



Article Microstructure and Properties of Direct Laser-Deposited CeO₂-Modified Cobalt-Based Composite Coatings

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Abstract: The seawater circulation pump is a significant piece of equipment in coastal nuclear power plants that is susceptible to erosion and corrosion in the seawater. In this work, CeO₂-modified cobalt-based composite coatings were prepared on the surface of martensitic stainless steel by direct laser deposition. The effect of CeO₂ on the phase composition, microstructure, microhardness, corrosion resistance, and erosion properties of the cobalt-based composite coatings was systematically investigated. While the addition of CeO₂ did not affect the phase composition of the coatings that comprised γ -Co, γ -Ni, M₇C₃, and M₂₃C₆ (M = Cr, W, Fe) metallic carbides, the eutectic organization showed an obvious phenomenon of contiguous aggregation. Microscopic pores were found in the coatings with 2 wt.% CeO₂, and the number of pores increased with the increase in CeO₂ content. Despite the higher self-corrosion potential (-0.27668 V) of cobalt-based alloy coating compared to the substrate (-0.37019 V), indicating enhanced corrosion resistance, the difference in self-corrosion potential among coatings with varying CeO₂ addition amounts is small (0.027 V), and the corrosion current densities are within one order of magnitude (10^{-8} A/cm²). These findings suggest that the addition of CeO₂ has no significant impact on the coating's corrosion resistance.

Keywords: direct laser deposition; cobalt-based composites; CeO₂; corrosion resistance; erosion properties

1. Introduction

The seawater circulation pump is one of the key pieces of equipment in the circulating cooling systems of nuclear power plants [1]. Seawater is mainly used as circulated water in coastal areas since the freshwater resources are normally short in these areas, and nuclear power plants require a large amount of recycled water. The performance of the seawater circulation pump directly affects the operation of the entire nuclear power plant's stability [2]. Super martensitic stainless steel is often used as the main material for seawater circulation pumps because of its good plastic toughness, high strength and hardness, high fracture toughness, and anti-abrasion properties. However, due to long-term seawater corrosion and scouring abrasion, it is easy to produce surface pitting and pan wear, resulting in equipment failure or structural incompleteness [3]. For the above-mentioned problems, surface modification technology is widely used because of economic considerations. Currently, direct laser deposition is a promising technology for surface modification due to the advantages of high energy density, low dilution rate, fine organization, high comprehensive mechanical properties, and interfacial metallurgical bonding, which lead to excellent wear resistance and surface hardness [4]. Though direct laser deposition is an efficient method to improve surface quality, it is difficult to avoid the formation of defects, such as cracking and holes in coatings [5,6]. Therefore, the application of direct laser deposition in some special fields is still limited.



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Stellite series of cobalt-based alloys have excellent wear resistance and corrosion resistance, and are widely used in metallurgy, petroleum, chemical and other fields [7]. Cobaltbased alloys consist mainly of chromium, nickel, tungsten, silicon, and iron. Chromium enhances the corrosion resistance of the cobalt-based matrix and facilitates the formation of chromium carbides [8]. Due to the high cost of cobalt-based alloys, surface modification techniques are typically used to create cobalt-based alloy coatings that improve surface properties while reducing costs.

