

Formation of corrosion products protecting surfaces of the boiler proper tubes from the combustion chamber

S. Król ^{a,*}, M. Pietrzyk ^b

^a Opole University of Technology, Faculty of Mechanical Engineering, Opole, Poland

^b BOT Power Station of Opole, Brzezie, Opole, Poland

* Corresponding author: E-mail address: stanislaw.krol@po.opole.pl

Received 09.11.2006; accepted in revised form 15.11.2006

Properties

ABSTRACT

Purpose: The aim of this paper is to determine how the oxidation product layer of the steel applied for the radiant tubes should increase if we are going to obtain the lowest possible corrosion losses.

Design/methodology/approach: Boiler tubes, made of 13CrMo4-5 steel were subjected to tests. In the boiler BP-1150, the tubes $\varnothing 30 \times 5$ mm are joined by fins and form a membrane shield. According to the maps of tube wall thickness, in the zone of the highest heat load, sectors of the shield were sampled in the places where the tube wall thickness was equal or greater than 4.3 mm, i.e. the minimum calculation thickness, according to the specifications given by the boiler manufacturer. It means that the corrosive loss could be determined as small, in spite of a long operation time (more than 60,000 hours).

Findings: The authors have determined structure and chemical and phase compositions of products and deposits forming in the radiant tubes in the regions of low corrosive losses after long-lasting operation (up to 60,000 hours). Then, they discussed a mechanism of formation of a compact layer protecting a steel surface against excessive oxidation under combustion gases.

Practical implications: The layer on the tubes with small losses of wall thickness are characterized by the following properties: good compactness, very good adhesion to the metallic base, low amount of sulfur, especially in magnetite, no aggressive components at the phase boundary product – steel, small development of the phase boundary product-steel. Owing to those properties, even presence of sulfur in the products do not reduce their passivation qualities.

Originality/value: Determination of the oxidation product layer of the steel applied for the radiant tubes.

Keywords: Corrosion; Radiant tubes of the boiler; Hard coal combustion gas

1. Introduction

Durability of the boiler proper tubes within the combustion chamber is influenced by many factors, for example aggressiveness of the corroding medium (combustion conditions and combustion gas composition), temperature of the tube material, operation time, a type of the material [1-3]. From the measurements of tube wall thickness after various operating

times, and from the elaborated maps of thickness distributions [3, 4] it appears that different reductions of the wall thickness can be observed on one wall and on the adjacent walls of the combustion chamber. In the boilers BP-1150 with tangential furnaces, as operation time rises, low corrosive losses could be seen on the prevailing area of the chamber walls (tubes on the walls). The estimated corrosion rate on that area was less than 0,15 mm per year [3]. However, a high reduction of the tube wall thickness

could be seen on a wide area on the chamber wall. In such a case, the estimated corrosion rate for those places exceeded 0,7 mm per year. Position of such places is determined by height of the burner zone and a horizontal distance between the wall fragments and the powdered-fuel burners.

The aim of this paper is to determine how the oxidation product layer of the steel applied for the radiant tubes should increase if we are going to obtain the lowest possible corrosion losses.

2. Experimental procedures

Boiler tubes, made of 13CrMo4-5 steel according to PN-EN 10028-2; 1996 (previous 15HM), were subjected to tests. In the boiler BP-1150, the tubes $\varnothing 30 \times 5$ mm are joined by fins and form a membrane shield. According to the maps of tube wall thickness, in the zone of the highest heat load, i.e. between the levels + 22.6 m and + 36.0 m, sectors of the shield were sampled in the places where the tube wall thickness was equal or greater than 4.3 mm, i.e. the minimum calculation thickness, according to the specifications given by the boiler manufacturer. It means that the corrosive loss could be determined as small, in spite of a long operation time (more than 60,000 hours).

The products and deposits occurring on the external surface of the tubes directed to the combustion chamber were subjected to the following tests:

- quantitative assessment of products and deposits,
- analysis of water extracts from products and deposits in order to determine pH, electrostatic conductivity σ , and amounts of SO_4^{2-} and C^- ,
- tests of spectrum in the infrared radiation FT-IR with use of the interference spectrometer with Fourier transformation (Philips Analytical PU 9804),
- derivatography in nitrogen and in air with use of Instruments Thermal Analysis,
- structural tests with scanning microscopy and X-ray microanalysis at the electron microscope,
- tests with X-ray phase analysis at the diffractometer X'Pert made by Philips with quantitative analysis according to Rietveld algorithm.

3. Results and discussion

Fig. 1 shows a typical structure of the oxidation products layer in the boiler proper region with small losses of tube wall thickness. The layer quantitative portion per a tube area unit increases with time, but after about 50,000 hours of the boiler service it does not exceed 930 g/m².

