Investigation into corrosion and wear behaviors of laser-clad coatings on Ti6Al4V

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Abstract
TiAlCoCr_xFeNi high-entropy alloys (HEAs) coatings were fabricated on the surface of Ti6Al4V by laser cladding. Their microstructural evolution with the increase in x value (x = 0, x = 1.0, x = 2.0) was investigated in detail. Besides that, the investigation into the effects of the Cr content on their corrosion behaviors and mechanical properties (in terms of hardness and wear resistance) was also carried out comprehensively. The results indicated that two kinds of phases (a solid solution with the hexagonal close-packed (HCP) structure and Ti_2Ni) were synthesized in the coatings, and the HCP content was gradually increased with the increase in x accompanied with the decrease in Ti_2Ni content. A HEA coating only composed of single HCP was successfully prepared when x reached 2.0. The electrochemical and immersion tests all confirmed that the coating with x = 2.0 demonstrated the most excellent corrosion resistance in a 0.1 mol L^-1 HCl solution from different aspects including corrosion tendency and corrosion rate without the applied potential, the formation efficiency/stability of the passive film and the dissolution rate in the passive state, and corrosion surface morphology. The average microhardness values of the coatings were gradually increased from 656HV_0.2 to 800HV_0.2 with increasing x from 0 to 2.0, which were about double that of the substrate (350 HV_0.2). Wear resistance of the coatings also exhibited the upward tendency with increasing the x values (0.562 mm^3 at x = 2.0, 0.640 mm^3 at x = 1.0, 0.641 mm^3 at x = 0 and 1.419 mm^3 for the substrate). More Cr addition into the cladding material will contribute to the formation of a HEA coating composed of single HCP with excellent corrosion and wear resistance.

1. Introduction
Titanium alloys exhibit excellent corrosion resistance in the static corrosion environment since a thin and compact oxide layer spontaneously formed on their surfaces can protect them from corrosion. However, the thin protective layer easily suffers from the serious damage and peels off from the surfaces when titanium alloys contact with the other components and do a relative motion under the friction condition. The exposed titanium alloys will be subjected to the severe chemical/electrochemical dissolution, accompanied with the sharp micro-cutting loss due to their very low hardness of about 350 HV_0.2. The interaction between corrosion and wear will further accelerate the failure of titanium alloys. Wear and corrosion all stem from the surfaces of titanium alloys, therefore improving the surface properties becomes an urgent problem in the application process of titanium alloys.

Up to now, many surface modification methods have been explored and applied to improve surface properties of titanium alloys [1], including electroplating [2], physical vapor deposition [3], chemical vapor deposition [4], micro-arc oxidation [5], and so on [6-9]. However, the protective coatings prepared by above methods are usually thin (micrometer scale in thickness) and loose in microstructure, and have a weak bonding with the substrate, whose applications are greatly limited in the harsh corrosion wear environment. Comparatively speaking, laser cladding as a new and promising technique can resolve the above shortcomings and endow titanium alloys with excellent corrosion/wear resistance. The laser-clad coating exhibits an excellent
metallurgical bonding with the substrate, and its thickness can be flexibly adjusted from micrometers to several millimeters by controlling the thickness of the pre-placed layer or the feeding rate of the powder, and regulating the processing parameters. Most importantly, the cladding material will undergo a process of rapid melting and solidification under laser irradiation, resulting in a dense and fine microstructure obtained in a very short period of time. Many investigations into the laser-clad coating prepared on titanium alloy have been carried out.

A large number of metal-based composite coatings had been synthesized on different metals and alloys. Lei et al. [10] prepared carbon fiber reinforced nickel-based composite coatings on the surface of 1Cr13 stainless steel by laser cladding. Compared with the coating without carbon fibers, the hardness of the coatings with 6 vol.% carbon fibers was increased by 30%. In addition, the corrosion current density and the wear rate were reduced by 93% and 45%, respectively. Shi et al. [11] also applied laser cladding to prepare carbon fiber reinforced nickel-based composite coatings on the surface of Q235 steel. The results showed that the distribution of carbon fibers and metal carbides was more uniform, and the combination between carbon fibers and matrix also became better when the content of carbon fibers was gradually increased from 0 vol.% to 9 vol.%. The average microhardness of the coating with carbon fibers was 678 HV 0.2, which was 1.7 times higher than that of the coating without carbon fibers. The ultimate tensile strength was evaluated from 164 MPa to 608 MPa when the content of carbon fibers was increased from 0 vol.% to 9 vol.%. The coatings were also fabricated on the other alloys such as copper alloys [12], aluminum alloys [13], magnesium alloys [14] and titanium alloys [15–20] etc. With respect to titanium alloys, considerable metal-based composite coatings reinforced by the ceramic particles had been synthesized on their surfaces (TaC-reinforced TiNi/Ti 3 Ni matrix [15], ZrO 2 reinforced TiNi matrix [16], TiC reinforced α-Ti matrix [17], TiB 2 /TiC/TiN reinforced α-Ti matrix [18] and so on [19, 20]). Wear resistance of these coatings is all greatly improved when compared with that of titanium alloys due to their very high hardness of about 750–1400 HV resulting from a combination of the refinement/solution/dispersion strengthening effects. However, the intermetallic compounds involved in the above-mentioned composite coatings will bring about some new issues, such as poor machinability and high cracking susceptibility [21, 22]. In addition, the further improvement in their comprehensive properties is also greatly restricted by the main components.