Rare earth elements in deposited coatings can play a role in enhancing the mechanical properties, wear resistance, and corrosion resistance of the coatings. This is because of the high chemical activity of rare earth elements, which can refine the grains and increase the density of grain boundaries during the solidification of the coating, and promote the formation of intermetallic compounds, thus strengthening the coating. It can also enhance the fluidity and wettability of the powder during the melting process and reduce the microporous structure of the coating, which results in better macroscopic forming of the coating [9]. CeO₂, La₂O₃, and Y₂O₃ are relatively common rare earth oxide materials used in direct laser deposition [10]. Gao et al. [11] investigated the effect of CeO_2 addition on the crack sensitivity, microstructure, phase composition, solute segregation, and microhardness of Ni60 coatings. It was found that the Ni60 coating with the addition of 4% CeO₂ had a more uniform solute distribution and a more homogeneous cross-sectional structure. The addition of 4% CeO₂ can effectively suppress cracks and porosity, promote grain refinement, and improve the tissue uniformity of the Ni60 coating. Liu, et al. [4] prepared TiC/Ti₂Ni-reinforced Ti-based composite coatings on the surface of Ti811 titanium alloy using $TC_4 + Ni_{60}$ hybrid powders with different CeO₂ contents (0, 1, 2, 3, and 4 wt.%). It was shown that the effect of CeO_2 on the phase composition of the coating was negligible, but significantly improved the microhardness and wear resistance of the coating and refined the microstructure of the coating by adding an appropriate amount of CeO_2 .

CeO₂ can effectively strengthen the properties of deposited coatings, however the effect of the addition of CeO₂ on the corrosion of cobalt-based alloy coatings and the erosion property of slurry has been less studied. In this paper, we deposited four groups of cobalt-based composite coatings with different CeO₂ additions successfully by coaxial direct laser deposition technology. Subsequently, the effect of CeO₂ on the phase composition, microstructure, electrochemical corrosion properties, and slurry erosion performance of the modified coatings was studied. The results can provide an experimental basis for the application of CeO₂ in direct laser-deposited cobalt-based coatings.

2. Materials and Methods

The substrate was G-X5CrNiMo13-4 martensitic stainless which was used as the material of the seawater circulation pump, and its chemical composition is shown in Table 1. The substrate was cut to a thickness of 14 mm with an electrical discharge machining wire cutter, and the oxide was removed from the surface with a grinder. To ensure the surface finish of the substrate, the surface was polished to 200 mesh using metallographic sandpaper and then cleaned with alcohol. The main body of the composite powder material is Stellite F cobalt-based alloy powder, and its chemical composition is shown in Table 2. As shown in Figure 1, the morphology of the Stellite F particles (45~150 μ m) and CeO₂ particles (1~40 μ m, purity \geq 99.99%) exhibited a spherical shape. The powders were evenly mixed for 3.5 h at a speed of 220 rpm with a planetary ball miller, and four groups of composite powders were prepared with different CeO₂ addition (0 wt.%, 1 wt.%, 2 wt.% and 3 wt.%), which are hereinafter referred to as "0% Ce", "1% Ce", "2% Ce", and "3% Ce", respectively. Before the deposition, the powders were put into a vacuum-drying oven at 393 K for 2 h to remove any possible moisture in the powders.

Element	С	Si	Mn	Р	S	Cr	Ni	Fe
Substrate	≤ 0.05	0.7	≤1.5	0.04	≤ 0.015	12~14	3.5~4.5	Bal.

Table 1. Chemical composition of G-X5CrNiMo13-4 substrate (wt.%).

Table 2. Chemical composition of Stellite F cobalt-based alloy powders (wt.%).

Element	С	Cr	Si	W	Fe	Ni	Со
Stellite F	1.7	22.8	1.2	12.5	1.2	22.8	Bal.



Figure 1. SEM morphology of the (a) Stellite F cobalt-based alloy powder and (b) CeO₂ powder.

Coaxial powder-blown direct laser deposition was performed by an n-Light CFL-4000 fiber laser (Vancouver, BC, Canada). During the deposition process, the lapping rate of 30% was maintained and other process parameters were optimized according to the criteria of high efficiency and fewer defects, such as entrapment and porosity. The process parameters optimized by the response method are laser power 2500 W, scanning speed 350 mm/min, and powder feeding rate11 g/min. High-purity argon gas is used as the protective gas, and the gas flow rate is 40 L/min.

The phase composition analysis was performed using an X-ray diffractometer (Malvern Panalytical Empyrean Alpha-1, Westborough, MA, USA). The target material was Cu target, and the experimental parameters are as follows: The characteristic wavelength was 0.154060 nm, the operating voltage was 40 kV, the operating current was 40 mA, the scanning speed was 5° /min, the scanning range was 20° to 110° , and the scanning step was 0.02° .

