



## EVALUATION OF HIGH-TEMPERATURE CORROSION ON 13CrMo4-5 STEEL OPERATED IN THE POWER INDUSTRY

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### Abstract

The paper presents results of studies of steel and the oxide layer formed during a long-term operation ( $t = 130,000$  h) on 13CrMo4-5 steel at an elevated temperature ( $T = 455^\circ\text{C}$ ). The oxide layer was studied on a surface and a cross-section at the inner site of the pipe (in the flowing medium – steam side). The paper contains results of studies such as: light microscopy, scanning electron microscopy, X-ray phase analysis.

### Introduction

Both in Poland and worldwide there are attempts to ensure the energy security both on an industrial and household scale. This makes that the research and development of structural materials to be used in a modern conventional and nuclear power industry are still relevant. The basic objective of proper repairing of power units is to increase their reliability and efficiency and to extend their life at minimised costs (TRZESZCZYŃSKI 2010, BRUNNÉ et al. 2011).

In recent years, as demonstrated by Polish studies, a substantial share in part failure frequency is that of corrosion. Among others, such parts as superheater coils of secondary steam boilers get damaged due to excessive reduction of wall

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thickness. It is due to corrosion, from the inside as well as from the outside. Such a reduction is due to the widely understood high temperature corrosion, a contribution to which is made by oxides formed on the surface (or absence of such oxides), which do not always perform a protective role (DOBOSIEWICZ, BRUNNÉ 2007, KLEPACKI, WYWROT 2010).

Protective layers of oxides, which are formed during the normal operation exert equally important influence upon the longevity of operation of parts of turbines and boiler, dependent on mechanical properties, including creep strength and creep limit. Their good adhesion is important, as well as very slow growth, and slight susceptibility to scaling. Excessive growth of oxide layer from the steam side (internal wall of pipe) has negative consequences during long term operation, because:

- it reduces the bore of pipes, especially in heavy wall tubes with small inside diameter;

- the oxide layer causes reduction of wall thickness and increase of stresses, moreover – scaling of oxide layer may lead to erosion inside the turbine.

Scaling of oxide layer is an extremely harmful phenomenon, as the scaled particles may get to the turbine, and lead to fatal consequences. Scaled oxide layers may clog the bore of superheater pipe, as well as other steam pipelines, causing local overheating, which often leads to pipe burst.

On the flue gas end, besides oxide layers also ash deposits are frequently formed, which most often insulate.

DOBOSIEWICZ and BRUNNÉ (2007) showed that the main reasons for the wear of superheater coils are physicochemical processes occurring in steel associated with the simultaneous impact of: high temperature, aggressive exhaust and significant stress. To this processes belong to: creep, high-temperature corrosion, steam corrosion, erosion. The result of these processes are: degradation of the structure under the influence of high temperature and corrosive and erosive wall thickness degradation.

Steels for use in elevated temperatures find wide application first of all in the power sector. This steels are used mainly for boiler pipes, superheater coils, chambers, pipelines, parts of boilers, steam turbines, as well as other devices. Such steels include inter alia 10CrMo9-10, 13CrMo4-5 and also a high-chromium steel X10CrMoVNb9-1 (LAVERDE et al. 2004, PRISS et. al. 2014, GWOŹDZIK 2016a, 2016b).

## Material and Experimental Methods

The material studied comprised specimens of 13CrMo4-5 steel operated at 455°C during 130,000 hours (the base steel material and the oxide layer). The oxide layer was studied on a surface and a cross-section at the inner surface

(in the flowing medium – steam side) of the tube wall. Through examinations of material comprised:

- macroscopic and microscopic examinations using an Olympus SZ61, GX41 light microscope (LM) and Jeol JSM-6610LV scanning electron microscope (SEM);
- thickness measurements of formed oxide layers;
- chemical composition analysis of oxides using Jeol JSM-6610LV scanning electron microscope working with an Oxford EDS electron microprobe X-ray analyzer;
- XRD measurements (studying the phase composition, crystallite sizes ( $D_{hkl}$ )); the layer was subject to measurements using a Seifert 3003T/T X-ray diffractometer and the radiation originating from a tube with a cobalt. A computer software and the PDF4+2009 crystallographic database were used for the phase identification. Based on the width and the position of the main coat and substrate reflections, the size of the crystallites ( $D_{hkl}$ ) of hematite and magnetite were determined using the Scherrer formula. X-ray studies were carried out on the surface, and then the layer surface was polished down. The next the diffraction measurements were performed again to determine individual oxide layers. After removal of the  $\text{Cu}_2\text{O}$ , X-ray measurements were carried out, then for each case, the iron oxide layer was removed ( $5\mu\text{m}$ ) cyclically, each time making XRD measurements. The main reflections originating from planes (104) for  $\text{Fe}_2\text{O}_3$  and (311) for  $\text{Fe}_3\text{O}_4$  have been analysed;
- a quantitative evaluation of ferrite and perlite/bainite was carried out. The microstructure of the steel was analyzed by analyzer of image. Then the average size of phase and their volume share were calculated.

## Results of examinations

The microscopic observations of the surface of the oxide layer showed a significant degree of layer development. Directly on the surface, the spheroidal character of the oxide layer was observed (Fig. 1). EDS studies have shown (Fig. 2) that the oxide layer is composed of copper oxides and iron oxides, where the dominant element is iron. Three zones have been distinguished in the oxides layer formed.  $\text{Cu}_2\text{O}$  occurs at the surface, then hematite ( $\text{Fe}_2\text{O}_3$ ), under which a magnetite ( $\text{Fe}_3\text{O}_4$ ) exists (Fig. 3).

Copper compounds appearing on the internal surfaces of energy equipment elements and in the entire water-steam system are the result of progressive erosion and corrosion processes in supply and condensation systems, where these waters are enriched in trace amounts of copper compounds (ŚLIWA, GAWRON 2009, GAWRON 2014). One of the main sources of copper compounds emission to the circulating medium are such elements of power devices as: condensers and regeneration heat exchangers. In this type of elements, the progressive