Such amount is not significant because similar amount of corrosive products can occur on internal surfaces of tubes in superheaters of live steam P4 and re-steam MC, made of the high-chromium martensitic steel X20CrMoV12.1 [5].

In the formed layer, two basic sublayers can be distinguished: deposits and products. In the products occurring just near the deposits there are also spheroidal particles of deposits. Deposits can

be a "site" and a "source" of the compounds which can influence corrosive destruction of tubes through reactions with the products or/and diffusion or penetration through pores. Thus, information about both products and deposits were obtained while the tests.

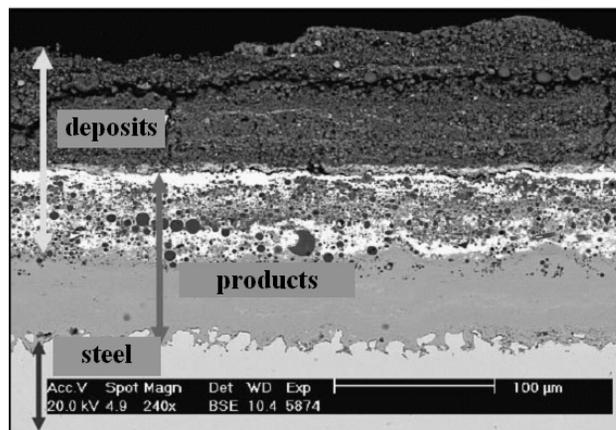


Fig. 1. Corrosion products and deposits formed on the external surface of the radiant tubes; magnification 240 x

Chemical tests of water extracts did not show any important differences, taking into account pH ($5.1 \div 5.8$), electrolytic conductivity ($70 \div 200 \mu\text{Scm}^-$), or content of SO_4^{2-} ($0.06 \div 0.40 \%$) and Cl^- ($0.3 \div 4.4 \%$), though conductivity and fraction of SO_4^{2-} and Cl^- were always higher in deposits in comparison of products. The deposits included mainly compounds containing groups SiO_4^{4-} , i.e. silicates and aluminosilicates; the products included mainly oxides Fe_2O_3 , Fe_3O_4 (Fig.2). The sublayer of deposits was not homogeneous, however it contained mainly very small particles, some micrometers in diameter (Fig.3). In the deposits, oxygen, silicon and aluminium were the dominating elements, and Na, Mg, S, K, Ca, Ti, Fe were the accompanying ones (Fig. 4a,b). Fine-spherical crystals were fly-ash being a set of chemically active and inactive crystallites.

In the combustion chamber, passage of coal dust through the high temperature area causes vitrification of the ash grains, and unburned components SiO_2 , Al_2O_3 , also MgO , K_2O , CaO remain inside the grains forming eutectics subjected to fusion, and next they congeal as glass.

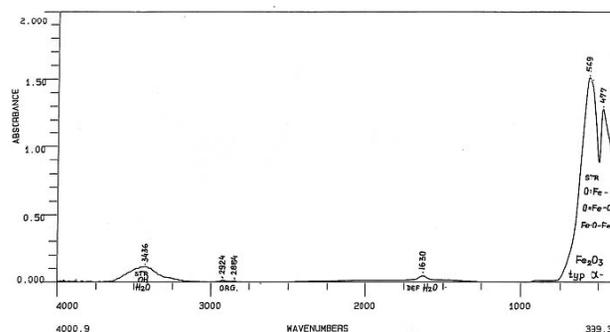


Fig. 2. FT-IR spectrum of corrosion products and deposits on the internal surface of the radiant tube

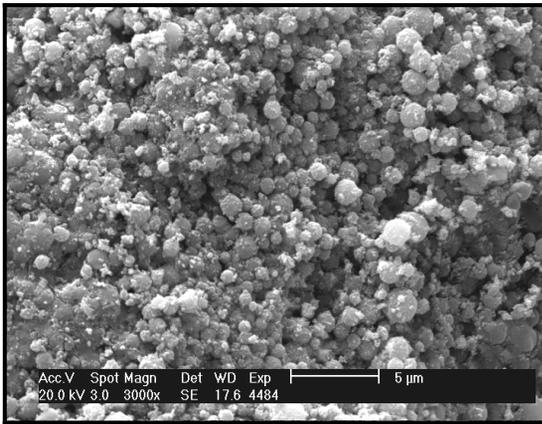


Fig. 3 Morphology of deposits from the external side with characteristic very fine spherical particles. Magnification 3000 x

