Corrosion Behavior of High-Cr–Ni Materials in Biomass Incineration Atmospheres

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ABSTRACT: In this paper, the corrosion test of high-Cr–Ni tubes was carried out in a biomass incinerator by replacing the original heated surface tube with a test tube. The investigated materials are high-Cr–Ni stainless steels (TP347H, SP2215, and Sanicro25) and alloy (HT700T). Long-term services (>4000 h) to investigate the corrosion rates and corrosion characteristics of the materials have been carried out. The appearance, element content, and composition of corrosion products after corrosion of the specimens were analyzed. Analysis indicates that the deposits are mainly composed of alkali metal salts, iron oxides, iron sulfates, and complex salts. Moreover, the corrosion morphology of the materials with different Cr–Ni contents varies greatly. TP347H has a high corrosion rate (0.11 mm/1000 h) with intergranular corrosion cracks and pitting on the windward side. However, the corrosion pattern of HT700T is comprehensive corrosion and the corrosion rate is low (0.015 mm/1000 h). Using corrosion rate as a criterion for corrosion resistance, HT700T has the highest corrosion resistance, while TP347H has the lowest. The corrosion behavior is also related to the corrosion resistance index (CI) value based on the content of critical elements. The order of material corrosion resistance predicted by the CI value is the same as reflected by the corrosion rate.

1. INTRODUCTION

As an important energy conversion method in the new biomass energy utilization technology, biomass power generation is characterized by low cost, high efficiency of direct combustion, and no thermal energy conversion in some technologies.1–5 Biomass power generation is one of the key technologies promoted worldwide in recent years. However, with the improvement of biomass boiler parameters, the corrosion problems caused by high-temperature combustion are gradually exposed. Severe alkali metal molten salt corrosion occurs when straw-based biomass is burned at high temperatures. In addition, the combustion of biomass mixed with coal reduces the corrosion effect of elemental chlorine but deepens the corrosion effect of sulfur corrosion and KCl. Moreover, the conversion of domestic waste to biomass incineration will produce different degrees of HCl gas-phase corrosion. At present, the corrosion problem has become a major obstacle to the conversion and utilization of biomass into energy.6–13 In the high-temperature combustion state of biomass, the corrosion resistance of metals is particularly prominent as an environmental adaptation, and the corrosion resistance of heat-resistant metal materials in the combustion environment of graduate materials is of great significance to the development and application of biomass power generation.

Lots of research has been done on the corrosion of materials under a biomass incineration atmosphere. Wang et al.14 compared the corrosion behavior of 304, 316L, and Q235A in LiCl–KCl molten salts at 450 °C, which demonstrates that the Mo-containing 316L stainless steel has better corrosion resistance. Gomez-Vidal et al.15 investigated the corrosion behavior of Inconel 702, Haynes 224, and Kanthal APMT alloys in MgCl2–KCl molten salts under an argon atmosphere by a mass loss method and electrochemical methods, confirming the role of elemental Ni in the resistance to elemental chloride corrosion. Montgomery16–18 revealed the relationship between the corrosion rate and metal wall temperature, flue gas temperature, and coal-to-biomass blending ratio by using eight different materials (including low-alloy steel, stainless steel, and nickel and alloys) in service at the Masnedø CHP power plant. Brady19 investigated the corrosion performance of stainless steel and coatings using a homemade combustion device to simulate a biomass boiler service environment. Thomas Gruber20,21 studied the corrosion rates of different steel grades in biomass boiler
service and the influencing factors and proposed an empirical formula for corrosion rates. By comparison, it is indicated that the corrosion behavior of different alloys under a biomass incineration atmosphere varies greatly, so research is still needed for specific materials and specific corrosion environments.

