

Article

Microstructure and Tribological Properties of FeCrCoMnSi_x High-Entropy Alloy Coatings

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Abstract: For shaft parts, 45 steel has been widely used due to its favorable mechanical properties and low cost. However, the relatively low wear resistance of 45 steel limits its application. In this work, high-entropy alloy of FeCrCoMnSi_x ($x = 0, 0.3, 0.6, 0.9, 1$) coatings were prepared on the surface of a 45 steel substrate using laser cladding technology to improve the wear performance of 45 steel. The effect of the Si element on the microstructure and tribological property of these coatings is investigated. The results show that the structure of FeCrCoMn coatings is mainly an FCC + HCP dual-phase solid solution, grown in equiaxial crystals. When a small amount of Si ($x = 0.3$) is added, the BCC phase is generated in the coating; meanwhile, the microstructure is transformed into the divorced eutectic character. When the content of Si is $x = 0.6$, the eutectic structure is promoted, and the microstructure is refined and becomes denser. When the content of Si increases to $x = 0.9$ and 1.0 , the metal silicate phase containing Mn and Cr is formed due to the precipitation of supersaturated solid solution. At the same time, the microstructure is transformed into dendritic crystals due to the composition super-cooling effect by the excessive Si element, inducing serious element segregation. The hardness of FeCrCoMnSi_x high-entropy alloy coatings increases to 425.8 HV when the Si content is 0.6 under the synergistic effect of the solid-solution and dense eutectic structure. The friction and wear analysis shows that the friction and wear mechanisms of the coating are mainly abrasive wear and oxidative wear. The coefficient of friction and the wear rate of the FeCrCoMnSi_x high-entropy alloy coating decreases to 0.202 and $4.06 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$, respectively, when the content of Si is 0.6 due to the dense microstructure and high hardness. The above studies prove that the presence of Si in the FeCrCoMnSi_{0.6} high-entropy alloy coating induces a refined eutectic microstructure and improves the coating's anti-wear properties by increasing hardness and decreasing the coefficient of friction.

Keywords: high-entropy alloy coatings; laser cladding; microstructure; tribological properties; wear resistance



Citation: Zhang, S.; Jiang, D.; Sun, S.; Zhang, B. Microstructure and Tribological Properties of FeCrCoMnSi_x High-Entropy Alloy Coatings. *Coatings* **2024**, *14*, 1476. <https://doi.org/10.3390/coatings14121476>

Academic Editor: Rafael Comesaña

Received: 25 October 2024

Revised: 16 November 2024

Accepted: 21 November 2024

Published: 22 November 2024



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1. Introduction

45 steel is a medium-carbon high-quality structural steel with good strength. It has been widely used in mechanical manufacturing, in which 45 steel is primarily used for the shaft parts materials [1,2]. However, the relatively low hardness and wear resistance of 45 steel cannot meet the requirements of engineering. Surface engineering is feasible and economical in improving the hardness and wear resistance of 45 steel materials.

Recently, high-entropy alloys (HEAs) have received a lot of attention in surface engineering, which usually refer to alloys consisting of at least five major elements, and the content of each element is between 5% and 35% [3]. With the increase in related research and the advancement of technology, HEAs have been extended to new alloy systems such as qua-ternary alloys, ternary alloys, and non-equal-atomic alloys [4]. Due to the higher

mixing entropy, HEAs are conducive to the formation of simple solid-solution structures after solidification, which mainly include FCC, BCC, and HCP solid-solution structures [5,6]. From a thermodynamic point of view, HEAs have four effects, namely, high entropy, slow diffusion effect, lattice distortion effect, and “cocktail” effect, which exhibit unique properties such as high strength, high hardness, excellent abrasion resistance, and corrosion resistance [7,8]. Therefore, they have attracted wide attention.

FeCrCoMn HEAs have a simple solid-solution structure due to the similar atomic radii and electronegativity of the constituent elements, causing the random distribution of elements on the crystal matrix. It has been shown that the FeCrCoMn HEAs coating with an equal molar ratio possesses the FCC + HCP dual-phase solid-solution structure; therefore, the alloy has a better plastic deformation ability [9,10]. However, the relatively low hardness limits its further application in engineering.

It has been shown that metallic elements can improve the mechanical properties of FeCrCoMn HEAs. For example, as an oxide-forming element, Al forms dense and stable protective oxide layers, which inhibit alloys from further oxidation [11]. Moreover, adding Al can increase the lattice distortion and hinder the diffusion of atoms, which promotes the refinement of the grains, thus inducing an increase in the strength and toughness of alloys [12,13]. Mo possesses a moderately large atomic size that facilitates both solid solution and precipitation hardening; therefore, the existence of Mo in HEAs may enhance the strength of the alloys [14]. In addition, the Mo element has the characteristics of corrosion resistance and lubrication, which not only improve the stability of the passivation film in corrosive media but also can improve the contact interface between the friction pair and the alloy, increasing the wear resistance of the alloy [15,16]. In contrast to Fe, Cr, Co, and Mn elements, metallic Ti has a larger atomic radius, which tends to produce more considerable lattice distortion and creates solid solution strengthening, enhancing the alloy's comprehensive properties [17,18]. Meanwhile, Ti has high corrosion resistance in different aqueous conditions due to its low passivation potential. Therefore, Ti can also enhance the corrosion resistance of HEAs [19].

Recently, many scholars have investigated the enhancement of the performance of HEAs by adding non-metallic elements (such as Si, B, and C), among which, Si is widely utilized in various alloys [20–22]. The addition of Si can promote the formation of the Si-contained phases, which can promote the strength of the alloy [23]. Moreover, due to the small atomic radius of Si, when Si is added to the alloy, it can occupy the vacancies of metals in the lattice structure and enhance the densification of the alloy, increasing the hardness and wear resistance of the alloy [24]. Huang et al. [25] showed that due to the substitution effect of the Si element, the lattice distortion of FeCoCrNiSi_x HEAs has been enhanced, which prevents the movement of dislocations and deformation of the substrate, thus improving the mechanical properties. Chen et al. [26] found that the density of sp² graphite is reduced in the DLC films by doping Si elements, stabilizing the sp³ bonding and enhancing the wear and corrosion resistance.

