Preparation and molten salt corrosion behaviors of TiO$_2$/Al$_2$O$_3$/Inconel625 composite coatings on the surface of Q235 alloy at 900 °C

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Abstract: Sol-gel method combined with plasma surfacing was used to prepare TiO$_2$/Al$_2$O$_3$/Inconel625 composite coatings on the surface of Q235 alloys. To investigate the corrosion resistance of this coatings, samples with Inconel625 single coating and TiO$_2$/Al$_2$O$_3$/Inconel625 composite coating were corroded with NaCl and Na$_2$SO$_4$ salts with the weight ration of 1:1 at 900 °C in air for 24 h. Molten salt corrosion thermodynamic results show the composite coatings caused lower oxidation weight gain than the sample with single coating. Combination of XRD and SEM results illustrates that the surface and cross-sectional morphology were composed of an outermost loose and cracked NiO and iron oxides layer for the Inconel625 coated sample. For the composite coating sample, the oxide film was composed of more compact NiO and Cr$_2$O$_3$ as the main layer. There were inner oxidation regions for both samples, but region for sample with composite coating was more thinner than that for sample with single coating. This work shows that TiO$_2$/Al$_2$O$_3$/Inconel625 composite coating improves the molten salt corrosion resistance properties of the Q235 alloy at 900 °C by promoting the formation of the protective Cr$_2$O$_3$ film on the sample surface.

1. Introduction

Along with the growth of living standard, people make more and more garbage in their daily lives, so the environmental pollution problem has become more and more serious, researchers pay close attention to how to deal with so much garbage through an environmental-friendly method. In consideration of air and soil pollution for the compost and landfill ways, waste incineration shows obvious advantages, such as saving space, energy regeneration, harmlessness[1]. When deal waste with incineration process, the most serious problem is the corrosion on the surface of the combustion furnace, which directly causes the hidden danger during the incineration process and also the invalid of the furnace. Among these corrosions, chlorine corrosion was considered to be the most impotent one, during this kind of process, Cl$_2$ plays the part of catalytic agent, it would not be consumed but causes continuous chemical corrosion of the matrix alloy. For these reasons, modification of the furnace surface such as coating preparation has been paid more attention recently.

Inconel625 alloy coating has been proved to be effective to resist chlorine corrosion during the garbage incineration process [1-3]. But the Cl$^-$ still could permeate Inconel625 coating just in more slow speed, as far as the high cost and low preparing speed of the protective coating, another more protective film should be prepared on the surface of Inconel625 coating to further resist the chlorine corrosion of the matrix alloy. At a relatively high temperature, Cl$^-$ can nearly react with all metallic oxides and create metal chlorides with very low boiling point, just in this way, will the protective
metallic oxides formed on the surface of the matrix be consumed and be volatilize in the form of gases. Nevertheless, the Gibbs free energy enthalpy change in the chemical reaction between the Cl⁻ and Al₂O₃ is very high, which makes the very low probability of the corrosion to Al₂O₃ by Cl⁻, so in this research, the sol-gel method was combined with the plasma surfacing process to obtain TiO₂/Al₂O₃/Inconel625 composite coatings on the surface of Q235 alloys in order to find new way to produce more effective films in actual production.

2. Experimental

Q235 alloys plates used in this work were bought in the market, and then were cut to pieces with the size of (15x15x15) cm. X-ray diffraction (XRD) was used to analysis the phase compositions of the materials obtained on the surface of Q235 alloy after molten salt corrosion at the temperature of 900 °C. Scanning electron microscope (SEM) and energy spectrometer (EDS) were used to observe the surface profile of the samples.

After washed in ethanol and acetone, the Q235 alloy was coated with 2.5 mm thick Inconel625 film by plasma surfacing method (cold metal transfer CMT), and then dipped into Al₂O₃ gel for 120 seconds, then pulled up with a speed of 2000 mm·s⁻¹ and following by being kept in air for 300 seconds. This procedure was repeat one more time, then the same operation was carried out just with the difference of dipping into TiO₂ gel. After these progresses, the sample was dried in muffle furnace for 10 min and 30 min at the temperature of 90 °C and 300 °C, respectively. The above dipping and dry procedure were repeat for 3 times. In the next step, the sample put into muffle furnace kept on 500 °C, 700 °C and 900 °C for 30 min, 30 min and 50 min, respectively.

To investigate the protective function of the composite coating, the samples obtained with Inconel625 coating and TiO₂/Al₂O₃/Inconel625 composite coating were dealt with molten salt corrosion at 900 °C for 24 h, the salt was composed of NaCl and Na₂SO₄ with the weight ratio of 1:1.