A novel concept of “multi-component high-entropy alloys (HEAs)” was defined by Yeh et al [23], in which a single solid solution with body-centered cubic (BCC) structure [24], face-centered cubic (FCC) structure [25] and hexagonal close-packed (HCP) structure [26] is synthesized. Owing to the high entropy effect in a multicomponent system, the formation of intermetallic compounds can be greatly inhibited during the solidification. It can be concluded that the HEA coating can effectively resolve the above-mentioned shortcomings involved in the traditional composite coating. However, the present investigations in terms of HEAs mainly focus on the component optimization in different bulk HEAs prepared by the melting method. Some multicomponent systems have been explored (CrMnFeCoNi [27, 28], CoCrCuFeNi [29, 30], AlCoCrFeNi [31, 32], AlCoCrFeNiTi [33, 34] and so on [35, 36]), among which AlCoCrFeNiTi attracts more attentions due to its higher plasticity/toughness, hardness and excellent corrosion resistance. However, there are few reports about the AlCoCrFeNiTi coatings prepared on titanium alloys (especially by laser cladding). Moreover, Cr as a main corrosion-resistant component in HEAs plays an essential role in improvement of corrosion resistance. Unfortunately, its effect on corrosion resistance of HEAs was not revealed in detail in present studies. The relationship between content of Cr and wear resistance of HEAs was also not established.

In this study, three multicomponent systems with different contents of Cr (TiAlCoCr x FeNi, x = 0, 1.0, 2.0) were used to fabricate the HEAs coatings on Ti6Al4V by laser cladding. Microstructural evolution of the coatings with the change in x was investigated. The mechanical properties in terms of wear resistance and microhardness, and corrosion behaviors of the coatings were also analyzed in detail.

2. Experimental procedures

Ti6Al4V as the substrate was machined into the cylinders with 50 mm in diameter and 10 mm in thickness. Al, Co, Cr, Fe, and Ni powders with high purity (≥99.5 wt.%) were selected as the cladding materials, which were dried for 1 h at 80 °C and weighted in three different mole ratios (x = 0, 1.0, 2.0 in AlCoCr x NiFe) using a Sartorious BSA124S analytical balance (0.1 mg resolution), then uniformly mixed by a QM-3SP2 planetary ball milling.

The substrate surface was ground with 150# silicon carbide abrasive paper and ultrasonically cleaned in acetone. A pre-placed layer with a thickness of approximately 1.0 mm was prepared by the modification binding method [37]. Laser cladding was operated using an YLS-5000 fiber laser. The parameters were optimized as follows: applied power of 3 kW, scanning rate of 5 mm s −1 , and spot diameter of 6 mm. Three TiAlCoCr x FeNi HEAs coatings were named as Coating I (x = 0), Coating II (x = 1.0) and Coating III (x = 2.0).
The macromorphologies and microstructures of the coatings were characterized using a VHX-600 K optical microscope (OM) and a HITACHI S-3400 scanning electron microscope (SEM). Their chemical compositions were detected by a GENESIS EDAX energy dispersive spectrometer (EDS). Phase constituents were analyzed using a PANalytical X’ Pert Pro x-ray diffractometer (XRD) with Cu target radiation (\( \lambda = 0.154060 \text{ nm} \)). Microhardness distribution across the coatings’ cross-section was measured by an HXD-1000TMSC/LCD microhardness tester with a load of 200 gf and a duration time of 15 s. Wear resistance of the coatings and the substrate was evaluated by using the ball-on-disk reciprocating mode on a CFT-1 friction machine at room temperature (25 °C). Prior to the tests, the surfaces of the coatings were ground to acquire an approximately same surface roughness. YG6 ceramic balls (5 mm in diameter) were selected as the counterparts. The sliding time was 120 min, the applied load was 30 N and the sliding speed was maintained at 0.1 m s \(^{-1} \). Morphologies and chemical compositions of wear surfaces were characterized by SEM coupled with EDS. Wear volumes of the samples were measured for four times by a surface mapping profilometer, and the average value was obtained.

The electrochemical tests (including potentiodynamic anodic polarization tests and electrochemical impedance tests) were performed on an AUTOLAB PGSTAT302 electrochemical workstation in a 0.1 mol L \(^{-1} \) HCl solution at room temperature (25 °C). The traditional three-electrode system was applied, in which the coatings and the substrate were selected as the working electrode, a Pt sheet and a saturated calomel electrode were chosen as the counter electrode and the reference electrode. For the potentiodynamic anodic polarization tests, the potential was swept from −0.8 to 1.0 V with a scanning rate of 1 mV s \(^{-1} \). The electrochemical impedance spectrograms were recorded with the frequency from 100 kHz to 0.01 Hz and the amplitude of 10 mV around the open circuit potential (OCP). In order to investigate the corrosion mechanisms of the coatings, an Escalab 250XI X-ray photoelectron spectroscope (XPS) with a monochromatic Al Kα excitation was applied to detect chemical valence states of metal elements involved in the passive film formed on Coating III in the EIS tests. The binding energy scale was calibrated by the C1s peak (284.67 eV). To further study corrosion resistance of the coatings, 30 days immersion tests were conducted in a 0.1 mol L \(^{-1} \) HCl solution at room temperature (25 °C). The surface morphologies of the samples after immersion tests were observed by OM.

