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Effect of Processing Parameters on the Microstructure and Corrosion Properties of AlCrFeCoNi High-Entropy Alloy Coatings Fabricated by Laser Cladding

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Abstract: AlCrCoFeNi high-entropy alloys (HEAs) have been successfully synthesized by laser cladding. The AlCrFeCoNi HEA coatings were composed of planar crystal, columnar grain, and equiaxed grain from bottom to top. Face-centered cubic (FCC) was the major phase in coatings, and its content decreased when increasing laser power or reducing scanning speed. The precipitation in the HEA coatings were Al-Ni enriched B2 phase and FeAl₃ intermetallic compounds. The interface zone had higher microhardness than the cladding zone due to the addition of Fe from the dilution role. The C2 (3 kW, 4 mm/s) and C9 (3.5 kW, 6 mm/s) coatings displayed the best corrosion resistance when taking the E_{corr} (−0.327 V, −0.335 V), I_{corr} (0.236 $\mu\text{A}\cdot\text{cm}^{-2}$, 0.475 $\mu\text{A}\cdot\text{cm}^{-2}$), and R_{ct} (224.2 $\text{k}\Omega/\text{cm}^2$, 121.1 $\text{k}\Omega/\text{cm}^2$) into consideration. Pitting dominated the corrosion process of the AlCrFeCoNi HEA coatings. Large grain boundary areas generated by the fine grain in the C2 and C9 coatings enhanced difficulty of ion transport along the grain boundary. Then, multiple corrosion sites on the surface promoted uniform corrosion and formed a protective oxide film, inhibiting serious pitting. This work provided an approach of laser cladding AlCrCoFeNi HEAs with different laser powers and scanning speeds, and insights into the correlation of anti-corrosion properties with the microstructure of AlCrCoFeNi coatings.



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Keywords: laser cladding; high-entropy alloys; process parameters; electrochemical behavior; pitting

1. Introduction

To enhance the corrosion resistance of Q235 steel for broader applications in various industries, numerous techniques have been utilized or investigated to enhance its corrosion resistance through the application of protective coatings, such physical vapor deposition [1], thermal spraying [2], electroplating [3], and laser cladding [4]. Laser cladding is a very promising material manufacturing process, widely used in many industrial fields such as automobiles, aerospace, and ships [5–7]. This technology has the characteristics of high laser power density, fast cooling speed, small heat affected zone, and complete metallurgical bonding between the cladding layer and the substrate material [8,9]. Huang et al. [10] effectively created a Fe_{37.5}Cr_{27.5}C₁₂B₁₃Mo₁₀ coating using laser cladding technology. This coating demonstrated an increased corrosion potential of −0.41 V and a decreased passive current density of $2.29 \times 10^{-7} \text{ A}\cdot\text{cm}^{-2}$ in a 3.5 wt% NaCl solution, compared to the values for 45# steel, which were −0.64 V and $4.57 \times 10^{-6} \text{ A}\cdot\text{cm}^{-2}$, respectively. The superior

corrosion resistance of the coating was primarily due to the enhanced microstructural and compositional homogeneity, as well as the incorporation of Cr and molybdenum Mo. Additional studies have also confirmed that laser cladding is an effective technique for enhancing the corrosion resistance of steels [11,12].

High-entropy alloys (HEAs) consist of several principal elements with equal or near-equal molar fractions, and are an emerging metal material proposed by Yeh et al. [13]. Numerous research findings indicate that, influenced by the “high-entropy effect”, HEAs predominantly comprise one or more types of simple solid solution, such as face-centered cubic (FCC), body-centered cubic (BCC), or hexagonal close-packed (HCP) phases [14], occasionally with a minor presence of intermetallic compounds. Tao et al. [15] reported that the phase of the laser-clad $\text{NiCoFeCrSiAl}_x\text{Cu}_{0.5}\text{TiMoB}_{0.4}$ HEA coatings changed from FCC + BCC to BCC as the main phase with increasing Al content. Aside from the solid solution phase, Juan et al. [16] identified an intermetallic compound with a high concentration of Fe and Mo within the FeCrCoNiAlMo_x laser cladding coating. Among the most thoroughly researched HEA systems are AlCrFeCoNi, which garners attention due to the combination of its constituent elements’ relative abundance, low cost, and outstanding mechanical properties. It has been reported that AlCoCrFeNi exhibited impressive 1.37–1.45 GPa yield stress, 2.96–3.53 GPa ultimate stress, and 15.5–24.5% strain [17]. The AlCrFeCoNi HEAs are characterized by the coexistence and phase transitions between the softer FCC and harder BCC phases, enabling a range of mechanical properties that encompass both strength and ductility [18,19]. FeCrNiMnMo_xB_{0.5} HEA coatings were also produced on Q235 steel via laser cladding, and the influence of molybdenum on their corrosion resistance was examined in a saturated salt solution [20]. The coating with $x = 0.4$ exhibited the best corrosion resistance, showcasing a significant improvement in corrosion potential by 69.6% and a reduction in corrosion current density by 97% compared to the substrate. Wu et al. [21] found that a FeNiCoCrMo_{0.3}Nb_{0.40} cladding layer demonstrated superior corrosion resistance, with a corrosion current density of $1.24 \pm 0.6 \mu\text{A}/\text{cm}^2$. This enhanced resistance was attributed to the fact that Nb facilitated the formation of a passivation film, thereby improving the material’s corrosion resistance. Qiu et al. [22] examined the corrosion characteristics of $\text{Al}_2\text{CrFeCo}_x\text{CuNiTi}$ HEA coatings, which were deposited on Q235 steel substrates using laser cladding techniques. The findings indicated that the coating with $x = 2$, consisting of a BCC solid solution phase, exhibited superior corrosion resistance to 304 stainless steel when immersed in 0.5 mol/L H_2SO_4 solution. Current research primarily concentrates on the selection and refinement of alloy constituents, upon which a relationship between microstructure and corrosion resistance is delineated, ultimately identifying an optimal alloy composition that offers the highest level of corrosion resistance. It is worth noting that the microstructure and corrosion resistance of laser-cladded materials are considerably affected by the laser cladding parameters, such as laser power (LP) and scanning speed (SS). Reports on the preparation of laser-clad AlCoCrFeNi HEA coatings are few, and the evolution in the corrosion behavior of coatings with changes in the processing parameters of LP and SS is unexplored.

In this work, AlCrFeCoNi was employed to create HEA coatings on Q235 steel through laser cladding. To create a high-quality cladding coating without macroscopic flaws and with excellent mechanical properties, it is necessary to optimize process parameters and study the effects of parameters on the corrosion resistance of HEA coatings. A systematic study was conducted to explore the influence of LP and SS on the microstructure, microhardness, and corrosion resistance of the coatings. Additionally, the underlying mechanisms were examined in relation to the microstructure and corrosion characteristics. The findings are anticipated to serve as a reference for enhancing the corrosion performance of AlCrFeCoNi HEA laser-cladding coatings.

2. Materials and Methods

2.1. Materials and Preparation of Coatings

The Q235 steel with a BCC lattice structure was composed of ferrite and pearlite. It was chosen as the substrate with a size of 300 mm × 100 mm × 10 mm. The substrate surface was smoothed and sanitized using a grinding apparatus to eliminate rust and oils. High-purity (99.5 wt.%) Al, Fe, Co, Cr, and Ni were chosen as the cladding powders, which were then dried for one hour at 80 °C and measured out in equal molar proportions. The powder was introduced into a grinding tank equipped with agate balls of varying diameters ranging from 6 to 15 mm, followed by milling at 300 revolutions per minute for 8 h using a QM-3SP2 planetary ball mill (Nanjing NanDa Instrument Co., Ltd., Nanjing, China). A 4 wt.% polyvinyl alcohol was blended with the mixed powder, and then evenly spread on the substrate. Laser cladding was carried out using a fiber-coupled semiconductor laser (Laser-line LDF 8000-60, Laserline GmbH, Mulheim-Karlich, Germany) with a spot diameter D of 7.4 mm. The shielding gas was an argon gas with a purity of 99.99% and a flow rate of 15 L/min. The detailed processing parameters are shown in Table 1.

Table 1. Detailed parameters of LP (kW) and SS (mm/s) used in laser cladding.

Coatings	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
LP	2.5	3	3.5	4	4.5	3.5	3.5	3.5	3.5	3.5
SS	4	4	4	4	4	2	3	5	6	7

2.2. Microstructure Characterization

Samples for observation were extracted from the cladded coatings through wire-cut. The cross section was defined as perpendicular to the cladding direction and used for microstructure characterization. Before observation, the metallographic specimens were sequentially ground with silicon carbide sandpaper ranging from 150 to 1500 grit, then refined using 1 mm diamond polishing compounds, and finally ultrasonically cleaned in acetone for a duration of 2 min. Subsequently, they were subjected to etching with aqua regia, a mixture of HNO₃ and HCl in a volume ratio of 1:3, for 30 s. A scanning electron microscope (SEM, model SU-PRA40 by Carl Zeiss AG, Jena, Germany) fitted with an energy dispersive spectrometer (EDS) was utilized for the analysis of the microstructure and elemental composition. Electron backscatter diffraction (EBSD) was performed on a Tescan Mira 4 FEG SEM (Tescan, Brno, Czech Republic) with the Oxford HKL EBSD detector (Oxford Instruments, Abingdon, Oxfordshire, UK).

