Novel $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$ Eutectic High-Entropy Alloys with Excellent Combination of Mechanical and Corrosion Properties

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Received: 16 February 2020 / Revised: 28 March 2020 / Published online: 3 June 2020

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Abstract

The emergence of eutectic high-entropy alloys (EHEAs) offers new insights into the design of next generation structural alloys, which is due to their stable dual-phase microstructure and outstanding mechanical properties from room to elevated temperatures. In this work, a series of $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$ ($0 \leq x \leq 12$) EHEAs were designed and prepared via vacuum arc-melting. Typical eutectic microstructure composing lamellar face-centered cubic solid solution phase and C14 Laves phase appears in the as-cast EHEA when $x=9$. The microstructure turns to hypoeutectic or hypereutectic when x is below or beyond that critical value accordingly. The volume fraction of the hard Laves phase is proportional to the Nb addition, leading to the strength increment yet at the expense of ductility at room temperature. In particular, the EHEA having 4 at% Nb shows a compressive strength of 2.1 GPa with an elongation to fracture of 45%, while EHEAs containing 9 and 10 at% Nb exhibit ultrahigh yield strengths of over 1.4 GPa. The effect of Nb addition on the corrosion resistance of this Cr-free EHEA system was also studied. The EHEA containing 9 at% Nb has the best anti-corrosion performance in the 3.5 wt% NaCl solution at 298 ± 1 K, indicating a good combination of mechanical and corrosion properties.

Keywords Eutectic high entropy alloys · Laves phase · Microstructure · Mechanical properties · Corrosion property

1 Introduction

Since 2004 [1, 2], high entropy alloys (HEAs), also referred to as compositionally concentrated (or complex) alloys (CCAs), have received considerable attention due to their simple solid-solution structure and excellent mechanical performance [1–9]. This high-entropy concept enables a breakthrough of the traditional alloy design strategy with single principal element towards a much vaster composition scope. Following this line, single-phase face-centered cubic (FCC)

and body-centered cubic (BCC) structured HEAs appeared [1–4]. However, due to the lacking of effective strengthening and/or ductilizing mechanisms additional to the intrinsic high solid-solution effect, their mechanical performance is still far from application as advanced structural materials.

Solving the strength–ductility trade-off dilemma is an everlasting challenge not only for traditional alloys but also for HEAs nowadays. Recently, Lu et al. [6] have presented a successful trial to deal with this dilemma by developing a new group of HEAs, i.e. the eutectic high-entropy alloys (EHEAs). These EHEAs exhibit an ideal in situ composite structure of intermetallic reinforcing phase (e.g. B2 phase [6] and Laves phase [10–12]) and FCC matrix phase, leading to high rupture strengths and good creep resistances. The direct casting of the EHEAs is also reported for future industrial application [6, 7]. As one of the constituted phases in the EHEAs, Laves phases are well known for their high strength and oxidation resistance [13–15], which might impact the mechanical properties of EHEAs at both room and elevated temperatures. For example, the FCC/Laves phase EHEAs containing niobium [10]/zirconium [11]/tantalum [12] show excellent mechanical properties including compression strength over 2 GPa at a ductility of 20%.

Available online at <https://link.springer.com/journal/40195>.

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However, their plastic deformation capacity at room temperature and softening resistance at elevated temperature are still far from satisfactory.

To further widen the composition spectrum of EHEAs potential for practical application, in this work, we designed a new EHEA system based on a HEA matrix $\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2}$. The alloying of vanadium and molybdenum is selected due to their relative high melting points and large atomic radii, which might further enhance the lattice distortion in the solid solution matrix, thereby benefiting the mechanical properties. Different amount of niobium was selected and added into this $\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2}$ HEA system to achieve an EHEA composite architecture. Both the mechanical and corrosion responses are investigated, with the underlying mechanism discussed in relation to the microstructure features characterized in arrays of microscopy methods.

