Microstructure and Corrosion Behavior of Laser-Cladding CeO$_2$-Doped Ni-Based Composite Coatings on TC4

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1. Introduction

Titanium alloys are widely adopted for aerospace, defense, automobile, medical, and other applications due to their low density, high specific strength, good corrosion resistance, and fatigue resistance. Nevertheless, titanium alloys have many limitations, which include a high friction coefficient, weak erosion-corrosion, poor machinability, and relatively poor ability to resist high-temperature oxidation [1, 2]. The limitations have negatively affected the safety and reliability of Ti alloy components and limited their applications. Titanium and its alloys can be corroded in certain environments, especially in environments containing chloride ions. In such environments where the concentration of chloride ion is high, the corrosion attacks will be severe and thus the alloys are corroded. Ti-6Al-4V (TC4) alloy is generally resistant to corrosion, but it can also be rapidly corroded in corrosive environments where the protective oxide layer is destroyed. On the other hand, titanium has a great tendency to react with oxygen. Therefore, it is of importance to protect titanium alloys from corrosion attacks by forming a stable and continuous surface layer.

Different protection approaches such as plasma nitriding [3, 4], physical vapor deposition (PVD) [5–7], chemical vapor deposition (CVD) [8, 9], and plasma spraying process [10, 11] have been applied on Ti-6Al-4V for improving the corrosion resistance. Among these approaches, laser cladding is considered as a promising and effective method because of its large coating thickness, improved compact structure, and excellent performance [12–17]. Also, thanks to the high hardness, good wear resistance, and high-temperature oxidation resistance, Ni-based self-fluxing alloys are widely used in surface-strengthening technologies, such as laser cladding and thermal spraying. As such, this strategy
is often employed not only in academic research but also in industry practice. For instance, it is well known that the laser cladding of Ni-based alloys on the surface of steels can greatly improve the surface properties of the substrate materials. Other representative works are cited in the following. Li et al. [18] fabricated Ni-based composite coatings added with La₂O₃ on carbon steel through laser cladding. Liu et al. [19–21] examined the microstructure and tribological properties of laser-clad Ni-based high-temperature, self-lubricating, and wear-resistant composite coatings. Zhang et al. [22] prepared a Ni₆₀ alloy-cladding layer added with rare earth CeO₂ on the surface of 6063 Al alloys through laser cladding, and they achieved outstanding results. Farahmand et al. [16] investigated the effects of synthesizing a nano-WC powder and rare earth element (RE) on the obtained coatings were thoroughly evaluated.设计，laser-cladding experiments were carried out, and the obtained coatings were thoroughly evaluated.

2. Experimental Details

The substrate material of this experiment is the TC4 titanium alloy sheet. The chemical composition of TC4 titanium alloy is shown in Table 1. The substrates were prepared from a large TC4 titanium alloy sheet, which was cut to 100 mm × 100 mm × 10 mm by a wire electrical discharge machining (EDM) system. The Ni₂5 alloy powder and CeO₂ powder with different mass ratios were weighed by a balance. By using a QM3SP04L planetary ball-milling machine, the two powders were mixed and milled to ensure uniformity. The typical physical properties of CeO₂ and the chemical composition of Ni₂5 are shown in Tables 2 and 3.

Before laser cladding, the surfaces of TC4 substrate plates were cleaned by sandpapers, washed with alcohol, and then dried. An LDM2000 fiber laser processing system was employed for laser cladding, which consists of a 2000W fiber laser system, a powder feeder, and a 3-axis CNC mechanism. Argon gas was used as a protective gas for the cladding operation. The laser-cladding process parameters are listed in Table 4. After cladding, the samples were cut into rectangular specimens of dimensions of 10 mm × 10 mm × 3 mm with the wire EDM system.

The longitudinal section of the specimen was used for characterization. After being well polished with diamond paste and etched with an HF : HNO₃ : H₂O = 2 : 5 : 43 solution, the microstructure of the specimen was examined using a scanning electron microscopy (Nova Nano SEM 450) equipped with energy-dispersive X-ray spectroscopy (EDS) unit. The X-ray diffraction (XRD) data were recorded using a PW 1730 X-ray diffractometer (Philips, The Netherlands) with monochromated Cu Ka radiation at 40 kV and 40 mA in the 2θ range of 10–90°. Microhardness of the specimen was measured by using an HDX-1000 digital microhardness tester (Taiming Test Co., China), which consists of a square-based pyramidal diamond indenter with a 136° angle between two opposite faces. The static load applied was 50 g and the dwell time of loading was 15 sec. An average value of microhardness was taken from at least five different measurements. Immersion corrosion analysis was carried out using a CS310H electrochemical workstation. The 3.5% NaCl solution was chosen as the immersion medium and its pH was maintained at 6.5.