3. Results and discussion

3.1. Structural characterization

3.1.1. Macromorphologies and dilution rates

Figure 1 shows the cross-sectional macromorphologies of the samples. The samples can be divided into three regions: corresponding to coating, heat-affected zone and substrate. The coatings’ surfaces are comparatively smooth and basically parallel to the base surface. The fusion line can be clearly observed between coating and substrate surface.

The dilution rate can be calculated as follows [20]:

\[
\eta = \frac{S_1}{S_1 + S_2} \times 100\% \tag{1}
\]

in which \( S_1 \) refers to the area of the coating below the substrate surface, \( S_2 \) signifies the area of the coating above the substrate surface.

The cross-sectional profile of the coating can be considered as a combination of an ideal arc and a rectangle (figure 2). Therefore, \( S_1 \) and \( S_2 \) can be calculated according to the geometric relationship [38]:

\[
S_1 = \left( \frac{(W/2)^2 + H_i^2}{2H_i} \right)^2 \left( \frac{2\pi}{360} \right) \sin^{-1} \left( \frac{WH_i}{H_i^2 + \left( \frac{W}{2} \right)^2} \right) - \frac{W \left( \frac{W}{2}^2 - H_i^2 \right)}{4H_i} \tag{2}
\]
where $H_1$ and $H_2$ represent the depths of the coating below and above the surface of the substrate, respectively, and $W$ denotes the width of the coating.

Based on the measured values of $H_1$, $H_2$, and $W$, the dilution rates of three coatings were calculated according to equations (1)–(3). As shown in Table 1, the dilution rate has no significant changes with the increase in $x$ (70.9% for $x = 0$, 72.4% for $x = 1.0$ and 70.1% for $x = 2.0$).

The dilution rate mainly depends on the absorption energy of the given substrate, which is closely related to the processing parameters and the pre-placed layer (surface roughness, thickness, compositions and phase constituents and so on). The chemical compositions can be regarded as a most important factor responsible for...
For the metal elements (Al, Co, Cr, Ni, Fe) involved in the cladding materials, the absorptivity of Cr to YAG laser with a wavelength of 1.06 μm is 0.42, which is higher than that of the other elements (0.09 for Al, 0.33 for Co, 0.26 for Ni, 0.35 for Fe). It is clear that the cladding material containing more Cr can absorb more laser energy, which contributes to the melting of the substrate. However, the absorbed energy for melting the cladding material containing more Cr will be enhanced correspondingly due to its higher melting point than the other elements (2178 K for Cr, 1768 K for Co, 1726 K for Ni, 933 K for Al, 1809 K for Fe), which weakens the melting of the substrate. The two factors resulting from the addition of Cr will play the role against each other in the dilution rate. No significant change should result from the interplay between the two.

3.1.2. XRD analyses
Figure 3 shows the X-ray diffraction patterns of the coatings with different x values (x = 0, 1.0, 2.0). The diffraction patterns of Coatings I-III are very similar, in which eight diffraction peaks are involved. Two strong diffraction peaks are located at 40.2° and 41.4°, besides which the other six weak peaks can also be detected. An interesting phenomenon is observed when x is increased from 0 to 1.0, namely, the intensity ratio between two peaks (40.2° and 41.4°) presents the increasing tendency. When x is further increased to 2.0, the majority of peaks completely disappear and only two peaks are reserved (a strong peak at 40.2° and a weak peak at 76.2°). Those peaks were fitted by the HighScore Plus software and compared with d values in Joint Committee on Powder Diffraction Standards (JCPDS) cards. The results show that the coating is composed of a solid solution with the HCP structure (JCPDS card: 01-089-2762) and an intermetallic compound of Ti2Ni (JCPDS card: 01-072-0442). The volume fraction of the two phases can be calculated from the XRD patterns by the Jade 5.0 software. The volume fraction of Ti2Ni and HCP is 65% and 35% in Coating I. Ti2Ni is gradually reduced to 44% and 7% when x is increased to 1 and 2, accompanied with the increase to 56% and 98% in volume fraction of HCP. That is to say, a HEA coating composed of the single solid solution was successfully synthesized when x reaches 2.0.

For the HEAs, only the solution solid is expected to be synthesized in a multicomponent system. However, some unfavorable intermetallic compounds are also easy to be simultaneously formed in such a system. Therefore, it is very essential to establish the criterions for effectively predicting phase constituents of the HEAs, which will greatly simplify the design of the multicomponent system and reduce the processing costs. Some criterions in terms of the mixing enthalpy ($\Delta H_{\text{mix}}$), the mixing entropy ($\Delta S_{\text{mix}}$) and the atomic size difference ($\delta$) had been established to predict phase constituents. Zhang et al. [39] proposed the criterions based on a large number of data obtained from numerous prepared HEAs, namely the simple solid solutions can be synthesized when they satisfy $12 \leq \Delta S_{\text{mix}} \leq 17.5 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $-19 \leq \Delta H_{\text{mix}} \leq 5 \text{kJ} \cdot \text{mol}^{-1}$, $0 \leq \delta \leq 6.5$. The similar criterions were also established by Guo et al. [40], which are followed: $11 \leq \Delta S_{\text{mix}} \leq 19.5 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $-22 \leq \Delta H_{\text{mix}} \leq 7 \text{kJ} \cdot \text{mol}^{-1}$, $0 \leq \delta \leq 8.5$. 

