Impact of Iron-Sulfide Deposits on Oxidized Austenitic Steels as Simulation of Corrosion and Fireside-Tube Wastage in Coal Combustion

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The sulfidation effect of molten iron sulfides was studied on oxidized austenitic steels as a simulation of furnace-wall corrosion in PC combustion environments. The test coupons were oxidized to produce an external oxide scale and pyrite was placed on the oxide and thermally treated in an inert atmosphere to decompose the pyrite into pyrrhotite. DSC-TGA and XRD indicated that FeS interacts with the Fe_2O_3 oxide layer, even at 700°C if the contact is good, changing the oxidation state of iron and the physical structure. On the other hand, the interaction of FeS with Cr_2O_3 between 1100 to 800°C, 24 hr in the inert atmosphere, consisted of the formation of a chromium sulfide layer beneath the oxide scale. SEM-EDX showed that the diffusion of sulfur in the steel matrix can be 30 μm deep, indicated by small particles of chromium sulfide. It is demonstrated that iron sulfide deposits could be responsible for sulfidation of the alloys.

KEY WORDS: fireside corrosion; sulfidation; iron sulfide.

INTRODUCTION

In recent years there has been a major concern about the low availability loss due to repeated boiler tube failures in fossil-fuel plants. Of all the failure mechanisms surveyed, fireside corrosion is most intensely studied, since the implementation of low NO_x burner technology.¹ Corrosion of furnace wall tubes during pulverized-fuel combustion is believed to be

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enhanced by the establishment of localized reducing conditions in the vicinity of the furnace walls, because the new configurations in boilers retrofitted with low NO_x burner systems involve higher partial pressures of H_2S . The study of corrosion on tube life has been studied in terms of resistance to moderately reducing environments representative of low NO_x gas compositions.² On the other hand, recent studies of the Electric Power Research Institute have demonstrated that FeS deposits on mild steels are the main culprits causing excessive waterfall fire-side wastage.³ The authors proposed that those deposits promoted the sulfidation attack by maintaining a constantly reducing sulfidizing environment in the ash. This binary system of melted iron sulfides–surface iron oxides has, for a long time, focused great interest in the chemical interaction between the deposits and oxide scales as detected by SEM.^{4,5} The mechanism of interactions of molten iron species on hematite surfaces (Fe_2O_3) as a simulation of boiler waterfall has been studied recently by differential scanning calorimetry,⁶ suggesting that both di- and mono-iron sulfides can react with the oxide layer, changing the oxidation state of iron in the oxide scale to Fe^{2+} or even Fe^0 . This would imply a change in the protective ability of the scale, causing increased corrosion.

Solutions to the fireside corrosion are available from changes in operating procedures and design. However, for some boilers, there will remain areas with unacceptably high corrosion rates. Material-engineering solutions to this problem involve the use of a more corrosion-resistant alloy (SS type-310 stainless steel or 50Cr–50Ni), either as a coextruded outer layer over the low alloy, or deposited as a coating.⁷ Their major objective is to form a slow-growing protective scale of Cr_2O_3 that is well bonded to the substrate alloy. The weld overlays and diffusion coating seem to exhibit satisfactory resistance to the reducing gas.⁸ A number of research works propose that coatings such as SiN_x or CeO_2 applied to low- and high-alloy steels increase the corrosion resistance, because of a change in oxidation mechanism that leads to a more compact and uniform scale.^{9–11} All these studies have a temperature range of 400 to 600°C, this being the waterwall temperature range of the most efficient fossil-power plants. It is expected that steam temperatures will rise another 50–100° in the next 30 years, provided that suitable materials and technology are developed.¹² In this way, behavior of steels and alloys should be studied at higher temperatures under oxidizing and sulfidizing atmospheres, assuming that fireside temperatures could exceed 800°C. Sulfidation of chromium oxide has been studied extensively¹³ in terms of attack of gaseous sulfides. In this paper, we demonstrate another way for sulfidation of the protective layer, caused by molten iron sulfide particles, to reach the tube wall. Simulation by differential scanning calorimetry (DSC) of the pyrite decomposition and pyrrhotite interaction with oxidized stainless steels, and further analysis by EDX and SEM,

showed the formation of sulfur spots in the Cr_2O_3 –Fe interface. Previously, DSC has been used to describe deposition and fluxing phenomena under slagging conditions,¹⁴ and to test the corrosion behavior of SS316 in different atmospheres.¹⁵ Changes in composition were studied by XRD and SEM.^{10,16}

EXPERIMENTAL PROCEDURES

The materials used in this work were: SS304, SS316, and SS310 from Goodfellow (composition in Table I) as sheets 0.25-mm thick. Discs (ϕ = 6 mm) were cut from the sheet and ultrasonically cleaned in ethanol. Although these steels are not the alloys of choice for tube walls, they were selected for this study due to their composition, which involves a progressive tendency to form chromium oxides with increasing chromium content.

