Corrosion Behavior of C4 Coating Produced by Cladding Laser in Sulfuric Acid

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Abstract—C4 coating was prepared by high power multilayer laser cladding. Corrosion behavior of the C4 coating and 316 stainless steel in sulfuric acid solution was investigated. The corrosion rate was measured by using the mass loss method. Obvious corrosion morphology and serious exfoliation corrosion of 316 stainless steel are noticed in sulfuric acid solution. While C4 coating after corrosion test shows nearly unchanged surface morphology. The results show that corrosion resistance of C4 coatings is higher than 316 stainless steel. The corrosion morphology was observed by SEM (Scanning Electron Microscope), and the elements distribution of corrosion products was analyzed by EDS (Energy-Dispersive X-ray Spectroscopy). The results show that the S element content increased with the extension of corrosion time, while the Cr content decreased. For the 316 stainless steel, with the extension of corrosion time, the content of C increased. The sulfur-containing corrosion products on the surface are all dissolved in the acid solution. The contents of Cr and Ni decreased, and their passivation ability was weakened. The results indicate that C4 coating exhibits better corrosion resistance in sulfuric acid solution due to the stable formation of dense oxide film on the surface.

1. Introduction

The emission of acidic gases such as SO\textsubscript{2} resulting from the combustion of coal in thermal power plants can cause a serious air pollution. In recent years, a technology termed as flue gas desulfurization (FGD) has been widely used to reduce the emission of SO\textsubscript{2}. The limestone–gypsum wet FGD is one of the most popular processes. The flue gas after desulfurization contains a lot of vapor whose temperature may fall below its dew point. As a result, condensates with high concentrations of acids can form on the surface of the chimney lining, which can cause serious corrosion to the chimney lining materials. Therefore, the selection of the material with high corrosion resistance concerns with the safe operation and service lifetime of FGD systems. Ni-Cr-Mo alloy exhibits excellent corrosion resistance in many acidic aqueous solutions, which is recommended as one of the candidate materials for anticorrosion linings of chimneys [1].

C4 is a kind of Ni-Cr-Mo alloy with excellent anticorrosion property. It is widely used in the chemical industry for the superior corrosion performance in different environments. However, high cost of C4 limits its large-scale applications. In recent years, Ni-Cr-Mo alloy coatings have been rapidly developed by laser cladding which is an effective and promising way to produce coatings with superior mechanical and chemical properties [6].

Bellenage and Rameau [9] and Takeuchi et al [10] reported the corrosion behavior of C22 steel and C-276 in strong acid solution, respectively. Laser cladding is widely used to produce metallurgical well-
bonded coating due to the advantages of high power, small heat-affected-zone (HAZ) and minimal distortion of the substrate [11]. In this study, the corrosion behavior of C4 alloy cladding layer and 316 stainless steel in sulfuric acid solution were investigated by the corrosion test, and the corresponding corrosion mechanisms were revealed in detail.

2. Experimental

2.1. Materials
The chemical compositions of C4 coating and 316 stainless steel are listed in Table 1. The as-prepared samples were cut into dimensions of 50 mm×30 mm×2.5 mm. Prepare six parallel samples for each sample. The surface of samples were grinded with 600~1500 mesh abrasive papers and then polished with corundum powders of 3−5μm, finally ultrasonically cleaned in distilled water followed by ethanol. After drying, the original weight (0.1mg analytical balance) was weighed after 4h.