Biomass boilers with high parameters can improve the utilization of biomass energy, which is the direction of biomass boiler development. However, the increase of boiler parameters, especially the temperature, will inevitably bring more serious problems of high-temperature corrosion of existing materials. Instead of the existing steels, a high-Cr–Ni alloy to manufacture the high-temperature heating surface of boilers is one of the solutions to the above problems. Noteworthily, some of the austenitic stainless steels, such as TP304H and TP347H, used to produce the superheater and reheater for coal-fired power plant boilers can also be used for biomass boilers. Therefore, some new high-Cr–Ni materials, such as SP2215, Sanicro25, and HT700T, developed for high-parameter power plant boilers are equally promising for biomass boiler applications. However, the corrosion behavior of these materials under a biomass incineration atmosphere has not been reported. In this study, the corrosion resistance of four commercially available high-Cr–Ni tubes (TP347H, SP2215, Sanicro25, and HT700T) has been investigated based on the Biomass Power Plant of China, and the corrosion characteristics and mechanisms of different materials in the biomass incineration environment are discussed.

2. MATERIALS AND METHODS

The Biomass Power Plant has one stalk-fired water-cooling vibrating stoker boiler. The boiler generates 30 MW of steam and district heating. In addition, the rated evaporation capacity of the boiler is 130 t/h, the superheated steam temperature is 540 °C, and the flue gas temperature is 1090 °C under rated working conditions. According to the structural design and operation experience, it is found that SH3 has the worst service environment. Thus, the test tube was welded to replace the original superheater tubes of SH3 to obtain the corrosion state of the high-Cr–Ni materials in the worst service environment. The location of the test tube inside the biomass boiler is shown in Figure 1. Additionally, the distribution of the high-Cr–Ni tubes in the test tube is also shown in Figure 1. All tubes are solid solution-treated and pickled with no subsequent surface treatment on the outer surface. Since the material of SH3 is TP347H, TP347H is distributed at both ends of the test tube to facilitate welding of the same steel in the field. The compositions of the high-Cr–Ni tubes are listed in Table 1. The roughness of the outer surface of the high-Cr–Ni tubes before corrosion is measured using a TR200 handheld surface roughness meter. Five points were randomly selected for roughness measurement, and the results are shown in Table 2.

Long-term exposures (4000 h) were conducted to evaluate the high-Cr–Ni tube performance. After exposure, the specimens were removed from the superheater panel and put into individual canisters containing silica gel to prevent uptake of water from the surrounding environment as metal chlorides are known to be very hygroscopic. An APOLLO300 field emission scanning electron microscope was chosen to observe the morphology of the corrosion layer with an acceleration voltage of 15 kV. The composition of the corrosion layer was examined using a Bruker Quantax EDS detector. The physical phase analysis of the corrosion layer on the outer surface of the samples was performed using an X-ray diffraction (XRD) meter. A Rigaku D/max 2200 diffractometer was used in the 2θ–2θ model with Cu Kα radiation (λ = 1.54 Å). Moreover, the operating voltage, current, and scanning speed are 15 kV, 30 mA, and 3°/min, respectively. In order to obtain the corrosion rate of the material, the size of microcracks or corrosion products on the windward side of the material was measured. The samples were initially observed, and five areas of severe corrosion were selected for marking. A Vickers hardness tester was used to make reference points within the marked area. Then, the wall thickness of the uncorroded sample and the distance between the reference point and the inner surface of the corroded sample were measured using a stereo microscope (Figure 2a). The distance between the reference point and the sample corrosion layer was measured by SEM at 500× (Figure 2b). The corrosion rate of the sample is expressed as

\[ v = \frac{(L_0 - L_1 - L_2)}{t} \]

where \( v \) is the corrosion rate and \( t \) is the test time.

3. RESULTS

3.1. Deposit Analyses. Thick deposits are present on the windward side of the tube after service, while no deposits are

![Figure 1. Location of the test tube inside the biomass boiler.](Image)
present on the leeward side. The powder from the windward side was randomly taken for XRD analysis to determine its chemical composition, and the results are shown in Figure 3. It should be noted that the chemical compositions shown in Figure 3 are the ones that appeared more frequently in this study. It is indicated that the phase compositions of the deposits on the outer surface of the samples are random, that is, the phase compositions of the deposits are different at different locations. Additionally, the substances in the sediments are mainly alkali metal salts (K₂SO₄, MgCl, and NaCl), iron oxides (Fe₂O₃), iron sulfates [Fe₂(SO₄)₃], and complex salts [Ca₂₂(SiO₄)₈S₂O₄]. Among the elemental composition, alkali metals and corrosive elements mainly originate from fuel combustion, while Si originates from the adhesion and accumulation of silica-containing bed materials in high-temperature environments.

