



# Article Effect of Minor Mo Addition on Microstructure and Corrosion Resistance of High-Velocity Air Fuel-Sprayed Fe-Based Amorphous Coatings

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**Abstract:** In this work, Fe<sub>64</sub>Nb<sub>3</sub>B<sub>17</sub>Si<sub>6</sub>Cr<sub>6</sub>Ni<sub>4</sub> and Fe<sub>60</sub>Nb<sub>3</sub>B<sub>17</sub>Si<sub>6</sub>Cr<sub>6</sub>Ni<sub>4</sub>Mo<sub>4</sub> (at. %) coatings were prepared with a high-velocity air fuel spraying method, and the effects of minor Mo addition on the microstructure, glass formation, and corrosion resistance of the coating were studied. It was found that the Mo addition improves the glass-forming ability of the alloy and a fully amorphous structure with a higher compactness was obtained in the Mo-containing coating. The thermal stability of the coating is enhanced by Mo addition and the onset crystallization temperature was increased by 20 K. In addition, the Mo-containing amorphous coating exhibited higher corrosion resistance than the Mo-free coating. The superior corrosion resistance can be attributed to the increased proportion of protective, stable Cr, Nb, and Mo oxides in the passive film and fewer defects of the Mo-containing coating.

Keywords: Fe-based amorphous coating; HVAF; microstructure; corrosion resistance

# 1. Introduction

Compared with crystalline alloys, amorphous alloys show characteristics of no vacancies, dislocations, and other defects, which renders amorphous alloys which exhibit significantly better mechanical and physicochemical properties than those of crystalline materials [1–3]. Fe-based amorphous alloys, one of the most commonly studied amorphous alloys, have drawn quite a bit of attention for their advantageous mechanical characteristics, strong corrosion resistance, and comparatively inexpensive cost [4,5]. Irrespective of the limitations of glass-forming ability (GFA), amorphous alloys fabricated as protective coatings instead of bulk show great application prospects [6–8]. Currently, the major techniques for preparing Fe-based amorphous coatings are thermal spraying and laser cladding [9–11]. Fe-based amorphous coatings prepared by laser cladding have fewer holes and the coating size can be precisely controlled. However, due to the high laser energy, most of the prepared coatings have crystalline phases and crack [11,12]. In comparison, the high-velocity air fuel (HVAF) thermal spraying technique, which provides the advantages of high flight of sprayed particles and large kinetic energy, is widely used in the creation of Fe-based amorphous coatings [13–15].

Among Fe-based amorphous alloys, Fe-(B, Si)-Nb amorphous alloys are receiving more attention due to their high GFA, excellent corrosion resistance, and fairly low cost [16,17]. Based on the Fe-(B, Si)-Nb system, the authors' group has been dedicated to its component optimization to further improve its corrosion resistance and GFA. The addition of minor alloying elements is a well-known method in component optimization of Fe-based amorphous alloys, and Cr, Ni, and Mo are three common alloying elements. Among them, Cr



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). is crucial to further improve the corrosion resistance, because it can form a dense passive film on an alloy's surface to prevent further erosion of the internal alloy by the corrosive medium [17,18]. Additionally, Ni can improve the forming ability of Fe-based amorphous alloys, because it belongs to the same period as Fe with the adjacent position in the periodic table, sharing similar atomic radii, outer electronic structures, and physicochemical properties with Fe. Similar atomic substitution can improve the chaos of amorphous alloy systems [4,19]. Therefore, Ni and Cr elements were added to the Fe-(B, Si)-Nb amorphous alloy system to form the FeNbBSiCrNi alloy. In addition, Mo has been found to be effective in the regulation of composition to improve the corrosion resistance and GFA of Fe-based amorphous alloys [17,20]. However, the role of Mo in the FeNbBSiCrNi system is not clear and needs further study. In order to better understand the factors affecting the GFA and the corrosion resistance of coatings through micro-alloying, the focus of the current work is to explore the effect of adding a small amount of Mo on FeNbBSiCrNi amorphous coatings.

