CARBON DIFFUSION COEFFICIENTS OF OXIDISED VALVE STEEL GRADE 4H14N14W2M AT HIGH-TEMPERATURES

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Abstract

In the paper was discussed the obtained results of carbon diffusion coefficients $D_c$, after oxidation of highly-alloyed valve steel grade 4H14N14W2M acc. to PN in air. Decarburising annealing was carried out in chamber electrical furnace at various temperatures from 940 do up to 1100\degree C with gradually rise of temperature at 40\degree C intervals. The calculations of $D_c$ values for each temperature was determined graphically by Boltzman’s-Matano method by using the values of carbon distribution concentrations in function of its distances from surface to core of oxidised samples respectively to the times of oxidation. During analyses the big concentration of carbon at subsurface was neglect.

The aim of this research has been comparison the values of carbon diffusion coefficients $D_c$ for valve steel grade 4H14N14W2M with Fe-C alloy containing similar concentration of carbon and chromium as tested steel (i.e. 14\% wt. Cr).

The analysis shows, that values of carbon diffusion coefficients in tested valve steel are about four times orders smaller, than carbon diffusion coefficients in Fe-C+14\%Cr alloy.

1. INTRODUCTION

The high temperature oxidation of steels for valves in air and other gas environments as $O_2$, $CO_2$ and steam of $H_2O$ causes the forming of scale layers containing oxides; $FeO$, $Fe_3O_4$, $Fe_2O_3$ and $Cr_2O_3$, $Al_2O_3$, $SiO_2$ \cite{1}. High temperature oxidation beyond of scale formation is influencing on the gradient of carbon concentration ($dc/dx$), and differentiate the concentration of alloy elements in subsurface of steel layers. Diffusion flux of carbon $J$ from the core of oxidised specimens (with rise of annealing time), is defined by first Fick’s law \cite{2},

$$J = - D_c (dc/dx) \quad (1)$$

where:

$(dc/dx)_t$ – gradient of carbon concentration,

$D_c$ – coefficient of carbon diffusion.

According to the Arrhenius dependence the rate of carbon diffusion in steel is determined by values of carbon diffusion coefficient $D_c$ \cite{3}.

$$D_c = D_0 \cdot \exp \left( \frac{-Q}{RT} \right), \quad (2)$$

where: $D_0$ – constant frequency, $Q$ – activation energy of carbon diffusion, kJ/mol,

$R = 8.31436 \times 10^{-3}$ kJ/mol K, Boltzmann’s constant, $T$ – temperature , °K.

The aim of the experiment has been determination of carbon diffusion coefficients of 4H14N14W2M valve steel oxidised at high-temperatures in air and comparison obtained values with literature data for alloy Fe-C containing similar concentration of carbon and chromium i.e. 0.4\%C and 14\% wt. Cr.
2. SELF STUDY

The research was carried out on the cylindrical specimens φ 50, \( l = 200 \) mm made of industrial valve steels grade 4H14N14W2M with chemical composition given in table 1.

<table>
<thead>
<tr>
<th>Grade of steel</th>
<th>Chemical composition of tested valve steel %wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>4H14N14W2M</td>
<td>0.41</td>
</tr>
</tbody>
</table>

The polished specimens were treated by annealing in electrical furnace at different temperatures i.e. 940, 980, 1020, 1060 and 1100°C with accuracy ± 2°C. Times of oxidation annealing \( t_1, t_2, ..., t_5 \) for steel 4H14N14W2M in followed temperatures \( T_1, T_2, ..., T_5 \) was determined from the relation which insurance the same thickness of decarburised layers \( \xi_{t_1} = \xi_{t_2} = \ldots = \xi_{t_5} \) for alloy Fe-C with similar chromium content to tested valve [4].

\[
\xi_{i(j-s)} = \sqrt[5]{D_{c1} t_1} = \sqrt[5]{D_{c2} t_2} = \ldots = \sqrt[5]{D_{c5} t_5}
\]  

Carbon diffusion coefficients \( D_{c1}, D_{c2}, ..., D_{c5} \) were calculated from eq. (4) substituting temperature \( T \) in °K and parameters \( Q \) (kJ/mol) and \( D_o \) (cm²/s), which are given in literature data for alloy Fe-C+14%Cr [5].

\[
D_{c(i-5)} = 0.293 \cdot \exp\left[\frac{-193.8}{8.31436 \cdot 10^{-3} \cdot T_{(i-j)}^0}\right]
\]  