Table 1. Chemical compositions of C4 coating and 316 stainless steel(wt.%)

|   | Cr  | Ni  | Fe  | C   | Mn  | Si  | P  | Mo |
|---|-----|-----|-----|-----|-----|-----|----|----|
| C-4 | 14.0 | Bal | 3.0 | 2.0 | 1.0 | 0.0 | 0.0 | 8.0 |
| 316 | 16.0 | 0   | 15.0| -   | -   | 2.0 | 1.0 | 0.0 |
|    |     |     |     |     |     |     |     | 2.50| |

2.2. Methods
The sulfuric acid solutions with concentrations of 15% and temperature of 80 °C was used in the corrosion test. The test temperature was controlled by HH-2 constant temperature water bath. Six parallel samples are used for each group. The sample should avoid contact with the beaker, the upper of the sample should be kept at a certain distance from the surface of the solution. Place the beaker in a constant temperature water bath to make the solution reach the specified temperature (80°C) as soon as possible. Corrosion time is set to 30 days, replace the solution every 7 days, take out a set of samples every 5 days. Clean the surface corrosion products, measure the weight after corrosion. Corrosion rate was calculated by the quality loss and corrosion time.

2.3. Weight loss method
Gravimetric method is a classic and reliable method for measuring metal corrosion rate. When the corrosion products on the metal surface are relatively easy to clean and will not damage the base metal, the weight loss method is used. After the sample is corroded, the change of weight and size is measured, and the corresponding corrosion rate is calculated. The calculation formula (1) is as follows:

\[ V = \frac{m_2 - m_0}{S t} \]  

\( V \): Corrosion rate (g/(m²*h));  
\( m_2 \): Original mass(g);  
\( m_0 \): Final mass (g);  
\( S \): Corrosion area(m²);  
\( t \): Corrosion time (h);

2.4. Characterization method
The surface morphology of C4 coating and 316 stainless steel were observed by scanning electron microscopy (SEM, FEI Quanta 200FI). EDS (Energy-Dispersive X-ray Spectroscopy) was used to analyze distribution of elements.
3. Result and DISCUSSION

3.1. Corrosion rate

Table 2. Corrosion weightlessness data of C4 coating

| Time (days) | Mass change (mg) | Corrosion rate (g/㎡*h) |
|------------|------------------|-------------------------|
| 5          | 1.1              | 0.0032                  |
| 10         | 1.4              | 0.0021                  |
| 15         | 2.4              | 0.0023                  |
| 20         | 4.2              | 0.0032                  |
| 25         | 4.4              | 0.0026                  |
| 30         | 5.7              | 0.0029                  |

Table 3. Corrosion weightlessness data of 316 stainless steel

| Time (days) | Mass change (mg) | Corrosion rate (g/㎡*h) |
|------------|------------------|-------------------------|
| 5          | 20.57            | 22.58                   |
| 10         | 24.86            | 27.29                   |

Corrosion data of C4 coating and 316 stainless steel are listed in the Table 2 and Table 3. The corrosion rate of 316 stainless steel is about 24.94mm/a, while the corrosion rate of C4 coating is about 0.0030mm/a.

3.2. Weightlessness-curve

The fitting curve of corrosion weightlessness is shown in Fig.1. The fitting equation is shown in formula (2). The correlation coefficient of the fitting curve of C4 cladding layer is 0.9263, and the fitting result is reasonable.
3.3. **SEM Examination**

![SEM image](image)

**Figure 2.** Surface morphologies of C4 coatings for (a) 5 days; (b) 20 days; (c) 30 days

**Figure 3.** SEM image of 316 stainless steel after corrosion
(a) Corroded for 5 days (b) Corroded for 10 days

The corrosion morphology of C4 coating and 316 stainless steel surface were observed by scanning electron microscopy. EDS was applied to analyze the elements of corrosion product.

Fig. 2 shows the surface morphology of C4 coating after corrosion. After the coating was corroded, the surface morphology is nearly unchanged, did not demonstrate distinct corrosive trace. Morphology of corrosion presents pitting corrosion character. The pitting formation mechanism is that the laser cladding coating causes defects such as crack, hole and inclusion due to thermal stress and the rise of bubbles in the molten pool. The matrix metal in the hole is in a low-potential activation state, which is the anode, and the large surface outside the hole is in a high-potential passivation. As the cathode of the battery is corroded, the inside and outside of the hole constitute an activated-passivated battery characterized by a large cathode and a small anode.
Surface morphology of the C4 coating corroded in sulfuric acid solution for 5 days is shown in Fig.2a. It can be seen that there is no obvious corrosion trace on the surface of the coating, but pitting was observed as well. The surface morphology of the C4 coating in sulfuric acid solution for 20 days is shown in Fig.2b. Compared with Fig.2a, the size of the pitting has increased, but there are no obvious corrosion traces can be found in surface. Surface morphology of the C4 coating after 30 days in sulfuric acid solution is shown in Fig.2c. The coating surfaces are a little rough and white in acid solutions, which is related with the oxidization of coating surface.

