
Effect of Microstructural Variation of a Martensitic Stainless Steel on High Temperature Degradation Behavior

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Abstract: Martensitic stainless steels are chromium steels with a small addition of Ni. They have a good combination of mechanical properties and corrosion resistance, due to their Cr content [12]. The degradation processes are present in several industrial equipments and, generate repair or replacement actions in a periodic way. In an attempt to minimize these problems, several studies have been developed with this purpose. However, due to the several variables involved in the process, both in design and equipment operation, there is still a fertile field for an effective understanding of these degradation problems. For example, one can cite the effects that the different microstructures developed in martensitic stainless steels, materials commonly used in severe service conditions, present on the behavior of resistance to oxidation of the material. And, also, the environment in which the material is inserted. In a high-temperature environment, impurities are found, among them, compounds such as vanadium pentoxide, which act vigorously in the progression of the oxidation process. Oxidation tests are necessary to relate the behavior and influence exerted on the oxide layer by grain refinement. Thus, the present work aims to analyze the influence of the microstructure of the martensitic stainless steel AISI 420, with application of different treatments. The behavior of this steel was evaluated under different oxidation conditions, in contact with a solution containing Vanadium Pentoxide, and as a control parameter the mass variation of the samples. Analysis of the microstructures and the corrosion/oxidation products were carried out via Optical Microscopy, Scanning Electron Microscopy. As result it was verified the importance of the microstructure in the material's resistance to the action of degradation by oxidation, and its influence on the oxide layer formation process.

Keywords: Degradation, Martensitic Stainless Steel, Vanadium Pentoxide

1. Introduction

Approximately 20% of the world's steel production is destined to repair damage generated by the oxidation process. Many studies were developed in order to reduce expenses caused by this problem and there was progress related to the development of techniques used to combat oxidation action. However, this factor still causes concern to sectors that suffer losses, including financial losses, as a result of oxidation.

In view of the above, the present work aims to develop a study in order to gain an understanding of the influence of microstructure on the behavior of the material against the aggressive oxidation environment present in thermoelectric boiler tubes, that is, the influence of refinement of grain in the oxidation rate in these environments, also known as

fireside corrosion [1].

The different microstructures developed in martensitic stainless steels from heat treatments are factors that influence the resistance to oxidation of the material [7]. Tests are necessary to establish a relationship between the behavior and the influence exerted on the oxide layer [4] by grain refinement. Therefore, tests were carried out at high temperatures, as a way to simulate oxidative environments, such as those in boiler tubes in thermoelectric plants, through analyzes of the influence of the microstructure of martensitic stainless steel 420, with quench heat treatment and without treatment.

In general, grain size refinement results in increased oxidation resistance, but this increase in strength is dependent on the process used to obtain the refined structure.

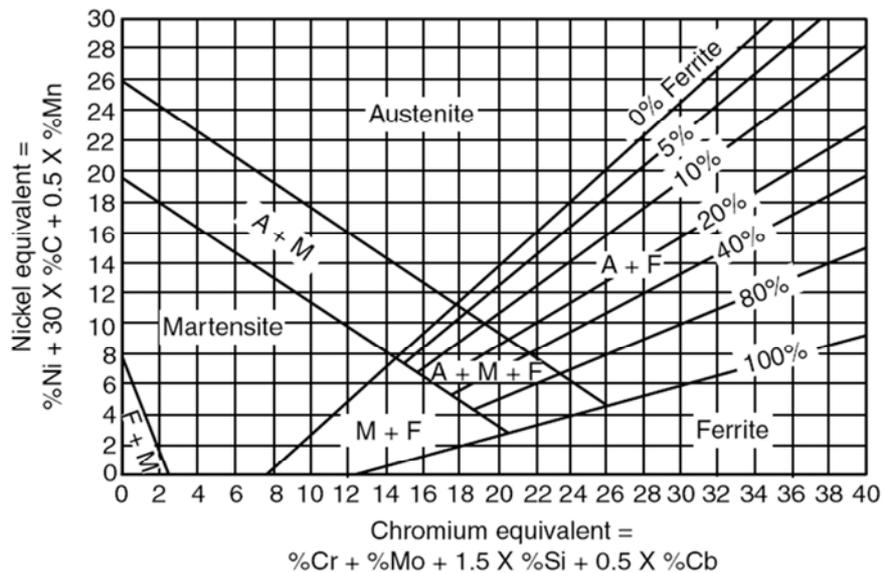
Because, the method used in the process affects characteristics such as chemical homogeneity, grain size distribution and grain size fraction volume [5].