Currently, the surface technology of high-entropy alloy coating mainly includes laser cladding [6,27], physical vapor deposition [16], thermal spraying [28], and cold spraying [29–31]. Among them, laser cladding technology has become a common method due to its ability to form a good metallurgical bond between the coating and the substrate, its small dilution rate and heat-affected zone, and its dense structure, with only small defects in the coating [17,32]. Ren et al. [27] prepared a NbMoTaWTi high-entropy alloy coating on the surface of the TC4 alloy via laser cladding. They have found that the hardness of the coating is as high as 600 HV and exhibits excellent wear resistance. In this paper, a FeCrCoMnSi_x HEAs coating was prepared on 45 steel substrates with laser cladding technology. The influence of the Si element on the microstructure and tribological properties of this coating was investigated.

2. Experimental Detail and Methods

2.1. Coating Preparation

The substrate for the experiments was 45 steel, which was cut into a $70 \times 30 \times 8$ mm piece via wire cutting (DK7745, Taizhou Zhenghua CNC Machine Tool Factory, Taizhou, China), and the surface of the substrate was polished and smoothed with sandpaper of different meshes and then ultrasonically cleaned in anhydrous ethanol to make surface clean. The Fe powder, Cr powder, Co powder, Si powder, and Mn-Fe alloy powder, with a purity of 99.99% and with a particle size of about $45 \mu\text{m} \sim 80 \mu\text{m}$, were selected and weighed using an electronic balance (JJ1000Y, Shanghai Jing Sheng Scientific Instrument Co., Ltd., accuracy of 0.01 g, Shanghai, China) against the nominal composition of FeCrCoMnSi_x ($x = 0, 0.3, 0.6, 0.9, 1.0$) according to the atomic ratio. The atomic percentage is shown in Table 1. Then, the powder was mixed using a planetary ball mill (XQM-1L, Hunan Focus Laboratory Instruments Co., Ltd., Changsha, China). The rotation speed was 120 r/min, and the milling time was 120 min. In the friction test, ceramic balls were employed as grinding balls with a diameter of 3 mm and a ball-to-powder ratio of 3:1.

Table 1. Composition of the FeCrCoMnSi_x HEAs coating (at. %).

	Fe	Cr	Co	Mn	Si
FeCrCoMn	25.00	25.00	25.00	25.00	0.00
$\text{FeCrCoMnSi}_{0.3}$	23.26	23.26	23.26	23.26	6.98
$\text{FeCrCoMnSi}_{0.6}$	21.74	21.74	21.74	21.74	13.04
$\text{FeCrCoMnSi}_{0.9}$	20.41	20.41	20.41	20.41	18.37
$\text{FeCrCoMnSi}_{1.0}$	20.00	20.00	20.00	20.00	20.00

Prior to the cladding, the HEAs powder with the thickness of 2 mm was pre-laid on the surface of the 45 steel substrate with the adhesive (anhydrous ethanol). Then, it was placed into the drying oven (101-1AB, Tianjin Taiste Instrument Co., Ltd., Tianjin, China) and dried at 120°C for 150 min. The fiber laser (ROFIN-FL020, ROFIN Company, Hamburg, Germany) was used for multi-channel lap experiments. The laser power was 1600 W, with a scanning speed of 10 mm/s. The laser spot diameter of 4 mm was selected, and an overlapping rate of 50% was used. Furthermore, high-purity argon (99.99%) was used to protect against the influence of the atmosphere during the entire cladding process (i.e., from oxidation).

2.2. Characterization Method of Coating

The coating samples were cut into 15×10 mm via wire cutting, ground with different sizes of sandpaper, and then polished before surface observation and other performance tests were carried out. The phase composition of the coating was identified using an X-ray diffractometer (XRD, D8 advance, Bruker, Ettlingen, Germany) with $\text{Cu K}\alpha$ radiation. This XRD testing was operated at 40 kV and 40 mA via a continuous scan mode with the rate of $5^\circ/\text{min}$, ranging from 20° to 90° .

The coating was subjected to metallographic corrosion using a metallographic corrosion solution (hydrochloric acid–nitric acid–hydrofluoric acid–water = 1:1:1:1) for 45 s. Then, the macroscopic morphology of the coating surface was observed using an optical microscope (LEICA DM1750 M, LEICA, Wetzlar, Germany). The microstructure of the coating surface was observed using a scanning electron microscope (SEM, Sigma 300, Zeiss, Jena, Germany), and the elemental distribution of the coating was analyzed by combining it with the energy dispersive spectrometer (EDS, Alteglofsheim, Germany).

The coatings' microhardness was determined via a micro-Vickers hardness tester (HV-1000, Shanghai Yishai Precision Technology Co., Ltd., Shanghai, China). Test data were taken every 0.5 mm along the longitudinal section of the coating cross-section, and five test data examples were taken randomly at the same horizontal position and averaged. The loading force was 1 kg, and the pressure holding time was 10 s.

The tribological test were carried out using a reciprocating friction and wear tester (Bruker UMT-3, Goleta, CA, USA). The stable load was 30 N, the frequency was 2 Hz, the reciprocating motion stroke was 6 mm, the wear time was 1800 s, and the GCr15 ball was the grinding pair with a diameter of 9 mm. The whole friction and wear test process was completed in the simulated seawater environment. Three repetitions of the experiment were performed for each sample to ensure the accuracy of the experimental data. The wear scar morphology and element distribution of the coating were observed by SEM, and the wear mechanism of the coating was analyzed. The three-dimensional morphology of the wear surface of the coating was observed with a laser confocal microscope (VK-X1000, Keyence, Tokyo, Japan), and the abrasion scar's depth, width, and wear volume were measured. The wear rate of the coating was calculated using the following formula [33]:

$$Q = \frac{V}{F \cdot L} \quad (1)$$

In the formula, Q is the wear rate, $\text{mm}^3/\text{N} \cdot \text{m}$; V is the wear volume of the coating, mm^3 ; F is the friction load, N; and L is the friction reciprocating sliding distance, m. All the observations and tests above were carried out at room temperature.

