Oxidation and Wear Mechanisms of FeCoCrNiMnAl\textsubscript{x} Cladding Layers at High-Temperature Condition

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Abstract: FeCoCrNiMnAl\textsubscript{x} high-entropy alloy (HEA) cladding layers were successfully fabricated on H13 steel by laser cladding. The microstructure and properties of the FeCoCrNiMnAl\textsubscript{x} HEA cladding layers were systematically studied. The influence of Al content on high-temperature wear resistance of HEAs was investigated by depth-of-field microscopy, XRD, SEM and EDS. Addition of Al element affected the mechanism of oxidation and strengthening of the cladding layers, and effectively promoted its anti-oxidant and abrasion resistance. Compared with the FeCoCrNiMn cladding layer, the FeCoCrNiMnAl\textsubscript{0.75} cladding layer enhanced the anti-plastic deformation capacity by 7.1\% and reduced oxidation weight gain and total wear weight loss at high temperature by 36.79\% and 79.0\%, respectively. The wear mechanisms of the cladding layer at high temperature were mainly oxidation wear and abrasive wear, while adhesive wear took a backseat.

Keywords: laser cladding; high-entropy alloy; high-temperature oxidation; high-temperature wearing

1. Introduction

Due to high-entropy \cite{1}, severe lattice distortion \cite{2}, sluggish diffusion \cite{3} and cocktail effects \cite{4}, high-entropy alloys (HEAs) have excellent properties such as high hardness, high wear resistance, high-temperature resistance and high specific strength \cite{5-9}. Performance in the high-temperature service environment (such as high-temperature oxidation, high-temperature wear, etc.) determine the application prospect of HEAs in the high-temperature field. Therefore, the high-temperature properties of HEAs have been widely studied and discussed.

Liu et al. \cite{10} studied the oxidation behavior of AlCoCrFeNi HEAs with different Al content in supercritical water at different temperatures. They found that oxide particles on the surface of Al\textsubscript{0.15}CoCrFeNi and Al\textsubscript{0.4}CoCrFeNi HEAs were smaller than those on HR3C steel, leading to better oxidation resistance and electrochemical corrosion resistance. Butler et al. \cite{11} researched the effect of Al content on the oxidation behavior of Al\textsubscript{x}CoCrFeNi HEAs. It was found that the oxide layer was mainly composed of Cr\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3}, and increasing the Al content could improve the thickness and uniformity of Al\textsubscript{2}O\textsubscript{3} film, resulting in improvement of the high-temperature oxidation resistance of the HEAs. Kai et al. \cite{12} studied the oxidation behavior of three equimolar HEAs (i.e., FeCoNiCrMn, FeCoNiCrSi and FeCoNiCrAl). Oxidation rates of all the alloys were parabolic regardless of alloy composition and temperature. The oxides formed by Al elements at high temperature had a significant effect on the high-temperature oxidation resistance of HEAs.

Tribological behavior of materials is very important for their service life. Investigation of high-temperature friction and wear behavior of HEAs in the air is increasing rapidly. Chen et al. \cite{13}
found that the \(\sigma\)-CrFe phase was formed in as-cast \(\text{Al}_{0.6}\text{CoCrFeNi}\) HEA after cold rolling and annealing treatment, so the high-temperature wear resistance (600 \(\degree\)C) of the alloy was three times that of the GCr15 alloy. Joseph et al. [14] studied the influence of Al content on the high-temperature wear resistance of \(\text{Al}_{x}\text{CoCrFeNi}\) (\(x = 0, 0.3, 0.6, 1\)) HEAs. The results indicate that \(\text{AlCoCrFeNi}\) HEA had an ultra-high microhardness (630 HV\(_3\)) and the highest wear resistance at room temperature due to formation of dense oxide films and grain refinement of the subsurface.

Although a large number of scholars have studied high-temperature oxidation and wear resistance of different kinds of HEAs, there are few studies on high-temperature wear resistance of HEAs prepared by laser cladding (LC). LC is characterized by high energy density, fast cooling speed, small heat input, low dilution rate of cladding layer and small thermal impact on matrix [15,16]. Thus, it can not only achieve surface modification of materials but also reduce the cost of processing [17,18]. Therefore, LC has been increasingly used to manufacture HEAs.