In this work, 4 at. % Mo was added to FeNbBSiCrNi to examine the impact of minor amounts of Mo on the alloy's microstructure and corrosion resistance. Two Fe-based alloy coatings were prepared with the HVAF spraying technique. The microstructures, morphologies, and corrosion resistances of Mo-free and Mo-containing alloy coatings were systematically studied, and the microscopic mechanism of Mo was analyzed in Fe-based alloy coatings.

#### 2. Experimental Section

#### 2.1. Preparation of Powders and Coatings

 $Fe_{64}Nb_3B_{17}Si_6Cr_6Ni_4$  (FeNbBSiCrNi) and  $Fe_{60}Nb_3B_{17}Si_6Cr_6Ni_4Mo_4$  (FeNbBSiCrNiMo), at. % powders for spraying were prepared by gas atomization. An HVAF C7 spraying system (Kermetico, San Francisco, CA, USA) was used for the coating–spraying, and the detailed spraying parameters of the HVAF process are shown in Table 1. Before spraying, the surfaces of 45 carbon steel substrates were degreased, ground, and sand-blasted. The sand blasting material was 80 white corundum.

Table 1. HVAF spraying parameters for FeNbBSiCrNi and FeNbBSiCrNiMo coatings.

Parameter	FeNbBSiCrNi	FeNbBSiCrNiMo		
Spray distance (mm)	240	240		
Air pressure (psi)	91	94		
Fuel pressure (psi)	87	89		
Hydrogen flow rate (SLPM)	35	35		
Nitrogen flow rate (SLPM)	25	25		
Powder delivery rate (rpm)	3	3		
Traverse velocity (mm/s)	1000	1000		

# 2.2. Microstructural and Phase Composition Analysis

We used scanning electron microscopy (SEM, ZEISS Sigma 300 system, Oberkochen, Germany) and an energy-dispersive X-ray spectrometer (EDS, Oxford Xplore 30, Oxford, England) in secondary electron (SE2) mode to observe the morphologies of the powder and coating. The porosity of the coating was calculated from 15 randomly selected SEM images of the coating cross-section, utilizing Image-Pro Plus 6.0 image analysis software. To determine the phase of coatings, X-ray diffraction (XRD, Rigaku SmartLab SE system, Tokyo, Japan) was used and the coatings were exposed to Cu K $\alpha$  radiation with 2 $\theta$  ranging from 20° to 90° and a step size of 2°/min. A differential scanning calorimeter instrument was used to perform differential scanning calorimetry (DSC, STA 449F3 Jupiter, NETZSCH, Selb, Germany) measurements of the coatings at a rate of 20 K/min in an Ar atmosphere. Transmission electron microscopy (TEM, FEI Talos F200X, Thermo Fisher Scientific, Waltham, MA, USA) was used to further characterize the structure of the coatings.

### 2.3. Corrosion Analysis

To investigate the corrosion resistance of the coatings, electrochemical tests were performed on a CHI660E electrochemical workstation. These tests included a potentiodynamic polarization test, an electrochemical impedance spectroscopy (EIS) test, and a Mott–Schottky (M-S) plot test. Saturated potassium chloride/calomel electrodes were used as the reference electrode, platinum electrodes as the auxiliary electrode, and coating samples as the working electrodes with a nominal area of 1 cm<sup>2</sup> in a standard three-electrode setup. All experiments were performed after 12 h immersion in 3.5 wt. % NaCl solution. The potentiodynamic polarization tests were carried out with a scanning rate of 5 mV/s. The EIS tests were executed with a sinusoidal potential perturbation of 10 mV in a frequency range of  $10^5$  Hz $\sim 10^{-2}$  Hz and the data from the EIS were fitted using Zsimpwin 3.60 software. The M-S plot was swept at a frequency of 5000 Hz in 10 mV steps. Each electrochemical test was repeated three times to assess the data's reproducibility.