![Figure 3. X-ray diffraction patterns of the coatings.](image-url)
The above parameters were defined as following [38]:

$$\Delta S_{\text{mix}} = -R \sum_{i=1}^{n} C_i \ln C_i$$  \hspace{1cm} (4)

$$\Delta H_{\text{mix}} = \sum_{i,j=1, i \neq j}^{n} \Omega_{ij} C_i C_j$$  \hspace{1cm} (5)

$$\delta = \frac{\sum_{i=1}^{n} C_i (1 - R_i / R_a)^2}{R_a}$$  \hspace{1cm} (6)

where $n$ means the number of components in multi-component alloy system, $R$ denotes the gas constant ($R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), $C_i$ and $C_j$ are the atomic percentage of the $i$ and the $j$ components in the system, $\Omega_{ij} = 4H_{\text{mix}}^{\text{ref}}$ refers to the interaction parameter between the $i$ and $j$ components in the system ($H_{\text{mix}}^{\text{ref}}$ signifies the mixing enthalpy of a binary liquid alloy system and can be tracked in literature [41]), $R_a$ is the atomic radius, and $R_i$ is the atomic radius of the $i$ component.

It is clear that the calculations of the three parameters are closely related to the contents of different elements in HEAs. The components involved in the laser-clad HEAs coatings are derived from two parts, corresponding to the cladding materials ($\text{AlCoCr}_{x}\text{NiFe}$) and the substrate ($\text{Ti6Al4V}$). A model had been established to calculate the contents of those components [38]. Based on that, the contents of all components in the three coatings were calculated (shown in table 2). The values are also measured by EDS (shown in table 3), which are approximately same to the calculated values. Then, $\Delta S_{\text{mix}}, \Delta H_{\text{mix}}$ and $\delta$ were figured out by Eqs. (4)-(6) (shown in table 4). For the three coatings, the values of $\Delta S_{\text{mix}}$ and $\delta$ can satisfy the criterions proposed by Guo et al. However, the values of $\Delta H_{\text{mix}}$ in Coatings I and II are deviated from the criterions except for that in Coating III. It can be conclude that the simple solid solution can only be synthesized in Coating III, which agrees well with the XRD results.

Besides the above-mentioned parameters, a new parameter ($\Omega$) defined as the net driving factor was also put forward to further strengthening the prediction of phase constituents in HEAs. $\Omega$ can be calculated by the following equation [42]:

$$\Omega = T_m \Delta S_{\text{mix}} / |\Delta H_{\text{mix}}|$$  \hspace{1cm} (7)

where $T_m = \sum_{i=1}^{n} C_i T_{mi}$ denotes the melting point of the coating, in which $T_{mi}$ represents the melting point of the $i$ component.

$\Delta S_{\text{mix}}$ and $\Delta H_{\text{mix}}$ can be regarded as the driving force and the resistance force, respectively. When $\Omega$ exceeds 1, the solid solution is inclined to be synthesized owing to the driving force is larger than the resistance force, whereas the unfavorable intermetallic compound tends to be precipitated. As shown in table 4, the values of $\Omega$ exhibit the upward tendency with increasing the addition content of Cr in the cladding materials, resulting in the

### Table 2. Calculated chemical compositions in the coatings (in at.%).

| Coatings | Al  | Fe  | Co  | Ni  | Cr  | Ti  | V  |
|----------|-----|-----|-----|-----|-----|-----|----|
| I        | 12.52 | 8.58 | 8.58 | 8.58 | 0   | 59.12 | 2.62 |
| II       | 10.94 | 7.04 | 7.04 | 7.04 | 7.04 | 58.29 | 2.61 |
| III      | 9.65  | 5.71 | 5.71 | 5.71 | 11.42 | 59.17 | 2.63 |

### Table 3. Measured chemical compositions in the coatings by EDS (in at%).

| Coatings | Al  | Fe  | Co  | Ni  | Cr  | Ti  | V  |
|----------|-----|-----|-----|-----|-----|-----|----|
| I        | 13.09 | 8.84 | 8.09 | 7.99 | 0   | 60.41 | 1.58 |
| II       | 11.46 | 7.41 | 7.92 | 7.45 | 6.48 | 57.46 | 1.82 |
| III      | 11.63 | 7.54 | 5.27 | 3.78 | 11.30 | 57.08 | 3.40 |

### Table 4. Some parameters for predicting phase constituents in the coatings.

| Coatings | $\Delta S_{\text{mix}}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ | $\Delta H_{\text{mix}}/\text{kJ} \cdot \text{mol}^{-1}$ | $\Omega$ | $\delta/%$ |
|----------|------------------------------------------------|-----------------|--------|-------|
| I        | 10.80                                             | -28.12          | 0.68   | 7.61  |
| II       | 11.63                                             | -24.75          | 0.85   | 7.12  |
| III      | 11.39                                             | -22.04          | 0.95   | 6.67  |
value is approximately equal to 1 in Coating III. The result further validates the conclusion that the solid solution can be formed more easily in Coating III.

