

Article

A Cobalt-Free Multi-Principal Elements Alloy with Balanced Mechanical Properties and Exceptional Corrosion Resistance

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Abstract

This study investigates the mechanical properties and corrosion behavior of a Co-free Fe₄₀Ni₃₀Cr₂₀V₈Mo₂ (at.%) multi-principal elements alloy (MPEA) designed for potential applications in aggressive environments. The alloy exhibits a balanced combination of strength and ductility, with a yield strength of approximately 258 MPa, an ultimate tensile strength of about 647 MPa, and a fracture elongation of around 52%, of which deformation is primarily governed by dislocation-mediated plasticity. In terms of corrosion performance, the alloy demonstrates excellent resistance in chloride-containing environments. Potentiodynamic polarization tests reveal a wide and stable passive region of approximately 1.28 V_{SCE} and a high pitting potential of about 0.975 V_{SCE}, indicating exceptional stability of the passive film. Electrochemical impedance spectroscopy (EIS) further confirms the high impedance and protective nature of the surface layer. X-ray photoelectron spectroscopy (XPS) analysis reveals that the superior anti-corrosion property is attributed to the formation of a passive film enriched with protective Cr₂O₃ and V, Mo oxides, which collectively construct an effective barrier against chloride-induced attack by reducing donor density. This work provides valuable insights for the development of alternative alloys to replace Co-containing systems in demanding corrosive applications.

Keywords: high-entropy alloy; mechanical properties; corrosion properties; passive film

1. Introduction

The rapid advancement of industries such as aerospace, marine engineering, and energy generation imposes increasingly stringent demands on structural materials, particularly for service in extreme environments characterized by high stress, corrosive media, and thermal loads. Traditional alloys, constrained by their traditional compositional design, increasingly fall short of meeting these multifaceted requirements. The emergence of high-entropy alloys (HEAs), also called “multi-principal elements alloys (MPEAs)”, brought a new direction to design high-performance alloys [1]. MPEAs exhibit an unprecedented synergy among their constituent elements. This unique feature facilitates the integrated design of good mechanical properties, wear resistance, oxidation resistance, high thermal stability, and corrosion resistance capabilities, often mutually exclusive in conventional alloys [2–15]. The defining feature of MPEAs is their profound “cocktail effect”, which



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enables a synergy among constituent elements that transcends simple property averaging. This intrinsic characteristic positions MPEAs as a highly promising platform for next-generation engineering materials.

Among the vast MPEA family, the CoCrFeNi MPEA system have become a quintessential model due to their stable face-centered cubic (FCC) structure, which provides an excellent foundation for combining high toughness with notable corrosion resistance [16–18]. The system's corrosion performance is largely attributed to the formation of a robust, Cr-rich passive film. However, a critical impediment to the sustainable and large-scale application of this promising system is its reliance on Cobalt (Co). Co is associated with significant drawbacks, including documented bio-toxicity, high cost, and complex recyclability, raising environmental and economic concerns. Consequently, the development of high-performance, Co-free alternatives has emerged as a paramount objective within the field [19].

The strategic substitution of Co with carefully selected elements presents a viable pathway to achieve this goal. Extensive research has identified Molybdenum (Mo) as a particularly potent additive for enhancing corrosion resistance in the CoCrFeNi system, Mo enriching within the passive film, preferentially forming stable, high-valent oxides (e.g., MoO_2 , MoO_3) that act as a formidable barrier against corrosive ion ingress [20–22]. In Mo-modified CoCrFeNi-based MPEAs, the native oxide film and the passive films formed at potentials such as $0.5 V_{\text{SCE}}$ and $0.8 V_{\text{SCE}}$ are primarily composed of Mo and Cr as core components, with Mo being the key element responsible for the improved corrosion resistance, as Mo can form stable high-valent oxides and promotes the densification of the passive film and reduces defects, effectively blocking the penetration of corrosive media. The enrichment of Mo within the film fundamentally strengthens the passivation capability and corrosion resistance, serving as the core driving factor for the superior corrosion performance of this system [23,24]. Vanadium (V) introduces severe lattice distortion due to its large atomic radius mismatch with elements like Iron (Fe), Chromium (Cr), and Nickel (Ni), leading to potent solid-solution strengthening without readily precipitating brittle intermetallic phases in FCC matrices [25–27]. This effect can dramatically increase yield strength and hardness while preserving appreciable ductility and strain-hardening capability [26,28]. Furthermore, V exhibits a synergistic interaction with Mo; it can co-partition in the passive film, contributing to a denser, more protective oxide structure and thereby offering an additional boost to corrosion resistance [29,30]. Therefore, the co-addition of Mo and V is theoretically predicted to create a synergistic effect, simultaneously addressing the critical needs for enhanced corrosion protection and mechanical robustness in a Co-free alloy.

Guided by this rationale, the present study is designed to comprehensively investigate the effects of substituting Co with synergistic additions of Mo and V in a novel Co-free MPEA, with a focused inquiry into the resultant corrosion mechanisms. We evaluate its mechanical properties via tensile testing and elucidate deformation mechanisms using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD). Electrochemical corrosion behavior in 3.5 wt.% NaCl solution is examined by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and Mott–Schottky analysis. The elemental valence states of passive films are characterized by X-ray photoelectron spectroscopy (XPS), enabling a direct correlation between film characteristics and macroscopic performance. This work aims to provide a comprehensive understanding of how Mo and V co-addition governs the microstructures, mechanical behaviors, and corrosion mechanisms of this Co-free MPEA.

2. Experiments

2.1. Materials Preparation

The Fe₄₀Ni₃₀Cr₂₀V₈Mo₂ (at.%) high-entropy alloy ingot was fabricated using vacuum arc melting. The Fe₄₀Ni₃₀Cr₂₀V₈Mo₂ (at.%) alloy ingot was prepared by vacuum arc melting using high-purity elemental metals (Fe: 99.9 wt.%, Ni: 99.9 wt.%, Cr: 99.9 wt.%, V: 99.9 wt.%, Mo: 99.9 wt.%, provided by Beijing Yanbang New Materials Co., Ltd. (Beijing, China). The ingot was remelted four times to ensure compositional homogeneity. The chemical compositions of the MPEA and the reference alloy (316L SS) were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, SPECTRO BLUE SOP, Kleve, Germany), as displayed in Table 1. The as-cast ingot was subsequently rolled at room temperature into plates with a thickness of 10 mm. Disk-shaped specimens with an area of 1 cm² and dog-bone-shaped tensile specimens (with a gauge length of 21 mm and a gauge width of 7.5 mm, and a thickness of 1 mm) were cut from the sheets by electrical discharge machining (EDM). The surface oxide layers of all specimens were removed by SiC abrasive paper. Both the disk and dog-bone specimens were then subjected to heat treatment. They were placed in a pre-heated muffle furnace at 1100 °C for 1 min, followed by quenching. Subsequently, the specimens were polished with SiC paper from 180# to 2000# grit. The disc-shaped specimens were embedded in epoxy resin for electrochemical tests, while the dog-bone specimens were prepared for tensile mechanical property testing.