2.3. Microhardness Tests

The samples were ground and polished before being tested for microhardness. The microhardness of the sample was measured using a microhardness tester (HXD-1000MZ, Shanghai KaiKang Optical Instrument Factory, Shanghai, China). The testing load was 1.98 N (HV0.2) and the dwell time was 15 s. To ensure reproducibility, the hardness value was determined by taking an average of measurements from more than three distinct locations.

2.4. Electrochemical Measurements

The samples were evaluated at ambient temperature with the three-electrode testing setup on an electrochemical workstation (PARSTAT4000, Princeton Applied Research, Princeton, NJ, USA). Since Cl[−] can degrade the passive film on the coating's surface, its presence aids in assessing the coating's corrosion resistance under more severe service conditions. Therefore, 3.5% NaCl solution was selected as the corrosion medium. Prior to

the tests, specimens were immersed in the solutions for 30 min to stabilize the open current potential. Two testing methodologies were utilized: potentiodynamic anodic polarization tests and electrochemical impedance spectroscopy (EIS) studies. The potentiodynamic polarization tests were carried out over a potential range from -0.2 V to 1.5 V, with a scanning rate of 0.5 mV/s. The EIS measurements were performed across a frequency spectrum ranging from 10 kHz to 0.01 Hz.

3. Results

3.1. Coatings' Morphology

The macro photographs of the HEA cladding coatings are displayed in Figure 1. All cladding coatings exhibited smooth macro-morphology without spatter; furthermore, the coatings from C1 to C5 show no characteristics of burning loss, while the C6 and C7 coatings incurred obvious burning loss owing to the lower SS causing an increase in heat source residence time. In addition, the burning loss reduced with increasing SS (C8, C9 and C10 coatings).

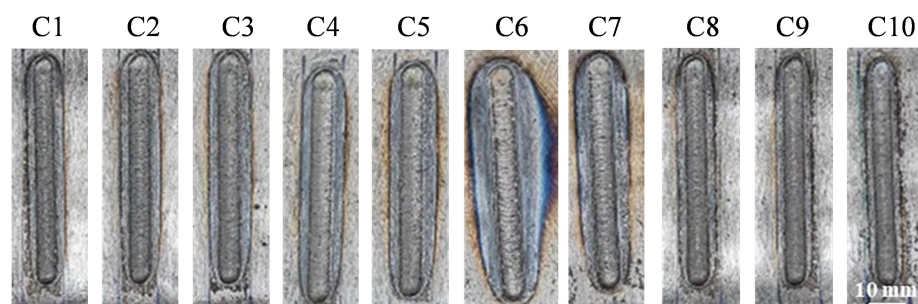


Figure 1. Macro photographs of the HEA cladding coatings from C1 to C10.

Figure 2 shows the cross-sectional macro-morphologies of the HEA coatings with changing LP and SS. Insufficient LP can lead to the formation of local pores and cracks within the cladding layer, which in turn can result in inadequate metallurgical bonding between the base material and the applied coating. However, a large LP increases dilution rate, making more elements in the matrix enter the coatings. A SS that is too rapid may prevent the alloy powder from melting completely, thus failing to establish a proper metallurgical bond between the coating and the substrate. Conversely, if the SS is too slow, the powder is at risk of being excessively burned. All coatings apart from the C1 coating exhibited a dense structure, free of any cracks or pores. As shown in Figure 2a1, a crack in the C1 coating passed through the cladding zone and then expanded about 0.5 mm to the substrate. A lower LP was accompanied by a higher cooling rate of the molten pool; thus, a large shrinkage stress was generated, resulting in the formation of a crack in the C1 coating.

The cross-sectional profiles of the coatings can be seen as a fusion of two perfect arcs with distinct radii, as schematized in Figure 2a3. W , H , and h represent the width, height, and penetration depth of the coatings, respectively. These dimensional features were measured and are shown in Figure 2a2,b2. Laser energy increased with the rise of LP, thus the melting range of the substrate expanded, leading to an increase in h and a broadening of W , as depicted in Figure 2a2. The cooling rates of the molten metal during the solidification process were faster as SS increased, and the solidification time of the molten metal was shorter. The wettability and spread ability of the molten metal decreased, which caused an increase in H , as shown in Figure 2b2, while W decreased. Meanwhile, the substrate's absorption of laser energy diminished, and consequently, the h of the molten pool was reduced.

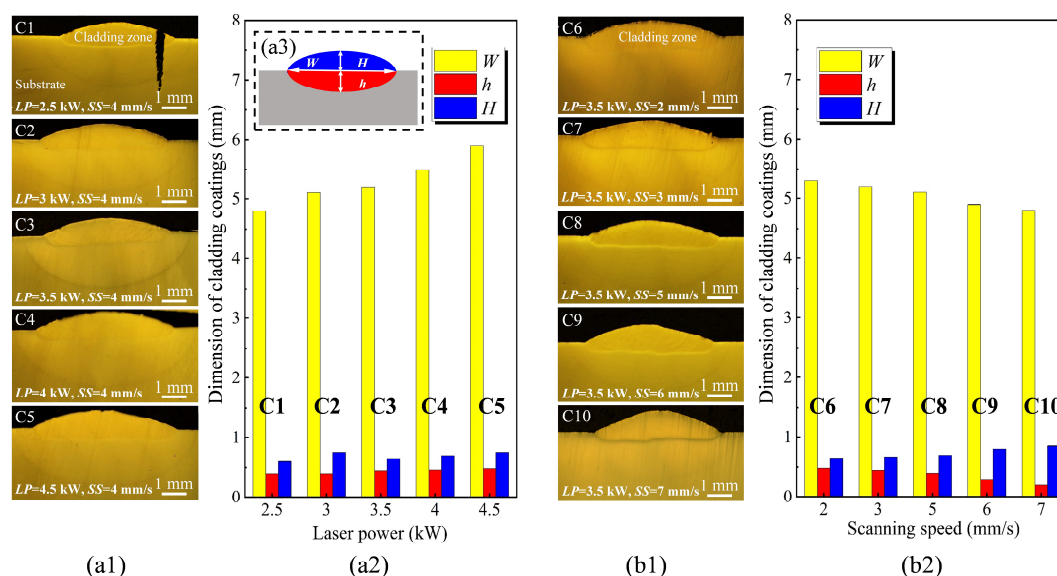


Figure 2. Macro-morphologies and dimensions of the HEA coatings: (a1,a2) LP as a variable, (b1,b2) SS as a variable, (a3,a2) a schematic drawing of the simplified profiles of the coatings.

The dilution rate (η) is a characteristic that holds a pivotal and decisive role in assessing the geometry of a single pass welding. A low η can result in inadequate metallurgical bonding between the cladding layer and the substrate. Conversely, a high η may lead to excessive dilution of the substrate by the coating, which can compromise the coating's integrity, diminish its properties, and enhance the likelihood of cracking. The η is based on a combination of the single pass height and penetration depth parameters, which is derived using Equation (1):

$$\eta = h / (H + h) \times 100\% \quad (1)$$

The LP and SS are the key processing parameters that collectively control the energy input into the molten pool, thereby influencing the η of the coatings. The laser specific energy (E), which serves as a standard measure of the impact of laser processing parameters on the properties of the coating, can be calculated using the subsequent equation:

$$E = LP / (D \times SS) \quad (2)$$

As illustrated in Figure 3a, the η exhibits a rising trend in conjunction with the augmentation of LP. The LP affected the η of the coating by changing the heat input. When LP was raised, the η increased due to the higher absorption of E. The SS played as important a role as the LP. When the SS was fast, the laser specific energy would decrease, thus causing a decrease in η .

The typical microstructure at different zones of the coating is shown in Figure 4. The cladding layer was composed of planar crystal, columnar grain, and equiaxed grain from bottom to top. The type of crystallization and the orientation of grain growth are predominantly dictated by the crystallization parameter G/R, where G represents the temperature gradient and R denotes the solidification rate [23]. At the bottom of the cladding layer close to the substrate, the temperature gradient was very high, and the crystals grew on the flat interface to form a clear planar crystal as shown in Figure 4d, suggesting the establishment of a strong metallurgical bond between the cladding layer and the substrate. With the decrease in temperature gradient and solidification rate from the bottom (Zone D) to the middle area (Zone E) of the coating, the cladding layer was predominantly composed of extended columnar grains. The dendrites grow in a direction opposite to the temperature gradient [24]. Owing to the substantial temperature gradient

at the coating's base, the crystals exhibited distinct growth orientation, leading to the formation of columnar grains, as shown in Figure 4d. The orientation of columnar crystal and dendrite growth in the coating's midsection was predominantly influenced by the direction of heat flow, causing the inconsistent grain growth shown in Figure 4e. In the side region of the coating (Figure 4b), a large number of columnar crystals were also present. In addition to this, under the influence of multiple forces [25], the metallic liquid in the molten pool created a circulation, which fostered the existence of a circulating flow line within the fully solidified microstructure, as demonstrated in Figure 4c. Meanwhile, there were some equiaxed grains in the middle area. In the top area, the cooling rate was large due to the convective heat transfer between molten pool, and fine equiaxed grains were formed, as shown in Figure 4a.

