

Research Article

Effect of CeO₂ on High-Temperature Oxidation Performance of Electron Beam Cladding NiCoCrAlY Coating on Ni-Based Alloy

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In order to enhance the high-temperature oxidation resistance properties of Inconel 617 alloy, NiCoCrAlY and NiCoCrAlY CeO₂ composite powder coatings metallurgically bonded to substrate were prepared on the surface of Inconel 617 alloy by electron beam cladding. The effect of rare earth oxide CeO₂ on the oxidation resistance of NiCoCrAlY coating was investigated. The isothermal oxidation behavior of the substrate and NiCoCrAlY cladding layer with different CeO₂ contents (1%, 2%, 3%, and 4%) and without CeO₂ oxidized at 1050°C for 20 h, 40 h, 60 h, and 100 h was analyzed. The microstructure and phase composition of the coating after electron beam treatment were tested. The results show that the self-repair of Al₂O₃ and Cr₂O₃ oxide film can be improved under a high-temperature oxidation environment with the addition of CeO₂, and the oxidation resistance of NiCoCrAlY coating can be effectively strengthened by adding CeO₂. The improvement effect is most obvious when the content of CeO₂ is 2%.

1. Introduction

The Inconel 617 is a solid-solution-strengthened nickel-chromium-cobalt-molybdenum alloy. It has excellent properties such as high-temperature yield strength, creep strength, and good corrosion resistance. Therefore, it is used widely in turbine blades, guide vanes, and other high-temperature structural components. With the development of aerospace technology, turbines are developing in the direction of high flow ratio and high thrust-weight ratio. The temperature and pressure in the gas chamber are continuously improved, and the service environment faced by the engine and gas turbine blades is becoming more and more demanding, so the performance requirements of the blade are becoming stricter and stricter [1]. In order to improve the high-temperature properties of the matrix, a thermal barrier coating is usually used to reduce the working temperature of the hot-end alloy and prevent the high-temperature oxidation, corrosion, and wear of the alloy [2]. The selection of thermal barrier coating materials is limited by some basic conditions, such as high melting point, low thermal conductivity, thermal expansion coefficient

matching with high-temperature alloy matrix, no phase transformation occurring between room temperature and working temperature, and good chemical stability [3].

The oxidation resistance of NiCoCrAlY bonded coating is one of the most important high-temperature protection properties, which has a vital impact on the service performance and service life of the double-layer thermal barrier coating [4, 5]. Under high-temperature conditions, Cr and Al in NiCoCrAlY coating can form a dense oxide film on the surface to prevent further oxidation of the coating and matrix. However, as time goes on, the thickness of the oxide film increases. When the oxide film increases to the critical thickness, the stress between the oxide film and the NiCoCrAlY coating promotes the crack initiation and propagation, which eventually leads to the oxide film spalling and the failure of the whole coating. In addition, for low-Al NiCoCrAlY coating, a small amount of Al₂O₃ and Cr₂O₃ are formed by high-temperature oxidation, while Cr₂O₃ film is easily converted to volatile CrO₃ at high temperatures above 900°C, thus gradually thinning the oxide film and reducing the oxidation performance of the coating [6].

Doping rare earth compounds can increase coating activity. It has a significant effect on reducing the critical content of Cr_2O_3 film, decreasing the growth rate of Cr_2O_3 film, and improving the adhesion of Cr_2O_3 film [7–9]. CeO_2 is a commonly used rare earth oxide to modify the material. The introduction of CeO_2 into the electron beam cladding NiCoCrAlY coating can simultaneously exert the fine grains obtained by the electron beam cladding and the active effect of rare earth elements, so as to improve the high-temperature oxidation resistance of the coating. In this paper, the isothermal oxidation experiments of NiCoCrAlY coating with Inconel 617 matrix, rare earth, and CeO_2 (1%, 2%, 3%, and 4%) were systematically studied, and the mechanism was discussed.