X-ray photoelectron spectroscopy (XPS, Thermo Fisher Nexsa, Waltham, MA, USA) was used to analyze the passive film that formed on the coating following a 12 h immersion in a 3.5% NaCl solution. Avantage 5.9 software was used to process the XPS analysis data, and the other peaks were calibrated using the standard C1s peak at 284.8 eV.

#### 3. Results and Discussion

#### 3.1. Structure and Thermal Stability of the Coatings

An SEM image of the powders of FeNbBSiCrNi and FeNbBSiCrNiMo is shown in Figure 1. It is seen that the powders are spherical or nearly spherical with smooth surfaces, demonstrating a good fluidity, which is conducive to the stability of the spraying process and the uniformity of the coating. The cross-sectional morphologies of both coatings are shown in Figure 2, both of which exhibit a uniform structure. Significant deformation was caused as the heated particles impacted rapidly on the surface of the substrate or the deposited particles during the HVAF process. The particles' shape changed from spherical to lamellar after deposition. The main structural defect of HVAF sprayed coatings is the interlayer porosity, which is due to the formation of some non-contact areas among two deformed lamellar structures during the spraying process. As clearly displayed in Figure 2, the FeNbBSiCrNiMo coating contains fewer and smaller pores, as the porosity of the FeNbBSiCrNi coating and the FeNbBSiCrNiMo coating were calculated to be 2.26% and 1.53%, respectively. This indicated that the 4 at. % Mo addition improves the compactness of the coating.



Figure 1. SEM images of the (a) FeNbBSiCrNi and (b) FeNbBSiCrNiMo metallic powders.



Figure 2. SEM images of the cross sections of (a) FeNbBSiCrNi and (b) FeNbBSiCrNiMo coatings.

The XRD patterns of the Fe-based coatings are shown in Figure 3. The presence of broad diffraction peaks as well as  $\alpha$ -(Fe, Cr) and Fe<sub>2</sub>B crystalline phases in the FeNbBSiCrNi coating suggests that the coating is an amorphous/crystalline composite structure. The amorphous content of the coating was estimated to be about 87.5% based on the area ratio of the crystalline peaks to the amorphous peaks, while the FeNbBSiCrNiMo coating merely exhibits a broad diffraction peak without any crystalline phase peaks, illustrating a single amorphous structure of the as-sprayed Mo-containing coating. The addition of a minor amount of Mo changes the phase structure of the Fe-based coating and increases the amorphous content of the coating, and the higher amorphous content indicates better corrosion resistance of the Mo-containing Fe-based coating [20]. Figure 4 shows the DSC curves of the coatings. The presence of amorphous structures in both coatings is further evidenced by the obvious crystallization-induced heat absorption peaks in the curves. The onset crystallization temperature  $(T_x)$  can be taken as a criterion to compare the relative thermal stability of the two Fe-based coatings. The higher the  $T_x$ , the better the thermal stability of the coating [21]. The  $T_x$  of the FeNbBSiCrNiMo coating is about 20 K higher than that of the FeNbBSiCrNi coating, indicating that the addition of minor Mo significantly improved the thermal stability of the Fe-based coatings, as reported in the study by Zhang et al. [17]. The 4 at. % Mo addition enhanced both the GFA and the thermal stability of the Fe-based coating while inhibiting crystallization.



Figure 3. XRD patterns of the as-sprayed Fe-based coatings.



Figure 4. DSC curves of the as-sprayed Fe-based coatings.