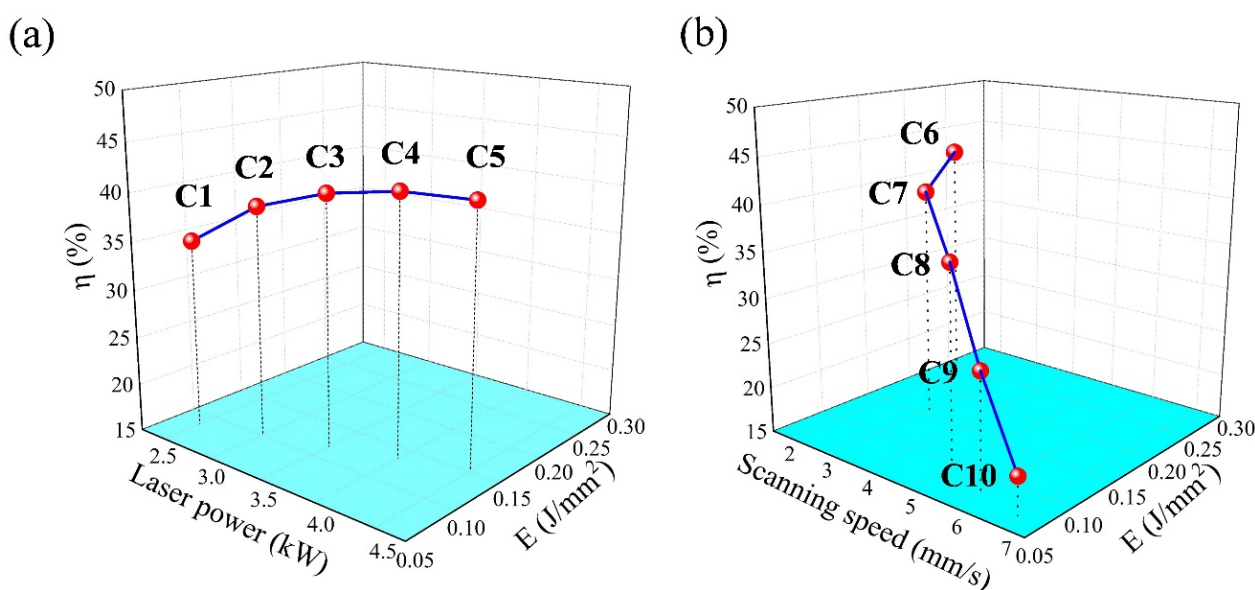


Figure 3. The η of the HEA coatings: (a) LP as a variable, (b) SS as a variable.

3.2. Microstructure Analysis

The large columnar grain and equiaxed grain in middle region of the coating were composed of small sub-grains, as shown in the SEM images in Figure 5a1–a3. The sub-grain was outlined by clear sub-grain boundary (SGB), along with a number of precipitates. Crystals epitaxially grew on the surface of the initial planar growth layer upon solidification, followed by the solidification of the remaining liquid as the process continued. Upon rapid solidification, insufficient solute mixing and complex fluid flow in the melt pool greatly influenced the local solidification conditions and led to the formation of interwoven sub-grains with irregular geometries. Thus, the inter-polygonal boundary was a solidification feature that occurred in grain interior. The EDS results in Figure 5a4 demonstrate that the grain boundary (GB) and SGB have almost the same composition content. Therefore, the sub-grains can be used as the smallest unit of cladding layer, and its size can be used to evaluate the microstructure and properties of materials.

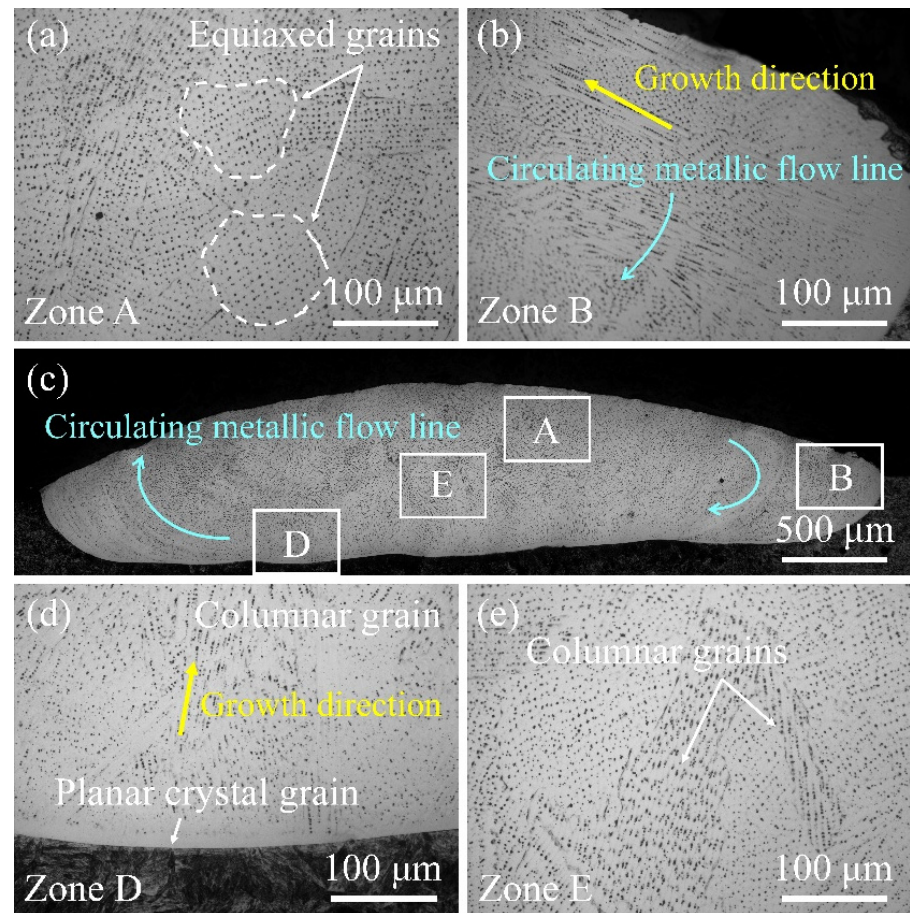


Figure 4. Microstructure of the coating of C3 coating cladded at a LP of 3.5 kW and SS of 4 mm/s: (a) Zone A at the top region of coating, (b) Zone B at the side region of coating, (c) overall view, (d) Zone D at the bottom region of coating, and (e) Zone E in the middle region of coating.

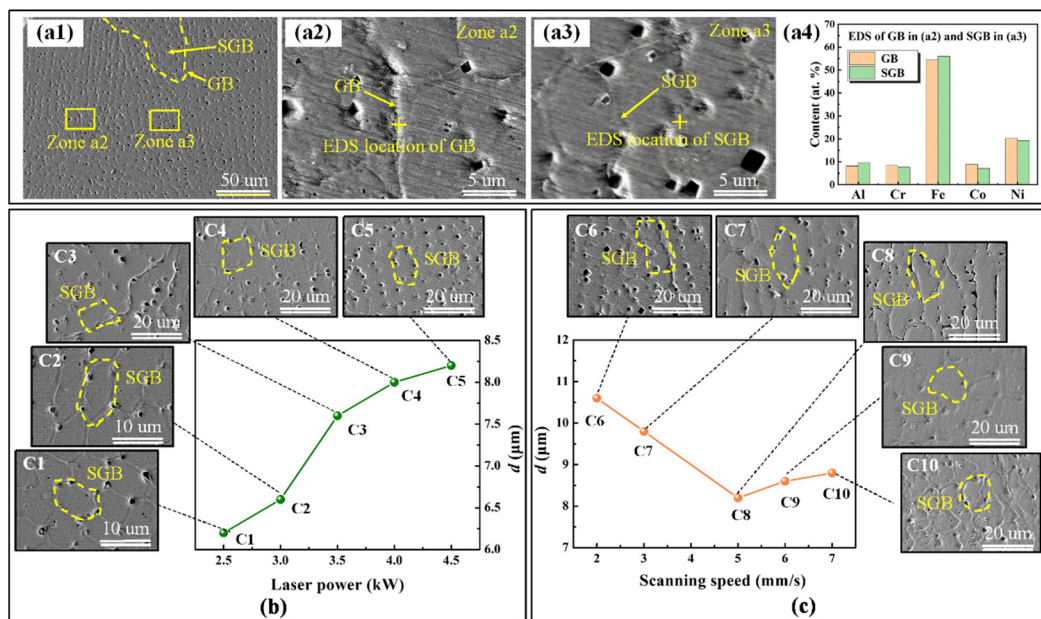


Figure 5. Microstructure and size of sub-grains in the cladding coatings: (a1) microstructure of the cladding coating for C3 coating, (a2) Zone a2 in (a1, a3), Zone a3 in (a1, a4), EDS results of GB and SGB corresponding in (a2, a3); (b) sub-grain size of the coatings with LP as a variable; (c) sub-grain size of the coatings with SS as a variable.

