1. Introduction

Life extension of industrial boiler’s components is subject of great interest and is directly related to the components that operate at elevated temperatures. Among the failure mechanisms that act in piping and boiler components operating under creep regimes, overheating due to the formation of the internal oxide layer has a large influence on the life of components. The presence of these films and deposits on the wall of the tubes increases the metal temperature, which accelerates the damage mechanisms, thereby reducing the material’s life\(^{[1]}\).

The oxide layer formed on the internal surface of low alloy steel tubes (up to 3% Cr) exposed to the steam generated in boilers consists of a layer with different levels. When the metal temperature is below 560°C and there is a high partial pressure of oxygen, a film consisting of magnetite (Fe\(_3\)O\(_4\)) and other of hematite (Fe\(_2\)O\(_3\)) is found. At higher temperatures, an additional layer of wustite (FeO) may appear. If the steel has more alloying elements, a spinel oxide (Fe, Cr, Mo)\(_3\)O\(_4\), can be generated, as the oxide layer grows in the direction of the tube wall. These oxides are formed according to the following reactions\(^{[2]}\):

\[
\begin{align*}
\text{Fe} + \frac{1}{2} \text{O}_2 & \rightarrow \text{FeO} \\
\text{Fe} + \frac{3}{2} \text{O}_2 & \rightarrow \text{Fe}_3\text{O}_4 \\
\text{Fe} + \text{Cr} + \frac{2}{3} \text{O}_2 & \rightarrow \text{Fe}_2\text{CrO}_4
\end{align*}
\]

Overheating due to the formation of the internal oxide layer has a large influence on the life of boiler components. The aim of this study consisted in assessing the effect of the internal oxide layer on the microstructural degradation in boiler tubes. Three samples of 2.25 Cr-1Mo superheater steel tubes were used. The methodology of the study compared the microstructures of the samples received by optical, scanning electron, and transmission electron microscopy. Tensile and hardness tests were performed. At the end of the tests it was proved the deleterious effect of the internal oxide layer on the life of the component. From the measurements of the internal oxide thickness, the remaining lives of the pipes operating under creep regime were estimated with a methodology established in the literature.

KEY WORDS: Oxide scale thickness; Microstructural degradation; Remaining life.

© 2012 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda.
• Fe(s) + ½ O₂(g) = FeO(s);
• 3 FeO(s) + ½ O₂(g) = Fe₃O₄(s);
• 2 Fe₃O₄(s) + ½ O₂(g) = 3 FeO₂(s).

In practice, magnetite is the oxide most present on the internal surface of boiler tubes that operate with conventional chemical cycles. The effects of the oxidation process in the mechanical behavior of a component may be[3]:
• Reduction in the cross section area of resistant material which is subjected to mechanical loading, which leads to an increase in stress;
• thermal insulation of the tube. The oxide layer has a considerable effect in the heat transfer of the tube, increasing its temperature and accelerating materials degradation;
• spalling of oxide scales. The spalling of thick oxide scales would be beneficial in terms of reducing the above-mentioned thermal insulation effect. However, the spalled oxide itself can lead to tube overheating if it becomes trapped in the system, thus reducing the flow rates inside the tubes.

The main goal of this paper is to evaluate, by means of a comparative study, the effect of the internal oxide layer in the microstructural degradation and in the reduction of mechanical strength of tubes used in superheaters of boilers. In this study, characterization and mechanical tests were performed in order to demonstrate the deleterious effect of the internal oxide layer in the life of the component. At the end of the tests, remaining life values were estimated from readings of oxide scale thicknesses that were made during the inspection of the component.

2. Materials and Methods

2.1 Study Material

Three tube samples of 10 CrMo910 steel, a 2.25 Cr-1Mo steel widely used in high temperature applications were sent. Samples were named as follows:
• Tube 1 - new material;
• tube 2 - tube removed after 191,000 hours of operation, presenting an internal oxide layer of approximately 130 μm;
• tube 3 - tube removed after 191,000 hours of operation, presenting an internal oxide layer of approximately 850 μm.

Tubes 2 and 3 were taken from a superheater of a boiler of a thermal power plant in Brazil. Fig. 1 shows a schematic drawing of the analyzed component. The tubes were removed from the region called 7X, identified in Fig. 1 by an arrow. The nominal conditions of operating pressure and temperature are 10.8 MPa (110 kgf/cm²) and 510°C, respectively. The nominal thickness and outer diameter of the tubes are 5.6 mm and 31.8 mm, respectively.

