Corrosion Behavior of the Ni–Cr–Fe Base Superalloy GH984G in a Synthetic Coal Ash and Flue Gas Environment

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Received: 16 December 2016 / Revised: 22 March 2017 / Published online: 22 June 2017
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Abstract The corrosion behavior of the new Ni–Cr–Fe base superalloy GH984G in a synthetic coal ash and flue gas environments was studied at 700 °C. The results showed that the corrosion rate was slow during the initial corrosion stage, then followed by a stage of faster mass loss. During the corrosion test, the scale trended to spall slightly, resulting in the formation of corrosion pits on the sample surfaces. The main corrosion products were identified as NiFeCrO₄ and a small amount of Cr₂O₃. The scale microstructure involved the presence of three corrosion layers. The outer layer contained Cr, Ni, Fe, O and a small amount of S. Many micro-cracks were detected in the Cr-rich intermediate oxide layer. The inner corrosion layer was thin and rich in S. Internal sulfidation and internal oxidation occurred in the substrate. Because of its relatively high Cr content, the GH984G superalloy exhibited a good corrosion resistance under the test conditions.

KEY WORDS: Ni–Fe–Cr base superalloy; Coal ash; SO₂; Corrosion

1 Introduction

The aim of increasing the efficiency of future coal-fired power plants requires more critical steam conditions. The requirement of high efficiency and reduced emissions requires the use of advanced ultra-supercritical (A-USC) conditions with steam temperatures up to 700–760 °C and pressures up to 35–37.5 MPa [1–3]. The goal of A-USC is to generate 760 °C steam, although the metal surface temperature of the key components, including the superheater and reheater tubes will be 800 °C or even higher [4].

Ni-based superalloys are expected to be the best candidates for A-USC steam boiler applications in coal-fired power generation systems [5]. The alloy GH984G (Ni-20.7, Fe-20.9, Cr-3.4, (Mo + Nb)-2.3, (Ti + Al)-1.4, wt%) is a new Ni–Fe–Cr-based wrought superalloy with high creep strength [6, 7]. This superalloy is a candidate for superheater and reheater tubes application due to its comprehensive mechanical properties and long-term thermal stability [8, 9]. The aim of the present work is to examine the corrosion resistance of this alloy in synthetic flue gases atmosphere at high temperature.

2 Experimental Procedures

The alloy GH984 was received from Dongfang Boiler Group Co., Ltd, Material Research Institute. Square specimens with dimensions of 10 mm × 15 mm × 3 mm were cut by electrical discharge method. The surfaces were ground down to 800 SiC paper. The sample surfaces were cleaned in acetone and distilled water in an ultrasonic bath before testing. The synthetic coal ash powders were prepared from mixture of Na₂SO₄, K₂SO₄ and Fe₂O with molar ratios of

Available online at <http://link.springer.com/journal/40195>

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3:3:2. The synthetic coal ash suspension was prepared by adding ethanol. Then the samples were placed on a hot plate and coated with the suspension to form a continuous layer of synthetic coal ash with a loading of about 40 mg/cm². The synthetic flue gas was composed of: 15% CO₂, 3.5% O₂, and 0.25% SO₂, and bal. N₂. The gas flow was set to a rate of 20 mL/min, while the test temperature was 700 °C. At selected time intervals, the samples were taken out from the furnace and washed with boiling distilled water, followed by drying and weighing. After this, the samples were coated again with the synthetic coal ash powder and put back into the furnace to continue the test. In order to compare the corrosion resistance of this superalloy with that of other materials, the corrosion kinetics of the other three superalloys 740H (Cr-25.0, Co-20.0, Mo-0.5, Nb-1.5, Ti-1.35, Al-1.35, wt%), 617B (Cr-21.8, Fe-1.3, Mo-9.2, Co-12.4, Al-0.92, Ti-0.45, wt%) and C263 (Cr-20.0, Co-20.0, Mo-6.0, Ti-2.2, Fe-0.55, wt%) were tested under the same conditions.