All cladding coatings showed a similar microstructure in overall view, whereas the sizes of sub-grains were not the same. As shown in Figure 5b, coarse sub-grains appear as the LP increases further. Raising the LP can improve laser absorption, followed by an increase in heat input according to Equation (2). This indicates that LP is a critical parameter for directly managing the sub-grain size in laser cladding coatings. Conversely, an increase in SS caused a higher thermal gradient. In addition, the cooling rate tended to increase and the laser specific energy decreased when SS increased. Consequently, a reduced amount of heat was applied to specific areas during the cladding process. Thereby, the nucleation rate increased and the sub-grains were refined under higher SS as shown in Figure 5c. Broadly speaking, the mechanical properties of materials with a finer microstructure tended to be enhanced to some extent. This improvement was primarily attributed to the increase in GBs and the consequent rise in resistance to dislocation movement, which augmented the metal's resistance to plastic deformation. Simultaneously, a greater number of grains allowed the plastic deformation of the metal to be distributed among more grains, and the GBs can also impede the propagation of cracks, thereby enhancing the mechanical properties of the metal.

The EBSD phase mapping shown in Figure 6 indicates that the major phase in coatings is FCC, with a small element of BCC phases simultaneously precipitated within the FCC phase. However, the volume fractions of the FCC and BCC phases in the coatings with different processing parameters were different. As shown in Figure 6a, the EBSD phase mapping illustrates a higher BCC content and a reduced FCC content when the LP increases. The existence of BCC as precipitated phase is related to the segregation during cladding. The laser specific energy increases and the cooling rate slows down as LP increases; thus the decelerated solidification process promotes alloying element to aggregation. Hence, the BCC phase appears gradually as LP increases. On the other hand, the proportion of the BCC phase in coatings can be significantly decreased with much higher SS. As discussed above, increasing the laser SS creates the characteristics of rapid solidification; the diffusion of the alloying element is inhibited, causing suppression of segregation. Thereby, an increase in the SS decreases the number of BCC phases and increases the FCC phases, as shown in Figure 6b. In general, it is well known that the FCC phase has good plasticity [26]. No matter how the processing parameters change, the FCC is the predominant solid solution phase due to the high entropy effect in thermodynamic, which ensures the coating has good plasticity due to the high content of FCC [27].

During the solidification of the molten pool of HEA, phase transition relies on atomic diffusion. The sluggish diffusion in the HEA promotes the creation of supersaturated solid solutions. This effect causes the appearance of precipitates on the laser cladding coating of HEAs [28]. Non-continuous precipitates were noted (seeing Figure 7a) on the SGBs for the C1 coating. As shown in the magnified image in Figure 7b, the precipitates display a square shape in this view. The two-dimensional shapes of the precipitates are different when observed from different angles. As for the C4 coating in Figure 7c, precipitates present in the shape of triangles (outlined in green color) and hexagons (outlined in pink color). In addition, the trapezoid (outlined in yellow color) precipitates are observed for the C7 coating in Figure 7d. According to the EBSD results, these precipitates are BCC-phase. As illustrated in Figure 7e, the two-dimensional shapes of square, triangle, hexagon, and trapezoid can be acquired when slicing a cube in different planes. Therefore, all of these precipitates observed in SEM images may be the same three-dimensional phase.

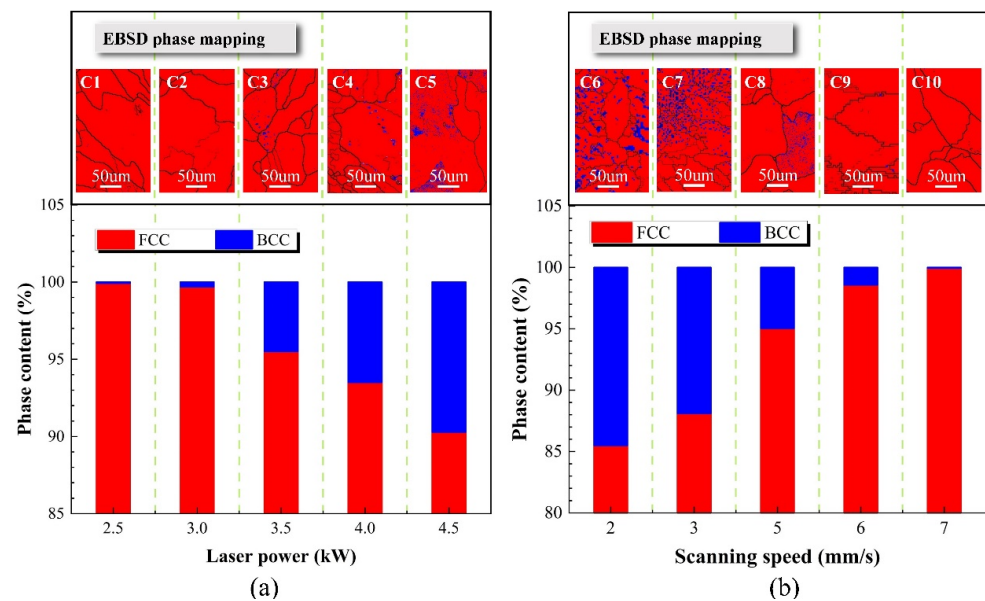


Figure 6. EBSD phase mapping results for all cladding coatings: (a) LP as a variable, (b) SS as a variable. Red represents the FCC phase and blue represents the BCC phase, both in the EBSD phase mapping image and bar charts.

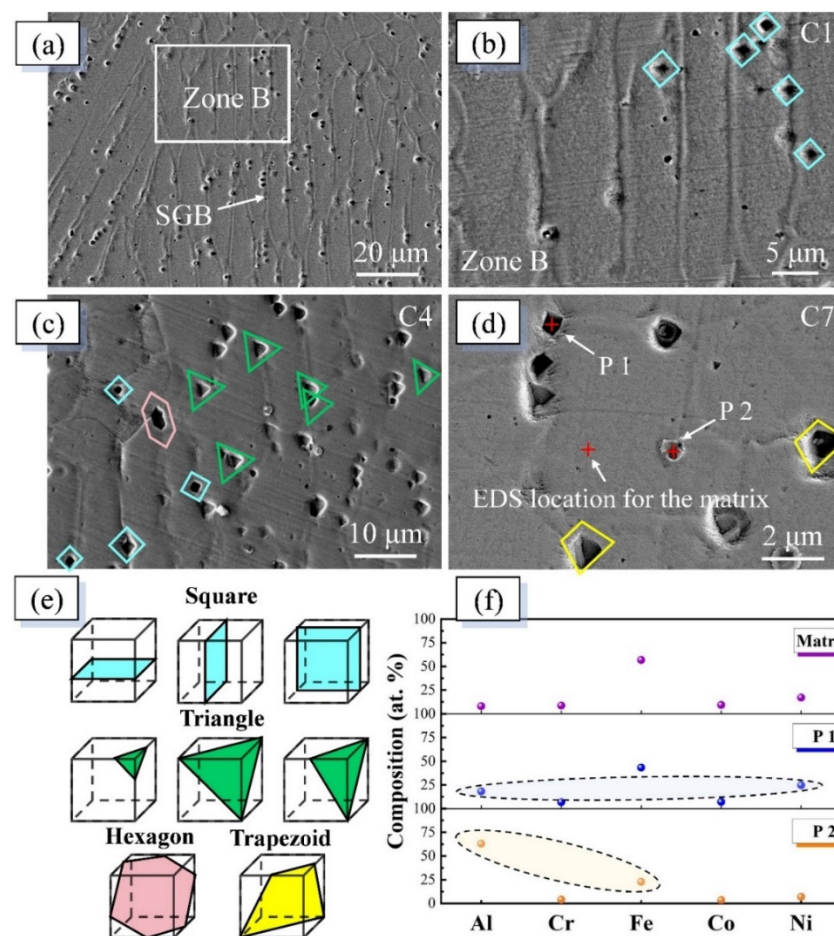


Figure 7. Investigation of the precipitates in cladding coatings: (a) low-magnification image of C1 coating, (b) Zone B marked in (a), (c) microstructure of precipitate in C4 coating, (d) microstructure of precipitate in C7 coating, (e) shapes observed from different views of the precipitates, (f) EDS analysis results of the P1, P2, and matrix.