Table 1 presents the chemical compositions of the samples, which are in accordance with the 10 CrMo910 steel[4]. Only the chromium content of Tube 1 was lower than the standard specification.

Fig. 2 presents the received samples in which the test specimens were obtained. The tubes were grinded in the outside surface to remove the external oxide layer.

### Table 1  Chemical composition of the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>%C</th>
<th>%Si</th>
<th>%Mn</th>
<th>%Cr</th>
<th>%Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube 1</td>
<td>0.129</td>
<td>0.196</td>
<td>0.350</td>
<td>1.902</td>
<td>0.90</td>
</tr>
<tr>
<td>Tube 2</td>
<td>0.14</td>
<td>0.237</td>
<td>0.461</td>
<td>2.142</td>
<td>0.90</td>
</tr>
<tr>
<td>Tube 3</td>
<td>0.129</td>
<td>0.218</td>
<td>0.459</td>
<td>2.140</td>
<td>0.91</td>
</tr>
<tr>
<td>10 CrMo910</td>
<td>0.08 - 0.14</td>
<td>Max 0.50</td>
<td>0.30 - 0.70</td>
<td>2.00 - 2.50</td>
<td>0.90 - 1.10</td>
</tr>
</tbody>
</table>
2.2 Study Methodology

The methodology used to evaluate the microstructural degradation in boiler tubes due to the presence of the internal oxide layer was determined from the experience gained from previous studies of boiler tubes degraded in field and in laboratory\textsuperscript{[3]} (Fig. 3).

Microscopy techniques were used to compare the microstructures of the samples. Optical microscopy was performed for a preliminary evaluation and possible correlation with the Toft and Marsden criterion\textsuperscript{[4]}. Analysis of the interface between the microstructure and the oxide layer was performed by scanning electron microscopy. By means of extraction replicas of each of the samples, the precipitates were observed and identified by transmission electronic microscopy. The precipitates were identified by means of EDS results presented in the literature\textsuperscript{[5]}.

Room temperature tensile tests with flat specimens were obtained from the samples at a strain rate of $3.3 \times 10^{-4}\text{s}^{-1}$ on an EMIC DL 30,000 system (Fig. 4a). For the $600^\circ\text{C}$ tensile tests, a strain rate of $1.2 \times 10^{-4}\text{s}^{-1}$ was applied; the tests were performed on a Time Groups WDW-100 system. For these tests, round specimens were machined (Fig. 4b).

Vickers hardness tests were performed in four different regions of the cross section of each sample; a 0.5-mm space between indentations was adopted (Fig. 5). Tests were made in an Emcotest 750G3 durometer.

From the oxide scale thickness readings, the geometrical data, the operating conditions and time, the remaining life of the tubes operating under creep conditions was estimated. There is a well-established methodology for that in the literature\textsuperscript{[6]}.

The calculation method for estimating residual life based on measurements of the internal layer of magnetite can be divided into three modules\textsuperscript{[7]}. The modules and the input data for each are presented below:

Module 1 - Geometric data of the tube under investigation and loading conditions. The inputs in this module are:
- The internal and outer radii of the tube at time $t = 0$ (i.e., the nominal or design values informed before the operation of the equipment);
- the number of operating hours until the moment of the inspection;

---

**Fig. 3** Methodology applied to evaluate the microstructural degradation due to the effect of the internal oxide layer in boiler tubes.
Module 2 - Estimation of the oxide layer evolution on the internal wall of the tube and the effective metal temperature. The input data are:
- The average thickness of the oxide layer measured in the field;
- Growing model of the oxide layer: linear or quadratic. The quadratic model was adopted due to the fact that this one presented conservative results. The output data is the effective metal temperature at the time corresponding to the moment of the analysis.

Module 3 - Remaining life and total damage accumulation. In this module, the remaining life may be calculated from two methods. In the first one, the mechanical stress is calculated, afterwards, the intersection points between the curves of stress and creep strength of the material is obtained. Then it is possible to estimate the total time of operation. Subtraction of the operating time from the total time gives the remaining life of the component. The second method uses Robinson’s linear damage accumulation rule to calculate the creep damage obtained at the moment of the inspection. For both methods, the creep strength curves of the ASTM A387 Grade 22 steel were used. This steel is equivalent to the 10 CrMo910 steel. The literature recommends the use of the most conservative result[8].

The analysis was performed using readings of oxide scale thickness obtained by ultrasonic tests during a planned stop of the unit.

3. Results and Discussion

Fig. 6 presents the micrographs obtained from optical microscopy. In all the samples a microstructure composed by ferrite and pearlite was found. From the presented reads: 

- the minimum measured value of the outer radius of the tube during the inspection of the unit;
- the steam pressure.