Natural pyrite, sieved to $\phi < 40$ microns, was stored in an inert atmosphere.

Tests were run with bare-alloy surfaces and oxidized surfaces. The samples were oxidized in air in a muffle furnace at 800 and 1000°C for times ranging from 3 to 240 hr. The phase constitution of the oxide layer was investigated by X-ray diffraction (XRD) using a Siemens D500 diffractometer with $\text{CuK}\alpha$ radiation. The diffraction angle scanned was 20–70° 2θ using a step size of 0.05° 2θ .

Thermogravimetric and colorimetric experiments were performed in a TA SDT 2960 thermobalance, in Pt pans, with a constant 90 ml/min flow of argon. Three different types of experiments were performed in the thermobalance:

1. Thermal treatment of pyrite to study its thermal history and its decomposition into iron monosulfide (pyrrhotite). The heating ramp to 1300°C was 80°C/min. These experiments were performed in a Pt crucible with pyrite, which was laid onto different discs: hematite, SS304, SS310, oxidized SS304, and oxidized SS310.
2. It is well known that the iron species that impacts on the tube wall is iron monosulfide as molten droplets. The simulation of that

Table I. Composition of the Stainless Steels

AISI grade	Typical analysis					%Fe
	%Cr	%Ni	%Mo	%Mn	%Si	
304	17–20	8–11		< 2		Balance
316	16.5–20	9–14	2.0–3.5	< 2		Balance
310	24–26	19–22		< 2	< 1	Balance

impact was done by decomposing pyrite at 80°C/min to 1100° (to ensure its fusion) and holding times of 24 hr at 800 and 900°C, deposited over oxidized coupons. Similar experiments were performed without heating to 1100°C.

3. Several experiments were performed in alternating heating-cooling cycles in argon and in air, to study the oxidation of the sulfur species formed.

The microstructure of the samples was studied by scanning-electron microscopy (SEM), in a JEOL microscope, model JSM 6400, equipped with Si(Li) energy-dispersive spectroscopy (EDX).

RESULTS

Oxidation of Steels

The first experiments performed revealed that pyrite did not show any interaction over bare SS304 and SS310 when heated in argon to 1300°C: the decomposition heat and weight loss, as well as the melting endothermic phenomena, showed the same values as obtained for pure pyrite over empty Pt pans. On the other hand, polished coupons would not be a realistic approach to the deposition attack, provided that the surface of tubewalls inside burners should present an oxidized surface to impacting particles. Thus, the main objective of this work was to study the interaction of iron sulfide with the oxide scales. For this purpose, the coupons were oxidized for 72 and 240 hr in a muffle furnace at 800 and 1000°C. The external surface of SS304 oxidized at 800° for 3 days has a composition of hematite, as can be seen in Fig. 1. XRD profile of pure hematite is displayed for comparison. SEM-EDX indicated that the oxide scale formed is enriched in Fe (Fig. 2). On the other hand, for oxidized SS310, the XRD profile seems to indicate the presence of hematite (peaks at 33 and 54 2 θ), but to a minor extent. The main structure presented in XRD in Fig. 1 are peaks at 35 and 57 2 θ , corresponding to chomite (FeCr₂O₄).¹⁰ SEM-EDX of this sample is shown in Fig. 3a (cross section) and b (surface). The oxide scale has a composition enriched in Cr (89% Cr, 9% Fe), whereas the coupon core showed the expected composition of SS310: 51% Fe, 27% Cr, 18% Cr, 1% Mn. SS316 has a XRD diffractogram similar to that of SS304, and the SEM-EDX (Fig. 3c) confirmed, as well, the environment of Fe in the outer oxide layer. These results indicate that there are two different systems to study in the iron sulfide interaction: iron sulfide-Fe₂O₃ and iron sulfide-Cr₂O₃. The system iron sulfide-pure hematite has been studied thoroughly in a previous work,⁶ and the next section expands the study of pyrite oxidized-steel system, in a more realistic approach.

Fig. 1. X-ray diffractograms of pure hematite, SS304, and SS310, and oxidized SS304 and SS310 at 800°C for 72 hr.

Fig. 2. SEM photomicrograph and EDX composition of SS304 oxidized for 72 hr at 800°C.

