Preparation and high temperature oxidation 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. Oxidation 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 innermost continuous but not compact enough Cr$_2$O$_3$ layer, the outer layer next to Cr$_2$O$_3$ was loose and cracked NiO, and the outermost layer was composed of iron oxides for the Inconel625 coated sample. For the composite coating sample, the oxide film was composed of NiO as the outermost layer, Cr$_2$O$_3$ as the inner layer, there was a very thin but continuous layer consisted of Cr$_2$O$_3$ and Al$_2$O$_3$ as the innermost layer. This work shows that TiO$_2$/Al$_2$O$_3$/Inconel625 composite coating improves the high-temperature oxidation resistance properties of the Q235 alloy at 900 °C by promoting the formation of the protective Cr$_2$O$_3$ and Al$_2$O$_3$ film.

1. Introduction
With the development of the society, people's living standards continue to improve. At the same time, more and more garbage is produced, the environmental pollution problem has become more and more serious, so researchers pay close attention to how to deal with so much garbage through an environmental-friendly way[1-3]. Comparing to compost and landfill, waste incineration shows obvious advantages, such as saving space, energy regeneration, harmlessness. For the waste incineration process, the most serious problem is the corrosion on the surface of the combustion furnace, which directly cause the invalid of the furnace and also make hidden danger during the incineration process. So modification of the furnace surface such as coating preparation has been paid more attention recently. In some countries, Inconel625 alloy coating has been prepared on the furnace surface to prevent the corrosion during incineration process because of its excellent oxidation and chlorine corrosion behavior[4,5]. Usually, high-temperature alloys include doping active elements(Al, Si, Cr, et.al) into the matrix, which will be oxidized firstly and the obtained thin films (Al$_2$O$_3$, Si$_2$O$_3$, Cr$_2$O$_3$, et.al) on the outermost layer of the alloys which can prevent the further oxidation of the inner matrix[6-8]. The preparing method of coatings including magnetron sputtering, plasma spraying, thermal spraying, as well as sol-gel method. The sol-gel method has distinctive advantages, but the process usually needs long time to repeat the dipping and pulling procedure to obtained the required
thickness of the film. The research in this work, the sol-gel method was combined with the plasma surfacing process to obtain protective 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 oxidation 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 progress, 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 was 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 cyclic oxidation at 900 °C for 24 h.

3. Results and Discussion

3.1 Oxidation thermodynamics

Figure 1 shows the Oxidation thermodynamics of Q235 alloys with Inconel625 and TiO2/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 high-temperature oxidation resistance of the alloy obviously. Sample with Inconel625 coating showed nearly linear growth law during the 24 h oxidation process, while the coated sample showed different oxidation rate at different stage. TiO2/Al2O3/Inconel625 composite coating gives the specimen less mass gain and slower oxidation rate, which means more protective film could have been prepared in this research.

![Figure 1. Oxidation thermodynamics of Q235 alloys with different coatings oxidized at 900 °C for 24 h](image)

3.2 XRD analysis

Figure 2a shows the XRD patterns of sample covered by TiO2/Al2O3/Inconel625 composite coating.
The analysis of the results show 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 oxidation at 900 °C in air. Sample with the composite coating showed relatively simple phases while the other one showed more complex surface component. Both samples had NiO (89-7101) as their main phases, the appearance of Al₂TiO₅(70-1434) for the composite coating sample might restrain the further oxidation of the matrix alloy.

3.3 SEM morphology
Figure 3 shows the surface morphology of samples with Inconel625 and TiO₂/Al₂O₃/Inconel625 composite coatings oxidized 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 structure, which were composed of NiO and Cr₂O₃ 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 could hardly protect the inner matrix from oxidizing.

As a comparison to sample A, sample B was covered by TiO₂/Al₂O₃/Inconel625 composite coating, after oxidization, a relatively smooth surface was obtained, which was composed of NiO and Cr₂O₃, many small regions which were composed of carbon made the sample had different surface morphology with the other sample. When this region was magnified to 2000 times, colloidal substances covered the loose oxides were found as in Fig. B2, the substances seal up the space on the surface which might become passageway for further oxidation of the matrix alloy. So this kind of structure could protect the matrix and obtained materials with higher oxidation resistance.
Figure 4 shows the cross-section morphology of the samples covered by Inconel625 coating and TiO$_2$/Al$_2$O$_3$/Inconel625 composite coating after oxidized 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 were composed of three layers. The innermost Cr$_2$O$_3$ layer is continuous but not compact enough. The outer layer next to Cr$_2$O$_3$ was loose and cracked NiO, and the outermost layer was composed of iron oxides. 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 as the outermost layer, Cr$_2$O$_3$ as the inner layer, between these two layers, it was TiO$_2$ thin layer, there was a very thin but continuous layer consisted of Cr$_2$O$_3$ and Al$_2$O$_3$ was found as the innermost layer. At the same time, in this kind of condition, more inner oxidized areas were found near the grain boundaries of the Inconel625 coating, which were also composed of Cr$_2$O$_3$ and Al$_2$O$_3$. TiO$_2$ and Al$_2$O$_3$ addition to the surface coating promoted the formation of the protective film.

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, for it can gain continuous and compact Cr$_2$O$_3$ and Al$_2$O$_3$ layer to prevent further oxidation of the matrix alloy.

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 oxidized 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 high-temperature oxidation resistance properties of the Q235 alloy at 900 °C by promoting the formation of the protective Cr$_2$O$_3$ and Al$_2$O$_3$ film.

(3) Colloidal substances covered the loose oxides were found when the sol-gel method was used to get the coating, this special structure seal up the space on the surface which might become passageway for further oxidation of the matrix alloy.

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