3.1.3. Microstructural characterization

Figure 4 shows the backscattered electron (BSE) images of the TiAlCoCrₓFeNiHEAs coatings. As shown in figure 4(a₁), the island-like structure is uniformly distributed within the amorphous structure in the coating with x = 0. When x is increased to 1.0 and 2.0, the amorphous structure is greatly reduced in volume fraction, accompanied with the increase in volume fraction of island-like structure (figure 4(b₁) and (c₁)). BSE images with a high magnification clearly present the microstructural evolution of the coatings with the change in x (figure 4(a₂, b₂, c₂)). For the amorphous structure, plenty of fine stripped/equiaxed particles are uniformly scattered within the amorphous matrix. EDS was applied to identify the chemical compositions of three phases.

### Table 5. EDS results of the zones illustrated in figure 4 (a₂) (in at%).

| Phases   | Ti   | Ni   | Fe   | Co   | Al   | V    | Cr   |
|----------|------|------|------|------|------|------|------|
| Point 1  | 58.03| 5.61 | 6.05 | 5.02 | 19.40| 2.95 | 2.95 |
| Area 1   | 58.65| 3.01 | 6.69 | 4.30 | 19.33| 4.00 | 4.01 |
| Area 2   | 54.13| 12.99| 6.02 | 8.63 | 13.72| 1.08 | 3.42 |

Figure 4. BSE images of the coatings with different contents of Cr: (a₁), (a₂) Coating I; (b₁), (b₂) Coating II; (c₁), (c₂) Coating III.
with different morphologies. As shown in table 5, the island-like phase and the stripped/equiaxed particle are very similar in chemical composition (rich in about 58 at.% Ti and about 19 at.% Al). For the matrix in the amorphous structure, the contents of Ti and Al are reduced to about 54 at.% and 13 at.%, however the content of Ni is sharply increased from about 4 at.% to 13 at.%. 

Combined with the XRD results, the island-like phase and the stripped/equiaxed phase in the amorphous structure can be confirmed as α(Ti) with a HCP structure, and the matrix in the amorphous structure is identified as the intermetallic compound of Ti2Ni. Obviously, Coating I is composed of coarse primary α(Ti) grains and the eutectic structure (α(Ti) + Ti2Ni). Along the increase in x, the island-like grains become coarser and gradually swallow the amorphous structure, resulting in the amorphous structure mainly distributed along the boundaries of the former. When x reaches 2.0, the coating is almost filled with island-like phase, and the amorphous phase is hardly observed. α(Ti) with a HCP structure presents the increasing tendency in volume fraction together with the opposite change in Ti2Ni, and the single solid solution of α(Ti) is obtained in the coating with x = 2.0.

### Table 6. Electrochemical parameters obtained from figure 5.

| Samples   | Ecorr/V   | Ep/V    | Icorr/A·cm−2 | Ip/A·cm² |
|-----------|-----------|---------|--------------|----------|
| Substrate | −0.273(±0.008) | −0.087(±0.002) | 1.58E−7(±0.09) | 2.48E−6(±0.13) |
| Coating I | −0.238(±0.011) | −0.155(±0.006) | 1.28E−7(±0.12) | 8.86E−7(±0.28)  |
| Coating II| −0.192(±0.016) | −0.114(±0.004) | 1.57E−7(±0.15) | 5.99E−7(±0.32) |
| Coating III| 0.125(±0.013) | 0.184(±0.009) | 1.61E−7(±0.13) | 3.69E−7(±0.38) |

Figure 5. Potentiodynamic anodic polarization curves recorded on the samples in a 0.1 mol·L−1 HCl solution.

3.2. Corrosion behaviors

#### 3.2.1. Electrochemical tests

Figure 5 shows the potentiodynamic anodic polarization curves recorded on the coatings and the substrate in a 0.1 mol·L−1 HCl solution. Some electrochemical parameters were obtained from figure 5 (shown in table 6). The corrosion potential (Ecorr) of the coatings is increased from −0.238 V (Coating I) to −0.192 V (Coating II), finally to 0.25 V (Coating III) with increasing the Cr addition content, which is higher than that of the substrate (−0.273 V). The corrosion potential characterizes the electrochemical dissolution tendency of a given material. When the other material is involved in the corrosion environment, the material with a high corrosion potential is more likely to be protected due to its strong ability to acquire electrons. Therefore, the corrosion tendency of the four samples is arranged in the following order: Coating III < Coating II < Coating I < Ti6Al4V. The corrosion current density (Icorr) represents the corrosion rate without the applied current. Clearly, there are no significant differences in corrosion rate for the four samples due to their similar Icorr (about 1.5E−7 A·cm−2). The samples will step into the active state when the applied potential exceeds Ecorr, causing the rapid increase in current. When the potential reaches the passive potential (Ep), the samples are transformed from the active state into the passive state due to a thin and compact oxidation film formed on their surfaces. The transformation difficulty is closely associated with the difference between Ep and Ecorr. Obviously, it is easier for the samples with
indicated that the microstructural evolution caused the difference in corrosion resistance of two alloys. The SLM prepared Ti6Al4V by selective laser melting polarization tests. Dai et al. [46] compared the corrosion resistance of as-prepared Ti6Al4V by selective laser melting (SLM) to that of commercial Grade 5 sample. The results indicated that the microstructural evolution caused the difference in corrosion resistance of two alloys. The SLM smaller difference value to enter the passive zone. The difference value of Coating III is the smallest (about 0.059 V), followed by Coating II (0.078 V) and Coating I (0.083 V), which are lower than that of the substrate (0.186 V). The passive current density (Ip) is used to evaluate the stability of the passive film. Coating III exhibits a minimum passive current density of 3.69E-7 A·cm⁻², followed by Coating II (5.99E-7 A·cm⁻²), Coating I (8.66E-7 A·cm⁻²). Compared with the coatings, Ip of the substrate is increased almost one order of magnitude (2.48E-6 A·cm⁻²). It is clear that corrosion resistance of the coatings is significantly improved when compared with that of the substrate. As far as the coatings are concerned, their corrosion resistance is also gradually enhanced with the increase in addition content of Cr.