Consequently, this investigation systematically studied high-temperature oxidation and wear properties of \(\text{FeCoCrNiMnAl}_{x}\) laser coatings, and the influence of Al content on mechanisms of high-temperature oxidation and wear were discussed in detail.

2. Experimental Procedures

2.1. Materials and Fabrication of Laser Cladding Coating

4Cr5MoSiV1 die steel (H13 steel) was used as the matrix material for LC of HEAs, and the chemical composition is listed in Table 1. The specific size of the matrix material sample was 80 \(\times\) 60 \(\times\) 12 mm\(^3\). \(\text{FeCoCrNiMnAl}_{x}\) HEA powder prepared by gas atomization was used in the experiment. The molar ratios of alloying elements in the HEAs powders were 1:1:1:1:1:\(x\) (\(x = 0, 0.25, 0.5,\) and \(0.75\)), and the particle size was approximately 15–53 \(\mu\)m.

| Chemical composition of 4Cr5MoSiV1 die steel (wt.%). |
|---|---|---|---|---|---|---|
| C | Si  | Mn  | Cr  | Mo | V  | Fe  |
| 0.37 | 1.0 | 0.36 | 5.02 | 1.26 | 0.91 | Bal. |

A JK2003SM Nd:YAG solid-state laser machine was used to conduct LC. The powder was compacted and flattened by mechanical extrusion, so that the thickness of prefabricated cladding powder was about 1 mm. The laser cladding parameters were about 6 mm/s scanning velocity, 1300 W laser power, 3 mm laser beam spot diameter (negative defocus), 30% overlap ratio of multi-track, argon shielding gas, and 25 mL/min flow rate.

2.2. Microstructure Characterization

The samples were polished according to standard procedures and then etched by using nitrohydrochloric acid for about 30 s. A JSM-7800F scanning electron microscope (SEM, JEOL, Tokyo, Japan) was used to observe the microstructures of \(\text{FeCoCrNiMnAl}_{x}\) cladding layers. The distribution and content of alloying elements were determined by energy dispersive spectroscopy (EDS, JEOL, Tokyo, Japan). The phase compositions of the coatings were identified by a MiniFlex600 advanced X-ray diffractometer (40 kV, 15 mA, Cu K\(\alpha\) radiation, 8\(^\circ\)/min scanning speed, Rigaku, Tokyo, Japan), and Origin Pro 9 software was used to analyze the data.

2.3. High-Temperature Oxidation Test

A high-temperature oxidation test was conducted in a high-temperature electric furnace. The maximum service temperature of 4Cr5MoSiV1 die steel is 600 \(\degree\)C. In order to verify improvement of high-temperature oxidation of substrate metal by the \(\text{FeCoCrNiMnAl}_{x}\) cladding layers, the temperature of the high-temperature oxidation test was set at 600 \(\degree\)C, and the test duration was 100 h. The specimens
with the size of $10 \times 10 \times 1 \text{ mm}^3$ were cut from the cladding layers. Samples were put into the corundum porcelain boat, and a digital balance with 0.1 mg accuracy was used to measure the weights of the porcelain boat and sample as the initial mass ($m_0$). After the high-temperature oxidation test, the porcelain boat and oxidation sample were weighed as $m$. The ratios of mass changes to the surface area were the weight gain per unit area of cladding layers ($\Delta G$).

$$\Delta G = \frac{m - m_0}{S}$$  \hspace{1cm} (1)

where $m_0$ is the initial mass (mg) of the porcelain boat and sample before the high-temperature oxidation test, $m$ is the mass (mg) of the porcelain boat and sample after the high-temperature oxidation test, and $S$ is the total area of the sample ($\text{cm}^2$). To ensure the accuracy of the test results, the samples with the same process parameters were tested three times under the same oxidation environment parameters and then averaged. The microstructures and element distributions of the oxidation layer after 100 h high-temperature oxidation test were characterized using SEM and EDS, respectively.