Figure 5 shows the TEM micrographs and selected area electron diffraction (SAED) patterns of the coatings. Localized lattice streaks with well-defined grain boundaries were observed in the FeNbBSiCrNi coatings (Figure 5a). In addition, some bright spots scattered near the diffuse ring were observed in the SAED pattern, confirming the presence of crystalline phases in the coating. The amorphous phase regions of the coatings in Figure 5b are uniformly lined and homogeneous in composition, and the SAED pattern consists only of halo rings, which indicates the presence of a completely amorphous structure in the coating. In contrast, the Mo-added coating showed no lattice fringes from the TEM images and no evidence of crystallization and the SAED pattern showed a bright spot in the center and the presence of a uniform diffuse ring around the periphery (Figure 5c,d), indicating the presence of a completely amorphous structure. These results are consistent with the XRD results.

The mixing enthalpy of each constituent element of the Fe-based coatings is shown in Table 2, and large negative mixing enthalpies among the different components typically result in highly stable supercooled liquids. It can be seen that Mo has large negative mixing enthalpy with Nb, B, and Si. FeNbBSiCrNi and FeNbBSiCrNiMo coatings have mixing enthalpies of  $-40.0 \text{ kJ} \cdot \text{mol}^{-1}$  and  $-42.2 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively. The larger the negative enthalpy of mixing between the alloy system, the more favorable the formation of amorphous alloys [22]. As a result, the addition of minor amounts of Mo increases the mixing enthalpy of the Fe-based coatings and, thus, increases the GFA. In addition, the strong interactions among the transition metal and metalloid atoms are established through s-d hybridization bonds. In the present study, Mo and Nb possess one 5s electron, while Si and B possess two 2s and 3s electrons, respectively. One 5s electron is considered to be more active than the energy levels of two 2s and 3s electrons because a pair of s electrons with opposite spin directions have significantly lower energy levels than one *s* electron. Therefore, compared to the 2s electron of the B atom and the 3s electron of the Si atom, the 5s electrons of the Mo and Nb atoms are more mobile. As a result, the addition of Mo enhances the *s*–*d* hybrid bonding property, as Mo atoms provide more *s* electrons and Fe atoms provide more empty "d" shell layers, which causes an increase in the GFA [23]. In addition, the large atomic size of Mo is favorable for the filling of the local structure, which enhances the GFA by increasing the local filling rate, suppressing the long-range diffusion of atoms, and facilitating the formation of amorphous structures [23]. Additionally, the HVAF process has great potential for the preparation of amorphous coatings because the cooling rate is fast enough (about  $10^{7}$  K/s) to prevent the remote diffusion of atoms and thus avoid crystallization [24]. Therefore, the amorphous structure in FeNbBSiCrNiMo coatings can

be attributed to the appropriate alloy composition as well as the fast-cooling suppression of nucleation of completely molten particles from the highest temperature of the flame (about 1600 K) through the impact-cooled substrate surface [24]. As demonstrated by the XRD and TEM results, the FeNbBSiCrNiMo coating exhibits a completely amorphous structure.



**Figure 5.** TEM images of the coatings. (**a**,**b**) The FeNbBSiCrNi coating and (**c**,**d**) the FeNbBSiCrNiMo coating.

Element	Fe	Nb	В	Si	Ni	Cr	Мо
Fe	0	-16	-26	-35	-2	-1	-2
Nb	-	0	-54	-56	-30	-7	-36
В	-	-	0	-14	-24	-31	-34
Si	-	-	-	0	-40	-37	-35
Ni	-	-	-	-	0	-7	-7
Cr	-	-	-	-	-	0	0
Mo	-	-	-	-	-	-	0

**Table 2.** Mixed enthalpies between the principal elements of the alloy (unit:  $kJ \cdot mol^{-1}$ ) [25].

#### 3.2. Corrosion Resistance of the Coatings

3.2.1. Potentiodynamic Polarization and Electrochemical Impedance Spectroscopy

To evaluate the impact of a small Mo addition on the corrosion resistance of Febased coatings, potentiodynamic polarization behaviors and EIS tests were performed on FeNbBSiCrNi and FeNbBSiCrNiMo coatings, and the results are shown in Figure 6. The self-corrosive potential ( $E_{corr}$ ) responds to the ease with which the material can be corroded, and the self-corrosive current density ( $I_{corr}$ ) responds to the actual corrosion rate of the material [26]. From Figure 6a, it can be seen that with the addition of minor amounts of Mo, the  $E_{\rm corr}$  of the Fe-based coatings increased from -597 mV to -491 mV, and the  $I_{\rm corr}$  decreased from 4.44  $\mu$ A/cm<sup>2</sup> to 3.78  $\mu$ A/cm<sup>2</sup>. The polarization resistance ( $R_{\rm p}$ ) was calculated according to the Stem-Geary formulation as follows [27]:

