

High temperature corrosion behavior of superalloy GH984G in synthetic flue gases environments

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ABSTRACT: High temperature corrosion behavior of Ni-Fe-based Superalloy GH984G was studied in the synthetic flue gas environments with different SO₂ concentration at 800°C. The micro-structure and composition of the scales were investigated by scanning electron microscope/energy dispersive spectroscopy and X-ray diffraction. The Cr₂O₃-rich scale with a mount of TiO₂ formed on the sample surface. With the SO₂ increasing, corrosion became serious and more TiO₂ was detected in the scale. Sulfides could be detected even the SO₂ concentration decreased to 0.5%.

Introduction

The aim of increasing the efficiency of future coal-fired power plants requires designs for more critical steam conditions. The requirement for high efficiency and reduced emissions requires the use of advanced ultra-supercritical (A-USC) conditions with steam temperature of up to 700~760°C and pressure of up to 35~37.5 MPa. 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.

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

Experiments

GH984 alloy was received from Institute of Metal Research, Chinese Academy of Science. Square specimens with dimensions of 10 × 15 × 3 mm were cut by the 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 flue gas was composed of: 15% CO₂, 3.5% O₂, (1%, 0.5% and 0.25%) SO₂, bal. N₂. The gases flow was set to a rate of 20 mL/min, the test temperature was 800°C.

After corrosion test, the surface morphology and phase composition of the specimens were investigated in scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) and in X-ray diffraction (XRD).

Experiment results

Corrosion kinetics and corrosion equations of materials

Fig.1 shows the Corrosion kinetics of GH984G after exposed for 1000h in the synthetic flue gas environments with different SO₂ concentration. The fitting results are shown in Table 1. The corrosion of the samples in the test conditions for 1000h is slight (<0.6mg/cm²). The results showed that the samples had good corrosion resistance in fuel gases environment.

The phase composition and microstructure of corrosion products

Fig.2 shows the X-ray diffraction patterns of the samples corroded in synthetic flue gas with various SO_2 concentrations. The XRD analysis revealed that

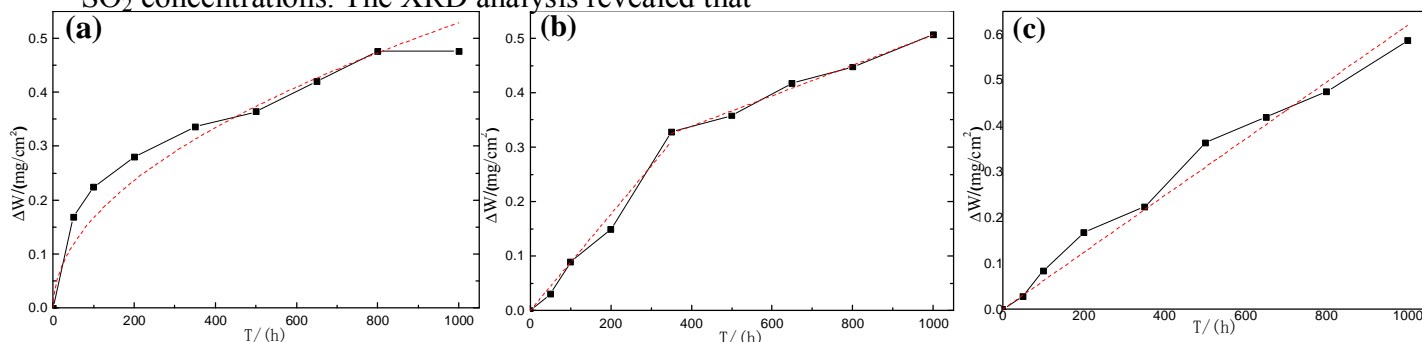


Figure 1. Corrosion kinetics and fitted curves of the samples in the various SO_2 concentration. (a) 0.25% SO_2 ; (b) 0.5% SO_2 ; (c) 1% SO_2 ;

Table 1. Fitted results of samples under different corrosion conditions.

