Study on Oxidation Resistance Technology for Aluminium Electrolysis Anode Stubs

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Abstract

The anode stubs in aluminium electrolysis operate under high-temperature and corrosive conditions for extended periods. To improve their oxidation resistance, this study used a molten infiltration coating method to prepare an anti-oxidation coating on the surface of conventional stubs. Through metallographic microscopy, scanning electron microscopy (SEM), oxidation tests, thermal shock tests, and friction-wear tests, the microstructure, high-temperature oxidation resistance, thermal shock resistance, and abrasive wear performance of the molten infiltration coating were analysed. The results indicate that the molten infiltration coating and the stub substrate undergo elemental interdiffusion, forming a strong metallurgical bond. The oxidation rate of the coating at 850 °C is only 0.52 mg/cm^2·h. Industrial tests conducted at a Chinese aluminium smelter demonstrated that the oxidization rate of the anode stubs with molten infiltration coating was reduced by 2.14 mm/cycle compared to currently used anode stubs, significantly extending the service life of stubs. This technology is important for reducing production costs in the aluminium smelter.

Keywords: Aluminium electrolysis, Anode stubs, Molten infiltration coating, Oxidation resistance.

1. Introduction

In 2024, China's electrolytic aluminium output reached 43.393 million tonnes (according to International Aluminium Institute statistics), maintaining its position as the world's largest producer for 24 consecutive years and producing more aluminium than the rest of the world for the last 12 years. In the aluminium electrolysis process, anode stubs are subjected to oxidation due to high-temperature, abrasion from electrode materials, and corrosion by the electrolyte, leading to the formation of a "narrow neck" phenomenon (as shown in Figure 1), which shortens their service life. Additionally, iron oxides formed by the oxidation of stubs enter the electrolyte, increasing iron impurity content and degrading the quality of primary aluminium [1, 4]. Currently, the protective methods for anode stubs mainly focus on technologies such as anode stub protection rings, anti-oxidation coating spraying (as shown in Figure 2), and stub wrapping [5, 8]. Among these, while the protection ring can isolate the stub from the covering material, it fails to address the issue of air oxidation and corrosion. The anti-oxidation coating spraying technology is effective in preventing anode stub corrosion. However, the coating is prone to peeling off under high temperatures and requires reapplication during each anode replacement [4, 6]. This paper investigates the oxidation resistance technology of anode stub materials. By employing a coating molten infiltration method, an oxidation-resistant alloy layer is formed on the surface of the stubs. Under high-temperature conditions, this layer can in situ generate a ceramic protective coating, which is uniform, dense, and free from cracking or peeling, thereby providing effective protection for the anode stubs.

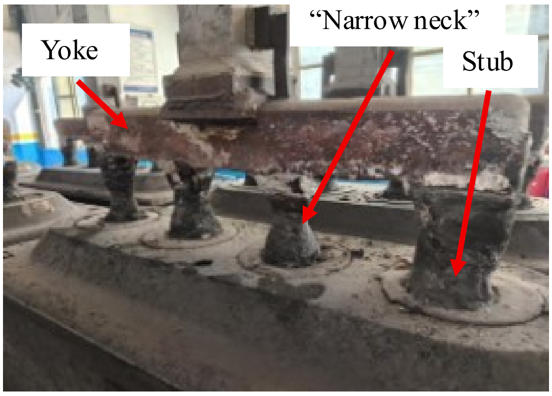


Figure 1. Morphology of oxidized/corroded stubs with "narrow neck".

Figure 2. Application of anti-oxidation coating.

2. Test

2.1 Test Materials

This test used Q235B, a type of section stub material, as the base material for the anode stubs. The molten infiltration coating material used was a powder material developed by our institute, primarily composed of a composite of alloy powder and ceramic powder. Its specific microstructure is shown in Figure 3.