2 Experimental

The $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$ ($x=0, 2, 4, 6, 8, 9, 10, 12$ in at%, denoted as Nb0, Nb2, Nb4, Nb6, Nb8, Nb9, Nb10, Nb12, respectively, hereafter) EHEAs were fabricated in a vacuum induction melting furnace via mixed high-purity elements (higher than 99.95 wt%) under a Ti-gettered high-purity argon atmosphere. The ingot was flipped and remelted for at least five times to eliminate the inhomogeneity. All investigated samples in this work were in as-cast condition.

The crystal structure was identified by X-ray diffraction (XRD, EMPYREAN) with $\text{Cu K}\alpha$ radiation and a 2θ scattering range of 20° – 100° at a scanning rate of $4^\circ/\text{min}$, a voltage of 40 kV and a current of 40 mA. A Zeiss supra 55 field-emission-gun scanning electron microscope (SEM) equipped with the energy-dispersive spectrometry (EDS) was used to characterize the microstructure of the materials and relative chemical compositions.

High-temperature differential scanning calorimeter (DSC) tests were conducted on a Netzsch STA 449 F3 machine at a heating/cooling rate of 10 K/min.

Hardness was measured using a Vickers hardness testing machine (MH-50) under a load of 500 g with 15 s holding time. Five measurements were made on each sample, and the average values were used in this work. Compressive test was conducted using a uniaxial compression tester (WPM) at a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$. Specimens of $\varnothing 5 \text{ mm} \times 10 \text{ mm}$ were wire-cut directly from the as-cast ingot, with the surface ground down to 1500# grid-paper.

Corrosion resistance was measured by an electrochemical workstation (Reference 600) in the 3.5 wt% NaCl solution at room temperature of $298 \pm 1 \text{ K}$. The dimension of the active section of the electrochemical test samples was 0.6 cm in diameter and 0.2827 cm^2 in area. A

conventional three-electrode system was used, with the investigated samples as the working electrode, a platinum foil of $20 \text{ mm} \times 20 \text{ mm}$ as the counter electrode and an Ag/AgCl electrode (saturated KCl with electrode potential of 0.1981 V vs. standard hydrogen electrode) as the reference electrode. The polarization test was commenced at a scan rate of 1 mV/s after reaching a steady open circuit potential (OCP). The potential scanning range was -1 V versus the OCP level of the samples to 1.5 V versus OCP. The electrochemical test results were analyzed by Tafel extrapolation from polarization curves using the Cview software.

3 Results and Discussion

3.1 Phase and Microstructure

Figure 1a shows the XRD patterns of the $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$ EHEAs. The two groups of peaks that belong to different crystalline structures were identified. One is an FCC solid solution phase, and the other is a $\text{Fe}_2(\text{Nb}, \text{Mo})$ -type C14 Laves phase with a hexagonal close-packed (HCP) lattice structure (Fe_2Nb : $a=0.4813 \text{ nm}$, $c=0.7849 \text{ nm}$; Fe_2Mo : $a=0.4730 \text{ nm}$, $c=0.7720 \text{ nm}$). Increasing Nb addition, i.e. the increase in x value, the intensity of Laves phase peaks increases gradually. This likely indicates a growing amount of Laves phase in the material. Figure 1b presents the lattice parameters of FCC solid solution and Laves phase. As x increases, the lattice parameter of the FCC phase first increases slightly when x is below 8 but decreases sharply after that. This is probably due to the increasing solid-solution of Nb in the FCC matrix phase that results in the lattice distortion and therefore expansion before reaching the solution limits for original FCC structure, i.e. $x=8$ in the current alloy. Lattice parameters c and a of the Laves phase show a similar trend as the FCC phase. However, why these parameters from both phases decrease when $x \geq 9$ is still not clear. A possible explanation is the denser atomic stacking in the lattices of the two constituent phases triggered by a critical amount of Nb alloying that changes the elemental occupation state. Nevertheless, Nb, together with the Mo from the HEA matrix, as two of the strong Laves stabilizer in steels and superalloys [16, 17], reasonably tends to partition into the lattice of Laves phase in the current EHEAs, composing the multi-components $(\text{Co}, \text{Fe}, \text{Ni}, \text{V})_2(\text{Nb}, \text{Mo})$ -type Laves phase as revealed in the EDX results in Table 1.