$$R_{\rm p} = \frac{\beta_{\rm A} \times \beta_{\rm C}}{2.203 \times I_{\rm corr} \times (\beta_{\rm A} + \beta_{\rm C})} \tag{1}$$

where  $\beta_A$  and  $\beta_{Cc}$  indicate the slope of the anode and cathode of the polarization curve, respectively. From Equation (1), the  $R_p$  values of the FeNbBSiCrNi coating and the FeNbB-SiCrNiMo coating are 8783  $\Omega$  and 14,334  $\Omega$ , respectively.



**Figure 6.** (**a**) Potentiodynamic polarization curves, (**b**) Nyquist plots, and (**c**) Bode phase angle plots of the Fe-based coatings; (**d**) electrical equivalent circuits.

Higher  $E_{\rm corr}$ , lower  $I_{\rm corr}$ , and greater  $R_{\rm p}$  values were found for the FeNbBSiCrNiMo coating than for the FeNbBSiCrNi coating, indicating a higher corrosion resistance and better passivation ability of the Mo-containing Fe-based coating. The improved corrosion performance of the FeNbBSiCrNiMo coating can be attributed to three aspects. Firstly, Mo elements can interact with Cr elements, as they have a synergistic effect in corrosion resistance. Adding 4 at. % Mo provides Mo<sup>6+</sup> compounds, which act as corrosion inhibitors, and accelerates the formation of Cr-containing passive films on the FeNbBSiCrNiMo coating surface [28]. Secondly, the FeNbBSiCrNiMo coating shows an amorphous structure with fewer defects, such as grain boundaries and dislocations, so the local corrosion sprouting strength around the active site (crystalline/amorphous interface) is reduced and the probability of liquid corrosion through grain boundaries is reduced. Thirdly, the FeNbBSiCrNiMo coating has lower porosity, as shown in Figure 2.

The EIS test was studied to further understand the influence of minor Mo additions to Fe-based coatings on corrosion resistance. The Nyquist plots and Bode plots are shown in Figure 6b,c, respectively. The corrosion resistance is related to the arc radius of the Nyquist

plots [29]. A larger radius is observed in the FeNbBSiCrNiMo coating, indicating its higher corrosion resistance. In addition, a higher phase angle value for FeNbBSiCrNiMo confirms its superior corrosion properties. Based on the above analysis, an equivalent electrical circuit to describe the electrochemical cell for all the glassy coatings is proposed and shown in Figure 6d, which was used in EIS data fitting, and the fitting parameters are displayed in Table 3.  $R_{\rm s}$  is the solution resistance;  $R_{\rm c}$  and  $R_{\rm ct}$  are the coating resistance and charge transfer resistance, respectively. Since the coating surface shows an absence of perfect smoothness and exhibits defects like porosity and roughness, the constant phase angle element CPE was used instead of ideal capacitance.  $Q_c$  and  $Q_{dl}$  are the coating capacitance and electric double-layer capacitance, respectively;  $n_c$  and  $n_{dl}$  are the dispersion coefficients of  $Q_c$  and  $Q_{dl}$  away from the pure capacitance, respectively [30]. Similar ionic conductivity is indicated by a slight variance in  $R_s$  values between the two coatings. The  $n_c$  and  $n_{dl}$ values for both coatings are less than one, indicating that the coating exhibits nonideal capacitance behavior as a result of its surface heterogeneities. The  $Q_c$  value and passive film thickness are inversely correlated, decreasing the  $Q_c$  value as the passive film thickness increases [31]. The lesser  $Q_c$  value of the FeNbBSiCrNiMo coating points out that a relatively thicker passive film is formed. Additionally, a lesser corrosion area is indicated by a lower value of  $Q_{dl}$  for the FeNbBSiCrNiMo coating. The correlation between the  $R_c$  and  $R_{ct}$ values along with the material's corrosion resistance is positive [32]. The FeNbBSiCrNiMo coating has a relatively high  $R_c$  value, indicating that the degree of being corroded is small, and a high *R*<sub>ct</sub> value, indicating that charge transfer is difficult during the reaction. FeNbBSiCrNiMo coatings' higher R<sub>c</sub> and R<sub>ct</sub> values provide additional evidence of their excellent corrosion resistance.

