



# Durability evaluation of protection coatings on water-wall tubes of low-emission boilers

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## ABSTRACT

**Purpose:** of the paper is presentation of diagnostic research on durability of protection coatings on water-wall tubes in low-emission boilers.

**Design/methodology/approach:** Thermal spraying  $Al_2O_3/Ni-30Cr$  and hybrid paint coatings were evaluated. Durability of the coatings was evaluated after one and two years of service in direct action of flame, flue gas, and air flux from a blower. For evaluation of a level of degradation examinations of chemical composition and morphology of coatings and scales have been performed with the use of scanning electron microscope (SEM) equipped with EDS (energy dispersion X-ray spectroscopy) spectrometer.

**Findings:** Ceramic  $Al_2O_3/Ni-30Cr$  coatings are resistant to flame corrosion, but failed due to cracks generated by thermal stresses. Hybrid paint coatings do not protect steel tubes against hot corrosion (flame corrosion) since oxygen, sulphur and chlorine can easily diffuse throughout the coating. Resulting sulphide scale under the coating causes spalling of the coating. Sulfidation attack results in accelerated corrosion (wastage rate).

**Research limitations/implications:** Initial state of the coatings, and chemistry of combustion atmosphere have not been exactly known.

**Practical implications:** Generation of  $NO_x$  is limiting by firing fuel with lower amount of oxygen than required for complete combustion, i.e. under sub-stoichiometric conditions. Under these conditions carbon and sulfur present in coal are released as CO and  $H_2S$  gases. Additionally, unburned carbon particles arrive at water walls, which lead to high temperature oxidation, sulfidation and sometimes molten salt attack. Sulfidation mechanism results in accelerated corrosion rate, and additional costs due to unscheduled outages and replacement of water-wall tubes.

**Originality/value:** It has been found that the coatings do not protect heating surface of water-wall tubes from hot corrosion, including sulfidation under sub-stoichiometric burning. Durability of the coatings is from one to two years of exploitation of a boiler only.

**Keywords:** Corrosion; Low-emission boilers; Hot corrosion; Protection coatings

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## PROPERTIES

## 1. Introduction

For last 20 years legislation and law regulations [1-3] have forced to reduce emission of harmful substances from combustion in power plants equipment, including ashes and gases ( $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ), which substantially reducing environment pollution. Nitrogen oxides ( $\text{NO}_x$ ) are among the most toxic exhaust gases and contribute to acid rain, smog, destruction of the ozone layer of the Earth and the greenhouse effect (the last effect with  $\text{CO}_2$ ). Emission of volatile depends on the properties of the fuel burned and the combustion process parameters. Ashes and  $\text{SO}_2$  can be easily captured from flue gases by electro filters and desulfurization unit respectively. Emissions of nitrogen oxides ( $\text{NO}_x$ ) may be limited only in industrial conditions by modifying the combustion process, i.e. combustion atmosphere with low partial pressure of oxygen (sub-stoichiometric combustion).

Under such combustion conditions, fuel – in a reducing atmosphere – carbon and sulfur contained in the solid fuel (hard coal) are released in the form of gases:  $\text{CO}$  and  $\text{H}_2\text{S}$  [4, 5]. In the reducing atmosphere, resulting products of high-temperature corrosion on water-wall pipes made of low-alloy steel are not only iron oxides (hematite and magnetite) but also iron sulfides. Scale containing iron sulfides is brittle and easily fall off from the pipes surface, a phenomenon known as sulfur corrosion. The intensity of corrosion depends on the concentration of sulfur in the firing coal and combustion conditions. Lack of oxygen causes that the forming layer of iron oxides is thinner, and the presence of iron sulfide in the scale make it porous and more "permeable" for ions (increasing the rate of diffusion of iron ions by a layer of scale), which increases the corrosion rate. In addition, particles of unburned carbon and pyrite ( $\text{FeS}_2$ ) reaching a heated surface of boiler water walls, leading to severe hot corrosion attack (or, more broadly flame corrosion), and sulfur corrosion, resulting in accelerated wastage rate of water-walls. The rate of loss of pipe wall thickness (wastage rate) is about ten times higher in sub-stoichiometric combustion conditions (ranging from 0.8-1 mm per year), with respect to stoichiometric combustion conditions [6]. With high concentrations of sulfur in the coal, i.e. a high concentration of  $\text{H}_2\text{S}$  in the flame, the corrosion rate can be up to 2-5 mm per year [7]. Then rapidly increasing operating costs associated with dust boilers related to frequent and unplanned outages, and the replacement of water-walls, thereby increasing the cost of production of electricity and heat.