Figure 2 shows the SEM backscattered electron images showing the microstructures of the as-cast EHEAs with different amount of Nb addition. Nb0 alloy exhibits a dendrite morphology in Fig. 2a, with single FCC solid solution structure according to the XRD results. This dendrite architecture is due to the as-cast segregation of high melting-point

Fig. 1 **a** XRD patterns of $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$ EHEAs, **b** lattice parameters of the FCC solid solution and the Laves phase extracted from the XRD results in **a**, as a function of the Nb addition

Table 1 EDS results of $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$ EHEAs (at%)

Alloys	Region	Co	Fe	Ni	V	Mo	Nb
Nb0	DR	21.36	44.27	21.07	9.37	3.94	—
	ID	20.02	39.10	18.86	13.63	8.40	—
Nb2	DR	20.91	42.64	20.34	10.28	4.58	1.26
	ID	21.83	39.36	19.91	10.62	6.07	2.21
	E	16.49	34.56	19.25	12.19	9.89	7.62
Nb4	DR	19.83	43.63	20.49	9.94	3.88	2.24
	ID	20.08	42.31	18.72	11.53	4.66	2.70
	E	17.50	31.13	13.96	7.02	10.50	19.89
Nb6	A	20.41	42.23	19.36	10.61	3.96	3.42
	E	18.36	35.32	17.15	8.82	5.63	14.71
Nb8	A	18.91	43.00	20.60	10.60	3.36	3.53
	E	19.33	30.20	14.03	6.77	5.88	23.79
Nb9	E	19.00	35.25	17.38	8.59	5.29	14.49
Nb10	E	19.15	35.79	18.46	9.72	4.49	12.37
	B	17.97	34.15	12.19	5.04	7.56	23.08
Nb12	E	18.60	37.15	24.86	13.64	2.10	3.65
	B	18.31	33.72	11.55	5.01	6.62	24.80

elements Mo/Nb in the dendrite regions (marked by DR in Fig. 2a, while ID represents the inter-dendrites regions). As the increase in the Nb amount, the EHEAs firstly show hypoeutectic microstructures and then become fully eutectic in the Nb9 alloy, as shown in Fig. 2b–f. Finally, the microstructure turns to be hypereutectic as observed in the Nb10 and Nb12 alloys in Fig. 2g, h, respectively. EDS results of regions A (FCC solid solution) and B (Laves phase) in Table 1 indicate that the FCC solid solution phase is enriched in Co, Fe, Ni and V, while the Laves phase is enriched in Mo and Nb. Before reaching fully eutectic, the volume fraction of eutectic regions (marked by E in Fig. 2b) containing the proeutectic Laves phase increases sharply as the increase in Nb amount. In the Nb9 alloy as presented in

Fig. 2f, the bright Laves phase and dark FCC solid solution lamellas exhibit a radial pattern in the eutectic cells. This is due to that during the eutectic reaction, Laves phase and FCC solid solution grow in parallel with each other, forming fine coupled lamellae. The eutectic composition of this Nb9 EHEA is further confirmed by the DSC curve in Fig. 3 where only one sharp exothermic/endothermic peak in the cooling/heating curve is observed. Interestingly, the primary Laves phase in both the Nb10 and Nb12 alloys shows a flower-like six-lobe morphology. The only difference is that in the later case this flower feature grows even coarser. Figure 4 shows the elemental mapping of the Nb10 alloy via electron probe micro-analyzer (EPMA) method. Together with EDX results in Table 1, the region B in the Nb10 alloy

Fig. 2 SEM images of **a** Nb0, **b** Nb2, **c** Nb4, **d** Nb6, **e** Nb8, **f** Nb9, **g** Nb10, **h** Nb12, showing the microstructure evolution from hypoeutectic to fully eutectic and finally hypereutectic with flower-like primary Laves phase

Fig. 3 DSC curve of the as-cast (CoFe₂NiV_{0.5}Mo_{0.2})₉₁Nb₉ alloy, only one sharp exothermic/endothermic peak was observed in the cooling/heating curve

is clearly a Nb/Mo-rich primary Laves phase. The large consumption of Nb/Mo elements of the Laves phase leads to the decrease in their amount in FCC matrix phase and thus lattice distortion, which is consistent with the XRD results. The segregation of V and Nb at the edge of the eutectic cell (marked by red dotted line in Fig. 4d, f) is likely driven by the lowering of the local free energy at the interface regions such as phase boundaries.

