BCC and Laves phases. Attempts have been made to illustrate the Laves phase or TCP phase formation in the HEAs [54–56]. The formation of the Laves phase is largely related to the δ and electronegativity difference ($\Delta\chi$). For instance, Yurchenko et al. [56] suggested that the formation of the Laves phase is observed when $\delta > 5.0\%$ and $\Delta\chi_{\text{Allen}} > 7.0\%$. To summarize, it is noted that not all the parameters could accurately predict the phase formation in HEAs. In contrast, the CALPHAD modeling seems to be a more reliable and effective tool to predict the phase formation in HEAs as shown in the present work and Refs. [57–61].

3.3 Hardness and Mechanical Properties

The measured hardness values of the MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi are 826 ± 11 , 792 ± 8 , and 699 ± 22 HV, respectively. Therefore, the MoNbFeCrV alloy exhibits the highest hardness. The different volume fractions of Laves phase for the MoNbFeCrV alloy (53.0%) and the MoNbFeCrTi alloy (49.5%) may result in the minor hardness difference. Figure 8a shows the compressive engineering stress–strain curves for the MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys, and the 0.2% offset yield strength

Table 5 Calculated enthalpy of mixing (ΔH_{mix}), the entropy of mixing (ΔS_{mix}), atomic size difference (δ), Ω , γ , Λ , and electronegativity difference ($\Delta\chi$, calculation based on Allen electronegativity)

Alloy	ΔH_{mix} (kJ/mol)	ΔS_{mix} (J/(mol K))	δ (%)	Ω	γ	Λ	$\Delta\chi_{\text{Allen}}$ (%)
MoNbFeCrV	−6.72	13.38	5.36	4.71	1.167	0.47	8.84
MoNbFeCrTi	−9.28	13.38	6.69	3.34	1.192	0.30	10.34
MoNbFeVTi	−8.48	13.38	5.77	3.65	1.191	0.40	9.89

Fig. 8 **a** Compressive engineering stress–strain curves of MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys and fracture surfaces of **b** MoNbFeCrV alloy, **c** MoNbFeCrTi alloy, **d** MoNbFeVTi alloy

Table 6 The 0.2% offset yield strength ($\sigma_{0.2}$), compressive strength (σ_p), and fracture strain (ϵ_f) of the MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys

Alloy	Yield stress, $\sigma_{0.2}$ (MPa)	Compressive stress, σ_p (MPa)	Fracture strain, ϵ_f (%)
MoNbFeCrV	2663	2688	2.7
MoNbFeCrTi	1647	1811	0.9
MoNbFeVTi	1707	1729	1.7

($\sigma_{0.2}$), compressive strength (σ_p), and fracture strain (ϵ_f) are presented in Table 6. It is noted that the MoNbFeCrV alloy also shows the highest yield strength of 2663 MPa and the highest compressive strength of 2688 MPa. It can be seen from Table 6 that the ductility of these three HEAs is significantly limited, which should be mainly attributed to the presence of the brittle Laves phase or B2 phase. The SEM images of fracture morphologies for MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys are shown in Fig. 8c, d, respectively. A large number of cleavage planes and cleavage steps can be seen from the fracture surfaces of all the three alloys, which indicates that the fracture patterns for

the three alloys are typical brittle cleavage fracture. Further composition adjustment and/or thermomechanical processing is required to enhance the mechanical properties of the three alloys.

3.4 Corrosion Behavior

The potentiodynamic polarization curves of the MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys in deaerated 1 mol/L NaCl solution are given in Fig. 9a. The relevant electrochemical parameters are listed in Table 7. All alloys exhibit spontaneous passivation and pseudo-passive behavior in 1 mol/L NaCl solution due to the lack of distinct active–passive transition characteristic. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) are calculated from Fig. 9a using Tafel analysis [62]. It is seen from Table 7 that the MoNbFeCrV alloy has the most negative E_{corr} of -671 mV, which is about 200 mV lower than those of MoNbFeCrTi and MoNbFeVTi alloys. However, the MoNbFeCrV alloy shows the lowest i_{corr} of $0.07 \mu\text{A}/\text{cm}^2$, which is about one-fifth of the i_{corr} for the MoNbFeCrTi and MoNbFeVTi alloys. The passivation current densities (i_{pass}) of the three alloys are similar. It is noted that all the alloys are still under passivation

Fig. 9 **a** Potentiodynamic polarization curves of MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys in deaerated 1 mol/L NaCl solution and SEM images of **b** MoNbFeCrV, **c** MoNbFeCrTi, **d** MoNbFeVTi alloys after electrochemical test

even when the potential is about 1.0 V above the OCP. The breakdown potential (E_b) has not been observed for the three alloys, indicating that the three HEAs exhibit excellent corrosion resistance in the deaerated 1 mol/L NaCl solution. The pitting corrosion resistance of the three HEAs is better than that of 304 stainless steel [63]. Moreover, Fig. 9b–d shows the SEM images of the MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys, respectively, after the potentiodynamic polarization test. There are no pits formed on the sample's surfaces. For the MoNbFeCrV and MoNbFeCrTi alloys, the dominant BCC and Laves phases can be distinguished. Moreover, the BCC and B2 phases can also be easily observed in the MoNbFeVTi alloy from Fig. 9d.