2.4. Mechanical Properties

Nano-indentation test specimens ($10 \times 10 \times 5 \text{ mm}^3$) were cut, and the surface of the laser cladding layer was ground, polished and etched. The load-displacement data and elastic moduli of the cladding layers were obtained by a KLA-Tencor G200 Nanoindenter (KLA-Tencor, Milpitas, CA, US) at room temperature. The experiments were conducted at a loading rate of 0.1 s$^{-1}$ and a holding time of 10 s, and the indentation depth of the diamond head was 500 nm.

An MDW-02 abrasive wear tester was used to measure the high-temperature wear properties of the FeCoCrNiMnAl$_x$ cladding layers at 600 $^\circ$C. The upper sample for wear test was YG6 tungsten steel ball (WC + 6 wt.% Co) with the diameter of 6.35 mm, and its hardness was HRA92. The thickness and diameter of the specimens were 3 and 20 mm, respectively. The test parameters were 30 N load, 1 Hz test frequency, 65 r/min rotational speed, 60 min wear time, and 4 mm/s radial feed speed. An analytical balance with 0.1 mg accuracy was used to measure the weight of the specimens before and after the wear test. Then the wear loss, friction coefficient and friction force were obtained. The microstructure of the worn surface was characterized using SEM.

3. Results and Discussions

3.1. Phase and Microstructure of the FeCoCrNiMnAl$_x$ Coatings

Figure 1 shows the XRD detection results and SEM microstructures of FeCoCrNiMnAl$_x$ cladding layers. Due to the high mixing entropy, no complex intermetallic compounds were produced in the laser cladding layers. Only FCC (Face-Centered Cubic structure) phase exists in the FeCoCrNiMn, FeCoCrNiMnAl$_{0.25}$ and FeCoCrNiMnAl$_{0.5}$ cladding layers, as shown in Figure 1a–c. The FeCoCrNiMnAl$_{0.75}$ cladding layer has a dual phase structure (FCC and BCC phases), as shown in Figure 1d. This is similar to the conclusions of some scholars [2,4]. Therefore, Al element (0.75 mol) promoted partial conversion of the FCC phase in the HEA coating into the BCC (Body-Centred Cube structure) phase.

Grain boundaries and phase distribution of FeCoCrNiMnAl$_x$ cladding layers were detected by EBSD, and the results are shown in Figure 2. The FCC phase uniformly distributed in the cladding layers when the contents of Al element were 0, 0.25 and 0.5 mol, respectively. The BCC phase structure appeared in the FeCoCrNiMnAl$_{0.75}$ cladding layer, and it is located at the grain boundaries, as shown in Figure 2d2.

Moreover, dendritic morphologies can be observed on the surface of FeCoCrNiMnAl$_x$ cladding layers, as shown in Figure 1a1–d1. The average grain sizes of the four coatings are 10.37, 8.61, 7.54 and 5.32 $\mu$m, respectively, indicating that Al element has the effect of refining grains. EDS detection results of dendritic and interdendritic spaces of FeCoCrNiMnAl$_x$ cladding layers are listed in Table 2.
Interdendritic space in the FeCoCrNiMn cladding layer contained more Cr elements than dendritic spaces. The distribution patterns of alloying elements in the remaining cladding layers were basically similar, that is, the content of Cr and Al elements in the interdendritic space were higher, while the dendritic space contained more other four alloying elements (Fe, Co, Ni and Mn).