3.2 Phase Selection

Previous studies clearly indicated that there were several factors critical for the final phase construction and relative phase stability in HEA fields. Based on the Hume-Rothery rules, Zhang et al. [18, 19] proposed the phase selection criteria including ΔH_{mix} (mixing enthalpy), δ (atomic size difference), ΔS_{mix} (mixing entropy) referring HEAs in a wide composition spectrum:

$$\Delta H_{\text{mix}} = \sum_{i=1}^n \sum_{j=1, j \neq i}^n \Omega_{ij} C_i C_j = 4 \sum_{i=1}^n \sum_{j=1, j \neq i}^n \Delta H_{ij}^{\text{mix}} C_i C_j, \quad (1)$$

$$\delta = \sqrt{\sum_{i=1}^n C_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}, \quad (2)$$

$$\Delta S_{\text{mix}} = -R \sum_{i=1}^n (C_i \ln C_i), \quad (3)$$

where C_i is the atomic percent of the i th element, ΔH_{mix} is the mixing enthalpy between the i th and j th elements, r_i is the Goldschmidt atomic size of the i th element, R is the gas constant and equivalent to $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and T_m is the average value of the melting temperature. Among these, ΔH_{mix} characterizes the formation tendency of stable intermetallic, δ gives the degree of the atomic size mismatch, while ΔS_{mix} stands for the entropy of mixing of the HEA system. It is concluded that small atomic size differences ($< 6.6\%$) and near-zero values of the mixing enthalpy (in between -15 and 5 kJ mol^{-1}) prefer the formation of solid solutions phases [20, 21]. A criterion Ω is further developed to characterize the effect of mixing entropy over mixing enthalpy [22–25]:

$$\Omega = \frac{T_m \Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|}, \quad (4)$$

where Ω should be larger than 1.1 to avoid intermetallic phases [26]. In the current alloy variant, $\Delta H_{\text{AB mix}}$ is calculated using the Miedema model [20] and listed in Table 2. Therefore, ΔH_{mix} , δ , ΔS_{mix} , T_m , and Ω are given in Table 3.

Fig. 4 Elemental mappings of the Co, Ni, Fe, V, Mo and Nb in the Nb10 alloy using EPMA, the concentration of Nb/Mo in primary Laves phase and the segregation of V/Nb at the edge of eutectic cell were shown

Table 2 Values of ΔH_{mix} (kJ/mol) and atomic sizes of the elements

	Co	Fe	Ni	V	Mo	Nb
Co (1.251 Å)	0	−1	0	−14	−5	−25
Fe (1.241 Å)	−	0	−2	−7	−2	−16
Ni (1.246 Å)	−	−	0	−18	−7	−30
V (1.316 Å)	−	−	−	0	0	−1
Mo (1.363 Å)	−	−	−	−	0	−6
Nb (1.429 Å)	−	−	−	−	−	0

Table 3 Calculated parameters of (CoFe₂NiV_{0.5}Mo_{0.2})_{100-x}Nb_x EHEAs

Alloys	ΔH_{mix} (kJ/mol)	δ (%)	ΔS_{mix} (J/(K mol))	VEC	ΔX	$\bar{M}d$	T_m (K)	Ω
Nb0	-5.831	3.00	11.60	8.23	0.103	0.915	1867.1	3.71
Nb2	-7.079	3.64	12.18	8.17	0.107	0.939	1884.6	3.24
Nb4	-8.272	4.16	12.53	8.10	0.111	0.963	1902.1	2.88
Nb6	-9.410	4.59	12.79	8.04	0.115	0.987	1919.6	2.61
Nb8	-10.491	4.96	12.99	7.98	0.119	1.011	1937.0	2.40
Nb9	-11.011	5.13	13.07	7.94	0.121	1.023	1945.8	2.31
Nb10	-11.517	5.29	13.14	7.91	0.123	1.035	1954.5	2.23
Nb12	-12.487	5.58	13.26	7.85	0.126	1.060	1972.0	2.09