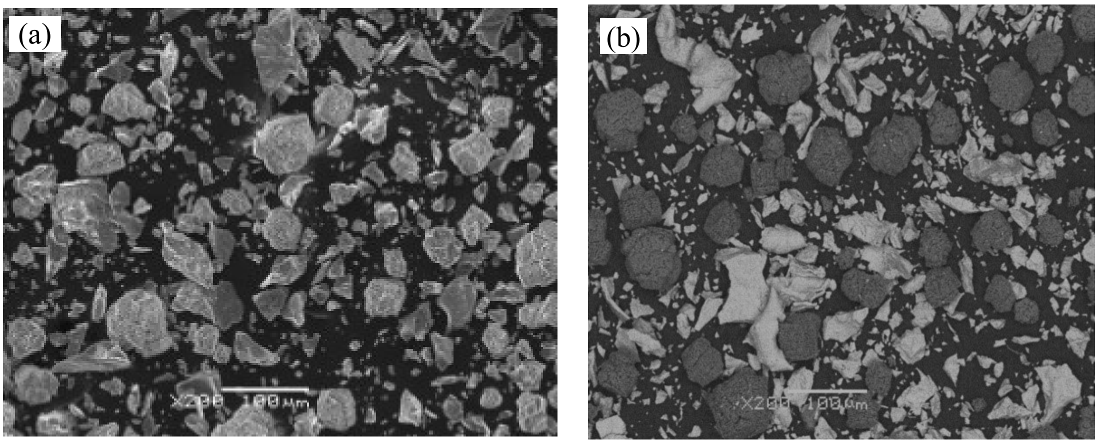


Figure 3. Morphology images of molten infiltration agent (a) SEM-SEI; (b) SEM-BEC.

2.2 Test Method

After surface derusting, the Q235B material is placed in a prefabricated molten infiltration box, which is then sealed and heated in a resistance furnace to facilitate high-temperature diffusion of elements. The molten infiltration box is equipped with a one-way exhaust device to discharge volatilized gases at high temperatures while preventing air ingress, thereby avoiding oxidation of the Q235 material.

3. Results and Discussion

3.1 Morphology Analysis

Figures 4 and 5 show the macroscopic morphologies of Q235B samples (diameter 10 mm × length 100 mm) with and without molten infiltration coating. As observed, the Q235B material maintains a certain metallic luster after surface derusting. In contrast, after high-temperature molten infiltration coating treatment, the surface is evidently covered with a gray-white coating, completely losing its metallic luster, with visible traces of high-temperature interdiffusion.

Figure 4. Q235B material without molten infiltration coating.

Figure 5. Q235B material with molten infiltration coating.

Figure 6 shows the metallographic images of the cross-section of the Q235B material and the molten infiltration coating. As can be observed from the images, the molten infiltration coating has unidirectional growth on the substrate surface, forming a distinct fusion interface with the substrate, achieving a strong metallurgical bond between the coating and the substrate. Figure 7 shows the SEM images of the cross-section of the Q235B material and the molten infiltration coating. The images reveal that the molten infiltration coating and the substrate are bonded in a dendritic diffusion manner, with the coating being continuous and dense, free of cracks or pores. Figure 8 displays the EDS elemental mapping of the cross-section of the Q235B material and the molten infiltration coating. The results demonstrate that the oxidation-resistant elements in the molten infiltration coating have a gradient distribution on the Fe-based substrate surface, with clear evidence of elemental interdiffusion.