3. Results and Discussion

3.1. Microstructure of the Coating

Figure 1 shows the XRD patterns of the FeCrCoMnSi_x HEAs coating. From Figure 1a, it can be seen that the FeCrCoMn HEAs coating is an FCC phase solid solution rich in Fe and Cr, with a small amount of a Co-rich HCP phase. After the addition of a small amount of Si element ($x = 0.3$), the BCC phase is observed near 45° . When the content of the Si element is 0.6, the diffraction peak intensity near 43° becomes weaker but the diffraction peak at 45° is enhanced, indicating that the amount of BCC phase is increased. When the content of the Si element is further increased to 0.9 and 1.0, Mn_4Si_7 and Cr_3Si metal silicate phases are observed in the XRD patterns.

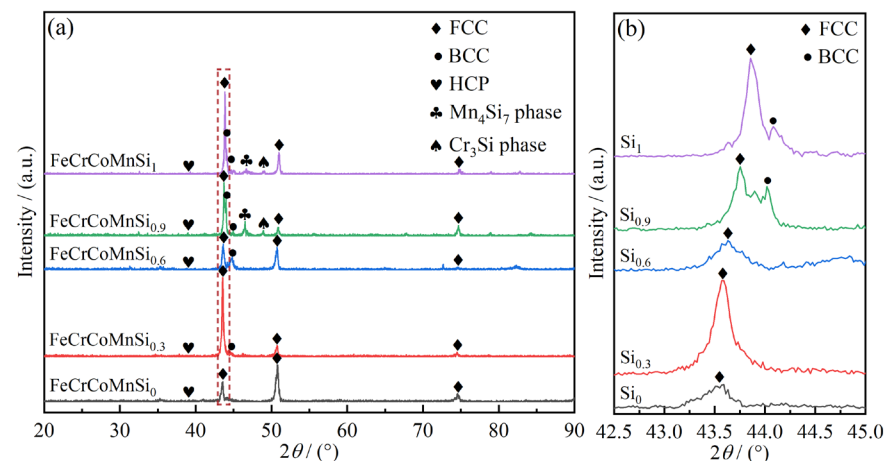


Figure 1. XRD patterns of the FeCrCoMnSi_x HEAs coating: (a) XRD pattern of the coatings; (b) magnification of the localized FCC phase.

Figure 1b shows the local magnification of the FCC diffraction peak in the XRD pattern of the FeCrCoMnSi_x HEAs coating. It is observed that the main diffraction peak is gradually shifted to the right when the content of Si is increased from $x = 0$ to $x = 1.0$, signifying that the lattice parameter decreases with this coating. According to the Bragg diffraction law [34] and the crystal plane spacing formula [35], the lattice parameter of the FCC phase is reduced from $3.5728 \text{ \AA}$ to $3.5522 \text{ \AA}$. These phenomena are related to the strong substitution ability of the relatively small atomic radius of the Si element [36,37]. Meanwhile, it can be observed from Figure 1b that when $x = 0.6$, the diffraction peaks are obviously broadened,

and it is speculated that there may be small amounts of new phases. Due to the limitations of XRD analysis, the micro structure of the coatings will be further characterized.

Figure 2 shows the cross-sectional morphology of FeCrCoMnSi_x high-entropy alloy coatings, and it is observed that under different Si contents, the continuous distribution of the Fe elements proves the favorable metallurgical bond between the coatings and the substrate.

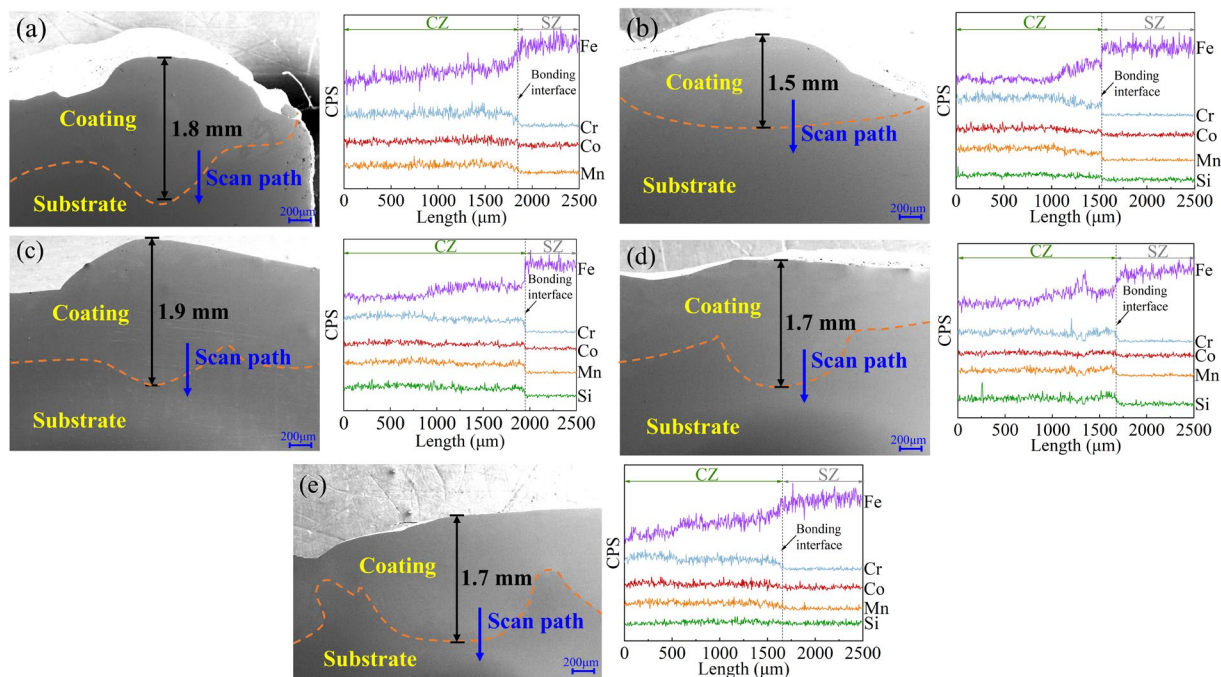


Figure 2. Cross-sectional morphology of the FeCrCoMnSi_x HEAs coating: (a) $x = 0$; (b) $x = 0.3$; (c) $x = 0.6$; (d) $x = 0.9$; (e) $x = 1.0$.