Iron Sulfide–Iron Oxide Interaction

The kinetic models used for the interpretation of excluded pyrite transformation inside coal burners propose that the particles, which impact in tube banks, are low-viscosity, molten FeS droplets. Even for oxidizing conditions, the particles impacting are actually molten droplets of the eutectic

Fig. 3. SEM photomicrograph of steels oxidized for 72 hr at 800°C. (a) SS310 cross section; (b) SS310 surface; (c) SS316 surface.

FeS–FeO.¹⁷ In this way, the particles adhere, upon impact, in the liquid state, reaching a high degree of contact with the exposed surface. The interaction of iron sulfide with hematite has been studied previously in terms of chemical mechanism and enthalpy changes.⁶ The mechanism proposed that the decomposition of pyrite into pyrrhotite at around 700°C is as follows (Fig. 4, line a):

The gas atmosphere has no influence on temperature and the extent of decomposition. Weight change vs. temperature of pyrite decomposition on hematite discs is displayed in Fig. 4, line b. A mechanism we proposed⁶ to explain the differences was that iron monosulfide interacts with the hematite as follows:

This interaction occurs at high temperature (1000–1100°C) if pyrite is placed on a hematite disc. If a high degree of contact is achieved by pelletizing pyrite in excess hematite, the hematite reduction into magnetite occurs at 500–700°C (line c, Fig. 4).

As mentioned above, when SS304 and SS316 are oxidized, an external scale of Fe₂O₃ forms. When the SS304 is oxidized at 800°C for 3 hr, the

Fig. 4. Weight loss (in pyrite basis) during thermal decomposition of pure pyrite (a); pyrite on hematite disc (b); pellet of pyrite/hematite in excess hematite (c); pyrite on SS304 oxidized at 800°C for 3 hr (d); pyrite on SS304 oxidized at 800°C for 72 h (e); pyrite on SS316 oxidized at 800°C for 72 hr (f).

monosulfide starts to react with the thin oxide layer, as can be seen in the mass loss in line d, Fig. 4, but the amount of available hematite is substoichiometric and the mass-loss line subsequently shows a weight gain. When SS304 is oxidized at 800°C for 3 days, the mass-loss profile of pyrite decomposition (line e, Fig. 4) is close to that shown in line b—pyrite placed on an excess of pure hematite. The same interaction is found for SS304 coupons oxidized at 1000°C for 24 hr. On the other hand, SS316 oxidized at 1000°C for 24 hr seems to offer a different chemical surface to interact with decomposing pyrite, Fig. 4, line f, although SEM indicated the Cr in the surface was minimal. Provided that the waterwall temperature in coal burners is considered to be between 500 and 700°C, a chemical interaction between the iron sulfide and the iron-oxide scale in low alloys can occur, if the contact is high. All the findings discussed above imply that the mechanism of wetting and adherence of molten pyrrhotite over the outer surface of the tube banks, is not only physically, but chemically, induced—iron monosulfide interacts with the Fe_2O_3 layer, changing the oxidation state of iron and the physical structure. This would imply a change in the protective ability of the scale, increasing corrosion, as can be seen in Fig. 5. This figure shows that the iron sulfide melted and adhered to the porous oxidized surface and that, upon shearing, parts of this oxide layer break off the substrate. This would indicate that the adherence between the oxide layer and ash drop is stronger than the adherence of the oxide layer to the metal.⁴

Fig. 5. SEM photomicrograph of pyrite placed on oxidized SS304 and treated to 1300°C. (a) Cross-sectional cut; (b) surface.

Iron-Sulfide–Chromium-Oxide Interaction

The interaction of iron sulfides over oxidized SS310 coupons was tested in the same way as described for SS304: coupons of SS310 were oxidized at different temperatures and times to ensure the formation of the protective chromium scale. Pyrite was placed on the oxidized coupon and heated in an inert atmosphere to 1300°C to allow complete melting of the iron monosulfide. Figure 6a shows an overview of the sample and the compositions of the coupon surface and the melted pyrrhotite decrease. The weight-loss profile for pyrite did not show large differences with that for pure pyrite, which indicates at first glances that a chemical interaction between chromium oxide and iron sulfide did not occur. EDX analysis of a cross section of the coupon (Fig. 6b) confirmed the formation of the chromium oxide outer scale. Chromium depletion occurs beneath the alloy–scale interface, as expected. The outer layer is comprised of melted iron sulfide adhered to the oxide scale. The main information given by EDX is evidence of sulfur penetration in the subsurface. Two percent exists in the outer deposited mass (zone 1, Fig. 6b). Zone 2 contains 11% and the dark spots in the subsurface area contains 52% S; 3% S exists 50 μm into the alloy in zone 3. Similar results were obtained for all oxidation times and temperatures. Thus, the penetration of sulfur at high temperature is not dependent on the oxide scale thickness. Provided that the importance of these findings is related to tube-banks exposure in normal boiler operation, the chemical interaction and sulfur penetration should be studied at lower temperatures.