2. Experiment

The substrate used in the present work is Inconel 617 alloy, the size is a thickness of 10 mm and a square shape of 30×10 mm, and the chemical composition is shown in Table 1. Before cladding, the Inconel 617 matrix should be smoothed by 240#-800#SiC sandpaper and finally with acetone for soaking and scrubbing. The cladding layer is NiCoCrAlY alloy powders of particle size 140 + 350 (average particle size is $75 \mu\text{m}$). The CeO_2 reinforced composite powder was prepared by the method described in the literature [10]. For all samples, the content of CeO_2 was 1%, 2%, 3%, and 4%. The composite powder was deposited on the substrate surface by thermal spraying pre-coating method. Then, the optimized electron beam process parameters (scanning beam current 85 mA, frequency 60 Hz, high voltage 60 kV, focusing current 350 mA, bias sweep amplitude 4%, and scanning speed 1000 mm/min) were used for electron beam scanning cladding in a vacuum of 1.33×10^{-2} Pa.

The experimental samples with sizes of $6 \text{ mm} \times 6 \text{ mm} \times 6 \text{ mm} \times 6 \text{ mm}$ were obtained from the surface of the cladding coating and the matrix samples of the same size were prepared. In this experiment, the discontinuous weighing method was used. Under the static atmospheric pressure conditions, the matrix and the NiCoCrAlY/ CeO_2 + NiCoCrAlY alloy layer samples were simultaneously placed in the same high-temperature resistance furnace and stored for 100 hours at 1050°C . During the oxidation process, the weight gain of the sample was weighed by an electronic balance of model AR2130 with an accuracy of ± 0.1 mg, weighed once every 20 hours. Then, the function relationship between the weight gain ΔW (mg/cm^2) of the samples and time t was calculated, and the constant temperature oxidation kinetic curves of each sample was plotted. SEM and XRD were used to observe the surface and cross-sectional morphology of the oxidized coating and the composition of the oxide film.

3. Results and Analysis

3.1. Oxidation Power Curve. Figure 1 shows the isothermal oxidation kinetic curves of the original NiCoCrAlY coating and the NiCoCrAlY coating modified with 1%, 2%, 3%, and 4% CeO_2 at 1050°C . In order to facilitate the comparison

TABLE 1: Chemical composition of Inconel 617 alloy (wt.%).

Ni	Cr	Co	Mo	Al	C	Fe	Mn	Si	S	Ti	Cu
Remains	22	12.5	9	1.2	0.07	1.5	0.5	0.5	0.008	0.3	0.2

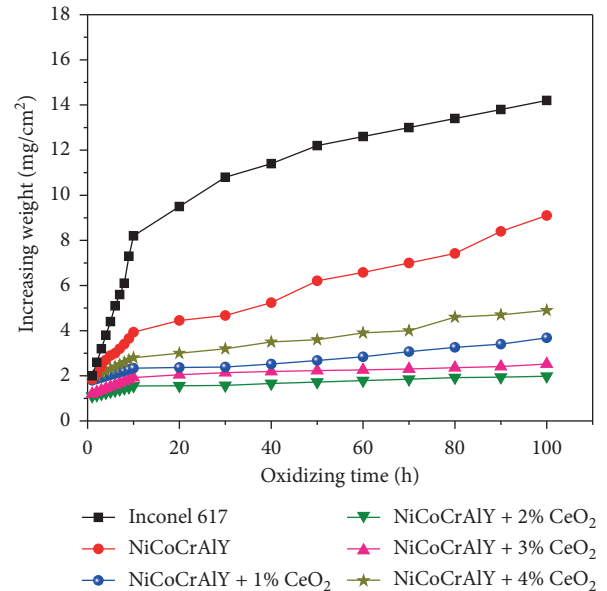


FIGURE 1: Oxidation kinetics of the substrate and coating.

with Inconel 617 matrix, the oxidation kinetic curves of the Inconel 617 matrix are included in Figure 1.