Table 3. The fitted results for the EIS of the coatings.

Sample	$R_s$ ( $\Omega \cdot \mathrm{cm}^2$ )	$Q_{ m c}  imes 10^{-5}$ (S·cm <sup>-2</sup> ·s <sup>n</sup> )	n <sub>c</sub>	$R_c$ ( $\Omega \cdot cm^2$ )	$Q_{dl}  imes 10^{-4}$ (S·cm <sup>-2</sup> ·s <sup>n</sup> )	n <sub>dl</sub>	$R_{\rm ct}$ ( $\Omega \cdot {\rm cm}^2$ )	$\chi^2  imes 10^{-4}$
FeNbBSiCrNi	11.73	9.190	0.8080	545	2.711	0.4361	15,360	3.07
FeNbBSiCrNiMo	11.67	7.092	0.7556	8714	2.164	0.6026	77,360	3.58

3.2.2. Mott-Schottky

The corrosion behavior of Fe-based coatings is closely related to the types of passive film. Within different ranges of potentials, electrons move out or in from the surface of the semiconductor passive film. When the space charge layer is in a depleted state, there is an M-S relationship between the applied voltage (E) and the space charge layer (C) [33]:

For *n*-type semiconductors:

$$\frac{1}{C^2} = \frac{2}{e \times \varepsilon \times \varepsilon_0 \times N_{\rm D}} \left( E - E_{\rm FB} - \frac{K \times T}{e} \right)$$
(2)

For *p*-type semiconductors:

$$\frac{1}{C^2} = -\frac{2}{e \times \varepsilon \times \varepsilon_0 \times N_{\rm A}} \left( E - E_{\rm FB} - \frac{K \times T}{e} \right) \tag{3}$$

where  $\varepsilon_0$  is the vacuum permittivity (8.85 × 10<sup>-14</sup> F·cm<sup>-1</sup>);  $\varepsilon$  is the relative dielectric constant of the passive film at room temperature (15.6) [34]; *T* is the absolute temperature; *K* is the Boltzmann constant (1.38 × 10<sup>-23</sup> J·K<sup>-1</sup>); e is the elementary charge (1.602 × 10<sup>-19</sup> C);  $E_{\text{FB}}$  is the flat band potential; and  $N_{\text{A}}$  and  $N_{\text{D}}$  are the acceptor and donor densities, respectively.

Figure 7a shows M-S plots of the passive film formed on Fe-based coatings. Depending on the applied potential, both Fe-based coatings showed two linear regions with a positive slope and a negative slope, indicating that the passive films all exhibit duplex semiconducting characteristics. The point defect model states that cation vacancy defects are electron acceptors and exhibit a *p*-type semiconductor, while oxygen vacancies and/or cation interstitial defects are electron donors and exhibit an *n*-type semiconductor [35]. Therefore, the passive films of both Fe-based coatings are mainly cation vacancy defects in the region below -0.5 V (*p*-type semiconductor), while above -0.5 V they are mainly oxygen vacancies and/or cation interstitial defects (*n*-type semiconductor).