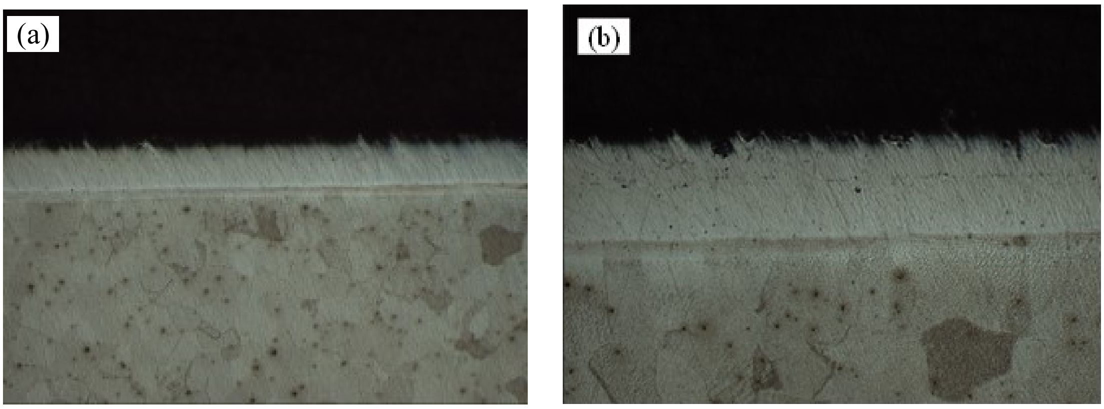


Figure 6. Metallographic images of molten infiltration coating: (a) 50×; (b) 100×.

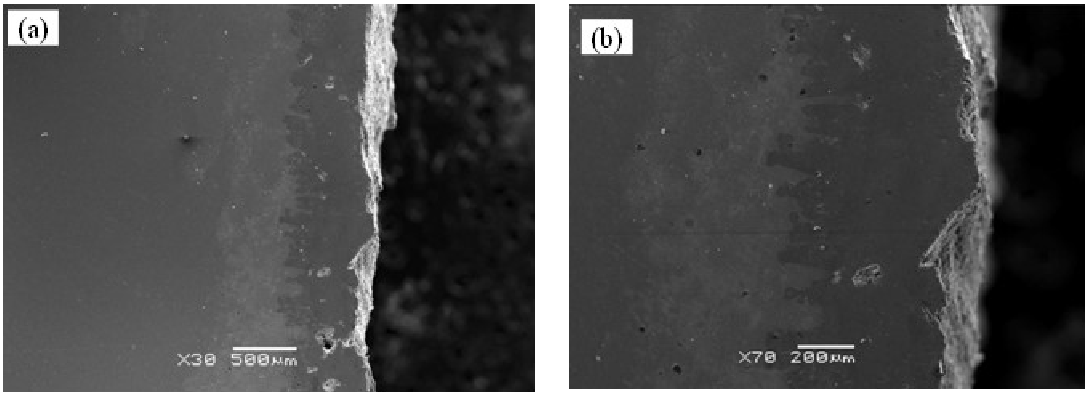


Figure 7. SEM images of molten infiltration coating: (a) 30×; (b) 70×.

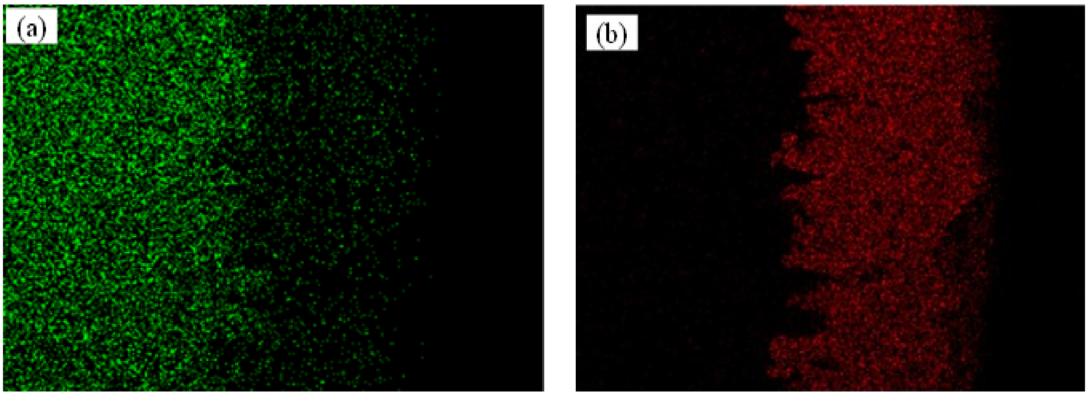


Figure 8. EDS elemental mapping of molten infiltration coating: (a) Distribution of Fe element; (b) Distribution of oxidation-resistant element X.

