OXIDATION OF AN AUSTENITIC STAINLESS STEEL PIPE CONTAMINATED BY PETROLEUM PRODUCTS

Ion PALAMARCIUC, Dan-Gelu GALUȘCĂ, Maricel AGOP, Dragoș ACHIȚEI, Cătălina MANOLIU NUȚESCU DUDUMAN

“Gheorghe Asachi” Technical University of Iasi, 700050, Romania, palamion@gmail.com

Abstract
The experimental researches of this paper were carried out in order to investigate the characteristics of the oxide layers obtained on the internal and external surfaces of an austenitic stainless steel pipe. The external surface did not present any corrosion results but the internal surface of the analysed pipe was contaminated by sulphur during the transportation of petroleum products. In spite of this fact it was found that the mechanical properties of such a surface can be improved by air oxidation. The surfaces were investigated by Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) analysis. Also the microindentation hardness was measured, on the both surfaces and between them, in order to detect and verify the improvement of the mechanical properties. Therefore it was found that oxidation at lower temperatures (300°C) resulted in formation of harder coatings. For comparison and better interpretation this paper presents the results of the analysis and measurements performed before and after the oxidation and cleaning, demonstrating the effectiveness of this simple method of reconditioning.

Keywords:
austenitic stainless steel, corrosion in petroleum products, oxide layer, surface hardening.

1. INTRODUCTION
The impact of corrosion on the industrial sectors, the public and daily life is very significant. Corrosion and materials reliability affect industrial complexes, public infrastructures, personnel safety and health, along with severe damages to the environment and sustainable development. The deleterious effects of corrosion are often described in economic terms as materials degradation/replacement costs and as financial losses [1].

It is known that austenitic stainless steels possess high corrosion resistance. They have virtually no inclination to corrosion cracking and offer good resistance to corrosion. But nonmetallic inclusions, both sulfides and oxysulfides, are preferential centers of pit formation in stainless steels [2].

Most kerosene fuels contain relatively large amounts of sulphur and sulphur products. The presence of free sulphur and hydrogen sulfide are key factors in causing fuel to be corrosive [3].

Sulphur and its compounds react strongly with nickel forming nickel sulphide with which nickel forms eutectic series of alloys. The penetration of sulphur in nickel steels is therefore pronounced due to the influence of nickel in increasing the solubility of sulphur in steel. Nickel offers, therefore, very little resistance to sulphur atmospheres and failure chiefly takes place through intercristalline embrittlement. Even contamination of nickel with sulphur results in intense pitting [4].

The technological processes of increasing the quality and operating characteristics of the protective layers imply high costs of raw materials, expensive and sophisticated (from constructive point of view) equipment, residual wastes and high energy expenses. Therefore it would be more rational to obtain protective layers by thermal air
oxidation that results in formation of oxide layers with low porosity and high antifriction properties. This method does not require additional materials, high-qualified staff or special parameters of the room or environment [5].

The aim of the paper is to detect the effects of corrosion, obtain oxide layers and compare the results obtained before and after oxidation, in order to demonstrate their importance by comparing the characteristics of the internal contaminated surface of the pipe with the external not contaminated surface.

2. INVESTIGATION OF THE SAMPLES BEFORE OXIDATION

The specimens used in the experimental analysis were taken from a fuel pipe that has been used in the fuel system of an aircraft turbofan engine for jet fuel transportation. The analysed pipe is made from J92603 austenitic stainless steel with the chemical composition presented in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Min.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.20</td>
<td>0.40</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>2.00</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>2.00</td>
</tr>
<tr>
<td>Ni</td>
<td>8.00</td>
<td>12.00</td>
</tr>
<tr>
<td>Cr</td>
<td>18.00</td>
<td>23.00</td>
</tr>
<tr>
<td>Mo</td>
<td>-</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 1 Chemical composition (%) of the J92603 austenitic stainless steel.