ΔH_{mix} of (CoFe₂NiV_{0.5}Mo_{0.2})_{100-x}Nb_x EHEAs is in a range from -5.8307 to -12.487 kJ mol⁻¹, while δ stays in between 3.00 and 5.58%, both falling in the predicted single-phase region. However, all Nb-doped (CoFe₂NiV_{0.5}Mo_{0.2})_{100-x}Nb_x alloys ($x > 0$) have a dual-phase structure. This suggests that the above criteria proposed by Zhang et al. seem not suitable for the studied EHEAs in this work. Wang et al. presented another criterion γ [27]:

$$w_s = 1 - \sqrt{\frac{(\gamma_s + \bar{r})^2 - \bar{r}^2}{(\gamma_s + \bar{r})^2}}, \quad (5)$$

$$w_L = 1 - \sqrt{\frac{(\gamma_L + \bar{r})^2 - \bar{r}^2}{(\gamma_L + \bar{r})^2}}, \quad (6)$$

$$\gamma = w_s / w_L = \frac{1 - \sqrt{\frac{(\gamma_s + \bar{r})^2 - \bar{r}^2}{(\gamma_s + \bar{r})^2}}}{1 - \sqrt{\frac{(\gamma_L + \bar{r})^2 - \bar{r}^2}{(\gamma_L + \bar{r})^2}}}, \quad (7)$$

where single solid-solution phase is claimed to form when γ is smaller than 1.175. This agrees with our experimental observation on the CoFe₂NiV_{0.5}Mo_{0.2} HEAs without Nb addition ($\gamma = 1.1073$), however still fails to predict the EHEAs having Nb dopant ($\gamma \approx 1.167$). This is probably due to the further increased enthalpy over entropy of the EHEA system as the Nb addition, which might trigger an earlier instability for the original FCC lattice and consequently the secondary phase formation.

Valence electron concentration (VEC) [23, 28–30], ΔX (electronegativity difference) [31] and $\bar{M}d$ (d-orbital energy level) [32] were also proposed to predict the phase construction in HEAs, where the latter two mainly deal with the appearance of topological close-packed (TCP) phases. They are expressed as:

$$\text{VEC} = \sum C_i \text{VEC}_i, \quad (8)$$

$$\Delta X = \sqrt{\sum_{i=1}^n C_i (X_i - \bar{X})^2}, \quad (9)$$

$$\bar{M}d = \sum_{i=1}^n C_i (Md)_i, \quad (10)$$

where X_i is the Pauling electro-negativity of the i th element, $\bar{X} (= \sum_{i=1}^n C_i X_i)$ is the average value of the Pauling electro-negativity, and $(Md)_i$ is the d-orbital energy level of the i th element in the M-element centered cluster in the i -M binary solid solution alloy, in which i is a solvent and M is a solute. The Pauling electronegativity of Co, Fe, Ni, V, Mo, and Nb is 1.88, 1.83, 1.91, 1.63, 2.16 and 1.60, respectively [12, 31].