The mixed entropy values ($\Delta S_{\text{mix}}$) of the FeCoCrNiMnAl$_x$ cladding layers were calculated using the Boltzmann equation, as follows [19]:

$$\Delta S_{\text{mix}} = -k \ln w = -R \sum_{i=1}^{n} x_i \ln x_i$$

(2)

where $k$ is the Boltzmann constant ($1.38054 \times 10^{-23}$ J/K), $w$ is the degree of confusion, $R$ is the gas constant (8.314 J/(K·mol)), $n$ is the number of elements and $x_i$ is the composition of the $i$th element. According to the EDS detection results of the FeCoCrNiMnAl$_x$ cladding layers, as shown in Table 3, the mixing entropies ($\Delta S_{\text{mix}}$) of the four cladding layers were 1.606, 1.708, 1.751 and 1.772 R, respectively. Therefore, the FeCoCrNiMnAl$_x$ laser cladding layers belong to the HEAs according to the perspective of thermodynamics.

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**Figure 1.** XRD detection results and microstructure of the FeCoCrNiMnAl$_x$ cladding layers: (a,a1), $x = 0$; (b,b1), $x = 0.25$; (c,c1), $x = 0.5$; and (d,d1), $x = 0.75$. 

![XRD detection results and microstructure of the FeCoCrNiMnAl$_x$ cladding layers](image-url)
Figure 2. EBSD detection results of the FeCoCrNiMnAl\textsubscript{x} cladding layers: (a\textsubscript{1}) \textit{x} = 0, FCC (Face-Centered Cubic structure) phase (red zone); (b\textsubscript{1}) \textit{x} = 0.25, FCC phase; (c\textsubscript{1}) \textit{x} = 0.5, FCC phase; (d\textsubscript{1}) \textit{x} = 0.75, FCC phase; (a\textsubscript{2}) \textit{x} = 0, grain boundaries; (b\textsubscript{2}) \textit{x} = 0.25, grain boundaries; (c\textsubscript{2}) \textit{x} = 0.5, grain boundaries; (d\textsubscript{2}) \textit{x} = 0.75, grain boundaries and BCC phase (blue zone).

Table 2. EDS detection results of dendritic and interdendritic spaces of FeCoCrNiMnAl\textsubscript{x} cladding layers (at.%).

| Regions | Fe  | Co  | Cr  | Ni  | Mn  | Al  |
|---------|-----|-----|-----|-----|-----|-----|
| A       | 23.4| 22.9| 10.1| 23.5| 20.1| 0   |
| B       | 20.2| 19.8| 21.7| 18.7| 19.6| 0   |
| C       | 23.6| 21.9| 9.7 | 22.1| 19.0| 3.7 |
| D       | 21.9| 17.6| 19.1| 17.9| 18.0| 5.5 |
| E       | 25.4| 21.5| 10.2| 18.5| 19.9| 4.5 |
| F       | 20.3| 21.6| 17.3| 16.8| 17.0| 7.0 |
| G       | 25.2| 20.0| 9.5 | 17.6| 18.4| 8.8 |
| H       | 17.7| 15.7| 18.3| 17.2| 17.1| 13.6|
Table 3. EDS results of the FeCoCrNiMnAl\(_x\) cladding layers (at.%).

| Cladding Layers | Al     | Cr     | Mn     | Fe     | Co     | Ni     |
|-----------------|--------|--------|--------|--------|--------|--------|
| FeCoCrNiMnMn    | -      | 20.06  | 19.96  | 20.03  | 19.93  | 19.48  |
| FeCoCrNiMnMnA\(_{0.25}\) | 3.76  | 18.64  | 18.54  | 19.4   | 19.91  | 19.75  |
| FeCoCrNiMnMnA\(_{0.5}\) | 7.01  | 18.74  | 18.76  | 19.95  | 17.93  | 17.91  |
| FeCoCrNiMnMnA\(_{0.75}\) | 10.01 | 18.34  | 17.92  | 19.59  | 17.03  | 17.11  |