The following can be seen from Figure 1. (1) The initial weight gain of Inconel 617 matrix is obvious, the oxidation weight gain shows a large slope rising linearly at 0~10 h, the weight gain slows down within 20 h~70 h and then increases small slope straight line after 70 h, and the weight gain after oxidation for 100 h reached $13.96 \text{ mg}/\text{cm}^2$. (2) When the rare earth CeO_2 is not added, the weight gain of the NiCoCrAlY cladding coating is obvious at the initial stage of oxidation. It is oxidized for 10 h at 1050°C and has gained $4.132 \text{ mg}/\text{cm}^2$. During the oxidation for 40 h~70 h with the increase of oxidation time, the rate of change in oxidative weight gain is gradually decreasing. When the oxidation time reaches 70 h, the rate of change of oxidative weight gain gradually becomes larger. After oxidation of 100 h, its weight gain has reached $9.658 \text{ mg}/\text{cm}^2$. (3) The high-temperature oxidation resistance of the cladding coatings with 1% CeO_2 and 3% CeO_2 was improved and the weight gain was stable during the later oxidation process. After high-temperature oxidation for 100 h, the oxidative weight gain was $4.058 \text{ mg}/\text{cm}^2$ and $2.915 \text{ mg}/\text{cm}^2$. (4) The addition of 2% CeO_2 cladding coating has the best high-temperature oxidation resistance and the oxidation weight gain is the smallest at the initial stage of oxidation; it enters the steady oxidation stage after oxidation for 10 hours. After high-temperature oxidation for 100 h, the oxidation increment is only $1.65 \text{ mg}/\text{cm}^2$. (5) The high-temperature oxidation resistance of the 4% CeO_2 cladding coating is relatively poor; at the initial stage of oxidation, the oxidation weight gain is also larger, but it is still smaller than the oxidation weight gain of the unadded

rare earth CeO₂ cladding coating; the oxidation weight gain was 1.942 mg/cm² within 10~60 h; it tended to be gentle after 60 h oxidation until the weight gain reached 6.153 mg/cm² at 100 h.

The analysis shows that the oxidation kinetic curves of Inconel 617 matrix and NiCoCrAlY cladding coating without the addition of rare earth CeO₂ follow the straight-line law within 1 h~10 h and follow the parabolic law within 10 h~70 h, which indicates that the coating enters the steady oxidation stage. After 70 h, the oxidation weight gain of the coating showed a linear change, and the slope changed greatly, indicating that the coating entered the oxidation instability stage. The oxidation kinetic curve of the coatings with rare earth CeO₂ follows the parabolic law at the initial stage of oxidation, which indicates that adding rare earth CeO₂ can reduce the time for the coating to enter the steady-state oxidation, and there is no oxidative instability in the whole experimental stage. On the one hand, in the initial stage of oxidation, the coating will be oxidized rapidly in a high-temperature oxygen-rich environment. At this time, Al in the coating and O in the air form a continuous and dense oxide film on the surface of the coating. With the continuous oxidation at high temperature, five kinds of NiCoCrAlY coatings successively entered the steady-state oxidation stage. At this time, the loss of oxide film coexisted with the formation, but the rare earth CeO₂ slowed the out-diffusion rate of Al in the coating and the formation rate of Al₂O₃ decreased. On the other hand, the rare earth CeO₂ can improve the coating structure, reduce the dilution ratio of the coating, and inhibit the interdiffusion of elements between the coating and the matrix, and some Cr in the NiCoCrAlY coating without adding CeO₂ is also involved in the high-temperature oxidation process, which also accelerates the oxidation rate of the coating. In addition, with the addition of rare earth CeO₂, the critical content of Cr element formed by Cr₂O₃ decreased, which accelerates the selective oxidation of Cr, so that the coating can form a continuous dense oxide film in a short time, thus shortening the coating time with antioxidant capacity. And due to the active effect of rare earth CeO₂, the oxidation rate of the Cr₂O₃ oxide film is also reduced. The addition of CeO₂ has a great influence on the improvement of the high-temperature oxidation resistance of the cladding layer. In order to make the chemical activity of rare earth more easily to play a role, it is necessary to select a reasonable amount of CeO₂. When the content of CeO₂ is 2%, the cladding layer can obtain the best high-temperature oxidation performance.

3.2. Coating Surface Oxide Film Morphology. Table 2 shows that the percentage of chemical elements in the NiCoCrAlY coating material is 18.64% Cr, 3.39% Al, 2.60% Co, 0.55% C, and 1% Y; the remainder is Ni. The composition of the samples was tested by spectroscopy and elemental analyzer; SEM and XRD were used to observe the surface and cross-sectional morphology of the oxidized coating and the composition of the oxide film after oxidation at 1050°C for 100 hours. The CeO₂ doped NiCoCrAlY coating was treated in the same way as shown in Figure 2.