Another synergistic mechanism of degradation of pipe heated surfaces in boilers (evaporators, superheaters) is corrosion caused by molten salt effects. Combustion of fuel containing a high content of chlorine and sodium, potassium, vanadium can cause the rise of ash and salt deposits forming eutectics with the low melting point. If the surface temperature of the metal/pipe is above the eutectic temperature, form the dangerous conditions that cause melting of oxides protective layer or direct dissolution of the metal. This type of corrosion occurs in waste incinerator boilers, recovery boilers, boilers firing black liquor, or coal with biomass.

The purpose of this paper is to present methods of preventing hot corrosion (low-oxygen and sulfur corrosion), and assessment of durability of protective coatings used on water-walls in the power plants low- $\text{NO}_x$  emission boilers.

## 2. Methods of preventing hot corrosion in low emission boilers

Power industry uses a variety of surface modification technologies to prevent premature degradation of boiler tubes:

- cladding – bimetallic tubes with outer layer of corrosion-resistant steel,
- diffusion aluminizing (calorizing),
- nitriding,
- chromizing,
- boriding,
- pre-oxidation,
- pad welding,
- thermal spraying,
- deposition of multilayer hybrid coatings (inorganic matrix and organic) methods of painting.

Thermal spraying appears to be the most cost effective technology of coatings deposition on water-walls of the firing chamber [5]. Other advantages of thermal spraying include the possibility of application of materials with different chemical and phase composition (alloys, ceramics), the possibility of multi-layer, composite and gradient coating deposition, the possibility of spraying coatings on finished objects and the ability to carry out repairs. The following processes are used in thermal spraying coatings in power plant boilers [8-10]:

- cold powder flame spraying (subsonic),
- hot powder flame spraying (subsonic) a two-stage process with remelting of a coating (Spray and Fuse),
- HVOF – High Velocity Oxy Fuel (supersonic),
- HP-HVOF – High Pressure-High Velocity Oxy Fuel (supersonic at high pressure),
- wire arc spraying,
- APS – Air Pressure Plasma (plasma spraying at atmospheric pressure).

## 3. Coating materials

Coating materials used to protect the heated surface of boilers against hot corrosion and erosion are a very broad group ranging from corrosion-resistant and heat-resistant steels (ferritic and austenitic), by NiCrSiB and NiCr alloys, nickel superalloys (e.g. Inconel 625), intermetallic based alloys of binary FeAl system, and ceramic materials (e.g.  $\text{Al}_2\text{O}_3$ ). There are also used metal matrix composites reinforced with ceramic particles, such as NiCr alloy reinforced with  $\text{Cr}_3\text{C}_2$  and TiC particles [11]. With the ceramic coatings employed at cycle variable high temperature it is necessary to apply an intermediate layer between the metal tube and the ceramic layer, typically 50/50 NiCr alloy is used [5, 10].