3.2. High-Temperature Wear Test Results of the FeCoCrNiMnAl\(_x\) Coatings

Figure 3 shows the high-temperature wear test results of the FeCoCrNiMnAl\(_x\) cladding layers. The wear mass losses of the four cladding layers were 19, 15, 7 and 4 mg, respectively. The wear loss weights of the FeCoCrNiMnAl\(_{0.25}\), FeCoCrNiMnAl\(_{0.5}\) and FeCoCrNiMnAl\(_{0.75}\) cladding layers, respectively, reduced by 21.1%, 63.1% and 79.0% compared with the FeCoCrNiMn cladding layer. Figure 3a–d shows the relationship curves between the friction coefficients of the FeCoCrNiMnAl\(_x\) cladding layers and the friction time at 600 °C. Friction coefficients in the initial stage are lower because the tungsten steel ball had not been adequately contacted with the cladding layer. The average friction coefficients of the four HEA cladding layers, at the stable wear stage, were 1.1591, 1.0202, 1.0596 and 0.7982, respectively. The change rules of the wear mass losses and friction coefficients indicate that Al element significantly improved the high-temperature wear resistance of the HEA cladding layers.

The wear widths of the FeCoCrNiMnAl\(_x\) cladding layers were 2.24, 1.62, 1.18 and 1.04 mm, respectively, as shown in Figure 3a1–d1. All the four HEA cladding layers contain oxidation wear morphologies. In addition, the worn surface of the FeCoCrNiMn coating appeared to have serious bulking and accumulation due to plastic deformation. Therefore, the wear morphology of the
FeCoCrNiMn coating is combined with oxidative wear and adhesive wear. The wear morphologies of the FeCoCrNiMnAl_{0.25} and FeCoCrNiMnAl_{0.5} coatings consist of oxidative wear, adhesive wear and a small amount of abrasive wear because of ploughing that appeared on the worn surfaces. The worn surface of the FeCoCrNiMnAl_{0.75} coating shows no obvious peeling and adhesion, and the wear mechanism is oxidation wear and abrasive wear.

3.3. High-Temperature Wear Mechanism of the FeCoCrNiMnAl_{x} Coatings

3.3.1. Anti-plastic Deformation Mechanism of the FeCoCrNiMnAl_{x} Coatings

Nano-indentation load-displacement curves of the FeCoCrNiMnAl_{x} cladding layers are shown in Figure 4. The peak loads of the four cladding layers are 19.503, 19.664, 19.833 and 20.884 mN, respectively. The anti-plastic deformation abilities of the FeCoCrNiMnAl_{0.25}, FeCoCrNiMnAl_{0.5} and FeCoCrNiMnAl_{0.75} cladding layers were, respectively, increased by 0.8%, 1.7% and 7.1% compared with the FeCoCrNiMn cladding layer. Meanwhile, the average elastic modulus of the four HEA cladding layers are 210.02, 191.104, 179.138 and 173.953 GPa, respectively. The results show that the FeCoCrNiMnAl_{0.75} coating has a higher hardness and stiffness than other three HEA coatings.

On the one hand, the significant difference of the atom radii between the Al element (1.43 Å) and the other four elements (i.e., Fe (1.26 Å), Mn (1.27 Å), Co (1.25 Å), Cr (1.28 Å) and Ni (1.25 Å)) aggravated the lattice distortion effect of the HEA. The increased content of Al element gradually increased the lattice distortion effect. Ultimately, normal grain growth was limited because the diffusion of atoms was hindered [20]. Therefore, fine-grain strengthening is one of the main methods for anti-plastic deformation of the cladding layers. On the other hand, both FCC and BCC structures contain 12 slip systems. However, FCC structures have four slip directions, while BCC structures have only 2. The direction and magnitude of the total dislocations in FCC structures are $1/2<110>$ and $\sqrt{2}/2$, respectively, while those in BCC structures are $1/2<111>$ and $\sqrt{3}/2$, respectively. An FCC structure has more slip direction and smaller Burgers vector than a BCC structure. It also contains more slip-conducive edge dislocation for motion, which is more likely to cause plastic deformation [21–25]. Therefore, the BCC phase has a greater ability to resist plastic deformation and plays a solid solution strengthening role in the FeCoCrNiMnAl_{0.75} coating.

As a result, major hardening in the FeCoCrNiMnAl_{0.75} HEA cladding layer is by a combination of refinement of the microstructure and presence of the hard BCC phase.

