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Materials Chemistry and Physics 90 (2005) 275–281
MATERIALS CHEMISTRY AND PHYSICS
www.elsevier.com/locate/matchemphys

The corrosion of INCONEL alloy 740 in simulated environments for pulverized coal-fired boiler

Shuangqun Zhao [a,b,*], Xishan Xie [a], Gaylord D. Smith [c], Shailesh J. Patel [c]

[a] Department of Physics, Ningxia University, Wencui Road, Xixia District, Yinchuan 750021, China
[b] High Temperature Materials Research Laboratories, University of Science and Technology Beijing, Beijing 100083, China
[c] Special Metals Corporation, Huntington, WV 25705, USA

Received 5 February 2004; received in revised form 23 March 2004; accepted 19 April 2004

Abstract

The corrosion of a new nickel base superalloy, INCONEL alloy 740, has been studied at 550 and 700 °C on exposure to the synthetic coal ash/flue gas environments by means of XRD, SEM, and EDX. Low temperature hot corrosion of the new alloy occurred at two temperatures. The corrosion started to form the thin Cr_2O_3 scale on the alloy at 550 °C and developed as pitting attack resulted from sulfidation. The frontal attack at 700 °C consisted of two successive stages in which the corrosion mechanism started from the sulfidation and ended up in the fluxing of oxide. The compact and protective Cr_2O_3 scale formed and the internal sulfidation took place during the initial stage. The severe hot corrosion occurred due to the presence of the molten $CoSO_4$ during the propagation stage. The loose and porous outer layer and the compact inner layer consisted of spinels and oxides, respectively. The sulfides of Cr, Ti, and Nb formed on the front of oxide scale and in Cr-depletion zone. The rapid degradation of corrosion resistance of the alloy can be attributed to the dissolution of both cobalt and cobalt oxide on the surface. The alloy of 25% Cr exhibited better resistance to coal ash/flue gas corrosion as compared to the alloy of 23% Cr in the present case.

Keywords: INCONEL alloy 740; Synthetic coal ash/flue gas; Low temperature hot corrosion; Corrosion mechanism

1. Introduction

Increasing demand for more electricity, reduced plant emissions and greater efficiency is forcing power plants to increase steam temperature and pressure of pulverized coal-fired boilers. Ultra-supercritical steam conditions greater than 31 MPa and 600 °C have been adopted and the thermal efficiency of pulverized coal-fired boiler of up to 45% has been obtained. Steam conditions up to 375 bar and 700 °C, being planned by both the European THERMIE project and the German MARCKO project, will increase the efficiency of boiler to about over 50%. The superheater and reheater materials will therefore be required which have a high creep rupture strength (100 MPa/10^5) at temperatures of about 750 °C, together with high corrosion resistance (=2 mm cross-section loss in 2×10^5 h) [1]. To meet this new strength and temperature requirement of future boiler tube alloy, the usual ferritic and solid solution austenitic alloys heretofore employed for this service, such as modified T91, TP304H, TP347H, and Super304H, etc. must be excluded. A new nickel-based superalloy, INCONEL alloy 740, is under development at Special Metals Corporation, Huntington, WV, to meet these stringent material targets [2,3]. This alloy maintains good microstructure stability to at least 750 °C and exhibits the stress rupture strength no less than 100 MPa at 750 °C [4,5]. Possible corrosion problems may result from fireside attack to be envisaged for tubular components due to highly aggressive ash deposits that contain alkali metals and sulfur from the coal. Compared with steels, much less is known about the coal ash corrosion resistance of nickel-based alloys [2,3,6]. This paper presents the results of an investigation on laboratory simulated superheater/reheater fireside corrosion of this new superalloy. The possible corrosion mechanisms are elucidated on the basis of experimental results of microstructural examination.

* Corresponding author. Tel.: +86 951 206 1004;
fax: +86 951 206 1003.
E-mail address: shuangqunzhao@sina.com (S. Zhao).

0254-0584/$ – see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.matchemphys.2004.04.006

2. Experimental materials and procedures

The chemical compositions (wt.%) of two heats of INCONEL alloy 740 employed in this investigation are pre-

Table 1
Chemical compositions of INCONEL alloy 740 (wt.%)

	Heat 1	Heat 2
C	0.03	0.06
Cr	22.96	24.97
Co	19.27	19.80
Nb	1.87	2.01
Ti	1.63	1.69
Al	0.72	0.87
Fe	1.01	0.71
Si	0.40	0.47
Mn	0.28	0.30
Mo	0.51	0.58
Ni	Balance	Balance

sented in Table 1. The alloy was vacuum induction melted, and then vacuum arc remelted. The ingot was homogenized at 1204 °C for 16 h and subsequently hot-worked to 15 mm bar at temperature no less than 1050 °C. The final heat treatment was solution-annealed at 1150 °C for 30 min and water quenched.