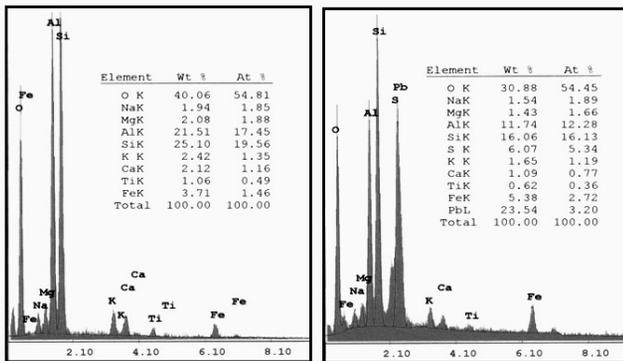


Fig. 4. Spectrum and chemical composition on the deposit surface (examples from various areas)

It is assumed that in the aluminosilicate skeleton formed while 50 milliseconds at the temperature of 1400° C there are not only the mentioned elements, but also nitrogen and carbon dioxide. Some of these particles are chemically active – that can be proved by a reduced pH and courses of derivatographic curves TG and DTG in nitrogen and air (Figs. 5 and 6), or by a mass reduction within 260° C, related to release of gaseous compounds occurring among particles of deposits. In the parts of deposits close to the product sublayer, anglesite $PbSO_4$ can be seen. Thus, not only the gas atmosphere of the combustion chamber, but also the deposit can be a source of sulfur. Anglesite $PbSO_4$ can be seen as light points (Fig. 3) or even a continuous band (Fig.1) in the cross sections observed by scanning microscopy. Thus, we should answer the question why there is so much compounds of lead on the surfaces of radiant tubes. Its amount in the applied fuel (hard coal) is rather low (from 0 to about 30 ppm) [6]. However, similar amounts of lead compounds occurred on the fragments of tubes drawn from the shields of the combustion chambers after various operation periods (from about 12,000 to about 65,000 hours). In the case of lead compounds coming only from the fuel, their amount would be a function of the operation time. Thus, we must assume that they are a component of the minium covering the shield surface before its assembly into the boiler (protection against corrosion while storage).

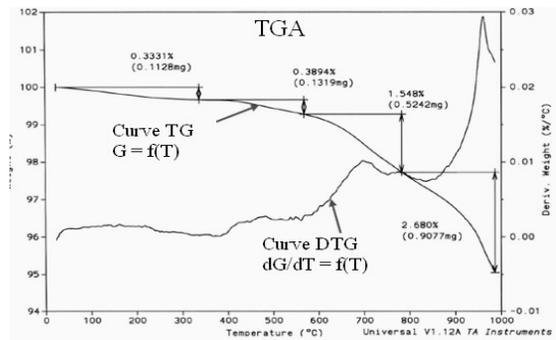


Fig. 5. TG and DTG curves showing mass variations versus temperature for deposits heated in nitrogen at the temperature $20 \pm 1000^\circ C$

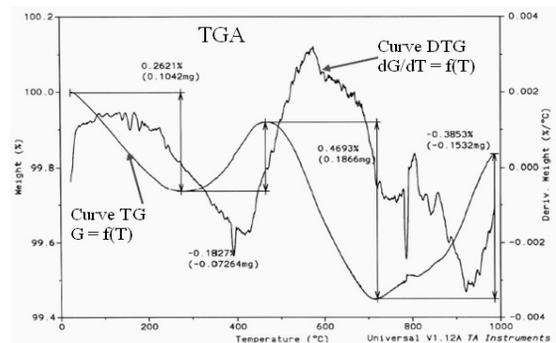


Fig. 6. TG and DTG curves showing mass variations versus temperature for deposits heated in air at the temperature $20 \pm 1000^\circ C$

In the product sublayer we can distinguish a magnetite band near the metallic base, and a hematite band over the magnetite. In the hematite band, near the interface with magnetite, there are agglomerates of sulfides (bright areas), and near the external phase boundary with the deposits we can observe spherical ash particles. It can be proved by X-ray microanalysis of particular regions of the layer (Figs. 7 and 8) and X-ray phase analyses (Fig.9).

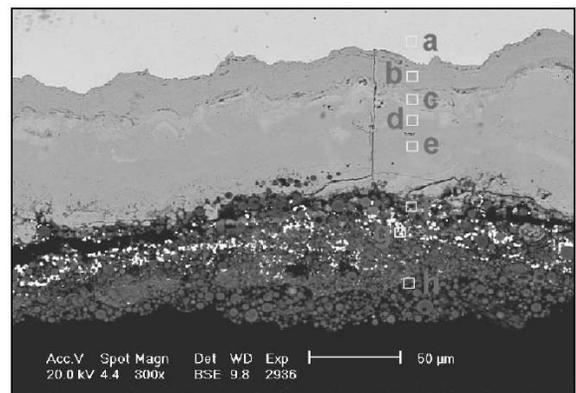


Fig. 7. Corrosion products and deposits formed on the external surface of the radiant tube. Magnification 300 x

