Evaluation of cast GX40CrNiSiNb24-24 steel after-service conditions

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Abstract

In this study, an attempt was made to assess changes in the microstructure of centrifugally cast tubes from GX40CrNiSiNb24-24 steel after a long-term operation under the conditions of a catalytic conversion of methane with steam. Changes in phase morphology occurring as a result of high temperature were identified.

Keywords: Metallography, Heat resistance Cr-Ni cast steel, Microstructure, High temperature degradation, Carbides

1. Introduction

Hydrogen, which is one of the sources of so-called “clean energy”, has become an alternative to the drastically diminishing fossil fuel resources. Due to the fact that the product of hydrogen burning is water, this element is an ideal fuel used in internal combustion engines or fuel cells. Currently, hydrogen is produced mainly from fossil fuels and used in the processes of chemical synthesis (e.g. the synthesis of ammonia, aldehydes, ketones), in metallurgy and aerospace (rocket fuel) [1]. Hydrogen is produced mainly from natural gas in the process of steam reforming at temperatures of up to 950°C under the pressure of 2÷4MPa. This process is carried out in a reformer, whose basic element is the furnace composed of the centrifugally cast chrome-nickel steel tubes. Placed vertically in the furnace, the tubes are filled with nickel catalyst (ceramic rings coated with a nickel-based alloy). The working tubes are exposed to corrosive environments (air, water vapour, carbon and sulphur) for approximately 100000 hours [2÷4].

Tubes operate in installations for the reforming and pyrolysis are made, among others, from the cast GX40CrNiSi25-20 steel [5−8]. This material has good resistance to gas corrosion (appropriately high content of chromium) and shows reasonable resistance to stress, even at temperatures down to 1050 °C. In as-cast state, the structure of cast GX40CrNiSi25-20 alloy is composed of an austenitic matrix with large precipitates of carbides, located mainly at the grain boundaries. To improve the performance properties of the alloy, nickel content is increased and an addition of niobium is introduced, the latter one being a strongly carbide-forming element. Niobium forms carbide eutectic at grain boundaries; scarce carbide particles are also present inside the grains. In as-cast niobium-inoculated alloys, one can find fine precipitates of niobium carbides (NbC), adhering to the carbides of M23C6 type. Carbides of M23C6 type contain in their composition besides chromium also certain amounts of Fe [9].

2. Methods investigation

The material for studies were samples of the cast GX40CrNiSiNb24-24 steel taken from a tube operatine in installations for the catalytic conversion of methane with steam. Samples were cut out from an area distance by about 1.5 m from the tube inlet operating at about 800°C for 110000 hours.
Metallographic studies were carried out on surfaces perpendicular to the tube axis using a Nikon light microscope and a Hitachi S-3500L scanning microscope, and also a NORAN attachment for analysis of the chemical composition. Samples were etched with a Mi 15Fe reagent.

The chemical composition of the examined cast steel is shown in Table 1.

Table 1. Chemical composition of the examined cast steel

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical composition, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>GX40CrNiSiNb</td>
<td>0.3</td>
</tr>
<tr>
<td>24-24(^1)</td>
<td>0.5</td>
</tr>
<tr>
<td>MB(^2)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

\(^1\) according to PN-EN10295  
\(^2\) examined material

To get more information on the phase composition of the examined material, an X-ray phase analysis was carried out. Diffraction studies were conducted on a Siemens Kristalloflex 4H diffractometer. The radiation of copper anode tube of \(\lambda = 1.54 \text{ Å}\) was used. Diffraction lines were recorded at a voltage of 35kV and 20mA current intensity in the 2θ angle range.

The aim of the conducted studies was to obtain structural characteristics of material used for the tubes centrifugally cast from heat-resistant steel GX40CrNiSiNb24-24.

3. Results and discussion

Figure 1 shows structure of the examined casting. On the tube section one can distinguish the three major structural zones, viz. of chill grains, columnar and equiaxial. The zone of frozen grains in the examined material has been partly destroyed by the effect of the corrosive environment (Fig. 1.1).

