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High-Temperature Oxidation Property and Corrosion and Wear Resistance of Laser Cladding Co-based Coatings on Pure Zr Surface

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Abstract: Co-based alloy coating was prepared on Zr alloy using laser melting and cladding technique to study the difference in the high-temperature oxidation behavior between pure metal Co coatings and Co-T800 alloy coatings, as well as the wear resistance of the coatings. Besides, the effect of changing the laser melting process on the coatings was also investigated. The oxidation mass gain at 800-1200 °C and the high-temperature oxidation behavior during high-temperature treatment for 1 h of two coated Zr alloy samples were studied. Results show that the Co coating and the Co-T800 coating have better resistance against high-temperature oxidation. After oxidizing at 1000 °C for 1 h, the thickness of the oxide layer of the uncoated sample was 241.0 μ m, whereas that of the sample with Co-based coating is only 11.8–35.5 μ m. The friction wear test shows that the depth of the abrasion mark of the coated sample is only 1/2 of that of the substrate, indicating that the hardness and wear resistance of the Zr substrate are greatly improved. The disadvantage of Co-based coatings is the inferior corrosion resistance in 3.5wt% NaCl solution.

Key words: Zr metal; laser cladding; Co-based coating; high-temperature oxidation resistance; wear resistance

1 Introduction

Zirconium (Zr) and Zr alloys are chemically stable metallic materials with high strength, good ductility, and fine corrosionresistance, and they have a small thermal neutron absorption cross-section that other metals do not have^[1-5]. Metal Zr has an indispensable place in many significant capacity areas despite their exceptional benefits, which include good mechanical properties in high-temperature and high-pressure water environments, good corrosion resistance, and the ability to effectively prevent the escape of nuclear fission products^[6]. However, Zr has several disadvantages, including pitting corrosion, low hardness, poor wear resistance, and oxidization at elevated temperatures^[7]. It is crucial to improve the stability of Zr metal and to enhance its resistance against oxidation, corrosion, and surface wear to prolong its service life.

Many surface modification techniques have emerged in recent years, including laser cladding^[8], magnetron sputtering^[9-12], hot and cold spraying^[13], micro-arc oxidation^[14-15], and ion implantation^[16]. Nowadays, a common research focuses on the improvement in surface properties. Surface modification can be used to achieve desired qualities and to provide a notable improvement in the performance of specific area. The benefits of surface modification include a short research and development cycle, rapid result output, little raw material usage, energy saving, reduced emission,

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and adaptability to various environments with different coatings^[17].

The laser cladding technique creates a protective layer by rapidly melting the cladding material and the material surface under laser irradiation followed by cooling the melt pool^[18]. The coating is typically in a strong metallurgical bond with the base metal because of the special mechanism of laser cladding. As a result, the material surface experiences a variety of surface property changes depending on the type of coating materials^[19]. The laser cladding technique offers several advantages^[20-21], including the fine grain organization, high hardness, a small heat-affected region, compatibility with a wide range of materials, high material utilization rate, and absence of chemical contamination. Kim et al^[22] employed the laser cladding approach to fabricate a uniform chromium coating on the surface of zinc alloy. The oxidized mass gain of the Crcoated samples was only 1/29 of that of the uncoated samples. Furthermore, after oxidation at a high temperature of 1200 °C for 2000 s, the oxidized thickness of the Cr-coated samples was significantly smaller than that of the base samples.

Co-based alloys and their composites exhibit favorable characteristics, such as excellent high-temperature performance, notable resistance against corrosion and wear, and a diverse array of uses in high-temperature settings^[23]. Generally, cobalt alloys exhibit two distinct crystal structures: face-centered cubic structure and densely organized hexagonal structure. The clustered hexagonal structure is characterized by higher hardness and comparatively lower ductility^[24]. The incorporation of cobalt (Co), chromium (Cr), tungsten (W), and other elements into the powder has the potential to enhance the wear resistance of the coating and to enhance the performance under high-temperature conditions. The incorporation of silicon (Si) facilitates the process of grain refinement while concurrently promoting the deoxidation of slag. Currently, there is a growing interest in using cobaltbased alloy coatings to modify the surface of Ti alloys, but the cobalt-based alloy coatings on Zr alloys are rarely studied. Tong et al^[25] applied a Co coating onto the titanium alloy surface and observed that the coating primarily consisted of columnar crystals with a minor presence of dendritic crystals and other structures. Additionally, the coating hardness is approximately three times greater than that of the substrate.

The utilization of cobalt-based materials exhibits significant promise in the realm of laser cladding materials. Shahroozi et $al^{[26]}$ showed that the modest quantities of elements Ti and C in Co-based powders can enhance the coating hardness. The rationale behind this phenomenon is in the ability of these two elements to undergo reactions with Co, resulting in the formation of compounds. The presence of these compounds facilitates nucleation, thereby contributing to the process of grain refinement and enhancing the wear resistance of the coating. Weng et $al^{[27-28]}$ found that incorporating TiN, B_4C , and SiC hard particles into cobalt-based alloys can enhance the hardness and wear resistance of the coatings. Additionally, a strong correlation between the organization of the coating and the shape of the melt pool could be observed. Consequently, it is evident that both the formation and duration of the melt pool play a crucial role in achieving optimal coating organization.