Table 1. The chemical compositions of the MPEA and 316L SS.

Alloys		Fe	Ni	Cr	Mo	Mn	Si	V
Fe ₄₀ Ni ₃₀ Cr ₂₀ V ₈ Mo ₂	wt.%	Bal.	31.81	18.07	3.47	-	-	6.90
	at.%	Bal.	30.57	19.60	2.04	-	-	7.64
316L SS	wt.%	Bal.	9.81	17.20	2.10	2.0	0.10	-
	at.%	Bal.	9.33	18.47	1.22	2.03	0.20	-

2.2. Tensile Test

Room-temperature uniaxial tensile experiments were performed using an MTS Landmark universal testing system at a fixed strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ (MTS Systems Corporation, Eden Prairie, MN, USA). Three duplicate specimens were tested per processing condition to ensure result reproducibility. Local strain distribution during tensile deformation was characterized by the digital image correlation (DIC) technique.

2.3. Electrochemical Tests

Electrochemical tests, including potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and Mott–Schottky analysis, were conducted using a standard three-electrode system connected to a CHI electrochemical workstation in a 3.5 wt.% NaCl solution. After the samples reached a stable open circuit potential (OCP), all electrochemical tests were performed. The specimen served as the working electrode, with a Saturated Calomel electrode (SCE) and a platinum sheet acting as the reference and counter electrodes, respectively. All electrochemical tests were performed after the samples reached a stable open circuit potential (OCP). The stable OCP of our alloy was approximately $-0.29 \text{ V}_{\text{SCE}}$, and that of 316L SS was approximately $-0.35 \text{ V}_{\text{SCE}}$. Subsequently, EIS measurements were performed by applying a sinusoidal potential perturbation with an amplitude of 10 mV over a frequency range from 10^{-2} to 10^5 Hz . The potentiodynamic polarization curve was measured at a scan rate of 1 mV/s, starting from a potential of $-0.6 \text{ V}_{\text{SCE}}$ until the current density reached to 10^{-3} A/cm^2 . All electrochemical tests were repeated at least three times to ensure the reliability of the data. At a frequency of 1 kHz,

Mott–Schottky plots were obtained using an amplitude signal of 10 mV and a step rate of 25 mV in the cathodic direction.

2.4. Microstructural Analysis

For microstructural characterization, specimens cut from tested tensile samples using electrical discharge machining were hot-mounted. The mounted samples were ground with SiC abrasive paper from 400# to 3000# grit and then polished with a colloidal silica suspension. X-ray diffraction (XRD) was employed to identify the initial phase constituents of the MPEA specimens. Measurements were conducted on a D/max 2550 in conjunction with Cu $K_{\alpha 1}$ ($\lambda = 1.5418 \text{ \AA}$) radiation at 40 kV and 30 mA. Diffraction patterns were recorded over a 2θ range of $30\text{--}110^\circ$ with a step size ($\Delta 2\theta$) of 0.02° and a scanning rate of $5^\circ/\text{min}$. Using backscatter electron imaging (BSEI) and electron backscatter diffraction (EBSD), microstructural characterization of both undeformed and tensile-tested samples (with varying local strains) was carried out in a TESCAN CLARA microscope (TESCAN ORSAY HOLDING a.s., Brno, Czech Republic), operated at 30 kV and 20 kV, respectively, with a step size of 50 nm for EBSD mapping. Corresponding chemical compositions were analyzed using EDS, an EDAX system at an accelerating voltage of 15 kV.

2.5. Characterization of Passive Films

On a SHIMADZU/Kratos AXIS SUPRA+ spectrometer (Kratos Analytical Ltd., Manchester, UK), X-ray photoelectron spectroscopy (XPS) was employed to characterize the passive films formed on the alloy surfaces.

Disk-shaped specimens were embedded in epoxy resin, ground with SiC abrasive paper (400# to 2000# grit), mechanically polished to a $1 \mu\text{m}$ finish, and then rinsed with deionized water and anhydrous ethanol. Prior to XPS analysis, stable passive films were established on the sample surface by potentiostatic polarization at $0.1 V_{\text{SCE}}$ for 3600 s. The obtained spectra were processed using XPSpeak software (version: Fitv4.1). Peak fitting was performed using mixed Gaussian–Lorentzian functions after Shirley background subtraction. The binding energy scale was calibrated against the C1s peak at 284.6 eV.

3. Results and Discussion

3.1. Microstructural Analysis Prior to Deformation

Figure 1a shows XRD patterns of the MPEA subjected to annealing. The patterns exhibit five typical FCC peaks, corresponding to the (111), (200), (220), (311), and (222) planes, indicating that the annealed sample predominantly consists of a stable FCC phase. The lattice constant was calculated to be $3.62 \text{ \AA}$, which is slightly larger than that of the equiatomic CoCrFeMnNi MPEA ($3.56 \text{ \AA}$) [31], referring to the lattice strain was enhanced by the addition of V and Mo. Figure 1b,c displays the EBSD IPF image and phase, respectively. Figure 1c is the corresponding EDS elemental mapping of an MPEA sample in Figure 1b. The annealing twins can be easily detected in the IPF map, similar to those observed in the majority of transition MPEAs. However, the phase map (Figure 1b) indicates the presence of a minor BCC phase. The EDS mapping in (c) reveals a relatively uniform distribution of all five constituent elements without significant segregation in the FCC matrix. Analysis suggests the coexistence of the FCC matrix with a small fraction of BCC phase, which may be related to the role of Cr and Mo as a BCC phase stabilizer [29,30]. Due to its low volume fraction, this BCC phase was not detected by XRD. Therefore, the MPEA sample is considered a predominantly single-phase FCC structure.