EDS was applied to identify the chemical compositions of the phases marked as matrix and P1 in Figure 7d. According to the EDS results in Figure 7f, Fe was the major component (56.79 at.%) and the four other elements (Cr with 8.76 at.%, Al with 8.01 at.%, Co with 9.27 at.%, and Ni with 17.17 at.%) can be found in the matrix, suggesting that the matrix is the FCC solid solution. The EDS results hint that the square precipitate of P1 in Figure 7d is a segregation of the BCC(B2) phase, since the particles are enriched in Ni (24.69 at.%) and Al (18.14 at.%) elements [29]. Fe, Cr, and Co, with small differences in atomic size, tend to form solid solutions. There is a substantial difference in atomic size between Al and Ni, which are enriched in the B2 phase; thus, Al and Ni are apt to form precipitates as a role of the lattice misfit. The AlCrFeCoNi system is engineered based on the distribution of the mixing enthalpy (ΔH_{mix}) among elements. Elements readily form a solid solution when their ΔH_{mix} is close to zero, whereas Al and Ni, having the most negative ΔH_{mix} (−22 kJ/mol), are more inclined to form precipitates [30]. Precipitates might trap dislocations, resulting in a higher concentration of dislocations and consequently enhancing the coatings' strength and wear resistance [31,32]. In addition, there is a particle (P2 marked in Figure 7d) with an irregular shape which is rich in Fe (22.7 at.%) and Al (62.85 at.%) and contains small amounts of Cr (4.04 at.%), Co (3.59 at.%), and Ni (6.81 at.%). Thus, Fe and Al might form an intermetallic compound of FeAl_3 owing to their negative ΔH_{mix} (−11 kJ/mol) [33].

3.3. Interface Characteristics and Microhardness

A transition layer named the interface zone appeared in all the coatings, which was related to element diffusion behavior. As shown in Figure 8a, the interface seemed clean without any precipitation. During laser cladding, as temperatures rise, the activated metal atoms at the interface move from their equilibrium positions to vacant sites. Then, adjacent atoms will occupy these newly created vacancies, proceeding via the vacancy diffusion mechanism to achieve macroscopic migration. As a result of the mutual diffusion of metal atoms at the coating and substrate, the transited interface zone is formed.

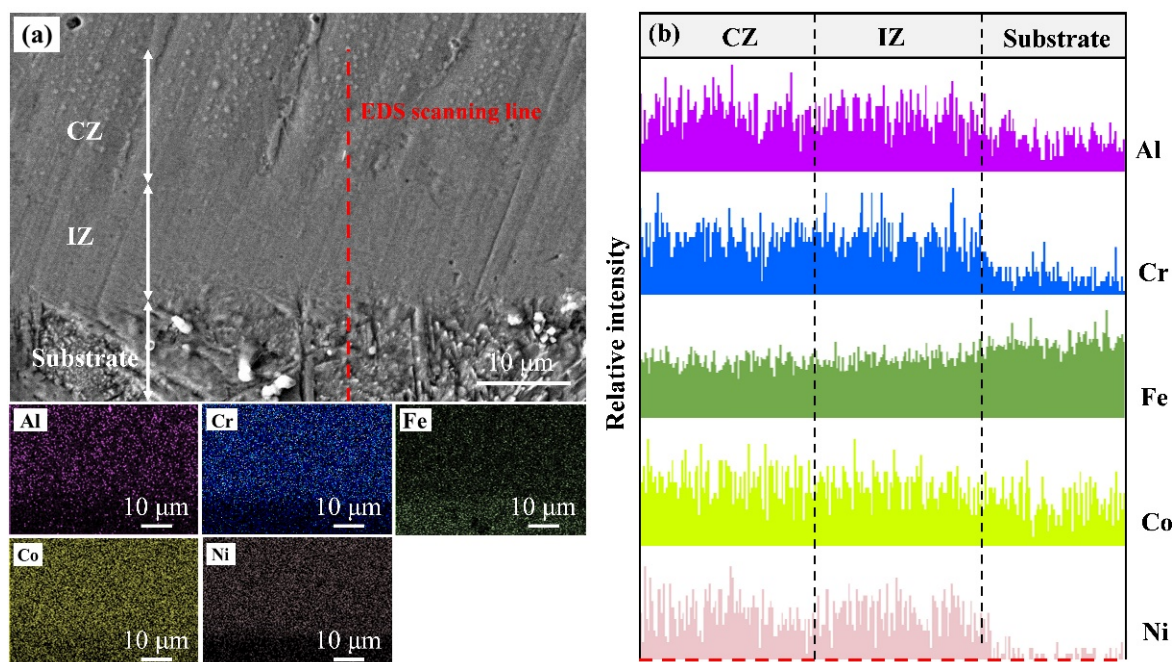


Figure 8. The influences of diameter and volume of precipitates on the microhardness of the AlCrFeCoNi coating when respectively changing the LP (a) and SS (b).

The EDS mapping in Figure 8a indicates that the distribution of elements is uniform in the interface zone. Compared with the substrate, the elements of Al, Cr, Co, and Ni were rich in the IZ, while Fe concentrations displayed the opposite trend. It can be found in Figure 8b that the Fe concentration gradually rises from the substrate to the IZ. The involvement of Fe can improve the compatibility between the coating and the substrate. The concentrations of Al, Cr, Co, and Ni reduced in the substrate, but these elements more or less appeared. During laser processing, Fe diffused from the substrate to the AlCrFeCoNi coating, driven by chemical potential, while Cr and other elements diffused to the substrate and filled existing vacancies left by Fe atoms. This feature of element distribution indicates that dilution takes place during the cladding process. When the LP is increased, the thickness of the interface rises from 12.8 μm to 24.6 μm , as shown in Figure 9, suggesting an increasing η . The interface thickness of C10 is 14.2 μm , which is much narrower than that of C6 (27.7 μm), indicating that the dilution rate can be greatly reduced by increasing the SS.

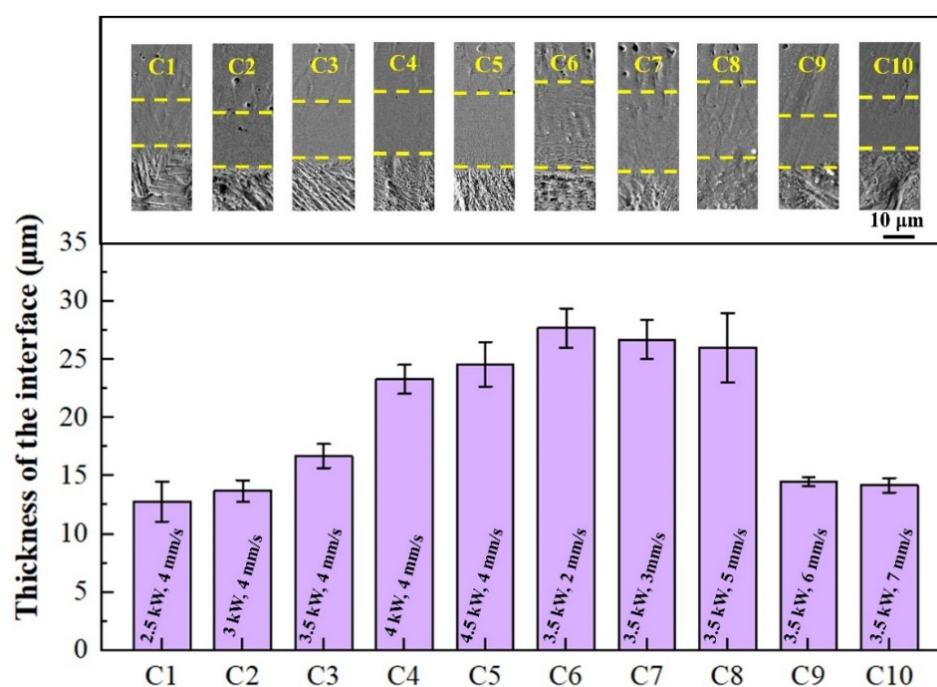


Figure 9. Interface thicknesses of the coatings with changing cladding processes.

Figure 10 illustrates the microhardness of the AlCrFeCoNi coatings, including the CZ and the IZ. The microhardness of the CZ is approximately 200 HV0.2, and it is worth noting that the microhardness of the IZ is higher than that of the CZ. The hard interface is commonly regarded as a conduit for managing non-uniform plastic deformation under tensile stress by accumulating and/or generating a dense array of geometrically necessary dislocations [34], thereby offering an optimal balance of strength and ductility. Due to the dilution role during the laser cladding process, the content of Fe in the IZ increases significantly, as displayed in Figure 9. Thus, the solid solution strengthening induced by Fe plays pivotal roles in the considerable increase in microhardness for the IZ compared with the CZ.