In this research, the laser cladding technique was used to prepare Co-based alloy coatings on the surface of metallic zirconium, which is innovative in the selection of both the preparation technique and the used materials. The influence of Co-based coatings on the surface properties of metal Zr was investigated, such as high-temperature oxidation behavior, corrosion resistance, hardness, and wear resistance. This research provides a theoretical basis for the surface treatment method of metal Zr.

2 Experiment

2.1 Sample preparation

Pure Zr plates were used as the experiment material in this experiment. Before experiment, the Zr plates underwent a wire-cutting process to obtain samples with dimensions of 100 mm×200 mm for laser cladding process. To eliminate oxides from the metal surface, the cut sheet was subjected to sanding using 60# sandpaper. Additionally, alcohol cotton was employed to eliminate the surface oil.

Two types of cladding powders were used in this experiment. One was the 99.99%-pure spherical Co-metal powder and the other was Co-T800 alloy powder. The chemical composition of Co-T800 alloy is shown in Table 1. Scanning electron microscope (SEM) was used for microstructure observation. Fig. 1 shows SEM images of cladding powders.

YLS-4000-KC CO_2 fiber laser model was implemented through the synchronized delivery of powder. At the operation table, a prefabricated metal Zr plate was positioned, and the

Table 1 Chemical composition of Co-T800 alloy (wt%)

Cr	Ni	Fe	Si	Mo	С	S	S	Co
17.50	1.41	0.22	3.14	28.1	0.01	0.01	0.01	Bal.



Fig.1 SEM images of Co powder (a) and Co-T800 powder (b)

experiment was conducted with synchronized argon gas surrounding the laser head to protect the material. It was necessary to conduct vacuum seal to preserve the powder before and after experiment. Before laser melting, the powder material underwent sieving using a sieve of 106 μ m in specification to separate the larger particles to maintain the smoothness of the powder during the melting process. The sieved powder was then dried in a vacuum drying oven at 200 °C followed by sealing and preservation.

The preparation of Co-coated and Co-T800-coated Zr samples was conducted with certain process parameters: powder feed rate of 1.2 L/min and lap rate of 50%. The scanning speed for the preparation of Co coating was 50 mm/s. The scanning speed for the preparation of Co-T800 alloy coating was 50 and 30 mm/s, and the corresponding samples were denoted as Co-T800₁ and Co-T800₂, respectively. The laser powder for the preparation of Co coating was 1800 W. The laser powder for the preparation of Co coatings was 1800 and 2000 W, and the resultant samples were denoted as Co₁ and Co₂, respectively. Table 2 presents the process parameters of laser cladding for the preparation of different coatings.

The laser-coated samples were cut into cubes of 10 mm×10 mm×10 mm using EDM wire cutter. The coating surface was then ground by sandpaper. The samples were then cleaned in alcohol using ultrasonic cleaner for 10 min to get rid of all surface contaminants. Then, the samples were completely dried.

2.2 Experiment methods

The morphologies were observed by high magnification SEM (JSM-7100). The phases of the coated surface were analyzed by X-ray diffractometer (XRD, Bruker D8). The scanning speed was set at 6°/min, and the scanning range was $10^{\circ}-90^{\circ}$. MDI Jade analytical software was used to analyze XRD patterns. The element distribution of the coated samples was investigated by energy dispersive spectrometer (EDS).

A high-precision electronic balance (FA1204B) was used to measure the starting mass of the coated sample. A muffle furnace (KSL-1200X) was used to investigate the hightemperature oxidation behavior in air atmosphere of coated and uncoated Zr metal samples. The samples were subjected to high-temperature oxidation at 800, 900, 1000, 1100, and 1200 °C for 1 h to examine the alterations in coating surface morphology, diffusion layer thickness, and other related factors. The protocol for high-temperature oxidation is as follows. The temperature was initially set at 20 °C with a heating rate of 5 ° C·min⁻¹. The temperature was then

Table 2 Laser cladding process parameters for preparation of different coatings

Centing	T	Scanning	Powder feeding	
Coating	Laser power/w	speed/mm \cdot s ⁻¹	capacity/L·min ⁻¹	
Co-T800 ₁	1800	50	1.2	
Co-T800 ₂	1800	30	1.2	
Co ₁	1800	50	1.2	
Co ₂	2000	50	1.2	

maintained at a steady rate as it gradually increased to the goal temperature for 1 h. Subsequently, the temperature was cooled to room temperature in furnace. To ensure precise quantification of the mass alteration of the samples before and after high-temperature oxidation, all samples subjected to high-temperature oxidation were positioned within a ceramic crucible. After the oxidation process, the mass of the oxidized coating samples was recorded once again using an electronic balance. To determine the oxidized mass gain per unit area of the coating, the mass change and surface area of the sample were taken into account.

