



Effect of coal ash on the performance of alloys in simulated oxy-fuel environments



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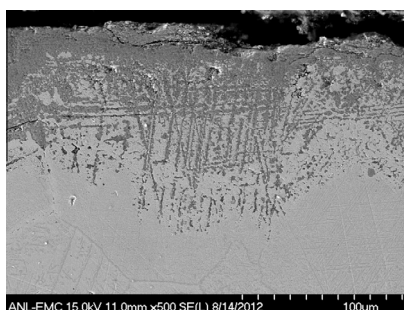
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HIGHLIGHTS

- Long-term performances of alloys in oxy-fuel environment with ash at 750 °C were evaluated.
- Two stages were found for ash corrosion: incubation stage and rapid corrosion stage.
- Mo, W, and Nb in alloys reduce the incubation time.
- Severe carburization was observed after incubation time in oxy-fuel environment with high CO₂ content.
- The corrosion rates in an oxy-fuel environment were higher than or close to the rates in an air combustion environment.

GRAPHICAL ABSTRACT



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ABSTRACT

Oxy-fuel combustion can increase efficiency and reduce pollution from coal power plants. To study material performance in an oxy-fuel environment, both Fe- and Ni-based alloys were exposed to simulated oxy-fuel environments at 750 °C for long terms up to 6300 h. The effects of ash and gas compositions (SO₂, CO₂, H₂O and O₂) on the performance of alloys were studied. Results from these tests are used to address the role of CO₂, steam, and ash in the long-term corrosion performance of alloys. Detailed results are presented on weight change, scale thickness, internal penetration, microstructural characteristics of corrosion products, and cracking of scales for the alloys. Oxide scales were studied by synchrotron nano-beam X-ray diffraction.

An incubation period and a propagation period were observed for ash corrosion. Before incubation time, alloys gain weight. After incubation time, localized corrosion damages the protective scales, alloys lose weight and corrosion rates dramatically increase. Since the incubation time can be over 4000 h, long-term test results are more helpful in evaluating the alloy performance in an oxy-fuel combustion environment with ash than the results from a short-term test. The mechanism of ash corrosion is also discussed.

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1. Introduction

Electricity is the world's fastest-growing form of energy consumption. Coal provides the largest share of world electricity generation. Since coal is plentiful, its share of the global energy mix

continues to rise, and it could surpass oil as the world's top energy source. However, it is well known that coal combustion to produce a given amount of electricity produces more CO₂ than oil or natural gas. The U.S. Department of Energy's Office of Fossil Energy is intensely promoting research and development of oxy-fuel combustion systems that employ oxygen, instead of air, for burning the fuel. The oxy-fuel combustion systems (without the diluent nitrogen gas) can enable recycling of the carbon dioxide to the

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compressor, the use of novel gas turbines, and advance reuse. The resulting flue gas consists primarily of H₂O and CO₂, which facilitates sequestration of CO₂ or its use in a turbine to generate electricity, thereby leading to reduction in CO₂ emissions. Also, because the oxidant is bereft of N₂, NO_x emissions are minimized in the exhaust gas. Studies at National Energy Technology Laboratory have indicated that oxy-fuel combustion can increase efficiency in the power plants from the current 30–35% to 50–60%. However, the presence of H₂O/CO₂ and trace constituents such as sulfur and chlorine in the gas environment and coal ash deposits including alkalis at the operating temperatures and pressures can have adverse effects on the corrosion and mechanical properties of structural alloys [1]. The concentration of CO₂, SO₂, and H₂O in oxy-fuel environments are higher than under air combustion conditions, because of the absence of airborne N₂. Alloy corrosion behaviors of steel materials in H₂O and CO₂ environments have been studied [2–7]. Increasing steam content can lead to break-away oxidation [3]. Carburization was observed when alloys were exposed to CO₂ at elevated temperature [4]. High CO₂ and H₂O concentrations also assist in partially oxidizing SO₂ to SO₃ [8]. The concentration of SO₃ in oxy-fuel environment is typically three or more times higher than under air combustion condition. SO₃ and steam can react to form sulfuric acid through the following reaction:



Higher SO₃ and H₂O concentrations lead to higher concentration of corrosive H₂SO₄ under oxy-fuel conditions. Thus there is a critical need to evaluate the response of structural and turbine materials in simulated oxy-fuel environments in an effort to select materials that have adequate high-temperature mechanical properties and long-term environmental performance.