After 1000h corrosion test, the surface morphology and phase composition of the corrosion films grown on the sample surfaces were investigated by a scanning electron microscope (SEM) equipped with an energy-dispersive spectroscope (EDS), a three-dimensional optical microscope and by X-ray diffraction (XRD).

3 Results

3.1 Corrosion Kinetics

Figure 1a compares the corrosion kinetics of GH984G with those of the other three superalloys in the synthetic coal ash/flue gas environment at 700 °C. The corrosion of the GH984G was slight (about 2.4 mg/cm²) in the test conditions for

1000 h, showing that these alloys exhibit good corrosion resistance in the flue gas environment. The corrosion kinetics of GH984G and 740H were almost identical. It is noteworthy that the corrosion rate of GH984G was slow during the early corrosion stage ($t < 350$ h). Conversely, large mass losses were observed for 617B and C263 during the corrosion test. Furthermore, In particular, 617B suffered from a severe corrosion, with corrosion products spalling extensively from the sample surfaces.

3.2 Phase Composition and Microstructure of the Corrosion Products

Figure 2 shows the XRD patterns of GH984G corroded in the synthetic coal ash/flue gas environment at 700 °C. Based on the XRD analysis, the main corrosion products were identified as NiFeCrO₄ and a small amount of Cr₂O₃.

Fig. 2 X-ray diffraction patterns of GH984G after corrosion in the synthetic coal ash/flue gas environment at 700 °C

Fig. 1 Mass change per unit surface area for the hot corrosion of GH984G in the synthetic coal ash/flue gas environment at 700 °C as a function of time (**a** for 740H, 617B, C263 and GH984G; **b** for GH984G)

Moreover, it is noteworthy that even after 1000h corrosion test, strong peaks of substrate were also observed. Combining the results of XRD and the corrosion kinetics, we concluded that the corrosion layer on the sample surface was thin and this alloy had good corrosion resistance.

Figure 3 shows the three-dimensional morphology, surface microstructure and corresponding EDS X-ray spectra of the GH984G alloy after corrosion in the synthetic coal ash/flue gas environment at 700 °C. Many corrosion pits with diameters of 200–300 μm were observed on the corroded sample surface. According to three-dimensional reconstructed image

of the pits, the average depth of the pits was about 74 μm. These pits were originated by spallation of the corrosion products. Actually, the surface morphology around the pits was differentiated into three typical regions. In region 1, some large grains were observed. The EDS analysis revealed that these large grains were composed of Fe, Ni, Cr, O and a small amount of Ti. Combining the results of XRD and EDS, we could reasonably conclude that these grains were mainly composed of NiFeCrO_4 , and Cr_2O_3 . At places where the corrosion layer of region 1 spalled, region 2 and 3 became exposed. Many pores were detected in region 3. The EDS

Fig. 3 Three-dimensional morphology **a**, surface microstructure **b**, corresponding EDS X-ray spectra **c–e** of the GH984G alloy after corrosion for 1000 h

Fig. 4 Cross sections **a**, **b**, the corresponding EDS patterns **c–g** of GH984G after corrosion

analysis revealed that regions 2 and 3 were composed of Ni, Fe, Cr, Al, O and S, indicating that sulfides formed under the outer corrosion layer.

Figure 4a, b shows the cross-sectional microstructures of the GH984G alloy after corrosion in the synthetic coal ash/flue gas environment at 700 °C. In Fig. 4a, SEM observation showed that the corrosion layer has an average thickness of about 3–5 µm. Moreover, some corrosion pits with a depth of 15–20 µm filled with corrosion products were detected. Figure 4b is a higher magnification of the corrosion pit in Fig. 4a. In Fig. 4b, the SEM observations revealed that the scale was composed of three layers. The outer layer was compact, and the EDS analysis showed that it contained Cr, Ni, Fe, O and a small amount of S. The intermediate layer presented many micro-cracks, and according to the EDS analysis, this layer contained Cr and O and a small amount of S. The inner layer was very thin and rich in S by the EDS analysis. It is noteworthy that the substrate presented some dark gray sites rich in S and O, showing that internal oxidation and sulfidation occurred.

