Identification of scale formed on Cr-Ni cast steel

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Received 02.07.2010; accepted in revised form 09.07.2010

Abstract

An attempt has been made to identify the scale formed on austenitic chromium-nickel cast steel with additions of Ti and Zr during oxidising at temperatures of 820 and 1000 °C. The scale identification was done by the technique of scanning microscopy, by X-ray diffraction phase analysis in Bragg-Brentano geometry with constant angle of incidence, and by scratch test.

Keywords: Fe-Cr-Ni alloys, Titanium, Zirconium, High temperature corrosion, Morphology of scale

1. Introduction

Austenitic chromium-nickel cast steels for pipes systems operating in the installations for catalytic steam conversion of methane are exposed to long-term (up to 10-12 years) effect of high temperatures (around 1050 °C) and aggressive environments of air, steam, and carbon and sulphur compounds [1÷3]. To improve the corrosion resistance of the above mentioned alloys, their compositions are enriched with metals, which belong to the group of high-melting metals like Ti, Zr, V and Nb. These elements form oxides and sulphides, characterised by greater thermodynamic stability than the oxides and sulphides of chromium, of which most of the scales formed on ferrous alloys are composed [4÷6].

Alloys used in these investigations were enriched with titanium and zirconium. Titanium belongs to the group of elements characterised by strong affinity to oxygen, forming oxides of very high stability. Titanium oxides are formed under the scale composed of Cr₂O₃, but owing to a strong diffusion of titanium through the scale, the surface of this scale soon becomes coated with oxides rich in titanium. The thickness of the scale is increasing in function of time. Adding small amounts of titanium (~ 0,1%) to alloys with high content of Cr and Ni (above 20% of each of these elements) reduces the oxidation rate [7, 8].

The role of zirconium is mainly that of driving changes in the morphology of the formed scale. Compared to the scale formed on zirconium-free alloys, the layer of the products of oxidation is characterised by smaller thickness, and on the surface there are lamellar precipitates formed as a result of the oxidation of zirconium-containing phases, exposed to a direct effect of the oxidising environment. Moreover, in zirconium-free alloys, the presence of numerous and large pores has been observed at the scale/metal phase boundary. In alloys modified with zirconium these pores are of a smaller size. The scale formed on zirconium-containing materials is characterised by better adhesion, resulting from better contact between the scale and metallic substrate (smaller number of pores) [6].

2. Methods investigation

The test material were centrifugally cast laboratory pipes made from austenitic chromium-nickel steel modified with Ti+Zr.
The chemical compositions of the tested materials are compared in Table 1.

### Table 1.
#### Chemical composition of the examined cast steel [wt%]

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical composition [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>TZ</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The investigations of the oxidation rate were carried out on a LABSYS apparatus made by SETARAM in the atmosphere of laboratory air under the atmospheric pressure and at temperatures of 820 and 1000 °C.

To identify the scale, the following tests were carried out on the examined material:
- microscopic examinations on JOEL 5500 LV scanning microscope equipped with EDS system for X-ray microanalysis made by IXRF,
- phase analysis by X-ray diffraction technique in Bragg-Brentano geometry at a constant angle of incidence, performed on D 500 Siemens diffractometer,
- testing the scale adhesion to substrate by scratch test using Nano-Scratch Tester made by CSM Instruments.

### 3. Results and discussion

The kinetic tests have proved that the run of the oxidation curves of the tested material can be in approximation described with a parabolic law.

Figure 1 shows the results of observations of the sample surface oxidised at a temperature of 820 °C, while Figure 2 shows the same results obtained for the temperature of 1000 °C.

#### Table 2.
#### Chemical composition of the examined cast steel [wt%]

<table>
<thead>
<tr>
<th>Area</th>
<th>Chemical composition [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>1</td>
<td>28.0±1.4</td>
</tr>
<tr>
<td>2</td>
<td>38.7±1.1</td>
</tr>
<tr>
<td>3</td>
<td>40.5±1.2</td>
</tr>
</tbody>
</table>

The surface of the scale formed at 820°C during oxidation in air was compact, adhering strongly to the substrate and coated with crystalline forms of a relatively uniform distribution. The conducted phase analysis revealed in these forms the presence of elements such as Cr, Nb and O (Fig. 1 - spectra 1, 3). Moreover, in some of these precipitates also the presence of Mn was traced. The analysis of the areas free from the precipitates showed that, like crystalline forms, they were also rich in Cr and O (Fig. 1 - spectrum 2). No niobium was traced in the examined areas, instead small amounts of Fe occurred.

The increase of oxidising temperature to 1000 °C contributes to severe degradation of the formed scale (Fig. 2).

On the surface of the samples taken from the examined material, the following characteristic areas can be distinguished:
- areas with damaged scale (marked in Fig. 2) – enriched with matrix elements– Mn, Si, Cr, O,
- areas with residual scale – enriched with Cr, Mn and O,
- areas without the scale– enriched with matrix elements– Ni, Si, Cr, Fe and O.

In the area free from the scale, numerous porosities were observed in the metallic core after the scale detachment from the substrate. Most probably they occurred as a result of carbide precipitates chipping in areas corresponding to alloy grain boundaries. Attention deserves the fact that not all of the carbide precipitates were detached. In areas of the ternary boundaries, the residual forms of the precipitates were observed with discontinuities in core material present between them (Fig. 3c). The EDS analysis revealed in these precipitates large amounts of elements like Nb, Si and Ni as well as Fe and Cr, originating most probably from the alloy matrix.

