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## Oxidation behavior during prolonged service of boiler tubes made of 2.25Cr1Mo and 12Cr1Mo0.3V heat resistance steels

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### Abstract

During service of thermal power plant (TPP) units, different components are exposed to high temperature due to technological cycle of TPP unit. Service lifetimes of these components, especially boiler heating surfaces, may be limited due to creep, fatigue or oxidation, but materials designed for use at high temperatures have been developed primarily for their creep properties and microstructural stability during long term exposures at elevated temperatures. Having in mind that oxidation in steam environment on the inner surface of boiler tubes and in flue gas on the outer surface of boiler tubes could lead to a different consequences regarding service life of tubes, either directly through metal wastage or indirectly through raising local temperatures due to the lower thermal conductivity of the oxide scale, the oxidation behaviour of a different heat resistant steels become very important characteristics. In this paper are presented some data about the oxidation behavior of boiler tubes made of 2.25Cr1Mo and 12Cr1Mo0.3V steel after service of approximately 130.000 and 200.000h in two 620MW TPP units. Characterization of oxide scales on the inner side on tubes made of two steels with different chromium content, after two different prolonged periods of service, were compared and also their influence on the service life of tubes and kinetics of oxide scale growth were analyzed.

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## 1. Introduction

Damages of the boiler tubes present one of the primary causes of thermal power plant (TPP) forced outages in many utilities worldwide. This is due to a very complex interconnection of design and history of operation of the each particular boiler unit [Sijacki et al., 2008]. Structural integrity of boiler tubes presents the major goal in maintenance of modern TPP, with plant life extension as its economic goal [Sijacki et al., 2010]. Life extension of ageing plants is mainly related to the materials degradation of high temperature components. Materials degradation and ageing is of a particular importance in the steam generating systems of TPP, which are commonly made from ferritic steels alloyed with chromium, molybdenum and vanadium [Sijacki et al., 2008; Aghajani et al., 2009] which provides satisfactory high temperature mechanical properties, weldability, and oxidation resistance [Singh Raman et al., 2002; Liu et al., 2006]. Superheaters (SH), located in boilers of TPP are exposed to severe operating conditions which are usually accompanied by simultaneous activity of a multiple damage mechanisms of material which can considerably reduce their designed service life, Fig.1. The most important damage mechanisms are long-term creep and oxidation. Particularly endangered and exposed to the most severe operating conditions are the final SH that provide fresh steam of the highest parameters.

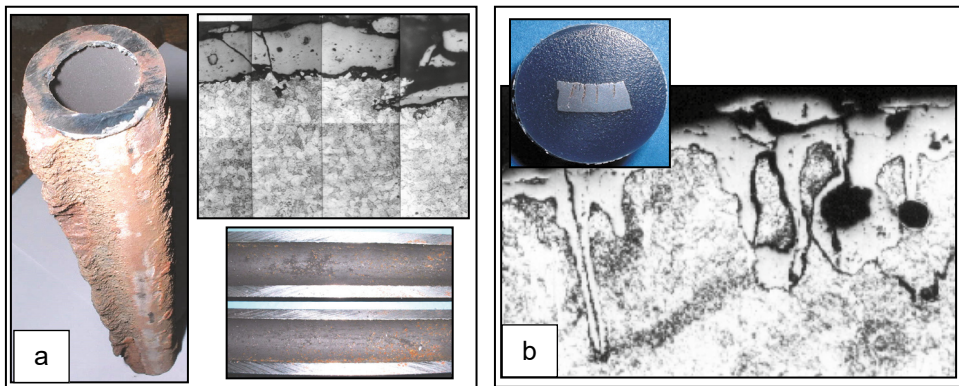


Fig. 1. Superheater damage: (a) Scales and microstructural degradation; (b) Thermal fatigue.

Having in mind that oxidation in steam environment on the inner surfaces of boiler tubes and in the flue gases on the outer surfaces of boiler tubes could lead to a different consequences regarding service life of tubes, either directly through metal wastage or indirectly through raising local temperatures due to the lower thermal conductivity of the oxide scale, the oxidation behaviour of a different heat resistant steels become very important characteristics.