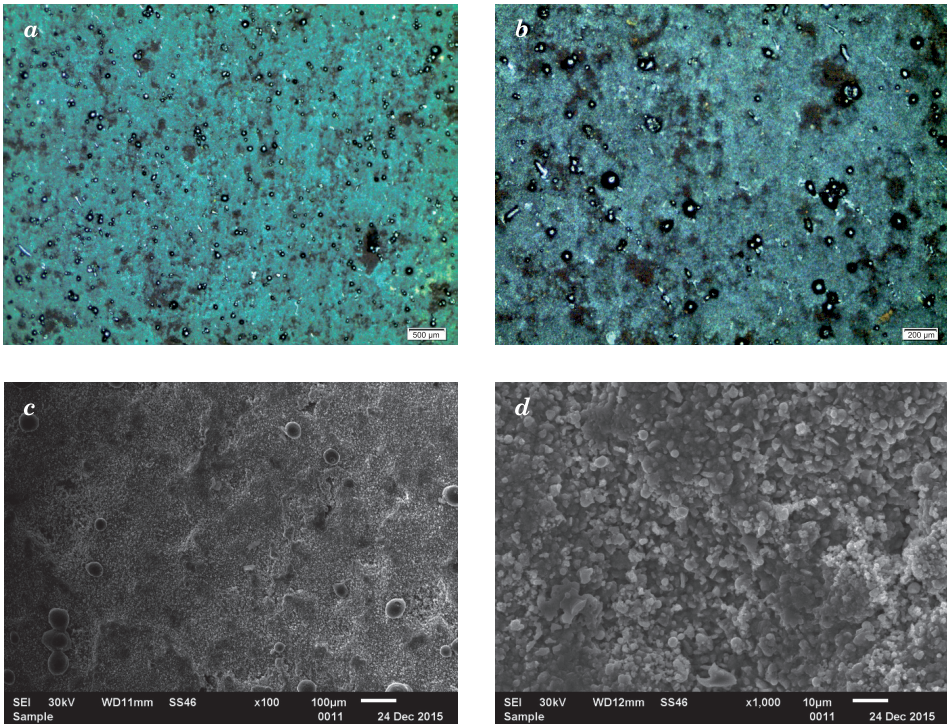


Fig. 1. Oxides formed on 13CrMo4-5 steel, inner surface:  
*a* – LM, 20×, *b* – LM, 45×, *c* – SEM, 100×, *d* – SEM, 1000×

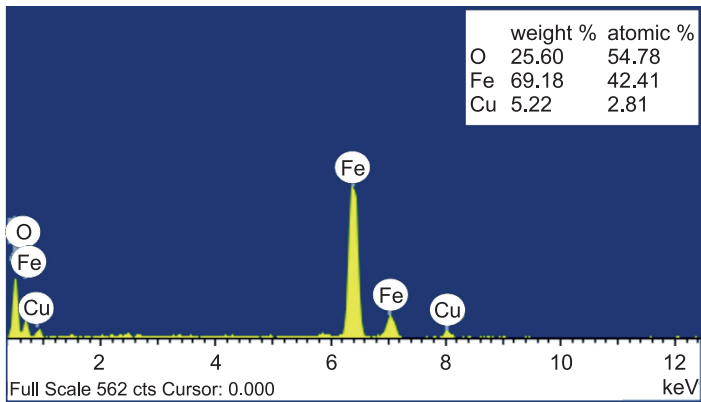


Fig. 2. EDS analysis of surface of oxides

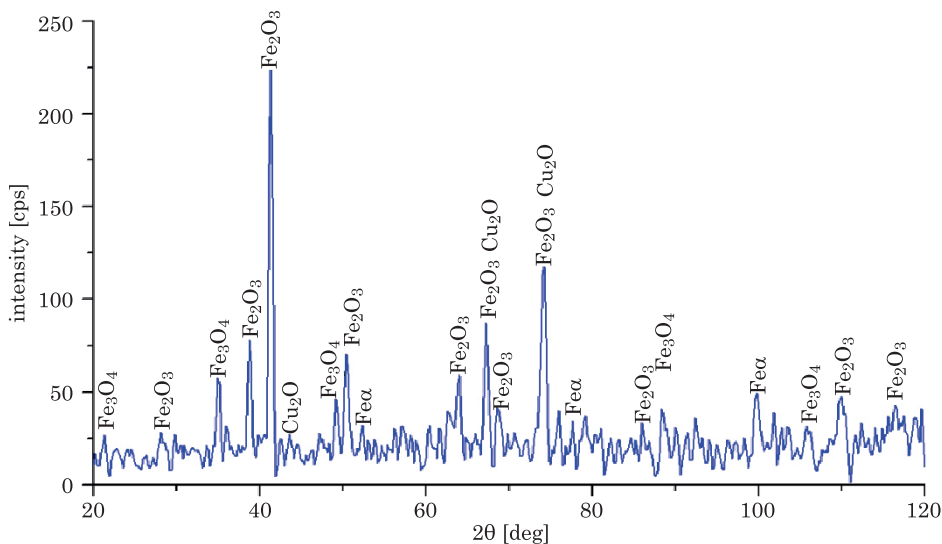


Fig. 3. X-ray diffraction patterns from the surface of oxide layer

corrosion processes result in the transfer of copper to the water in an ionic form. Copper then reacts with other compounds found in the circulating medium, which in turn causes uncontrolled emission of copper compounds, which under the temperature conditions of the boiler is released in the form of sediments. In addition, copper can pass into feed water in the form of copper oxides and copper metallic. This is caused by erosion or corrosion-erosion processes. These processes are caused by the influence of droplets on the condenser tubes or too high velocities of water flow through the tubes of the low-pressure regenerative heat exchangers (ŚLIWA, GAWRON 2009). However, from the side of the flue gas flow on this steel, as shown by previous tests,  $\text{SiO}_2$  (GWOŹDZIK 2016b) occurs.  $\text{SiO}_2$  precipitates in electrofilters after burning coal in various types of furnaces of power facilities (LELUSZ 2012).

