Process and performance of ultra-high-speed laser cladding corrosion-resistant layer on the surface of tungsten cathode

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Abstract. Ultra-high-speed laser cladding technology is used to clad the surface anti-corrosion layer of tungsten cathode for molten salt electrolysis. Using MSC. Marc finite element simulation software, optical microscope (OM), scanning electron microscope (SEM), energy spectrum (EDS), X-ray diffractometer (XRD) and microhardness tester and other analytical testing methods, respectively, the cladding process, the cladding layer microstructure morphology, phase composition, phase distribution and microhardness are simulated, and the structure is observed and analyzed. The simulation results show that the preheating process before cladding for the tungsten substrate can effectively avoid the cracking phenomenon caused by internal stress; the structure and performance observation results show that the cladding layer has a dense structure and no cracks, forming a good metallurgical bond with the substrate, the difference in the structure of the cladding layer affects the hardness of the cladding layer.

1. Introduction
Rare earths, known as "industrial monosodium glutamate", are my country's important strategic resources and are widely used in various fields. Rare earth elements have strong activity, so it is difficult to reduce and prepare them by ordinary methods. At present, the most effective method is molten salt electrolysis. The production of rare earth metals/alloys by molten salt electrolysis has the advantages of low cost, uniform composition, easy control, good quality and easy realization of continuous production \cite{1,2}. The production of rare earth metals by molten salt electrolysis requires the use of refractory and corrosion-resistant metals such as tungsten and molybdenum as the cathode. Because tungsten and molybdenum are relatively stable to rare earth metals and their halides below 1400°C, especially tungsten due to its high melting point, slow evaporation at high temperatures, low thermal expansion coefficient, high hardness, high density, good high-temperature strength and electron emission performance. Good and other characteristics, so it is the first choice for the cathode material. The working conditions of the tungsten cathode vary with the proportion of different rare earth oxides added. Generally, it is 1000–1100°C, the molten salt working voltage is 10V, and the working current is 5500–6000A.
The tungsten cathode is located 100mm–150mm above the molten salt surface, and the temperature is 700–800℃. Local rapid erosion and consumption will occur. The reason is that the rare earth oxide molten salt electrolyte volatiles adhere to the surface of the tungsten cathode to promote high-temperature oxidation and promote damage caused by thermal corrosion \[^4\], so that its service life generally does not exceed 6 months. For the life extension method of tungsten cathode, in recent years, enterprises and researchers have been continuously exploring and improving, but the effect is not very satisfactory. After half a year, the entire tungsten cathode is still scrapped, and the service life is still not long. In view of local rapid corrosion of tungsten cathode, the patent \[^5,6\] proposed the method of adding stainless steel protective sleeve to protect the bottom of the protective sleeve and the liquid level of the electrolyte. However, in the process of using this method, corroded iron elements intruded into rare earth products, making the iron content exceed the standard.

In recent years, ultra-high speed laser cladding technology has been widely developed. Compared with conventional laser cladding, high-speed laser cladding has the advantages of high processing efficiency, high processing accuracy, low subsequent processing cost, small heat input to the workpiece and can reduce the deformation of the workpiece\[^7,8\].

In order to make the tungsten cathode have excellent high temperature oxidation resistance and corrosion resistance of rare earth molten salt, the ultra-high speed laser cladding process was adopted in this experiment. The tungsten cathode was used as the substrate, and the self-fused Mn15 powder with high bonding strength, excellent corrosion resistance and good heat resistance was used as the cladding material to prepare the tungsten cathode substrate. The microstructure and hardness of the coating and substrate were studied in this paper.

2. Test materials and methods

2.1. Experiment material

The test matrix material was carried out on a tungsten rod with a volume ratio of 3:1 to the tungsten cathode. The coating material is MN15de self-fluxing alloy powder with a particle size of 200 mesh to 300 mesh, and its chemical composition is shown in Table 1.

| chemical element | Cr  | Fe  | Si  | Mo  | C   | Ni  | W  | B  |
|------------------|-----|-----|-----|-----|-----|-----|----|----|
| Wt%              | 25  | <5  | 2.5 | 14.96 | 0.03 | Bal. | 3.2 | 0.8 |

2.2. Preheat temperature simulation

The simulation adopts MSC. Marc finite element simulation software, which is modeled according to the actual tungsten electrode size. The finite element model is shown in Figure 1. Due to the axisymmetric characteristics of the round bar, the finite element model adopts an axisymmetric model. In order to ensure the accuracy of calculation, dense grids are used near the cladding layer during grid division (blue area in Figure 1), and looser grids are used in other areas. The left side and the lower side of the model are restrained by a fixed displacement, a total of 25 passes are cladding, and finally the natural cooling is performed.
2.3. Cladding layer preparation
Before cladding, the sample was pre-treated with sandblasting to make the surface appear a certain degree of roughness; the preheating temperature of the substrate was 800 ℃. The ZMZK6000 ultra-high-speed laser cladding machine is used to carry out the cladding process of the anti-corrosion layer on the surface of the sample. The specific parameters are as follows: the first layer cladding power: 45%, powder feeding rate: 0.6 (18g/min), protective gas: 20L/min, powder feeding gas: 1.6L/min. The subsequent cladding parameters are: power 85% and gradually increase according to the thickness of the cladding layer, powder feeding amount: 0.8 (24g/min), protective gas: 22L/min, powder feeding gas: 1.8L/min.