3.2. Microscopic Morphology and EDS Analysis of the Cross Section. The tubes were cut in half along the longitudinal direction, and the cross sections were polished for SEM image analysis and EDS analysis. The microscopic morphology of the sample before corrosion is shown in Figure 4. It indicates that all samples are intact with no corrosion on the outer surface. In addition, primary niobium carbide particles are present in the samples, with larger particles in HT700T and Sanicro25 and smaller particles in SP2215. The microscopic morphology of the sample after corrosion is shown in Figure 5. It is shown that the corrosion layer on the outer surface of the TP347H specimen is porous and loosely bonded to the matrix (Figure 5a). Intergranular corrosion and pitting corrosion occurred on the TP347H matrix. In addition, the corrosion at some locations has extended from the grain boundaries into the grain, causing grain detachment. As presented in Figure 5b, the corrosion of the SP221S specimen is mainly pitting corrosion, and the corrosion products show an obvious delamination phenomenon. Large-size holes are found in the corrosion products of the outer layer, while the inner layer is intact and dense. Additionally, pitting pores are diffusely distributed between corrosion products and the matrix. For Sanicro25 (Figure 5c), few corrosion products with no delamination inside are found on the outer surface of the specimen. In addition, the corrosion form of Sanicro25 is intergranular corrosion which is the same as TP347H. However, the corrosion penetrates only about one grain size into the matrix and no grain detachment occurs. It can be seen in Figure 5d that the corrosion layer thickness of HT700T is basically the same. The corrosion layer is dense and contains a small number of holes. There are regional honeycomb corrosion pits with a width of about 10 μm at the combination of the corrosion layer and the matrix.

The results of EDS analysis of corrosion products on the outer surfaces of different materials are shown in Table 3. From EDS results at point A, we find that the corrosion products on the outer surface of TP347H contain more O, Cr, Fe, S, and Cl and a small amount of alkali metal elements, which is consistent with the XRD results. TP347H grain boundary corrosion products (point B) contain Cr, Fe, Ni, and Cl and no alkali metal elements and sulfur elements. The content of Cl at point B is lower than that at point A, which may be attributed to the hindering effect of the corrosion layer on the chloride and the consumption of grain boundary carbides by reaction with the chloride (discussed in Corrosion

| C   | Si   | Mn   | Cr   | Ni   | Nb   | N   | Cu | B | Co | Al | other |
|-----|------|------|------|------|------|-----|----|---|----|----|-------|
| TP347H | 0.06 | 0.41 | 1.14 | 17.48 | 10.42 | 0.75 |
| SP2215 | 0.069 | 0.28 | 0.58 | 22.89 | 15.33 | 0.48 | 0.245 | 3.63 | 0.002 |
| Sanicro25 | 0.064 | 0.18 | 0.51 | 22.35 | 25.36 | 0.49 | 0.23 | 2.98 | 0.0035 | 1.44 | 0.023 | W: 3.37 |
| HT700T | 0.048 | 0.10 | 0.04 | 20.00 | Bal. | 0.01 | 0.007 | 0.002 | 2.13 | 1.96 | Fe: 26.10, Ti: 2.60 |

Table 3. Composition (wt %) of the High-Cr−Ni Tubes

| C   | Si   | Mn   | Cr   | Ni   | Nb   | N   | Cu | B | Co | Al | other |
|-----|------|------|------|------|------|-----|----|---|----|----|-------|
| TP347H | 1.854 | 1.749 | 1.981 | 2.072 | 1.922 | 1.915 |
| SP2215 | 1.534 | 1.842 | 1.589 | 1.821 | 1.572 | 1.672 |
| Sanicro25 | 1.685 | 1.361 | 1.608 | 1.621 | 1.473 | 1.550 |
| HT700T | 1.591 | 1.748 | 1.639 | 1.639 | 1.627 | 1.649 |

Table 2. Roughness of the Outer Surface of the High-Cr−Ni Tubes

Figure 2. Schematic diagram of external surface corrosion layer measurement. (a) Measurement of L₋₀ and L₋₁; (b) enlarged view of area A in (a): measurement of L₋₂.
Mechanism Analysis). SP2215 also conforms to the above rule, but the content of Fe is relatively high while that of Cr and Ni is low. Sanicro25 corrosion product composition is mainly Cr and O with a low content of corrosion elements S and Cl. For HT700T, the corrosion products contain mainly Cr and O but no S and Cl, which is different from other materials.

