Study on Oxidizing Chlorine Induced Corrosion Behavior of Several Stainless Steel Alloys

Changhui Miao¹, Longfa Jiang², Lingyun Bai*, Tuchun Chen¹

¹Jiangxi Science and Technology Normal University, Nanchang 330013, China;
²Nanchang Customs Comprehensive Technology Center, Nanchang 330013, China.

* email: 1020101028@jxstnu.edu.cn

Abstract: High temperature chlorine corrosion tests were performed on several stainless steels, which were 622, 316, A59, 686, 2#825, and 3#825. After corrosion under 70N₂-2CO₂-1O₂-0.2HCl oxidizing gaseous environment at 800 °C for 120 h, the corrosion dynamics of alloys were obtained, which showed the ability of alloys' high temperature chlorine corrosion resistance. The corrosion resistance sequence from high to low was A59>686>622>3#825>2#825>316. This order is consistent with the Mo element content in the alloy. SEM/EDS analysis was used to observe the surface and cross-section morphology of the corroded samples. Alloys with high chlorine induced corrosion resistance formed Cr₂O₃ oxide layers on the surfaces of the samples, such as 622, 686 and A59. Iron oxides formed alloys, such as 316 and 2#825, had lower corrosion resistance, because of the loose and porous oxides, which had very high vapor pressure. The formation of TiO₂ could also enhance the corrosion resistance.

1. Introduction

Waste incineration treatment has gradually replaced composting and landfill as the preferred technology for the harmless, quantitative and resource-using of waste. Garbage contains a certain amount of alkali metal, heavy metals and other substances, which will corrode the matrix seriously[1,2]. This puts high demands on the corrosion resistance of the alloys used for boiler equipment such as water walls and super-heaters.

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[3-5]. 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, has been widely used in the waste incineration equipment[6-8]. Most of the other alloys have not been adopted in this kind of conditions, 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, chlorine induced corrosion was carried out on 622, 316, A59, 686, 2#825 and 3#825 alloys under 70N₂-2CO₂-1O₂-0.2HCl oxidizing gaseous environment in this research.
2. Materials and methods

2.1 Materials
In this study, chlorine induced corrosion was carried out on 622, 316, A59, 686, 2#825 and 3#825 alloys under 70N₂-2CO₂-1O₂-0.2HCl oxidizing gaseous environment at 800 °C for 120 h. 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 a lathe. Finally, the test specimens in size of 2.5x5x10 mm were obtained by wire-electrode cutting. Table 1 shows the component contents of these specimens.

| Alloy | Fe  | Cr  | Ni  | Mo  | Nb  | W   | Cu  | Ti  | Mn  | V  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|
| 686   | 4.16| 20.00| 56.88| 14.93| 0.18| 3.03| 0   | 0.219| 0.56| 0  |
| 622   | 2.98| 21.17| 59.37| 12.92| 0   | 3.01| 0   | 0   | 0.309| 0  |
| A59   | 2.28| 21.97| 59.83| 15.47| 0   | 0   | 0   | 0   | 0   | 0.163|
| 316   | 66.68| 18.72| 10.65| 2.11| 0.025| 0   | 0.132| 0   | 1.32| 0.098|
| 2#825 | 32.10| 24.63| 39.26| 3.19| 0   | 0   | 0   | 0.112| 0.498| 0  |
| 3#825 | 26.84| 22.69| 42.58| 3.28| 0   | 0   | 2.79| 1.34| 0.486| 0  |

2.2 Corrosion tests
Corrosion exposures with duration of 120 h were carried out below oxidizing and chlorine containing gaseous environment at 800 °C. Each sample was tested for two parallel samples to ensure the accuracy and stability of the data results, which were put into individual quartz crucibles, and then the exposures were carried out in a three-zone tube furnace under 70N₂-2CO₂-1O₂-0.2HCl gaseous environment. The gas flow was 75 ml/min and the heating rate of the tube furnace was 15°C/min. The corrosion process was stopped every 10 h. Samples were cooled naturally with the furnace and then an electronic balance with a precision of one in 100,000 was used to weigh the samples’ weight. After that process, the corrosion was carried on until to 120 h.

2.3. Examination of exposed samples
After chlorine induced corrosion under 70N₂-2CO₂-1O₂-0.2HCl gaseous environment at 800 °C for 120 h, the corrosion dynamics curves of test samples were obtained by the mass change measured during the process, and the surface morphology and composition of samples were checked by XRD and SEM/ EDS analysis technique. Samples were molded in resin and then grinded without any lubricants to conduct the cross-section analysis of corrosion layers.

3. Results

3.1 Corrosion kinetics
The weight changes of each sample after chlorine induced corrosion under 70N₂-2CO₂-1O₂-0.2HCl oxidizing gaseous environment at 800 °C for 120 h are shown in Fig.1. All alloys show mass loss during this corrosion condition. These phenomena were mainly caused by the boiling points of the metal chlorides formed in these corrosion processes, which were all below 800 °C. Among them, 316 alloy is the least resistant to corrosion, which has a mass loss value of nearly 100 mg/cm². 2#825 also shows poorer corrosion resistance than other Ni-based alloys.