**Figure 7.** (a) Mott–Schottky plots of the passive film and (b)  $N_D$ ,  $N_A$ , and  $E_{FB}$  values of the passive film.

Figure 7b shows the  $N_A$ ,  $N_D$ , and  $E_{FB}$  values of the passive film formed on Fe-based coatings, calculated from Equations (2) and (3), and the slope of the linear regions of the M-S plots. A higher  $E_{FB}$  value of the FeNbBSiCrNiMo coating indicates a higher energy barrier, more difficult electron transfer, and more stable passive films formed [33]. In general, a higher  $N_A$  value indicates faster electron transfer rates at the passive film–electrolyte interface, and a higher  $N_D$  value indicates more oxygen vacancies in the passive film and the corrosive  $Cl^-$  is adsorbed more easily [36]. The  $N_A$  values of FeNbBSiCrNi and FeNbBSiCrNiMo coatings are  $3.21 \times 10^{20}$  cm<sup>3</sup> and  $1.08 \times 10^{20}$  cm<sup>3</sup>, and the  $N_D$  values are  $2.98 \times 10^{20}$  cm<sup>3</sup> and  $1.64 \times 10^{20}$  cm<sup>3</sup>, respectively. The higher  $N_A$  and  $N_D$  values of the FeNbBSiCrNi coating indicate that the passive film has more defects and deterioration of the corrosion resistance. The lower  $N_A$  and  $N_D$  values in the FeNbBSiCrNiMo coating indicate passivation film with fewer defects and better protection of the substrate. Therefore, the addition of minor amounts of Mo reduces the defects in the passive film and improves the corrosion resistance of Fe-based coatings.

# 3.2.3. XPS

An XPS analysis of the chemical composition of the passive film on the surfaces of the two coatings further verified the impact of minor amounts of Mo on the corrosion resistance of Fe-based coatings. The detailed XPS spectra of Fe 2p, Nb 3d, Cr 2p, Mo 3d, and O 1s peaks are shown in Figure 8. Metallic  $Fe^0$ , FeOOH, and  $Fe_2O_3$  were found in Fe 2p spectra; metallic Nb<sup>0</sup> and Nb<sub>2</sub>O<sub>5</sub> were found in Nb 3d spectra; metallic  $Cr^{0}$ ,  $Cr(OH)_3$ , and  $Cr_2O_3$  were found in Cr 2p spectra; and metallic  $Mo^0$  and  $MoO_3$  were found in Mo 3d spectra, which indicates the passive film of Fe-based coatings included mixed metal oxides and/or hydroxides. The metal oxide/hydroxide contents obtained from XPS analysis were normalized and their relative fractions in the passive film were calculated, which are shown in Figure 9. It can be seen that the primary component of the passive film on the FeNbBSiCrNi coating is Fe-oxide/hydroxide at about 79%. In contrast, the passive film of the FeNbBSiCrNiMo coating has less Fe-oxide/hydroxide content at about 48% and higher Cr-oxide/hydroxide, Nb-oxide, and Mo-oxide contents. In general, Feoxides are loose and porous and easily destroyed by corrosive solutions, while Cr, Nb, and Mo oxides are dense and stable and can effectively prevent the intrusion of corrosive Cl<sup>-</sup> [37,38]. Regarding this, the increased content of Cr, Nb, and Mo oxides provides the FeNbBSiCrNiMo coating with its excellent corrosion resistance. Previous research has shown the bilayer structure of the passive film formed from Fe-based amorphous alloys in

neutral liquids. While the inner layer is dense, stable, and oxide-based, the outside layer is loose, porous, and hydroxide-based [39,40]. Therefore, when the coating is corroded, the passive film's outer layers, FeOOH and Cr(OH)<sub>3</sub>, first play a protective role and are gradually destroyed with the erosion of Cl<sup>-</sup>. Then, Cr<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub>, and MoO<sub>3</sub> in the passive film's inner layer provide more effective protection. It is worth mentioning that  $Mo^{6+}$  can be dissolved in water to form molybdate ( $MoO_4^{2-}$ ), which can then adhere to the surface of the FeNbBSiCrNiMo coating to block further Cl<sup>-</sup> penetration and reduce the devastation of the coating [28]. The above analysis confirms that minor amounts of Mo are beneficial to improve the corrosion resistance of Fe-based coatings.