Figure 10a shows the potentiodynamic polarization curves of the MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi

alloys in deaerated 0.5 mol/L H_2SO_4 solution. The relevant electrochemical parameters are tabulated in Table 8. These three alloys again show spontaneous passivation and pseudo-passive behavior in 0.5 mol/L H_2SO_4 solution. The E_{corr} values for the three alloys are almost the same. The MoNbFeCrTi alloy has the largest i_{corr} of 1.35 $\mu A/cm^2$, followed by the i_{corr} of the MoNbFeCrV alloy of about 0.91 $\mu A/cm^2$ and the MoNbFeVTi alloy of about 0.70 $\mu A/cm^2$. It is interesting to note that the E_b is observed for the MoNbFeCrV alloy at 969 mV in 0.5 mol/L H_2SO_4 solution, which indicates that the passive films are broken when the potential is too high versus OCP. While the breakdown potentials for the MoNbFeCrTi and MoNbFeVTi alloys are still absent that implies the MoNbFeCrTi and MoNbFeVTi alloys are still in the passive state, the SEM images shown in Fig. 10b–d further confirm these observations. It can be seen from Fig. 10b that one particular phase in the MoNbFeCrV alloy is preferentially dissolved. The dissolved phase is found to be the V-rich Sigma phase when comparing Fig. 10b with Fig. 2b, c. Figure 10c, d shows the morphologies of the MoNbFeCrTi and MoNbFeVTi alloys, respectively. It is noteworthy that the MoNbFeCrTi and MoNbFeVTi alloys remain unaffected after the potentiodynamic polarization measurement.

Table 7 Electrochemical parameters of the MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys in deaerated 1 mol/L NaCl solution

Alloy	E_{corr} (mV _{SCE})	i_{corr} ($\mu A/cm^2$)	i_{pass} ($\mu A/cm^2$)
MoNbFeCrV	−671	0.07	5.01
MoNbFeCrTi	−477	0.38	4.35
MoNbFeVTi	−457	0.33	6.26

Fig. 10 **a** Potentiodynamic polarization curves of MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys in deaerated 0.5 mol/L H_2SO_4 solution and SEM images of **b** MoNbFeCrV, **c** MoNbFeCrTi, **d** MoNbFeVTi alloys after the electrochemical test

Table 8 Electrochemical parameters of MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys in deaerated 0.5 mol/L H_2SO_4 solution

Alloy	E_{corr} (mV _{SCE})	i_{corr} ($\mu\text{A}/\text{cm}^2$)	i_{pass} ($\mu\text{A}/\text{cm}^2$)	E_b (mV _{SCE})
MoNbFe-CrV	-275	0.91	14.09	969
MoNbFe-CrTi	-258	1.35	7.86	—
MoNbFe-VTi	-285	0.70	12.77	—

4 Conclusions

- (1) Three equiatomic HEAs MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi were prepared by vacuum arc melting. The microstructure, mechanical properties, and corrosion behaviors have been investigated. The MoNbFeCrV and MoNbFeCrTi alloys mainly consist of one BCC phase and one Laves phase. The MoNbFeVTi alloy is mainly composed of one BCC phase and an ordered B2 phase.
- (2) All the three HEAs have a dendritic microstructure. For the MoNbFeCrV alloy, the dendrite is recognized as the BCC phase and the interdendritic regions consist of the Laves phase and Sigma phase. For the MoNbFeCrTi alloy, the dendrite is identified as the BCC phase and the interdendrite is recognized as the Laves phase. The MoNbFeVTi alloy mainly consists of one BCC phase and one B2 phase. Additionally, a small number of Ti-rich phases in both MoNbFeCrTi and MoNbFeVTi alloys are suggested to have an ordered BCC (B2) structure according to the experimental results and CALPHAD calculations.
- (3) The MoNbFeCrV alloy has the highest hardness of 826 ± 11 HV and the highest yield strength of 2663 MPa. The fracture strains of the MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys are 2.7%, 0.9%, and 1.7%, respectively. Further studies need to optimize the chemical compositions and improve the mechanical properties, especially to enhance the ductility.
- (4) The MoNbFeCrV, MoNbFeCrTi, and MoNbFeVTi alloys exhibit a spontaneous passivation and pseudo-passive behavior in both deaerated 1 mol/L NaCl and 0.5 mol/L H_2SO_4 solutions. In deaerated 1 mol/L NaCl solution, pitting corrosion is not observed in all three

alloys even when the potential is 1.5 V higher than the OCP. In deaerated 0.5 mol/L H₂SO₄ solution, the MoNbFeCrTi and MoNbFeVTi alloys are still in the passive state although the potential is 1.5 V higher than the OCP. However, the breakdown potential is observed in the MoNbFeCrV alloy due to the preferential dissolution of the V-rich Sigma phase.

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