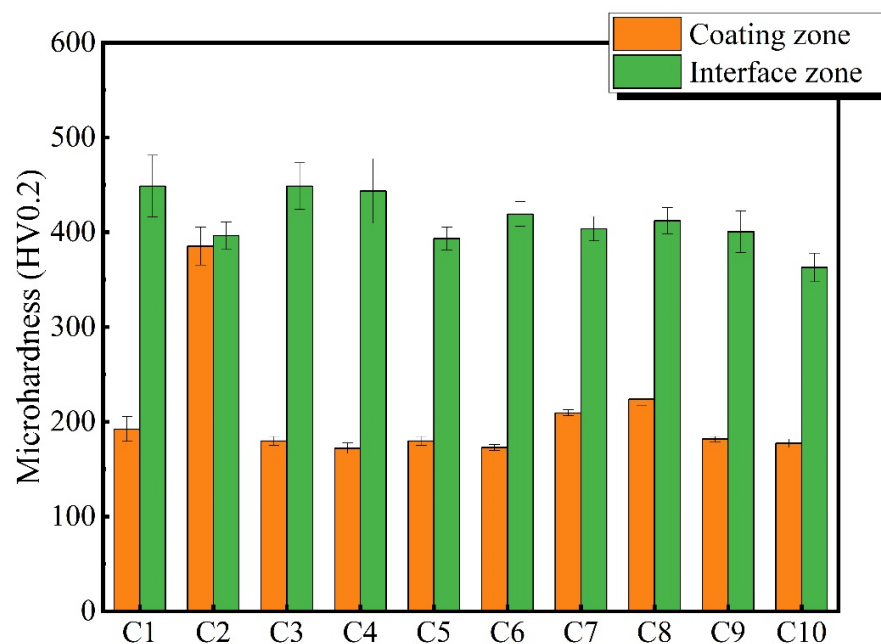


Figure 10. Microhardness of the coating zone and interface zone with changing cladding processes.

3.4. Electrochemical Corrosion Behavior

Figure 11a1,b1 shows the potentiodynamic polarization curves of the AlCrFeCoNi coatings. All coatings except the C1 and C10 coatings display typical activation–passivation–overpassivation characteristics. The passivation potential (E_{pp}) and breakdown potential (E_b) of the coating can be determined at the point of inflection where there is a marked change in the slope of the potentiodynamic polarization curve [35]. The passivation current density (i_p) of the coating is derived by averaging the current density within the passivation region, spanning from E_{pp} to E_b . The passivation parameters for various coatings are presented in Table 2. These coatings have roughly similar E_{pp} and E_b . The i_p of coatings changed with the processing parameters, and the C2 (3 kW, 4 mm/s) and C9 (3.5 kW, 6 mm/s) coatings had the lowest i_p in the corresponding experimental group.

The corrosion potential (E_{corr}) and current density (I_{corr}) of the coating was obtained using the Tafel fitting method. A comparatively high E_{cor} and a comparatively low I_{corr} suggest that the material possesses superior corrosion resistance. The electrochemical parameters of different coatings are shown in Figure 11a2,b2. Although the C7 coating attains the highest E_{cor} and the lowest I_{corr} , its passivation current density is higher. When the LP is 3 kW, the C2 coating achieves the higher E_{cor} (-0.327 V), corresponding to the lowest I_{corr} ($0.236 \mu\text{A}\cdot\text{cm}^{-2}$). When the SS is 6 kW, the C9 coating achieves the higher I_{corr} (-0.335 V), corresponding to the lowest I_{corr} ($0.475 \mu\text{A}\cdot\text{cm}^{-2}$). By comparison, the C2 and C9 coatings have little difference in E_{corr} and I_{corr} compared to C1 and C7; meanwhile, they have lower passivation current density. E_{corr} and I_{corr} are important parameters in the anti-corrosion resistance of materials. Therefore, the results of the potentiodynamic polarization curve testing indicate that the C2 (3 kW, 4 mm/s) and C9 (3.5 kW, 6 mm/s) coatings possess excellent anti-corrosion ability.

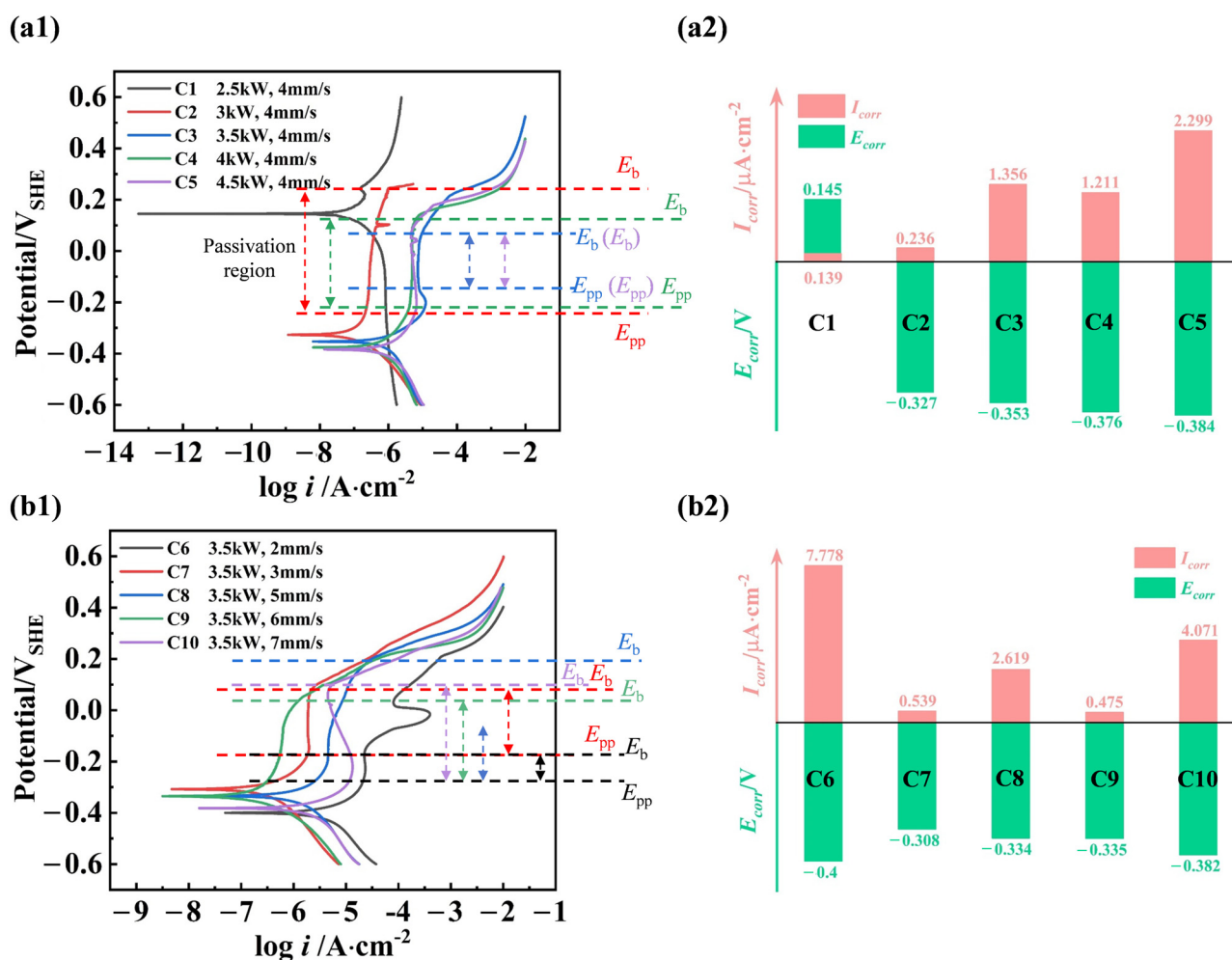


Figure 11. The testing results of potentiodynamic polarization for AlCrFeCoNi coatings: (a1,b1) potentiodynamic polarization curve, (a2,b2) the *E*_{corr} and *I*_{corr} of different coatings.

Table 2. *E*_{pp}, *E*_b, and *i*_p of the AlCrFeCoNi HEA coatings.