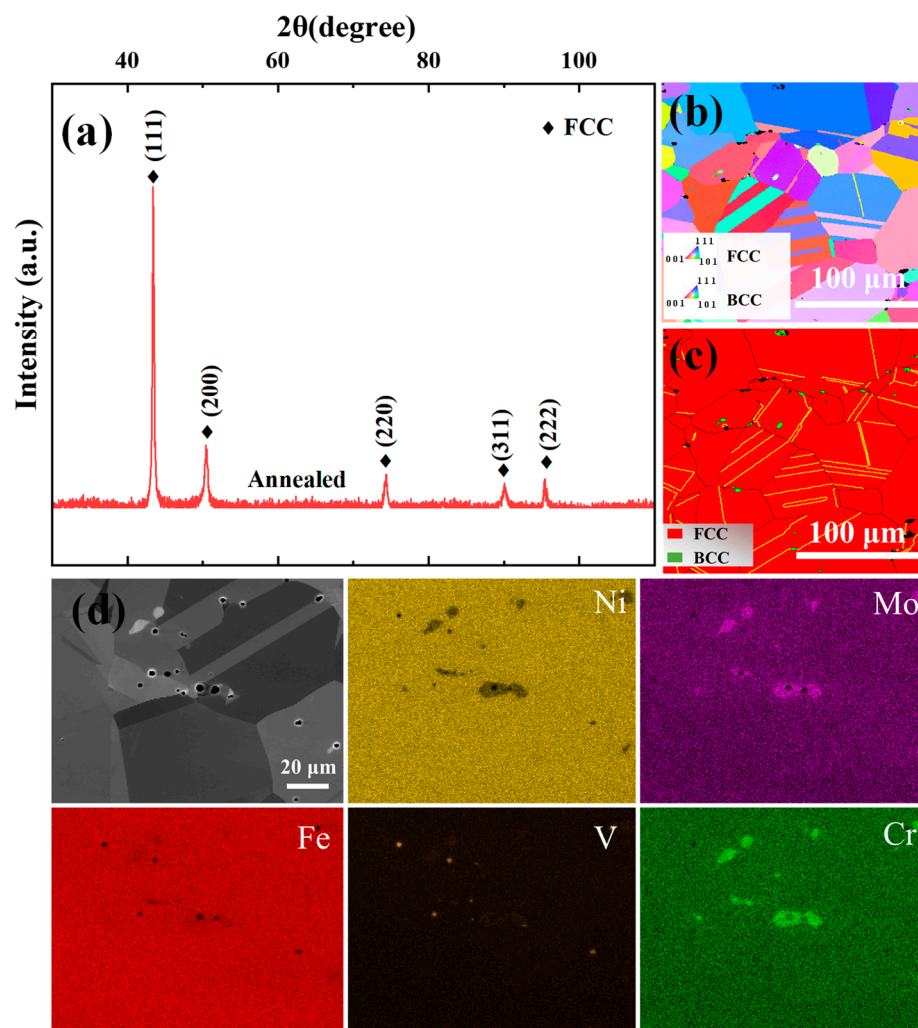


Figure 1. (a) XRD patterns of the annealed MPEA; (b) EBSD inverse pole figure (IPF) map and (c) phase map of the MPEA after heat treatment at 1100 °C; (d) EDS elemental maps obtained from the same sample region indicated by the yellow rectangle in (c).

3.2. Mechanical Behaviors

3.2.1. Tensile Deformation Behaviors

Figure 2 displays the mechanical response of the MPEA. The MPEA exhibits a yield strength (YS) of ~258 MPa, an ultimate tensile strength (UTS) of ~647 MPa, and a fracture elongation of ~52%, as shown in Figure 2a. Figure 2b shows the true stress–strain curve and the corresponding work-hardening rate curve of the MPEA. The work-hardening rate generally decreases with increasing true strain. Three distinct stages can be clearly distinguished: a sharp decline in the work-hardening rate at low true strain ($\epsilon < 0.025$), followed by a plateau-like region with a moderated decrease from 0.025 to 0.15, the rate of decrease moderates, resulting in a relatively flat profile in the curve, and finally a pronounced drop as the true strain exceeds 0.15.

3.2.2. Deformation Microstructures

Figure 3a–f display the EBSD maps of the MPEA at tensile strains of approximately 15% and 40%, respectively. At ~15%, microstructure is primarily characterized by high-angle grain boundaries and annealing twin boundaries, and grains are almost equiaxed (Figure 3a). Noticeable dislocation accumulation is observed according to Kernel Average Misorientation (KAM) maps (Figure 3b), primarily concentrated at grain boundary regions.

In contrast, the IPF map at a strain of ~40% shows that grains are prolonged along the tensile direction (Figure 3d). KAM map shows that grain boundaries and twin boundaries are still the accumulation sites for dislocations, and dislocation density in the grain interior is much higher than that of the 15-strain location (Figure 3e). Throughout the tensile process, no deformation twin structures and martensitic transformation are detected, evidenced by the corresponding phase map (Figure 3c,f), indicating that dislocation activity was the dominant deformation mechanism, which is consistent with XRD results. Notably, what we should focus on is that the KAM value around (Cr, Mo)-rich BCC phase is even higher than that at grain boundaries, indicating that the hard BCC phase led to premature cracking due to stress concentration, deteriorating the elongation.

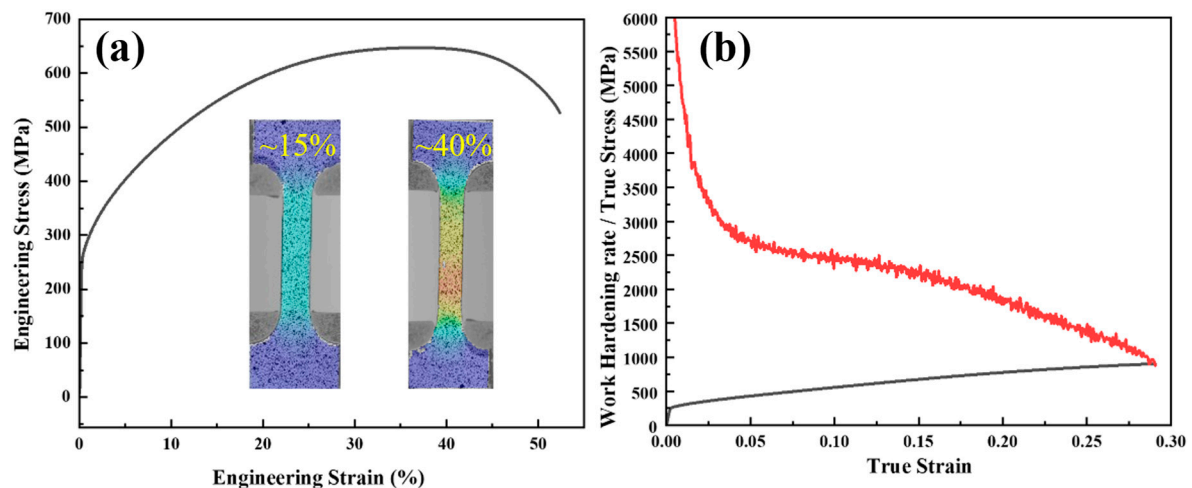


Figure 2. (a) Typical engineering stress–strain curve; (b) True stress–strain curve and the corresponding work-hardening rate curve of Fe₄₀Ni₃₀Cr₂₀V₈Mo₂ MPEA.