**Figure 8.** High-resolution XPS spectra of (**a**) Fe 2p, (**b**) Nb 3d, (**c**) Cr 2p, (**d**) Mo 3d, and (**e**) O 1s. Comparison of the chemical composition of passive film of the coatings.



**Figure 9.** Cation fraction in the passive film of the coatings obtained by XPS analysis: (**a**) FeNbBSiCrNi coating; (**b**) FeNbBSiCrNiMo coating.

## 3.2.4. Corroded Surface Morphology

The surface morphologies of the Fe-based coatings after 12 h of immersion in 3.5 wt. % NaCl solution are shown in Figure 10. The FeNbBSiCrNi coating was discovered to have a large area of white flocculent corrosion products as well as a few pits (Figure 10a). In contrast, the surface of the FeNbBSiCrNiMo coating is relatively flat with only a few corrosion products, indicating that the addition of minor amounts of Mo reduces the damage to the coating. Figure 11 shows the Fe-based coating's EDS images following the immersion test. Oxygen elements are abundant on the FeNbBSiCrNi coating's surface, indicating the occurrence of severe oxidation behavior. In comparison, the FeNbBSiCrNiMo coating surface had only a few oxides, indicating excellent corrosion resistance. The results also demonstrate that a minor Mo addition is beneficial to improve the corrosion resistance of Fe-based coatings.



**Figure 10.** SEM images of the surface of the (**a**) FeNbBSiCrNi and (**b**) FeNbBSiCrNiMo coatings after an immersion corrosion test.



**Figure 11.** EDS mapping of the coatings after immersion corrosion test. (a) FeNbBSiCrNi and (b) FeNbBSiCrNiMo coating.

## 4. Conclusions

In this work, FeNbBSiCrNi and FeNbBSiCrNiMo coatings were prepared using HVAF spraying. The effects of a minor Mo addition on the microstructure and corrosion behavior of the Fe-based coatings were studied. The principal conclusions are as follows:

- (1) The addition of minor amounts of Mo improves the GFA of Fe-based coatings and decreases the porosity. A 4 at. % Mo addition improved the coating's thermal stability, and a 20 K increase in the crystallization onset temperature was made.
- (2) A lower corrosion current density, a higher corrosion potential, and a greater charge transfer resistance indicate that adding Mo significantly increased the corrosion resistance of Fe-based coatings. In addition, the fully amorphous structure of Mocontaining coatings and the lower porosity also contribute to the corrosion resistance.
- (3) The addition of minor amounts of Mo reduces the defects in the passive film and increases the content of Cr, Nb, and Mo oxides, as well as inhibiting oxidative corrosion. Thus, the FeNbBSiCrNiMo coating has excellent corrosion resistance.

The addition of minor amounts of Mo improves the GFA of Fe-based coatings and increases corrosion resistance. It can be inferred that FeNbBSiCrNiMo coatings can be suitable candidates for corrosion-induced degradation applications and have the potential to be used in engineering applications.

In future work, the effect of different Mo contents on the microstructure and physicochemical properties of the coatings will be investigated in further detail. **Author Contributions:** Conceptualization, P.S., Z.J. and B.Z.; Funding acquisition, Z.Z. and J.C.; Investigation, P.S., Z.Z., Y.G. and L.X.; Methodology, Z.J., Z.Z., L.X. and X.L.; Project administration, J.C.; Resources, J.C.; Supervision, Z.Z. and J.C.; Validation, B.Z.; Writing—original draft, P.S. All authors have read and agreed to the published version of the manuscript.

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