Effect of silicon content on the resistance of ductile iron to high-temperature oxidation

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Abstract: This paper analyses the oxidation resistance of ductile irons containing 2.11, 3.4, 4.28, 4.49 and 4.81 wt.% Si that were held at 850 °C for 32 hours. A scale was formed on all the samples and their weight increased. The scale thickness and increase in weight were decreased with increase of the silicon content, especially when the silicon content > 4 wt.%. The compactness of the scale on the sample surface is significantly higher at higher silicon contents. The results obtained indicate that the resistance of ductile iron to high-temperature oxidation increases with increasing silicon content.

Keywords: DUCTILE IRON, SILICON, HIGH-TEMPERATURE OXIDATION

1. Introduction

Ductile iron is a kind of cast iron containing graphite particles in a microstructure [1 – 3]. Since the graphite particles have a spherical shape, ductile iron has significantly different properties than gray and compacted graphite iron. Through variations in chemical composition and microstructure, different properties can be achieved. Because of this, ductile iron castings are widely used, even at low and high temperatures. Certainly the most famous high-temperature applications are exhaust manifolds and turbocharger housings of the internal combustion engines.

Long exposure of iron to air at high temperatures results in oxidation [4 – 11]. Because of that, a scale (oxide layer) is formed on the surface consisting of three oxides: the outer layer is FeO, the middle layer is Fe₃O₄, and the inner layer (layer to base material) is FeO. The rate of oxidation, i.e. penetration into the material, depends on the diffusion of oxygen through the oxide layer. An oxide layer which is compact and tightly connected to the base material acts as a protective barrier, resulting in a decrease in the rate of oxidation. On the other hand, an oxide layer that is porous and contains cracks and is not firmly bonded to the base material will not act as a barrier to oxygen diffusion. As a result, oxidation continues and the thickness of the oxide layer increases, which becomes prone to cracking and to spallation.

The resistance of graphitic cast irons to high-temperature oxidation also depends on the shape of the graphite particles. Oxidation mainly progresses along the graphite phase. Therefore, the oxidation rate in the ductile iron is lower than in the gray and compacted graphite iron [12].

Silicon is the most significant and economically most suitable element to improve the resistance of cast iron to high-temperature oxidation. When the silicon content > 4 wt.%, β-SiO₂ barrier layer is formed at the oxide/base material interface [12]. SiO₂ is significantly more compact than Fe-oxides. Therefore, the transport of oxidizing substances to the interior of the material is reduced, which ultimately results in a decrease in the rate of oxidation. The scale (oxide layer), observed from the surface towards the interior of the silicon alloyed ductile iron, consists of Fe₂O₃, Fe₃O₄, FeO + Fe₂SiO₄ and finally β-SiO₂ separating the oxide layer from the base material [13].

This paper analyses the influence of silicon content on the resistance of the ductile iron to oxidation at 850 °C.

2. Experimental

The five ductile iron (DI) melts were made with the following targeted silicon content: 2.1 wt.%, 3 wt.%, 4.2 wt.%, 4.5 wt.% and 4.8 wt.%. A 25 mm thick Y-shaped sample (type II according to EN 1563:2012) was cast from each melt. The moulds are made by sodium silicate/CO₂ process. High-temperature oxidation resistance test specimens were cut from Y-shaped samples and then placed in porcelain bowls that were annealed to constant mass at 850 °C. The heating of the samples was carried out in a furnace in an oxidizing atmosphere. Samples were held for 32 hours at 850 °C. Weighing the samples together with porcelain bowls was carried out on a digital scale before and after heating in the furnace. Scale (oxide layer) on the surface of the samples after heating was analysed using light metallographic microscope with a digital camera.

3. Results and discussion

The chemical composition of the analysed ductile irons is shown in Table 1. The scale on the surface of the samples is shown in Figures 1 and 2. The effect of silicon on the change in samples weight and scale thickness is shown in Figures 3 and 4.

Table 1: Chemical composition of ductile irons

<table>
<thead>
<tr>
<th>Element content, wt.%</th>
<th>DI 1</th>
<th>DI 2</th>
<th>DI 3</th>
<th>DI 4</th>
<th>DI 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.61</td>
<td>3.56</td>
<td>3.32</td>
<td>3.15</td>
<td>3.05</td>
</tr>
<tr>
<td>Si</td>
<td>2.11</td>
<td>3.4</td>
<td>4.28</td>
<td>4.49</td>
<td>4.81</td>
</tr>
<tr>
<td>Mn</td>
<td>0.1</td>
<td>0.14</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>Fe</td>
<td>0.034</td>
<td>0.028</td>
<td>0.032</td>
<td>0.03</td>
<td>0.029</td>
</tr>
<tr>
<td>S</td>
<td>0.013</td>
<td>0.011</td>
<td>0.012</td>
<td>0.012</td>
<td>0.009</td>
</tr>
<tr>
<td>Mg</td>
<td>0.052</td>
<td>0.048</td>
<td>0.066</td>
<td>0.065</td>
<td>0.045</td>
</tr>
<tr>
<td>Cu</td>
<td>0.019</td>
<td>0.015</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>0.032</td>
<td>0.038</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Mo</td>
<td>0.002</td>
<td>0.009</td>
<td>0.63</td>
<td>0.63</td>
<td>0.61</td>
</tr>
<tr>
<td>Ni</td>
<td>0.014</td>
<td>0.019</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Nb</td>
<td>0.003</td>
<td>0.001</td>
<td>0.002</td>
<td>0.001</td>
<td>0.008</td>
</tr>
<tr>
<td>V</td>
<td>0.01</td>
<td>0.007</td>
<td>0.009</td>
<td>0.009</td>
<td>0.009</td>
</tr>
<tr>
<td>Sn</td>
<td>0.0044</td>
<td>0.0052</td>
<td>0.007</td>
<td>0.006</td>
<td>0.007</td>
</tr>
<tr>
<td>Al</td>
<td>0.011</td>
<td>0.008</td>
<td>0.009</td>
<td>0.009</td>
<td>0.012</td>
</tr>
<tr>
<td>Ti</td>
<td>0.016</td>
<td>0.009</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