4 Discussion

The corrosion rate of boiler superheaters and reheaters is accelerated when sodium sulfate, potassium sulfate, and iron sulfate are deposited on their surfaces. It is reported that the melting point of the ternary sulfate (Na, K)₃Fe(SO₄)₃ is 560 °C when the mole ratio of Na:K is 1:1 [10]. However, high concentrations of SO₃ are required to form the low melting point ternary sulfate [11]. In this experiment, only SO₂ was introduced instead of SO₃. However, SO₂ may react with O₂ to form SO₃. The presence of a catalyst (such as Pt, Fe) in the environment tends to accelerate the conversion rate of SO₂ to SO₃. Generally, Fe₂O₃ existing in the synthetic coal ash, as well as the oxides Fe₂O₃ or NiO formed in scale could act as catalysts for this reaction. Furthermore, SO₃ could also be produced from the decomposition of sulfates at high temperatures. Therefore, the concentration of SO₃ on the sample surface might be high enough to form low melting point multiple sulfates over some restricted regions. In addition, the thermodynamic phase diagram of the Ni–S–O system indicated that NiSO₄ is stable under experiment condition, suggesting the possibility of formation of the double sulfate Na₂SO₄–NiSO₄ with a low melting points (671 °C) [12]. Therefore, low melting point molten sulfates could be formed locally on the sample surface at 700 °C. According to the experiment results, GH984G showed good corrosion resistance after 1000h test, with only some corrosion pits on the sample surface. This could be ascribed to the fact that molten salts formed only in some local regions, not on the whole sample surface. In these local regions, the

corrosion rate accelerated, while corrosion products spalled during the test. Moreover, the presence of Al₂O₃ and Cr₂O₃ in the oxide layer was not favorable to the formation of stable sulfates under our experimental conditions [12], which could have contributed to inhibit severe hot corrosion.

During the initial corrosion stage, a Cr₂O₃-rich oxide film was probably formed rapidly on the sample surface because of the high Cr content of the alloy [13]. Moreover, Ti and Al could have easily formed the corresponding oxides due to their high affinity to O. Generally, Ti may diffuse rapidly outward, forming titanium oxide in the outer corrosion layer. On the contrary, the rate of outward diffusion of Al is slower than that of Ti. Therefore, alumina was enriched in the inner corrosion layer [14, 15], possibly contributing to inhibit the hot corrosion of the substrate. In addition, as mentioned above, a Cr₂O₃-rich oxide layer formed initially on the sample surface. Therefore, the corrosion rate was relatively slow during the initial corrosion stage ($t < 350$ h).

With an increase in the oxide layer thickness, the oxygen partial pressure in the oxide layer is much lower than that of flue gas environment. Under this condition, S might diffuse inward through the external corrosion layer, leading to a high activity of sulfur in the inner region of the corrosion layer. S is expected to react preferentially with Cr than that of Fe, Ni [16]. Then the sulfide would migrate outward and react with oxygen according to following reaction:

A rather porous Cr₂O₃ layer formed on the sample surface. The free S produced in this way may penetrate inward again to form new sulfide. The fact that the inner layer was rich in S might be related to the above reactions. The formation of sulfide in the corrosion layer may produce more defects in the corrosion layer, which can favor a fast diffusion outward of Ni and Fe. Under this condition, the corrosion rate accelerated after the initial corrosion stage. This is the reason that the EDS analysis could detect Ni and Fe in the outer corrosion layer.

5 Conclusions

1. The alloy GH984G showed good corrosion resistance in the synthetic coal ash and flue gas environments at 700 °C for 1000 h.
2. During the initial corrosion stage, the corrosion rate was slow and then followed faster mass loss. Many corrosion pits formed on the sample surface, which originated from the spallation of the corrosion products. The main corrosion products were NiFeCrO₄ and a small amount of Cr₂O₃.

3. The corrosion layer was composed of three had layers. An S-rich layer formed at the interface between the external corrosion layer and the metal substrate. Internal sulfidation and internal oxidation occurred in the substrate.

Acknowledgements This work was financially supported by National Science Foundation of China (Grant No. 51161022) and the Science and Technology Foundation of Department of Education of Jiangxi Province, China (Nos. DB201301133, 201301050).

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