The electrochemical impedance behaviors of the four samples were also investigated in a 0.1 mol·L⁻¹ HCl solution by the electrochemical impedance spectroscopy (EIS). Figure 6 indicates the EIS Nyquist curves. Each curve has similar profiles, but the radius of the capacitance arc are different, which indicates that the corrosion mechanisms of the samples are similar and controlled by the charge transfer resistance. The equivalent circuit model was established by the Zview software and the values of different components in this model are presented in Table 7.

**Table 7.** Electrochemical parameters obtained from figure 6.

| Samples        | Rₛ(Ω·cm²) | Qₛ(F·cm⁻²) | n  | Rₓ(Ω·cm²) |
|----------------|-----------|------------|----|-----------|
| Substrate      | 25.32(±1.62) | 4.52E-5(±0.34) | 0.91 | 9.52E4(±0.78) |
| Coating I      | 25.13(±2.09) | 2.02E-5(±0.43) | 0.81 | 8.56E5(±0.84) |
| Coating II     | 24.53(±2.26) | 2.36E-5(±0.52) | 0.81 | 9.80E5(±0.88) |
| Coating III    | 23.25(±1.96) | 3.54E-5(±0.46) | 0.87 | 1.20E6(±0.11) |

Rₛ represents the solution resistance between counter electrode and workings electrode, which has no significant changes (about 23.25–25.45 Ω·cm²) in this tests. Qₛ denotes the interfacial capacitance, which is used to characterize the degree of the charge concentration around the electrode surface [43]. Among all samples, the substrate demonstrates the highest Qₛ value, indicating that the passive film formed on it is the most unstable and easy to be corroded. n signifies the deviation degree of the double layer capacitor from an ideal capacitor, which mainly depends on the surface state (roughness, inhibitor adsorption, etc.) of the samples [44]. The surfaces of the passive film adhering to all samples’ surfaces are similar due to their similar n values. Rₓ refers to the charge-transfer resistance, which is regarded as an essential parameter evaluating the resistance of reactions occurring on the samples surface [45, 46]. It is clear that the Rₓ value of Coating III (1.20E6 Ω·cm²) is evidently higher than those obtained at the other samples (9.80E5 Ω·cm² for Coating II, 8.56E5 Ω·cm² for Coating I, and 9.52E4 Ω·cm² for the substrate). Corrosion resistance of the samples is followed: Coating III > Coating II > Coating I > the substrate, which is well in consistent with that acquired in the potentiodynamic anodic polarization tests.

Corrosion behaviors are mainly related to the inner microstructure with respect to phase constituents, chemical compositions and grain size inside the coatings. Dai et al. [47] compared corrosion resistance of as-prepared Ti6Al4V by selective laser melting (SLM) with that of commercial Grade 5 sample. The results indicated that the microstructural evolution caused the difference in corrosion resistance of two alloys. The SLM