The surface morphology of 316 stainless steel corrosion in sulfuric acid solution is shown in Fig.3. Measuring the corrosion rate by the mass loss method, the results revealed that the corrosion rate of 316 stainless steel is higher than C4 coating, while according to their corrosion appearance, its tendency to local corrosion is remarkably higher than that of C4 coating. The loosened corrosion products and slightly inter crystalline corrosion are observed on the surface, which were corroded for 5 days and 10 days, respectively, as shown in Fig.3a and Fig.3b. In terms of corrosion form, uniform corrosion, and local corrosion. It is shown that the corrosion pits on the surface of the stainless steel are more compact. Peeling of the surface of the stainless steel was observed, and the furrow-like corrosion morphology was found in both Fig.3a and Fig.3b.

3.4. **EDS Examination**

![Figure 4](image.png)

**Figure 4** Energy spectral analysis of corrosion surface of C4 coating in sulfuric acid solution for (a) 5 days; (b) 30 days

**Table 4.** TABLE ELEMENTAL MASS PERCENTAGE (wt.%)  

| Element | a   | b   |
|---------|-----|-----|
| C       | 10.80 | 14.40 |
| O       | 03.06 | 02.17 |
| S       | 07.53 | 05.69 |
| Cr      | 24.18 | 21.01 |
| Fe      | 00.49 | 00.76 |
| Ni      | 37.98 | 42.11 |
| W       | 05.40 | 04.79 |
| Mo      | 10.55 | 09.08 |

EDS analyses of the C4 coating phases labeled in Fig.4 and element contents are given in Table 4. From the point of view of element changes, the contents of C and Ni have increased, and there are no obvious changes of the contents of other elements. The corrosion rate decreased significantly after 30 days of corrosion, which was related to the increase of Ni content that improve the passivation performance of the coating surface.
Figure 5 Energy spectral analysis of 316 stainless steel in sulfuric acid solution for (a) 5 days; (b) 10 days

The EDS analysis of 316 stainless steel corrosion surface area are shown in Fig. 5. Composition results are listed in Table 5. In terms of element content, the content of elements such as Cr, Fe, Ni, Mo, in the 316 stainless steel has increased significantly with increasing corrosion time, while the content of C, which shows a decreasing trend. The increase of C element is not conducive to the corrosion resistance of stainless steel. The reduction of Cr, Fe, Ni, Mo and other passive and stable elements will also accelerate the corrosion rate of stainless steel.

Table 5. TABLE ELEMENTAL MASS PERCENTAGE (wt.%)

| Element | a   | b   |
|---------|-----|-----|
| C       | --- | 06.56 |
| O       | 04.33 | 04.08 |
| P       | 00.43 | 00.07 |
| S       | 00.00 | 00.10 |
| Cr      | 16.39 | 15.41 |
| Fe      | 66.81 | 65.04 |
| Ni      | 08.02 | 07.55 |
| Mo      | 04.02 | 01.18 |

3.5. Corrosion mechanism of C4 coating

Electrochemical corrosion is the main corrosion mechanism under the experimental conditions of this study. The following three steps can be used to indicate the progress of the electrochemical corrosion process: (a) The metal on the anode in the etching solution begins to dissolve in the solution in the form of ions; (b) Cathode flow; (c) The H⁺ present in the etching solution will generate H₂ after flowing to the cathode to produce a reduction reaction. There three integral parts make up a whole organically [14]. By providing heat to the corrosive solution, the temperature of the corrosive medium is increased. On the one hand, the activation of dissolved ions in the solution is enhanced, which accelerates the dissolution rate of metal ions. The amount of hydrogen ions begins to increase, and the rate of hydrogen generation is accelerated. On the other hand, the dissolution rate of positive ions in the anode surface layer is accelerated. The two factors are superimposed to accelerate the electrochemical process to a large extent, which is the reason why the temperature resistance of the coating is higher than others.

