Study on Molten Salt Corrosion Behavior of Several Stainless Steel Alloys

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Abstract: Molten salt corrosion tests were performed on several stainless steels, which were 622, 316, A59, 625, 686, 2#825, 3#825 and M400. After corrosion at 680 °C for 120 h, the sequence of alloys’ mass loss was 625<3#825<A59<622< 2#825<316<686<M400. SEM/EDS analysis was used to observe the surface and cross-section morphologies of the corroded samples. The alloys with high molten salt corrosion resistance formed Cr2O3 oxide layers on the surfaces of the samples, the formation of TiO2 could also enhance the corrosion resistance. However, Mn element was harmful to the alloys used in chlorine induced corrosion environment.

1. Introduction
China is the world's most populous country, with the acceleration of urbanization process, a large number of people concentrated in the city, which provides an powerful impetus for the country's prosperity, but also make the city face a series of difficult problems, a large number of urban garbage has become a prominent problem. In order to adapt to the national urbanization development strategy, reasonable, efficient and clean treatment of urban garbage has become an urgent need. At present, household waste disposal technology mainly includes sanitary landfill, composting and incineration to generate electricity. In view of the current technological development and commercial effect, landfill treatment has problems such as oversized landfill, slow processing speed, high cost. Composting waste disposal has complex procedures, large land area occupied, long cycle, at the same time, soil is faced with heavy metal pollution and other problems. Compared with the above treatments, waste incineration has the advantages of small occupation of land, easy site selection, obvious reduction, and the ability to utilize residual heat. Waste incineration treatment has gradually replaced composting and landfill as the preferred technology for the harmless, quantitative and resource-using of waste in large and medium-sized cities in China.

Garbage contains a certain amount of alkali metals, heavy metals and other substances, which will corrode the matrix seriously. Because Ni-based alloy has good anti-high temperature oxidation ability and strong corrosion resistance, it is of theoretical and practical significance to adopt Ni-based alloy as the inner wall coating of incinerator [1-3]. Among them, Inconel625 as a typical representative of Ni-based deformation high temperature alloy, with high stretching performance, fracture strength, excellent thermal fatigue strength, antioxidant and excellent welding performance, where Ni, Cr and Mo can improve the ability of antioxidant atmosphere, Mo can also prevent pitting and crevice corrosion. Nb has very high resistance to chloride stress corrosion and high temperature oxidation. Compared with iron-based and cobalt-based high-temperature alloys, nickel-based high-temperature
alloys have the characteristics of high operating temperature, less harmful phase and stable structure[4].

In order to enrich the corrosion data of different Ni-based alloys and expand the range of the optional materials which can be use as the inner wall coating of garbage incinerator, molten salt corrosion test were used to study the properties of 622, 316, A59, 625, 686, 2#825, 3#825 and M400.

2. Materials and methods

2.1 Materials

In this study, molten salt corrosion tests were carried out on 622, 316, A59, 625, 686, 2#825, 3#825 and M400 alloys. First, the powders of these alloys were coated on the surface of 12CrMoV tubes by laser clad method, respectively. Then the inner 12CrMoV tubes were removed by lathe. Finally, the test specimens with size of 2.5x5x10 mm were obtained by wire-electrode cutting. Table 1 shows the component contents of these specimens.

Table1. Actual compositions of the tested materials(wt.%)

| Alloy | Fe  | Cr   | Ni   | Mo   | Nb   | W   | Cu | Ti  | Mn  | Zr  | V   |
|-------|-----|------|------|------|------|-----|----|-----|-----|-----|-----|
| 625   | 0.559 | 21.36 | 65.47 | 8.72 | 3.51 | 0   | 0  | 0   | 0   | 0.051 | 0   |
| 686   | 4.16 | 20.00 | 56.88 | 14.93 | 0.18 | 3.03 | 0  | 0.219 | 0.56 | 0   | 0   |
| 622   | 2.98 | 21.17 | 59.37 | 12.92 | 0   | 3.01 | 0  | 0   | 0.309 | 0   | 0   |
| A59   | 2.28 | 21.97 | 59.83 | 15.47 | 0   | 0   | 0  | 0   | 0   | 0.163 | 0   |
| 316   | 66.68 | 18.72 | 10.65 | 2.11 | 0.025 | 0 | 0.132 | 0 | 1.32 | 0 | 0.098 | |
| 2#825 | 32.10 | 24.63 | 39.26 | 3.19 | 0   | 0   | 0  | 0.112 | 0.498 | 0   | 0   |
| 3#825 | 26.84 | 22.69 | 42.58 | 3.28 | 0   | 2.79 | 1.34 | 0.486 | 0   | 0   | 0   |
| M400  | 3.42 | 0.366 | 61.63 | 0.131 | 0    | 32.35 | 1.03 | 0.963 | 0   | 0   | 0   |

2.2 Corrosion tests

Corrosion exposures with duration of 120 h were carried out at 680 °C below a synthetic salt deposit which was composed of NaCl, KCl and Na2SO4, with the weight ratio of 5:5:2. Samples were put into individual quartz crucibles and buried in salt, then the exposures were carried out in a three-zone tube furnace under atmosphere environment.

2.3 Examination of exposed samples

Each sample was tested for three parallel samples, two of which were used to measure weight changes after corrosion, i.e. after corrosion samples were washed by ultrasonic cleaning of ethanol and acetic acid solution for two hours, removing surface salts and most of the corrosion product layers, after which the samples were analyzed for surface morphology and composition by XRD and SEM/EDS analysis. After the removal of residual small amount of stubborn corrosion layer by sandpaper polishing for a short period of time, corrosion weight loss data could be obtained. Another parallel sample was molded in resin and then grinded without any lubricants for the cross-section analysis of corrosion layer.