In the tubes of boilers in thermoelectric plants, deposits are formed that can cause different types of oxidation [3]. These deposits are formed as a result of several reasons [8]. Depending on the chemistry of the fuel, salts can form through these deposits [10]. The elements present can form compounds such as sodium sulphate or potassium sulphate, chlorides and vanadium oxides. Oxidative salts are known for their attack on components, causing it to reduce its useful life, resulting in its premature failure [6].

2. Development

2.1. Martensitic Stainless Steel

Steel that has a high chromium content, producing high



Fonte: COLPAERT, 2008

Figure 1. Schaeffler diagram. Chemical composition regions of different families.

2.2. Vanadium Pentoxide

Components present in thermoelectric power plants, such as turbines, are subject to aggressive oxidizing environments. In these environments, the element Vanadium reacts with Oxygen in the combustion process to produce Vanadium Pentoxide (V_2O_5), which has a melting temperature of 674°C . These compounds act as oxygen carriers and dissolve in the oxide layer, as this occurs the defect mechanism increases, allowing for accelerated corrosive attacks. Vanadium oxide can react with other constituents, such as sodium, forming compounds with a low melting point. These compounds fuse, allowing the breakage of the protective oxide layer, exposing

hardenability and increased resistance to softening during tempering. Martensitic stainless steels are austenitized at relatively high temperatures, approximately $925 - 1070^\circ\text{C}$, causing the carbides to dissolve to obtain uniform austenite. Controlling the austenitic grain size is important to ensure tenacity [13].

Martensitic stainless steels are stainless steels with carbon contents less than 0.1%, chromium contents between 12 and 18% and nickel contents between 2 and 4%. Corrosion resistance is impaired as the C content increases, but is compensated for with an increase in the Cr content [15]. These steels at high temperatures present an austenitic microstructure, but in the subsequent rapid cooling (heat treatment called tempering) the austenite present is transformed into martensite, providing much higher hardness/mechanical resistance. They are widely used in the manufacture of cutlery items [14].

the metal to corrosion [6].

Vanadium pentoxide also acts by reducing the ash melting point, making the ashes adhere to the metal surface [11]. And, many metallic alloys, destined to be used in thermoelectric boilers, have their useful life reduced due to oxidation.

3. Materials and Methods

For the tests, samples of martensitic stainless steel 420 were used, whose composition, obtained through spectrometry (Spectromaxx), is shown in table 1. Samples were cut with dimension (40x40x3) mm.

Table 1. Chemical composition of the martensitic 420 stainless steel used (% by weight).

| %C | %Mn | %Si | %Cr | %Ni | %Mo | %P | %S | %Cu | %Fe |
|--------|--------|--------|---------|--------|--------|--------|--------|--------|---------|
| 0,3230 | 0,2880 | 0,4520 | 11,8300 | 0,2230 | 0,0198 | 0,0198 | 0,0100 | 0,0169 | 86,6000 |

A total of ten samples obtained were tempered at the austenitization temperature of martensitic steel, that is, at 1038°C, for a period of thirty minutes, with subsequent cooling in water with agitation. Another ten samples remained in the condition received.

The samples, both tempered and those of the state received, were embedded, sanded with sandpaper of different grain sizes, in the following order: #80, #120, #220, #320, #400, #600 and #1200. Then they were polished using a 3µm alumina suspension and later attacked with Vilella reagent (1g picric acid, 2.5 mL HCl and 50 mL EtOH) for an interval of 5 to 7 seconds. The microstructure obtained was analyzed using an optical microscope.

For the oxidation test, in order to simulate the aggressive environment of thermoelectric boilers, the samples were weighed and preheated at 250°C for 10 minutes, for better

adherence of the solution prepared with 50% Sodium Sulphate, 50% Vanadium pentoxide and distilled water that was applied to the samples at the rate of 5 mg/cm². After this period, the samples were involved in the solution, being weighed again. This procedure was performed in order to verify the mass variation that occurs during the sample oxidation process. Then, ten samples in the tempered state and ten samples in the received state were placed in the oven at 900°C [2], for a period of 50 hours, and every 5 hours a tempered and an annealed sample were removed from the oven, with air cooling. When removed, they were weighed to verify mass gain.