During long-term service of SH, microstructural degradation and creep damage typically occurred simultaneously causing also a drop in the mechanical properties of material. These processes can lead to premature damage of SH tubes and forced outages of TPP. In order to avoid and prevent forced outages during plant service it is necessary to implement monitoring of boiler heating surfaces and to assess the degree of exhaustion of the material, particularly after approximately half of the design service life spent in exploitation. The most common methods that are used are sampling and different types of non destructive testing.

In a 620 MW lignite-fired TPP unit, the SH2 (the second of 4 SH) consists of 5 sections with a different tube dimensions made of combination of two steels: 1Cr0.5Mo and 2.25Cr1Mo steel (grade 15HM and 10H2M, Polish - PN). The final SH4 is also made of sections with different dimensions, but from one type of steel: 12Cr1Mo0.3V (X20CrMoV121, German - DIN), Table 1. The flue gases temperature in the zone of boiler furnace for SH2 is approximately  $t_{\text{gas}}=700^{\circ}\text{C}$  and for SH4 is  $t_{\text{gas}}=900^{\circ}\text{C}$ .

The number of boiler outages due to the damages of SH4 tubes was not large during service, and SH2 had only one outage during the service life of 200.000 hours. In order to monitor the condition of boiler tubing system of two identical TPP units (620MW), the practice of periodic testing of tube samples was introduced after 80.000 hours of service. In addition to obtained material data during regular annual overhauls of TPP, also obtained data about the damage mechanisms during failure analyses, which were carried out before the start of the systematic monitoring of material state, was used.

Table 1. The section tube dimensions and service parameters of the SH2 and final SH4

SH No. 2	Steel	Tube dimension (mm)	SH No. 4	Steel	Tube dimension (mm)
section 1 (inlet)	1Cr0.5Mo	Ø33.7x4	section 1 (inlet)	12Cr1Mo0.3V	Ø38x4
section 2	2.25Cr1Mo	Ø33.7x4	section 2	12Cr1Mo0.3V	Ø38x4.5
section 3	2.25Cr1Mo	Ø33.7x4.5	section 3	12Cr1Mo0.3V	Ø38x5
section 4	2.25Cr1Mo	Ø33.7x5	section 4 (outlet)	12Cr1Mo0.3V	Ø38x5.6
section 5 (outlet)	2.25Cr1Mo	Ø33.7x5.6			

In this paper some data are presented about oxidation behavior of boiler tubes sections made of 2.25Cr1Mo and 12Cr1Mo0.3V steel after service life of approximately 130.000 and 200.000 hours in two 620MW TPP units. Particularly exposed to the most severe operating conditions are final SH that provide fresh steam of the highest parameters, but oxidation process take place in all SH surfaces exposed to high enough temperature.

Characterization of oxide scales on the inner side on tubes made of two steels with different chromium content, after two different prolonged periods of service, were compared and also their influence on the service life of tubes and kinetics of an oxide scale growth were analyzed.

## 2. Experimental setup

Testing of 4 samples of SH tube was done, Table 2. Selected tube samples were cutted out from the middle section of SH4, as well as from the outlet section of SH2. Samples are comparable by service temperature. Samplings of the same sections were performed after 130.000 (samples 1 and 3) and 200.000 (samples 2 and 4) hours of service.

Table 2. SH samples characteristics

Sample	Section of sample	Service metal temperature <sup>a</sup> (°C)	Material	Tube dimension (mm)
1,2	SH2 section 4	~550	2.25Cr1Mo	Ø33.7x5.6
3,4	SH4 section 3	~550	12Cr1Mo0.3V	Ø38x5

<sup>a</sup>calculated by addition of  $\Delta t=35^{\circ}\text{C}$  on steam temperature

Several experimental techniques have been used in order to characterize microstructural and oxide scale of the samples joints after prolonged service. The following experimental techniques were used during experimental research: visual testing and dimensional measurement, hardness measurement, microstructural characterization by optical microscopy and scanning electron microscopy (SEM).

Visual testing and macrographic examination of outer and inner surfaces of SH tubes were done in order to detect deposits and oxide scales presence. Tube samples dimensional measurements: tube outer diameter, tube wall thickness, outer surface deposit thickness and weld reinforcement measurement were done using a mechanical external measuring gauge, Kroeplin D1R10.