Sulfur can be transported through oxide scale and increase the oxidation rates of alloys. Radiometric analysis indicated that the inward transport of sulfur is primarily due to the SO₂/S₂ molecular transport. Sulfides were observed in the inner scale layer [9]. However, the effect of sulfur on corrosion in oxy-fuel system has scarcely been studied [10]. Coal ash can also lead to severe corrosion at high temperature [11–20]. The corrosion of alloys in the oxy-fuel and ash environments has also been scarcely reported [21,22]. Since coal power plants should be operated for long time, it is important to study the long-term performance of alloys. However, recent studies usually show only short-term test results. If the oxidation follows the parabolic law, short-term test results can provide useful information. However, if the oxide scale breaks down after the incubation period, the corrosion rate can dramatically increase. Short-term test results below the incubation time will not be enough to evaluate the alloy performance for coal power plants.

Therefore, this paper provides a study of long-term performance of alloy materials in oxy-fuel environments.

2. Experimental

2.1. Materials

The compositions of the alloys selected for the study are listed in Table 1. Several alloys, both ASME-coded and uncoded, were selected for corrosion evaluation. Fe-based alloys and Ni-based alloys (333, 617, 625, 602CA, 230, 693, 740, and 718) were included in the study, especially for application at temperatures above 700 °C. MA956 is a Fe–Cr alloy produced via mechanical alloying and subsequent extrusion. Apart from fireside and steam-side corrosion resistance, the alloy selected for application in steam superheaters and reheaters should possess adequate strength at elevated temperatures for the duration of service.

2.2. Gas compositions

To understand the effect of gas composition on alloy corrosion, the alloys were exposed to seven different gas compositions (see Table 2). Gas 1 and 2 were used to model the effect of gas composition on the corrosion of alloys in gas environments without ash. Gases 3 to 7 were used to study the corrosion of alloys in these gas environments in the presence of ash. Gas 3 simulates the gas environment under oxy-fuel combustion conditions when Gatling coal is used with ~4% oxygen excess. Gas 5 is used to compare the effect of the partial pressure of oxygen on alloy corrosion. The partial pressure of oxygen in Gas 5 is 6 times higher than it is in Gas 3. The partial pressures of steam and SO₂ remain similar between Gas 3 and Gas 7. Gases 4 and 6 do not contain steam, but the partial pressures of O₂ and SO₂ in Gas 4 are the same as in Gas 3. Gas 7 does not contain CO₂ and steam. The effect of steam and CO₂ on the corrosion of the alloys is studied by comparing their performance in the gas environments both with and without steam.

2.3. Experiments

Oxidation experiments without ash were conducted in an experimental system that consists of a horizontal, tubular, high-temperature furnace capable of operation up to 1000 °C. The reaction chamber consisted of a quartz chamber (104-cm length, 5-cm OD, 0.32-cm thick), which was centered in a 30-cm-diameter resistive heating furnace. Type 316 stainless steel (SS) flange caps with an O-ring seal were used to close the ends of the quartz tube. The flange caps provided port fittings for the gas flow, steam/vapor

Table 1
Nominal composition (in wt%) of alloys selected for corrosion study.

Material	C	Cr	Ni	Mn	Si	Mo	Fe	Other
153MA	0.05	18.4	9.5	0.6	1.4	0.2	Bal	N 0.05, Nb 0.07, V 0.2
304	0.08	18.0	8.0	1.6	0.6	–	Bal	
253MA	0.09	20.9	10.9	0.6	1.6	0.3	Bal	N 0.19, Ce 0.04
800H	0.08	20.1	31.7	1.0	0.2	0.3	Bal	Al 0.4, Ti 0.3
333	0.05	25.0	45.0	–	1.0	3.0	18.0	Co 3.0, W 3.0
617	0.08	21.6	53.6	0.1	0.1	9.5	0.9	Co 12.5, Al 1.2, Ti 0.3
625	0.05	21.5	Bal	0.3	0.3	9.0	2.5	Nb 3.7, Al 0.2, Ti 0.2
602CA	0.19	25.1	62.6	0.1	0.1	–	9.3	Al 2.3, Ti 0.13, Zr 0.19, Y 0.09
230	0.11	21.7	60.4	0.5	0.4	1.4	1.2	W 14, Al 0.3, La 0.015
693	0.02	28.8	Bal	0.2	0.04	0.13	5.8	Al 3.3, Nb 0.67, Ti 0.4, Zr 0.03
740	0.07	25.0	Bal	0.3	0.5	0.5	1.0	Co 20.0, Ti 2.0, Al 0.8, Nb + Ta 2.0
718	–	19.0	52.0	–	–	3.0	19.0	Nb 5.0, Al 0.5, Ti 0.9, B 0.002
MA956	–	20.0	–	–	–	–	Bal	Al 4.5, Ti 0.5, Y2O3 0.6
WASP	0.02	20	Bal	0.5	0.75	4.3	2.0	Co 12–15, Ti 2.6–3.25, Al 1.0–1.5, Zr 0.1
ANL5	0.2	25	71.1	–	–	–	–	Al 3.3, Ti 0.3, Zr 0.2, Y 0.1

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