3. Results and Discussion

3.1 Molten salt corrosion thermodynamics

Figure 1 shows the molten salt corrosion thermodynamics of Q235 alloys withInconel625 andTiO₂/Al₂O₃/Inconel625 composite coating oxidized at 900 °C for 24 h. The results indicated that the mass gain of the sample covered by the composite coating was smaller. Composite coating improves the molten salt corrosion resistance of the alloy obviously. Sample with Inconel625 coating showed nearly linear growth law during the 24 h corrosion process, the negative growth of the weight in the beginning stage was due to the falling off of the oxide film. While the composite coated sample showed relative slowly corrosion rate and did not appear falling off phenomenon, TiO₂/Al₂O₃/Inconel625 composite coating gave the specimen less mass gain and slower molten salt corrosion rate, which means more protective film could have been prepared in this research.
3.2 XRD analysis

Figure 2a shows the XRD patterns of sample covered by TiO₂/Al₂O₃/Inconel625 composite coating. The analysis of the results showed that anatase TiO₂ (83-2243), Al₂O₃ doped rutile (89-8301) and austenite (33-0397) which represents the Inconel625 were detected, these results mean that the TiO₂/Al₂O₃/Inconel625 composite coating was obtained by the method mentioned above. From the analysis of Fig.2 b, which revealed the differences of the surface phase composition between samples with TiO₂/Al₂O₃/Inconel625 composite coating and just Inconel625 coating after molten salt corrosion at 900 °C in air for 24 h. Sample with the composite coating showed relatively simple phases while the other one showed more complex surface components. Both samples had NiO (89-7101) as their main phases, but there were more iron oxides for sample with Inconel625 coating, also Nb₄P₂O₁₁₅ (25-0592) and KₓCrO₂ (28-0745) were found on the surface of this sample, these results might mean that for the sample with single coating, exfoliation of oxides film was occurred and oxides of the trace components of the alloy were exposed. For the sample with composite coating, the oxides film was more simple and adhesive.

3.3 SEM morphology

Figure 3 shows the surface morphology of samples with Inconel625 and TiO₂/Al₂O₃/Inconel625
composite coatings molten salt corroded at 900 °C in air for 24 h, A1 and A2 for Inconel625, B1 and B2 for TiO2/Al2O3/Inconel625 composite coating in different magnification. For specimen A, sample had a surface morphology with many split lamellar structures, which were composed of NiO and Fe2O3 through the EDS analysis, the relatively plat part on the surface was NiO. When enlarged to 2000 times as in picture A2, the surface presented characteristics with loose structure, which were composed of different forms of iron oxides, this structure could hardly protect the inner matrix from molten salt corrosion.

As a comparison to sample A, sample B was covered by TiO2/Al2O3/Inconel625 composite coating, after corrosion, a relatively compact surface was obtained, which was composed of NiO and Cr2O3, the loose structure with more lighter contrast degree were composed of the oxides of Zr, Mo and Na together with NiO and Cr2O3. From the analysis of the fractured regions of the oxide film, the inner and outer oxide films were composed of the same main oxides, that were still NiO and Cr2O3, the difference was that there were more Carbon and Sulphur in the inner film. These results were consistent with the XRD analysis of the sample surfaces.

Figure 3 shows the cross-section morphology of the samples covered by Inconel625 coating and TiO2/Al2O3/Inconel625 composite coating after molten salt corroded at 900 °C for 24 h. From the results we can see that, the oxide films on the surface of the sample with Inconel625 coating was fractured, which were composed of iron oxides and little NiO. The next layer was thick inner oxidation region with thickness of more than 30 micron. Components of the inner oxidation region were Fe2O3 and NiO. On the other side, the morphology for sample with composite coating was different from the above sample, which had more compact oxides films with little crack areas. The film was composed of NiO and Cr2O3 as the main layer, there was an internal oxidation zone with a thickness less than 20 micron. In this region, oxides of Nb, Mo, Al, Cr were detected. Where the outermost oxides film was loose or had other flaws, there would have thick inner oxidation region.

TiO2 and Al2O3 addition to the surface coating promoted the formation of the compact oxide film on the sample surface and effectively prevented inner oxidation of the matrix.
From the analysis of the results for the two samples, a more protective coating was obtained by the sol-gel method combined with plasma surfacing technology, which was composed of TiO$_2$/Al$_2$O$_3$/Inconel625 composite coating.

![Cross-section morphology](image)

Figure 4. The cross-section morphology of the samples covered by Inconel625 coating(a) and TiO$_2$/Al$_2$O$_3$/Inconel625 composite coating(b) after molten salt corrosion at 900 °C for 24 h

4. Conclusions

(1) Sol-gel method and plasma surfacing technology was successfully used to prepare TiO$_2$/Al$_2$O$_3$/Inconel625 composite coating on the surface of Q235 alloys.

(2) TiO$_2$/Al$_2$O$_3$/Inconel625 composite coating improves the molten salt corrosion resistance properties of the Q235 alloy at 900 °C by promoting the formation of compact and adhesive film just like Cr$_2$O$_3$.

(3) A lot of iron oxides with different forms could be found on the corrosion surface of the Inconel625 coated sample, the loose structure was detected in this study, which had little protective affection to the matrix.

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