TABLE 2: Chemical constituents of NiCoCrAlY (wt.%).

Elements	Cr	Al	Co	C	Y	Ni
Mass fraction	18.64	3.39	2.60	0.55	1	Bal.

It can be seen from Figure 2(a) that the coating without the rare earth CeO₂ particles has large pits, the surface has particles falling off, and the coating has poor oxidation resistance. After the addition of rare earth CeO₂, the coating remains intact after undergoing high-temperature oxidation. This is because the rare earth CeO₂ inhibits the diffusion of Cr in the matrix. The base layer is mainly composed of the NiAl phase with good oxidation resistance. As the oxidation time continues, a large amount of Al diffuses to the outer layer to form a dense Al₂O₃ film. It has a strong resistance to high-temperature oxidation, and the coating without adding CeO₂ is generally higher in the dilution rate during the preparation process, which results in higher Cr content in the coating. After initial high-temperature oxidation, Cr and Al on the surface of the coating participate in the oxidation reaction to form a mixed oxide film of Al₂O₃ and Cr₂O₃. With the advancement of the oxidation process, some Cr₂O₃ on the surface of the coating decomposes at a high temperature of 1050°C. Therefore, voids of different sizes appear on the surface oxide film, and these voids reduce the strength of the oxide film. Figures 2(b)–2(e) are the surface oxide film morphology of the coating after the isothermal oxidation of the 1%, 2%, 3%, and 4% rare earth CeO₂ coatings at 1050°C for 100 h. It can be seen that there is no obvious pit on the oxide film of the coating after the addition of rare earth CeO₂, but the surface oxide film added with 4% rare earth CeO₂ coating has poor adhesion, and the local oxide film peels off. The surface morphology of the rare earth CeO₂ modified coatings was compared comprehensively. The surface of the coating modified by 2% rare earth CeO₂ was the densest, and the dense and intact oxide film was maintained under high-temperature oxidation for 100 h.

Figure 3 shows the surface morphology of the coating after the Inconel 617 substrate is isothermally oxidized at 1050°C for 20 h, 40 h, 60 h, and 100 h. It can be seen from Figure 3(a) that the surface of the Inconel 617 substrate is relatively rough after being oxidized at 1050°C for 20 h, and the entire surface appears densely embossed and has a small number of agglomerates. Amplification of the oxidized topography reveals many voids, which are formed by the inward diffusion of the oxidation reaction. When the oxidation time reached 60 h, a large oxidation void appeared on the oxidized surface (Figure 3(c)), indicating that severe internal oxidation occurred at this time. When the oxidation time reaches 100 h, a large area of oxide film peels off on the oxidized surface, and the voids and cracks are obvious. This is because the substrate itself contains less Al, and the Al₂O₃ oxide film formed during the oxidation process is not dense and continuous; during the high-temperature oxidation period of 60 h~100 h, the Cr₂O₃ oxide film is easily volatilized or decomposed at a temperature above 1000°C. The O₂ diffuses inward when the oxide film is lost and continues to diffuse into the substrate, causing the appearance of