Coatings	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
<i>E</i> _{pp} /V	/	−0.256	−0.149	−0.216	−0.216	−0.271	−0.159	−0.213	−0.228	/
<i>E</i> _b /V	/	0.243	0.052	0.101	0.077	−0.156	0.074	−0.066	−0.035	/
<i>i</i> _p /μA·cm ^{−2}	/	0.286	8.25	4.95	5.62	22.5	2.03	4.61	1.09	/

Figure 12 shows the EIS of different coatings. The Nyquist plots exhibit typical semicircular capacitive arcs that span from high frequency to low frequency (Figure 12a1,b1). The radii of the capacitive arcs of the C1 and C2 coatings are relatively large. When changing SS, the C9 coating has the largest radius of capacitive arc. The equivalent circuits depicted in Figure 12c,d are employed to model the electrochemical impedance spectrum data of the coatings. The C4 coating utilized the $R_s(Q_{CPE} R_{ct})$ equivalent circuit model as shown in Figure 12d, while the others employed the $R_s(Q_{CPE1} R_f)(Q_{CPE2} R_{ct})$ equivalent circuit model illustrated in Figure 12c. R_s , R_f , and R_{ct} are the solution resistance, the passive film resistance, and the charge transfer resistance, respectively. CPE1 represents the constant phase element capacitance of the entire anode layer, whereas CPE2 denotes the constant phase element capacitance of the interfacial double layer. A relatively high R_{ct} indicates that the coating has excellent anti-corrosion. The R_{ct} values of the C1 and C2 coatings, shown in Figure 12e, are relatively close: 256.3 kΩ/cm² and 224.2 kΩ/cm², respectively. When the SS changes to 6 kW, the C9 coating achieves the highest R_{ct} (121.1 kΩ/cm²). The

electrochemical impedance spectrum demonstrates that the C2 and C9 coatings possess strong anti-corrosion ability, which is consistent with the previous polarization curve. What needs illustration is that the C1 coating cannot be considered as the best-performing coating because of the existence of a crack in it.

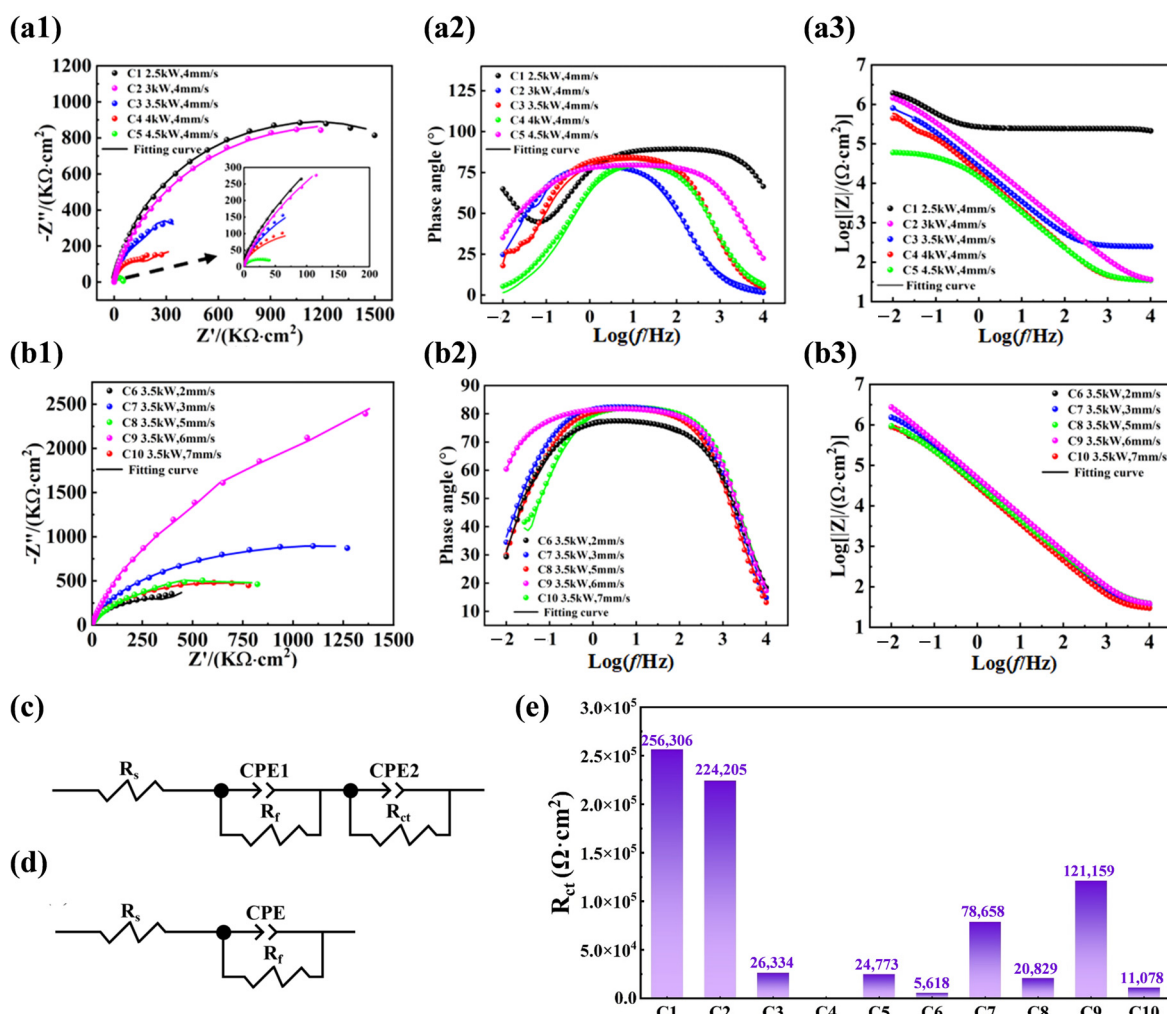


Figure 12. The EIS of the AlCrFeCoNi coatings: (a1,b1) Nyquist plots; (a2,a3,b2,b3) Bode plots; (c,d) the equivalent circuit model; (e) the R_{ct} of different coatings.

The anti-corrosion ability of C2 and C9 coatings may be attributed to the evolutions of phase structure and microstructure with the LP and SS. As noted in the previous microstructural analysis, the FCC matrix is rich in Cr, while the B2 phase is rich in Al and Ni. The C2 and C9 coatings had higher FCC content. High Cr content is beneficial to corrosion resistance. Consequently, the preferential corrosion of the B2 phase creates a galvanic coupling at the microscale between the FCC matrix and the B2 phase, with the FCC matrix serving as the cathode and the precipitated B2 phase functioning as the anode. When immersed in a 3.5 wt.% NaCl electrolyte solution, the coatings become electrically connected with an existing electric potential. This potential difference offers a more potent driving force for the dissolution of the less noble, Cr-depleted B2 precipitates. As a result of the coupling effects, the B2 phase tends to dissolve. Therefore, the C2 and C9 coatings can possess higher corrosion resistance.

4. Discussion

The processing parameters of laser cladding affected the microstructure, which could further influence the corrosion mechanisms of the AlCrFeCoNi coatings. As shown in Figure 13, pitting is the predominant corrosion form for all the cladding coatings under conditions of 3.5 wt.% NaCl solution. Figure 13a,b displays the round and uniform pitting holes in the C1 and C2 coatings with little corrosion pits around them. As LP increases, the sizes of the pits increase gradually. In addition, corrosion pits appear to merge in the C5 coating, as displayed in Figure 13e. On the other hand, the pits are irregular in shape and their size decreases when SS increases. Different pit sizes can indicate the dynamic process of metal dissolution during corrosion in 3.5 wt.% NaCl solution. The C2 and C9 coatings have smaller pit sizes, suggesting they possess better corrosion resistance, which is consistent with the electrochemical test results.

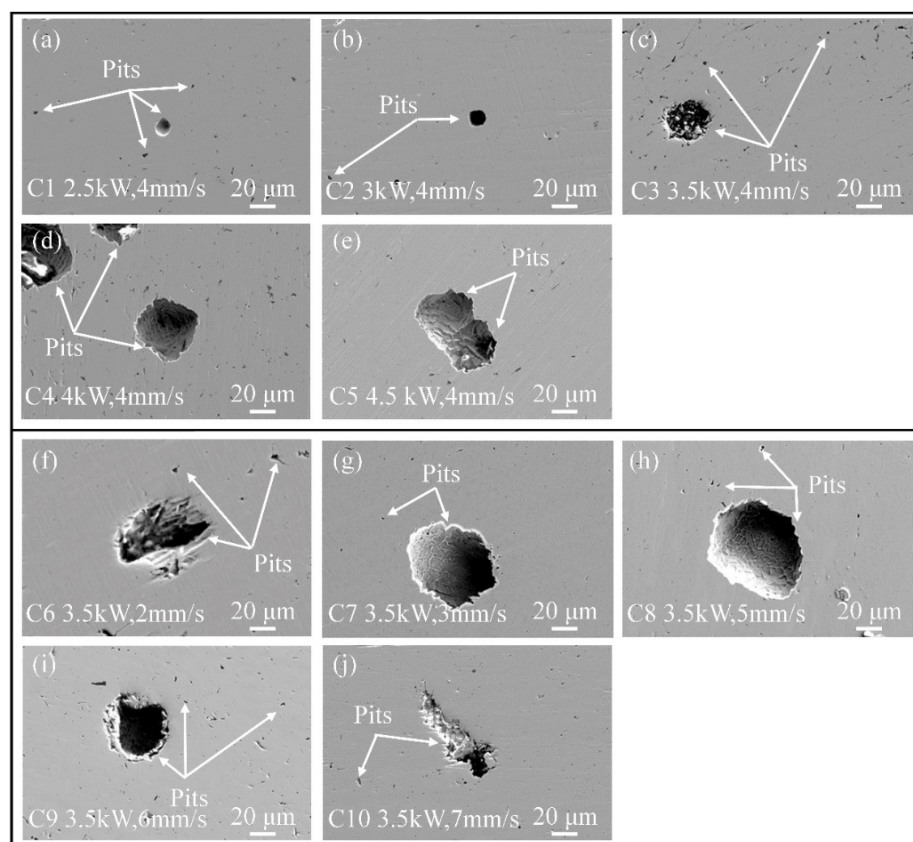


Figure 13. Morphology of the corrosion surface after electrochemical tests: (a–e) C1–C5 HEA coatings, (f–j) C6–C10 HEA coatings.