![Figure 6. EIS Nyquist curves recorded on the samples in a 0.1 mol·L⁻¹ HCl solution.](image-url)
sample was composed of 95.0 vol.% α’ martensite and 5.0 vol.%. However, the Grade 5 sample contained 86.7 vol.% α + 13.3 vol.%. α’ martensite belongs to a kind of metastable phase, which is easier to be dissolved. β with more V contents is considered as a phase with strong corrosion resistance, which implies that more β involved the alloys contributes to the improvement in corrosion resistance. The two factors caused the decrease in corrosion resistance of the SLM sample. Dai et al. [48] also confirmed that the grain size was another factor affecting corrosion resistance of the SLM samples. For this study, with the increase in content of Cr, the content of corrosion resistance of the SLM sample was composed of 95.0 vol.%. Based on the data provided in XPS, however, all Ti elements are oxidized to TiO2, contrary to the thermodynamics prediction. The abnormal phenomenon is mainly associated with the dynamics. The thermodynamics mainly clarifies the possibility of a reaction, in which no reaction rate related to the dynamics is involved. Although Reaction (10) is difficult to occur in thermodynamics, it may proceed at a higher rate. As a result, no titanium is maintained in the passive film. Reaction (12) is very easy to proceed since its ΔG° value is only less than that of Reaction (13). This implying that Cr2O3 can be formed preferentially in the passive film. The addition of Cr will contribute to the improvement in corrosion resistance of the coatings due to a dense layer of Cr2O3 with a higher resistance of corrosion. For the Grade 5 sample contained 86.7 vol.% α’ martensite belongs to a kind of metastable phase, which is easier to be dissolved. β with more V contents is considered as a phase with strong corrosion resistance, which implies that more β involved the alloys contributes to the improvement in corrosion resistance. The two factors caused the decrease in corrosion resistance of the SLM sample. Dai et al. [48] also confirmed that the grain size was another factor affecting corrosion resistance of the SLM samples. For this study, with the increase in content of Cr, the content of corrosion resistance of the SLM sample was composed of 95.0 vol.%. Based on the data provided in XPS, however, all Ti elements are oxidized to TiO2, contrary to the thermodynamics prediction. The abnormal phenomenon is mainly associated with the dynamics. The thermodynamics mainly clarifies the possibility of a reaction, in which no reaction rate related to the dynamics is involved. Although Reaction (10) is difficult to occur in thermodynamics, it may proceed at a higher rate. As a result, no titanium is maintained in the passive film. Reaction (12) is very easy to proceed since its ΔG° value is only less than that of Reaction (13). This implying that Cr2O3 can be formed preferentially in the passive film. The addition of Cr will contribute to the improvement in corrosion resistance of the coatings due to a dense layer of Cr2O3 with a higher resistance of corrosion.
approximately 10 Ω·cm rapidly formed on the coating. Therefore, Coating III with a highest Cr content can be quickly transformed from the active state into the passive state.

The stability of the passive film is responsible for the passive current density in the passive state. The dissolution process of those metallic oxides can be expressed as follows:

Figure 7. XPS results for the passive film formed on Coating III: (a) survey; (b) Ti 2p; (c) Ni 2p; (d) Al 2p; (e) Cr 2p; (f) Co 2p; (g) Fe 2p.
CoO + 2HCl = CoCl₂ + H₂O  
NiO + 2HCl = NiCl₂ + H₂O  
Fe₂O₃ + 6HCl = 2FeCl₃ + 3H₂O  
Cr₂O₃ + 6HCl = 2CrCl₃ + 3H₂O  
TiO₂ + 4HCl = TiCl₄ + 2H₂O  
Al₂O₃ + 6HCl = 2AlCl₃ + 3H₂O  

Similarly, thermodynamics calculations were also applied to predict the possibility and difficulty of above reactions. As shown in figure 9, besides TiO₂ and Al₂O₃, Cr₂O₃ is also very difficult to be dissolved in the HCl solution due to the ΔG° values of Reaction (17), (18) and (19) exceeding zero. It can be concluded that the lowest passive current density of Coating III is closely related to its high Cr content.

3.2.2. Immersion tests
To further verify the effect of Cr on corrosion resistance of the laser-clad coatings, immersion tests were carried out in a 0.1 mol·L⁻¹ HCl solution for 30 days at room temperature (25 °C). The surface morphologies of the coatings subjected to the immersion tests were observed by OM (figure 10). There are no large corrosion pits for Coatings I-III after immersion for 30 days. A close inspection reveals that Coating I suffers from the worst
intergranular corrosion when compared with the other coatings due to a large number of dendrites emerging from the initial polished surface. For Coating II, the dendrites can be clearly observed at local zones. Its surface is very smooth and the dendrites are hardly visible when $x$ is increased to 2.0, implying that the coating demonstrates excellent corrosion resistance. This result is also consistent with the electrochemical tests.

### 3.3. Mechanical properties

#### 3.3.1. Microhardness

Figure 11 shows the microhardness distribution across the coating’s cross sections. When $x = 0$, the average microhardness of Coating I is about 656 HV$_{0.2}$. With the increase in content of Cr, the average microhardness of Coating II and Coating III is enhanced to 763 and 800 HV$_{0.2}$. The microhardness of Coating III is improved...
about twice as much as that of the Ti6Al4V substrate (350 HV₀.₂). Obviously, the addition of Cr is beneficial to the improvement in hardness of the coatings.

The improvement in hardness of those coatings is mainly attributed to the solid solution strengthening from HCP and dispersion strengthening from Ti₂Ni. Ti₂Ni had been proved to possess a comparatively low hardness of about 616.9 HV [50], which is less than the average value of those coatings. Therefore, the solid solution strengthening from HCP plays a predominant role in the improvement in hardness of the coatings, which mainly depends on the difference in atomic radius between solvent and solutes, and volume fraction of the solutes. The atomic radii of all elements involved in the coatings are 1.460 Å (Ti), 1.432 Å (Al), 1.310 Å (V), 1.241 Å (Fe), 1.248 Å (Co), 1.246 Å (Ni), 1.249 Å (Cr). The atomic content of V is approximately the same in the three coatings, implying that the solid solution strengthening effect of V is roughly the same. The atomic content of Al presents a decline tendency with the increase in x. However, the change in volume fraction of Al does not produce a significant effect on the solid solution strengthening owing to its slight difference from Ti (about 2% in atomic radius). Fe, Co, Ni and Cr possess the approximately same atomic radii of about 1.246 Å (about 15% difference from that of Ti), whose total atomic content is gradually increased with increasing x (25.74 at.%, 28.16 at.% and 28.55 at.% for Coatings I, II and III), accompanied with the decrease in atomic content of Al. It can be concluded that the solid solution strengthening is gradually improved by adding more Cr into the cladding material. This agrees well with the above testing result.