## 4. Materials for research

Diagnostic tests were performed on pipes  $\varnothing 57 \times 5$  mm made of low-alloy steel grade 16Mo3 (16M by PN-75/H-84024), taken from the water-walls of the combustion chamber of OP-230 boiler working in a power plant. The pipes were covered by two types of coatings protecting against hot corrosion in sub-stoichiometric combustion conditions:

- thermally sprayed by plasma APS method ceramic coatings – the two layer coating with an outer layer made of  $Al_2O_3$  and an inner layer of NiCr alloy,
- hybrid coatings applied by painting technique – the HybridMD coating. The HybridMD type coating consisting of two layers. The inner layer with a thickness typically from 30 to 80  $\mu m$ , contains the inorganic phosphorus-based binder, and filler in the form of spherical aluminium powder. The outer layer with a thickness typically from 25 to 60  $\mu m$ , is a mixture of spherical and/or flake powders of aluminium and silicon, and a binder comprising a mixture of polysiloxane resins [8]. The polymer resin is a precursor, which by suitable heat treatment can be converted into a ceramic phase (called proceram) [12].

Application technology of hybrid protective coatings to surfaces consisting of the following steps [6]:

- cleaning the surface by abrasive blasting,
- applying the first layer by painting unit,
- annealing the first layer of coating at a temperature around 350°C,
- applying a second layer of coating by painting unit (the second layer annealing occurs during operation of pipes).

The rate of oxidation of a low alloy steel grade 16Mo3 coated with HybridMD is almost an order of magnitude lower than the uncoated steel. The coating is not completely sealed, which allows the access of oxygen to the substrate and formation of magnetite dense layer constituting the corrosion protection of steel. This coating adheres well to metal and is not peeling [6].

Aim of the diagnostic study was to evaluate stability of protective coatings after one and two years of operation in industrial conditions. Samples were taken from areas of direct impact of flame and exhaust (the level of the burners) and the air blower.

## 5. Methodology of research

To assess the degree of degradation of protective coatings and water-wall pipes the following tests were performed:

- chemical composition analysis, examination of microstructure and the degree of their degradation for the steel,
- macroscopic metallographic examinations of outer surfaces and cross-sections of the pipes,
- microscopic metallographic examinations of morphology of the pipes surface layers with the use of a scanning electron microscope (SEM) with EDS microanalysis spectrometer.

## 6. Description of achieved results

### 6.1. Water-wall pipes without a protection coating

Example of morphology of scale present on the surface of the water-wall pipes (without a protection coating) working in a low emission boiler is shown in Fig. 1. Thickness of the scale is larger in relation to the scaling occurring in classic combustion boilers, in this case is about 500  $\mu m$ . Scale consists of two layers – the interior and exterior. The inner layer is composed of iron oxides (magnetite and hematite) and iron sulfides, is compact but weakly bound to the substrate and brittle. On the border between the scale and the steel elevated concentration of chlorine is observed. The

outer layer is porous and outside the iron oxides contains large amounts of alkali metals (Na, K, Ca), and aluminium, silicon, magnesium, titanium and sulfur. In the case of co-firing biomass in the outer layer may be a large amount of lead in the form of pure lead precipitates.