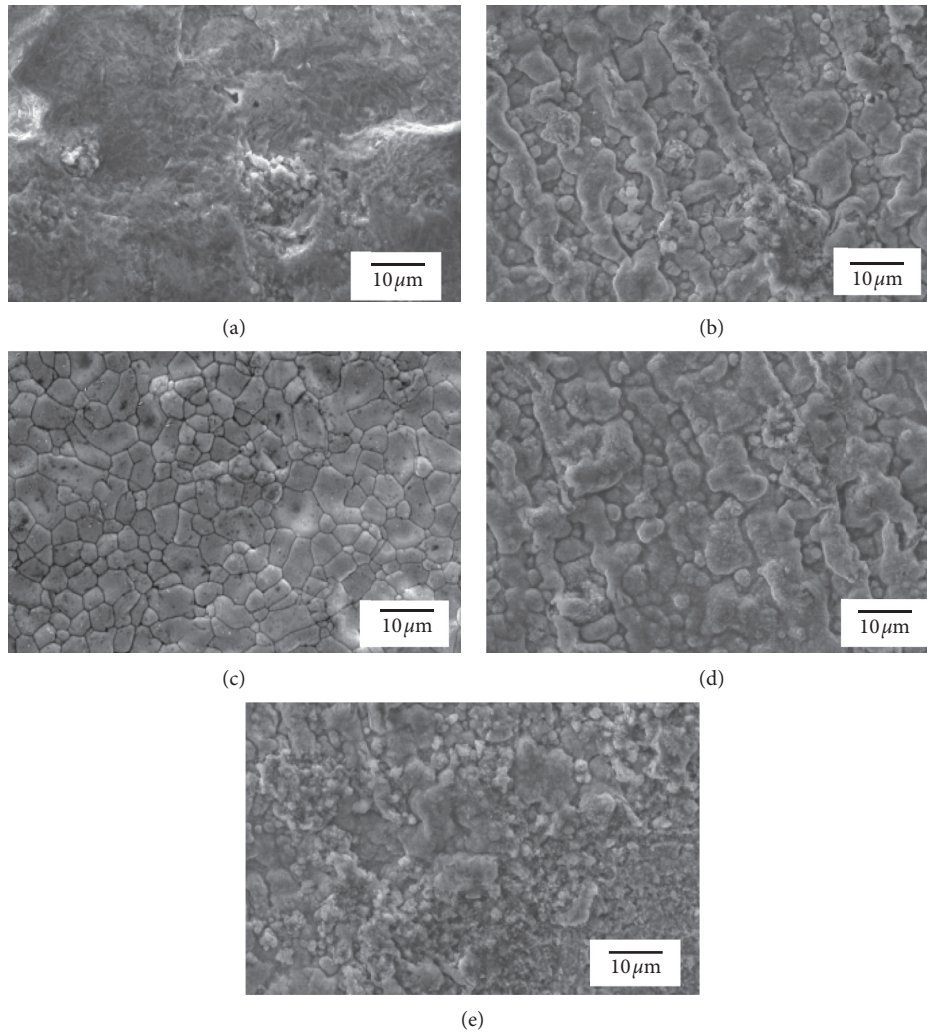


FIGURE 2: SEM morphology of the coating surface after isothermal oxidation for 100 h. (a) No CeO_2 . (b) Adding 1% CeO_2 . (c) Adding 2% CeO_2 . (d) Adding 3% CeO_2 . (e) Adding 4% CeO_2 .

cavities. The long-term high temperature causes the lost oxide film to peel off, and the surface is cracked [11–13].

3.3. Phase of Oxide Film. Figure 4 shows the XRD pattern of the surface oxide film of NiCoCrAlY coating after isothermal oxidation for 100 h at 1050°C. And Figure 5 shows the XRD pattern of the surface oxide film of NiCoCrAlY coating with 2% CeO_2 after isothermal oxidation for 100 h at 1050°C. It can be seen from Figures 4 and 5 that the surface oxidation product of the coating without adding rare earth CeO_2 is mainly composed of Cr_2O_3 and Al_2O_3 phases, containing a small amount of CrO_3 phase and NiCr_2O_4 phase, and there is no CeO_2 phase in the coating oxide film after adding rare earth CeO_2 , indicating that rare earth CeO_2 is decomposed by electron beam, the diffraction peaks of CrO_3 and NiCr_2O_4 phases disappear, while the intensity of diffraction peaks of Cr_2O_3 and Al_2O_3 phases is enhanced.

According to the analysis, it is slow-growing and stable oxide film can be formed on the surface of the coating, indicating that the coating has oxidation resistance. The

stability of the oxide film means that the oxide film does not melt, decompose, volatilize, crack, and peel off under oxidizing conditions. The Cr_2O_3 protective oxide film formed by NiCoCrAlY alloy has two crystal structures at high temperature, namely, rhombohedral $\alpha\text{-Cr}_2\text{O}_3$ which is stable at 300°C~900°C and transitional cubic crystal formed on the surface of metal chromium at the initial stage of oxidation- Cr_2O_3 . It is easy to oxidize volatile CrO_3 at a temperature higher than 900°C, causing the Cr_2O_3 film to become thinner so that the diffusion through this film is accelerated, the Al_2O_3 oxide film is much more stable than Cr_2O_3 at high temperature, and it has no volatilization [6]. In the high-temperature oxidation process of NiCoCrAlY coating without adding rare earth CeO_2 , although the standard free energy of forming Al_2O_3 is much lower than that of Cr_2O_3 , the Cr enriched on the surface of the coating is preferentially oxidized to form Cr_2O_3 , so in the surface oxidation of NiCoCrAlY coating. The membrane is mainly Cr_2O_3 . According to the surface activity theory of rare earth CeO_2 , rare earth atoms mainly diffuse along grain boundaries and other defects and segregate at grain boundaries, and large-

