EFFECT OF NICKEL, CHROMIUM, SILICON AND CARBON ON INCREASED RESISTANCE TO CARBURISING EFFECT OF Ni-Cr CAST STEEL

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SUMMARY

The study examines an effect of the basic chemical constituents in austenitic cast steel on an increase in its carburising resistance at a temperature of 900°C and with the carbon potential of atmosphere equal to 0.9%. It has been proved that the increment in sample weight is controlled mainly by the content of nickel, silicon and starting volume of carbon in alloy, while thickness of the carburised layer depends, first of all, on chromium content.

Key words: Fe-Ni-Cr alloys, carburisation, carbide formation

1. INTRODUCTION

The creep-resistant construction elements of carburising furnaces are usually made from austenitic cast steel. One of the main reasons of their reduced performance life is the formation of a carburised layer in the top part of elements. This highly unfavourable phenomenon can be kept under control by properly matching the chemical composition of steel [1, 2].

The mechanism due to which the alloying additions abate the process of austenitic steel/cast steel carburising has been investigated in every detail [3]. In view of a complex phase constitution of alloys and non-uniform distribution of alloying elements in austenite, carbon diffusion can be traced mainly through the results of experimental studies conducted on real alloys.

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The present study relates an output of laboratory research whose main aim was to determine the tendency and intensity of an effect of the main constituents present in austenitic cast steel on its resistance to carburising.

2. EXPERIMENTAL

Basing on ACI standard „Cast steel and heat-resistant cast alloys” [2], the variation range of chemical composition of the austenitic cast steel was selected in a way such as to cover all the most commonly used alloy grades: 18-40 %Ni, 17-30 %Cr and 0.05-0.6 %C (wt-%). It has also been assumed that the Si content will be maintained in a range of 1.2÷1.5%, and that of manganese in a range of 0.5÷0.8%. Eleven melts were made. The chemical composition of the experimental alloys is shown in Table 1.

Table 1. Chemical composition of the cast steels* (wt-%) and compiled results of measurements.

<table>
<thead>
<tr>
<th>Nr stopu</th>
<th>C</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>∆M/S</th>
<th>Zc</th>
<th>Z</th>
<th>Mc</th>
<th>W</th>
<th>Wcore</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.37</td>
<td>1.20</td>
<td>17.3</td>
<td>33.8</td>
<td>0.230</td>
<td>1.00</td>
<td>1.75</td>
<td>76</td>
<td>30.2</td>
<td>4.9</td>
</tr>
<tr>
<td>2</td>
<td>0.58</td>
<td>1.30</td>
<td>23.1</td>
<td>36.5</td>
<td>0.163</td>
<td>0.47</td>
<td>1.25</td>
<td>72</td>
<td>34.2</td>
<td>9.2</td>
</tr>
<tr>
<td>3</td>
<td>0.45</td>
<td>1.30</td>
<td>28.1</td>
<td>32.3</td>
<td>0.195</td>
<td>0.35</td>
<td>1.10</td>
<td>76</td>
<td>40.2</td>
<td>8.2</td>
</tr>
<tr>
<td>4</td>
<td>0.59</td>
<td>1.41</td>
<td>30.8</td>
<td>24.0</td>
<td>0.231</td>
<td>0.37</td>
<td>1.50</td>
<td>101</td>
<td>49.5</td>
<td>14.4</td>
</tr>
<tr>
<td>5</td>
<td>0.61</td>
<td>1.20</td>
<td>20.5</td>
<td>25.7</td>
<td>0.266</td>
<td>0.72</td>
<td>1.65</td>
<td>59</td>
<td>40.2</td>
<td>7.8</td>
</tr>
<tr>
<td>6</td>
<td>0.33</td>
<td>1.18</td>
<td>19.5</td>
<td>22.2</td>
<td>0.331</td>
<td>0.80</td>
<td>2.00</td>
<td>75</td>
<td>40.0</td>
<td>5.9</td>
</tr>
<tr>
<td>7</td>
<td>0.40</td>
<td>1.28</td>
<td>25.9</td>
<td>18.0</td>
<td>0.457</td>
<td>0.60</td>
<td>1.80</td>
<td>106</td>
<td>48.1</td>
<td>8.8</td>
</tr>
<tr>
<td>8</td>
<td>0.17</td>
<td>1.37</td>
<td>27.1</td>
<td>20.0</td>
<td>0.418</td>
<td>0.40</td>
<td>1.85</td>
<td>122</td>
<td>47.8</td>
<td>4.7</td>
</tr>
<tr>
<td>9</td>
<td>0.22</td>
<td>1.30</td>
<td>29.9</td>
<td>30.2</td>
<td>0.326</td>
<td>0.44</td>
<td>1.00</td>
<td>97</td>
<td>45.0</td>
<td>7.3</td>
</tr>
<tr>
<td>10</td>
<td>0.16</td>
<td>1.22</td>
<td>21.8</td>
<td>28.1</td>
<td>0.322</td>
<td>0.47</td>
<td>1.55</td>
<td>72</td>
<td>41.7</td>
<td>4.1</td>
</tr>
<tr>
<td>11</td>
<td>0.05</td>
<td>1.65</td>
<td>26.5</td>
<td>41.0</td>
<td>0.192</td>
<td>0.40</td>
<td>1.00</td>
<td>97</td>
<td>38.4</td>
<td>3.2</td>
</tr>
</tbody>
</table>