Nickel, chromium, silicon and other alloy elements have good passivation performance and strong oxidation resistance. The C4 coating contains much alloy elements like this, so the corrosion resistance has been greatly improved. It has compact structure phase, due to the fast cooling speed of laser cladding, the directional solidification structure will be produced, which will cause the grain structure on the surface of the coating. The similar crystal orientation can avoid and reduce the corrosion acceleration phenomenon caused by the different grain orientation in the galvanic cell. The electrode potential of the
solid solution structure is due to the solid solubility of alloy elements in the solid solution phase of nickel iron. As the solid solubility of alloying elements in the nickel-iron solid solution phase increases, the electrode potential of the solid solution also increases. The difference with the eutectic compound with high electrode potential is reduced, which can slow down the rate of electrochemical corrosion [15].

3.6. corrosion mechanism of 316 stainless steel
The nucleation positions of dense pitting pits appearing on the surface of 316 stainless steel are mostly in the unevenness of defects and magazines on the surface of stainless steel. Because the passivation film in these parts is relatively fragile, it is very susceptible to ring breakage (especially the effect of chloride ions is very obvious). Thus, it becoming an activated anode, surrounded by a cathode, and forming a pinhole-like etch pit by electrochemical corrosion[16].

During the grinding process of the sample, gaps and scratches are formed on the surface of the stainless steel, and the migration of the solution in the micro gaps is very difficult. In order to maintain the passive dissolution current, the surface of the stainless steel in the gap will consume the oxygen dissolved in the solution at a rapid rate, but the oxygen cannot be replenished. The passivation film on the surface of the stainless steel gap begins to dissolve due to the gradual consumption of oxygen in the solution in the gap, and the corrosion products will be gradually concentrated, and the PH value will also decrease[17]. When the PH value reaches a critical value, the passive state of stainless steel is destroyed, and a corrosion cell is formed in the gap, which intensifies the corrosion of the base metal.

The corrosion mechanism different with common steel, and the corrosion of stainless steel often occurs at the grain interface. Observation of the morphology of 316 stainless steel shows that the interface between the grains has undergone severe corrosion[18]. This is because corrosion begins to occur on the surface of the steel, and then develops along the grain boundaries, forming micro-cracks and breaking the connection between the grains. Reasonable explanation is that Cr and C have good mutual solubility. When C is precipitated, Cr will be carried out together, resulting in a lack of Cr content. When they are precipitated at the grain boundary, the Cr content of the matrix is reduced, resulting in Cr-depleted regions, so the passivation film is broken.

4. Conclusion
The C4 coating was prepared by multilayer laser cladding. The anticorrosion properties in acid solution are studied under combined concentrations and temperature, and corrosion time. The following conclusions are made based on detailed study.

1)C4 coating has excellent corrosion resistance in sulfuric acid solution, due to dense passive film on the surface mainly composed of Cr₂O₃, which has superior anticorrosion properties, surface morphology almost has no change. The corrosion rate is about 0.0030mm/a.

2)The corrosion rate of 316 stainless steel is about 24.94mm/a. Corrosion products are loosely attached to the surface of stainless steel, and most of them are dissolved in the corrosive medium. The surface passivation film cannot be recovered immediately after being damaged in hot sulfuric acid solution, and substrate is corroded rapidly.

3)The corrosion-resistant material of the chimney of the thermal power plant can choose the lining of the C4 coating, which can effectively extend the service life time.

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