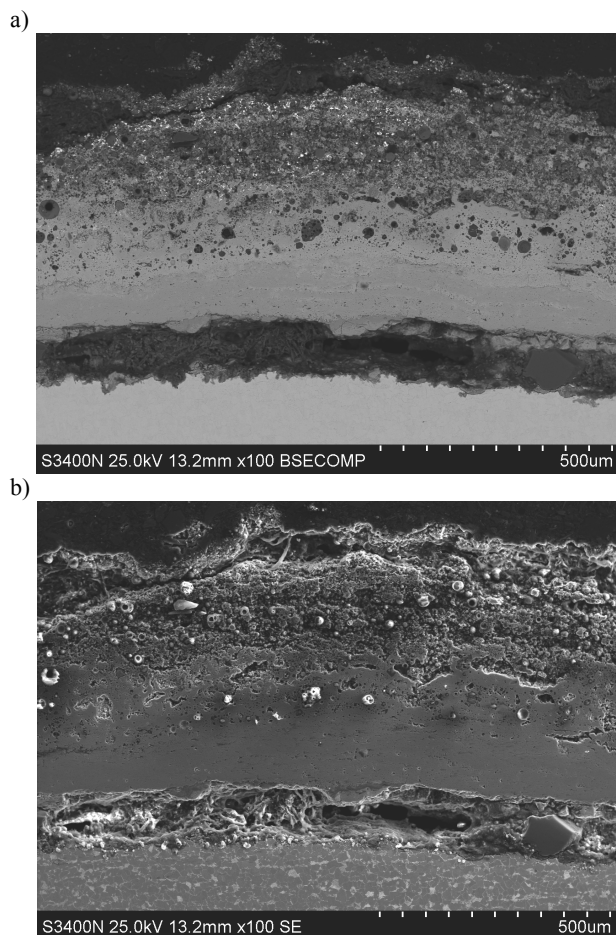


Fig. 1. Morphology of a scale on outer surface of a water-wall tube  $\varnothing 57 \times 5.0$  mm (without a protection coating). Longitudinal cross-section, SEM detector: a) BSE, b) SE

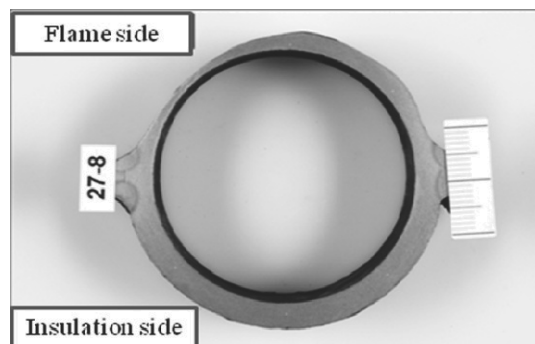


Fig. 2. Macrostructure of a cross-section of the water-wall tube  $\varnothing 57 \times 5.0$  mm (without a protection coating)

The described scale is the result of the synergistic effects of hot corrosion along with low-oxygen and sulfur corrosion, and does not protect against the destruction (wastage) of the pipe. The result is a rapid thinning of the pipe wall from the side of flame impact (Fig. 2). The final stage of a wall thinning is decohesion (open up) of a pipe, as a result of exceeding the allowable stresses.

## 6.2. Water-wall pipes with the ceramic protection coating

Morphology of the coating after one year of operation in the low- $\text{NO}_x$  emission boiler is shown in Fig. 3. On the outer surface of the tube there is a two-layer coating with a total thickness of approximately 650  $\mu\text{m}$ . The inner layer was applied with the Ni-30Cr alloy, has 250  $\mu\text{m}$  in thickness and a very good connection with the pipe base material. The outer layer was applied with aluminium oxide  $\text{Al}_2\text{O}_3$ , and has a thickness of about 400  $\mu\text{m}$ . The outer ceramic layer of the coating has only a slight degradation caused by a flame and exhaust gas at high temperature, but there was observed pores and cracks extending through the whole thickness of the ceramic layer [13].