SO_2 (vol%)	Fitted equation	Correlation coefficients
0.25	$y^2=2k_1t$	$k_1=1.396 \times 10^{-4}$
0.5	$y=k_2t$	$k_2=8.85486 \times 10^{-4}$
	$y=k_3t+b$	$k_3=2.79447 \times 10^{-4}; b=0.2268$
1	$y=k_4t$	$k_4=6.19936 \times 10^{-4}$

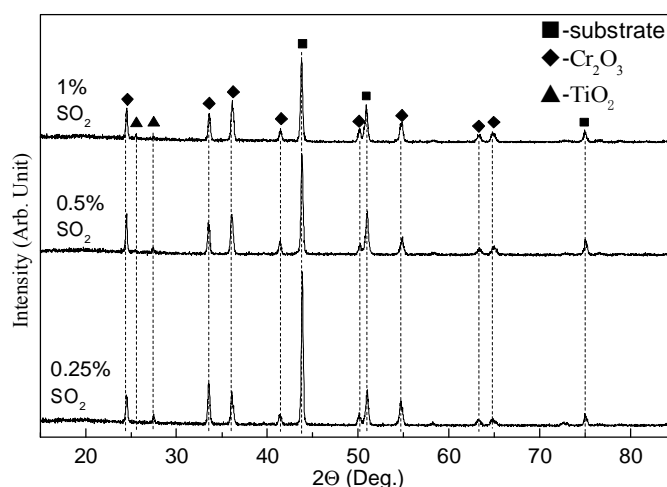


Figure 2. XRD pattern of the samples after corrosion 1000h.

the main corroded phases of all corroded samples were composed of Cr_2O_3 and TiO_2 .

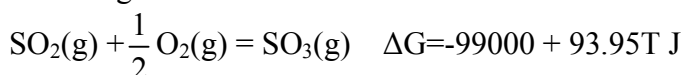
Fig.3 shows the surface microstructure corresponding EDS X-ray spectra of GH984G alloy corroded in synthetic flue gas with various SO_2 concentrations. Some large grains (marked as S) were observed on the sample surface. EDS analysis revealed that the large grains and other area (marked as P) consisted of Cr, Ti and O. However, EDS results revealed that the Ti concentration decreased with the SO_2 concentration increasing. When SO_2 concentration reached 0.5%, S element could be detected on the sample surface.

Fig.4 shows the cross-section and corresponding EDS X-ray spectra of the specimen corroded in synthetic flue gas with various SO_2 concentrations. SEM observation revealed that continuous and compact scale formed on the sample surface. A larger number of needle-like corrosion regions were observed in the alloy substrate. Fig.4(a) shows the cross-section of the sample tested in the gases contains 0.25% SO_2 , EDS analysis showed that Ti was not detected in the Cr_2O_3 -rich scale, combining the results of the XRD and the EDS on the surface, we could conclude that the TiO_2 formed

on the sample surface. In the needle-like corrosion regions, Ni, Fe, Cr, Al, S and O was detected. Fig.4(b) shows the cross-section of the sample tested in the gases contain 0.5% SO₂, EDS identified that Ti existed in the corrosion scale (2.02wt%). Moreover, S was detected at the interface of scale/substrate. When SO₂ concentration was 1%, Ti was found in the corrosion scale (3.50wt %), S mainly existed in the scale.

Discussion

Generally, SO₂ could react with O₂ and produce sulphur trioxide at high temperatures according to following reaction:



However, thermodynamic calculation result indicates the above mentioned reaction was not favored at 800°C. Therefore, the corrosion is mainly caused by oxidation and sulfur dioxide under the experiment conditions.

Table 2 shows the ΔG_m^0 values of different oxides. All the data in this Table are calculated by the software HSC Chemistry 6. According to Table 2 indicates that the affinity between metals and oxygen at 800°C decreased according to following sequence: Al, Ti, Cr, Fe, Ni. Meanwhile, the composition and microstructure of the scale formed on the alloys is not only affected by thermodynamics driving force, but also affected by the content of metal in the alloy.

Considering that the content of SO₂ was low in this test, GH984 alloy inevitably oxidized by O₂. F. Abe et al reported that Al ions are virtually immobile in the scale and that the growth of Al₂O₃ proceeds by inward diffusion of oxygen in the Cr₂O₃-rich scale at 800°C. Therefore, Al was detected in the needle-like products in the substrate. However, the high mobility of Ti ions makes it poss-