![Fig. 1. Structure of casting made from the GX40CrNiSiNb24-24 steel](image)

To evaluate the morphology of the dendritic structures, the secondary dendrite arm spacing (DAS) was determined. Measurements of the DAS parameter were taken only for the well-developed secondary arms located near the tube outer surface and middle wall part. It has been assumed that the width of the secondary dendrite arms is approximately equal to spacing between the precipitates found in the interdendritic spaces. The DAS parameter for both tube wall areas was similar and amounted to about 30 \(\mu\text{m}\).

Figure 2-4 shows after-service microstructure of the cast austenitic GX40CrNiSiNb24-24 steel as seen under a light microscope.

The metallographic analysis showed that the examined material is characterised by a dendritic structure with numerous precipitates of complex morphology present in both dendrites and interdendritic spaces.
Fig. 2. After-service microstructure of GX40CrNiSiNb24-24 cast steel - outer surface of tube, optical microscope

Fig. 3. After-service microstructure of GX40CrNiSiNb24-24 cast steel - middle part of tube, optical microscope

Fig. 4. After-service microstructure of GX40CrNiSiNb24-24 cast steel - inner surface of tube, optical microscope
For SEM examinations, areas located in middle part of the tube wall were chosen (Fig. 5÷7). The precipitates located in the interdendritic spaces, and visible on SEM images show clear enrichment in Nb, Ni and Si (Fig. 5, spectrum 2). It confirms the fact reported in the literature concerning the examined material that at high temperatures the precipitates of NbC are unstable, and after long-term operation at temperatures around 900°C undergo transformation forming an intermetallic Ni16Nb6Si7 type phase enriched in Si (G phase) [11]. The analysis of the chemical composition of these precipitates, located in different areas of the central zone of the tube wall, showed significant differences in the content of Nb (30÷45%wt), Si (6÷10%wt) and Ni (30÷40%wt). It can be concluded that the observed differences in the composition of these phases may be caused by varying degrees of advancement of the niobium carbide NbC transformation into the G phase [1].

The precipitates visible on SEM images as dark areas, showing mainly the enrichment in chromium, and less frequently in chromium and iron, are chromium carbides of Cr23C6 and (Cr,Fe)23C6 type (Fig. 5, spectrum 1).
In dendrites, the lamellar precipitates of an average size of about 5\(\mu\)m prevail. Typically, they are arranged in respect of each other at an angle of about 60 and 120 degrees. SEM examinations showed enrichment of this phase in Cr compared to the alloy matrix (Fig. 7). Based on the literature data, it can be concluded that these are probably the precipitates of \(\sigma\) phase, because operation of the examined material under the conditions of steam reforming in a temperature range of 850 ÷ 920ºC may contribute to the formation of acicular precipitates of this phase [1, 10].

Fig. 7. Microstructure on the cross-section of a tube cast from GX40CrNiSiNb24-24 steel with linear chemical analysis, SEM-EDS
Figure 8. The diffractogram of GX40CrNiSiNb24-24 cast steel

Figure 8 shows an example of diffraction pattern obtained on the examined material. The analysis of diffraction patterns revealed the presence of the following phases: \( \gamma \), \((\text{Cr, Fe})_{23}C_6\), NbC, Ni\(_{16}\)Nb\(_6\)Si\(_7\), Nb\(_3\)Ni\(_2\)Si.

4. Conclusions

- On the entire cross-section of the test tube, two types of precipitates were found: acicular (inside the dendrites) and complex of globular shapes (mainly in the interdendritic spaces).
- Complex precipitates show enrichment in Nb, Ni and Si (bright areas) and in Cr and Fe (dark areas).
- The phase enriched in Nb, Ni and Si is probably the G phase which is a product of the transformation of niobium carbide, while phases enriched in Cr and Fe are Cr\(_2\)C\(_6\) and/or \((\text{Cr, Fe})_{23}C_6\).
- The acicular precipitates enriched in Cr are probably the precipitates of \(\sigma\) phase.

The X-ray phase analysis revealed the presence of the following phases: \( \gamma \), \((\text{Cr, Fe})_{23}C_6\), NbC, Ni\(_{16}\)Nb\(_6\)Si\(_7\), Nb\(_3\)Ni\(_2\)Si.

References