Notably, the larger pits for the C4, C5, C7, and C8 coatings have clear patterns at the bottom of the pit, as shown in Figure 13d,e,g,h. It can be visibly observed in Figure 14 that the patterns are the GBs of sub-grains in the coatings. This indicates that the sub-grains were preferentially eroded away when immersed in 3.5 wt.% NaCl solution. Meanwhile, the outlines of all pits shown in Figure 14 are in the shape of zigzag. These all proved that preferential dissolution occurs at GBs for these coatings, which eventually cause grain cluster shedding during the corrosion process.

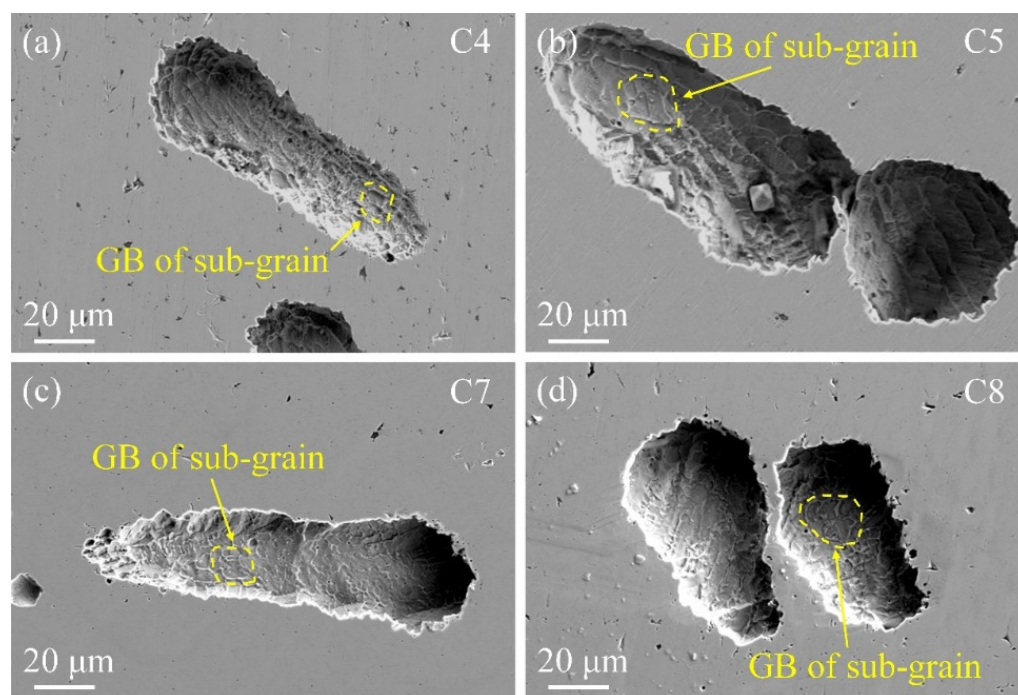


Figure 14. Morphology of the bottom of pits: (a) C4, (b) C5, (c) C7, and (d) C8 HEA coatings.

This corrosion process can be schematized, as shown in Figure 15a1–a3. For all the coatings, corrosion first took place in GB owing to the electrical potential difference from internal grain. Then, the invasion of Cl^- and the dissolution of the metal atom occurs along GB during electrochemical corrosion of the coatings, resulting in the entire grain spalling. The GB area is small when the grain size is large for the C4, C5, C7, and C8 coatings, which reduces the ion transport difficulty and promotes occurrence of electrochemical corrosion along the interconnecting channel composed by GBs of multi-grains. Thus, the grain cluster can be eroded off, forming a larger-size pit with an obvious GB pattern at the pit bottom. However, the pattern displayed in Figure 13 does not appear for the C1, C2, and C9 coatings. This means that the phenomenon of whole grain cluster shedding has scarcely taken place. The relatively mild corrosion process is attributed to the high FCC content and small grain size in the C1, C2, and C9 coatings, as indicated in Figure 15b1–b3. Small grain size means large GB area, which increases the difficulty of ion transport along GB. Thus, the electrochemical corrosion reaction tends to occur on the surface of the coating rather than along the GB. The multiple corrosion sites on the surface tend to be more uniform. The uniform corrosion can promote formation of a protective oxide film and inhibit the occurrence of serious pitting on the coating's surface, only forming some small pits by local metal dissolution. The passive film formed on the C2 and C9 coatings shows superior stability in preventing the processes of ion transfer and pitting corrosion compared to those coatings with coarse grains, which is consistent with the high R_{ct} they obtained in above electrochemical testing results.

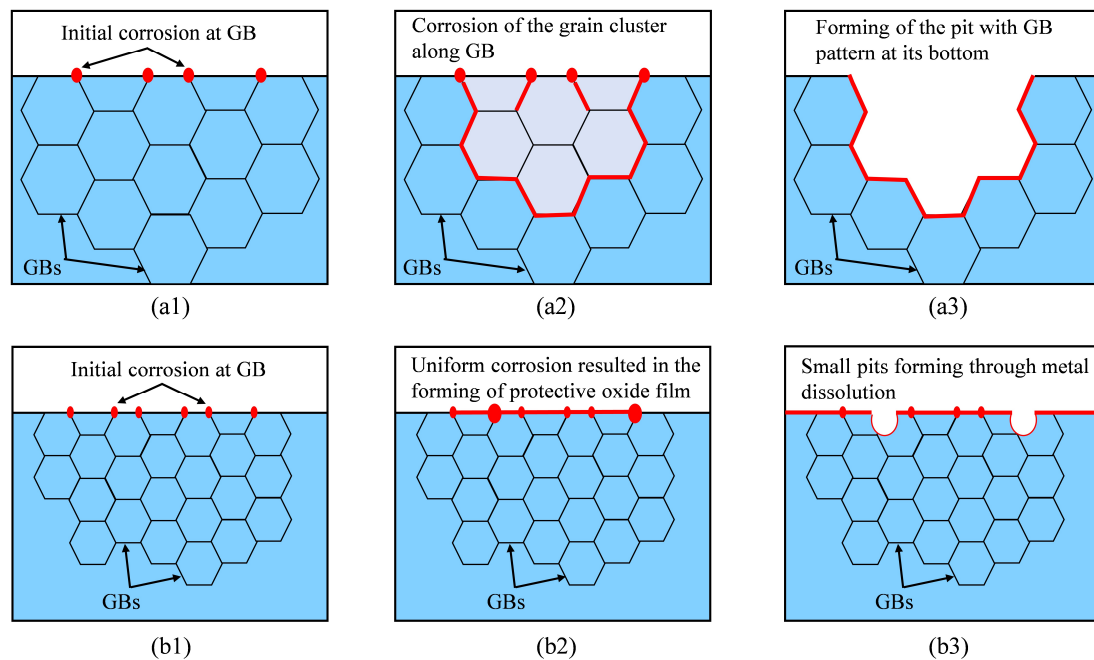


Figure 15. Schematic diagrams of the corrosion behaviors of the HEA cladding coatings: (a1–a3) coatings with coarse grains; (b1–b3) coatings with fine grains.

5. Conclusions

In this study, AlCrFeCoNi HEA coatings were fabricated using laser cladding technology, with adjustments made to LP and SS. The microstructure, hardness, and corrosion properties were examined systematically, leading to the following principal findings.

1. Except for the C1 coating with a crack, the coatings were dense and free from cracks and pores. The η of the coatings gradually rose by increasing LP, and it could be reduced by increasing SS.
2. The microstructure of the coatings was planar crystal, columnar grain, and equiaxed grain from bottom to top. Affected by the cooling rate, the sub-grain size decreased when the LP reduced or the SS increased. As LP increased, the phase in the HEA coatings changed from mainly FCC to a composition of FCC + BCC. By comparison, increasing SS made the FCC content rise.
3. The clean IZ without any precipitation formed as a result of the mutual diffusion of metal atoms at the coating and the substrate. The microhardness of the IZ was higher than that of the CZ, which was attributed to the dilution role in this zone.
4. The C2 (3 kW, 4 mm/s) and C9 (3.5 kW, 6 mm/s) coatings with fine grains displayed the best corrosion resistance when the E_{corr} , I_{corr} , and R_{ct} were taken into consideration. This was attributed to the increased grain boundary area, which hindered ion transport and promoted the formation of a more uniform and protective oxide film, inhibiting the serious pitting.

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