The corrosion resistance of the laser-cladding coatings was tested using an electrochemical work station. At the beginning of the experiment, the surface of each sample was polished with sandpapers and then wrapped with copper wire of 1 mm in diameter. The other exposed areas of the sample were sealed with 703 silicone rubber, and only a cylindrical surface of Φ6 mm was left on the surface of the sample. The sample was the working electrode, the saturated Mercury electrode was used as the reference electrode, the metal platinum sheet was used as the auxiliary electrode, and the reference electrode and the research electrode were connected by a salt bridge. A sodium chloride solution with a mass fraction of 3.5% was used as a reaction solution. The dynamic potential scan was performed at a scanning speed of 1 mV/s, and the scanning range was −1 V to +1.5 V.

3. Results and Discussion

Figure 1 shows the X-ray diffraction spectrum of laser-cladding coatings with different CeO₂ contents. The XRD result indicates that TiC, NiTi, Ni₃Ti, and Ti₃Ni exist in the laser-cladding coatings. It can be observed that the higher content of CeO₂ leads to the stronger the Ti₃Ni diffraction peaks. However, the types of other phases are not changed.

Figure 2 presents the macromorphology of coatings with different CeO₂ contents. It can be seen that there are no visible defects, such as lack of fusion and porosity, in the laser-cladding coatings. The number of cracks in the laser-cladding coatings varies with the rare earth CeO₂ content. When the content of CeO₂ is less than 2%, it can effectively reduce the crack generation of the laser-cladding coatings. When the content of CeO₂ is more than 2%, the number of cracks begins to increase again. As such, the proper amount of rare earth CeO₂ can effectively inhibit the laser-cladding cracks, and the excessive amount of rare earth CeO₂ can increase the number of laser-cladding cracks. The reason can be illustrated as follows. The addition of rare earth elements in the laser-cladding process can effectively refine the structure and increase the grain boundary. The crack propagation in the laser-cladding coatings is hindered and further reduces the harmful effect on the substances. All these lead to the improvement of strength and toughness of the laser-cladding coatings.
The formation of the crystal nucleus will bring about a free enthalpy reduction of the system which is the driving force of the nucleation. Moreover, the generated crystal nuclei are small and the degree of dispersion is high, which causes an increase in free enthalpy and resists the nucleation. It can be seen that the free enthalpy of the new grain boundaries plays an important role in the formation and development of crystal nuclei. With the increase of nucleation radius \( r \), the free enthalpy \( \Delta G \) of the whole solid-liquid system undergoes a process of rising first and then decreasing. Therefore, there exists a maximum value, which is the critical nucleation work. At this time, the nucleation radius of the whole solid-liquid system should be the critical radius \( r_k \) and \( r_k \) equation is calculated as \( r_k = 2\sigma/\Delta G \), in which \( \sigma \) is the surface tension on solid-liquid interface and \( \Delta G \) is the free volume change of unit volume.

Because of the strong electronegativity and active chemical properties of Ce atom, it is easy to fill the surface defects of alloy phase in liquid metal, so that the surface tension on the interface between the two phases is low. Based on \( r_k \) equation, it is understandable that the critical radius of the nucleus reduces after the reduction of surface tension, and the number of effective nucleation increases. As a result, the refinement of the microstructure can be achieved.

Figure 4 illustrates the point spectrum analysis of the cross section of sample S2, and it can be seen that the main elements in the coating are C, Ti, and Ni, and the atomic ratio of C and Ti is close to 1:1. Furthermore, the results of line scanning analysis from the substrate to the coating of sample S2 are shown in Figure 5. It can be seen that there are mainly Ti, Ni, C, and other elements in the coating. The Ni elements are mainly distributed in the coating layer, the Ti elements are distributed in the coating and the matrix, and the content in the substrate is higher. Other elements are distributed uniformly in the coating and the substrate, which indicates that the rare earth CeO\(_2\) is diffused into the substrate, and a metallurgical bond is developed between the coating and the substrate.

Figure 6 shows the microhardness distribution curves of laser-cladding coatings with various CeO\(_2\) contents. It can be seen that the curves follow a similar trend in which the microhardness is higher in the cladding layer and much lower in the substrate. More importantly, the hardness of cladding coatings appears to be different with various additions of CeO\(_2\). When the addition of CeO\(_2\) is at 0% and 1%, the maximum microhardness of cladding coatings is below 750HV\(_{0.05}\). When the amount of the rare earth CeO\(_2\) is 2%...
and 3%, the maximum microhardness of cladding coatings exceeds 900HV_{0.05}. The microhardness increase is expected in that the microstructure of the cladding layer is refined by the addition of rare earth elements. The rare earth oxide is dissolved in the solid solution and acts as a solid solution strengthening agent. The laser-cladding process is a non-equilibrium process, and it is possible to obtain the supersaturated solid solution of the rare earth element. The
Figure 3: Continued.
Figure 3: The SEM photographs of the laser-cladding coatings for different CeO₂ contents: (a–c) 0%, (d–f) 1%, (g–i) 2%, (j–l) 3%, (m–o) 4%, (p–r) 5%, and (s–u) 6%. (a, d, g, j, m, p, and s) The surface portion of coatings. (b, e, h, k, n, q, and t) The middle portion of coatings. (c, f, i, l, o, r, and u) The surface portion of coatings.