Carbon diffusion coefficients in alloy Fe-C+14%Cr calculated from equation (4)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>1100°C</th>
<th>1060°C</th>
<th>1020°C</th>
<th>980°C</th>
<th>940°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{c(1-5)} ) (cm²/s)</td>
<td>1.242 x10⁻⁸</td>
<td>0.746 x10⁻⁸</td>
<td>0.434 x10⁻⁸</td>
<td>0.244 x10⁻⁸</td>
<td>0.132 x10⁻⁸</td>
</tr>
</tbody>
</table>

Using data from table 2 at assumption that depth of decarburization will equals \( \xi_{(1-5)} \approx 0.24 \) mm were calculated times of oxidation annealing Fe-C+14%Cr at temperature 1100°C:

\[
t_1 = \frac{\xi_{1}^2}{D_{c1}} = \frac{0.024^2}{1.242 \times 10^{-8}} = \frac{0.0000576}{0.0000001242} = 46376.81 \text{s} \approx 12 \text{h} 30\text{'}
\]

and in followed temperatures, i.e. respectively 1060°C, 1020°C, 980°C and 940°C:

\[
t_2 = \frac{D_{c2} t_1}{D_{c2}} = \frac{1.242 \cdot 10^{-8} \cdot 45000}{0.746 \cdot 10^{-8}} \Rightarrow 1250\text{'} \approx 20 \text{h} 50\text{'},
\]

\[
t_3 = \frac{D_{c3} t_2}{D_{c3}} = \frac{0.746 \cdot 10^{-8} \cdot 75000}{0.434 \cdot 10^{-8}} \Rightarrow 2150\text{'} \approx 35 \text{h} 50\text{’},
\]
The calculated times of oxidation for steel Fe-C+14%Cr was used to 4H14N14W2 valve steel as well.

Temperatures and time of annealing oxidation

<table>
<thead>
<tr>
<th>Grade of steel</th>
<th>Temperatures and times of oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>940°C</td>
</tr>
<tr>
<td>4H14N14W2M</td>
<td>117h40’</td>
</tr>
</tbody>
</table>

In order of analysis of carbon concentration distribution \( c^{(1-5)}(x) \) on cross-section decarburised layers, samples after oxidation were cooled together with the furnace till the room temperature was reached. Than the specimens were protected by quartz sand and annealed at 750°C for 2h. Than again cooled to the room temperature, next the scale was mechanically removed and finally the metallographical specimen were prepared, which were etched with nital [6]. Measurements of carbon concentration \( c^{(1-5)}(x) \) were carried out from the surface to core by means of x-ray microprobe analyser JEOL type JCXA 733 at accelerating voltage 15KV.

3. RESULTS AND DISCUSSION

Microanalysis of carbon concentration distribution \( c^{(1-5)}(x) \) from surface to core of oxidised 4H14N14W2M steel reveals the same depth of decarburization c.a 2500 µm except of thin subsurface areas with big carbon concentration (fig.1).

![Fig.1. Distribution of carbon concentration on cross-section decarburised layers at temperatures after time of oxidation: 1 – 940°C/117h40’, 2 – 980°C/63h40’, 3 – 1020°C/35h50’, 4 – 1060°C/20h50’ i 5- 1100°C/12h30’. Steel 4H14N14W2M oxidised in air.](image-url)
The regression of curves of carbon distribution were approximated by average square method \(c^{(1-5)}(x)\) on the cross-section of decarburised layers except of thin subsurface layers (fig.2). These curves enable to calculated carbon diffusion coefficients \(D_c\).

Carbon diffusion coefficients \(D_c\) for followed temperatures were calculated graphically by Boltzman’s-Matano method [4, 5]. This method enables calculation of \(D_c\) values at different \(N(C)\) concentrations using the very same measured \(N(C,x)\) curves.

\[
D_c[c(x)] = -\frac{1}{2\cdot t \left( \frac{dc}{dx} \right)_x} \left\{ \int_{x'}^{\infty} \left( c(x) - c^1 \right) dx + \frac{c(x') - c^1}{c^0 - c^1} \int_{-\infty}^{x} \left( c^0 - c(x) \right) dx \right\} \tag{9}
\]

Changing boundary integration on \((x', -\infty)\) and \((x', \infty)\) in solution of Boltzman’s- Matano dependence from \(c^1\) to \(c^0\) by applying variable \(y = \frac{c(x') - c^1}{c^0 - c^1}\),

where: \(c^0\) i \(c^1\) respectively to carbon concentration in core on depth \(x_1\),

\(t\) – time of diffusion , \(\left( \frac{dc}{dx} \right)_x\) derivative in point \(x'\),

areas surfaces below and above concentration curve \(c(x)\) can be described as:

\[
A = \int_{x'}^{\infty} \left( c(x) - c^1 \right) dx \quad B = \int_{-\infty}^{x} \left( c^0 - c(x) \right) dx \tag{10}
\]

Boltzman’s – Matano method (9) require determination of point on depth \(x^M\) which divided area \(A\) below concentration curve \(c^{(1-5)}(x)\) and above area \(B\) with fulfilled a condition \(A = B\).