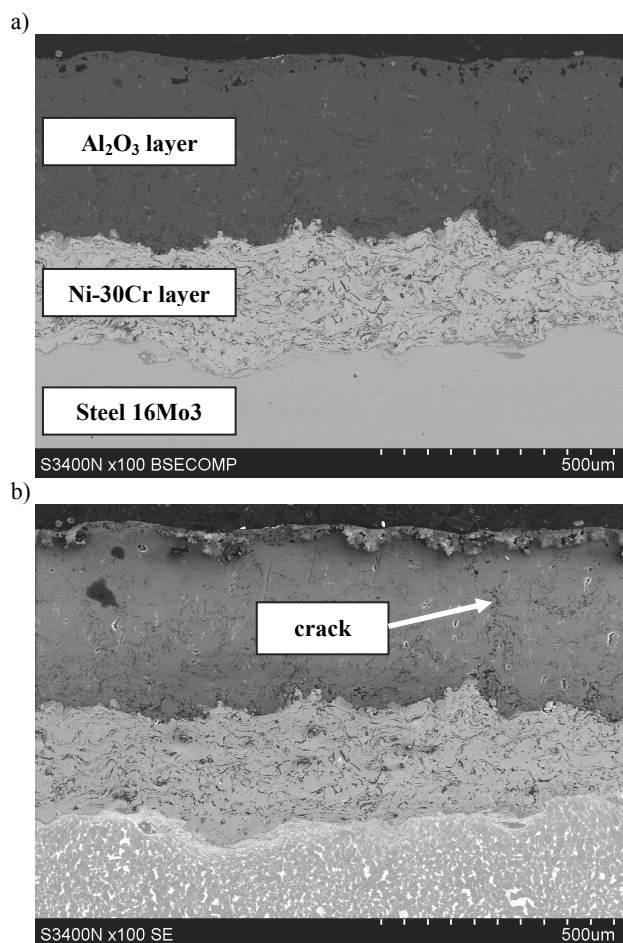


Fig. 3. Morphology of the ceramic protection coating on a surface of the water-wall tube  $\varnothing 57 \times 5.0$  mm, after one year of operation. Longitudinal cross-section, SEM detector: a) BSE, b) SE

Metallographic examination after two years of operation showed that the coating was almost completely degraded, and on the outer surface of the water-wall tubes, there are only remains of the sprayed ceramic coating (Fig. 4). On the outer surfaces of pipes characteristic scale for sub-stoichiometric combustion appeared. Elevated concentrations of aluminium in the scale may indicate that it was used a ceramic layer.

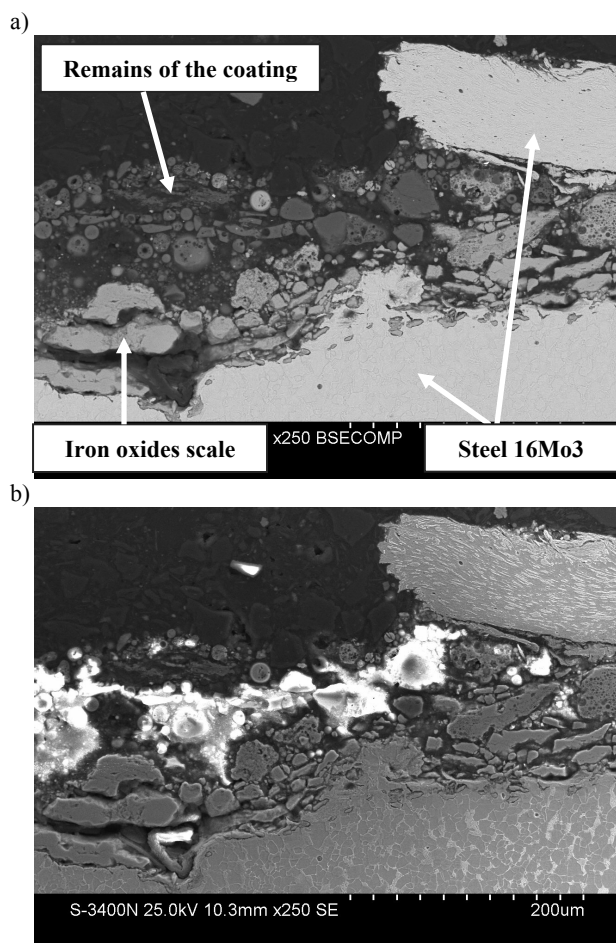


Fig. 4. Morphology of the ceramic protection coating on a surface of the water-wall tube  $\varnothing 57 \times 5.0$  mm, after two years of operation. Longitudinal cross-section, SEM detector: a) BSE, b) SE

## 6.3. Water-wall pipes with the hybrid coating applied by painting technique

After a one year of operation on the outer surface of the tube in the surface layer it was revealed the presence of the following layers (Fig. 5), starting from the pipe base metal to the surface:

- the iron oxides scale layer with a thickness of about 70  $\mu\text{m}$ , with iron sulfides (local concentration of sulfur in the scale reaches up to 22% by weight),

- porous, two-layer protective coating with a thickness of approximately 140  $\mu\text{m}$  – there was no damage to the coating in the form of voids, cracks and pitting corrosion,
- a layer of a scale and combustion products with thickness of approximately 20  $\mu\text{m}$ , which is composed of iron oxides and contains large amount of aluminium, silicon, sulfur, lead, and a small amount of phosphorus, potassium and calcium.