4. Results and Discussion

The result of mass gain over time is shown in Figure 2.

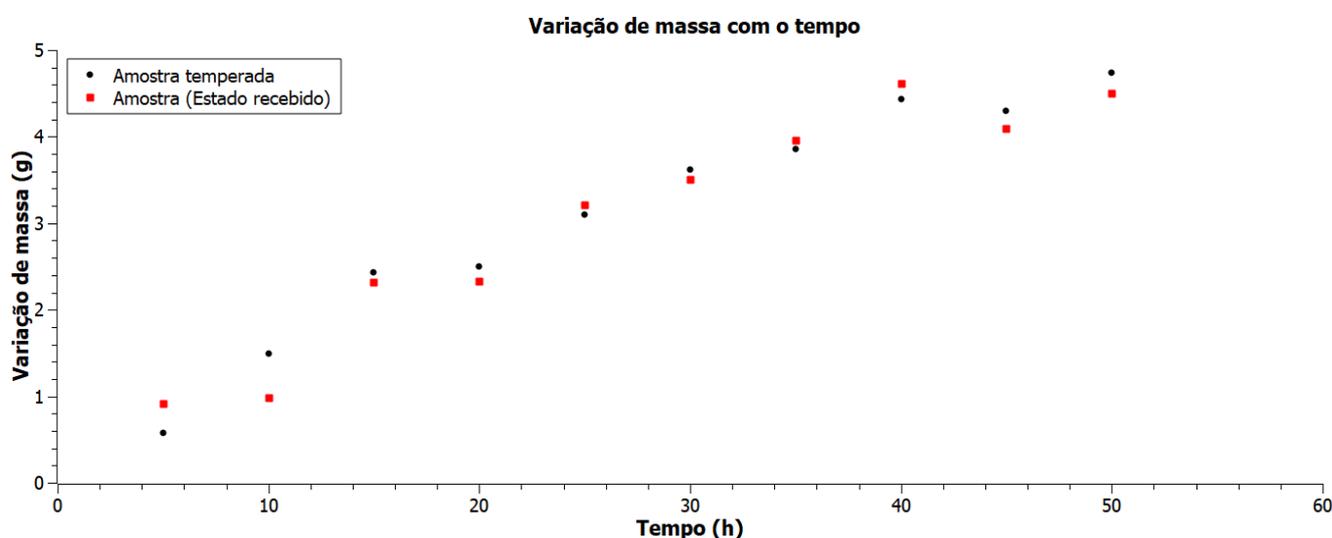


Figure 2. Mass variation with time after fireside corrosion test at 900°C in variable times.

In this graph, it is observed that although the variation between samples is different, there is a gradual increase in the mass variation in the samples, due to the increase in the oxide layer formed. Furthermore, even the samples presenting different microstructures, it can be verified that the process is controlled by the oxygen diffusion [9] through the formed layer. This is the main factor that determines the speed of formation of the oxide layer. As the thickness increases, the distance of diffusion through the oxide increases, which justifies the reduction of the oxide layer formation kinetics.

It is also observed that there is no great variation in mass gain between the two materials with different structures. The greater the gain in mass, the greater the tendency of the material to undergo oxidation, as the gain in mass is the result of an accumulation of an oxide layer deposited on the surface of the material.

It is known that the larger the contour area, the greater the amount of crystal defects, thus generating greater reactivity. The material was austenitized and later cooled abruptly, in the tempering process, forming martensite, with a refined

structure. While the samples in the received state remained with a coarser structure. Thus, the tempered samples remained more reactive after the oxidation test, when compared to the samples in the received state. It is notable that in the beginning the kinetics is fast, that is, when the oxide layer formed is not very thick. While this layer is still thin, oxygen reacts with the surface, as the layer becomes thicker, oxygen has to diffuse through the layer to react with the base metal. The thicker the oxide layer becomes, the more difficult it is for oxygen to diffuse through it, and this is noticeable in the graph shown above, that is, it is not the surface reactivity that determines the velocity, but the thickness of the oxide layer.

Through an optical microscope, it was possible to obtain images of the microstructure after 50 hours at 900°C.