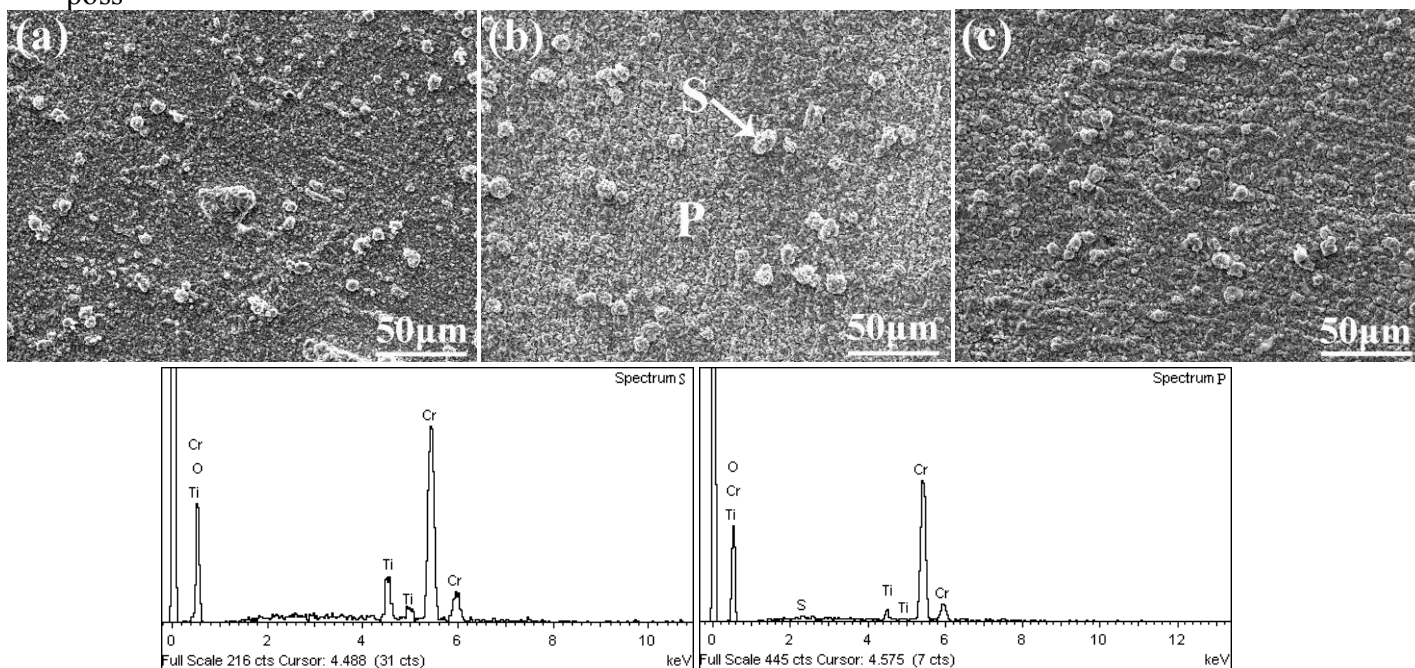


Figure 3. The surface microstructure and corresponding EDS X-ray spectra of samples corroded in synthetic flue gas for 1000h. (a) 0.25%SO₂; (b) 0.5%SO₂; (c) 1%SO₂;