The metallographic observation was performed using a Zeiss inverted metallographic microscope (Zeiss Observer.A1 m, Gottingen, Germany), and high magnification microstructure observation and quantitative analysis of composition were performed using a Schottky field emission scanning electron microscope (ZEISS Gemini 300, Jena, Germany) equipped with an energy spectrum analyzer (Smartedx).

A digital display microhardness tester (DHV-1000ZTEST, Beijing, China) was used for microhardness characterization. The load used for the microhardness test was 9.8 N, with a loading time of 15 s. The testing method was to take 9 points on the horizontal section of the coating and calculate the average value.

The potentiodynamic polarization curves and electrochemical impedance spectra (EIS) were conducted at room temperature ($22 \pm 2 \,^{\circ}C$) in a 3.5 wt.% NaCl solution by a CS310 electrochemical workstation. A platinum sheet electrode was the counter electrode, samples were the working electrode, and a saturated calomel electrode (SCE) was used as the reference electrode in a three-electrode system. After soldering the wires to the back of the samples, epoxy resin was used to seal the samples with an inlay mold, ensuring that only the test surfaces were in contact with the electrolyte. Before EIS tests, an open circuit potential (OCP) test was performed for 2 h until the open circuit potential was stable ($\Delta V_{OCP} \leq 0.03 \, \text{mV/s}$). The frequency span was from 100 kHz down to 0.01 Hz. Subsequently, the polarization curve was measured with a starting potential of $-0.8 \, \text{V}$ and an ending potential of 3 V, a potential

scan rate of 1 mV/s, and a cut-off current density of 0.1 A/mm². The self-corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of the polarization curves were obtained using the Tafel extrapolation method. Each electrochemical test group was repeated three times to ensure the reproducibility of the test data.

The jet impact method was used to evaluate the slurry erosion performance [12] under the erosion angle of 30° and 90°. The test surface was ground to 1500 grit using metallographic sandpaper and then polished. The mass loss of the samples was weighed using an electronic balance (FA1004, Liang Ping Instruments, Shanghai, China) with an accuracy of 0.001 mg. The total time for each sample was 60 min, and the samples were taken out and cleaned every 15 min and then weighed until the erosion test was completed. The detailed erosion test parameters are shown in Table 3.

Parameters Values Flow rate (L/min) 25 Stand-off distance (mm) 350 90/30 Eroding angle (°) 15 Erosion exposure increment (min) Total exposure time (min) 60 Erodent SiO₂ 200-400 Erodent size (µm)

Table 3. The parameters for the erosion test.

Erodent concentration (wt.%)

3. Results and Discussion

3.1. Microstructure Characteristics

Figure 2 shows the XRD results obtained for the Stellite F powders, and coatings with different CeO₂ addition. It can be seen from Figure 2 that the Stellite F cobalt-based alloy coatings comprised γ -Co, γ -Ni (face-centered cubic structure), and metallic carbide M₇C₃, and M₂₃C₆ (M = Cr, W, Fe). Metallic carbides of M₇C₃ and M₂₃C₆ are often present in high-temperature alloys as grain boundary strengthening phases, which are formed between the primary solid solution, and usually exhibit a brittle and hard eutectic organization and has a significant effect on the alloy's properties, such as high temperature creep resistance, tensile strength, fatigue properties, and pitting resistance [13–15]. Figure 2 illustrates that the addition of CeO₂ does not affect the phase composition. CeO₂-modified cobalt-based composite coatings still consist of γ -Co, γ -Ni, M₇C₃, and M₂₃C₆ (M = Cr, W, Fe). No diffraction peaks of CeO₂ are observed in the XRD patterns, which may be due to the relatively small mass fraction of CeO₂ powder (0–4 wt.%) and the very small particle size of CeO₂ in the cobalt-based composite alloy powder in the current experiment [16,17].