The corrosion resistance of the coatings was assessed using an electrochemical workstation (CHI660E). The corrosion process involved the utilization of 3.5wt% NaCl solution. This solution was composed of high-purity NaCl and deionized water. The corrosion characteristics of metal Zr in salt-rich environments can be replicated to simulate its practical application in the marine environment. The sample had a contact area of 0.5 cm². A fixture was used to securely attach the surface of the sample to the electrochemical workstation, ensuring direct contact with the corrosive solution. The initial measurement of the open-circuit potential (E_{orn}) of the sample under investigation was conducted, followed by the maintenance of a stable open-circuit potential for 1800 s. The initial potential of the electrochemical impedance was determined by inputting the measured value of the stabilized open-circuit potential. Subsequently, the electrochemical impedance spectra (EIS) of the samples were obtained, and impedance measurements were conducted within the frequency range from 10⁻² Hz to 10⁻⁵ Hz with an amplitude of 0.01 V. The data were obtained from curve fitting using the ZSimpWin impedance program to derive the fitted equivalent circuit and parameters. The electrochemical polarization curves were established with measurement conditions the speed of 0.01 V·s⁻¹ and the scanning range from -1.0 V to 2.5 V. The electrochemical polarization curves were acquired to determine the corrosion potential (E_{corr}) and breakdown potential $(E_{\rm h})$.

The Vickers hardness of the substrate and the surface of the coated samples after laser cladding was characterized using a microhardness tester (HMV-G-XY-S). A positive quadrangular conical diamond indenter was used as the indenter in the hardness tester. The Vickers hardness was determined by measuring the diagonal length of the indentation and subsequently calculating the associated Vickers hardness. Eight distinct places were randomly chosen to focus and spot in each sample plane. The applied stress load was 1.96 N with a symbol gauge of $HV_{0.2}$. The load retention duration was set at 10 s.

The comprehensive material surface property tester (CFT-I) was used to conduct reciprocal wear tests on the surfaces of the coating and the substrate. These test samples had a length of 5 mm. The computer recorded the changes in the coefficient of friction during the friction process. A profilometer was used to measure the profile of the abrasion marks after friction. The friction partner was chosen based on the friction of ceramic balls with diameter of 5 mm. The test

was conducted for 15 min with an applied load force of 20 N and a friction speed of 200 cycles/min.

3 Results and Discussion

3.1 Microstructure and physical phase

The post-laser cladding surface of the coating exhibits undulating streaks resulting from the superimposed laser movement on the substrate surface. Consequently, the coating surface was processed and ground using sandpaper. Fig. 2 displays SEM surface morphologies of Co-T800,, Co-T800, Co₁, and Co₂ coated samples. It can be seen that the coatings exhibit a relatively smooth and flat surface, which is devoid of apparent defects and possesses a high level of density. All four coatings have minuscule air holes, as indicated by the arrows in Fig.2. Besides, there are also minuscule cracks that cannot be readily detectable. The Co-T800 series coating surfaces have similar shapes to the Co series coating surfaces, and their overall performance is more compact and consistent, making it suitable to achieve a high-performance coating. Fig. 3 depicts SEM morphologies of the surfaces of Co series coatings. The surface microstructure exhibits dendrites and cellular crystals, which are intermixed with one another. This phenomenon results from the accelerated cooling of the laser fusion coating, which promotes dendritic growth. This hybrid structure exhibits exceptional mechanical capabilities. The development of this phase structure is primarily influenced by the cooling and shows no substantial association with the energy density of the laser.

The optimization of process parameters is of utmost importance in the context of laser cladding. To modify the energy density of the laser, it is necessary to decrease the scanning speed and to augment the laser power. The objective of these modifications is to attain coatings with superior quality and performance while maintaining the structural integrity of the substrate. Hence, it is imperative to conduct precise control and optimization over these process parameters to achieve the intended coating. The impact of process parameters on laser cladding coatings is highly intricate. For a comprehensive examination of the influence of process parameters on coating properties, it is necessary to conduct numerous repetitive experiments to analyze the underlying principles. However, this research primarily focuses on the performance evaluation of Co-based coatings, resulting in a relatively restricted investigation into the effects of laser energy density on coating performance.

Fig.4 displays XRD patterns of the surface of laser-melted Co-T800 series and Co series coatings. XRD patterns exclusively exhibit the diffraction peak associated with Co on both coating surfaces. XRD pattern of Co series coating exhibits a higher diffraction peak, which aligns with the standard diffraction card of Co metal. Conversely, XRD pattern of the Co-T800 series coating reveals a slight displacement in the position of the diffraction peak, but it is similar to the Co diffraction peak. However, the intensity of the diffraction peak is lower. Hence, the primary factor contributing to the decreased peak value of XRD diffraction peaks of the Co-T800 series coating can be attributed to the fact that the coating contains additional metal elements. These metal atoms are solidly dissolved within the Co lattice gap, leading to crystal structure distortion in the Co lattice. Consequently, the interference effect of X-rays on the crystal face is diminished, resulting in the manifestation of weak diffraction peaks in XRD pattern.

The thicknesses of Co series and Co-T800 series coatings are shown in Fig. 5. The Co-T800₁, Co-T800₂, Co₁, and Co₂ coatings have the thickness of 331.9, 613.1, 547.5, and 635.6 μ m, respectively. Through the optimization of laser process parameters, with the increase in laser energy density, the



Fig.2 SEM images of Co-T800₁ coating (a), Co-T800₂ coating (b), Co₁ coating (c), and Co₂ coating (d) on Zr substrate



Fig.3 SEM images of Co_1 coating (a) and Co_2 coating (b)



Fig.4 XRD patterns of Co series and Co-T800 series coatings

thickness of laser melted coating is increased. Furthermore, the cross-section morphology reveals a consistent transition

between the coating and the substrate in all samples. The interface between the coating and the substrate is apparent, which is devoid of any apparent defects.