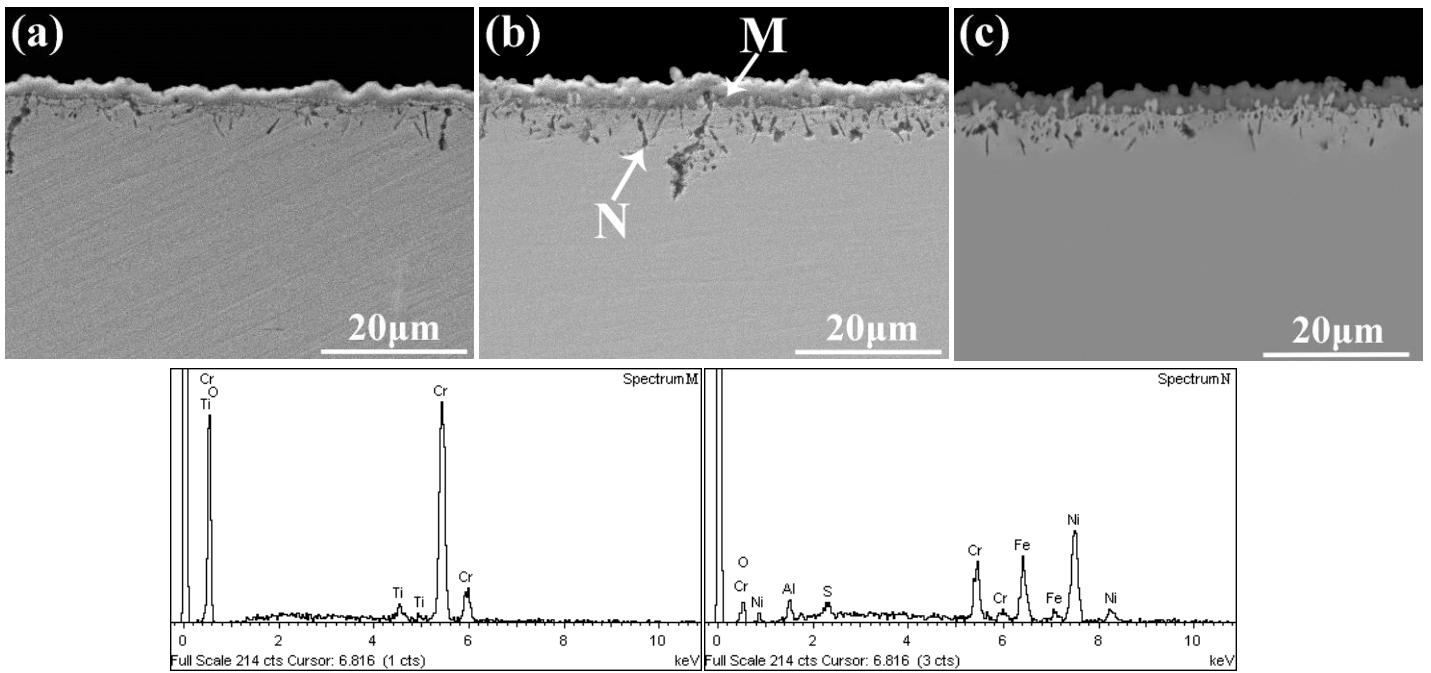


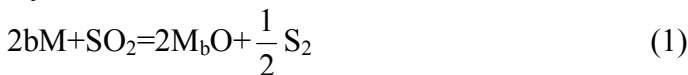
Figure 4. The cross-sections morphology and corresponding EDS X-ray spectra of samples corroded in synthetic flue gas for 1000h. (a) 0.25%SO₂; (b) 0.5%SO₂; (c) 1%SO₂;

Table 2. The calculated ΔG_m^0 values of different oxide at 800°C.

Oxide	Al ₂ O ₃	TiO ₂	Cr ₂ O ₃	Fe ₂ O ₃	NiO
ΔG_m^0 (kJ/mol)	-1336	-749	-853	-541	-142

ible to migrate through the Cr₂O₃ scale and to form TiO₂ on the sample surface.

As mentioned above, S was detected in the scale by EDS, combining the corrosion kinetics, we could conclude that SO₂ existed in synthetic flue gas led to corrosion accelerated. It can be seen that only formation of oxide and can proceed if sulphur partial pressure are too low. When the samples tested in the gases with 0.25vol% SO₂, No Sulphur was detected by the EDS. Actually, at high temperatures SO₂ could lead corrosion of some metals according to reaction (1). If the sulphur partial pressure was low enough, sulfides were instability, which would led to sulfides displace or decompose. Therefore, only oxides were detected in the scale when SO₂ concentration was set to 0.25vol%. It is reported that the direct reaction of the SO₂ with the metal has been considered rather than the reaction with, sulfur and oxygen, which accounted for the formation of the sulfide/oxide layer.



When SO₂ concentration up to 0.5%, the S was been found under the Cr₂O₃-rich scale, we can conclude that the internal sulfidation reaction occurred. When partial pressures increasing and scale became thicker on the sample surface, oxygen partial pressure would decrease, which could lead to local sulphur partial pressure increasing and formation of sulfide, especially, sulfide observed at the interface of scale/substrate. When SO₂ concentration was 1%, the S was been found on surface, scale, and the metal/scale interface. Under this condition, the following reaction probably occurred: $7Cr + 3SO_2 = 2Cr_2O_3 + 3CrS$ $\Delta G_{800}^0 = -1236$ KJ/mol (2)

According to above reaction, with SO₂ concentration increasing, sulfides would form in the corrosion products. Therefore, the oxidation kinetics of GH984G followed different kinetics law in various SO₂ concentration and corrosion rate accelerated with SO₂ concentration increasing.

Conclusions

GH984G have shown good corrosion resistance under the corrosion test conditions with difference SO_2 concentration. With the SO_2 concentration increasing, the corrosion of this alloy accelerated. The Cr_2O_3 -rich scale with small amount of TiO_2 formed on the sample surface under the test conditions. The Cr_2O_3 -rich scale could inhibit SO_2 penetration. Therefore, this scale showed good corrosion resistance in flue gas environment.

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