Figure 4: The point spectrum analysis of the cross section of sample S2: (a) the cross section of the S2 coating, (b) elements distribution of coating, and (c) the atomic ratio of elements.
formation of the solid solution will produce strong lattice distortion, resulting in significant solid solution strengthening. Nevertheless, with the further increase of CeO$_2$ content, the microhardness of the cladding layer gradually decreases because the excessive addition of rare earth oxides is easy to form internal inclusions with other components, which in turn decreases the density and the microhardness of the laser-cladding coating.

It can be seen from the above analysis that the amount of rare earth CeO$_2$ addition influences the phase composition, microstructure, density of cracks, and microhardness of the cladding coating. It is thus intuitive that the rare earth CeO$_2$ addition may have an effect on the corrosion resistance of the laser-cladding coating. The corrosion resistance of the laser-cladding coating with different contents of CeO$_2$ is obtained by an electrochemical work station.

Figure 7 shows the potentiodynamic polarization curves of samples added with different CeO$_2$ contents in 3.5% NaCl solution. For each sample, the test result consists of a cathode polarization curve and an anode polarization curve. The cathode polarization curves remain unchanged in the experiment, which means that none of all the cathode polarization processes are changed. With the increase of voltage, the anodizing starts to occur. It can be seen from the diagram that the self-corrosion potential of the sample with CeO$_2$ content of 2% is $-0.15 \text{ V}$, which is much higher than that ($-0.30 \text{ V}$) of the sample with rare earth content of 0%.

It shows that the addition of the proper amount of rare earth can improve the corrosion resistance of the laser-cladding coating. However, with the CeO$_2$ content higher than 3%, the corrosion potential decreases again. In particular, the corrosion potential of the coating decreases from $-0.2 \text{ V}$ (with 3% CeO$_2$) to $-0.45 \text{ V}$ (with 6% CeO$_2$). This is because the grains in the coating will be refined obviously when the amount of CeO$_2$ is moderate. With the increase of the number of crystals, the segregation of components can
be improved and the grain boundary can be prolonged, so the impurity density and the corrosion tendency at the grain boundary are reduced.

Figure 8 shows the Nyquist plot of the laser-cladding coating with different CeO$_2$ contents in a 3.5% NaCl solution. It can be seen that the diameter of the capacitive reactance circle in the Nyquist diagram is small, indicating that the laser-cladding coating is excellent in corrosion resistance in the high-frequency region. The Nyquist image is equivalent to a straight line at this time, indicating that the cladding layer is equivalent to an insulating layer with a large capacitance value and a small resistance value, which can effectively protect the titanium alloy substrate from corrosion. Moreover, the linear slope of 2% CeO$_2$ content is the largest, indicating that the corrosion resistance of the laser-cladding coating is the best when the rare earth content is 2%.

Figure 9 shows the bode plot of the laser-cladding coatings with different CeO$_2$ contents in a 3.5% NaCl solution. It can be seen that the high-frequency impedance increases with the increase of CeO$_2$ content, while the low-frequency impedance firstly increases and then decreases with the increase of CeO$_2$ content. The reduction of the low-frequency impedance means the decrease of the solution resistance, and the increase of the high-frequency impedance indicates that the grains in the coatings will be refined when the amount of CeO$_2$ is at a proper level.
4. Conclusions

In conclusion, this study shows that doping the Ni-alloy coatings with CeO₂ could change the microstructure and properties of the Ni-alloy coatings. The XRD result indicates that TiC, NiTi, Ni₃Ti, and Ti₂Ni phases exist in the laser-cladding coatings. The phase composition of the coatings does not change with the increase of CeO₂ content up to 6%. The microstructure of the sample with CeO₂ content of 2% is significantly refined, because the Ce atom reduces the critical radius of the crystal nucleus and the number of effective nucleus increases. When the rare earth addition exceeds the critical value, grain refinement effect starts to deteriorate, and the grains become coarser. The addition of CeO₂ can increase the microhardness of the coating. With 2% CeO₂, the maximum microhardness of the coating reaches over 900 HV₀.₀₅, while that of coating with 0% CeO₂ is below 750HV₀.₀₅. The addition of the proper amount of rare earth can significantly improve the corrosion resistance of the laser-cladding coating. This is because the grains in the coatings will be refined when the amount of CeO₂ is at a proper level.

Data Availability

The data used to support the findings of this study are included within the supplementary information files.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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