3.3.2. High-Temperature Oxidation Mechanism of the FeCoCrNiMnAl_{x} Coatings

Figure 5a–d shows that the oxidation mass gain curves of the FeCoCrNiMnAl_{x} cladding layers present a parabolic shape. The oxidation mass gain curves consist of a rapid oxidation stage (0–20 h) and a slow oxidation stage (20–100 h). The mass gains of the four cladding layers were 0.299, 0.261,
0.221 and 0.189 mg/cm², respectively. Oxides on the surface of the FeCoCrNiMn cladding layer present a microstructure of stacked clusters, and formation of an incomplete oxide film, as shown in Figure 5a1. Combined with EDS results in Table 4 and XRD results in Figure 6, it can be seen that the stacked cluster structure is composed of Mn₃O₄ (i.e., A zone), and the gap is Cr₂O₃ (i.e., B zone). After Al element was added to the cladding layers, the content of Mn₃O₄ in the oxide layer gradually decreased, while the compact small-sized oxide (i.e., D, F and G zones) appeared and gradually increased. EDS and XRD detection results show that this kind of oxide is Al₂O₃ instead of Cr₂O₃. A complete Al₂O₃ oxide film was formed on the surface of the FeCoCrNiMnAl₀.75 cladding layer, as shown in Figure 5d1. Therefore, this HEA cladding layer had the best high-temperature oxidation resistance.

Figure 5. Oxidation mass gains and microstructures of surface oxides of the FeCoCrNiMnAlₓ cladding layers: (a,a1) x = 0; (b,b1) x = 0.25; (c,c1) x = 0.5; (d,d1) and x = 0.75.

| Elements | O   | Al  | Cr  | Mn  | Fe  | Co  | Ni  |
|----------|-----|-----|-----|-----|-----|-----|-----|
| A        | 48.19 | 0   | 8.16 | 26.80 | 6.95 | 4.07 | 5.83 |
| B        | 50.90 | 0   | 33.21 | 5.39  | 4.34 | 2.69 | 3.47 |
| C        | 51.55 | 0.31 | 1.52 | 38.23 | 5.09 | 1.53 | 1.77 |
| D        | 53.56 | 35.71 | 2.33 | 2.72  | 2.79 | 1.51 | 1.40 |
| E        | 51.14 | 2.03 | 2.45 | 38.35 | 2.69 | 1.90 | 1.44 |
| F        | 53.56 | 35.70 | 2.41 | 2.69  | 1.71 | 1.96 | 1.97 |
| G        | 54.35 | 36.24 | 2.37 | 2.58  | 1.44 | 1.63 | 1.39 |
Figure 6. Phases in the oxidation layer of the FeCoCrNiMnAl\textsubscript{x} cladding layers after 100 h high-temperature oxidation.

The oxidation kinetics curves of the FeCoCrNiMnAl\textsubscript{x} cladding layers were fitted by using the high-temperature oxidation parabolic model. The high-temperature oxidation parabolic kinetic equation was used to calculate the oxidation rate:

\[ x^2 = at \]  \hspace{1cm} (3)

where \( x \) is the oxidation mass gain per unit area, \( a \) is the parabolic velocity constant of the oxidation reaction (the rate of oxidation) and \( t \) is the oxidation time. Oxidation kinetic data of the four HEA coatings at the slow oxidation stage are put into Equation (3) for linear fitting, and the results are shown in Figure 7. The relationships between the square of oxidation mass gain and the oxidation time are approximately linear. The oxidation mass gain rate of the FeCoCrNiMnAl\textsubscript{0.75} cladding layer was lower than those of other cladding layers, which further proved that the FeCoCrNiMnAl\textsubscript{0.75} cladding layer had a better high-temperature oxidation resistance capability.