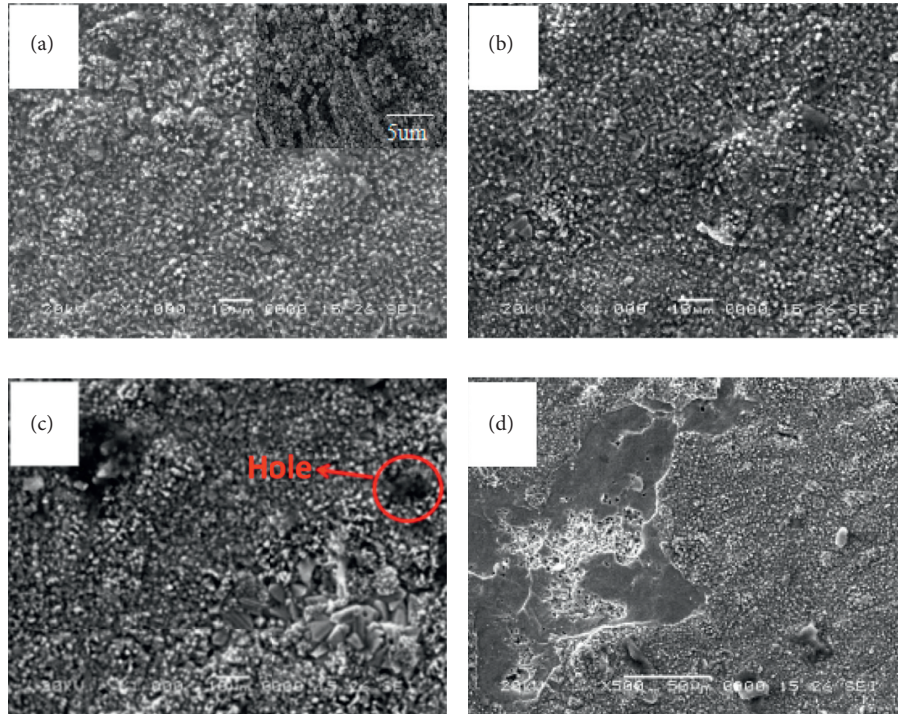


FIGURE 3: Surface morphology of substrate oxidized at 1050°C for 20 h, 40 h, 60 h, and 100 h. (a) Oxidizing the 20 h coating. (b) Oxidizing the 40 h coating. (c) Oxidizing the 60 h coating. (d) Oxidizing the 100 h coating.

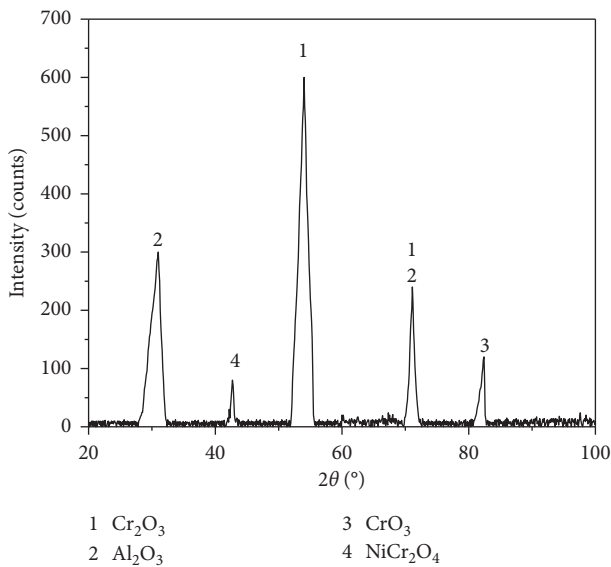


FIGURE 4: XRD pattern of the surface oxide film of NiCoCrAlY coating oxidized at 1050°C for 100 h.