The cross-section morphologies and corresponding EDS element distributions of the Co-T800 series and Co series coatings are shown in Fig.6. Fig.6a displays the cross-section morphology of Co-T800₁ coating, revealing that the upper half of the coating consists primarily of elements Co, Mo, and Cr with a little evenly distributed Si. The predominant element in the lower portion of the substrate is primarily Zr. In the coating, the concentration of Zr is comparatively lower than that in the substrate.

During the laser cladding process, the inclusion of a tiny quantity of Si atoms can effectively adsorb contaminants and enhance the purity of the melt pool on the substrate surface.

Additionally, the incorporation of elements Mo and Cr can contribute to the reinforcement of the coating. The coating exhibits a more homogeneous distribution of elements, which is devoid of element bias aggregation, establishing a solid basis for generation of coating with favorable performance characteristics.

The performance of the coating is contingent upon the compatibility and bonding process between the coating and the substrate. The establishment of robust compatibility between the coating and the substrate is crucial to prevent the occurrence of flaking and peeling, thereby enhancing the service life and stability of the coating performance.

In contrast to Co-T800 series coatings, the pure metal Co series coatings lack additional metal components, resulting in the absence of lattice distortions. Consequently, these coatings exhibit enhanced flexibility and improved resistance against high-temperature thermal shocks. However, it is worth noting that the strength of pure metal Co series coatings is relatively lower. According to Fig. 6c – 6d,



Fig.5 SEM cross-section images of Co-T800, coating (a), Co-T800, coating (b), Co, coating (c), and Co, coating (d)

elements Co and Zr exist in the coatings. Additionally, XRD analysis of these coatings reveals that Co is the predominant phase, whereas Zr is firmly dissolved within the lattice

interstitials within the solid solution of Co. Co_2 coating exhibits a comparable element distribution to Co_1 coating, but their thicknesses are different.



Fig.6 SEM cross-section morphologies and corresponding EDS element distributions of Co-T800₁ coating (a), T800₂ coating (b), Co₁ coating (c), and Co₂ coating (d) on Zr substrate

3.2 High-temperature oxidation properties

High-temperature oxidation experiments were conducted on the samples at 800, 900, 1000, 1100, and 1200 $^{\circ}$ C. Fig. 7 shows the surface morphologies of uncoated and coated samples after oxidation at 1000 $^{\circ}$ C for 1 h. After oxidation at elevated temperature, the uncoated sample exhibits a white surface, accompanied by prominent irregular cracks and heightened peeling phenomenon. These phenomena suggest that the substrate surface suffers significant oxidation. Conversely, the Co series coatings exhibit a little surface fissure after oxidation.

Cracks and holes can still be observed on the surface of Co-T800 series coatings, but their number is significantly lower than that of the uncoated sample. The morphology of the Co-T800 series coating demonstrates the consistent homogeneity and a dense surface with only a minor number of cracks. In contrast to the Co-T800 series coatings, the Co series coatings exhibit superior performance after oxidation at 1000 ° C. These coatings have highly dense surface without visible cracks or faults. This result suggests that the coating effectively protects the substrate and therefore significantly extends its service life at elevated temperatures.

The quantity of oxygen assimilated by the sample surface can be estimated by measuring the oxidation mass gain of sample. Fig. 8 displays the oxidation mass gain of different samples, indicating that the mass of all samples is increased with the increase in oxidation temperature. However, it is noteworthy that the difference in oxidation mass gain between the coated and uncoated samples becomes increasingly prominent with the increase in oxidation temperature. The difference in oxidation mass gain between uncoated and coated samples becomes more obvious when the oxidation temperature is 1100 and 1200 °C. It can be inferred that the samples with Co series coatings have superior oxidation resistance at high temperatures.

Fig.9 illustrates the oxide layer thickness obtained from the uncoated and coated samples along with the corresponding EDS results. The results indicate that the uncoated sample has more pronounced oxidation phenomenon, and the interfaces of the oxide layer display a crisp laminar structure.

Element O diffuses into the substrate, including the oxide layer, to a distance of nearly 241.0 μ m. The Co-T800₁ coating exhibits a surface oxidation thickness of approximately 11.8 μ m. Similarly, the Co-T800₂ coating displays a comparable oxidation thickness of approximately 11.8 μ m. The Co₁ coating displays a thickness of approximately 20.9 μ m, whereas the Co₂ coating exhibits a thickness of approximately 35.5 μ m. These results suggest that at elevated temperatures, the Co-based coating samples exhibit a slower oxidation rate compared with the uncoated Zr substrate. Additionally, the coated samples demonstrate superior antioxidant properties. EDS analysis reveals that the oxygen is predominantly localized within the oxide layer, where



Fig.7 SEM images of sample surfaces after oxidation at 1000 $^{\circ}$ C for 1 h: (a) uncoated, (b) Co-T800₁ coating, (c) Co-T800₂ coating, (d) Co₁ coating, and (e) Co₂ coating



Fig.8 Oxidation mass gain of uncoated and coated samples after oxidation at different temperatures

oxidation predominantly occurs on the coating surface. Briefly, the thickness of the oxygen diffusion layer in the coated samples is about 1/20 - 3/20 of that in the uncoated sample.