* average content of other elements: Mn ~ 0.63%, S ~ 0.011%, P ~ 0.032%.

From each alloy samples with casting skin were prepared for metallographic examinations [2]. The samples were carburised for 500 hours in a continuous process at a temperature of 900°C, using the atmosphere composed of a mixture of propane and hydrogen. The carbon potential of the atmosphere was 0.9%.

After carburising the samples were weighed at an accuracy of ± 0.05 mg. Mean values from four measurements (for given alloy) calculated in respect of the sample surface (∆M/S) are compiled in Table 1 (the confidence coefficient adopted in calculation was 1-α = 0.95).

Due to carburising effect, in the external layer of the examined alloys, carburised layers of varied thickness and with varied amount, size and type of carbide phases have been formed [6]. Figure 1 shows as an example the microstructure of a carburised layer in alloy no. 5.
The produced carburised layers were described by the characteristic parameters used in the studies described below.

**Linear carbon distribution.** This information, unfortunately only of a qualitative nature, was obtained by scanning of carburised layer with a measuring beam of 100 µm diameter, produced by a JEOL 50 SM microanalyser. By averaging carbon concentration comprised within this range, a „smooth” run of the curves was obtained. In Figure 2a, taking as an example the carburised layer in alloy no. 5, a result of such measurement was plotted in the form of a graphic diagram. Basing on the plotted diagrams of a linear carbon distribution it can be stated that the carburised layers consist of at least two zones. The division into the individual zones and the determination of their thickness are shown in Figure 2a. The rate of alloy carburising depends on carbon diffusion in the second transition zone between the carburised layer and uncarburised core [6]. An approximate evaluation of the value of carbon diffusion in this zone is possible due to the relationships described in [5]:

\[
D_c = \frac{(Z_c / 2)^2}{t} \quad (1)
\]

\[
\sqrt{\pi} \frac{x^2}{2} \text{erfc} x = \frac{Z_c c}{(Z_c c + S)} \quad (2)
\]

where:

- \(D_c\) – value corresponding to carbon diffusivity in transition zone,
- \(Z_c\) – coordinate (thickness) of carburised layer (Fig. 2a, Table 1),
- \(S\) – field under the carbon distribution curve in the second (transition) zone,
c – coordinate corresponding to carbon concentration at point Zc,
ξ – coefficient allowing for deviation of the diffusion process from parabolic law of saturation.

Thus measured parameters and calculated values Dc are compiled in Table 2. The value of ξ was selected after calculation of the right member of equation (2) using values of this function compiled in a table in [5].

Fig. 2. Plotted results of metallographic examinations of the carburised layer in alloy no. 5: a) linear distribution of carbon concentration, b) percent content of carbides.

Table 2. Calculated values of Dc.