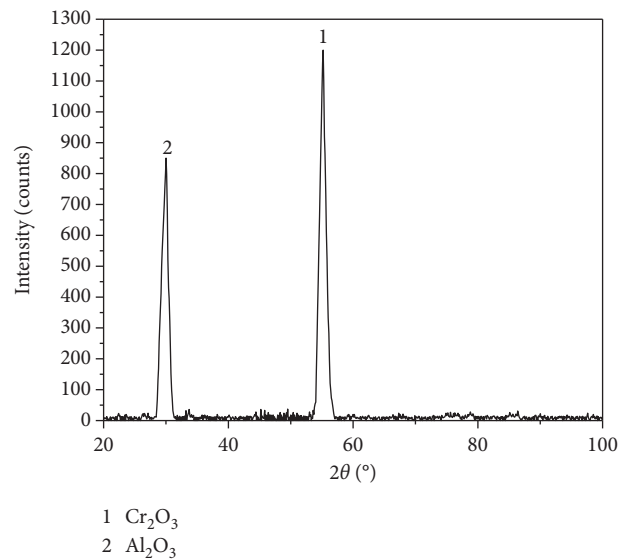


FIGURE 5: XRD pattern of the surface oxide film of NiCoCrAlY coating with 2% CeO_2 oxidized at 1050°C for 100 h.

scale rare earth atoms will hinder the movement of Al and Cr atoms along grain boundaries or dislocations; thereby, the addition of rare earth CeO_2 can suppress the diffusion of Cr element. The content of Cr from the inside to the outside is gradually reduced by the diffusion of elements in the matrix. At this time, selective oxidation of Al occurs. Secondly, rare earth elements can effectively reduce the growth rate of oxide film [14]. In a certain way, the rare earth element changes the relative short-circuit diffusion speed of the anion and cation

to a certain extent, so that the growth mechanism of the Cr_2O_3 film is reversed, which is the growth from the cation-diffusion-based growth to the anion-diffusion-based growth. The Cr_2O_3 oxide film has better stability at temperatures exceeding 1000°C. In addition, the addition of rare earth CeO_2 improves the self-healing property of the oxide film and reduces the consumption of oxide film forming elements in the self-repair process of the oxide film, the rare earth oxide particles are enriched in the grain boundary of

the oxide film, thereby the inward diffusion capacity of oxygen decreases, the partial pressure of oxygen in the channel is reduced, and the self-healing property of the oxide film is improved. Moreover, the consumption of Cr and Al in the oxide film self-repair process is much lower than that of the undoped rare earth CeO₂ coating. This explains the disappearance of the diffraction peak of the CrO₃ phase and the enhancement of the diffraction peaks of Cr₂O₃ and Al₂O₃ after the addition of rare earth CeO₂.

4. Conclusion

In this paper, the rare earth modified NiCoCrAlY coating was coated on the surface of Inconel 617 alloy by electron beam cladding technology, and then its high-temperature oxidation performance was studied. The main conclusions are as follows:

- (1) The oxide film formed by the NiCoCrAlY coating during the high-temperature oxidation period adheres to the surface of the coating to effectively suppress the occurrence of internal oxidation. The surface oxide film of the coating without adding rare earth CeO₂ is mainly composed of Cr₂O₃, Al₂O₃, CrO₃, and NiCr₂O₄, and local protrusion and shedding occur in the late oxidation stage. The outer oxide of the coating added with rare earth CeO₂ is mainly composed of Cr₂O₃ and Al₂O₃, which can remain dense and smooth after high-temperature oxidation for 100 h.
- (2) The addition of rare earth CeO₂ can improve the high-temperature oxidation resistance of NiCoCrAlY coating, and the addition of 2% is more significant. It not only effectively reduces the growth rate of the oxide film but also enhances the cohesive strength of the oxide film and reduces the tendency of the oxide film to peel off.
- (3) The NiCoCrAlY coating modified by CeO₂ can improve the self-repairability of Al₂O₃ and Cr₂O₃ oxide films in the high-temperature oxidation environment and promote the selective oxidation of antioxidant elements in the coating. Some rare earth CeO₂ particles are enriched in the grain boundary, interrupting the passage of O in the air to the inside of the coating and also slowing the oxidation in the coating.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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