The oxide layer formed on the studied steel on the inner side is  $54.82 \mu\text{m}$  thick. This layer is mostly degraded. This degradation occurs in the form of microcracks and fissures. Directly on the steel side, there is little corrosion on the grain boundaries. The pits covered with oxides have been directly from the steel side. The pits are  $76.37 \mu\text{m}$  thick.

Studies of crystallite sizes have shown (Fig. 4) that the hematite were existed to a depth of polishing  $15 \mu\text{m}$ . The crystallite size for this oxide was  $43.14 \text{ nm}$ ,  $42.15 \text{ nm}$ ,  $16.34 \text{ nm}$ , after removal of the layer by  $5 \mu\text{m}$ ,  $10 \mu\text{m}$  and  $15 \mu\text{m}$ , respectively. In contrast, the size of crystallites for magnetite gradually increases to a depth of  $30 \mu\text{m}$  and it was  $38.23 \text{ nm}$  (The crystallite size for this oxide was  $17.98 \text{ nm}$ ,  $19.10 \text{ nm}$ ,  $33.98 \text{ nm}$ ,  $35.54 \text{ nm}$ ,  $37.32 \text{ nm}$ ,  $38.23 \text{ nm}$  after removal of the layer by  $5 \mu\text{m}$ ,  $10 \mu\text{m}$ ,  $15 \mu\text{m}$ ,  $20 \mu\text{m}$ ,  $25 \mu\text{m}$  and  $30 \mu\text{m}$ , respectively).



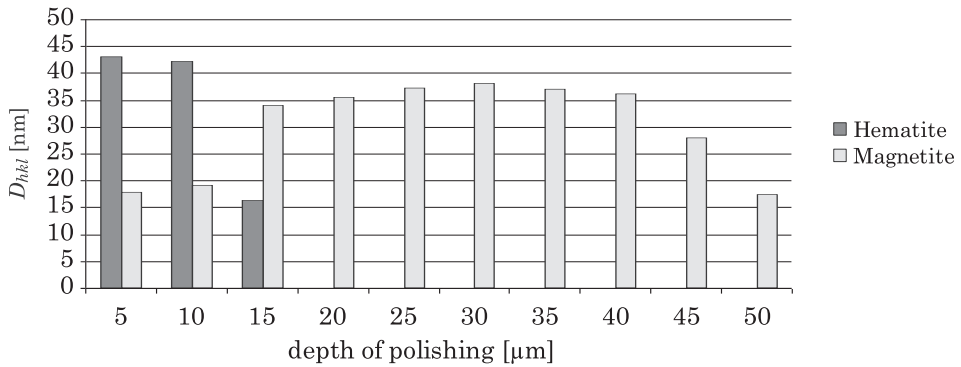


Fig. 4. Determination of crystallite size ( $D_{hkl}$ ) for main peaks  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$

The next, a slight decrease of crystallite size ( $D_{hkl}$ ) was observed (The crystallite size for this oxide was 37.11 nm, 36.12 nm, 27.98 nm, 17,54nm after removal of the layer by 35  $\mu\text{m}$ , 40  $\mu\text{m}$ , 45  $\mu\text{m}$ , 50  $\mu\text{m}$ , respectively).