Figure 3. Physical phase compositions of the deposits: (a) alkali metal salts; (b) oxides and iron sulfates; (c) oxides and complex salts.

Figure 4. Microscopic morphology of the high-Cr–Ni materials before corrosion (a) TP347H; (b) SP2215; (c) Sanicro25; (d) HT700T.

Figure 5. Corrosion morphology of the high-Cr–Ni materials: (a) TP347H; (b) SP2215; (c) Sanicro25; (d) HT700T.
corrosion rate and the worst corrosion resistance, while HT700T has the slowest corrosion rate and excellent corrosion resistance. Since the actual corrosion of each material is different, the error in the statistics of corrosion cracking or thinning varies. Specifically, the error of HT700T with full corrosion is small.

4. DISCUSSION

4.1. Sediment Mechanism Analysis. As can be seen in Figure 3, the deposition of the SH3 tube section is mainly a layer of alkali metal salts and iron oxides with a certain thickness. The position of the tube shows that the tube is located directly above the furnace chamber, and there are no heat transfer components in between. Therefore, the temperature of SH3 is low, while the flue gas temperature is high. Generally, alkali metals, chlorine, and sulfur exist in the flue gas in the gas-phase form at 700 °C and above.26–27 The flue gas carrying the gas-phase alkali metals condenses and forms deposits on the walls of the heated surface where the temperature is lower. As the deposition continues to thicken, the temperature of the tube increases, causing the deposition to melt. Moreover, the particles and bed material in the flue gas are continuously adsorbed by it to produce a hard initial deposit layer. During the thickening of the deposition layer, Si- and Al-containing bed materials, ash particles, and alkali metal salts in the flue gas enter the deposition layer at the same time. In addition, sulfur oxides in the flue gas enter as sulfates. As the deposition layer continues to form, the condensation rate of alkali metal salts slows down due to the higher temperature of the outer layer. At the same time, the adhesion of the outer layer of the deposit is reduced and the ability of the deposit to trap fly ash particles is diminished. As a result, the thickness of the deposited layer is gradually stabilized by the flue gas washout.

Generally, the chemical composition of the sediment varies with the type and source of the biomass burned. The biomass boiler where the test tube is located uses straw as the main fuel, and the main components of the ash are K, Na, Cl, S, Si, and Ca. According to the published literature, the elements exist in different compounds during combustion, such as KCl, SO3, SiO2, CaCO3,29 and so forth. Moreover, some of the deposits may be generated during combustion through the following chemical reactions.

\[
2KCl + SO_2 + 1/2O_2 + H_2O = K_2SO_4 + 2HCl \quad (2)
\]

\[
CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O \quad (3)
\]

\[
CaCl_2 + K_2SO_3 = CaSO_4 + 2KCl \quad (4)
\]

The phase composition of the sediment indicates that, except for the complex salts, the other substances are common components and oxidation products of the biomass combustion process.30 From the molecular formula of the complex salts, it is presumed that they may consist of sulfates and silicates of Ca. In addition, the low-melting-point eutectic content in the deposit increases due to the combined effect of the compound salt and alkali metal compounds such as K and Na, which accelerates the corrosion process.31

4.2. Corrosion Mechanism Analysis. The results of the sediment and corrosion products show that the samples are subjected to corrosion by both S and Cl elements. The published literature shows that NaCl under gas-phase conditions increases the oxidation rate by damaging the protective Cr2O3-containing oxide layer.32 The HCl generated in the reaction will continue to react with the matrix to form chromium chloride and nickel chloride, further accelerating corrosion. Moreover, the chloride in the sediment forms a low-temperature molten mixture to melt the oxide layer. The high chloride bias in the sediment causes a corrosion phenomenon similar to gaseous corrosion. All of the above processes add up to the formation of chlorine corrosion of the material. In addition to the attack of Cl, there is another corrosive element, S. The corrosion of S on metals is mainly reflected in the early stage of rapid corrosion. With the reaction, the sulfate with low activity produced by corrosion will be covered on the metal surface, playing a similar role to passivation.33 When SO2 coexists with HCl in equal amounts in the flue gas, the following reactions occur with the heated surface metal.