Figure 3 shows the surface morphology of the FeCrCoMnSi_x HEAs coating, and the element point scanning results of certain local areas are shown in Figure 4. From Figure 3a, it can be seen that the structure of the coating is mainly equiaxed crystals, and the average grain size is about 8.33 μm for the FeCrCoMn HEAs coating. The elements are uniformly distributed, and there is a small amount of Mn element segregation on the grain boundary, as shown in Figure 4a. When a small amount of Si element ($x = 0.3$) is added, the micro structure of the coating transforms into the divorced eutectic one. Fe-rich and Co-rich phases are within the crystal, but metal silicate phases are squeezed and gathered to form grain boundaries. Given that laser cladding is a rapid solidification process during the eutectic transition, the Si-rich phase will preferentially form and grow near the primary precipitated Si-rich phase due to the attachment of the composition and the micro structure, leading to the separation of these two phases in the eutectic structure, as shown in Figure 3b. When $x = 0.6$ (Figure 2c), the main micro structure of the coating is transformed into columnar dendritic crystals with obvious eutectic characteristics, and the micro structure is refined and denser [38]. The eutectic reaction is an isothermal transformation, so there are relatively few macroscopic defects, such as the internal elemental segregation phenomenon and holes. When the content of the Si element is increased to 0.9, the primary dendrites are short and coarse, the secondary dendrites are irregularly oriented, and the structure is petal-like, as shown in Figure 3d. It can be seen from Figure 3e that when the content of the Si element continues to increase to 1.0, the structure is a typical dendrite, with the primary dendrite being slender and well-developed, and the secondary dendrite aggregates and grows. Elemental analysis shows that Cr, Mn, and Si are mainly enriched in the dendrites (region B). In contrast, Fe and Co elements are enriched in the inter-dendrites (region A), and the segregation of the element is present, as shown in Figure 4e.

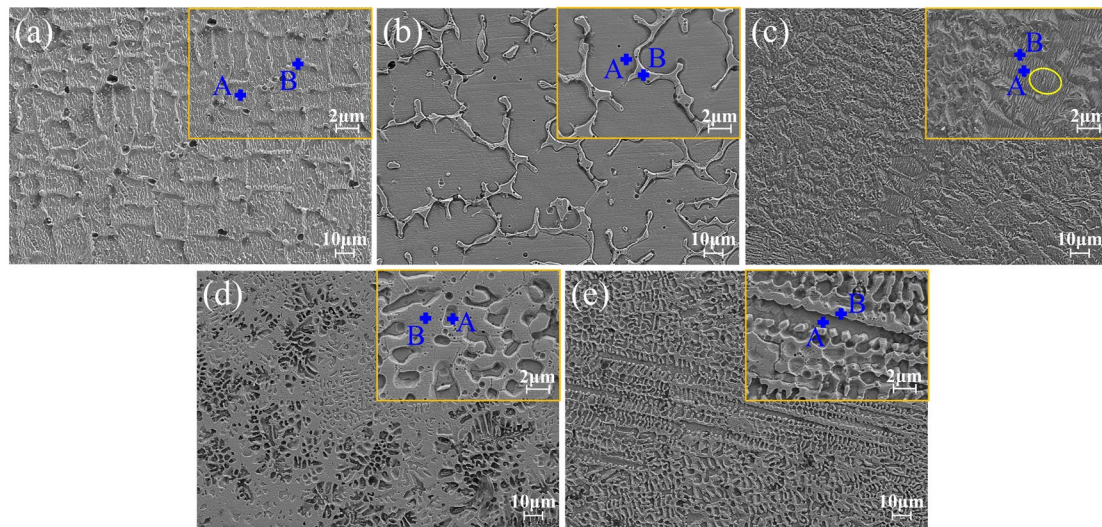


Figure 3. SEM diagram of the surface micro structure of the FeCrCoMnSi_x HEAs coating: (a) $x = 0$; (b) $x = 0.3$; (c) $x = 0.6$; (d) $x = 0.9$; (e) $x = 1.0$.