The size of crystallites, as well as the nature of stresses, affect the morphology and mechanical properties of the oxide layers (GWOŹDZIK 2014). The studies

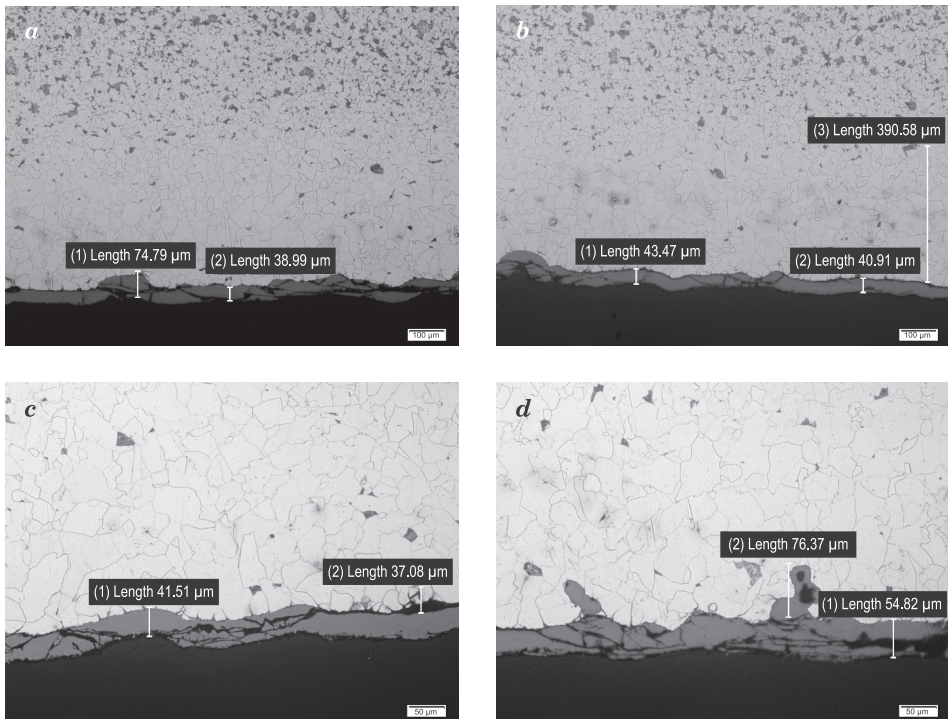


Fig. 5. The thickness of oxide layer formed on the steel examined, LM: a, b – 100 $\times$ , c, d – 200 $\times$

have shown that crystallites for hematite are larger in size than crystallites for magnetite. In papers (GWOŹDZIK 2011, GWOŹDZIK, NITKIEWICZ 2011) it was shown that the outer oxide layer, i.e. hematite, is more brittle and prone to cracking, which is related to the size of crystallites.

The microscopic examination of the structure (Figs. 5, 6) have shown significant decarburization directly from the surface, which reaches a depth of 390.58  $\mu\text{m}$ .

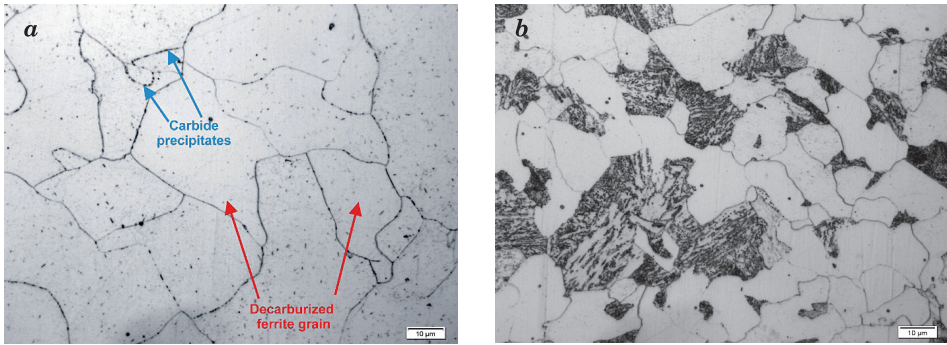


Fig. 6. Microstructure of 13CrMo4-5 steel, LM, 1000 $\times$ :  
 a – 200  $\mu\text{m}$  from oxide layer, b – 600  $\mu\text{m}$  from oxide layer