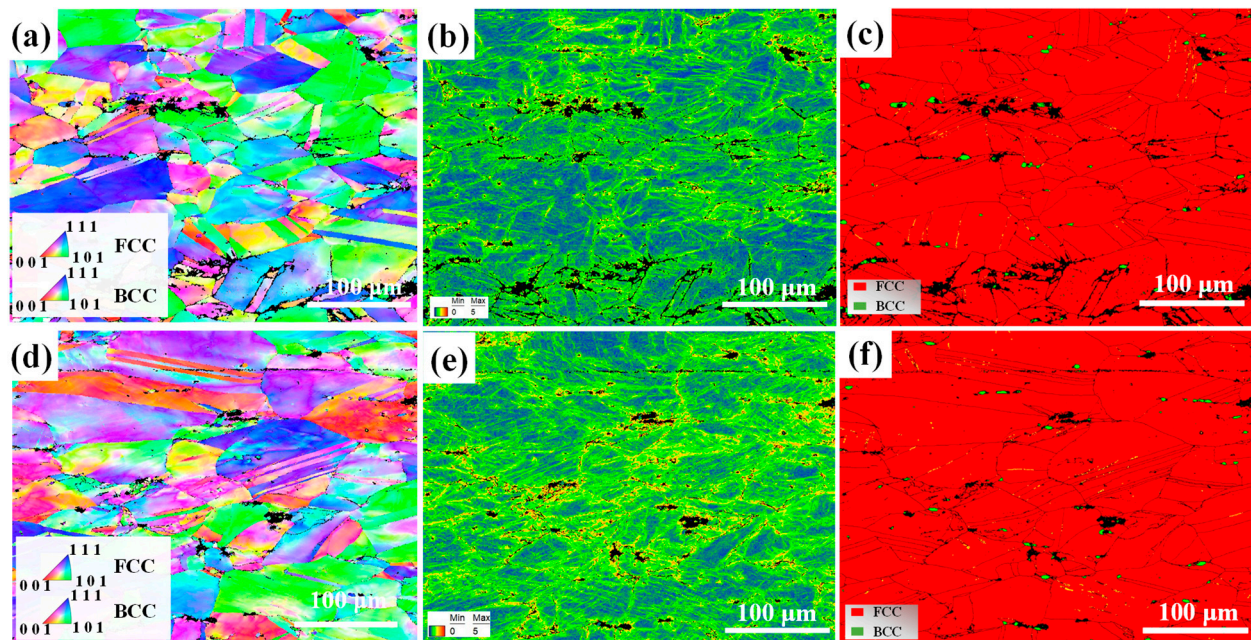


Figure 3. EBSD analysis at different strain levels of the MPEA. (a–c) correspond to the IPF map, KAM map and phase map at a strain of ~15%, respectively; (d–f) correspond to the IPF map, KAM map, and phase map at a strain of ~40%, respectively.

The BSE images in Figure 4 provide further insight into the post-deformation microstructures. At the relatively low local strain of ~15% (Figure 4a), the grains undergo slight deformation. While abundant dislocations are generated within the grains, significant dislocation pile-ups are evident (Figure 4c). This observation aligns with the EBSD results, indicating that deformation in the MPEA involves dislocation generation within the grains, thereby influencing its mechanical properties. Under a larger local deformation of ~40%, the grains experience severe plastic deformation, as shown in Figure 4d. The dislocation density within the crystals is considerably higher compared to the region with ~15% strain. Furthermore, numerous microbands are formed at this strain level, as seen in Figure 4e,f. Meanwhile, a few of the dislocation cells with a size of ~200 nm are found within the grains. Normally, dislocation cells are beneficial to ductility by consuming the dislocation-free zones [25]. However, the limited number of dislocation cells cannot provide enough zone to generate abundant dislocations to accommodate plastic deformation. Therefore, this is another reason for the ordinary elongation obtained in the MPEA.

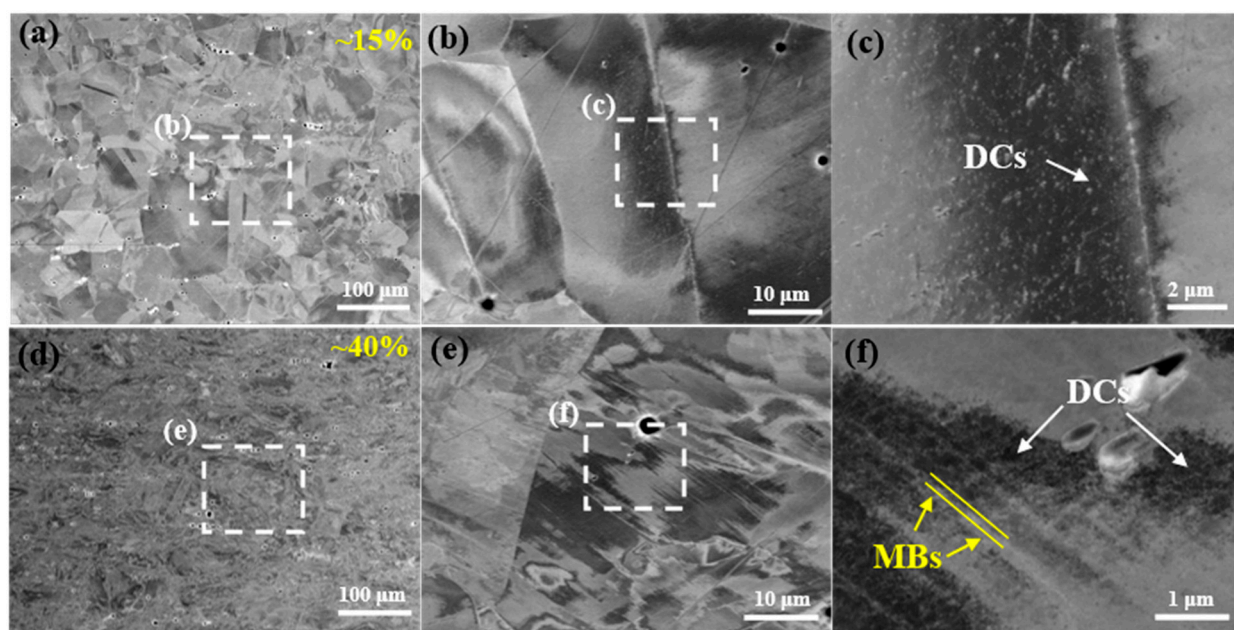


Figure 4. BSE images of sample regions with two representative local strains: (a–c) microstructures at a strain of ~15%; (d–f) microstructures at a strain of ~40%. “DCs” and “MBs” denote dislocation cells and microbands, respectively.

Based on the observed deformation microstructures, the strain-hardening behavior of the MPEA can be elucidated as follows. Initially, upon yielding, the work-hardening rate decreases rapidly (Figure 2b), which corresponds to the activation of dislocation slip and multiplication [26,27]. Subsequently, as strain increases, dislocations accumulate and pile up at grain boundaries, and multiple slip systems become active. The formation of dislocation microbands brings a significant increase in dislocation density, which is reflected in the moderated decline in the work-hardening rate. In the final stage, with further straining, the continued increase in dislocation density and the progressive exhaustion of dislocation-free regions accelerate the decrease in the work-hardening rate until necking.

3.3. Corrosion Behaviors

3.3.1. Electrochemical Corrosion Behaviors

The potentiodynamic polarization curves of 316L SS and the Fe₄₀Ni₃₀Cr₂₀V₈Mo₂ MPEA, measured in a 3.5 wt.% NaCl solution at ambient temperature is presented in

Figure 5a. These illustrate the characteristic anodic and cathodic electrochemical responses of both materials. Key quantitative parameters in this plot, including corrosion potential (E_{corr}), corrosion current density (i_{corr}), passive current density (i_{pass}), pitting potential (E_{pit}), and passivation range (ΔE), were extracted from these curves and listed in Table 2 for comparison.