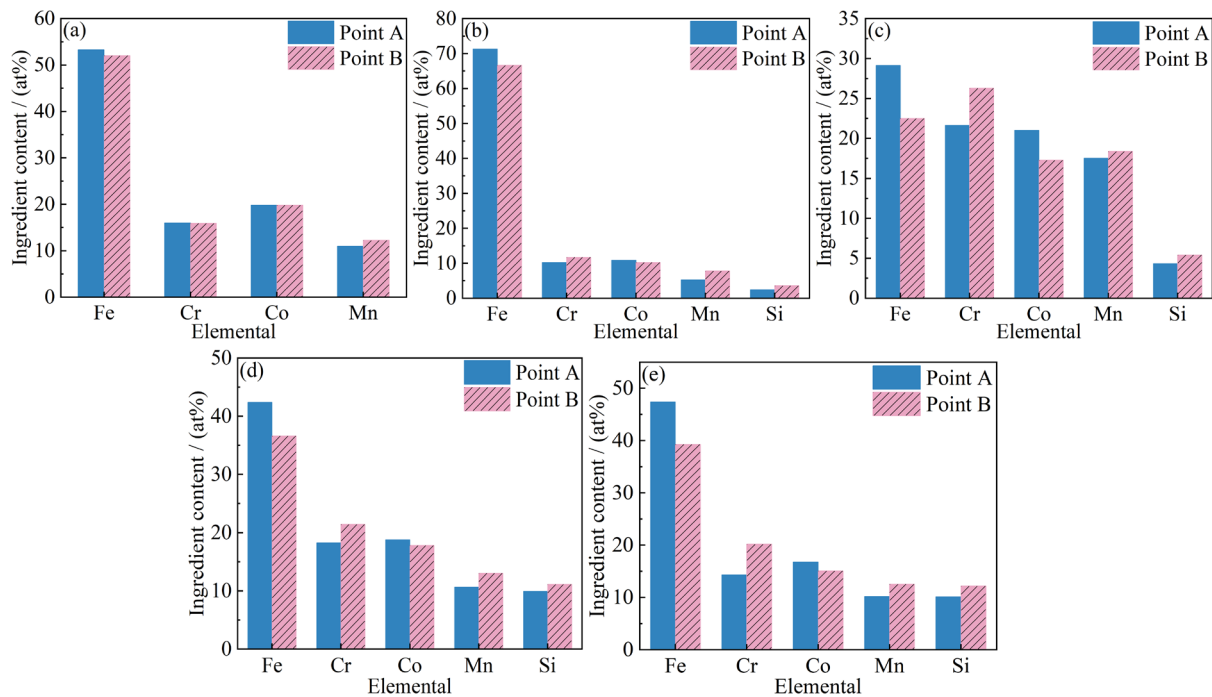


Figure 4. The EDS results of FeCrCoMnSi_x HEAs coating: (a) $x = 0$; (b) $x = 0.3$; (c) $x = 0.6$; (d) $x = 0.9$; (e) $x = 1.0$.

3.2. Hardness of Coating

Figure 5 shows the microhardness of the FeCrCoMnSi_x HEAs coating. The average hardness of the coating surface is 291.7 HV without the Si element. The hardness of the coating surface is obviously enhanced when the Si element is added, and the hardness increases to 425.8 HV when $x = 0.6$, which is about 1.5 times the FeCrCoMn HEAs coating. Although the hardness of the coating decreases slightly at $x = 0.9$ and 1.0 , it is still higher than that of the FeCrCoMn HEAs coating. Therefore, adding the Si element improves the hardness of the FeCrCoMn HEAs coating.

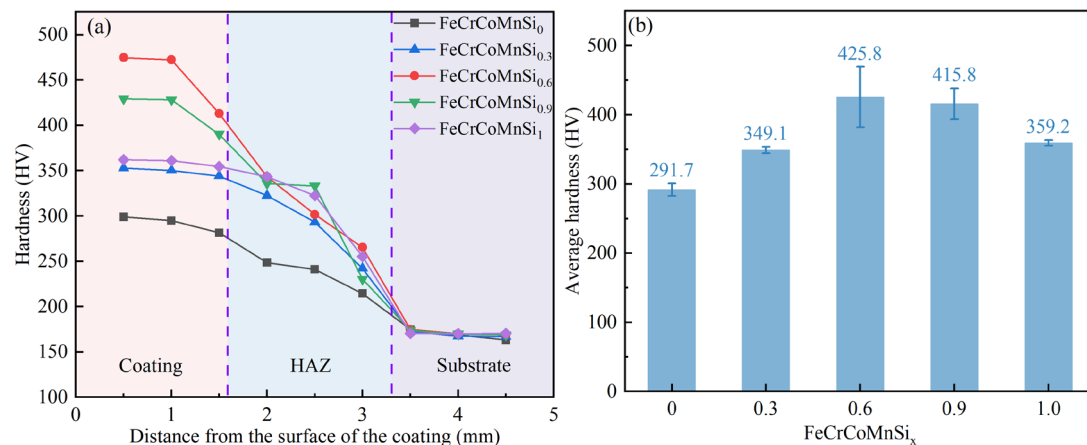


Figure 5. Hardness of the FeCrCoMnSi_x HEAs coating: (a) hardness distribution curves; (b) average hardness of the coating surface.

Because of the relatively small atomic radius of Si element, when the content of Si element is small ($x = 0.3$), the BCC phase is less (Figure 1a), and the phase structure of the coating is mainly FCC phase. The addition of the Si element will dissolve into the interstices of the FCC phase, leading to an increase in solid solubility and thereby improving the hardness due to the increased lattice distortion caused by the solid solution [39,40]. When the content of Si increases to 0.6, the content of the BCC phase in the coating is increased. Additionally, the added Si element would replace other metal elements partially related to the decrease in the interstitial solution and the increase in the displacement solution, and the lattice distortion is further enhanced by the difference in the interatomic radius, producing a significant solid solution effect [41]. Combining with the above analysis, it can be seen that the micro structure has obvious eutectic characteristics (Figure 3c), and a small number of hard metal silicate in the coating are uniformly dispersed in the matrix, which plays the role of dispersion strengthening [42,43]. Consequently, the hardness of the coating is greatly increased due to the combined action of refined crystalline strengthening, solid solution strengthening, and dispersion strengthening. As the Si content increases to 0.9 and 1.0, due to the exsolution and precipitation of the hard brittle metal silicate phases (Figure 1), the internal stress of the coating is reduced and the hardness of the coating decreases slightly.

3.3. Friction and Wear Properties of Coating

Figure 6a shows the coefficient of friction (COF) curves of FeCrCoMnSi_x HEAs coating in simulated seawater testing conditions. It can be seen from Figure 6a that the COF of the coatings are 0.270, 0.241, 0.202, 0.220, and 0.235 when the content of the Si element is 0, 0.3, 0.6, 0.9, and 1.0. It can be seen that during the running-in period, the COF of the coating shows a rapid upward trend due to the point contact between the grinding ball and the coating. When the friction is in the middle-later stage, the contact mode between the grinding ball and the coating transforms to surface contact, and the COF tends to be stable. When the Si content is 0.6, the dense eutectic structure and higher hardness lead to the lowest COF and the best wear performance. In addition, it is also observed that the COF of the coatings show an obvious fluctuation phenomenon when the content of Si is 0.9 and 1.0. As mentioned above, there are hard and brittle metallic silicate phases in the coating's structure, and the detachment of hard abrasive debris increases the roughness of the coating, thus producing large fluctuations in the COF.