The output data is the wear rate on the outer wall of the tube and the variation in external radius of the tube as a function of time.

Fig. 4 Specimens obtained for tensile tests: (a) room temperature and (b) high temperature, 600°C.

Fig. 5 Schematic drawing showing the regions where Vickers hardness tests were performed.

Fig. 6 Micrographs obtained by optical microscopy: (a) tube 1, no sign of degradation; (b) tube 2, few signs of degradation; and (c) tube 3, higher level of microstructural degradation.
sults, it is possible to see that Tube 1 is in stage A, which means that it does not present any signs of microstructural degradation by the Toft and Marsden criterion\(^6\). Tube 2 presents a microstructure in a C/D stage; as it was expected, due to the presence of a very thick internal oxide layer, tube 3 presented a higher level of degradation, in stage D/E.

The analysis of the microstructure/oxide layer interface carried out in tubes 2 and 3 indicated that the layer is formed at the expense of the tube walls (Fig. 7). It is possible to see a sublayer and the presence of voids in the tube walls, more clearly in tube 3 due to the detachment of the grains that were undergoing the oxidation process.

Fig. 8a presents a micrograph made by transmission electron microscopy in an extraction replica of tube 1. As expected, there were several regions composed by the \(M_3C\) precipitate, which confirms the presence of pearlite in the initial microstructure of the tube. Fig. 8b presents the EDS spectrum of the \(M_3C\) precipitate found in the sample. The spectrum is in accordance with previous results from the literature\(^7\).

Fig. 9a presents a micrograph made by transmission electron microscopy in an extraction replica of tube 2. The literature shows that boiler tubes exposed to long term operation conditions tend to present the coarsening of precipitates in the grain boundaries, as it was observed, also there is a loss in the pearlitic structure, this detail is shown in the left side of the micrograph\(^5,9\). However, the presence of \(M_2C\) precipitates in the ferritic grain of the

![Fig. 7](image_url) Micrographs obtained by scanning electron microscopy: (a) tube 2 presenting a sublayer; and (b) tube 3 presenting sublayer and voids due to the oxidation process.

![Fig. 8](image_url) Transmission electron microscopy analysis of the extraction replica of tube 1: (a) region rich in \(M_3C\) precipitates; and (b) EDS spectrum of the \(M_3C\) precipitate.

![Fig. 9](image_url) Transmission electron microscopy analysis of the extraction replica of tube 2: (a) region showing coarsening of precipitates in the grain boundary; and (b) EDS spectrum of the \(M_2C\)

precipitate.
material, right side of the micrograph, may indicate that it does not present an advanced degree of microstructural degradation. Fig. 9b presents the spectrum of the \( M_23C_6 \) precipitate, mostly found in the grain boundary of the micrograph. The spectrum is in accordance with previous results from the literature\(^7\).

Fig. 10a presents a micrograph made by transmission electron microscopy in an extraction replica of tube 3. The literature shows that boiler tubes exposed to long term effects of temperature and mechanical stress tend to show excessive coarsening of the precipitates in the grain boundaries\(^5\). In the specific case of tube 3, coarse \( M_6C \) precipitates were found. These precipitates are expected to be found for advanced stages of microstructural degradation\(^5,9\). Fig. 10b presents the spectrum of the \( M_6C \) precipitate, found in a higher amount in the grain boundaries of the sample. The spectrum is in accordance with previous results from the literature\(^7\).

As opposed to what was observed in tube 2, in all the samples of tube 3 there were no regions rich in \( M_3C \) precipitates to indicate the pearlitic region nor \( M_2C \) precipitates, which can offer some strength in the ferritic grains.

Considering that tubes 2 and 3 operate the same amount of time under the same design conditions, it is possible to say that the presence of a Magnetite layer with a significant thickness, which acts as a thermal insulator during operation, may have been responsible for the localized overheating of tube 3. Hence, the microstructural degradation was accelerated in this sample.

**Fig. 11a** presents the stress versus strain curves obtained at room temperature (25°C) and 600°C tensile tests. **Fig. 11b** presents the average hardness values through the wall of each of the samples. **Table 2** presents the average values of the mechanical properties of the analyzed samples.

The reason that tube 2 presented higher values for room temperature tensile properties and also higher hardness values than tube 1 may be associated to secondary hardening. This is related to the enhancement in the amount of precipitates, which is a consequence of long term high temperature exposure. However, the presence of coarsened precipitates in the grain boundaries contributed to reduce the strength of the material, when it was subjected to a tensile test at elevated temperatures and with a lower strain rate.