\[
4NaCl + Cr_2O_3 + 5/2O_2 \leftrightarrow 2NaCrO_4 + 2Cl_2 \quad (5)
\]
The calculated reaction free energy of eq 6 at 800 K is −246.6 kJ, while eq 7 is −115.7 kJ, which indicates that the affinity of SO2 for the matrix is significantly stronger than that of HCl.24 In other words, when SO2 and HCl are present in the flue gas at the same time, SO2 is able to form a dense protective sulfate film on the metal surface in preference to HCl. However, due to the small atomic radius of Cl, it can easily accumulate at defects on the metal surface and even penetrate the protective film, causing pitting corrosion.36,37

As shown in Figure S, it indicates that the corrosion morphology of different materials in the same environment is different. Specifically, pitting corrosion dominates in SP2215, intergranular corrosion occurs in TP347H and Sanicro25, while HT700T is uniformly corrosion. Moreover, the EDS results demonstrate that TP347H, Sanicro25, and HT700T have a high Cr content (29.15–49.80%) in the external surface corrosion products, while SP2215 has a low content (15%). It can be inferred that TP347H, Sanicro25, and HT700T generate the Cr2O3 protective passivation layer on their external surfaces except for SP2215. Thus, pitting corrosion occurs on SP2215 due to the lack of protection from the passivation layer. In addition, the corrosion products of SP2215 have obvious delamination, with a dense inner layer and a loose and porous outer layer. The EDS result shows that the corrosion products in the corrosion pits are mainly iron and chromium oxides, which differ significantly from the matrix in the coefficient of thermal expansion. As the expansion of corrosion products at high temperatures is smaller than the matrix, expansion tensile stress always accompanies the corrosion products. Furthermore, the loose holes of the outer corrosion products tend to grow and merge and eventually form delamination under the effect of expansion tensile stress. The intergranular corrosion of TP347H and Sanicro25 is associated with the precipitation of M23C6 carbides at grain boundaries during high-temperature service. The element Nb in both materials can retard the precipitation of M23C6 at the grain boundaries but cannot stop it completely.38 Compared to the metal matrix, the chloride generated by biomass combustion reacts preferentially with carbide, making the metal more susceptible to intergranular corrosion, which in turn causes intergranular corrosion of the matrix.39–41 However, the intergranular corrosion of Sanicro25 is less severe due to the high Cr content of the outer protective passivation layer. Similar to Sanicro25, HT700T generates a passivation layer with high content of Cr on the outer surface, which reduces the content of corrosive elements in contact with the matrix. In addition, due to the high content of Ti and low content of C, there is less precipitation of M23C6 carbide at the grain boundary during service. Under the combined influence of the above two factors, slight uniform corrosion occurs on HT700T rather than pitting and intergranular corrosion.

4.3. Relationship between Chemical Composition and Corrosion Resistance. EDS analysis of different materials after corrosion shows that O, Cr, Fe, Ni, S, and Cl are the main constituent elements of the corrosion products of metals other than HT700T. In general, the difference in the type of corrosion in the same environment is related to the content of alloying elements (such as Cr, Ni, and Mo). Cr reacts preferentially with oxygen in the atmosphere to form a dense and protective oxide film with good adhesion. Molybdenum and nickel improve the microstructure of metals, which effectively inhibits intergranular and pitting corrosion. However, unlike the element O, the element Cl is more strongly bound to Cr than Fe and Ni. Moreover, the chloride of Cr requires a lower critical oxygen partial pressure than the oxide transition, which leads to a greater growth stress in the oxide film of Cr compared to Fe and Ni. Furthermore, the adhesion of the oxide film to the matrix and the denseness of the oxide film are destroyed. Therefore, the oxide film is not effective in preventing the increase of corrosion, although it contains a certain amount of elemental Cr. In addition, it illustrates that the influence of elements other than element Cr on corrosion cannot be ignored. This phenomenon is particularly obvious for HT700T, where the corrosion products are composed of O, Cr, Ti, and Al. The published literature shows that Al-containing materials tend to generate dense Al2O3 in high-temperature environments. The following reactions occur when alkali metal chlorides come into contact with Al2O3:

\[
\text{Al}_2\text{O}_3 + 2\text{NaCl} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{NaAlO}_2 + \text{Cl}_2 \quad (8)
\]