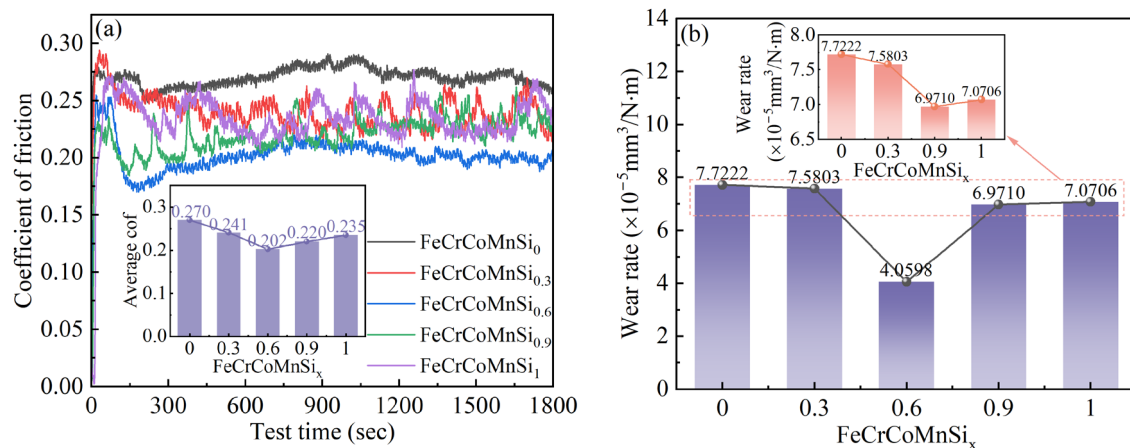


Figure 6. Coefficient of friction and wear rate of the FeCrCoMnSi_x HEAs coating: (a) coefficient of friction; (b) wear rate.

The wear rate of the FeCrCoMnSi_x HEAs coating is shown in Figure 6b. With the increase in Si element content, the wear rate first decreases, and the coating has the lowest wear rate of $4.06 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$ when $x = 0.6$, reflecting better wear resistance. This is related to the fact that when the addition of Si is sufficient, it promotes the formation of the BCC phase, decreasing the solid solubility and, simultaneously, inducing the formation of uniform and fine hard metal silicides. In addition, the hardness of the metal silicides is higher, and they are diffusely distributed, so the wear resistance of the coating is improved [44]. When the content of the Si element increases to 0.9 and 1.0, the wear rate of the coating increases. This is because of the increase in the hard metal silicides, which makes it easy to produce hard abrasive debris during the friction and wear process, causing serious damage to the coating surface and thus increasing the wear rate. The three-dimensional grinding mark morphology of the coating is shown in Figure 7. The depth and width of the grinding mark decrease to $445.364 \mu\text{m}$ and $8.426 \mu\text{m}$, respectively, when the content of Si is 0.6, indicating that the addition of the Si element significantly reduces the depth and width of the grinding mark of the coating, showing an anti-wear ability.

Figure 8 shows the abrasion morphology of the FeCrCoMnSi_x HEAs coating in the simulated seawater testing condition. As shown in Figure 8a, the spalling phenomenon is more obvious, and the furrows are deep and numerous on the coating without the Si element. And during the friction process, due to its lower hardness, it is easily squeezed by the GCr15 ball, generating deep furrows and severe abrasive and adhesive wear. It is also observed from Figure 8a that there is a slight plastic deformation on the worn surface of this kind of coating. The corrosion pits are also observed in Figure 8a, which indicates that the possibility of corrosion reactions is high. From Figure 8b, it can be seen that when a small amount of Si element ($x = 0.3$) is added, the furrows on the worn surface of the coating become shallow, and spalling is reduced. However, the number of corrosion pits on the worn surface of the coating increases, indicating that the corrosion reaction is enhanced, and this also induces the roughness of the coating surface, resulting in the fluctuation of COF and an increase in the wear rate, as observed in Figure 6a. When $x = 0.6$ (Figure 8c), the furrows on the coating surface are reduced and become shallow again, with decreased peeling and adhesion phenomena. Since the hardness of this coating is the highest, the deformation resistance of the coating is enhanced, and the plough effect of the friction pair on the coating is inhibited. On the other hand, there are fewer defects in the denser coating structure, with more uniformly distributed elements (Figure 2c), which can resist the migration of Cl^- effectively and improving wear and corrosion resistance. When the content of Si element increases to $x = 0.9$ and 1.0, it is found that the furrows on the worn surface of the coating become deeper again. The oxidation is more serious with small cracks on the worn surface, as shown in Figure 8d,e. As mentioned above, the structure

transforms to a dendritic crystal structure with the segregation of elements (Figure 3d,e), which leads to the formation of a corrosion cell due to the element concentration gradient, accelerating the friction loss in simulated seawater. In addition, the hard metal silicides are too brittle [45] to resist the strain, which is easy to peel off, and this exacerbates wear of the coating.