However, according to Fig.9b-9c, it becomes more evident that elevated levels of oxygen are also present within the cracks of the coatings. This observation implies that the oxygen has the potential to facilitate deeper oxidation towards the substrate through these cracks. In contrast to the Co-T800 series coatings, the metal Co series coatings do not have cracks after oxidation, thus preserving the integrity of the coatings. However, it is worth noting that the Co coating experiences a greater degree of oxidation, resulting in a greater thickness compared with the Co-T800 series coatings. Therefore, it can be inferred that the pure metal coating exhibits superior thermal stability compared with the alloy coating, but the alloy coating exhibits better oxidation resistance than the pure metal coating. Additionally, the pure metal coating demonstrates good molding quality, and the alloy coating has an inferior heat resistance and is prone to cracking and defects.

The difference in high-temperature oxidation between the coating and the substrate becomes increasingly evident as the oxidation temperature rises. After oxidation at 1200 °C for 1 h, the Co-T800 series coatings exhibit notable surface deterioration, characterized by extensive cracking and peeling of the coating, resulting in a substantial decrease in substrate protection. The Co series coating surfaces exhibit minimal cracks and maintain strong adhesion to the substrate. Therefore, Co-based coatings exhibit greater resistance against the high-temperature oxidation compared with the Zr substrate. For instance, Co-T800 series coatings subjected to high-temperature oxidation at 1200 °C have cracks. Despite the slightly thicker oxide layer than the alloy coating, the Co coating effectively prevents the further diffusion of oxygen atoms after high-temperature oxidation at 1200 °C. Therefore, the coating protects the substrate and enhances the oxidation resistance at elevated temperatures.

It is found that the surface of the uncoated substrate has serious cracking phenomenon after high-temperature oxidation, whereas the surface of the Co series coating remains intact after high-temperature oxidation. This is because ZrO_2 at 800 – 900 ° C has a transition from the tetragonal crystal structure phase to the monoclinic crystal structure with the volume expansion of 3%-5%, resulting in cracking. The thermal stability of CoO is better, and there is no structural transformation, so the coating surface remains intact.

3.3 Electrochemical corrosion property

Fig. 10a shows the open-circuit potential-time curves for the uncoated and coated samples in 3.5wt% NaCl solution. The results indicate that the open-circuit potentials of the Co series and the Co-T800 series coatings are larger than those of the uncoated sample (substrate). The polarization curves of the uncoated substrate and the coated samples in 3.5wt% NaCl solution are shown in Fig. 10b. The corrosion potential (E_{rear}) in the polarization curve represents the pivotal moment when the curve transitions from a downward trend to an upward trend, i. e., the minimum value point of the curve. The corrosion potential is indicative of the sample potential at the onset of corrosion. The higher corrosion potential indicates greater difficulty in initiating the corrosion reaction. The breakdown potential, denoted as $E_{\rm b}$, refers to the electronic breakdown of the passivation film on the sample surface. When the potential alters, the polarization curve undergoes a transition from a smooth increase to a sudden increase. This variation signifies the stability of the passivation film reaction and the strength or weakness of its breakdown potential. A higher potential value indicates greater stability of the passivation film, resulting in improved corrosion resistance.

The polarization curves demonstrate that the corrosion potentials of the Co series coatings exhibit higher values than those of the substrate. This observation suggests that the coatings exhibit greater corrosion resistance than the Zr substrate. Furthermore, the corrosion potentials align with the results obtained from the open-circuit potentials. Nevertheless, the Co series coatings exhibit reduced breakdown potentials compared with the Zr substrate, suggesting that the passivation film on the coating surface has diminished corrosion resistance. The phenomenon of higher corrosion potential and lower breakdown potential is common, which can be attributed to the presence of small cracks on the laser-melted coating surface, which significantly impacts the stability of the passivation film. Consequently, the equilibrium state of the passivation film is disrupted, leading to the corrosion of the sample. From a kinetic perspective, the initiation of corrosion will lead to an escalation in the corrosion rate of the sample. The electrochemical polarization curve characteristics of different samples in 3.5wt% NaCl solution are shown in Table 3. The electrochemical polarization curves reveal that Co series coatings exhibit lower corrosion resistance compared with the Zr substrate. However, Co-T800 series coatings demonstrate slightly higher corrosion resistance than pure metal Co series coatings. Furthermore, enhancing the process parameters has a minimal effect on the corrosion resistance of Co series coatings.