The oxide film thicknesses of the FeCoCrNiMnAl\textsubscript{x} cladding layers were 2.38, 1.93, 1.66 and 0.82 \( \mu \)m, respectively, as shown in Figure 8a1–d1. The oxide film of the FeCoCrNiMn cladding layer exclusively contains Cr and Mn elements, while Co, Ni and Fe elements are undetectable, as shown in Figure 8a2. The oxide film can be divided into two layers: a thicker Mn-rich outer layer and a thinner Cr-rich inner layer (near the bottom of the HEA cladding layer). The Al element began to distribute in the oxide films of the FeCoCrNiMnAl\textsubscript{0.25} and FeCoCrNiMnAl\textsubscript{0.5} cladding layers, and the content was increasing gradually, as shown in Figure 8b2,c2. The oxide film on the surface of the FeCoCrNiMnAl\textsubscript{0.75} coating could be divided into three layers: a Cr-rich inner layer, a Mn-rich middle layer and a thinner Al-rich outer layer, as shown in Figure 8d2.
The oxidation kinetics curves of the FeCoCrNiMnAl\textsubscript{x} cladding layers were fitted by using the high-temperature oxidation parabolic model. The high-temperature oxidation parabolic kinetic equation was used to calculate the oxidation rate:
\[ \dot{x} = a t \]
where \( \dot{x} \) is the oxidation mass gain per unit area, \( a \) is the parabolic velocity constant of the oxidation reaction (the rate of oxidation) and \( t \) is the oxidation time. Oxidation kinetic data of the four HEA coatings at the slow oxidation stage are put into Equation (3) for linear fitting, and the results are shown in Figure 7. The relationships between the square of oxidation mass gain and the oxidation time are approximately linear. The oxidation mass gain rate of the FeCoCrNiMnAl\textsubscript{0.75} cladding layer was lower than those of other cladding layers, which further proved that the FeCoCrNiMnAl\textsubscript{0.75} cladding layer had a better high-temperature oxidation resistance capability.

The oxide film thicknesses of the FeCoCrNiMnAl\textsubscript{x} cladding layers were 2.38, 1.93, 1.66 and 0.82 μm, respectively, as shown in Figure 8(a1–d1). The oxide film of the FeCoCrNiMn cladding layer exclusively contains Cr and Mn elements, while Co, Ni and Fe elements are undetectable, as shown in Figure 8(a2). The oxide film can be divided into two layers: a thicker Mn-rich outer layer and a thinner Cr-rich inner layer (near the bottom of the HEA cladding layer). The Al element began to distribute in the oxide films of the FeCoCrNiMnAl\textsubscript{0.25} and FeCoCrNiMnAl\textsubscript{0.5} cladding layers, and the content was increasing gradually, as shown in Figure 8(b2,c2). The oxide film on the surface of the FeCoCrNiMnAl\textsubscript{0.75} coating could be divided into three layers: a Cr-rich inner layer, a Mn-rich middle layer and a thinner Al-rich outer layer, as shown in Figure 8(d2).

Figure 7. Oxidation kinetics regression curves of the FeCoCrNiMnAl\textsubscript{x} cladding layers.

Figure 8. Microstructures and EDS results of the cross-sections of oxide films on the surface of the FeCoCrNiMnAl\textsubscript{x} cladding layers: (a1,a2) \( x = 0 \); (b1,b2) \( x = 0.25 \); (c1,c2) \( x = 0.5 \); and (d1,d2) \( x = 0.75 \).
As the oxidation process continued, a few O atoms entered the areas between the cladding layer and the inner film (i.e., Cr$_2$O$_3$ oxide) and inner film (i.e., Cr$_2$O$_3$ oxide) were formed, as shown in Figure 9(d2). Moreover, transient Cr$_2$O$_3$ was used as a nucleated particle of the steady Al$_2$O$_3$ due to the same corundum crystal structure of these two oxides [30]; thus, formation of Al$_2$O$_3$ oxide in the oxidation process was further accelerated [31].

