



# HOKKAIDO UNIVERSITY

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| Title               | Study on High-Temperature Corrosion of Ni-based Alloys in Atmosphere Containing Alkali Metal Chloride Vapor [an abstract of entire text]                              |
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## **DISSERTATION SUMMARY**

**Title of dissertation submitted for the degree**

**Study on High-Temperature Corrosion of Ni-based Alloys in Atmosphere  
Containing Alkali Metal Chloride Vapor**

With the high population growth and high solid solid waste generated in the world, the demands of new waste to Energy (WtE) power plants will always be increased; particularly in the China and other developing countries. While in the developed countries, they focused to modernize and increase the utilization factor their WtE power plants, such as increasing the boiler operation temperatures from 400 °C to 580°C in the last decade.

With such high temperature in the incinerator equipment, particularly boiler parts e.g. heat exchange tube and superheater are having major problem due to a material degradation by high temperature corrosion. In the incineration environments, the corrosion becomes the major problem due to high chlorine concentration in waste and its rapid corrosion process particularly during the combustion process. During combustion, the alkali salts were released, and it will be deposited later on the surface of boiler parts and the chlorine corrosion becomes accelerated leading faster degradation materials. In the Internal Circulation Fluidized Bed (ICFB) which has a steam operating temperature at 570 °C, the bed material such as sand particle containing high chlorine

concentration is circulated continuously during the combustion from the main combustion chamber into the heat exchange cell where the heat exchange tubes (HET) were installed. Continuous hitting of the bed material to the surface of HET caused corrosion induced erosion. Thus, improving the corrosion resistance of the material used in the boiler component directly links to the lifetime of the materials.

NiCr-based alloys and coatings with are widely used for the boiler component because their excellent corrosion performance. Although Fe has less corrosion resistance than Ni and Cr, Fe has better mechanical strength and cheaper alloys than both alloys. Meanwhile, Mo is widely accepted to enhance the corrosion resistance of Ni-based alloys and coatings. In the power plant industries, particularly the WtE power plants, further improvement of the corrosion resistance is still necessary to increase the lifetime and operation temperature. In order to develop new alloys, it is necessary to understand the mechanism of the corrosion, effects of alloying elements on the corrosion. Thus, in this study, the corrosion behavior of Ni20Cr-based alloy with Mo or Fe additions in atmospheres containing air and salt-vapor at 570 °C was evaluated.

This thesis consists of seven chapters in total. Chapter 1 introduced the research background from current status and trend of WtE industry, different types of incineration technologies and corrosion problem in the WtE incinerators; the literature studies of high temperature corrosion in the chlorine atmosphere; the scope and aims of research study; and the outline of study.

Chapter 2 described the details of experimental methods. Ni20Cr-based alloys were used with variations of Mo (0, 1, 3, 7 in wt.%) and Fe (0, 4, 30 in wt.%) additions. The corrosion was performed at 570 °C in oxidizing atmosphere (with air and salt vapor) and low oxidizing atmosphere (with Ar and salt vapor) for 100 h. A salt mixture composed of 40% NaCl + 40% KCl + 20% CaCl<sub>2</sub> (mol %) was used as the source of the salt-vapor. During the tests, the salt mixture was placed upstream of the specimens with the respect of the gas flow with a linear velocity of 0.33 cm/sec at 600°C. After the given corrosion time (25, 50, or 100 h), the corrosion mass change was measured at room temperature.

In order to investigate corrosion performance, all reaction products formed on the corroded samples were removed by chemical treatments based on ISO 17248:2015(E). This chemical treatment procedure was performed to measure the total consumed mass or mass loss due to corrosion. Then, by using the calculation, we evaluated  $\Delta W_g$ ,  $\Delta W_l$ , and  $W_M^{\text{in MCl}_2(\text{g})}$  in this study.

Then, we performed the X-ray diffraction (XRD) to analyse formed phases of the corrosion products. The cross-section of all samples prior and after the corrosion tests including their distributions of each element were examined by using field-emission scanning electron microscopy-energy-dispersive X-ray spectroscopy (FESEM-EDS). The cross-section of all samples were prepared by focused ion beam milling to avoid the loss of metal chlorides.

Chapter 3 investigated the corrosion performance of Ni-Cr alloys with combinations of 1-7 wt. % of Mo, and 4 or 30 wt. % of Fe addition, and evaluated the effect of each combination on the corrosion performance in the salt vapor containing atmosphere. The results show that combination of Mo and Fe addition gives better corrosion resistance to the Ni20Cr-based alloys. The evaporation of metal chlorides during corrosion decreased with Fe addition to Mo containing alloys, and further decreased with the higher Fe contents in the alloys. To achieve the optimum of combination results to give better corrosion performance and minimize the evaporation of metal chlorides, with more Mo addition was added into the Ni20Cr-based alloys, higher Fe contents need to be added too.

The microstructure of cross-section of the alloys after the corrosion showed that the alloys formed an outer Ni-Fe oxide scale and an inner porous of Cr-Mo oxide and oxychlorides scale. The composition of Ni and Fe on the outer oxide scale depended on the Fe content in the alloys.