EIS results of different samples in 3.5wt% NaCl solution



Fig.9 SEM images and corresponding EDS element distributions of different samples: (a) uncoated, (b) Co-T800₁ coating, (c) Co-T800₂ coating, (d) Co₁ coating, and (e) Co₂ coating



Fig.10 Open-circuit potential (a) and polarization curves (b) of uncoated and coated samples

are shown in Fig. 11a-11c. The fitted equivalent circuits are used to analyze the data. The Nyquist diagram in Fig. 11a displays the real and imaginary components of the impedance, which are represented by the horizontal and vertical coordinates of the diagram, respectively. The diameters of the arcs correspond to the magnitude of charge transfer capacity between the test sample and the electrolyte solution, namely capacitive arcs^[29]. The resistance against the charge transfer between the sample and the electrolyte solution is increased proportionally with the increase in the diameter of the capacitance arc, which infers the improved corrosion resistance.

Both the Co-T800 series and Co series coatings have smaller capacitive arc diameters compared with the Zr

samples in 5.5wt% NaCl solution							
Parameter	Uncoated	Co-T800 ₁	Co-T800 ₂	Co ₁	Co ₂		
$E_{\rm corr}/{ m V}$	-0.51	-0.37	-0.49	-0.46	-0.53		
$E_{\rm b}/{\rm V}$	0.34	0.25	0.26	-0.01	-0.17		

Table 3 Electrochemical polarization characteristics of different samples in 3 5wt% NaCl solution

substrate. This result suggests that the corrosion resistance of Co-T800 series and Co series coatings is weaker than that of the Zr substrate. In Fig.11b, the Bode mode diagram illustrates the relationship between the impedance of the mode value and the frequency of the wave. The resistance of the passivation film is represented by the intersection value of the data line and the vertical coordinate axis^[30]. During the low-frequency stage, the curve exhibits a slope of approximately -1, indicating a straight line. At this point, the resistance primarily arises from the capacitance response. When the curve intersects with the longitudinal coordinate axis, the passivation film resistance can be approximated. As the frequency increases, the curve exhibits a progressive shift towards a more gradual pattern. During this period, the resistance of the passivation film decreases, suggesting that the resistance at this stage is mostly influenced by the response of the electrolyte resistance.

The Bode phase angle diagram in Fig. 11c illustrates the relationship between the impedance of the phase angle and the frequency of the electric wave. A greater phase angle peak corresponds to a wider range of peaks, suggesting a higher level of corrosion resistance of the material^[31]. The Bode

phase diagram, Bode mode diagram, and Nyquist diagram all vield consistent results that the order of corrosion resistance of the samples from strong to weak is Zr>Co-T800 series coatings>Co series coatings. The impedance measurements exhibit concurrence with the result of electrochemical polarization curves. Therefore, the primary cause for the disparity in performance can be attributed to two factors: one is the laser melting procedure, which generates minor fissures on the coating surface, thereby impairing the corrosion resistance of the coating; the other is the comparatively weaker corrosion resistance of Co in comparison to Zr alloys. Consequently, the application of laser melting technique to Co coatings on Zr substrate does not effectively enhance the corrosion resistance. Furthermore, the enhancement of the process parameters does not yield a substantial alteration in the corrosion resistance of the coating. Hence, the laser cladding process parameters solely influence the molding characteristics of the coating, such as coating thickness and dilution rate. Conversely, the chemical properties of the coating have an indirect impact on the coating performance.

Table 4 displays the impedance parameters of different samples. The equivalent circuit diagram in Fig. 11d is fitted using the ZSimpWin software. This model demonstrates a strong correspondence with the experimental data^[32]. In this model, R_s denotes the resistance of the electrolyte solution, R_1 represents the resistance of the passivation film, and R_2 represents the coating resistance. R_1 and R_2 are connected in parallel with capacitors with capacities, separately. The two parallel circuits are then connected in series with R_s to create the overall fitted circuit. The initial parallel circuit depicts the phenomenon of ion diffusion over the passivation film after



Fig.11 Nyquist diagram (a), Bode mode diagram (b), Bode phase angle diagram (c), and equivalent circuit diagram (d) of uncoated and coated samples

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Table 4 Impedance parameters of different samples								
C	$R_s/\Omega \cdot \mathrm{cm}^2$	$R_1/\Omega \cdot \mathrm{cm}^2$	CPE ₁		$P/O m^2$	CPE ₂		
Sample			$Y_0/\mathbf{s}^n \cdot \mathbf{\Omega}^{-1} \cdot \mathbf{cm}^2$	n	$R_2/\Omega^2 \cdot \mathrm{cm}$	$Y_0 / \times 10^{-5} \mathrm{s}^n \cdot \Omega^{-1} \cdot \mathrm{cm}^2$	п	
Uncoated Zr	7.08	8.31×10^{2}	2.79×10 ⁻⁶	0.89	3.34×10 ⁵	2.45	0.91	
Co-T800 ₁	7.71	1.32×10 ⁴	3.25×10 ⁻⁵	0.96	3.91×10 ⁵	4.52	0.92	
Co-T800 ₂	7.24	2.61×10 ⁵	7.32×10 ⁻⁵	0.89	1.35×10^{4}	5.06	0.87	
Co ₁	7.73	9.41×10 ⁷	4.24×10 ⁻⁵	0.90	7.29×10 ³	2.62	0.96	
Co ₂	7.49	8.06×10 ³	6.39×10 ⁻⁶	0.95	2.64×10 ⁵	3.45	0.87	