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Figure 3 shows the microstructure of the cobalt-based composite coatings with different CeO₂ content. Figure 4 shows the EDS mapping results of the rectangular region in Figure 3d. As shown in Figure 4, the cobalt-based alloy coating with 3 wt.% CeO₂ content has a significant elemental segregation phenomenon, especially for Co, Ni, Cr, and W elements. Combining the EDS results in Table 4 and the previous XRD patterns, it can be induced that the coating consists of the Co-rich cellular solid solution (S1) and reticular eutectic carbides (S2) mainly composed of M_7C_3 and $M_{23}C_6$ (M = Cr, W, Fe).

Co has two allotropes, face-centered-cubic (FCC) γ -Co transforms to hexagonal-closepacked (HCP) ε -Co during cooling, which is a non-diffusive martensitic phase transformation. The distribution of the different stabilizing elements has a significant effect on the martensitic phase transformation. C, Ni, and Fe are γ -Co stabilizing elements, while Cr, W, and Mo are ε -Co stabilizing elements. During the rapid cooling process of direct laser deposition, reticular eutectic carbides M₇C₃ and M₂₃C₆ (M = Cr, W, Fe) are precipitated from the eutectic solid solution and the content of ε -Co stabilizing elements, such as Cr and W, is reduced, allowing γ -Co to be retained to room temperature [18].



Figure 2. XRD patterns of Stellite F powders and coatings with different CeO_2 addition.



Figure 3. SEM microstructure of the coatings. (a) Stellite F, (b) Stellite F + 1 wt.% CeO_2 , (c) Stellite F + 2 wt.% CeO_2 , (d) Stellite F + 3 wt.% CeO_2 .



Figure 4. EDS mapping results of the element Co, Ni, Cr, W, Fe and C in the rectangular region in Figure 3d Stellite F + 3 wt.% CeO₂.

Table 4. EDS analysis of the cobalt-based composite coatings in Figure 3a (wt.%).

Spot	Со	Cr	Ni	Fe	W	С
S1	34.67	19.11	24.50	9.17	8.46	4.09
S2	15.82	47.44	7.14	4.83	11.00	13.77

A closer look reveals that the eutectic organization in the CeO_2 -modified coatings is significantly increased and shows an obvious phenomenon of contiguous aggregation. The

atomic radius of metallic elements Co, Ni, Cr, and Ce in CeO₂-modified coatings is 125.1 pm, 124.59 pm, 124.91 pm, and 182.47 pm, respectively [19]. Among these elements, Ce had the largest atomic radius, therefore, it tends to cause lattice distortion and increase the free energy of the system. However, the system always develops spontaneously toward the lowest free energy, which leads to the enrichment of Ce elements at the grain boundaries [20]. During the growth of primary solid solution grains, the enrichment of Ce elements at grain boundaries produces a dragging effect that hindered grain growth [9]. This changed the morphology of the reticular eutectic carbide precipitates on the grain boundaries.

When the addition of CeO_2 exceeds 2 wt.%, microscopic pores have been found in the coatings, and the number of pores shows a significant tendency to increase with the increase in CeO_2 content. These pores are usually considered to be caused by the inclusion of gas produced by the decomposition of the oxide at high temperatures [21].

3.2. Microhardness

Figure 5 shows the hardness of the upper surface of the coatings with different CeO_2 addition and the substrate. The hardness of each coating is much higher than that of the substrate, and the hardness of the coatings shows a decreasing trend with the addition of CeO_2 . When the content of CeO_2 is up to 3 wt.%, the hardness of the coating was 428 HV1, which is 16.08% lower compared to the coating without the addition of rare earth oxides. Adding rare earth oxides to the coating leads to an increase in the dilution rate and microporosity occurs in the coatings when too much rare earth oxide is added, which leads to a decrease in the hardness of the coatings.



Figure 5. Microhardness of the cobalt-based composite coatings with different CeO₂ addition and the substrate.