3.3.2. Wear resistance

Figure 12 shows the wear profiles of the substrate and coatings with different contents of Cr after the sliding tests. The substrate demonstrates a largest wear volume of about 1.419 mm³. For Coatings I and II, their wear volumes are similar (0.640 mm³), decreased obviously by 54.8% compared with that of the substrate. When x is increased to 2.0, the wear volume of the coating is further reduced to 0.562 mm³, and about 80% of that obtained in Coatings I and II. Therefore, the increase in content of Cr in the cladding material can weaken the wear volume.

In order to reveal the mechanism of the samples, SEM was applied to characterize the surface morphologies of the substrate and Coating III. As shown in figure 13(a) and (b), the wear track presents an oval shape. However, whether the width or the length in the wear track of Coating III are all significantly smaller than those obtained in the substrate, which further confirms that Coating III exhibits more excellent wear resistance than the substrate. High-magnification SEM images clearly presents significant differences between their morphologies. A large number of furrows coupled with severe plastic deformation are distributed throughout the whole wear surface of the substrate, indicating that the substrate is subject to severe microcutting. For Coating III, its surface is comparatively smooth and no obvious furrows are observed. A portion of zones are covered with a thin layer of products. Other than those, many sheets loosely adhere to the wear surface. EDS results indicate that Area 1 is rich in O (68.08 at.%) and Area 2 is mainly composed of Ti and Al (shown in table 8). It can be concluded that the surface suffers from oxidation during sliding. The sheets can be identified as the debris from the coating, which peel off from the surface and is oxidized, and finally rolled into the sheets. The oxidation layer and flaky debris will protect the coating from microcutting to a certain extent. Wear loss of the substrate and Coating III mainly results from the microcutting effect.
Wear loss of the coatings presents the slight difference, which should be mainly attributed to the change in phase constituent of the coatings with \( x \). Besides HCP, the comparative content of Ti\(_2\)Ni (65 vol.%) is involved in the coating when \( x \) is zero. Along with the increase in \( x \), the content of Ti\(_2\)Ni was gradually reduced to 44vol.% (\( x = 1.0 \)) and 7 vol.% (\( x = 2.0 \)). As far as the two phases are concerned, Ti\(_2\)Ni possesses the weaker resistance to plastic deformation than HCP due to its lower hardness than that of HCP. Moreover, Ti\(_2\)Ni with a complex cubic structure also has more slip systems than HCP with a close-packed hexagonal structure, which implies the former possesses better ductility than the latter. When the friction pairs contact at an applied load and do a relative motion, the sharp protrusions on YG6 ceramic balls are easier to penetrate into the soft Ti\(_2\)Ni with weak resistance to plastic deformation, and produce more serious microcutting. Therefore, wear loss of the coatings presents the downward tendency with the increase in \( x \) due to the reduction in content of Ti\(_2\)Ni. Accompanied with the cyclic reciprocating, stripped debris gradually peels off from the surface, leaving many furrows. The oxidation layer and the flaky debris can also be formed on the substrate surface, but cannot exist steadily since the soft substrate is unable to provide the enough structural support for them. On the contrary, they can adhere to the surface of the coatings with a high hardness, resulting in the significant reduction in wear loss.

### 4. Conclusions

1. TiAlCoCr\(_x\)FeNi HEAs coatings were prepared on surface of Ti6Al4V by laser cladding. The volume fraction of Ti\(_2\)Ni was decreased accompanied with the increase in volume fraction of HCP along the increase in \( x \) (0, 1.0, 2.0). When \( x = 2.0 \), the coating was only composed of the single solid solution of HCP. The evolution in phase constituent was closely associated with the change in Ti\(_2\)Ni. When \( x \) was close to 1 when \( x \) reached 2.0, implying that the unfavorable intermetallic compound was avoided due to the high resistance force in the system.

2. The coating with \( x = 2.0 \) exhibited the optimum corrosion resistance in electrochemical and immersion tests carrying out in 0.1 mol·L\(^{-1}\) HCl solution, which demonstrated a stronger corrosion tendency, a higher
passivation tendency and a lower active dissolution rate when compared with the substrate and the other coatings \((x = 0, 1.0)\). It should be attributed to the rapid formation of oxides containing Cr, which shielded the coating from further dissolution. Moreover, the oxides containing Cr with a high stability also made a partial contribution to the improvement in corrosion resistance of the coating.

(3) The hardness of the substrate was significantly improved by preparing the TiAlCoCr,FeNiHE as coatings. A high Cr content contributed to the improvement in hardness of the coatings (enhanced about 20% with \(x\) increased from 0 to 2.0). Correspondingly, wear resistance of the coatings was improved than that of the substrate, and their wear resistance presented an increasing tendency with increasing \(x\) values. The change mainly resulted from the evolution in phase constituent of the coatings. The content of HCP with a high hardness and a low ductility was gradually increased, accompanied with the decrease in content of Ti2Ni with a low hardness and a high ductility. This improved the resistance to microcutting, resulting in the decrease in wear loss.

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