Figure 4 shows the diffraction patterns of scales formed on the samples of cast steel oxidised in the atmosphere of air at a temperature of 820 °C.

Comparing the results of examinations of the effective X-ray penetration depth with the true thickness of the scale (mean thickness amounts to about 4 μm) formed on materials oxidised at a temperature of 820°C, it can be stated that the effective X-ray penetration to a depth of 1.5 μm gives us information on areas lying at the external surface of the scale, while the depth of about 5 μm enables obtaining the results from the sample areas lying in a metallic core directly under the layer of oxidation products (Table 2).
The morphology of the scale surface is shown in Fig. 2.

Fig. 3. The morphology of the scale surface is shown in Fig. 2.

Fig. 4. Diffraction patterns of scale formed on the examined cast steel oxidised at a temperature of 820 °C; patterns obtained in Bragg-Brentano (B-B) geometry with constant angle of incidence (angles of incidence: \( \alpha = 2^\circ, \alpha = 5^\circ, \alpha = 7^\circ \))

Table 2.
The values of the effective depth of X-ray penetration compared for the examined materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Effective penetration depth [( \mu \text{m} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2°</td>
</tr>
<tr>
<td>TZ</td>
<td>1.56</td>
</tr>
</tbody>
</table>

The analysis of the obtained diffraction patterns of the examined scales revealed the presence of the following phases: \( \text{Cr}_2\text{O}_3 \), \( \text{MnCr}_2\text{O}_4 \), \( (\text{Cr}, \text{Fe})_2\text{O}_3 \), \( \text{SiO}_2 \) and \( \text{CrNbO}_4 \). The \( \text{CrNbO}_4 \) phase was present in the diffraction patterns obtained at an angle of incidence amounting to 2° (~1.5 \( \mu \text{m} \)). With the increasing effective depth of penetration, the intensity of peaks originating from the oxide phases present in the scale was reduced, and peaks originating from the matrix of the examined material, i.e. austenite, started appearing. An increase in the peak intensity was directly related with the increasing amount of a given phase in the examined material.

The scale adhesion to the substrate was determined by scratch test. Table 3 gives the values of loading \( L_{c1} \) at which the first buckling and chipping of the scale was observed to occur; the value of loading \( L_{c2} \) is the one at which continuous damages along the scratch left by an indenter appear, and the depth of scale penetration obtained in the examined material oxidised at a temperature of 820 °C assumes its highest value.

Table 3.
The values of critical stress and the maximum depth of penetration obtained in scratch test during examination of the scale adhesion to substrate

<table>
<thead>
<tr>
<th>Material</th>
<th>Critical load [mN]</th>
<th>Depth of penetration ( G [\mu \text{m}] )</th>
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<tbody>
<tr>
<td></td>
<td>( L_{c1} )</td>
<td>( L_{c2} )</td>
</tr>
<tr>
<td>TZ</td>
<td>18,25±1,82</td>
<td>36,15±4,11</td>
</tr>
</tbody>
</table>
In the scale formed on alloy modified with Ti+Zr, the first deformations and chipping appeared at a loading amounting to 18.25 mN, while continuous damages of the scale related with indenter operation were observed at a loading of 35.15 mN.

Figure 5 shows the appearance of sample surface after scratch test at the previously mentioned values of loading, i.e. Lc1 and Lc2. Loading Lc2 removed the scale from an entire length of the scratch left by indenter. During the test, a grave scale degradation in the form of material losses affecting not only the subsurface layers but penetrating to a metallic core was observed. Additionally, a loosening and detachment of the scale from the substrate also took place.

At this point it should be stressed that the indenter penetration depth depended on the thickness of the built up scale [9]. Attention also deserves the fact that „ridging” of the scale formed on the tested material was uniform and covered a large surface area of this scale.

Through the test, a grave scale degradation in the form of material losses affecting not only the subsurface layers but penetrating to a metallic core was observed. Additionally, a loosening and detachment of the scale from the substrate also took place.

4. Conclusions

Carried out examinations lead to the following conclusions:

- the oxidation curves for both test temperatures have an approximately parabolic run,
- the scale formed on samples during oxidation in air at a temperature of 820 °C is characterised by good adhesion to the cast steel surface, revealing no cracks and/or discontinuities,
- the analysis of diffraction patterns obtained in Bragg-Brentano geometry at constant angle of incidence allows stating if in the examined scales the phases of Cr2O3, MnCr2O4, (Cr, Fe)2O3, SiO2 and CrNbO4 are present. With the increasing angle of incidence, the oxide phases disappear and instead peaks originating from the alloy matrix appear,
- based on the scratch test results it has been observed that the introduced microadditions affect the scale adhesion to the metallic substrate, when the scale is formed during oxidation of the tested material at a temperature of 1093K for 24h in the atmosphere of air. In the case of the tested material, the scratch on the scale surface is uniform, and the first scale chipping and detachment appear no sooner than under a load of 18 mN,
- the scale formed on the tested materials oxidised at a temperature of 1000 °C suffered nearly total degradation. Three typical areas were distinguished in this scale.

References