VEC, ΔX and $\bar{M}d$ values of the EHEAs are calculated and listed in Table 3. Guo et al. [28] concluded that HEAs are supposed to form BCC phases when $\text{VEC} < 6.87$ whilst FCC phase when $\text{VEC} > 8$. In this study, the VEC of the EHEAs varies from 8.23 to 7.85 with the increase in Nb content. This indicates that the alloys tend to form multiphase, giving a quite good accordance with the experimental results. TCP phases is believed stable when $\Delta X > 0.133$ except for some Al-containing HEAs [31]. The value of ΔX of this Al-free (CoFe₂NiV_{0.5}Mo_{0.2})_{100-x}Nb_x EHEAs ranges from 0.103 to 0.126, indicating a much broader range of $\Delta X > 0.103$ for the formation of TCP phases. $\bar{M}d > 1.09$ is also proposed to have the appearance of TCP phases in a certain alloy [32]. However similarly, the stable range for TCP phases in our EHEAs is to some degree expended, i.e. $\bar{M}d \geq 0.915$, although in good accordance with a reported CoCrFeNiTa_x [12] HEA system with $\bar{M}d \geq 0.906$ for the appearance of TCP phases.

Table 4 presents the calculated enthalpies [20] evaluated by first-principles “high-throughput” density functional theory calculations in the HEA system. Some ΔH_f values of the binary components are beyond the limits for single solid solution ($37 > \Delta H_f > -138$ meV/mol), suggesting the possible occurrence of secondary phase formation. Based on this fact, the criterion ΔH_f seems

Table 4 Calculated enthalpies of formation of the lowest energy structures of binary compounds relative to phase separation into pure elements (meV/atom)

	Co	Fe	Ni	V	Mo	Nb
Co	0	-60	-21	-199	-52	-150
Fe	-60	0	-97	-176	-484	-2505
Ni	-21	-97	0	-250	-100	-316
V	-199	-176	-250	0	-127	-56
Mo	-52	-484	-100	-127	0	-133
Nb	-150	-2505	-316	-56	-133	0

Energy scale (meV/atom)

suitable for the current EHEA system. Since Mo and Nb have a larger atom radius than the other transition metals in this study, their alloying will lead to a large lattice distortion, thereby destabilizing the FCC matrix lattice and in turn promoting the formation of the Mo/Nb-enriched Laves phase. In addition, Mo and Nb also have relatively larger negative enthalpies of mixing with the other alloying elements. This might explain the early formation of Mo/Nb-enriched Laves phase formation at a low Mo/Nb content in the EHEAs.

3.3 Mechanical Properties

Figure 5a displays the compressive engineering stress–strain curves of the $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$ EHEAs, and the corresponding yield strength, compressive fracture strength, plastic strain and fracture strain are listed in Table 5. We observe that the Nb0 and Nb2 EHEAs show excellent compressive ductility without fracture. The Nb4 EHEA exhibits its high compressive strength of 2120 MPa and plausible fracture strain at 45%, but followed by slight drop in the Nb6 alloy. All eutectic and near-eutectic EHEAs (Nb8, Nb9, Nb10) show compression strength of over 2000 MPa and fracture strain at around 27%. Among these, Nb10 has the best comprehensive performance. This seems reasonable

Fig. 5 **a** Compression curves of $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$, **b** map of compressive strength and fracture strain combinations of various HEAs including $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$ EHEAs showing advantages

Table 5 Mechanical properties of the (CoFe₂NiV_{0.5}Mo_{0.2})_{100-x}Nb_x EHEAs

Alloys	Yield strength (MPa)	Compressive strength (MPa)	Plastic strain (%)	Fracture strain (%)	Vickers hardness (HV)
Nb0	199.0	—	> 60	> 60	147.6
Nb2	261.7	—	> 60	> 60	216.6
Nb4	476.4	2120.1	35.3	45.3	270.6
Nb6	883.4	2059.7	23.1	32.7	342.7
Nb8	1118.2	2050.8	19.3	28.2	393.5
Nb9	1449.2	2191.7	17.4	26.7	501.8
Nb10	1469.3	2433.2	19.4	27.7	476.1
Nb12	1310.5	1704.2	3.7	10.5	524.9

that the addition of Nb increases the volume fraction of brittle Laves phase that leads to a dramatic strengthening effect as well as a deterioration of ductility. Nevertheless, our (CoFe₂NiV_{0.5}Mo_{0.2})_{100-x}Nb_x EHEAs in this study clearly outperformed many other HEAs such as the CoCrFeNi-based HEAs [10, 12, 27, 30–40] in mechanical response, indicating potential in developing as future engineering structural materials.