3.3. Electrochemical Analysis

To investigate the effect of CeO_2 on the corrosion resistance of cobalt-based composite coatings, the samples were detected by electrochemical tests in 3.5 wt.% NaCl solution. The polarization curves of the substrate and the coatings with different CeO_2 addition are shown in Figure 6 and the polarization curve fitting parameters obtained by the Tafel extrapolation method are shown in Table 5.



Figure 6. (**a**) Polarization curves of the coatings for each component and the substrate, (**b**) enlarged view of the rectangular region in (**a**).

Sample	$E_{\rm corr}$ (V)	i _{corr} (A/cm ²)	<i>i</i> _p (A/cm ²)	$E_{\rm tr}$ (V)
Substrate	-0.37019	$1.89 imes10^{-6}$	$1.61 imes 10^{-6}$	0.191
Stellite F	-0.27668	$7.26 imes10^{-8}$	$2.09 imes10^{-7}$	0.639
Stellite F + 1 wt.% CeO ₂	-0.28853	$8.20 imes10^{-8}$	$2.65 imes10^{-7}$	0.656
Stellite F + 2 wt.% CeO_2	-0.26919	$5.38 imes10^{-8}$	$1.77 imes 10^{-7}$	0.654
Stellite F + 3 wt.% CeO_2	-0.29607	$6.12 imes10^{-8}$	2.06×10^{-7}	0.664

Table 5. Electrochemical parameters of the coatings for each component and the substrate.

The self-corrosion potential (E_{corr}) of the coatings shows a process of decreasing, then increasing, and then decreasing with the increase in CeO₂ content, which means that the effect of CeO₂ on the corrosion reaction of the coatings in 3.5 wt.% NaCl solution is not linear. The self-corrosion potential of the coating with the addition of 2 wt.% CeO₂ was -0.26919 V, which is the highest among the Stellite F cobalt-based alloy coating, indicating that the corrosion reaction was more difficult to make occur. The corrosion current densities (i_{corr}) of the coatings without and with CeO₂ are in the same order of magnitude, indicating that the addition of CeO₂ does not have a significant effect on the corrosion reaction rate of the coatings in 3.5 wt.% NaCl solution. The overpassivation potential (E_{tr}) is the potential at which the passivation film is struck, which marks the beginning of pitting on the working electrode surface, and the corrosion resistance of the passivation film is characterized by the passivation current density (i_p). The difference in the overpassivation potential for the four compositions is small, with a maximum difference of only 0.025 V. The coatings with the addition of CeO₂ undergo secondary passivation after the breakdown of the primary passivation film, which enhances the pitting resistance of the coatings in 3.5 wt.% NaCl solution with a secondary overpassivation potential near 0.947 V.

Figure 7 displays the surface morphology of the coatings with different CeO₂ addition and the substrate after electrochemical corrosion. Figure 7a shows that there are many tongue-like pitting pits on the surface of the substrate, indicating that its corrosion type is localized pitting corrosion. The surface morphology of the coatings with CeO₂ added is not significantly different from that of the cobalt-based composite coating, both of which exhibited reticular protrusions and cellular depressions. Combined with Figure 3, it can be seen that the reticular protrusions should be reticular eutectic carbides mainly composed of M_7C_3 and $M_{23}C_6$, while the cellular depressions should be Co-rich solid solutions. This corrosion morphology of the coating surface where the solid solution is corroded and the carbide is exposed indicate that the corrosion type was selective corrosion [22].



Figure 7. SEM images of the corroded surface after potentiodynamic polarization testing of (**a**) substrate, (**b**) Stellite F, (**c**) Stellite F + 1 wt.% CeO₂, (**d**) Stellite F + 2 wt.% CeO₂, (**e**) Stellite F + 3 wt.% CeO₂.