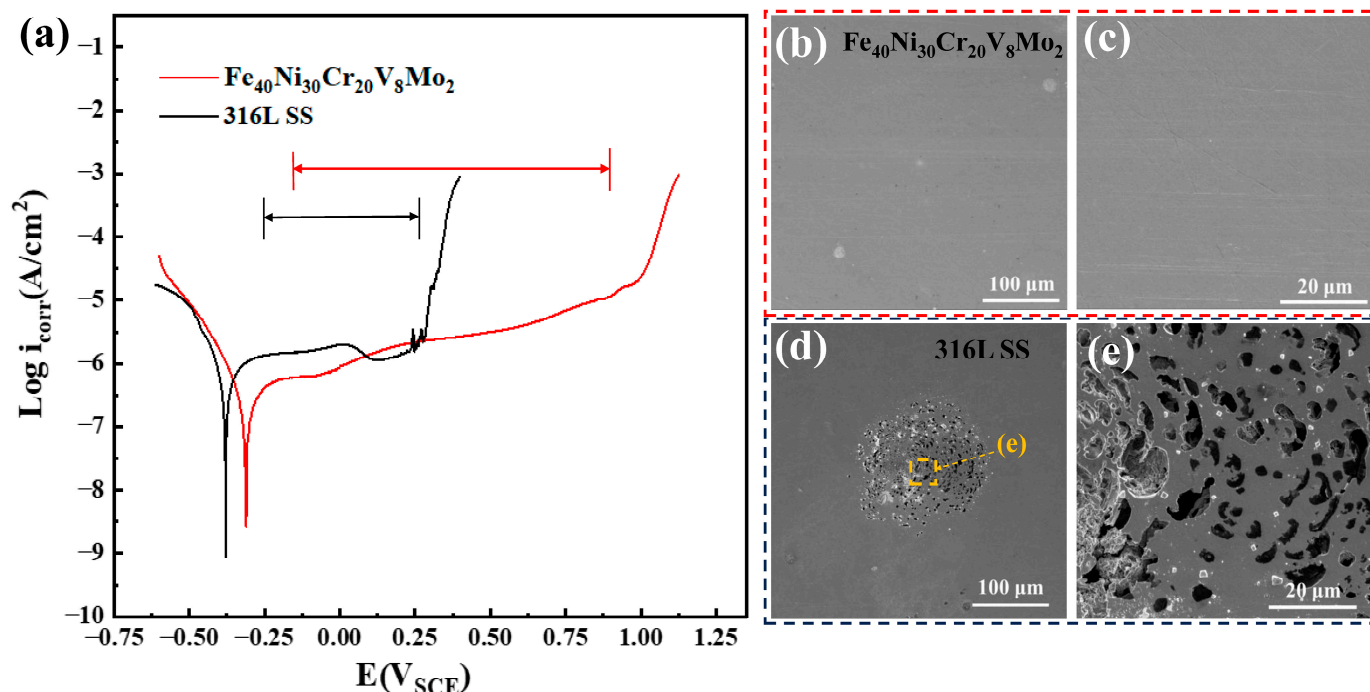


Figure 5. (a) Potentiodynamic polarization curves of the MPEA and 316L SS; (b–e) Corroded surface morphologies of the $\text{Fe}_{40}\text{Ni}_{30}\text{Cr}_{20}\text{V}_8\text{Mo}_2$ MPEA after polarization within the potential range of $-0.5 \text{ V}_{\text{SCE}}$ to $0.5 \text{ V}_{\text{SCE}}$.

Table 2. Electrochemical parameters of the two samples derived from Figure 5a.

Samples	E_{corr} (V)	i_{corr} (A/cm^2)	E_{pit} (V)	ΔE (V)
$\text{Fe}_{40}\text{Ni}_{30}\text{Cr}_{20}\text{V}_8\text{Mo}_2$	-0.306	6.423×10^{-7}	0.975	1.281
316L SS	-0.379	5.941×10^{-6}	0.256	0.635

As a general principle, superior corrosion resistance is associated with a nobler E_{corr} and a lower i_{corr} [28]. Combining the data in Table 2 with the polarization curves in Figure 5, it is evident that the $\text{Fe}_{40}\text{Ni}_{30}\text{Cr}_{20}\text{V}_8\text{Mo}_2$ MPEA possesses a clear advantage over 316L SS. The MPEA exhibits a more noble corrosion potential ($E_{corr} = -0.306 \text{ V}_{\text{SCE}}$) and a lower corrosion current density ($i_{corr} = 6.423 \times 10^{-7} \text{ A}/\text{cm}^2$) compared to 316L SS ($E_{corr} = -0.379 \text{ V}_{\text{SCE}}$, $i_{corr} = 5.941 \times 10^{-6} \text{ A}/\text{cm}^2$). This convincingly demonstrates the superior corrosion resistance of the MPEA. Furthermore, the results in Figure 5 and Table 2 indicate that the MPEA possesses a broader passivation range and maintains passive stability at higher anodic potentials, suggesting that it can maintain good corrosion resistance even in more severe corrosive environments, thereby exhibiting stronger service adaptability.

In the polarization curve of 316L SS (Figure 5a), a rise in current density occurs at a high potential of $0.028 \text{ V}_{\text{SCE}}$, which is closely related to the selective dissolution of Cr [32]. Under high potential, the protective Cr^{3+} in the passive film is oxidized to the more soluble Cr^{6+} . Compared to Cr^{3+} , Cr^{6+} is prone to dissolution and depletion at higher voltage, leading to the breakdown of the passive film integrity and the abnormal change in current density. Furthermore, severe fluctuations in current density are observed in the

potential range of 0.216–0.288 V_{SCE} for 316L SS. Within this potential range, the passive film is in a critically unstable state, undergoing a dynamic imbalance between continuous film formation and localized breakdown. Finally, when the potential reaches the pitting potential ($E_{pit} = 0.256$ V_{SCE}), the film loses its ability to repassivate, marking the onset of stable pitting corrosion.

In contrast, the pitting potential (~ 0.975 V_{SCE}) of the Fe₄₀Ni₃₀Cr₂₀V₈Mo₂ MPEA is significantly higher than that of 316L SS ($E_{pit} = 0.256$ V_{SCE}), indicative of a stable and dense passive film formed within its passivation range. In addition, unlike 316L SS, the oxidation of Cr³⁺ to soluble Cr⁶⁺ is suppressed in the MPEA, likely due to the synergistic effects of its constituent elements. Accordingly, no significant current density fluctuations are observed in the potential interval of 0.884–1.024 V_{SCE}, confirming the enhanced stability of the passive film. Moreover, compared to some representative MPEAs [33–38], as shown in Figure 6, the alloy in this work possesses a relatively positive E_{corr} and a lower i_{corr} , thus superior corrosion resistance is obtained in the present MPEA.