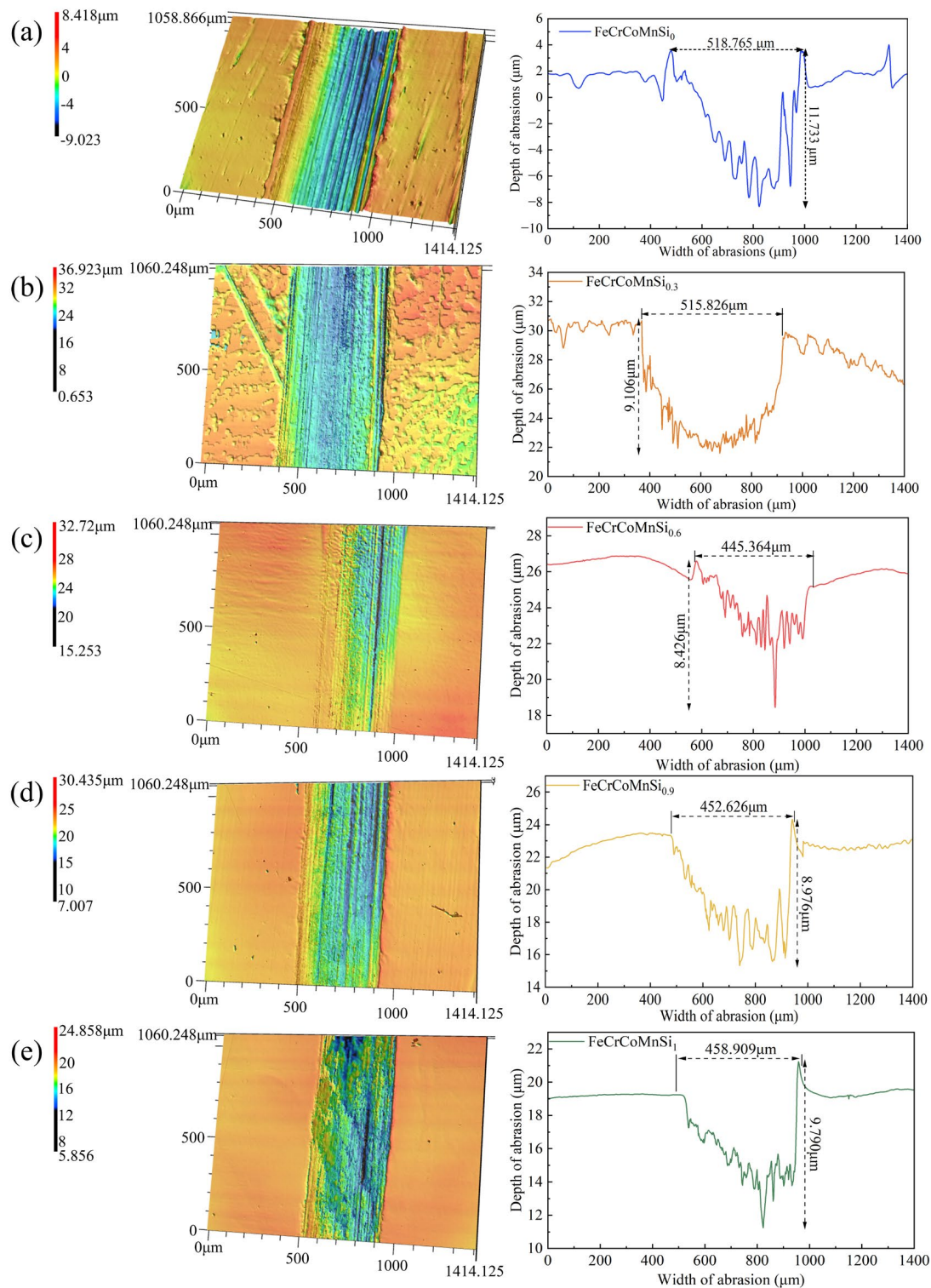


Figure 7. The three-dimensional contours topographies of the worn scars for the FeCrCoMnSi_x HEAs coating: (a) $x = 0$; (b) $x = 0.3$; (c) $x = 0.6$; (d) $x = 0.9$; (e) $x = 1.0$.

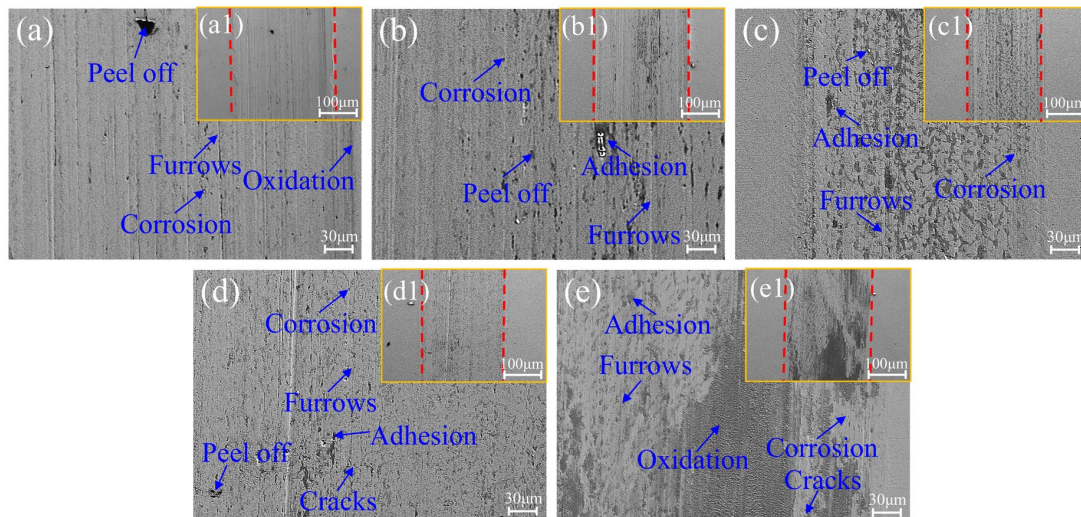


Figure 8. The micro-wear morphology of the FeCrCoMnSi_x HEAs coating: (a) $x = 0$; (b) $x = 0.3$; (c) $x = 0.6$; (d) $x = 0.9$; (e) $x = 1.0$; (a1–e1) Small multiple wear morphology.