Careful observation reveals that the surface of the cellular solid solution has a fragmented film structure, and its composition is found to contain more O and Cr by EDS analysis (Table 6), indicating that the material is a Cr_2O_3 film produced on the surface of the Co-rich solid solution. It has been shown that Cr_2O_3 films generated by Cr-containing alloys in a corrosive environment can effectively prevent further corrosion reactions from occurring [23]. Moreover, the distribution of O elements on the reticular eutectic carbide phase is also found by EDS. From the above, the corrosion mechanism in the coatings is presumed to be as follows. In the anodic polarization stage of the electrode polarization process, the potential of the carbide is more positive than that of the solid solution, so that a microcell is formed between them, then the solid solution acted as the metal anode for the oxidation reaction (as in Equation (1)) and reacted with Cl^{-} in solution to form hydrolyzable compounds. So that the anode solid solution continues to dissolve, and the electron from the anode dissolution flows to the carbide phase, the reduction reaction of oxygen occurs on the surface of the carbide phase (as in Equation (2)), which leads to the protection of the carbide phase as a cathode eventually exposed to precipitation. This mechanism is similar to graphite corrosion in gray cast iron. While the microcell reaction occurs, due to the potential difference between the elements in the solid solution phase and the easy oxidation of Cr elements to generate passivation film Cr₂O₃, which makes the potential of Co and Ni elements more negative than that of Cr₂O₃, resulting in the continuous corrosion leaching of Co and Ni elements, and finally the formation of a porous structure composes of reticulated carbides on the surface of the coating.

$$M \to M^{n+} + ne^- \tag{1}$$

$$O_2 + 2H_2O + 4e^- \to 4OH^-$$
 (2)

Table 6. EDS results of the corroded surface in Figure 7b (wt.%).

Spot	Со	Cr	Ni	Fe	W	0	С
S3	24.54	16.75	16.80	8.30	18.43	9.22	5.96
S4	15.75	40.32	7.76	5.25	16.69	2.62	5.96

From the Bode plot of Figure 8b, it can be seen that the phase angles of the impedance of all the samples are always less than 90°. This is caused by frequency dispersion that makes the interfacial properties deviate from the ideal capacitance and is generally considered to be caused by the unevenness in the electrode surface or material transport, such as electrode surface roughness, grain boundaries, dislocations, impurities, material adsorption, and porous layers [24,25]. Usually, a constant phase element (CPE) is used as a substitute for the "ideal" capacitance (C) in the mathematical characterization of impedance for this constant phase angle phenomenon [26]. The impedance of CPE is defined as follows:

$$Z_{\rm CPE} = 1/Q(j\omega)^n \tag{3}$$

In this definition, Q is the device conductance as a constant; j is the imaginary number $(j^2 = -1)$, ω is the angular frequency, and n is an adjustable parameter indicating deviation from pure capacitive behavior, whose value is usually between -1 and 1. Qiao et al. [27] and Metikoš et al. [28] defined CPE as ideal capacitance when n = 1, n = 0.5 as Warburg impedance with diffusion characteristics, n = 0 as ideal resistance, and n = -1 as pure inductance.

As seen in Figure 8a, all samples show a capacitive arc in the Nyquist plot, which indicate the predominance of electrochemical reactions occurring at the electrodes in the measured frequency range [29]. The semicircular arcs in these plots also represent the charge transfer mechanism on an uneven surface [30]. In general, a larger diameter of the capacitive arc indicated a higher corrosion resistance [31]. The capacitive arcs of the modified coatings are significantly larger than that of the substrate, indicating better corrosion resistance.



Figure 8. (a) Nyquist plot, (b) enlarged Nyquist plot, (c) Bode plot of the coatings with different CeO₂ addition and the substrate.

To gain further insight into the reaction process and surface state of the substrate and the coatings in 3.5 wt.% NaCl solution, the EIS data are fitted using Zview according to the corrosion characteristics of the electrochemical reaction system. The equivalent circuit corresponding to the EIS impedance spectrum is shown in Figure 9, and the fitting results are shown in Table 7. In this equivalent circuit, R_s is the resistance of 3.5 wt.% NaCl solution, R_p is the film resistance dependent on passivation film and coating, and CPE is the constant phase element of the films. The value of χ^2 is under 10^{-2} , which indicates that the selected equivalent circuit is reasonable, and the fitting result is reliable. Among the four compositions of the coatings, the coating with 3 wt.% CeO₂ addition had the highest film resistance (640,750 $\Omega \cdot \text{cm}^2$), which is about 22 times higher than that of the substrate (28,632 $\Omega \cdot \text{cm}^2$).