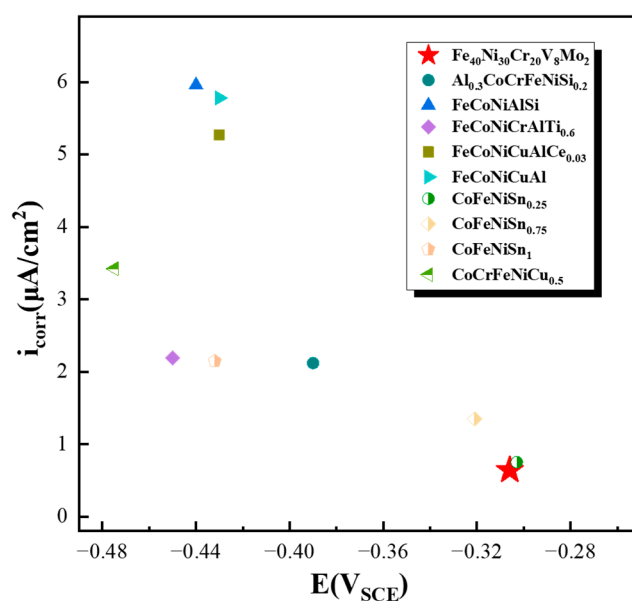


Figure 6. The self-corrosion voltage and currents of the reference and as-prepared MPEAs [33–38].

Figure 5b–e show the surface morphologies of the two alloys after polarization within the potential range of -0.5 V_{SCE} to 0.5 V_{SCE}. Notably, there are no obvious corrosion pits observed in the surface of the MPEA, as shown in Figure 5b,c. In contrast, Figure 5d,e reveal the distinct pitting traces and corrosion pits of varying sizes on the 316L SS surface. These observations are consistent with the polarization behavior discussed earlier: within this potential window, the passive film of the MPEA remained intact, whereas that of 316L SS underwent localized breakdown. The absence of pitting on the MPEA surface further confirms the superior stability of its passive film and its excellent corrosion resistance, even at elevated potentials. Moreover, as summarized in Table 2, the pitting potential of the MPEA approaches ~ 1 V_{SCE}, suggesting that the alloy is likely to retain its corrosion resistance under even higher applied potentials or in more concentrated aggressive environments.

Figure 7 displays the EIS results for the Fe₄₀Ni₃₀Cr₂₀V₈Mo₂ MPEA and 316L SS in a 3.5 wt.% NaCl solution, containing Nyquist plots (Figure 7a) and Bode plots (Figure 7b). The capacitive arc radius in the Nyquist plot provides an overview of the charge transfer resistance, providing a comparative assessment of the corrosion resistance of the two materials. The MPEA exhibits a well-defined capacitive arc with a radius significantly larger than that of 316L SS. A larger capacitive arc radius generally indicates that it is harder for the charge transfer process and, consequently, better corrosion resistance [21,28,39].

These observations suggest that the passive film of MPEA demonstrates higher corrosion resistance, which aligns with the findings derived from the potentiodynamic polarization tests discussed earlier.

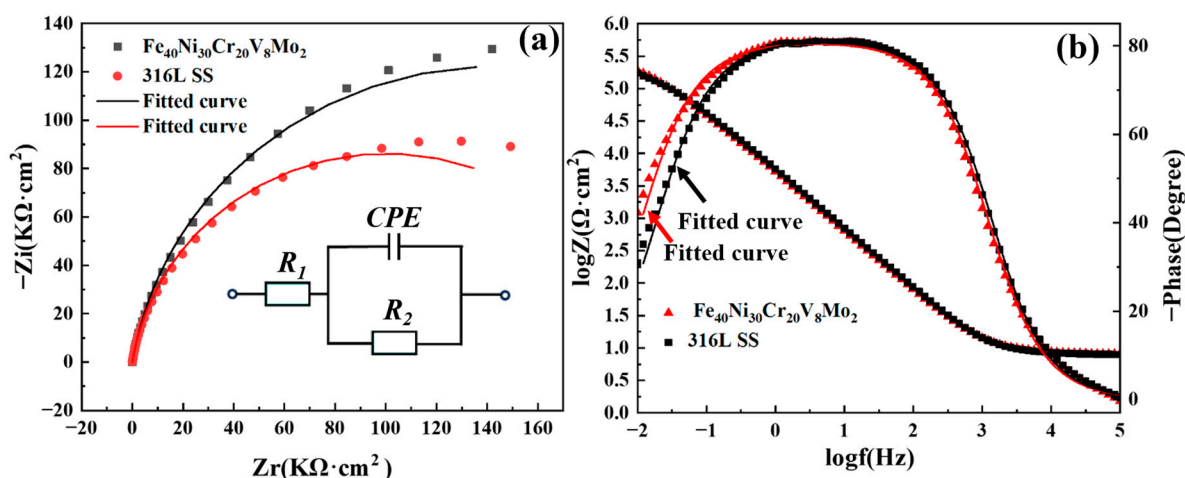


Figure 7. (a) Nyquist plots and (b) Bode plots for the MPEA and 316L SS in a 3.5 wt.% NaCl solution.

Figure 7b presents the Bode plots for the MPEA and 316L SS. The magnitude of impedance ($|Z|$) shows a nearly linear relationship with frequency, with a slope close to -1 , indicating capacitive behavior. The curves for both materials largely overlap. In the Bode phase angle plot, notable differences emerge in the low-frequency region (below 0.1 Hz), where the MPEA maintains a higher phase angle than 316L SS, implying enhanced stability and protectiveness of its passive film. In the mid-to-high-frequency region, both materials exhibit similar phase angle values, with a maximum approaching 80° , indicative of a near-ideal capacitive response and the formation of a compact, insulating passive layer.

An R(Q(R)) equivalent circuit model was employed to fit the EIS spectra, with the resulting fitting parameters summarized in Table 3. The fitted chi-squared values were all below 10^{-3} , indicating good agreement between the selected EEC model and the experimental data. In these models, R_1 represents the solution resistance; the values of two systems are equivalent; R_2 is defined as the charge transfer resistance at the metal/electrolyte interface. To account for non-ideal behaviors arising from surface roughness, material heterogeneity, or current leakage, constant phase elements (CPEs) are introduced in place of ideal capacitors. CPE is parallel to R_2 , indicating the double-layer capacitance here. The MPEA exhibits a significantly higher charge transfer resistance ($R_2 = 2.862 \times 10^5 \Omega \cdot \text{cm}^2$) compared to 316L SS ($2.006 \times 10^5 \Omega \cdot \text{cm}^2$), indicating superior passivation and corrosion resistance of the MPEA. Additionally, the n value of CPE is close to 1, suggesting that this capacitive element behaves nearly like an ideal capacitor, consistent with the formation of a compact and stable passive layer.

Table 3. Fitting parameters of the EEC model for the EIS data shown in Figure 7.