<table>
<thead>
<tr>
<th>Alloy No</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>c, mm</td>
<td>34</td>
<td>45</td>
<td>52</td>
<td>71</td>
<td>40</td>
<td>39</td>
<td>63</td>
<td>85</td>
<td>75</td>
<td>58</td>
<td>83</td>
</tr>
<tr>
<td>S, mm²</td>
<td>8.80</td>
<td>7.60</td>
<td>12.75</td>
<td>10.63</td>
<td>9.60</td>
<td>13.07</td>
<td>16.30</td>
<td>29.55</td>
<td>13.55</td>
<td>16.47</td>
<td>19.08</td>
</tr>
<tr>
<td>ξ</td>
<td>1.20</td>
<td>0.95</td>
<td>0.55</td>
<td>0.85</td>
<td>1.00</td>
<td>0.85</td>
<td>0.80</td>
<td>0.50</td>
<td>0.85</td>
<td>0.65</td>
<td>0.65</td>
</tr>
<tr>
<td>Dc×10⁻⁶, cm²/s</td>
<td>0.0965</td>
<td>0.0340</td>
<td>0.0562</td>
<td>0.0263</td>
<td>0.0263</td>
<td>0.1230</td>
<td>0.0781</td>
<td>0.0889</td>
<td>0.0372</td>
<td>0.0726</td>
<td>0.0726</td>
</tr>
</tbody>
</table>

Volume content of carbides W. The measurements were taken in a direction normal to the sample surface in fields of 100 µm width using a CLEMEX 1024C image analyser. On each sample the measurements were taken at six locations chosen at random in the layer. An analysis of the carbide phase was made after etching of the samples with
Beraha reagent (10% aqueous solution of HCl with an addition of 1 g K₂S₂O₅ per 100 ml of solution). Figure 2b shows as an example a result of measurements taken in alloy no.5, while Figure 3 shows microstructure of the carbide phase. Table 1 compiles for the examined alloys the results of measurements of percent carbide content in the first subsurface layer (W) and in the core – (W_core).

<table>
<thead>
<tr>
<th>Alloy 5</th>
<th>Distance from surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 µm</td>
</tr>
</tbody>
</table>

The results of measurements compiled in Table 1 and 2 were mathematically processed on a Multiple Regression module in STATISTICA PL. v.5.1 packet. The computations also allowed for silicon content changing in the alloy. Under the conditions applied in the experiment, the course of the reaction has proved to be too complicated and hence impossible to be kept under control, which resulted in larger than expected scatter of the silicon content values in molten steel. Below the determined relationships have been compiled along with parameters of the statistical estimation, coefficient of determination R² and statistics F.

\[
\Delta M/S = 0.269 - 0.235 \times C - 0.157 \times Si + 8.145 \times Ni^2
\]

\[
Z_c = 6.03 - 0.34 \times Cr - 0.06 \times Ni + 0.01 \times Cr^2 + 0.001 \times Ni^2
\]

\[
Z = 0.1 - 0.05 \times Ni + 36.13 \times Cr^3 + 0.94 \times Si
\]

\[
M_c = 59.1 - 140.3 \times C + 3.7 \times C \times Ni - 0.12 \times Cr \times Ni + 3.77 \times Si \times Cr
\]

\[
W = 47.3 - 37.3 \times C + 0.7 \times Cr - 0.7 \times Ni + 47.6 \times C^2
\]

\[
(W - W_{core}) = 46 + 0.6 \times Cr - 0.6 \times Ni + 51.8 \times C^2 - 41.2 \times C \times Si
\]

\[
D_c = -0.093 - 0.06 \times C + 1.642 \times Ni^4 + 2.846 \times Cr^3
\]
3. DISCUSSION OF RESULTS

Carburising of austenitic cast steel brings very important changes in microstructure of its outer layer. The deposited carburised layer is characterised on the cross-section by varied content and size of carbides – Fig. 1 and 3. Examining from the side of the surface chromium carbides present on the grain boundaries and in the matrix it can be observed that the process of carburising is accompanied by increasing content of those carbides and by the growth of individual precipitates. In [6] it has been proved that the layers contain carbides of $M_2C_3$, $M_7C_3$ and $M_23C_6$ type, the content of the first two carbides being predominant in the region of the highest carbon concentration. The precipitating high-chromium equilibrium phases reduce, first of all, chromium content in the matrix, thus reducing the heat-resistant behaviour of the material.

As proved by the carried out investigation, it is not possible, within the examined range of chemical content, to completely eliminate the carburising process of the austenitic cast steel, but it is possible to reduce it quite effectively. Basing on the calculated equations of regression it can be generally stated that increasing the content of nickel, chromium, silicon and carbon in the alloy reduces the process of carburising. Yet, the effect of the examined elements has not been sufficiently allowed for in all the derived relationships. Also the degree of this effect on the values of the examined parameters differs quite considerably.