Figure 9. Equivalent circuit of the coatings in 3.5 wt.% NaCl solution.

Table 7. Fitting results for EIS of the coatings for each component and the substrate.

Sample	$R_{\rm s}~(\Omega \cdot {\rm cm}^2)$	CPE-Y ₀	CPE-n	$R_{\rm p}~(\Omega \cdot {\rm cm}^2)$	x ²
Substrate	3.91	$6.32 imes 10^{-5}$	0.87	28,632	$3.64 imes10^{-4}$
Stellite F	3.005	$2.59 imes10^{-5}$	0.92	628,750	$4.93 imes10^{-4}$
Stellite F + 1 wt.% CeO ₂	6.9	$2.48 imes10^{-5}$	0.93	466,410	$2.87 imes10^{-3}$
Stellite F + 2 wt.% CeO_2	4.246	$2.87 imes10^{-5}$	0.91	523,650	$5.09 imes10^{-4}$
Stellite F + 3 wt.% CeO_2	3.839	$2.60 imes 10^{-5}$	0.89	640,750	$4.79 imes10^{-4}$

Combined with the above analysis, the coating with 2 wt.% CeO₂ addition has the best corrosion resistance with the lowest corrosion current density (i_{corr}) and highest film resistance of the passivation film, indicating that it has a low corrosion rate and weak charge transfer ability in 3.5 wt.% NaCl solution.

3.4. Erosion Test Results

Figure 10 shows the accumulated mass loss at an impingement angle of 90°. The average mass loss of coatings with different CeO₂ addition is about one-fifth of that of the substrate. All the curves show a decreasing slope, which indicates that the mass loss rate on the sample surface decreases slightly as the impact time of solid–liquid two-phase flow increases. Oka et al. [32] showed that modulating the material hardness can effectively control the scouring wear rate. The initial surface states of the scouring samples are all polished surfaces, while the impact of the solid phase particles on the sample surface deformed the metal, resulting in a strain-hardening-like effect on the sample surface, which eventually manifested itself as a decrease in the scouring wear rate. The mass loss of the unmodified cobalt-based alloy coating is 40.97 mg, which is 70.7% less than that of the substrate. The final mass loss of the coating with 1 wt.% CeO₂ added is the lowest, and with the increase in CeO₂ content, the mass loss increases.

To investigate the slurry erosion failure mechanism under the 90° impingement angle, the eroded surfaces are illustrated in Figure 11. Obvious furrows, cracking, cutting lips, and lamellar spalling are found on the surfaces of all coatings, indicating that the erosion on the sample surfaces is produced by a combination of three mechanisms: cutting, ploughing and subsurface deformation and cracking. Although the erosion failure mechanisms are the same, the surface morphology of the substrate and modified coatings differ significantly. The surface of the substrate has obvious cracking and lamellar spalling, and the ploughings and cutting lips are also more obvious compared to other samples, indicating that the substrate. This

mechanism has the most obvious ability to remove the surface of the material due to the impact of the solid phase particles on the sample surface at a 90° erosion angle.







Figure 11. Erosion morphology of the coatings and the substrate under an erosion angle of 90° . (a) Substrate, (b) Stellite F, (c) Stellite F + 1 wt.% CeO₂, (d) Stellite F + 2 wt.% CeO₂, (e) Stellite F + 3 wt.% CeO₂.