Alloys	$R_1 (\Omega \cdot \text{cm}^2)$	$R_2 (\Omega \cdot \text{cm}^2)$	CPE ($\Omega^{-1} \text{cm}^{-2} \text{s}^n$)	n
Fe ₄₀ Ni ₃₀ Cr ₂₀ V ₈ Mo ₂	8.409	2.862×10^5	3.773×10^{-5}	0.89
316L SS	8.131	2.006×10^5	3.395×10^{-5}	0.90

As can be seen from Figure 8a, the Mott–Schottky (M–S) curves of both the MPEA and 316L SS exhibit a well-defined linear relationship with a positive slope, indicating that the passive films formed on both materials in 3.5 wt.% NaCl solution presents typical n-type semiconductor characteristics, whose electrical conduction behavior is dominated by

donor-type defects (oxygen vacancies and metal interstitial atoms) within the passive films. No distinct negative slope segment is observed within the test potential range, suggesting that the passive films do not show noticeable p-type semiconductor characteristics [40–43]. From the calculation results shown in Figure 8b, the donor carrier concentration N_D of the passive film on the MPEA is significantly lower than that on the 316L SS. The donor carrier concentration is a direct quantitative indicator of the microscopic defect density of the passive film. A lower N_D indicates a smaller number of point defects, such as oxygen vacancies in the passive film, corresponding to a denser and more intact passive film. Such a passive film can effectively block the penetration and diffusion of aggressive ions such as Cl^- , greatly reduce the risk of dissolution and breakdown of the passive film, and thus improve the protection efficiency and long-term stability of the passive film [41,44]. Meanwhile, the flat band potential E_{FB} of the MPEA is significantly positively shifted compared with that of the 316L SS. For n-type semiconductor passive films, a more positive flat band potential corresponds to higher thermodynamic stability of the passive film and a higher potential threshold for pitting initiation, thus endowing the alloy with better pitting resistance and corrosion resistance in chloride-containing environments, which is consistent with the results of the potentiodynamic polarization curves in Figure 5a above.

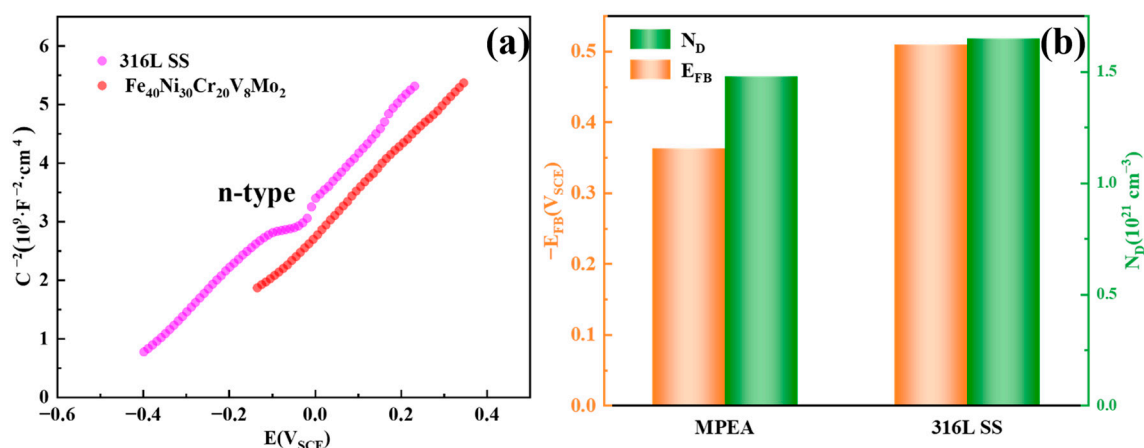


Figure 8. (a) Mott–Schottky plots and (b) calculated N_D and E_{FB} values for the MPEA and 316L SS in a 3.5 wt.% NaCl solution.

3.3.2. Characterization of Passive Films

From the electrochemical test results presented above, it is clear that the passive film plays a critical role in determining the corrosion resistance of the alloy. Therefore, XPS was used to characterize the chemical composition of passive films formed on the surfaces of both the MPEA and 316L SS. Figure 9 shows the Cr 2p3/2, Fe 2p3/2, Ni 2p3/2, Mo 3d, and V 2p3/2 XPS spectra collected from the passive films of these two alloys.

In the potentiodynamic polarization curve (Figure 5), the MPEA exhibited a more stable and wider passivation range compared to 316L SS [45,46]. This difference can be attributed to the lower chemical stability of Fe^{2+} . Fe^{2+} is prone to dissolution and further oxidation to Fe^{3+} , ultimately precipitating as FeOOH on the substrate surface. This “dissolution-reprecipitation” process compromises the denseness and stability of the passive film [47]. As illustrated in Figure 9a,g, the Fe 2p3/2 peak can be resolved into four components, corresponding to Fe^0 (706.9 eV), Fe^{2+} oxide (708.4 eV), Fe^{3+} oxide (710 eV), and Fe^{3+} hydroxide (711.8 eV) [48]. Notably, the relative intensity of Fe^{2+} in the MPEA’s spectrum (Figure 9a) is lower than that in 316L SS, indicating a higher content of Fe^{2+} in the passive film of 316L SS, which is in agreement with the proposed mechanism.