The pulverized coal-fired environment was simulated as coal ash plus flue gas. The synthetic coal ashes were composed of (wt.%): 5 Na_2SO_4, 5 K_2SO_4, 30 Al_2O_3, 30 SiO_2, 30 Fe_2O_3 and the synthetic flue gas were composed of (vol.%): 15 CO_2, 3.5 O_2, 0.25 SO_2, 81.25 N_2. Cylindrical test coupons 20 mm in length and 6 mm in diameter were ground to 120 grit SiC abrasive paper. The samples were ultrasonically cleaned in acetone and ethanol and then applied synthetic coal ash suspended in ethanol with a brushed to the samples surface until about 10 mg cm^{-2} coal ash were coated onto the surface. The coating procedure was repeated about every 500 h without cleaning the samples and the flow rate of pre-mixed flue gas was 200 ml min^{-1} during corrosion. Pt foil was applied as a catalyst for the reaction: $2SO_2 + O_2 \rightarrow 2SO_3$. The samples of heat 1 were exposed at 550 and 700 °C for times up to 2009 and 4001 h, respectively, and that of heat 2 at 700 °C for times up to 5008 h. According to ASTM G54-77 [7], the metal loss on the sample surface was determined by using scanning electron microscopy. The value was based on 24 measurements of the corrosion depth made along the sample cross-section, this corresponding with a distance of about 800 μm between the measurement points. The detailed structure analyses for corrosion products were carried out by XRD, SEM, and EDX.

3. Results and discussion

3.1. Corrosion of heat 1 at 550 °C

SEM surface images show that the oxide scale formed on the surface of heat 1 sample corroded at 550 °C for 1008 h was not compact and the surface of the sample was not entirely covered with oxide. The integrated but uneven oxide scale formed on the surface of the sample corroded at 550 °C for 2009 h and the oxide particles were fine. The cross-section morphologies of oxide scale formed on the samples corroded at 550 °C for 1008 and 2009 h are shown in Fig. 1. The oxide layer was found not to be compact, dense and adherent to the surface of the sample corroded for 1008 h (Fig. 1a) whereas the compact and adherent oxide scale was observed after exposure for 2009 h. The thickness of the scale was nonuniform and the alloy suffered the pitting attack (Fig. 1b). The original surface of the alloy can be discerned easily.

Fig. 2 shows the X-ray mapping of a pit on the sample after corrosion for 2009 h. Below the original alloy surface, the pit was rich in Cr, S, O and small amount of Co and Ti. The oxide formed above the original surface was rich in Ni, O, S and small amount of Co. No Cr-depletion zone was found beneath the pit. Combining the results of X-ray mapping with the X-ray diffraction result (Fig. 3), the products formed below the original surface were identified as major in Cr_2O_3 and CrS. The outer part of the pit consisted of NiO and Ni_3S_2.

3.2. Corrosion of heat 1 at 700 °C

The cross-section images of the samples of heat 1 corroded at 700 °C for 501, 1006, 1988, and 4001 h are shown in Fig. 4. Their average metal losses were 6.02, 6.75, 10.61, and 20.55 μm, respectively. The morphologies of the oxide scale of the samples corroded at 700 °C were observed to be different from that corroded at 550 °C in one important

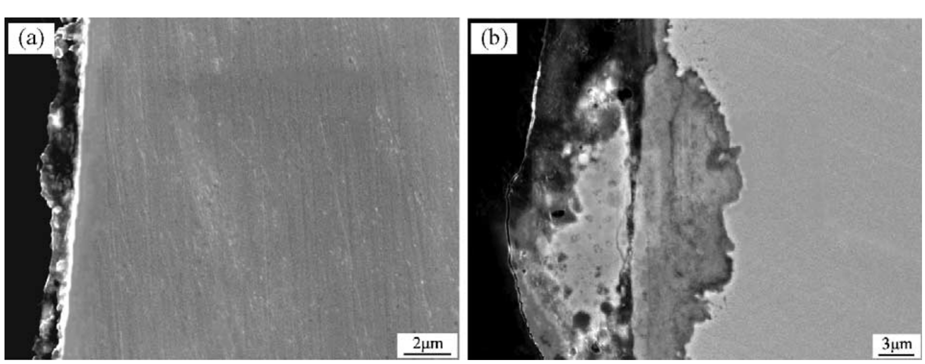

Fig. 1. Cross-section images of the samples corroded at 550 °C for 1008 h (a) and 2009 h (b).