2.4. Organization and performance testing
ObserverA1m Zeiss microscope was used to observe the microstructure and cracks; JBM-6510 scanning electron microscope and its attached energy spectrometer were used for tissue morphology observation and micro-area composition analysis, and D8 Advance X-ray instrument was used for phase analysis. The HXD-1000B electronic microhardness tester measures the cross-sectional hardness of the cladding layer when the loading load is 2N and the loading holding time is 15s, and the indentation distance is 0.1mm.

3. Results and discussion
3.1. The influence of preheating on stress and strain
The influence of preheating on the stress and strain in the material was investigated. Some results of preheating at 500℃ and 800℃ are shown in Figure 2 and Figure 3, respectively.

![Figure 2](image)
**Figure 2** Partial results of stress, strain and temperature in preheated material at 500℃

![Figure 3](image)
**Figure 3** Partial results of stress, strain and temperature in preheated material at 800℃
The above simulation results are drawn into a curve, as shown in Figure 4. It can be seen from the Figure 4 that as the preheating temperature increases, the axial, hoop, and Von Mises stresses have all decreased significantly, indicating that preheating is very effective in reducing the stress in the material. Quantitative calculations show that preheating at 500°C and 800°C reduced the axial stress by 16% and 28%, respectively, reduced the hoop stress by 22% and 32%, and reduced the Von Mises stress by 25% and 46%, respectively. Due to the large axial and circumferential stresses, these two stresses are the main forces affecting material cracking. Preheating at 800°C can cause the axial and circumferential stress to drop by 28% and 32%, respectively, which is very large.

![Figure 4 The influence of preheating temperature on stress](image)

3.2. Macroscopic morphology and phase analysis of the cladding layer

![Figure 5 Sample macro photos](image)

Figure 5 shows the MN15 cladding layer prepared on the surface of the tungsten cathode according to the above process parameters. From Figure 1, it can be seen that the surface of the cladding layer is obviously silvery white, with good flatness, and no obvious cracks and holes. Each layer is cladding. There is no obvious boundary between the layers, and the total height of the cladding layer is 4mm ~ 7mm.
Figure 6 shows the X-ray diffraction pattern of the cladding layer. It can be seen from Figure 6 that the phases in the cladding layer are mainly composed of γ-Ni, FeNi3, CrB, Ni3B, M23C6 and other phases.

3.3. Microstructure morphology of cladding layer

Figure 7 is the cross-sectional morphology of the MN15 alloy cladding layer. It can be seen from Figure 7 that the cross section is divided into three areas: the left side is the cladding layer, the right side is the matrix, and there is a bright white band between the two. The structure of the cladding layer is uniform without obvious cracks and pores. The interface between the cladding layer and the substrate is a bright white line. This bright white band is produced by the mutual diffusion of Cr and Ni elements in the coating and W elements in the substrate to reduce the hard phase, which also shows that there is a good metallurgical bond between the coating and the substrate. The appearance of bright white bands is a characteristic of induction heating cladding [9]. At present, it is generally believed that due to the difference in characteristics between the cladding layer and the substrate, the eddy current at the interface between the coating and the substrate is large, and the temperature at the interface is higher. At high temperatures, the elements in the cladding layer diffuse to the substrate, and during rapid cooling, the elements in the cladding layer remain in the substrate to form a bright white band.
It can also be seen from Figure 7 that the structure of the cladding layer has different morphologies such as fine needles, dry, small particles, and small blocks.

3.4. Microhardness test

Figure 8 shows the microhardness distribution curve of the sample. The results show that the average microhardness of the cladding layer is 523.8 (HV0.2), which is 1.49 times that of the base material 351.9 (HV0.2). The microhardness of the cladding layer has small fluctuations, which is because the difference in the structure of the cladding layer affects the hardness of the cladding layer. The maximum value in the bonding area at the bottom of the cladding layer is caused by the presence of large particles of Ni, Cr, W composite carbides in the bottom of the cladding layer, and the presence of these particles enhances the hardness and strength of the bonding area.

4. Conclusion

(1) The Mn15 alloy cladding layer was successfully prepared on the surface of the tungsten cathode using ultra-high-speed laser cladding technology. The structure of the cladding layer is uniform and dense, and the metallurgical combination of the substrate and the cladding layer is good;

(2) The simulation results show that as the preheating temperature increases, the axial, hoop, and Von Mises stresses have all decreased significantly. Preheating is very effective in reducing the stress in the material;

(3) The surface of the cladding layer is obviously silvery white, with good flatness, no obvious cracks and holes, no obvious boundary between each cladding layer, and the total height of the cladding layer is 4mm ~ 7mm;

(4) The average microhardness of the cladding layer is 523.8 (HV0.2), which is 1.49 times that of the base material 351.9 (HV0.2);

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