In Figure 1 it can be seen that all the samples oxidized during heating. However, it is clearly seen that the thickness of the scale (oxide layer) is greatest on DI 1 which has the lowest content of silicon (2.11 wt.% Si).

Figure 2 shows that the oxide layer on the surface of all the analysed ductile irons consists of two parts. The inner part of the oxide layer on DI 3, DI 4 and DI 5 is compact and tightly connected with the ductile iron, which hinders the penetration of oxygen into the material. With increasing silicon content in the DI 3, DI 4 and DI 5 the thickness of the inner part of the oxide layer increases. The outer part of the oxide layer is less compact, but does not separate from the inner part. The outer part of the oxide layer on DI 3, DI 4 and DI 5 is much more compact than the outer part of the oxide layer on DI 1 and DI 2.

The inner part of the oxide layer on DI 1 is not compact. It is significantly porous and not firmly bonded to ductile iron. The outer part of the oxide layer is also non-compact and separates from the inner part of the oxide layer. Such an oxide layer structure does not represent a significant barrier to oxygen penetration into the interior of the material. It is obvious that low-silicon ductile iron castings are not suitable for high-temperature applications.

DI 2 has higher silicon content than DI 1. For this reason, DI 2 has a different resistance to high-temperature oxidation. The inner part of the oxide layer on DI 2 is more compact than the inner part of the oxide layer on DI 1 and is more firmly connected with the ductile iron. However, its compactness and connection with ductile iron is lower than in DI 3, DI 4 and DI 5. According to the characteristics, the outer part of the oxide layer on DI 1 and DI 2 are similar. Taking all this into consideration, DI 2 has better resistance...
to high-temperature oxidation than DI 1, but less than DI 3, DI 4 and DI 5.

Fig. 1 Macrostructures of the samples after 32 hour of heating at 850 °C: a) DI 1 (2.11 wt.% Si), b) DI 2 (3 wt.% Si), c) DI 3 (4.28 wt.% Si), d) DI 4 (4.49 wt.% Si), e) DI 5 (4.81 wt.% Si).

The obtained results show that during heating the weight of all samples increased due to oxidation, i.e. formation of an oxide layer (scale) on the surface. However, it can be seen from Figure 3 that the increase in weight decreases with increasing silicon content. This shows that the resistance of ductile iron to high-temperature oxidation increases with increasing silicon content.

It can be seen from Figures 2 and 4 that the thickness of the scale is much smaller on ductile irons containing > 4 wt.% Si (DI 3, DI 4 and DI 5) than on DI 1 and DI 2 which have lower silicon contents. The thickness of the oxide layer is greatest on DI 1 which has the lowest silicon content (2.11 wt.%). The oxide layer is the thinnest on DI 5 which has the highest silicon content (4.81 wt.%). This shows that the thickness of the scale on the ductile iron decreases with increasing silicon content.

4. Conclusion

The results obtained show that the ductile iron oxidizes during prolonged exposure to high temperatures, resulting in an increase in its weight and the formation of a scale on the surface. However, with an increase in silicon content, especially > 4 wt.%, the increase in weight and thickness of the scale are significantly reduced. In addition, the scale on the surface of high-silicon ductile irons is largely compact, which hinders the penetration of oxygen in the ductile iron and the progress of oxidation. It can be concluded that silicon greatly increases the resistance of ductile iron to high-temperature oxidation.

Fig. 2 Microstructures of the surface part of the samples after 32 hours of heating at 850 °C (non-etched): a) DI 1 (2.11 wt.% Si), b) DI 2 (3 wt.% Si), c) DI 3 (4.28 wt.% Si), d) DI 4 (4.49 wt.% Si), e) DI 5 (4.81 wt.% Si).

Fig. 3 Influence of silicon content in the analysed ductile irons on the change in weight of the samples after 32 hours of heating at 850 °C.
Fig. 4 Influence of silicon content in the analysed ductile irons on the scale thickness formed during 32 hours of heating at 850 °C.

5. References