Corrosion Phenomena of High Temperature Alloys by Helium Impurities in the Primary Coolant of HTGR

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Abstract. The primary coolant circuit of the high temperature gas-cooled reactor (HTGR) contains trace impurities. A nickel base alloy would corrode when exposed to an atmosphere at a high temperature and for a long time. The protective oxide scale formed by chromium is an important factor to prevent severe corrosion of high temperature alloys. Corrosion tests were conducted on Inconel 617, Incoloy 800H, Hastelloy X, and T-22, which are commonly used in the steam generator of HTGR. The alloys were exposed to helium with trace impurities for 48 hours at 950℃. The corrosion results were analyzed by weighing, scanning electron microscopy (SEM) and electron probe microanalyzer (EPMA). All the four alloys formed oxide scales in this atmosphere, but they differ in the capacity to resist corrosion. Therefore, the carbon transfer phenomenon observed in this experiment varies for the different alloys. In addition, for Cr in Inconel617, the expected depletion phenomenon near the corrosion layer occurred, which is consistent with the results from theoretical analysis.

1. Introduction

The high temperature gas-cooled reactor (HTGR) is characterized by the high outlet temperature, which is up to 950℃. Meanwhile, there are trace impurities in the primary coolant circuit, such as CO, CH₄, H₂O and H₂ in the 0.1–10 Pa range [1]. The impure helium atmosphere puts forward new challenges to the material performance. Nickel-based alloys have been used in high temperature applications since long time due to their superior corrosion resistance, especially, they have been widely utilized in the heating surface tubes of the HTGR steam generator in recent decades.

Decarburization, carburization and internal oxidation are three main corrosion phenomena for the Nickel based alloy. According to a large number of previous experimental data [2-4], it is shown that the decarburization leads to a decrease in the creep performance, the severe carburization leads to the low temperature embrittlement of materials, and the internal oxidation leads to surface embrittlement. Therefore, this corrosion should be prevented. Generally speaking, Ni based Cr rich alloys can form the dense oxide scale, which effectively improves the corrosion resistance. The protective oxide scale can prevent the further rapid corrosion such as decarburization and carburization. Inconel 617 and Hastelloy X alloys were mainly used in the prototype plant for nuclear process heat (PNP) project in Germany and HTTR in Japan [5-6]. In Shandong province of China, the Pebble-bed Modular High-Temperature Gas-cooled Reactor (HTR-PM) has been designed and constructed by INET of Tsinghua University. In the heating surface tubes of the steam generator, the evaporation and overheat segment are made of Incoloy
800H and T-22 alloy [7-8]. At present, there are few engineering application examples of these two alloys in the HTGR field, so a lot of experiments should be conducted to verify the corrosion resistance of the materials.

The purpose of this work is to investigate the corrosion phenomena of the high temperature alloys used for HTR-PM and compare them with the corrosion behavior of the other two common alloys in the steam generator. Corrosion experiments of the four alloys were carried out for 48 hours at 950°C in an impure helium atmosphere. The quality change, surface morphology and element distribution of the samples were analyzed.

2. Experimental Procedures
The alloys used in this work are: Inconel 617, Hastelloy X, Incoloy 800H and T-22. The chemical composition of these alloys is shown in Table 1.

| Alloys         | C    | Cr   | Fe  | Mn  | Ti  | Al  |
|----------------|------|------|-----|-----|-----|-----|
| Inconel 617    | 0.01 | 24.3 | 0.29| 0.04| 0.72| 1.23|
| Hastelloy X    | 0.01 | 22.7 | 24.0| 0.68| 0.33| 0.18|
| Incoloy 800H   | 0.39 | 21.8 | Base| 0.53| 1.03| 0.79|
| T-22           | 0.01 | 2.11 | Base| 0.54|    | 0.1 |

The samples were processed into 20*40*2mm pieces. The final heat treatment temperature of the material was 1180°C, and water cooling was used for 10 mins. Both sides of the samples were mechanically polished by abrasive paper from 600# to 2000#. Then, the samples were ultrasonically degreened in an acetone mixture, dried in air, and weighed with an electronic balance with an accuracy of 0.1mg.