The microstructural characterization by optical microscopy at different magnifications was carried out on specimens cut out from tube samples, using an optical microscope Carl Zeiss Axiovert 25 equipped with a Panasonic WV-CD50 digital camera. All specimens were polished and etched in 10 ml HNO<sub>3</sub> + 30 ml HCl and 5g FeCl<sub>2</sub> + 50 ml HCl + 100 ml H<sub>2</sub>O solutions. Inner surface oxide scale thickness measurement was also done by optical microscopy.

Specimens for SEM examination of the microstructure were prepared in the standard way, by cutting, grinding, polishing, etching and vapor deposition of gold. A metallographic examination was carried out on SEM unit, type JEOL JSM-6460LV at different magnifications.

The chemical composition (qualitative and quantitative XRD diffraction analysis) of SH boiler tube scale deposits - powders on the tube inner surfaces was performed using a Siemens D500 PC diffractometer, CuK $\alpha$  radiation ( $\lambda=1.54056 \text{ \AA}$ ), in the  $2\theta$  range 10-70° with a step of 0.02°. Identification of phases was carried out using DIFFRACTplus software package and joint committee on powder diffraction standards (JCPDS) database for XRD peak identification.

### 3. Results and discussion

High chromium steels generally have good oxidation resistance at moderately high temperatures due to formation of a protective chromium-rich oxide scale  $(\text{Cr,Fe})_2\text{O}_3$ . Effect of Cr content in steels exposed to the high temperature oxidation is well understood, but mechanisms of scale formation and its integrity are still very interesting for researchers, especially in the case of prolonged service life of metal in a real service condition. However, it was observed that the behavior of a chromium containing steel in experimental environment differ from the data obtained in real service life where metal is in contact with steam. These differences are not well understood [Singh Raman et al., 2002].

It is well known fact that heat resistance steels alloyed with Cr tend to form chromium rich oxide layer within the scale on metal surface that protects the material against further oxidation and this protective property depends on chromium content in steel. Oxide scales on internal surfaces of three heat resistant steels with different chromium content (2.25%, 9% and 12%) at the same metal service temperature ( $\sim 550^\circ\text{C}$ ) are shown in Fig. 2. Oxides of 2.25Cr and 9Cr steels have distinctive layer structure with a lot of defects and voids that indicate on a higher scales growth rate at service temperature in comparison with scale on steel with higher chromium content (12%) at the same temperature. Also, service life time and oxide appearance indicate that 12Cr steel have much more protective and stable scale at this temperature. This is especially important having in mind creep properties and the high temperature range of service for these three steels. Despite the higher creep properties of 9Cr steel it could not maintain oxide scales with sufficiently high protective properties. Scaling rate generally follows parabolic growth kinetic, controlled by diffusion through areas that provide less resistance to diffusion, such as grain boundaries and defects [Nieto Hierro et al., 2005].

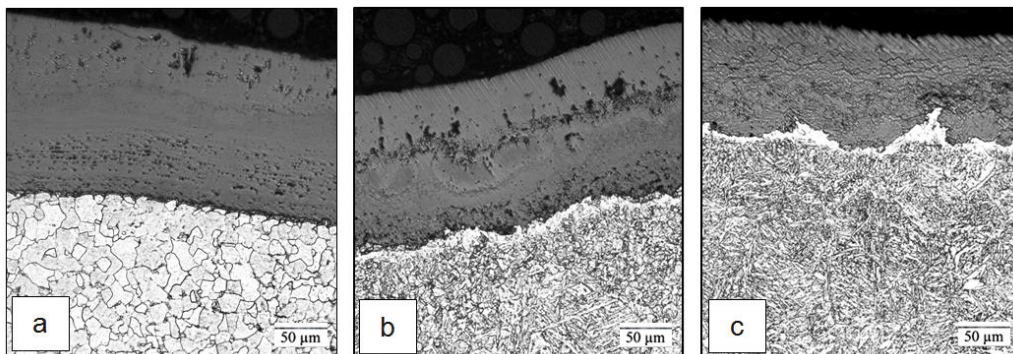


Fig. 2. Optical microscopy, steam side oxide scales: (a) 2.25Cr1Mo steel, 550°C, 60.000h; (b) 9Cr1MoVNb, 550°C, 60.000h; (c) 12Cr1Mo0.3V, 550°C, 240.000h