Note: R_s denotes the resistance of the electrolyte solution; R_1 represents the resistance of the passivation film; R_2 represents the coating resistance; *n* represents the dispersion index of CPE; CPE₁ is the capacitance of the diffusion layer of the passivation film; CPE₂ is the capacitance of the protective layer of coating; Y_0 indicates true capacitance of CPE.

traversing the parallel circuit, which indicates the process of substrate corrosion. The capacitance of the diffusion layer of the passivation film and the protective layer of the coating is denoted as CPE₁ and CPE₂, respectively. These capacities are quantified using the symbols Q_1 and $Q_2^{[33]}$. *n* represents the dispersion index of the constant phase angle element (CPE), which is associated with the surface roughness of the sample. When *n*=0, the capacitance of CPE is equivalent to the resistance. Similarly, when *n*=1, the capacitance is equivalent to the CPE value^[34].

3.4 Hardness and wear resistance

The evaluation of materials in applications is significantly influenced by hardness and wear resistance. The response of materials to wear is a complex phenomenon that depends on both the wear system and the wear process^[35]. It is crucial to carefully consider specific material tribology indications while doing linear reciprocating wear tests using controlled environment friction and a wear tester. The reliability of the tested material is contingent upon several critical aspects, namely volume loss, coefficient of friction, and surface abrasion pattern. Researchers can obtain significant insights into the wear properties of different materials under controlled testing conditions by closely monitoring these indicators^[36].

Hardness tests were conducted on uncoated and coated samples. The surface microhardness of different samples is shown in Fig.12. The Zr substrate exhibits a microhardness of approximately 198 $HV_{0.2}$, the Co-T800 series coatings display the microhardness of approximately 600 $HV_{0.2}$, and the pure Co series coatings exhibit a microhardness of approximately 400 $HV_{0.2}$.

Fig. 13 displays the surface morphologies and coefficient of friction of uncoated and coated samples after frictional wear. The uncoated sample has the greatest width of wear, accompanied by adhesive pits along the wear edge. This wear morphology demonstrates the characteristics of severe adhesive wear. The coated samples all show smoother wear edges and smaller widths of wear marks. The Co series coatings exhibit narrower abrasion mark width, compared with the Co-T800 series coatings. A profilometer was used to measure the depth of the abrasion marks. According to



Fig.12 Surface microhardness of uncoated and coated samples

Fig. 13f, the Co_1 and Co_2 coatings exhibit the shortest of abrasion marks, measuring around 1/4 of the substrate depth. The abrasion mark width of the $Co-T800_1$ and $Co-T800_2$ coatings is the second thinnest, which is roughly half of the substrate depth.

Fig. 13g displays the abrasion trace obtained from the profilometer. The profile traces reveal that the uncoated sample exhibits a significantly larger abrasion profile (both in terms of width and depth) compared with the samples with Co series coatings. The abrasion traces of the Co_1 and Co_2 coated samples are comparatively smaller. The Co-T800 series coatings demonstrate a modest level of abrasion. It can be seen that the alteration in laser cladding process parameters has a minimal impact on the shape of the abrasion marks.

The coefficient of friction of different samples is shown in Fig. 13h. It is observed that the coefficient of friction of uncoated substrate is gradually increased as the friction proceeds. Additionally, the coated samples demonstrate a relatively stable coefficient of friction, which is potentially attributed to the specific nature of the friction between the substrate and the friction vice. The experiment results indicate that the application of laser-melted Co series and Co-T800 series coatings can enhance the wear resistance of the Zr substrate, and the Co series coatings exhibit better wear resistance. The alteration in the laser cladding parameters has a minimal impact on the wear resistance of the coatings,



Fig.13 Abrasion mark morphologies on surface of uncoated Zr substrate (a), Co-T800₁ coating (b), Co-T800₂ coating (c), Co₁ coating (d), and Co₂ coating (e); abrasion depth (f), abrasion trajectory (g), and coefficient of friction (h) of uncoated and coated samples

resulting in a comparable level of wear resistance.

4 Conclusions

1) The compatibility of Co-based coatings and the bonding characteristics between the coating and the substrate are favorable. By reducing the scanning rate and increasing the laser power, the coating thickness is increased, leading to a slight improvement in coating quality. However, this alteration in the laser cladding process parameters has a minimal impact on coating properties.

2) The oxidation mass gain of the Co-based coated samples

is significantly reduced compared with that of the substrate. The thickness of the oxygen diffusion layer in the coated samples is about 1/20-3/20 of that in the uncoated sample.

3) Pure Zr has the best corrosion resistance, followed by the Zr substrate with Co-T800 series and Co series coatings.

4) The microhardness of the Co-T800 series coatings is higher than that of the Co series coatings and Zr substrate. The Co_1 and Co_2 coatings have the smallest depth of wear marks, which is about 1/4 of the substrate depth. The Co-T800 series coatings have the second smallest wear mark width, which is about half the thickness of the substrate depth.