In the figures 3 and 4 below, it is observed that the microstructure of the samples after 50 hours in the oven, shows a refined structure, with the presence of Martensite, Ferrite and carbides. However, the received state sample has a higher amount of carbides that, in some parts, form an alignment, being a weakening point for the oxidation process.

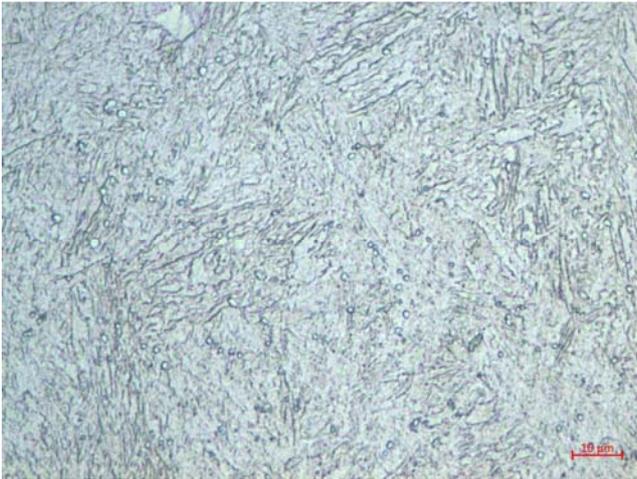


Figure 3. Sample microstructure (received state) after 50 hours in the oven.

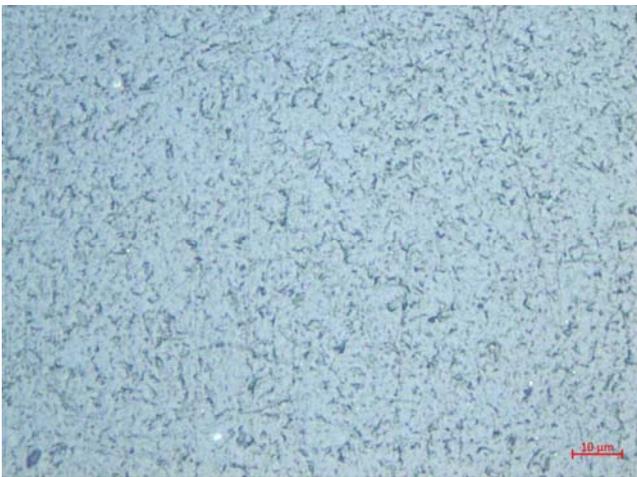


Figure 4. Microstructure of the sample (tempered) after 50 hours in the oven.

Grain size variation was performed so that the austenitic grain size showed variations and different reactivity during oxide formation. The analysis using the Scanning Electron Microscope indicates that the Vanadium has undergone a liquefaction process, diffusing through the material, keeping the traces of the structure. And, it acts on an intergranular corrosion process model. Microstructural variations in the material at a temperature of 900°C over 20 hours do not cause substantial effects.

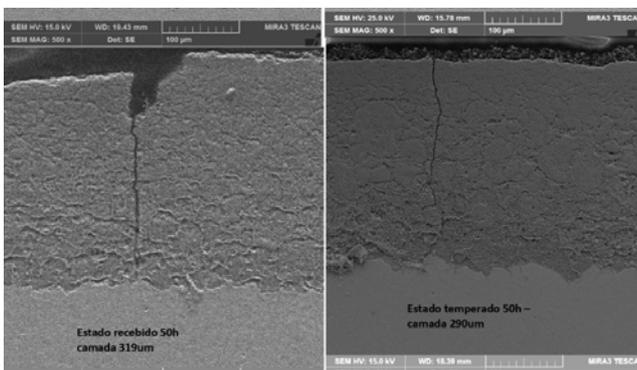


Figure 5. Analysis of the oxide layer in SEM.

5. Conclusion

The preliminary results point to the importance of the microstructure in the material's resistance to the action of degradation by oxidation, and its influence on the oxide layer formation process, especially regarding its stability and adhesion to the surface of AISI 420 steel.

As much as there are variations in surface reactivity, which can interfere in the initial process, the fact is that for long periods, what determines the oxidation behavior is the oxygen diffusion coefficient towards the base metal.

It is recommended, as a suggestion for future works, the analysis of the influence of the thickness of the oxide layer on the corrosive process.

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