3.2 Analysis of Oxidation Resistance

Figures 9(a) and (b) show the high-temperature oxidation morphologies of the Q235B samples with and without molten infiltration coating after exposure at 850 °C for 10 hours, respectively. As can be observed from the images, the uncoated Q235B has significant oxidation-induced shelling, forming a brittle and porous oxide layer with poor adhesion to the substrate, which is prone to expansion and spalling, indicating inferior oxidation resistance. The oxidation rate is measured at 42.36 mg/cm^2·h. In contrast, the sample with molten infiltration coating treatment shows no signs of shelling or spalling, maintaining its original appearance before oxidation, with an oxidation rate of only 0.52 mg/cm^2·h.

3.3 Analysis of Thermal Shock Resistance

Figures 10(a)-(e) show the thermal shock tests of Q235B material without molten infiltration coating and Q235B material with molten infiltration coating, respectively, under the cyclic condition of 3 h at 900 °C → air cooling to room temperature for five cycles. As seen in the images, the ordinary Q235 material oxidizes in air, forming a brittle iron oxide layer. Over time, the oxide layer on ordinary Q235B material thickens continuously. Under repeated thermal shock conditions, it eventually forms a "shell structure" that cracks and peels off in a bark-like manner, indicating that this layer lacks oxidation resistance. In contrast, the Q235B material sample with molten infiltration coating can in situ form a ceramic protective coating at high temperatures, achieving a metallurgical bond with the substrate. This layer is thin, uniform, and dense, exhibiting strong thermal shock resistance without cracking or spalling. Thus, it demonstrates excellent high-temperature oxidation resistance.

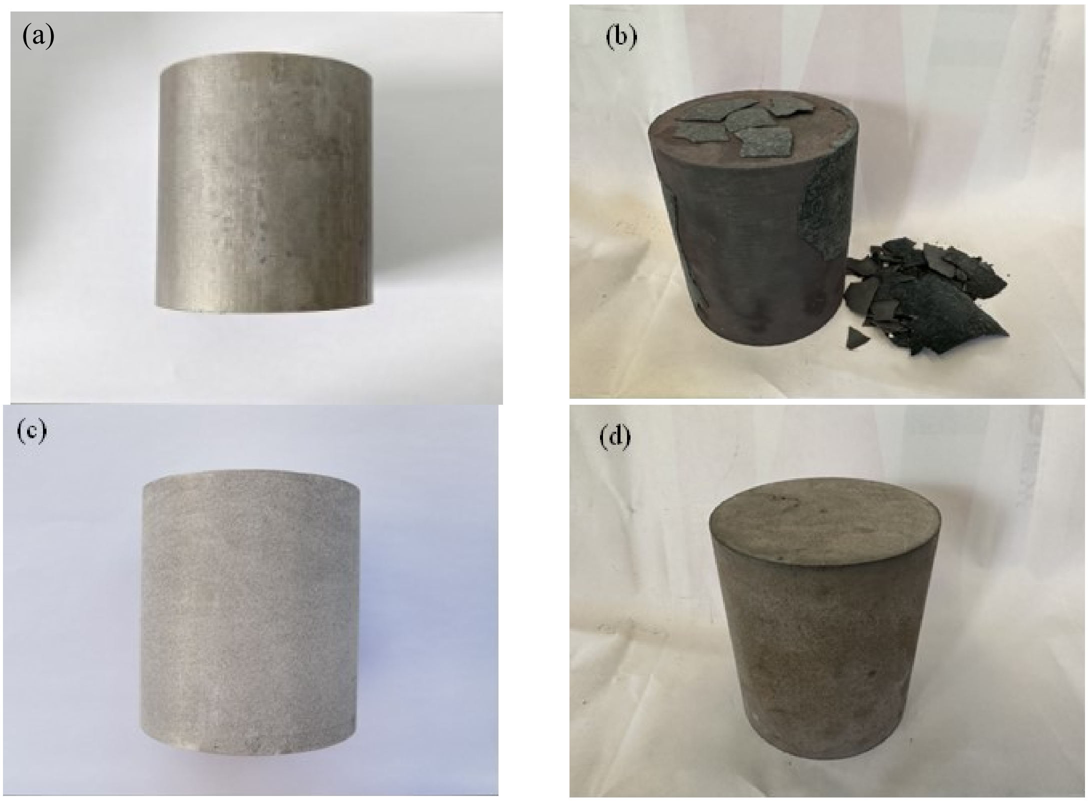


Figure. 9. Oxidation images after 10 h at 850 °C. (a) Original morphology of Q235B material. (b) Morphology of Q235B material after high-temperature oxidation. (c) Original morphology of Q235B material with molten infiltration coating. (d) Morphology of Q235B material with molten infiltration coating after high-temperature oxidation.