Tube 3 presented the lowest values of yield strength, tensile strength and hardness. The results confirm the deleterious effect of the presence of a very thick oxide layer in the mechanical properties of industrial boiler steel tubes.

For the remaining life assessment, the values of oxide scale thickness for tube 2 and tube 3 were 130 μm and
933 μm, respectively. Table 3 presents the main results obtained for each calculation method.

The oxide layer forms at the expense of the tube wall; consequently, an enhancement of the mechanical stress in the tube with the higher oxide thickness was already expected. The effective metal temperature calculated for tube 3 was 601.8°C, a value well above that specified for the safe operation of the material. This value can be securely related to the presence of a very thick oxide layer, which acts as a thermal insulator during operation of the boiler. Hence, the presence of such layer is directly responsible for the severe microstructural degradation and loss of mechanical properties of tube 3. For tube 2 the calculated metal temperature was in accordance with its nominal condition, indicating that a layer of 130 μm does not influence the heat exchange in the tube. It can be considered that tube 2 showed signs of microstructural degradation which were expected to the presence of a very thick oxide layer, which acts as a thermal insulator during operation of the boiler. Hence, the presence of such layer is directly responsible for the severe microstructural degradation and loss of mechanical properties of tube 3. For tube 2 the calculated metal temperature was in accordance with its nominal condition, indicating that a layer of 130 μm does not influence the heat exchange in the tube. It can be considered that tube 2 showed signs of microstructural degradation which were expected to the time and operating conditions for which it was designed.

The above results clearly show that the internal oxide layer can affect the remaining life of the material. It is possible to notice that the presence of a thick layer was able to reduce, approximately, by one order of magnitude the remaining life of tube 3, when it is compared with tube 2, for both methods of calculation. Following the recommendation of the literature to adopt the most conservative result, it is possible to assume that the remaining life of tubes 2 and 3 are 1.05 x 10^4 and 1.06 x 10^5 hours, respectively.

### 4. Conclusions

The proposed methodology had the main goal to evaluate the effect of the internal layer of magnetite in the microstructural degradation and in the loss of mechanical strength in tubes of industrial boilers.

Microstructural characterization tests clearly showed that tubes that present thick internal magnetite layers will suffer an accelerated microstructural degradation, due to the fact that the layer will act as a thermal insulator, causing a localized overheating of the tube. For 2.25 Cr-1Mo steels, the accelerated degradation was confirmed by the identification of coarse M₆C precipitates located at the grain boundaries of tube 3.

The reason that tube 2 presented higher values of room temperature tensile properties and also higher hardness values than tube 1 may be associated to the secondary hardening. This is related to the enhancement in the amount of precipitates, which is a consequence of long term high temperature exposure. However, the presence of coarsened precipitates in the grain boundaries contributed to reduce the strength of the material when it was subjected to a tensile test at elevated temperatures and with a lower strain rate. The same effect was observed more significantly in tube 3, which showed a higher level of microstructural degradation.

The results of the remaining creep life assessment show that a 130 μm internal layer does not contribute in a deleterious way for tube 2. In the case of tube 3, with an internal layer above 900 μm, the remaining life was reduced by one order of magnitude, when comparing tube 3 with tube 2. This implies that a thick internal layer may influence significantly the residual life of the tubes.

It can be assumed that the material presenting a significant layer of magnetite will be exposed to an operating condition into which it was not designed. This will mean a loss of mechanical strength more quickly than expected and may cause the failure of the tube before its expected life, leading to forced shutdowns, which represents costs to the maintenance of industrial boilers.

### References


---

**Table 3** Main results obtained by the calculation methodology for estimating the remaining creep life based on measurement of the internal oxide layer

<table>
<thead>
<tr>
<th>Tube</th>
<th>Oxide scale thickness (μm)</th>
<th>Mechanical stress (MPa)</th>
<th>Effective metal temperature (°C)</th>
<th>Remaining life Method 1 (h)</th>
<th>Remaining life Method 2 (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>130</td>
<td>28.2</td>
<td>509.8</td>
<td>2.04 x 10⁶</td>
<td>1.05 x 10⁶</td>
</tr>
<tr>
<td>3</td>
<td>993</td>
<td>31.6</td>
<td>601.8</td>
<td>2.57 x 10⁵</td>
<td>1.06 x 10⁵</td>
</tr>
</tbody>
</table>

---

*www.keytometals.com; **Creep Properties of Heat Resistant Steels and Superalloys.


