The effect of long-term service on carbide transformations in Cr-Mo steels

G.D. Pigrova, B.S. Kabanov, V.M. Sedov

Central Boiler and Turbine Institute
194021, Polytechnicheskaya 24, St. Petersburg, Russia

Time-temperature carbide diagrams are received for several industrial steels with 1%, 2% and 5% chromium content in the range 450-700°C. Areas of existence for various carbides are defined by alloying conditions and a type of the thermal pretreatment. Composition, structure and the amount of carbides formed have been investigated by phase analysis method. The results are obtained for alloying effect on various carbide formation and directivity of carbide reactions.

The rate of metal cooling from austenite has a great influence on the carbide phase diagram. Decrease in cooling rate will promote the formation of more stable carbides. Data of carbide analysis under laboratory ageing are examined together with the results of metal analysis after long term service during 200 thousand hours. Comparing received data for phase diagram with data of the phase analysis of materials after service exposure points the way for increasing the phase stability of materials.

Keywords: Cr-Mo steels, service, carbide transformations

1. INTRODUCTION

Cr-Mo steels are extensively used for service components in industrial equipments. Steels are used over a long period of time and under operation the structural changes occur in the metal which can result in deterioration of mechanical properties of materials 1,2. Results of investigation of phase changes against of temperature and aging time or operation time for different alloying steels can be used for an understanding of mechanism of alloying element redistribution in the course of phase transformations.

At this work the carbide transformations of steels with different Cr-Mo content after commercial operating over a long period of time have been investigated.
2. EXPERIMENTAL DETAILS

Steels of three compositions with different Cr-Mo content has been investigated (Table 1). After long-term service the studies of steels were conducted over the specimens taken from parts of equipment with different service time.

Table 1

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>12MoCr</td>
<td>&lt; 0.15</td>
<td>0.4 – 0.6</td>
<td>0.40 – 0.55</td>
<td>0.4 – 0.7</td>
<td>0.15 – 0.30</td>
</tr>
<tr>
<td>10Cr2Mo1</td>
<td>0.08 – 0.13</td>
<td>2.0 – 2.5</td>
<td>0.9 – 1.1</td>
<td>0.3 – 0.6</td>
<td>0.17 – 0.37</td>
</tr>
<tr>
<td>15Cr5Mo</td>
<td>&lt; 0.15</td>
<td>4.5 – 6.0</td>
<td>0.45 – 0.60</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Carbide transformations have been studied by phase analysis method. Carbides were extracted from matrix by means of electrochemical method in methanol base electrolyte. Obtained powders were studied by X-ray analysis in Co-radiation. Quantity and composition of carbides were determined by means of chemical analysis of obtained sediments.

3. RESULTS

3.1. 12MoCr steel

Carbides of three types are generated in 12MoCr steel: M₃C cementite on iron base, M₂C carbide on molybdenum base and a complex cubic carbide of M₂₃C₆ type. Data of phase analysis of 12MoCr steel after long-term service of metal under continuous use at temperatures of 510⁰C (Table 2).

Table 2

<table>
<thead>
<tr>
<th>Time, h</th>
<th>Carbides</th>
<th>Time, h</th>
<th>Carbides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial condition</td>
<td>M₃C</td>
<td>101000</td>
<td>M₂C, M₂₃C₆</td>
</tr>
<tr>
<td>68600</td>
<td>M₃C</td>
<td>132000</td>
<td>M₂₃C₆, M₂C, M₃C</td>
</tr>
<tr>
<td>79300</td>
<td>M₂C, M₂₃C₆</td>
<td>152000</td>
<td>M₂₃C₆, M₂C, M₃C</td>
</tr>
<tr>
<td>84300</td>
<td>M₂C, M₂₃C₆</td>
<td></td>
<td></td>
</tr>
<tr>
<td>98900</td>
<td>M₂C, M₂₃C₆</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

With increase in service hours the cementite decomposition occurs. Data of X-ray analysis show that M₂C carbide formation takes place after 70-80 thousand hours and after 100 thousand hours M₂₃C₆ carbide is formed which becomes the main carbide in following service
during 130-150 thousand hours. Precipitation of Mo is increasing uniformly according to service time while Cr precipitation changes less noticeable.

Investigation of metal phase composition after operation during 250 thousand hours at 400°C gave no change in comparison with the starting condition.

Thus, during long-term service of 12M0Cr steel at 510°C the following sequence of carbide transformations is being observed:

\[ M_3C \rightarrow M_3C + M_2C \rightarrow M_3C + M_2C + M_{23}C_6 \rightarrow M_2C + M_{23}C_6 \]

3.2. 10Cr2Mo1

10Cr2Mo1 steel is investigated after operating period of time of 80-200 thousand hours at temperature range of 490-530°C (Table 3). The main carbides after operational time are complex cubic carbides of \( M_{23}C_6 \) and \( M_6C \), cementite is completely absent. Chromium and molybdenum content is increasing as compared with initial one. The most considerably is increasing molybdenum content. Obtained data regarding to carbide state of 10Cr2Mo1 steel during operational time is conforming to data obtained by investigation of 2,25Cr-1.0Mo steel 3-5.

Table 3
Phase composition of 10Cr2Mo1 steel after long-term service

<table>
<thead>
<tr>
<th>Time, ths h</th>
<th>Carbides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial condition</td>
<td>( M_{23}C_6, M_7C_3, M_6C, M_2C )</td>
</tr>
<tr>
<td>80</td>
<td>( M_6C, M_7C_3, M_{23}C_6 )</td>
</tr>
<tr>
<td>100</td>
<td>( M_{23}C_6, M_2C, M_6C, M_7C_3 )</td>
</tr>
<tr>
<td>120</td>
<td>( M_2C, M_{23}C_6, M_6C, M_7C_3 )</td>
</tr>
<tr>
<td>200</td>
<td>( M_{23}C_6, M_6C, M_2C, M_7C_3 )</td>
</tr>
</tbody>
</table>

3.3. 15Cr5Mo steel

Specimens are been cut from tubes after different operating conditions at temperature range of 425-530°C. There have been recognized no change in metal after operating at 425-450: carbides of \( M_2C \), \( M_{23}C_6 \) and \( M_7C_3 \) types are available. Cr content in carbides is of 0.4%, Mo content is of 0.2%. In metal which has been in operation about 150 thousand hours at temperature of 520-530°C besides above carbides has been recognized \( M_6C \) carbide which has been the main phase at some samples. Molybdenum content is increasing in carbides up to 0.35-0.40% that corresponds to such a condition of metal.
4. CONCLUSIONS

1. Carbides of $M_3C$, $M_2C$, $M_{23}C_6$, $M_7C_3$ and $M_6C$ types are being formed in Cr-Mo steels. Their stability and relationship are determined by conditions of alloying and operating. The main directivity of carbide reactions in steels is:

   12MoCr: 
   $$M_3C \rightarrow M_2C + M_2C \rightarrow M_2C + M_{23}C_6$$

   10Cr2Mo1: 
   $$M_3C \rightarrow M_2C + M_2C + M_7C_3 \rightarrow M_{23}C_6 + M_6C,$$

   15Cr5Mo: 
   $$M_2C + M_2C + M_2C + M_7C_3 + M_{23}C_6 \rightarrow$$
   $$M_2C + M_{23}C_6 + M_6C.$$

2. Forming of complex cubic carbides of $M_{23}C_6$ and $M_6C$ types can be seen mainly during the long-term service. This corresponds to molybdenum extraction into carbide phases up to 60-70% of its initial content in steels.

REFERENCES