In investigated samples from SH2 and SH4 after 200.000 hours service (S2 and S4 samples, Table 2) oxide scales have different appearance, but the most significant difference is in composition of scales. Generally, low carbon and low alloy steels during service at elevated temperatures form an oxide scale consisting of several layers: wustite ( $\text{FeO}$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ). Each of these oxides is stable for a certain partial pressure of oxygen and temperature. However, in real service conditions magnetite and hematite have maximum stability. These oxides have a large number of structural defects.

The addition of chromium in steel promotes formation of low defect scale with a high  $\text{Cr}_2\text{O}_3$  content, which was observed in investigated samples, especially for 12Cr steel. XRD analyze, Fig.3, show that chromium content provide a larger amount of complex oxides in the scale containing  $(\text{Fe,Cr})_3\text{O}_4$ , while steel with lower Cr content has complex oxide  $\text{FeO}+\text{Cr}_2\text{O}_3$  and also significant amount of magnetite. All oxide layers also contained carbides which originate from steel matrix. During the long term oxidation process iron and other elements dissolved in a steel matrix are prone to oxidation, but carbides formed in microstructure, especially during aging (spheroidisation) are stable and most probable not active during oxidation process.

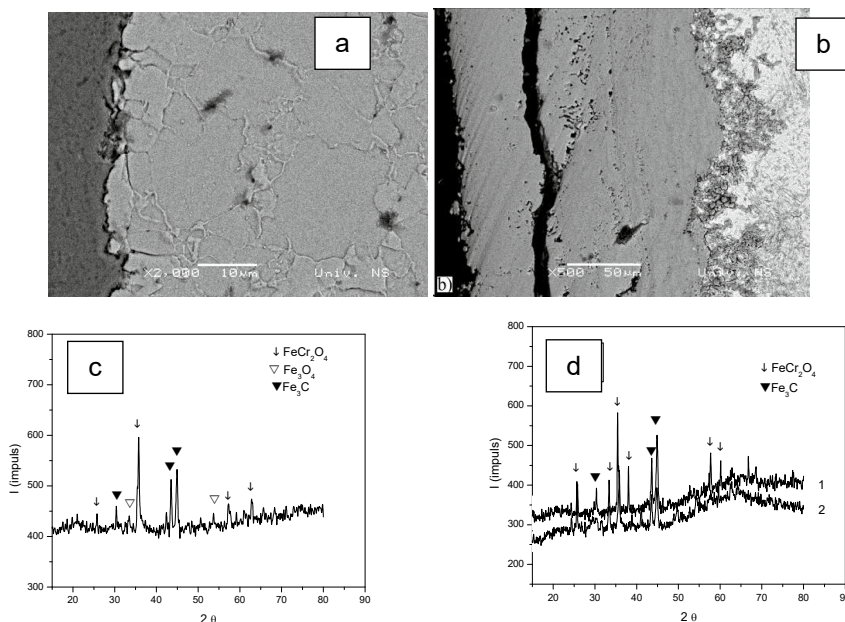


Fig. 3. Tubes inner side oxide scale after 200.000h of service at 550°C, SEM backscattering mode: (a) 2.25Cr1Mo steel; (b) 12Cr1Mo0.3V steel; (c, d) XRD analysis of 2.25Cr1Mo and 12Cr1Mo0.3V steels.