Based on resulted data, it is still difficult to understand the corrosion mechanism behind the improvement of corrosion performance by the combination of Mo and Fe addition. Thus, in the next chapters, the results of each addition of Mo and Fe will be explained.

Chapter 4 investigated only the effects of Mo addition up to 7 wt. % on the corrosion behavior of Ni20Cr-based alloy in oxidizing-chlorine containing atmosphere. The Mo-free Ni20Cr alloy corroded with a high corrosion rate due to a formation of

chromates. The chromate formation caused breakdown of the protective  $\text{Cr}_2\text{O}_3$  scale leading to the higher chlorine potential at the surface of  $\text{Cr}_2\text{O}_3$  oxide scale and the generation of chlorine. The generated chlorine penetrated in to the alloy substrate through cracks and/or pores in the oxide scale, promoting the internal precipitation of chromium chloride which consumed the Cr in the subsurface region to form a thick Cr-depleted zone. This condition resulted in a less protective  $\text{NiCr}_2\text{O}_4$  formation, and the alloy became oxidized rapidly to form a thick oxide scale.

Mo addition to the Ni20Cr alloy has given better corrosion performance. The optimal Mo content for this alloy was found to be 3 wt. %, and lower or higher Mo contents resulted in increased corrosion mass gain and metal chloride evaporation. Mo addition with the presence of Mo-oxide promoted NiO formation at the initial stage, which was able to prevent the chromate formation. Thus, the chlorine potential at the surface was not increased and a Cr-rich oxide scale could be formed continuously below the NiO. However, the oxygen potential the oxygen potential at the interface between oxide scale and alloy substrate decreased due to the NiO and the Cr-rich oxide, which promoted the Mo-oxy-chloride formation ( $\text{MoO}_2\text{Cl}_2$ ). The  $\text{MoO}_2\text{Cl}_2$ , then evaporated, forming pores in the inner oxide scale.

Preventing chromate formation by NiO scale formation is one of the key points for increasing the corrosion resistance of  $\text{Cr}_2\text{O}_3$ -forming alloys in salt vapor-containing environments.

Chapter 5 investigated the effects of Mo on the corrosion behavior of Ni20Cr-based alloy in the low oxidizing atmosphere in order to confirm the mechanism proposed in the chapter 4. The corrosion mass gain of Mo-free Ni20Cr-based alloy decreased significantly comparing to that in the oxidizing-chlorine containing atmosphere. Decreasing the corrosion rate in the Mo-free alloy was attributed that chromates was not formed because of the insufficient oxygen concentration in the low oxygen atmosphere. Thus, the chlorine potential at the surface remained low, which resulted in formation of a thin continuous protective  $\text{Cr}_2\text{O}_3$  scale that could protect the alloy substrate. This showed that the oxygen heavily affected the corrosion behavior of the Ni20Cr alloy in the chlorine containing atmosphere.

However, the corrosion rate of the Mo-containing alloys was found to increase. In the low oxidizing-chlorine atmosphere, the corrosion for the Mo containing alloys in the led formations of a continuously dense NiO as an outer oxide scale and dense inner oxide scale with “island-like” corrosion products composed of high Cr-Mo oxychlorides. No, protective  $\text{Cr}_2\text{O}_3$  scale formed below the NiO scale. Thus, a NiO formed on Mo containing alloys, allowed chlorine and KCl gas to penetrate into the alloy substrate. Then those gas species reacted with the Cr and Mo to form highly volatilized oxychloride, resulted in the corrosion products composed of high Cr-Mo oxychlorides.

The results in the chapter 5 confirmed that the proposed corrosion mechanism for corrosion behavior of Ni20Cr-based alloy in the oxidizing-chlorine containing atmosphere.

Chapter 6 investigated the effects of Fe on the corrosion behavior of Ni20Cr-based alloy in the oxidizing atmosphere. Fe addition to Ni20Cr-based alloy improved the corrosion resistance in the oxidizing-chlorine containing atmosphere. Although the oxide scale structure formed on the Fe containing alloys were similar to that formed on the Fe-free Ni20Cr-based alloy. However, at the initial corrosion stage, a Fe oxide scale was formed faster than Cr<sub>2</sub>O<sub>3</sub> scale. The Fe-rich nodules shape covered the Cr<sub>2</sub>O<sub>3</sub> and prevented the chromates formation on the Cr<sub>2</sub>O<sub>3</sub> surface leading low the chlorine potential at the alloy surface. Because the Fe oxide is not a protective scale, some alkali chlorides could react with Cr<sub>2</sub>O<sub>3</sub> to form the chromates. Low extent of chromate formation due to the Fe oxide formation resulted in thin internal Cr-chloride penetration and Cr-depleted zone. With more Fe addition, the chromates formation became less resulted in the thinner both internal Cr-chloride penetration and Cr-depleted zone. Thus, a continuous Cr<sub>2</sub>O<sub>3</sub> scale could be maintained to protect the alloy substrate for a longer period.

Finally, in the chapter 7, the general conclusion summarized the corrosion behavior and mechanism of Ni20Cr-based alloy in the chlorine containing atmosphere with high-low oxygen contents, including its alloying effects of Mo and Fe to the Ni20Cr-based alloy.