3.4 Analysis of Wear Resistance

Since the anode stubs inevitably undergo long-term contact and friction with alumina materials, resulting in wear damage characterized by low-stress scratching abrasion, enhancing the wear resistance of the stubs is also a critical indicator for their protection. In this test, a circumferential abrasive wear test was selected to evaluate the wear resistance. The test samples were processed into cylindrical rods and placed in the equipment, with industrial granular alumina used as the abrasive counterpart. The test was conducted at a rotational speed of 60 r/min for 24 hours. A schematic diagram of the abrasive wear is shown in Figure 11. According to the friction and wear test results, the Q235B material sample without molten infiltration coating demonstrated poor wear resistance, with a weight loss of 0.68 g. In contrast, the Q235B material sample with molten infiltration coating demonstrated excellent wear resistance, showing a weight loss of only 0.04 g, 17 times better than that of the Q235B material. This superior performance is attributed to the uniform distribution of high-hardness Fe-X alloy phases on the surface of the molten infiltration coating. These phases prevent the embedding of alumina particle tips into the substrate during friction, thereby hindering the sliding of abrasive particles across the surface and reducing the abrasive wear caused by the extrusion of alumina particles on the Q235B substrate. In comparison, the surface of the Q235B substrate lacks reinforcing phases, resulting in inferior wear resistance. As the wear duration increases, localized wear pits enlarge, leading to progressive material loss [9].