3.4 Relationship Between Microstructures and Mechanical Properties

Figure 6 shows the relationship between Laves phase volume fraction and yield strength/Vickers hardness. The volume fractions of the Laves phase were measured based on over 10 SEM images. An approximate linear increase with increasing volume fraction of Laves phase is observed, which can be expressed as $y_{HV} = 5.5285x + 151.49$, where y_{HV} is the hardness value, and x is the volume fraction of Laves phase (vol%). Yield stress shows the exact the same relationship with the volume fraction. The drop of the yield stress in the

Fig. 6 Volume fraction of Laves phase and hardness/yield strength of (CoFe₂NiV_{0.5}Mo_{0.2})_{100-x}Nb_x EHEAs

Nb12 alloy is probably because of the onset of early fracture before reaching its intrinsic yield point. Therefore, the Nb9 and Nb10 EHEAs show the highest yield strength. For lamellar eutectics, the strengthening effects mainly come from the second-phase, solid solution and boundaries [34]. Firstly, assuming an iso-strain deformation state, the stiffer and more elastic Laves phase aligned within the ductile FCC solid solution enables the rule-of-mixtures prediction [35] in consideration of the total strength of the lamellar eutectics,

$$\sigma_{\text{EHEA}} = V_{\text{Laves phase}} \sigma_{\text{Laves phase}} + (1 - V_{\text{Laves phase}}) \sigma_{\text{FCC}}, \quad (11)$$

where $V_{\text{Laves phase}}$ is the volume fraction of Laves phase and $\sigma_{\text{Laves phase}}$ and σ_{FCC} are the stress of Laves phase and FCC solid solution at a specific value of strain, respectively. This equation indicates the significance of the strength contribution from second phase, i.e. the Laves phase. Secondly, additional alloying of Mo and Nb also provides solid solution strengthening to the eutectic alloys not only in the FCC matrix phase but also in the Laves phase. And at last, lamellar eutectics can be further strengthened as the reducing of interlamellar spacing [36, 37]. This part of strengthening is proposed to follow the Hall–Petch relationship,

$$\sigma_{\text{EHEA}} = \sigma^* + \frac{k}{\sqrt{\lambda}}, \quad (12)$$

where σ^* is the frictional stress, k is a constant, and λ is the lamellar spacing, which will become relatively higher when the Laves phase volume fraction is too low or too much. On the contrary, the EHEA Nb9 with fine fully lamellar microstructure, that is, with the lowest λ value has the highest strength contribution from boundaries, leading to an optimized balancing of strength and ductility among all hypoeutectic and eutectic alloys.

Fig. 7 Polarization curves of (CoFe₂NiV_{0.5}Mo_{0.2})_{100-x}Nb_x

Table 6 Electrochemical data of $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$ alloy system obtained from potentiodynamic polarization testing in 3.5 wt% NaCl at 298 ± 1 K

Sample	E_{corr} (mV)	i_{corr} ($\mu\text{A cm}^{-2}$)	E_{pit} (mV)	Average $E_{\text{pit}} - E_{\text{corr}}$ (mV)
Nb0	-252.36	4.2606	-43.25	209.11
Nb2	-318.8	4.0963	20.48	339.28
Nb4	-322.87	3.1789	79.19	402.06
Nb6	-310.18	3.4967	132.5	442.68
Nb8	-287.15	3.2805	199.9	487.05
Nb9	-337.46	4.6428	195.9	533.36
Nb10	-294.55	5.0078	261.1	555.65
Nb12	-351.21	7.1288	247.3	598.51

3.5 Corrosion Performance

The polarization curve of the $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$ EHEAs is shown in Fig. 7, and the corresponding electrochemical data are listed in Table 6. The passive window ($E_{\text{pit}} - E_{\text{corr}}$) of the alloys increases with increasing Nb addition, indicating that Nb can effectively improve the passivation ability of this EHEA system. Interestingly Nb4, Nb6 and Nb8 alloys exhibit the lowest corrosion current densities