The Al$_2$O$_3$ oxide has a lower Gibbs free energy (−373.75 kJ/mol) than those of Cr$_2$O$_3$ and Mn$_2$O$_3$ oxides [26]. The Al$_2$O$_3$ oxide was preferentially formed and rapidly grew on the surface of the cladding layers, as shown in Figure 9a1,b1. The necessary conditions for the formation of the continuous dense oxide film are as follows: the volume of metal oxide film formed on the metal surface is larger than the volume of metal elements consumed to generate these oxide films, which is called Pilling-Bedworth Ratio (PBR) [28]. The PBR value of Al$_2$O$_3$ (1.28) is suitable among the oxides formed on the surface of the cladding layers due to rapid oxidation of Mn atoms. In addition, since Cr$_2$O$_3$ has a lower standard Gibbs free energy than other oxides, Cr atoms and oxygen atoms entered the oxide film, rapidly forming Cr$_2$O$_3$ oxide, which further increased the thickness of the oxide film, as shown in Figure 9c1. As the oxidation process continued, these Mn$_2$O$_3$ and Cr$_2$O$_3$ oxides separated the inward diffusing alloying atoms from the outward diffusing alloying atoms, and then the oxidation rate of the cladding layer was reduced.

Figure 9a1–c1 shows the oxidation mechanism of the FeCoCrNiMnAl cladding layer. The standard Gibbs free energies of the Mn$_2$O$_3$ oxide (−306.70 kJ/mol) and Cr$_2$O$_3$ oxide (−251.70 kJ/mol) are less than those of the other three oxides [26], and the Mn element has a diffusion rate two magnitudes faster than the Cr element [27]. Mn atoms in the FeCoCrNiMnAl cladding layer firstly oxidized with the O atoms on the surface to form an incomplete thin Mn$_2$O$_3$ oxide film, as shown in Figure 9a1,b1. As the oxidation process continued, the thickness of the Mn$_2$O$_3$ oxide film increased rapidly, and a complete oxide film was formed. A Mn-depleted zone was generated on the subsurface of the cladding layer due to rapid oxidation of Mn atoms. In addition, since Cr$_2$O$_3$ has a lower standard Gibbs free energy than other oxides, Cr atoms and oxygen atoms entered the oxide film, rapidly forming Cr$_2$O$_3$ oxide, which further increased the thickness of the oxide film, as shown in Figure 9c1. As the oxidation process continued, these Mn$_2$O$_3$ and Cr$_2$O$_3$ oxides separated the inward diffusing O atoms from the outward diffusing alloying atoms, and then the oxidation rate of the cladding layer was reduced.
used as a nucleated particle of the steady Al$_2$O$_3$ due to the same corundum crystal structure of these two oxides [30]; thus, formation of Al$_2$O$_3$ oxide in the oxidation process was further accelerated [31].

Insufficient content of Al element in the cladding layers (i.e., FeCoCrNiMnAl$_{0.25}$ and FeCoCrNiMnAl$_{0.5}$) made the dense Al$_2$O$_3$ oxide discontinuous, which could not play a good protective effect on the cladding metal. The Al element content in the FeCoCrNiMnAl$_{0.75}$ cladding layer was sufficient, and the continuous and dense Al$_2$O$_3$ effectively improved the high-temperature oxidation resistance of the cladding layer.

In conclusion, the good high-temperature oxidation resistance and anti-plastic deformation ability of the FeCoCrNiMnAl$_{0.75}$ cladding layer jointly determine its excellent high-temperature wear resistance. Therefore, the FeCoCrNiMnAl$_{0.75}$ cladding layer can effectively improve the high-temperature wear resistance of H13 steel.

4. Conclusions

(1) Adding Al element could not only refine the grain size of the FeCoCrNiMnAl$_x$ cladding layers, but also promotes formation of the second phase (i.e., BCC).

(2) Addition of Al element increased the hardness and wear resistance of the HEA coatings. Compared with the FeCoCrNiMn cladding layer, the high-temperature wear loss and anti-plastic deformation capacity of the FeCoCrNiMnAl$_{0.25}$ cladding layer were, respectively, reduced by 79% and increased by 7.1%.

(3) A dense Al$_2$O$_3$ oxide film was formed on the surface of the FeCoCrNiMnAl$_{0.75}$ cladding layer, whose oxidation resistance was enhanced by 36.79% compared to the FeCoCrNiMn cladding layer.

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