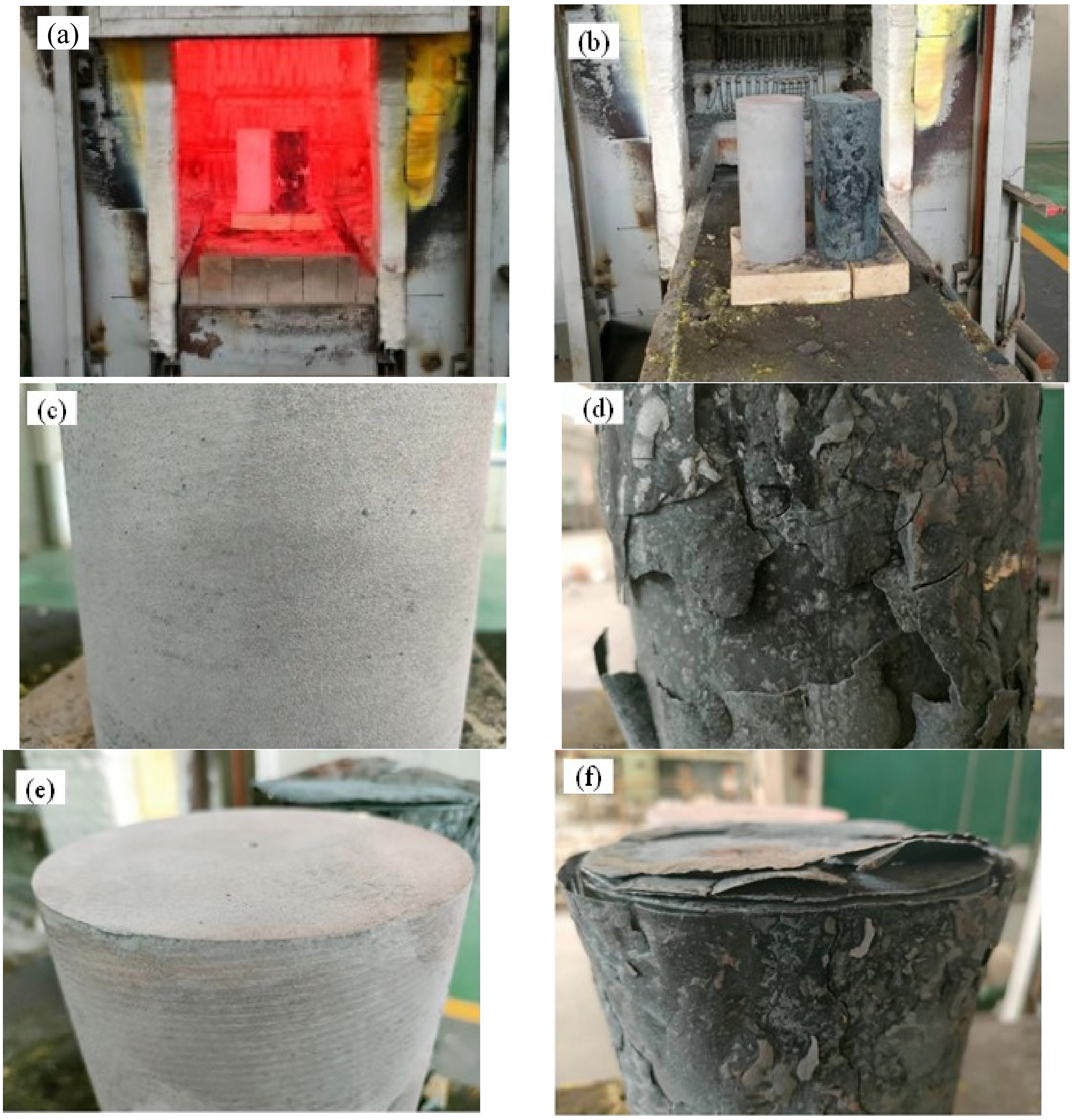
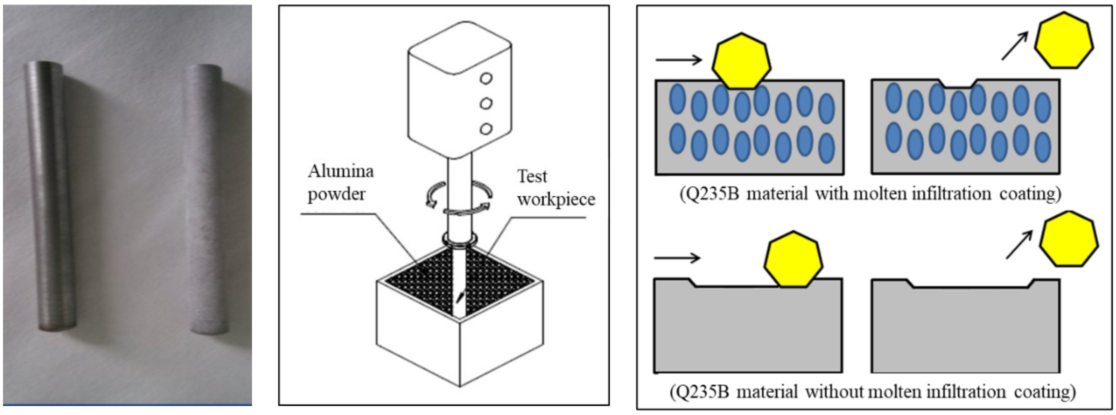


Figure 10. Thermal shock test.
(a) High-temperature morphology (b) Room-temperature morphology
(c) Circumferential morphology of Q235B material with molten infiltration coating. (d) Circumferential morphology of Q235B material without molten infiltration coating.
(e) Top morphology of Q235B material with molten infiltration coating. (f) Top morphology of Q235B material without molten infiltration coating.

3.5 Industrial Tests

Using Q235B section steel as the substrate, oxidation-resistant anode stubs were prepared by coating the molten infiltration method. Industrial tests were conducted on a 200 kA potline cell at a Chinese aluminium smelter, with the industrial application scenarios shown in Figure 12. The welding and casting methods for oxidation-resistant stubs are the same as those for conventional stubs, requiring no additional treatment. After four cycles of use, the average wear rate of conventional stubs was 2.35 mm/cycle, while that of oxidation-resistant stubs was 0.21 mm/cycle, demonstrating significant antioxidant effects. By adopting oxidation-resistant anode stubs, the service life can be extended from 3 to 4.5 years. For a 300 kt/y-capacity potline, it is projected to generate annual economic benefits of approximately RMB 3.94 million (545 kUSD/y approx.).