There was no corrosion damage to the applied coating after one year in service, but only slight thinning of the pipe wall from the heated side.

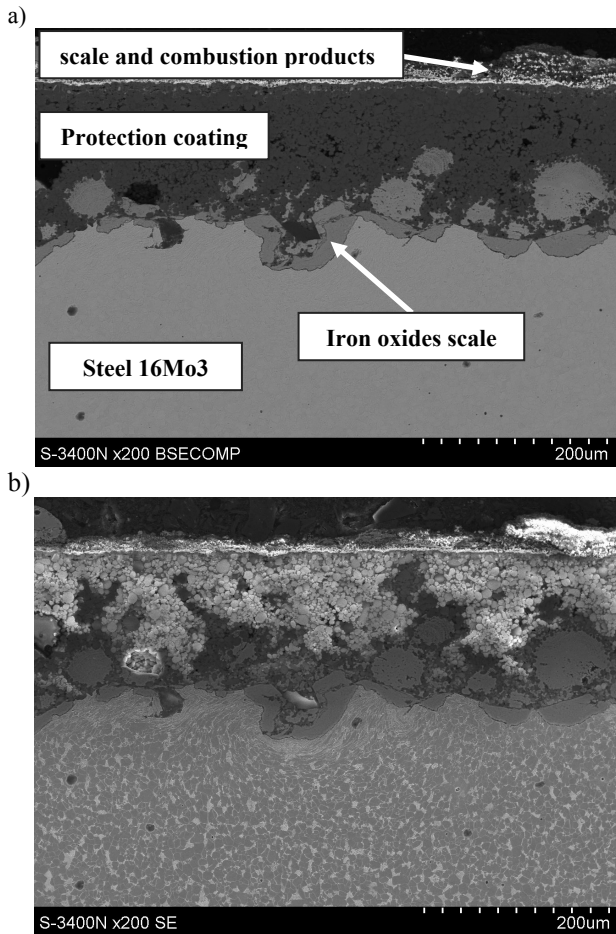


Fig. 5. Morphology of the painted protection coating on a surface of the water-wall tube  $\varnothing 57 \times 5.0$  mm, after one year of operation. Longitudinal cross-section, SEM detector: a) BSE, b) SE

Metallographic examination after two years of operation showed that on the outer surface of the pipe the protective coating was almost completely degraded and destroyed. There were only remains of the protective coating, and relatively thick (150-200  $\mu\text{m}$ ) layer of iron oxides and sulfides (Fig. 6). Increasing layer of iron oxides and sulfides slowly "surpassed" porous protective layer, thereby leading to its destruction.