For the corrosion test, eight samples (two samples for each alloy) can be exposed at the same time, being placed in a separate quartz tubes, which are housed in a high-temperature furnace. The corrosion test is carried out in a flowing impure helium gas at atmospheric pressure and at a flowing rate of 0.1 ml s⁻¹ cm⁻² sample surface. The tubes are made of quartz to avoid the influence of the test device in this test atmosphere. The impurities of the gas were configured before the test, and are shown in Table 2. The flow rate of the gas is controlled by the mass flow meter with 200 mL/min. The samples were heated at a rate of 5 °C/min and cooled at a rate of 10 °C/min in the test atmosphere.

| Impurities | O₂   | H₂   | CH₄  | CO   | H₂O  |
|------------|------|------|------|------|------|
| Content(ppm)| 1.0  | <0.1 | <0.05| <0.05| 6.0  |

After the corrosion test, the sample was weighed with EX224ZH balance, which is produced by OHAUS of USA, with an accuracy of 0.1mg. XQ-1 Metallographic Specimen Inlay Machine was utilized to press thermosetting plastics for the sample, which would be helpful for the observation. Just like before, samples were mechanically polished by abrasive paper from 600# to 2000# until there was no scratches and stains on the alloy surface. Finally, the samples characterized by the scanning electron microscopy (SEM) with the energy dispersive spectrometer (EDS) system and the electron probe microanalyzer (EPMA). The morphology, element distribution and content with the depth of the corroded samples were obtained in the following sections.
3. Results and Discussion

3.1. Mass Gain

![Mass Gain Graph](Image)

**Figure 1.** Mass gains of the four alloys after the test.

As shown in Fig. 1, the four alloys showed a mass increase after the corrosion test. They all showed a significant mass transfer from the atmosphere, where impurities were transferred to the alloys through surface reactions. Hastelloy X and T-22 have a low mass gain, indicating a potentially good corrosion resistance. This is consistent with the previous test results of Tsinghua University and the findings of C.J.Tsai [9]. This result needs to be further verified by SEM with EDS system and EPMA in the next section.

3.2. Inconel 617

![Inconel 617 SEM Images](Image)

**Figure 2.** The cross-sectional SEM micrographs with EDS for Inconel 617 alloy and the distribution of various elements.

Figure 2 presents the cross-sectional SEM micrographs with EDS for Inconel 617 alloy after 48 hours corrosion at 950°C. From figure b) to f), the EDS system shows the distribution of carbon, oxygen, aluminum, chromium and titanium. The chromium content in the alloy is high, so it combines with free oxygen to form a Cr₂O₃ scale. According to figures c) and e), it can be obviously seen that there are Cr₂O₃ scales on the Inconel 617 surface. In addition, large amounts of spinel can be observed below the surface oxide layers. The internal and inter-granular Al₂O₃ is well developed due to the preferential...
oxidation of Al in Alloy 617. The extensive development of internal oxides may prove the protection from the surface oxide scale of Inconel 617. This is consistent with the results of C. Jang et al [10].

Figure 3 shows the distribution of various elements in Inconel 617 alloy with the depth measured by EPMA. In this figure, the thickness of the oxide layer can be quantitatively determined to be about 4μm, and the scale is composed of chromium, aluminum and titanium oxides, of which chromium is the dominant element. According to the change of carbon content in Fig. 3, slight carburization occurred in the range of 15μm-30μm from the surface of the alloy. In addition, the chromium content below the oxide layer is very low. It is due to the migration of chromium to the surface, resulting in the emergence of a chromium depleted zone. This is consistent with the chromium depletion phenomenon researched by Quadakkers et al [5].

![Figure 3](image3.png)

**Figure 3.** The change curve of alloying element content with depth obtained by EPMA.

### 3.3. Hastelloy X

As shown in Fig. 4, Hastelloy X has also formed an oxide layer in this atmosphere. The thickness of the upper sample layer is about 1.3 μm and the thickness of the bottom layer is about 0.9 μm as measured by SEM in figures a) and b). This scale is dense, and it consists mainly of chromium and manganese oxides. According to the micrographs, there is less internal oxide in this alloy, which means the corrosion depth is shallow. This phenomenon also reflects the strong protective effect of the oxide layer on the Hastelloy X surface.

![Figure 4](image4.png)

**Figure 4.** The cross-sectional SEM micrographs with EDS for Hastelloy X and the distribution of oxygen, aluminum, chromium elements.
Figure 5 shows the depth dependent Hastelloy X element content. According to elemental analysis, there might be a very thin chromium carbide layer on the surface of the alloy, indicating that the slight carburization may have occurred on a surface. Relative to the other alloys, the manganese content in the surface layer of Hastelloy X is high. So, it formed the dense MnCr₂O₄ layer which is on the top of the Cr₂O₃ layer. It is the main contributor to the strong oxidation resistance of Hastelloy X. This is very similar to the Haynes 230 [10].