3. Results

3.1 Corrosion kinetics

The weight changes of each sample after molten salts corrosion at 680 °C for 120 h are shown in Fig. 1. Among them, M400 alloy is completely corroded, no residual sample is found, so its data is not shown in Fig.1. 686 sample also appears completely layered fragmentation phenomenon.

Since mass loss is contrary to the corrosion resistance of alloy, so the corrosion resistance sequence of the alloys from high to low is: 625>3#825>A59>622> 2#825>316>686>M400.
3.2 Surface morphology and composition

Fig. 2 shows the surface morphology and composition of the samples after cleaning the loose corrosion products by ultrasonic cleaning of ethanol and acetic acid solution for two hours.

![Surface morphology and composition](image-url)
From the analysis of corroded surface morphology and composition, it can be seen that 316 surface is mainly composed of iron oxides, iron oxides also appeared on 825 surfaces, especially for the 2#825, a large number of loose flakes of iron oxide area can be found under the discontinuous Cr$_2$O$_3$ layer, which is an important cause for poor alloy corrosion resistance, this structure is not conducive to preventing the internal diffusion of corrosive elements such as Cl, S ions and the external diffusion of metal chloride, and at last causes the large weight loss of the material. 622, A59, 625 and 686 surfaces are mainly composed of Ni and Cr oxides, which were more dense and also have better tolerance of Cl, S ions. For 686 alloy, due to special structural, parallel striped areas are formed on its surface, where salts are enriched and accelerate the infiltration and corrosion of molten salt. The surface composition of 622 is very similar to that of 625, but the former has a more loose and porous structure, which resulting in poor corrosion resistance.

Fig. 2 shows the cross-sectional morphology and composition of the corroded samples after clean the loose corrosion products cleaning (A for low magnification; B for high magnification)

Fig. 3 shows the cross-sectional morphology and composition of the corroded samples. Loose corrosion layer on 622 surface was found, which was the mixture of Cr$_2$O$_3$ and salt, and the Cr$_2$O$_3$ oxide did not form a continuous layer. 316 surface had been dissolved by molten salt, and a deep internal oxidation and corrosion region was obviously seen. A59 mainly formed NiO and Cr$_2$O$_3$ coating, a continuous Cr$_2$O$_3$ layer was formed between the corrosion layer and substrate, which was an important reason for high corrosion resistance of the alloy with. 625 surface formed a continuous Cr$_2$O$_3$ coating, there were some cracks between the coating and the matrix. The corrosion layer for 686 was the thickest and the most loosen one. The corrosion layer for 2#825 was mainly Cr$_2$O$_3$, a large number of oxides on the outmost surface were dissolved by molten salt. Although the inner coating was dense and continuous, but there were obvious cracks between the corrosion layer and the matrix, resulting in internal oxidation and Cl iron infiltration corrosion of the alloy substrate. The Cr$_2$O$_3$ coating on the surface of 3#825 was separated from the substrate, but the continuous TiO$_2$ and Cr$_2$O$_3$ mixed oxide coatings were visible on the surface of the substrate, which was highly protective. In summary, it can be known that the corrosion morphology and composition of the alloys are consistent with the corrosion dynamics, the former can explain the internal reasons for its corrosion resistance order.
4. Discussion
In this research, molten salt corrosion of alloys under atmosphere environment followed the activated oxidation mechanism, because there were enough oxygen for the metal chlorides volatilized from the surface of alloy matrix to change to metal oxides and chlorine, the latter would back to corrosion process of the alloy.

Alloy composition has very important effect on the corrosion degree, usually, Cr is the most effective element to chlorine induced corrosion because of the excellent stability of its oxide product Cr₂O₃, Ni element can promote the formation of protective layer of Cr₂O₃, so Ni-Cr alloys are usually used as high corrosion resistance materials in extreme conditions. In this work, 625, A59 and 622 have more higher Ni and Cr content, therefore, they have high corrosion resistance. The gaseous iron chloride has a high partial pressure at the test temperature. Thus for the 316 alloy, there was no oxides layers found after corrosion process, this cause the poor stability of this alloy under the corrosive condition. M400 has too much Cu element, which has high reducibility, but in this oxidizing atmosphere, the oxidation-reduction reaction was completely carried out and the alloy was totally corroded. TiO₂ has the similar function as Cr₂O₃ during the corrosion process, so 3#825 alloy which has high Ti content showed high corrosion resistance in this research. Mn element in stainless steel usually causes the decline of the corrosion resistance, this phenomenon is still applicative in this molten salt corrosion process of alloys.

![Fig.3. Cross-sectional morphology and composition of alloys after molten salt corrosion at 680°C for 120 h](image_url)
5. Summary and conclusions
1) Molten salt corrosion tests were performed on several stainless steels, which were 622, 316, A59, 625, 686, 2#825, 3#825 and M400. After corrosion at 680 °C for 120 h, the sequence of alloys’ mass loss was 625<3#825<A59<622< 2#825<316<686<M400.
2) M400 and 316 alloys are not suitable for molten salt corrosion condition, and can not be used in chlorine induced high temperature atmosphere.
3) Ti element is benefit to improve the molten salt corrosion resistance of alloys, Mn element has the contrary effect.

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