The generated chlorine gas continues to react with other elements within the matrix. Due to the negative Gibbs free energy of most metals reacting with Cl2 at high temperatures, metal chlorides are created at the matrix interface. Additionally, AlCl3 is preferentially generated and diffuses toward the interface of the oxide film and the gas phase as a result of its more negative Gibbs and greater vapor pressure relative to other metal chlorides (FeCl3, CrCl3, and NiCl2). At the above interface, AlCl3 is oxidized to Al2O3, and the generated Cl2 returns to the substrate and oxide film interface to continue corrosion.

\[
2\text{AlCl}_3 + 3/2\text{O}_2 \rightarrow \text{Al}_2\text{O}_3 + 3\text{Cl}_2 \quad (9)
\]

This cycle continues to form an Al2O3 oxide film, which provides protection to the matrix. The element Ti acts as a stabilizing element in the matrix to prevent the combination of C and Cr, which plays a role in avoiding the generation of intergranular corrosion.

There is a strong correlation between the composition of alloying elements and their corrosion resistance.42,43 Previous studies have investigated the relationship between the two by setting corrosion resistance parameters.

\[
\text{PREN} = \% \text{Cr} + 3.3\% \text{Mo} + 16\% \text{N} \quad (10)
\]

\[
\text{PREN} = \% \text{Cr} + 3.3(\% \text{Mo} + 0.5\% \text{W}) \quad (11)
\]

However, the corrosion parameters involve few types of elements, which do not contain critical elements such as Ni, Nb, Ti, and so forth.44 It is believed that Ni is the key element for the formation of the surface passivation layer in a biomass combustion atmosphere.45 Nb and Ti can improve the intergranular corrosion resistance of the material. Additionally, the surface passivation layer is made more stable by the addition of Mo and W.46 In view of the influence of the above elements on the corrosion resistance, the corrosion resistance index (CI) parameter was proposed by Antunes and de Oliveira47 based on the corrosion resistance parameters with improved and broadened element types.
It is indicated that the lower the CI value, the weaker the corrosion resistance. The calculated CI values for TP347H, SP221S, Sanicro25, and HT700T are 31.65, 40.62, 53.53, and 84, respectively. The CI values demonstrate that HT700T has the highest corrosion resistance, while TP347H has the lowest. If the corrosion type is not considered, the corrosion degree of the material is material. It illustrates that the order of material corrosion resistance predicted by the CI value is the same as reflected by the corrosion rate.

5. CONCLUSIONS

(1) The deposits on the windward side of the tube are mainly composed of alkali metal salts, iron oxides, iron sulfates, and complex salts. Except for the complex salts, the other substances are common components and oxidation products of the biomass combustion process. The complex salts may consist of sulfates and silicates of Ca.

(2) The corrosion behavior of the materials after service is different. TP347H has a high corrosion rate (0.11 mm/1000 h), while the corrosion rate of HT700T is low (0.015 mm/1000 h). Intergranular corrosion occurs in TP347H and Sanicro25, pitting corrosion dominates in SP221S, and HT700T exhibits uniform corrosion. Pitting corrosion occurs on SP221S due to the lack of protection from the passivation layer. Intergranular corrosion of TP347H and Sanicro25 is associated with the reaction of chlorides and grain boundary carbides. The corrosion performance of HT700T is mainly dependent on the presence of a dense passivation layer on the outer layer and the high Ti content and low C content of the matrix.

(3) The CI value is used to characterize the corrosion resistance of the material. The calculated CI values demonstrate that HT700T has the highest corrosion resistance, while TP347H has the lowest. If the corrosion rate is used to assess the degree of corrosion, the order of material corrosion resistance predicted by the CI value is the same as reflected by the corrosion rate.

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