![Figure 5. The change curve of alloying element content with depth obtained by EPMA.](image)

3.4. Incoloy 800H

![Figure 6. The cross-sectional SEM micrographs with EDS for Incoloy 800H and the distribution of oxygen, aluminum, chromium elements](image)

As shown in Fig. 6, an oxide scale of about 5 μm thickness has formed on the surface of Incoloy 800H the alloy, which is thicker than that of Inconel 617 and Hastelloy X. However, a thicker oxide layer does not mean better corrosion resistance. On the contrary, 800H alloy shows the worst oxidation resistance. Severe internal oxidation occurred in this alloy and a large amount of Al₂O₃ spinel oxide was formed. According to the SEM data, the corrosion depth was more than 30 μm, which indicates that the surface oxide layer provides poor protection.

According to the curve in Fig. 7, it can be clearly seen that there is obvious internal oxidation along the lines on the sample swept by EPMA, and the identified oxide is Al₂O₃. In the surface layer of the alloy, the change of oxygen content is completely consistent with that of chromium, indicating that the surface oxide is mainly Cr₂O₃. In addition, the carbon content inside the alloy is relatively high and
fluctuates constantly, which may be due to the deep carburizing behavior. Therefore, in this test atmosphere, the main corrosion phenomena of Incoloy 800H alloy are internal oxidation and deep carburization.

![Figure 7. The change curve of alloying element content with depth obtained by EPMA.](image)

3.5. T-22

![Figure 8. The cross-sectional SEM micrographs with EDS for T-22 and the distribution of oxygen, chromium elements.](image)

T-22 alloy is a low alloy steel, its composition and structure are different from the other three alloys. Figure 8 shows the cross-sectional micrographs of T-22 alloy under scanning electron microscope with the EDS system. It can be seen that the overall corrosion resistance is good, without decarburization and severe carburization occurring. Fig. 8 e) and f) show that there are large volumes of chromium oxide in the deep regime of T-22, which may be due to the changes of the material structure during processing of the alloy, and not being necessarily due to this corrosion.

![Figure 9. The relationship between the content and depth of the main elements in the T-22 alloy.](image)

Figure 9 shows the relationship between the content and depth of the main elements in the T-22 alloy. Due to the low content of chromium, aluminum and other elements in T-22, only a very thin oxide layer was formed on the surface. Except for some potentially attached carbon on the surface, the carbon content inside the alloy is the lowest among the four alloys, indicating that there is no carbon transfer between the alloy and the atmosphere. According to the test results, T-22 alloy has good corrosion resistance despite its low content of alloying elements, which may be related to the metallurgical structure (Ferrite + Bainite) [11] and material structure. At present, there are few tests for of the T-22 alloy in the HTGR field. Thus, more experiments are needed to study the corrosion resistance of T-22.
3.6. Discussion

![Figure 9. The change curve of alloying element content with depth obtained by EPMA.]

![Figure 10. SEM cross-sectional micrographs for the four alloys, followed by that a) Inconel 617; b) Hastelloy X; c) Incoloy 800H; d) T-22](image)

All the four alloys developed oxide scales in the test atmosphere, and the comparison of corrosion was shown in Figure 10. A dense oxide scale was formed on the surface of Hastelloy X, which can effectively avoid further corrosion. The internal oxidation is not obvious, which suggested that the oxide layer has better protection. Meanwhile, the mass gain of Hastelloy X alloy is very low, which indicates that this alloy has good corrosion resistance. The mass gain and corrosion behavior of Inconel 617 are similar to the Incoloy 800H. Both of them developed 4-5μm thick oxide layer, but spinel oxides could still be identified inside the sample, indicating that their protective effect were poor. Incoloy 800H has the highest mass gain and the deepest corrosion, so it can be determined to have the worst corrosion resistance. T-22 alloy has a thin oxide layer due to its low chromium content, but its corrosion resistance is also good according to the SEM figure. In particular, T-22 has a strong inhibition on carbon transfer between the alloy interior and the atmosphere.

4. Conclusion

The four Ni(Fe) base alloys foreseen to be used for the heat exchanger tubes of the steam generator in HTGR were corroded for up to 48 hours in an impure helium atmosphere at 950℃. The corrosion results were analyzed and discussed based on SEM and EMPA, and the four alloys showed different corrosion phenomena.
1. T-22 alloy and Hastelloy X alloy show the good corrosion resistance under the test conditions, and Incoloy 800H has the worst corrosion resistance;
2. The formation of the spinel oxides can be observed in Inconel 617 and 800H, which is similar to the previous research results on Hayens 230 alloy;
3. The chromium depletion occurs near the oxide layer of Inconel 617 and it may be caused by the migration of chromium;
4. A proper increase of manganese content may contribute to the formation of a dense oxide layer, thus improving the oxidation resistance of the alloy;

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