Each coating has a flatter surface and significantly less laminar spalling compared to the substrate. On the surface of the unmodified coating, furrows and cutting lips are mainly observed, indicating that ploughing and cutting dominated in this sample. As shown in Table 8, EDS analysis in S5 indicates that the black patches on the erosion surface of the sample were residual SiO₂ particles, and the cutting lips at the end of the furrows were rich in Cr and C, indicating that the organization here is mainly composed of carbide hard phases. The water flow will scatter in all directions at an impact angle of 90°, and when the solid phase particles reach the carbide hard phase, some solid phase particles will impact the sample and flow with the water, and the kinetic energy will be exhausted, resulting in furrows on the surface of the sample and the formation of deposits at the end of the subsequent solid phase particles, leaving the carbide hard phase that resisted the erosion of the solid phase particles exposed.

Table 8. EDS analysis of the erosion surface in Figure 11b (wt.%).

Spot	0	Si	Со	Cr
S5	52.10	41.29	2.58	4.03

Figure 12 shows the accumulated mass loss at an impingement angle of 30°, from which it can be seen that the mass loss of the unmodified coating is 19.51 mg, which is 73.13% less compared to that of the substrate.



Figure 12. Accumulated mass loss of the coatings and the substrate eroded at impingement angles of 30°.

Figure 13 shows the morphology of the eroded surfaces at a 30° impingement angle. On the surface of the substrate samples, the same ploughing cutting lips and cracks are found, but the samples have a flatter surface that increases ploughing length, and reduces lamellar spalling compared to the erosion angle of 90°. Similar changes are observed for the remaining coating, where the sample surface is generally flatter, and the furrows occupy most of the sample surface. This indicates that the ploughing of solid-phase particles is the main wear mechanism at a 30° impingement angle [33,34].



Figure 13. Erosion morphology of the coatings and the substrate under an erosion angle of 30°. (a) Substrate, (b) Stellite F, (c) Stellite F + 1 wt.% CeO₂, (d) Stellite F + 2 wt.% CeO₂, (e) Stellite F + 3 wt.% CeO₂.

The mass loss of all coatings at a 90° impingement angle is greater than 30° , which indicates that all coatings and substrates exhibit brittle erosion behavior under current conditions [35]. However, all samples exhibit ductile scouring behavior according to the eroded surface morphology. Based on the results of Sheldon and Finnie [36], it is thought that the larger solid phase particle size or impact velocity designed for the scour wear test in this subject may cause the discrepancy in erosion mass loss of the samples from the actual erosion behavior.

4. Conclusions

In this work, we deposited four groups set of cobalt-based alloy coatings on the surface of super martensitic stainless steel by adding different amounts of CeO_2 . The effect of rare earth oxide CeO_2 on the microstructure and properties of the coating was investigated. The following conclusions can be drawn:

- 1. The addition of CeO₂ has no effect on the phase composition. CeO₂-modified cobalt-based composite coatings still consist of γ -Co, γ -Ni, M₇C₃, and M₂₃C₆ (M = Cr, Fe, W, Co).
- 2. The eutectic organization in the CeO₂-modified coatings is significantly increased, and the eutectic organization shows an obvious phenomenon of contiguous aggregation.
- 3. Microscopic pores are found in the coatings with 2 wt.% CeO₂, and the number of pores increases with the increase in CeO₂ content. These pores are usually caused by the inclusion of gas produced by the decomposition of the oxide at high temperatures.
- 4. In 3.5 wt.% NaCl solution, the deposited coatings have a superior corrosion resistance compared to the substrate. However, the difference in self-corrosion potential for coatings with different CeO₂ addition amounts is small (0.027 V), and the corrosion

current densities of the coatings without and with CeO_2 are in the same order of magnitude (10^{-8} A/cm²), indicating that the addition of CeO₂ does not have a significant effect on the corrosion resistance of the coating.

5. Only the mass loss of the coating with 1 wt.% CeO₂ addition is less than that of the unmodified coating, and the mass loss increases with increasing CeO₂ content. This may be due to the microscopic pores in the coating becoming a weak point for erosion, and the decrease in hardness makes the coatings less resistant to impact.

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