Thus, pyrite was placed on oxidized SS310 discs and heated rapidly to 1100°C, to ensure pyrite decomposition and pyrrhotite fusion, and held for

Fig. 6. SEM photomicrograph of pyrite placed on oxidized SS310 and heated to 1300°C. (a) General overview. (b) Cross section, EDX composition (1) 2%S, 53%Fe, 39%Cr, 4%Ni; (2) 11%S, 38%Fe, 46%Cr, 5%Ni; (3) 3%S, 57%Fe, 15%Cr, 24%Ni.

24 hr at 800 and 900°C. Figure 7 shows the detailed SEM image and the EDX maps for the 800°C sample. Sulfur penetration of 30 µm in the sub-surface is clearly identified. Moreover, a bright area of sulfur overlapped with chromium at the surface, which indicates the formation of chromium

Fig. 7. EDX maps for S, Cr, and Fe of pyrite placed on oxidized SS310, heated in an inert atmosphere to 1100°C, and held at 800°C for 24 hr.

sulfide. This effect is even more clear when the pyrrhotite interacts with the oxidized coupon at 900°C for 24 hr, Fig. 8. The bulk atomic composition at 30 μm depth is 6% S, 54% Fe, 19% Cr, 19% Ni. The atomic composition of a circle of 2 μm centered in one of the dark spots (which are smaller than 2 μm diameter) is 27% S, 33% Fe, 22% Cr, 12% Ni. The bright layer of sulfur

Fig. 8. EDX maps for S, Cr, and Fe of pyrite placed on oxidized SS310, heated in an inert atmosphere to 1100°C, and held at 900°C for 24 hr.

Fig. 9. SEM image of cross section of oxidized SS310 and attacked by pyrite at 900°C for 24 hr.

Fig. 10. EDX maps for S, Cr, and Fe of pyrite placed on oxidized SS310 held at 900°C for 24 hr.

Fig. 11. EDX maps for S, Cr, and Fe of pyrite placed on oxidized SS310, heated to 1100°C in inert atmosphere, and another heating-cooling cycle in air for 30 min.

and chromium has an atomic composition of 51% S, 44% Cr, which indicates the formation of chromium sulfide.

The next two experiments were performed avoiding the pyrite melting stage in the heating program. Those studied the effect of iron sulfide over chromium oxide at 800 and 900°C for 24 hr. Neither diffusion nor interaction was detected at 800°C. On the other hand, although the melting point of pyrite was not reached at 900°C, visual observation of the oxidized SS310 coupon with pyrite in contact and heated to 900°C for 24 hr, indicated a certain degree of liquid adherence between the coupon and the pyrrhotite. Figure 9 shows a cross section of the sample. It is clearly seen in the figure that the subsurface attack extended to a depth of about 60 μm . Figure 10 shows the EDX maps of the surface: chromium sulfide formed on the surface, sulfur is present under the oxide layer, and spots rich in S are also present. It can be concluded that sulfur–chromium interaction is found when the iron sulfide has certain degree of fluidity onto the oxide layer. These conditions are expected in combustion boilers, where the melted pyrrhotite particles impact at high velocity over the tube banks.

The chemistry and thermal stability in oxygen of the chromium-sulfide inclusions should be studied thoroughly to describe the sulfidation corrosion likely to occur in duty cycles. For that, pyrite was placed on oxidized SS310 and heated rapidly to 1100°C, held at 900°C for 6 hr and cooled to 300°C. After a second heating to 1000°C in an inert atmosphere, the flowing gas was switched to air, and maintained for 6 hr. A third heating–cooling cycle was repeated in argon. The samples obtained were studied by SEM. A cross-sectional photograph of the coupon and the EDX maps of sulfur, chromium, and iron are displayed in Fig. 11. The bright particles of chromium sulfide (atomic composition: 51% S, 44% Cr) are stable to the treatment in oxygen, probably due to the thick layer of both chromium oxide and iron, preventing oxygen from penetrating into the subsurface. The oxidation effect of air is clearly seen in the absence of sulfur in the external deposits. In an inert atmosphere, the outermost surface was composed of iron sulfide and oxide, as mentioned above in the XRD composition and SEM analysis (Fig. 7). Thus, it has been demonstrated that iron sulfide deposits could be responsible for surface and subsurface sulfidation, which, combined with the loss of the protective scale by contraction–expansion cycles, would enhance corrosion, mainly in higher partial pressures of oxygen and water which arise in duty cycles.

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