Applying the determined relationships, cast steel resistance to carburising can be evaluated basing on the three adopted criteria, viz. weight increase after carburising – eq. (3), thickness of carburised layer – eqs. (4) and (5), and carbide phase content at the sample surface – eqs. (7) and (8).

Examining these criteria separately it becomes obvious that when the corrosive effect of environment on cast material has to be minimised, with the first criterion it is necessary to increase in alloy the content of, first of all, nickel, and then of carbon and silicon. The nature of this relationship results from the role that these elements play in reducing carbon solubility in austenite.

The form of the derived equation also indicates that maximum effect of these elements is beyond the range of the examined alloys. In the case of the second criterion it is mainly chromium content in the alloy {eq. (4), Fig. 4} that decides about the thickness of the carburised layer. Increasing the concentration of this element in steel promotes the nucleation within a given material volume of a large amount of chromium carbides. According to the third criterion, nickel and chromium are consistent as regards the degree of their effect on the examined parameter, but inconsistent as regards the direction of this effect. Hence it can be judged that this relationship allows for the role of both nickel and chromium, as expressed by eqs. (1) and (4), respectively. A similar interpretation holds true in the case of eq. (6). The value of the conventionally adopted, maximum carbon concentration in the top zone $M_{ce}$ is related to the chemical composition by a relationship of similar character. Therefore, in some definite cases, it is possible to use these relationships interchangeably to anticipate the results of a carburising process.
The above comparison of the criteria in evaluation of the carburising degree indicates that the recommended chemical composition of cast steel will depend on which criterion will be chosen for this evaluation. Therefore it is necessary to establish which criteria should be selected and recommended for use under a given set of operating conditions. It seems that, first of all, two criteria should be taken into consideration:

- $Z_c$, because it describes the thickness of the carburised layer characterised by a relatively constant carbon concentration, and so an area which has been overcarburised,

- $W$ or $(W - W_{core})$, because along with an increasing content of carbides in a given material volume its heat resistance is decreasing and brittleness is increasing [2, 8].

An increase in the values of $Z_c$ or $W$ provides a direct information about the degree of damage suffered by the material, i.e., about the unfavourable changes in microstructure of the top casting layer. As shown by eqs. (4) and (7), the direction of chromium effect on reducing the value of these two parameters is consistent (Fig. 4), with opposite positive effect of nickel. Due to the fact that chromium is a carbide-forming element, increasing its content in steel reduces the depth of carbon penetration, but on the cost of increasing its concentration in the respective layer due to the formation, within a given material volume, of a large amount of carbides. Therefore, to achieve higher resistance to carburising effect, yet such that would not cause overcarburising of the material, it is recommended to take into consideration rather the possibility of increasing nickel content in the alloy.

By transformation of eq. (1) into:

$$Z_c = 2\sqrt[4]{D_c / t}$$

(11)
the parameter \( \xi \sqrt{D_c} \) is created, which is typical of a given alloy and describes the kinetics of growth of the carburised layer. The lower is the value of this parameter, the higher is the cast steel resistance to carburising effect (the thinner is the carburised layer). If the value of this parameter is known, an increase in the thickness of the carburised layer after a time longer than 500 hours can be calculated for the conditions used in the carried out experiment.

4. CONCLUSIONS

The investigation of the resistance to carburising effect of austenitic cast steel assigned for parts of carburising furnaces has indicated the following:

- the increase in weight is mainly controlled by nickel content, and further by silicon and the starting content of carbon in steel,
- the thickness of the carburised layer depends, first of all, on the content of chromium which is also responsible for an unfavourable increase in carbides concentration in the top layer of the carburised material.

REFERENCES


Wpływ niklu, chromu, krzemu i węgla na wzrost odporności staliwa Ni-Cr na nawęglanie

STRESZCZENIE

W pracy analizowano wpływ podstawowych składników chemicznych stali austenitycznego na wzrost jego odporności na nawęglanie w temperaturze 900°C i przy potencjale węglowym atmosfery 0.9%. Wykazano, że przyrost masy próbek jest kontrolowany głównie zawartością niklu, krzemu i początkową ilością węgla w stopie, a grubość warstwy nawęglonej zależy przede wszystkim od zawartości chromu.

Recenzował Prof. Stanisław Jura