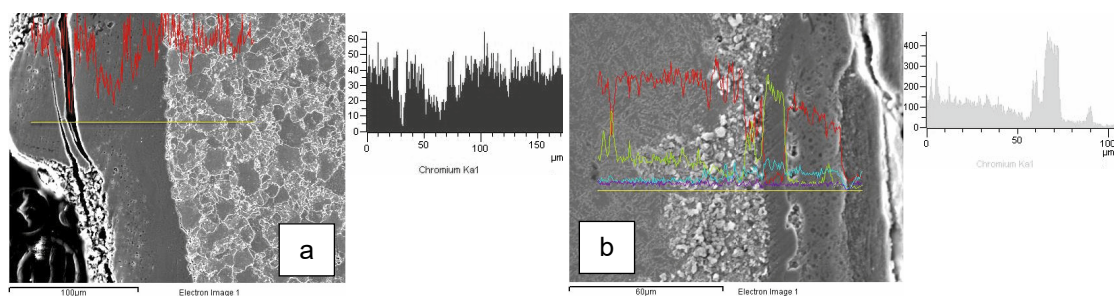


Fig. 4. Tubes inner side oxide scale after 200.000h of service at 550°C, EDS: (a) 2.25Cr1Mo steel; (b) 12Cr1Mo0.3V steel.

Oxide scales of 2,25Cr1Mo steel after 200.000h are well-adherent with metal matrix, Fig.4a. Low defect area of scale is in the vicinity of the metal surface, while external zone of scale contain higher defect density. At the same time EDS analysis indicate that porous layer has a lower chromium content, mainly consist of  $\text{Fe}_3\text{O}_4$ , which could explain higher defect density. Layer closer to metal is richer on Cr and therefore consists of  $(\text{Fe}, \text{Cr})_3\text{O}_4$  oxide ( $\text{FeO}+\text{Cr}_2\text{O}_3$ ).

Oxide scales of 12Cr steel after 200.000h of service are multilayered with a different Cr content across the thickness of the layer, Fig.4b. Closer to metal surface, oxide has the highest Cr content and the lowest defect density, that indicate formation of protective Cr-based oxide, while high defect density and lower Cr content indicate formation of  $(\text{Cr},\text{Fe})_3\text{O}_4$ . Under oxide scales internal oxidation is visible. Internal oxidation is consequence of oxygen diffusion trough the grain boundaries and Cr depletion of surface layers of metal and its diffusion in the oxide scales. This fact is confirmed by EDS analyses that show somewhat lower content of Cr in this zone, Fig.4b. The first stage of Cr depletion process in martensitic steel preceded the process of internal oxidation, hence lowering oxidation resistance of a steel. Internal oxidation in 2.25Cr steel was also detected, Fig.3a, but process of oxide forming is much faster and effects of an internal oxidation are relatively small (the size of a grain).

Process of internal oxidation was observed in specimens made of 12Cr1Mo0.3V steel after 130000h of service in the SH4 zone with the highest temperature ( $\sim 575^\circ\text{C}$ ), Fig.5c. In zones with lower service temperature, internal oxidation are not visible at all, Fig.5a, or slightly visible, Fig.5b.

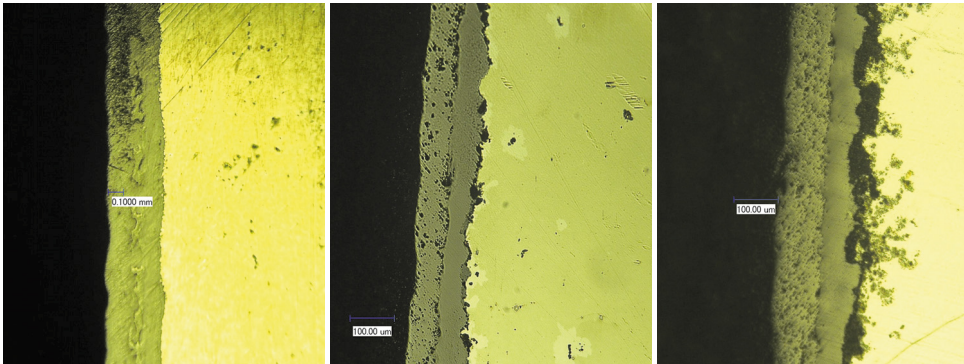


Fig. 5. 12Cr1Mo0.3V steel, tubes inner side oxide scale after 130.000h of service at: (a) 525°C; (b) 550°C; (c) 575°C.