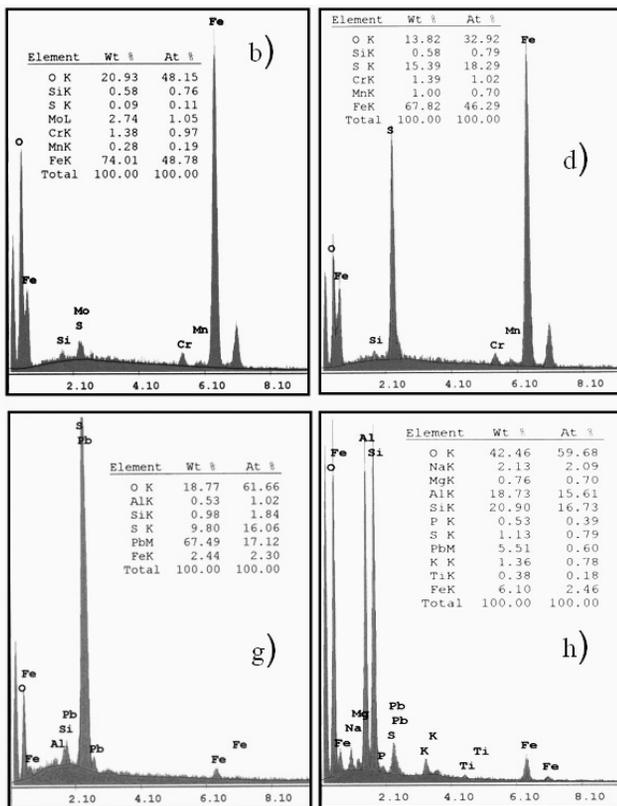


Fig. 8. Spectrum and chemical composition in points (b, d, g, h) marked on the cross-section by deposits and corrosion products in

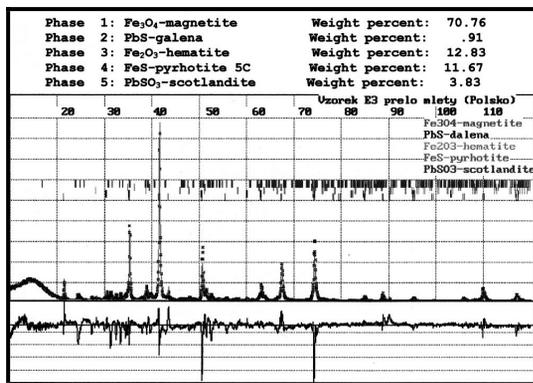


Fig. 9. A chosen representative diffraction pattern of the products from the external surface of the radiant tube (drawn for tests after the boiler cleaning for repair) with phase identification and results of calculations of mass fraction of particular phases

The phase analysis and the X-ray microanalysis allow to determine how such a layer forms:

- stage I - chemical reaction of Fe and oxygen from atmosphere; formation of Fe₂O₃; precipitation of ash becomes on this oxide,
- stage II - the product growth is not controlled by the chemical reaction rate, but by diffusion of ions through the scale between steel and hematite; magnetite Fe₃O₄ forms; the sequence Fe₂O₃ - Fe₃O₄ - Fe is obtained,
- stage III - ions Fe²⁺, Cr²⁺, Mo²⁺ diffusing from the core expand hematite and magnetite; chromium and molybdenum remain in magnetite, some ions of iron diffuse through Fe₂O₃, and hematite growth takes place at the phase boundary with the deposit, so some particles of the deposit are stopped in hematite; at the same time sulfur diffuse to the core forming FeS in hematite.

4. Conclusions

The layer on the tubes with small losses of wall thickness can be characterized by the following properties:

- good compactness,
- very good adhesion to the metallic base,
- low amount of sulfur, especially in magnetite
- no aggressive components at the phase boundary product - steel
- small development of the phase boundary product-steel.

Owing to those properties, even presence of sulfur in the products do not reduce their passivation qualities.

Acknowledgements

The work was realized within the project KBN 3T08C 015 26.

References

- [1] W. Kordylewski, „Burning and fuels, Wrocław 2001. (In polish)
- [2] St. Król, M. Pietrzyk, Corrosion of ferritic steels In burning chambers of steam boilers, Materials Science 1, 2005, 35-39 (in Polish).
- [3] M. Pietrzyk, Corrosion of ecraned boilers pipes in low emission conditions, PhD thesis, University of Opole, Opole 2005, (in Polish).
- [4] Repor tNr SPR/1/04/ET Power station Opole, unpublished, Wrocław 2004.
- [5] St. Król, J. Składzie, M. Pietrzyk, K. Przegaliński, X Conference. GRE 2006, Bielsko-Biała ZN PO nr 315, Opole 2006, 369-377. (In Polish).
- [6] Materials of chemical laboratory Power station. Opole, 2002-2004. (in Polish).