<table>
<thead>
<tr>
<th>Element</th>
<th>Internal</th>
<th>External</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>00.39</td>
<td>00.20</td>
</tr>
<tr>
<td>Ti</td>
<td>01.06</td>
<td>00.93</td>
</tr>
<tr>
<td>Cr</td>
<td>18.28</td>
<td>17.76</td>
</tr>
<tr>
<td>Fe</td>
<td>70.08</td>
<td>70.32</td>
</tr>
<tr>
<td>Ni</td>
<td>10.21</td>
<td>10.80</td>
</tr>
</tbody>
</table>

Table 2 Chemical composition (%) on the internal and external wall surface.

The main elements' chemical composition differences between the internal and the external wall were determined by EDX and shown in table 2 and figure 1.

Table 2 shows one of the effects of contamination with sulphur from the petroleum products' transportation – almost doubled the content of sulphur on the internal wall.

![Fig. 1 The EDX spectrum of the internal (left) and external wall (right).](image)
Transportation of jet fuel also resulted in the deposition of sulphur compounds, which have a specific dark color (Fig. 2).

The microindentation hardness tests (Fig. 3) showed that on the internal wall surface of the pipe the hardness was 231 daN/mm², on the external 253 daN/mm² and between the walls (in cross section) – 291 daN/mm².

3. EXPERIMENT AND RESULTS

For obtaining an oxide layer with better properties the specimens were cleaned by sandblasting, with foundry sand and air at the pressure of 100 bars. Before and after this they have been cleaned for 15 min in the ultrasonic cleaner at the frequency of f=46 kHz for removing the impurities that could worsen the adhesion of the layer.

The oxide layer was obtained by maintaining each specimen at 300, 400 and 600°C during 1 hour in a tube furnace and in continuous air flow.

Microindentation hardness measurements performed on the oxide layers of the J92603 austenitic stainless steel showed that higher temperature regimes reduce the hardness of the layers. Thus at 300°C the hardness of the layer was 504 daN/mm², at 400°C it reduced to 408 daN/mm² and at 600°C only 312 daN/mm². The main elements’ chemical composition differences between the internal and the external wall after oxidation were determined by EDX and shown in Table 3, Fig. 4 and Fig. 5.

| Table 3 Chemical composition (%) on the internal and external walls after oxidation. |
|---------------------------------------------|---|---|
| **Oxidation** | **At 300°C** | **At 400°C** |
|               | Internal | External | Internal | External |
| S              | 0.32     | 0.16     | 0.26     | 0.19     |
| Ti             | 0.83     | 0.79     | 0.85     | 0.89     |
| Cr             | 16.51    | 17.31    | 16.95    | 17.18    |
| Fe             | 60.88    | 61.16    | 62.91    | 62.12    |
| Ni             | 8.65     | 8.37     | 8.69     | 8.81     |
Fig. 4 and Fig. 5 show the results of the X-ray analysis and the differences between chemical compositions at different temperatures.

**Fig. 4** EDX spectrum of the internal (left) and external wall (right) after oxidation at 300°C.

**Fig. 5** EDX spectrum of the internal (left) and external wall (right) after oxidation at 400°C.

The X-ray diffraction analysis after oxidation showed that the layers, obtained on the J92603 steel by thermal oxidation, have mainly a four phase structure including intermetallic FeNi, Fe oxides TiO₂, Fe₂O₃ (Fig. 6). Cr and Ni oxides were present in small quantities, possibly it is related to their thermal stability, also to the difficulty of identification of some diffractive lines that have weak intensity.
Fig. 6 XRD pattern of the oxidized samples at 300°C (left) and 400°C (right) with the following phases: 1-Fe, 2-Fe$_2$O$_3$, 3-FeNi, 4-Ti$_2$O$_3$.

After the oxidation the layers appeared as in Fig. 7, where can be seen a slight difference in color.

Fig. 7 SEM micrograph of the oxide layers on the internal (left) and external (right) surface.

4. CONCLUSIONS

By experimental investigations of the physical, chemical and mechanical properties of the oxide layers, obtained on J92603 austenitic stainless steel by thermal oxidation, we demonstrated the principled technological possibility of obtaining hardening thermal oxide layers on corroded pipes’ surface.

We developed a method of obtaining hardened thermal oxide layers that can be used as wearproof surfaces and as corrosion resistant. It does not require additional materials, high-qualified staff or special parameters of the room; is not harmful for the environment; and the most important – it can be applied even for corroded surfaces.

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LITERATURE