References

- 1 Wang Z, Yang X, Wang J et al. Crystals[J], 2021, 11(11): 1437
- 2 Slobodyan M. Nuclear Engineering and Technology[J], 2021, 53(4): 1049
- 3 Huang K Y, Tsai C H. Journal of Nuclear Materials[J], 1985, 136(1): 16
- 4 Zhou L J, Wang F, Yang C et al. Materials & Design[J], 2015, 78: 25
- 5 Kondo R, Nomura N, Suyalatu *et al. Acta Biomaterialia*[J], 2011, 7(12): 4278
- 6 Sawarn T K , Banerjee S, Samanta A et al. Journal of Nuclear Materials[J], 2015, 467: 820
- 7 Casucci A, Mazzitelli C, Monticelli F et al. Dental Materials[J], 2010, 26(8): 751
- 8 Harooni A, Nasiri A M, Gerlich A P et al. Journal of Materials Processing Technology[J], 2016, 230: 263
- 9 Chen Q S, Liu C H, Zhang R Q et al. Corrosion Science[J], 2020, 165: 108378
- 10 Han X C, Chen C, Tan Y Q et al. Corrosion Science[J], 2020, 174: 108826
- 11 Han X C, Xue J X, Peng S M et al. Corrosion Science[J], 2019, 156: 117
- 12 Kashkarov E B, Sidelev D V, Syrtanov M S et al. Corrosion Science[J], 2020, 175: 108883
- 13 Yeom H, Maier B, Johnson G et al. Journal of Nuclear Materials [J], 2019, 526: 151737
- 14 Cheng Y L, Wu F, Dong J L et al. Electrochim Acta[J], 2012, 85: 25
- 15 Malinovschi V, Marin A, Negrea D et al. Applied Surface Science [J], 2018, 451: 169
- 16 Wang L, Luo Q, Zhang X et al. Bioactive materials[J], 2020, 5(2): 377
- 17 Mozetič M, Vesel A, Primc G et al. Thin Solid Films[J], 2018, 660: 120
- 18 Casucci A, Osorio E, Osorio R et al. Journal of Dentistry[J], 2009, 37(11): 891

- 19 Livingstone S, Xiao L, Corcoran E C et al. Nuclear Engineering and Design[J], 2015, 284: 97
- 20 Shang X, Bo S, Guo Y et al. Applied Surface Science[J], 2021, 564: 150466
- 21 Liu Y, Ding Y, Yang L et al. Journal of Manufacturing Processes [J], 2021, 66: 341
- 22 Kim H G, Kim I H, Jung Y I et al. Journal of Nuclear Materials [J], 2015, 465:531
- 23 Ocelík V, De Oliveira U, De Boer M et al. Surface and Coatings Technology[J], 2007, 201(12): 5875
- 24 Houdkov S, Pala Z, Smazalová E et al. Surface and Coatings Technology[J], 2017, 318: 129
- 25 Tong W H, Sun B W, Xu Q Q et al. Advances in Machinery, Materials Science and Engineering Application IX[M]. Amsterdam: IOS Press, 2023: 172
- 26 Shahroozi A, Afsari A, Khakan B. Surface and Coatings Technology[J], 2018, 350: 648
- 27 Weng F, Yu H J, Chen Z H et al. Journal of Alloys and Compounds[J], 2016, 686: 74
- 28 Weng F, Yu H J, Liu J L et al. Optics & Laser Technology[J], 2017, 92: 156
- 29 Xia C Q, Song L A, Liu S G et al. Materials Characterization[J], 2021, 174: 111045
- 30 Fu Q F, Zhu X Z, Li R J et al. Energy Storage Materials[J], 2020, 30: 401
- 31 Manhabosco T M, Tamborim S M, Dos Santos C B et al. Corrosion Science[J], 2011, 53(5): 1786
- 32 Li Q, Chen K, Xia C Q et al. Materials Science and Engineering A[J], 2021, 817: 141358
- 33 Maurya R, Siddiqui A R, Balani K. Surface and Coatings Technology[J], 2017, 325: 65
- 34 Xia C Q, Liu Q Y, Song T S et al. Surface and Coatings Technology[J], 2022, 446: 128756
- 35 Fu Y, Huang C, Du C W *et al. Corrosion Science*[J], 2021, 191: 109727
- 36 Yong Y W, Fu W, Deng Q L et al. Rare Metals[J], 2017, 36: 934

纯Zr表面激光熔覆Co基涂层的高温氧化及耐蚀耐磨性能

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摘 要:采用激光熔覆技术制备Co基合金涂层锆合金,研究了纯金属Co涂层与Co-T800合金涂层高温氧化行为的差异以及涂层的耐磨性,并探讨改变激光熔覆工艺对涂层的影响。研究了2种涂层Zr合金样品在800~1200 ℃下的氧化增重和高温1h的高温氧化行为。结果表明,Co涂层和Co-T800涂层具有更好的抗高温氧化性能。在1000 ℃下氧化1h后,未涂层样品的氧化层厚度为241.0 μm,而Co基涂层样品的氧化层厚度仅为11.8~35.5 μm。经过摩擦磨损测试表明,涂层试样的磨痕深度仅为基体的1/2,Zr基体的硬度和耐磨性得到了很大提高。Co基涂层的缺点是在3.5%(质量分数)的NaCl溶液中耐腐蚀性能较差。 关键词:金属Zr;激光熔覆;Co基涂层;高温氧化性;耐磨性

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