(i_{corr}) among all investigated alloys, showing better overall corrosion resistance than other Nb-doped EHEAs in the 3.5 wt% NaCl solution. This might be attributed to the fact that the concentration of Nb (often considered a passivating element) in FCC matrix increased first before reaching the eutectic composition, i.e. Nb4-8, while in the hypereutectic compositions, the presence of Nb/Mo-rich primary Laves phase will consume Nb largely from the matrix thereby degrade the overall corrosion resistance. Nevertheless, compared with 304 stainless steel ($i_{\text{corr}} = 0.601 \mu\text{A cm}^{-2}$), the corrosion resistance of EHEAs needs to be further improved.

Figure 8 presents the corroded morphologies of the Nb0, Nb4, Nb9, Nb12 alloys (which present typical dendrite, hypoeutectic, complete eutectic and hypereutectic structures respectively) after the potentiodynamic polarization test in the 3.5 wt% NaCl solution. According to the SEM images, the major type of corrosion was uniform corrosion. According to Table 1, the interdendrite of the $\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2}$ alloy is enriched in V and Mo, while the dendrite depletes them. This elemental redistribution particularly considering the corrosion-resistant element Mo, greatly activates the dendrite regions under electrochemical conditions as compared to the interdendrite regions. Therefore, the corrosion on the $\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2}$ alloy was concentrated to the dendrites. Figure 8b, c shows that

Fig. 8 Surface morphologies of **a** $\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2}$, **b** $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{96}\text{Nb}_4$, **c** $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{91}\text{Nb}_9$, **d** $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{88}\text{Nb}_{12}$ after corrosion in 3.5 wt% NaCl (at 298 ± 1 K)

a few pits were formed on FCC matrix after the potentiodynamic polarization test. It can be observed that both the number and size of pitting pits decrease, which is because the content of non-corrosion-resistant FCC phase in the complete eutectic structure decreased and the structure became denser. In addition, these corroded morphologies are quite like the microstructure shown in Fig. 2. Moreover, we find that there were many regular polygonal pits on the surface of Nb12 alloy, which is believed to be caused by the shedding of early nucleation of Laves phase without growing up during the corrosion process, to reduce the overall corrosion resistance, which is consistent with the previous results of increased corrosion current in Table 6.

4 Conclusions

In this work, novel $(\text{CoFe}_2\text{NiV}_{0.5}\text{Mo}_{0.2})_{100-x}\text{Nb}_x$ eutectic high-entropy alloys were prepared by vacuum arc-melting. The microstructure of the EHEAs was characterized, and the mechanical and corrosion behaviors were evaluated.

1. The XRD and SEM results reveal that the eutectic high-entropy alloys are transformed from hypoeutectic to hypereutectic solidification by increasing Nb content. The phase formation criteria, ΔH_f , appears to be suitable for predicting the phase formation in this alloy system. The eutectic composition, i.e., Nb9, shows a lamellar-like microstructure consisting of FCC solid solution and C14 Laves phases. With increasing volume fraction of C14 Laves phase, the alloys show enhanced strengths yet at the expense of ductility.
2. The eutectic and near-eutectic components, Nb8, Nb9, Nb10, with fine lamellar microstructure show the ideal combination among the second-phase, solid solution and boundary strengthening. They exhibit high compressive strength and yield strength, while the other hypoeutectic components show generally higher ductility.
3. The addition of Nb reduces the corrosion potential and significantly improves the passivation ability of the alloy. For another, the corrosion current density first decreased and then increased, which may be related to the Nb content solutioned in the matrix.

Acknowledgements This work was financially supported by the National MCF Energy R&D Program (No. 2018YFE0312400), the National Key Research and Development Program of China (No. 2019YFA0209901), the National Natural Science Foundation of China (Nos. 51822402 and 51671044), the Fundamental Research Funds for the Central Universities (No. DUT16ZD206), and the LiaoNing Revitalization Talents Program (No. XLYC1807047).

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