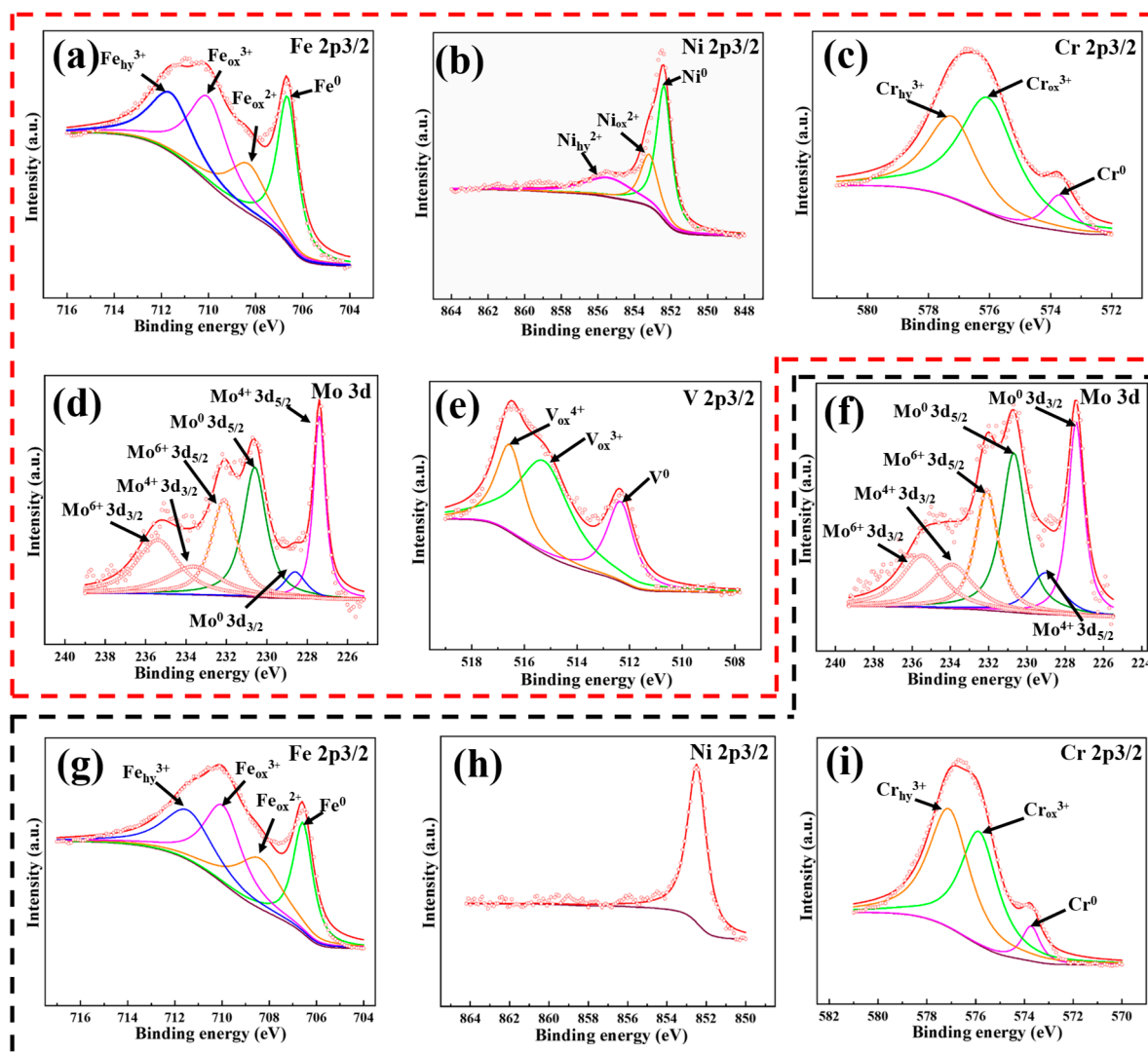


Figure 9. High-resolution XPS spectra after passivation at 0.1 V_{SCE} in 3.5 wt.% NaCl solution: (a–e) for the MPEA; (f–i) for 316L SS.

In contrast, Cr₂O₃ possesses high chemical stability within the passive film and is a key protective oxide for enhancing material corrosion resistance [42,49,50]. A higher ratio of Cr₂O₃ to Cr(OH)₃ in the passive film corresponds to superior corrosion performance [51,52]. In the XPS spectra (Figure 9c,i), the Cr 2p3/2 Cr³⁺ hydroxide (577.1 eV) [48]. The MPEA's passive film shows a higher Cr₂O₃ to Cr(OH)₃ ratio compared to that of 316L SS. This directly correlates with its higher pitting potential (E_{pit} , from Figure 5/Table 2) and charge transfer resistance (R_2 from Table 3), as a film richer in Cr₂O₃ is more effective at blocking the penetration of aggressive chloride ions [53]. The superior corrosion resistance of the MPEA's passive film is consistent with this finding.

Shown in (Figure 9d,f), the deconvolution results of the high-resolution Mo 3d XPS spectrum demonstrate that Mo element exists in three valence states in the passive film, with their characteristic binding energies as follows: metallic Mo⁰ (3d_{5/2}: 227.80 eV; 3d_{3/2}: 230.97 eV), tetravalent Mo⁴⁺ (3d_{5/2}: 229.17 eV; 3d_{3/2}: 232.32 eV) and hexavalent Mo⁶⁺ (3d_{5/2}: 232.46 eV; 3d_{3/2}: 235.71 eV) [54]. Mo⁶⁺, among them, mainly exists in the form of soluble molybdates (MoO₄^{2−}). These oxygen-containing molybdate species possess excellent self-healing capability and can rapidly migrate to the damaged regions of the passive film. They cannot only directly block the corrosion channels, but also synergistically

promote the reformation of the Cr_2O_3 passive layer, further enhancing the long-term protective performance of the passive film [54,55].

In Figure 9e, the V 2p_{3/2} peak can be deconvoluted into V^0 (512.5 eV), V^{3+} oxide (515.8 eV), and V^{4+} oxide (516.9 eV) [56,57]. The incorporation of V into the passive film contributes to an increased overall oxide content, promoting the formation of a denser and thicker passive layer, which in turn enhances the stability and protectiveness of the film [56]. This beneficial effect is reflected in the electrochemical behavior of the MPEA. Unlike 316L SS, which exhibits a distinct current density drop at high potentials attributed to the oxidation of Cr^{3+} to soluble Cr^{6+} , no such feature is observed in the polarization curve of the MPEA. This absence is likely associated with the presence of V oxides, which have been reported to suppress Cr segregation and mitigate the destabilization of the passive film [58–61]. Consequently, the V-containing MPEA maintains a more stable passivation range and a more robust passive film under anodic polarization.

To elucidate the role of Ni in the passive film, the Ni 2p_{3/2} spectrum of the MPEA in Figure 9b was deconvoluted into three components: Ni^0 (851.2 eV), Ni^{2+} oxide (852.1 eV), and Ni^{2+} hydroxide (857.6 eV) [62]. In contrast, no distinct components were resolved for the Ni 2p_{3/2} peak of 316L SS in Figure 9h, suggesting a substantially lower Ni content or a different chemical state distribution within its passive layer. Although the oxidation of Ni is thermodynamically less favorable compared to elements such as Cr and Fe, and metallic Ni^0 tends to enrich at the alloy/film interface [63], distinct Ni oxide species are nevertheless detectable in the passive film of the MPEA. According to the relative peak intensities, Ni^0 and Ni^{2+} oxide appear to be the predominant forms of Ni present. The incorporation of oxides in the passive film is significant, as Ni oxides enhance the densification and corrosion resistance of the film [30,64]. This aligns well with the higher corrosion resistance of the MPEA indicated by its higher impedance in the EIS Nyquist plot (Figure 7a), further corroborating the superior protectiveness of its passive film. It is worth noting that $\text{Cr}(\text{OH})_3$ typically exhibits a loose and porous structure, and its limited ability to inhibit chloride ion penetration restricts the denseness and corrosion resistance of the passive film [65]. The presence of Ni oxides in the MPEA's passive film may help mitigate this limitation by promoting a more compact and stable passive layer.

4. Conclusions

In this work, the mechanical properties and corrosion behavior of the $\text{Fe}_{40}\text{Ni}_{30}\text{Cr}_{20}\text{V}_8\text{Mo}_2$ MPEA were systematically evaluated. The principal findings are summarized as follows:

- (1) The alloy displays a balanced combination of strength and ductility. Room-temperature tensile tests yield a yield strength of ~258 MPa, an ultimate tensile strength of ~647 MPa, and a fracture elongation of ~52%. Deformation at room temperature of the MPEA is primarily governed by dislocation-mediated plasticity. The alloy demonstrates acceptable, though not exceptional, tensile ductility.
- (2) The alloy exhibits superior corrosion resistance in 3.5 wt.% NaCl solution, characterized by a broad and stable passive region, a high pitting potential (~0.975 V_{SCE}), and a low corrosion current density in the potentiodynamic polarization curve. Electrochemical impedance spectroscopy further confirms the high impedance and protective nature of the surface passive film. XPS analysis reveals that this superior performance arises from a high proportion of stable Cr_2O_3 , together with the synergistic enrichment of V and Mo oxides within the passive film. This oxide architecture effectively impairs localized corrosion initiation, endowing the alloy with outstanding resistance to chloride-induced attack.

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