(a) (b) (c)

Figure 11. Schematic diagram of abrasive wear. (a) Test samples. (b) Abrasive wear testing equipment. (c) Sample wear process.

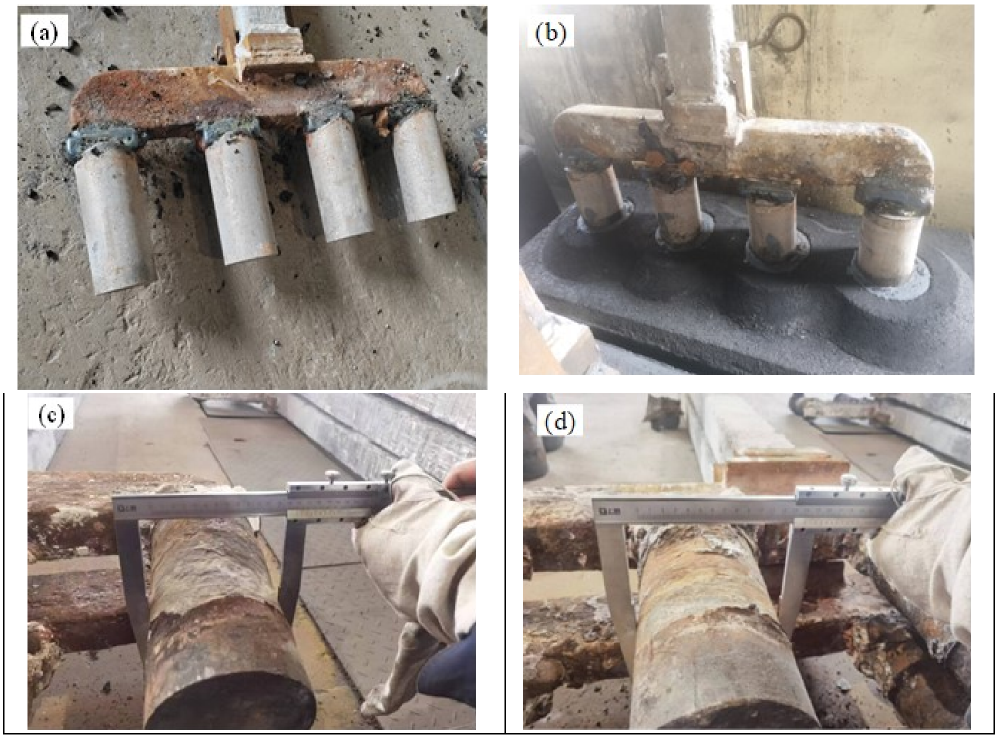


Figure 12. Industrial application scenarios.
(a) Welding of oxidation-resistant stubs. (b) Casting of oxidation-resistant stubs.
(c) Wear condition of conventional stubs. (d) Wear condition of oxidation-resistant stubs.

4. Conclusions

(1) Using the molten infiltration coating method, an oxidation-resistant alloy coating can be formed on the surface of Q235B steel. The oxidation-resistant elements in the coating interdiffuse with the substrate, exhibiting a gradient distribution on the surface of the substrate and forming a strong metallurgical bond.
(2) The Q235B material treated with the molten infiltration coating can in situ generate a ceramic anti-oxidation coating under high-temperature conditions. At 850 °C, the oxidation rate is only 0.52 $mg/cm^2 \cdot h$, and it shows no cracking or spalling after repeated thermal shocks at 900 °C, demonstrating excellent oxidation resistance and thermal shock resistance.

(3) The oxidation-resistant anode stubs prepared by the coating molten infiltration method have identical welding and casting processes as conventional stubs. Industrial tests have demonstrated that the oxidation-resistant stubs show an average wear rate of 0.21 mm/cycle, indicating significant oxidation resistance.

5. References

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