A59 shows the minimum mass loss and enters a stable stage after 30 h, which has nearly no mass change. This phenomenon is found for 686, however its total mass loss is higher than A59. 622 and 3#825 show much higher corrosion rates and still no tendency to stability of mass change during this 120 h test, especially for 3#825. Since mass loss is contrary to the corrosion resistance of alloy, so the corrosion resistance sequence of the alloys from high to low is: A59>686>622> 3#825>2#825>316.
3.2 Surface morphology and composition

Fig. 2 shows the surface morphology and composition of the corroded samples.

From the analysis of corroded surface morphology and composition, it can be seen that 316 surface is mainly composed of iron and nickel oxides, which have porous morphology and no protective affection, these holes are caused by the volatilization of the iron chlorides from the corrosion layer. Iron oxides also appear on 825 surfaces, especially for the 2#825, which has a larger porous and rough area. 3#825 has better corrosion resistance than 2#825, this result is on account of the formation of TiO2 as we can see in Fig. 2. A59 and 622 surfaces are mainly composed of Cr2O3, which are dense and have better tolerance of Cl ion. As far as 686 is concerned, Cr2O3 is also the main product on the rough surface. Oxides of Ni, Fe, Ti and W and their chlorides are found. Area where are rich of W element has a broken and porous morphology. This phenomenon might indicate that W is a harmful element for the alloy to resist chlorine corrosion.
3.3 Cross-section morphology and composition

Fig. 3 shows the cross-sectional morphology and composition of the corroded samples. The outermost loose corrosion layer on 622 surface has been dispersed in resin, which is composed of (Ni,Cr,Fe)O_y and Cl. The interlayer is consisted of Cr_2O_3, which is the most protective component of the corrosion process. Between the Cr_2O_3 layer and the matrix, (Ni, Fe),O_y and Cl are found, which means the Cl has penetrated from the Cr_2O_3 layer and damaged the matrix. 316 shows the most serious corroded cross section morphology, its loose outermost layer is not seen in this picture, but its large area of internal oxidation has been found, which is composed of (Ni, Fe),O_y, Cr_2O_3, Cl and Mo_2O_3. There are many holes in this region, so we can come to a conclusion that the 316 alloy will be corroded continuously until totally disappear which is in keeping with the corrosion dynamic curve. A59 mainly formed an inner Cr_2O_3 layer and an outer (Ni, Cr),O_y and Cl layer, and there is no obvious internal oxidation region found. A59 has the thinnest corrosion layer among these test alloys. The corrosion layer for 686 is also composed of Cr_2O_3, which is more thicker, but in its broken area, (Cr, Ni, W),O_y and Cl are found. 2#825 and 3#825 have similar components, but the higher iron content in the matrix of 2#825 causes the higher amount of iron oxide in the corrosion layer, which is more susceptible to chlorine corrosion for its low boiling point and high vapor pressure.

Fig.3. Cross-sectional morphology and composition of alloys the samples corroded under 70N_2-2CO_2-1O_2-0.2HCl oxidizing gaseous environment at 800 °C for 120 h

4. Discussion

In this research, high temperature chlorine corrosion tests under 70N_2-2CO_2-1O_2-0.2HCl oxidizing gaseous environment at 800 °C for 120 h were performed on several stainless steels, which were 622, 316, A59, 686, 2#825, and 3#825. Corrosion of alloys under this gaseous 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 once again back to corrosion process of the alloy.

Among the composition of the tested alloys, Cr and Ni are the beneficial elements to resist chlorine induced corrosion because of the excellent stability of their oxides product. Ni element can also promote the formation of a protective layer of Cr_2O_3, so Ni-Cr alloys are usually used as high corrosion resistance materials in extreme conditions. In this work, A59, 686 and 622 have high Ni and Cr content, therefore, they have high corrosion resistance. And the corrosion layers of them are all mainly composed of Cr_2O_3. 825 samples also have high Cr content, but they have too much Fe, which can not form protective layer for the matrix to face to chlorine containing environment, especially for
Mo is usually added into the alloys to improve the pitting resistance ability of alloy, in this research, the corrosion resistance sequence of the tested alloys is just consistent with the Mo content of these alloys, the mass loss becomes larger along with the Mo content turns smaller. Mn element in stainless steel usually causes the decline of the corrosion resistance. This phenomenon is still applicable in this high temperature chlorine induced corrosion process of alloys.

5. Summary and conclusions
1) High temperature chlorine corrosion tests under 70N2-2CO2-1O2-0.2HCl oxidizing gaseous environment at 800 °C for 120 h were performed on several stainless steels, the corrosion resistance sequence of the alloys from high to low is: A59>686>622>316>2#825>316.

2) 316 and 2#825 alloys are not suitable for this corrosion condition, and can not be used in chlorine induced high temperature atmosphere. A59 and 686 alloys are suitable to be used in this kind of corrosion condition.

3) Mo element is benefit to improve the high temperature chlorine corrosion resistance of these tested alloys.

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