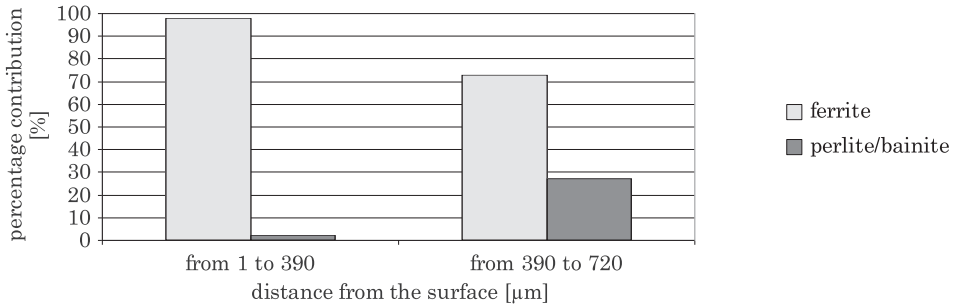


Fig. 7. Percentage contribution of ferrite and perlite/bainite

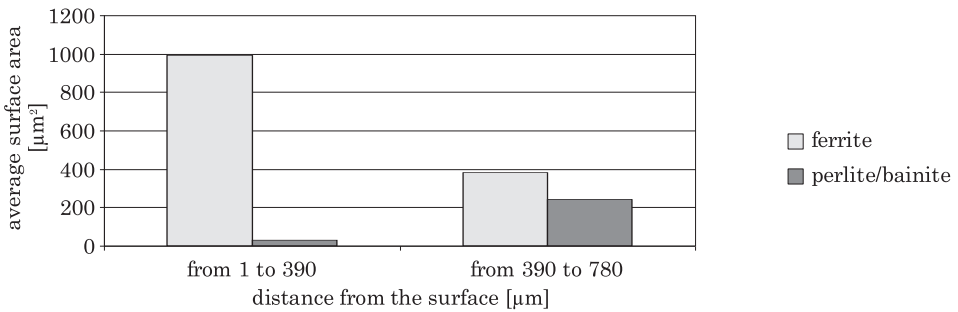


Fig. 8. Average surface area of ferrite and perlite/bainite

The quantitative phases analysis showed (Fig. 7) that only 2% perlite/bainite with a mean grain size of  $28.46 \mu\text{m}^2$  (Fig. 8) was present in this area. Instead, the decarburized ferrite grain size was  $992.25 \mu\text{m}^2$ . In turn, the proportion of perlite/bainite to ferrite at a depth of  $390 \mu\text{m}$  to  $780 \mu\text{m}$  was 27% to 73%. The average grain size in this area was  $382.46 \mu\text{m}^2$  and  $243.27 \mu\text{m}^2$  respectively for ferrite and perlite/bainite. In addition, especially in the decarburised layer, a significant share of carbide precipitates distributed mainly at the grain boundaries was observed.

## Summary

The research carried out on 13CrMo4-5 steel operated at  $455^\circ\text{C}$  for 130,000 h showed that:

- the structure of examined steel was ferrite and perlite/bainite with a share of 73% / 27%, respectively. The grain size of ferrite was  $382.46 \mu\text{m}^2$ , whereas perlite/bainite  $243.27 \mu\text{m}^2$ ;

- from the inside of the pipe wall, there is considerable decarburization. In this part ferrite prevails 98% (the grain size  $992.25 \mu\text{m}^2$ ), the rest was perlite/bainite, where the grain size was  $28.46 \mu\text{m}^2$ . In addition, there are the carbide precipitates along the grain boundaries that create chains in this places;

- the thickness of the oxide layer on the inner side of the pipe wall was  $54.82 \mu\text{m}$ . Numerous cracks and fissures were observed in this layer. Directly from the steel side there are pits covered with a layer of oxides;

- the phase analysis showed that the oxide layer is composed of  $\text{Cu}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ;

- the crystallite sizes for hematite is greater than for magnetite.

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