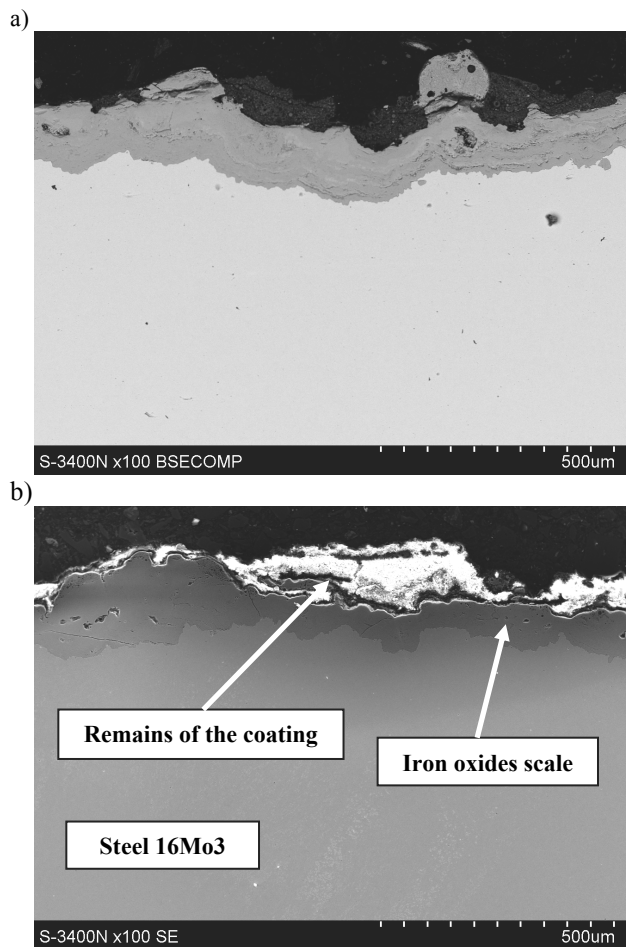


Fig. 6. Morphology of the painted protection coating on a surface of the water-wall tube  $\varnothing 57 \times 5.0$  mm, after two years of operation. Longitudinal cross-section, SEM detector: a) BSE, b) SE

## 7. Discussion of results

Double-layer thermally sprayed coating, with outer ceramic layer, fulfilled its protective role against flame, low oxygen and sulfur corrosion, by year of operation of the water-walls. However, investigations have shown that in  $\text{Al}_2\text{O}_3$  layer pores and cracks perpendicular to the tube surface are presented. The presence of pores is due to the thermal spray coating process and it is typical for this process. Cracks are due to cyclical changes in temperature and associated thermal stress, and the natural fragility of ceramic layers. It should be noted that thickness of ceramic layer is large (400  $\mu\text{m}$ ) which contribute to increase of coatings brittleness. Then, cracks and pores allowed a transport of oxygen, sulfur, and chlorine, through the coating to the base metal, and the formation of the oxide layer with iron sulfides beneath the coating. Increasing the coating layer of iron oxides and sulfides resulted in the gradual chipping of the coating, which after two

years of operation resulted in the almost complete destruction of the protective coating. The intermediate layer of Ni-30Cr alloy was completely destroyed probably by sulfur corrosion and intensive development of nickel and chromium sulfides. There was, however, no remnants of the intermediate layer, which indicates its low resistance to flame corrosion and exhaust in low-emission boilers.

Hybrid protective coating applied by painted technology has fulfilled its task by one year of operation in the combustion chamber. Evidence of the behaviour is a continuous coating of uniform thickness, and only a slight thinning of the pipe wall from the flame side. The formation of iron oxides scale on the outer surface of the coating shows that the coating was not fully dense (is permeable for ions), and the diffusion of iron atoms/ions throughout the coating was observed. As described in section 4, the hybrid painted coating is permeable, and is designed to only slow down the process of diffusion. At the same time the layer of iron oxides and sulfides was growing under the protection coating, as a result of incomplete dense of the coating and diffusion of oxygen and sulfur, which confirm an increase of the scale thickness from 70  $\mu\text{m}$  after one year of operation to 200  $\mu\text{m}$  after two years. The growing layers of iron oxides and sulfides above and below the protective coating resulted in "surpassing" the coating (trespassing of scale into the coating), which after two years of operation has led to the almost total destruction of the protective coating by spalling (peeling). Not be ruled out that the coating was also destroyed by erosion as a result of direct exposure to the burner (flame and exhaust) and the air flow from the blower.

## 8. Conclusions

The diagnostic research of following protection coatings: thermally sprayed  $\text{Al}_2\text{O}_3/\text{Ni-30Cr}$ , and hybrid applied by painting technique, operating for two years on water-walls in coal-fired low- $\text{NO}_x$  emission boilers allow to conclude that:

- the protection coatings do not shelter the surface of the heated pipes against hot corrosion (flame corrosion), including sulfur corrosion in a sub-stoichiometric combustion conditions,
- durability of coatings under direct flame and exhaust action, and the erosion effects of the blower, is only from one to two years of operation of the boiler,
- the additional cause of low durability of the coatings is a high concentration of sulfur and chlorine in a fired coal, and co-firing of biomass.

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