Carbon diffusion coefficients \(D_c\) is determined from followed equation

\[
D_c\left[c\left(x^M\right)\right] = -\frac{A}{2\cdot t \left( \frac{dc}{dx} \right)_{x^M}} \tag{11}
\]
Fig. 2. Regression curves of carbon distribution on cross-section decarburised layers of steel 4H14N14W2M oxidised in air at followed temperatures:
1 – 940°C/117h40', 2 – 980°C/63h40', 3 – 1020°C/35h50', 4 – 1060°C/20h50' and 5 – 1100°C/12h30' of steel 4H14N14W2M oxidised in air.

Table 5

<table>
<thead>
<tr>
<th>Temperature, T</th>
<th>940°C</th>
<th>980°C</th>
<th>1020°C</th>
<th>1060°C</th>
<th>1100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time of oxidation t [s]</td>
<td>423600</td>
<td>229200</td>
<td>129800</td>
<td>75000</td>
<td>45000</td>
</tr>
<tr>
<td>Area A=B, [cm²]</td>
<td>23.1·10⁻⁸</td>
<td>31.2·10⁻⁸</td>
<td>22.01·10⁻⁸</td>
<td>20.07·10⁻⁸</td>
<td>8.87·10⁻⁸</td>
</tr>
<tr>
<td>(dc/dx) for x^M</td>
<td>6,985·10⁻²</td>
<td>9,443·10⁻²</td>
<td>9.1·10⁻²</td>
<td>6,26·10⁻²</td>
<td>2,675·10⁻²</td>
</tr>
</tbody>
</table>

Carbon diffusion coefficients D_c in tested steel equals:

\[
D_c^{940°C} = \frac{23.1 \times 10^{-8}}{2 \times 42.36 \times 10^4 \times 6.985 \times 10^{-2}} = \frac{23.1}{591.77} \times 10^{-10} = 3.90 \times 10^{-12}, \quad [\text{cm}^2/\text{s}],
\]
Above calculations reveals, that carbon diffusion coefficients $D_c$ for tested steel are four-times order smaller, than carbon diffusion coefficients calculated from equation (4) for alloy Fe-C+14%Cr and its values increases with rising of temperature from 940 up to 1100°C respectively from $0.97 \times 10^{-12}$ up to $9.14 \times 10^{-12}$ [cm$^2$/s] (table 6):

### Table 6

The carbon diffusion coefficients $D_c$ [cm$^2$/s] for steel 4H14N14W2M and alloy Fe-C+ 14%Cr

<table>
<thead>
<tr>
<th>Temperature, T</th>
<th>940°C</th>
<th>980°C</th>
<th>1020°C</th>
<th>1060°C</th>
<th>1100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4H14N14W2M</td>
<td>3.90·10^{-12}</td>
<td>7.20·10^{-12}</td>
<td>13.0·10^{-12}</td>
<td>22.0·10^{-12}</td>
<td>36.8·10^{-12}</td>
</tr>
<tr>
<td>Fe-C+14%Cr</td>
<td>0.132·10^{-8}</td>
<td>0.244·10^{-8}</td>
<td>0.434·10^{-8}</td>
<td>0.746·10^{-8}</td>
<td>1.242·10^{-8}</td>
</tr>
</tbody>
</table>

### 4. CONCLUSION

The analysis of theoretical and experimental values of thickness of decarburised layers and carbon diffusion coefficients in alloy contains Fe-C+14%Cr and highly alloyed valve steel 4H14N14W2M reveals, that applied method of calculation of time of decarburization ensures the same thickness of decarburised layer oxidised at high-temperatures (i.e. in range from 940 up to 1100°C). These method of calculation was applied also for previous investigated H10S2M valve steel [7]. Whereas oxidation of steel 4H14N14W2M causes formation of thin subsurface layer with large concentration of carbon at simultaneous bigger concentration of alloy elements in valve steel i.e. 14.2%Ni, 2.26%W, 0.32%Mo, 0.60%Mn and 0.60%Si, which in consequences significantly decreases values of carbon diffusion coefficient values. These values are c.a. four times in order smaller in above range of temperatures.

### REFERENCES