The EDS analysis of the worn surface of the FeCrCoMnSi_x HEAs coating is shown in Figures 9 and 10. It can be found that the dark layer on the worn surface possess a high concentration of O element, suggesting the possible generation of oxide layers. From Figure 3c, it is observed that when the content of Si is 0.6, the micro structure is denser and uniform, so the oxide passivated film from Fe and Cr is evenly distributed on the wear surface of the coating (Figure 9c), which decreases the COF and protects the coating from further oxidation and corrosion during the friction process. Thereby the wear resistance of the coating in the seawater is improved [46]. However, as the content of the Si element increases to 0.9 and 1.0, it is observed from Figure 3d,e that the coating structure transforms into a typical dendritic structure. And the local segregation of the Fe element also results in the uneven formation of oxide film. Therefore, it is easy for the film to fall off into hard particles during the friction process, which cannot protect the coating effectively, and the wear rate of the coating slightly increases [47]. It is also observed from Figure 10 that when the content of Si is 1.0, the coating's worn surface has the highest content of Fe and O elements. By combining the wear morphology and the EDS analysis of the coating, it can be found that when $x = 0, 0.3, 0.6$, and 0.9 , the coating is mainly dominated by abrasive wear and accompanied by slight oxidative wear. When $x = 1.0$, the wear mechanism of the coating is dominated by oxidative wear.

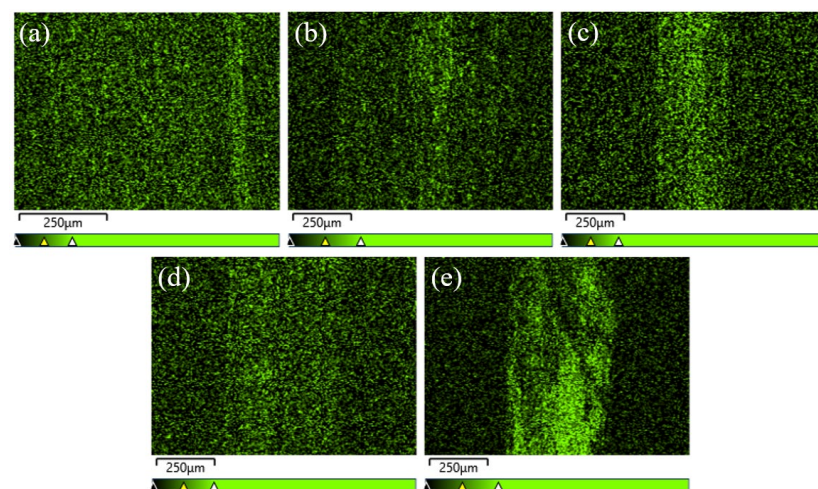


Figure 9. O element distribution on the worn surface of the FeCrCoMnSi_x HEAs coating: (a) $x = 0$; (b) $x = 0.3$; (c) $x = 0.6$; (d) $x = 0.9$; (e) $x = 1.0$.

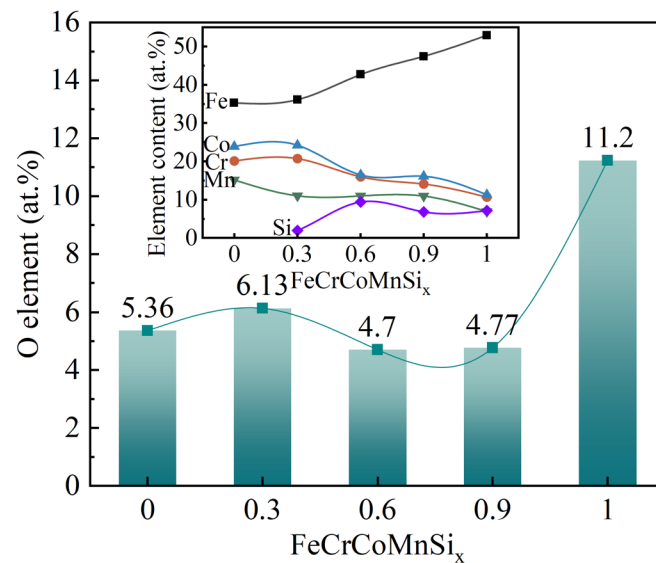


Figure 10. The element distribution on the worn surface of the FeCrCoMnSi_x HEAs coating.

4. Conclusions

A FeCrCoMnSi_x HEAs coating was prepared on 45 steel substrates via laser cladding technology, and the microstructure and friction properties of the coating were analyzed.

- (1) The addition of the Si element promotes the formation of the BCC phase solid solution, which transforms the main phase structure of the FeCrCoMnSi_x HEAs coating from FCC + HCP dual-phase to FCC + HCP + BCC three-phase solid solution. When $x = 0.6$, the structure is transformed from equiaxed crystals to finer and denser columnar dendritic crystals with obvious eutectic characteristics. When the Si content increases to $x = 0.9$ and 1.0 , the hard metal silicate phase is formed in the coating, the microstructure is typical dendritic crystals, and there is clear element segregation.
- (2) When $x = 0.6$, the coating has the highest hardness (425.8 HV) due to the solid solution strengthening and dispersion strengthening caused by adding Si elements and the dense and fine eutectic structure. However, with much greater Si content ($x = 0.9$ and 1.0), the increase in FCC phase solid solution and the decrease in the internal stress results in a slight hardness decrease.
- (3) The analysis of the coating's friction and wear properties in the simulated seawater environment shows that when the content of Si is 0.6 , the coating has the lowest COF (0.202) and wear rate ($4.06 \times 10^{-5} \text{ mm}^3/\text{N}\cdot\text{m}$) due to the dense structure, as well as the uniformly dispersed fine, hard metal silicide, thus exhibiting excellent wear resistance. With the increase in Si content, the coating's wear mechanism changes from adhesive and abrasive wear to oxidative wear.

Author Contributions: Software, B.Z.; Investigation, S.S.; Resources, S.Z.; Writing—original draft, D.J. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by National Natural Science Foundation of China (grant No. 52265015); and Natural Science Foundation of Ningxia (grant No. 2022AAC2003).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data will be made available on request.

Conflicts of Interest: The authors declare no conflicts of interest.

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