Internal oxidation is a result of long-term service and contact of steam with a metal. This type of damage is characterized by the separation along the grain boundaries due to segregation of oxides, their expansion and further progress along the grain boundaries, as an energy most favorable path, Fig. 4b. Internal oxidation is general and not localized, while has approximately constant depth of  $\sim 120 \mu\text{m}$  after 200.000 hours of service, Fig. 4b. Intensity of internal oxidation process depends on service temperature and service time, but kinetic of this process is highly dependent on time and process of microstructural degradation. Protectiveness of oxide scale in the case of Cr alloyed heat resistant ferritic steels depends on a fraction of Cr content in solid solution which could form Cr based oxide. The rest of Cr content in steel is mainly present in a carbide phase and do not have effect on the formation of oxides. During aging of steel exposed to creep condition this fact become more relevant, because most of Cr dissolved in the solid solution tend to migrates to carbide phases.

Fundamental changes in the content of alloying elements in ferrite matrix and carbide phase during long-term service of heat resistant steel, demonstrate that dynamic processes taking place in the material which leads to a redistribution of alloying elements between the ferrite matrix and carbides and also between carbides [Bakic et al., 2013]. Redistribution of alloying elements in ferrite matrix is essentially characterized by the solid solution matrix impoverishment due to the coagulation, coalescence and growth of carbides inside grains or at the grain boundaries.

Changes in the microstructure of materials are directly related to development of carbide precipitation processes, changes in the type and morphology of the carbide phases, chemical composition of particular carbide phase and the redistribution of alloying elements between the solid solution and carbide phase. According to Pigrova et al., [1997], alloying elements are included in the carbide phase during the initial period of service, and then during prolonged service tend to redistributed among the different types of carbide striving to increase M/C ratio.

During aging process and chromium depletion from matrix and formation of Cr rich carbide phase leading to the formation of oxide scale with a lower chromium content and lower protection properties. Lower Cr content in oxide in return has more defects density and oxygen diffusion to metal surface is much more promoted. This process lead to formation of multilayer scale which consists of at least three distinct regions, as it is visible in Figs. 4b and 5c: compact outer layer with a high defect density, compact inner layer with a low defect density rich on Cr and a region consisting of extensive internal oxidation. Grain boundaries as regions that are most prone to chromium depletion process have the higher oxidation process rate and also pronounced formation of oxide precipitates, Fig. 4b. The similar finding was published for outer surface oxide on the same 12Cr steel type, which confirmed that lower Cr content in the grain boundaries region promote oxidation process at grain boundaries, and also that a less protective oxide scale permitted a greater concentration of oxygen available for reaction with the chromium in steel matrix [Singh Raman et al., 2002; Singh Raman et al., 1995].

Chromium content change is not monotonic and has peak value during long-time service, which could be explained by dissolution of smaller carbide and increase of chromium content in matrix from which chromium is transported by diffusion to the larger carbides [Bakic et al., 2013]. This is main factor that has influence on formation of oxide layers at tube surface during service time with different protective properties. Impoverishment of matrix with alloying elements due to the microstructural changes and oxidation processes promotes creep damage formation that is visible in that region, even at the inner surface of tube.

## Conclusions

Oxidation behavior of boiler tubes made of 2.25Cr1Mo and 12Cr1Mo0.3V steel after service of approximately 130.000 and 200.000 hours in two 620MW TPP units show that oxidation behaviour of heat resistant steel alloyed with chromium during prolonged service at high temperatures has some special features regarding: chromium content, service time and temperature. Based on the results presented in this paper it could be concluded that:

- In formed oxides during prolonged service of these steels the Cr content in oxide depends on Cr content in steel, as well as the level of microstructural degradation during service time which influence the defects density in oxides and protectiveness of the scales.
- The oxide scale that is formed is multilayered and the layer closer to the metal surface is much more chromium rich with a lower defect density than the outer layer. The thickness of inner layer depend on Cr content in a steel and is much thinner in the case of 2.25Cr steel than for 12Cr steel despite the fact that both oxides are of the same  $(\text{Fe, Cr})_3\text{O}_4$  type.
- Process of oxidation is followed by process of internal oxidation of steel as a consequence of oxygen diffusion through oxide layers, which rate depend on: defect density. Grain boundaries and Cr depletion zones due to the aging process of metal exposed to creep are preferable locations for a higher rate of internal oxidation process. This process is less intensive in 2.25Cr steel due to the higher rate of general oxidation.

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