Mechanical properties characterization of a modified HP-type heat-resistant alloy

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ABSTRACT
The present research has designed a new HP-type heat-resistant alloy modified by adding niobium, cobalt and tungsten, reducing carbon, manganese, silicon and iron, and increasing molybdenum, and investigated the mechanical properties by means of metallurgical microscopy, Brinell hardness test, scanning electron microscopy, tensile test, impact test and creep-rupture strength test. The results show that the modified alloy has a fine microstructure consisting of an austenitic matrix with finely dispersed carbides, and an optimized combination of tensile strength (705 MPa), ductility, impact energy (53 J), and hardness (205 HRB) at room temperature and creep-rupture strength at elevated temperatures, attributed to the exceptionally fine scale of the austenitic microstructure and the associated tiny carbides.

KEYWORDS
Heat-resistant alloy; Austenitic steels; Elevated temperature; Microstructure; Mechanical properties.

INTRODUCTION
The heat-resistant (H-series) alloys now have been developed with high levels of Cr and Ni to provide the corrosion resistance, strength and austenite stability necessary for applications such as furnace tubes in the chemical and petrochemical industries. HP (Fe-25Cr-35Ni based) alloy is a kind of fully austenitic iron-nickel-chromium heat resisting steels, and extensively used in the petrochemical industry with extremely high temperatures. Modified-HP alloys are essentially Fe-25Cr-35Ni austenitic heat-resistant alloys dominating the market for steam reformer and steam cracker furnace tubes at elevated service temperatures above 850 to 1050°C. Starting with a base of iron, there are two important alloying elements in the alloys: Cr for oxidation resistance and Ni for strength and ductility. Nb, a strong carbide former, has been used in centrifugally cast tubes to form NbC precipitates for carbide stability to increase creep strength and creep ductility, as well as carburization resistance. Si is also added in conjunction with Ni to further increase the resistance to carburization, and the suitable Ni content is at a high level of 35 wt. % to prevent any embrittling sigma to form from the Si where the optimum carburization resistance and strength occur in the Fe-Ni-Cr alloy system.

Based on the fundamental theory of effect of alloying elements, the present study focuses on chemical composition design of a new HP-type heat-resistant
alloy modified with certain alloying elements and characterizes its excellent mechanical properties, with the purpose of improving performance parameters of furnace tubes in the chemical and petrochemical industries.

EXPERIMENTAL PROCEDURE

The chemical composition of the modified HP-type heat-resistant alloy given in TABLE 1 is designed according to the effect of alloying elements\textsuperscript{131}, and modified by adding Nb, Co and W, reducing C, Mn, Si and Fe, and increasing Mo. Metallurgically speaking, Ni tends to make the atomic structure “austenitic”, as well as small contents of some other austenitizing elements including C, N, Co and Mn. Furthermore, Ni can increase ductility and resistance to both carburization and nitriding, while Cr can enhance the high temperature strength and resistance to both carburization and oxidation. In order to obtain the expected mechanical properties, contents of some elements were limited to lower levels. Carbon is always present as small, hard particles called carbides\textsuperscript{141}, and was nevertheless reduced to 0.06 wt. % to protect ductility. Mn can improve hot workability, however, it is mildly detrimental to oxidation resistance so that it is limited to 0.80 wt. %. As one of effective elements that contribute carburization resistance, Si yet decreases the solubility of carbon in the alloys. Therefore, a restriction is also given to the Si content. Considering the weldability, S and P are restricted to a very low content of less than 0.03 wt. %. Some carbide forming elements are introduced in the composition design to strengthen the alloy. Nb is added at the 0.8 wt. % level for strength, and the limited amount can expectedly less harm oxidation resistance, practically speaking around 980°C and higher. As a large, heavy atom, W can react with the carbon to form a hard particle that may incorporate other carbide forming elements such as Cr. Co can not only improve strength slightly, but also enhance oxidation resistance at elevated temperatures. Ti is added in small amounts, about 0.1%, advantaging both strength and deoxidation of the alloy. Mo is another large, heavy atom that can help weldability and increase high temperature creep-rupture strength, and the Mo content is increased to 1.8 wt. %. In addition, a small amount of N can raise the tensile and yield strengths. As a deoxidizing agent for refining, Al is also used at a level of 0.4 wt. % for age hardening as a consequence of the precipitation of a ductile intermetallic phase Ni\textsubscript{3}Al.

The designed alloy was melted by vacuum-induction-melting (VIM) which can minimize the amounts of oxygen and nitrogen to get a better control on active atoms including Al and Ti, with less pollution of oxidation and dregs. Electro-slag-refining (ESR) was then employed to eliminate defects generated during the course of VIM, for example, coarse grains, porosity and segregation of alloying elements. The ingot with a diameter of 360 mm was forged with the initial forging temperature of 1150°C and the final forging temperature of 1000°C. The forged alloy was reheated to 1180°C for solution treatment holding for 4h and then water cooled down to the room temperature.

The specimens were machined with dimension of 12×12×15 mm, ground and polished using standardized techniques, and then etched in 3 vol. % natal-alcohol solution. Metallurgical observation of the alloy specimens was carried out on an XJP-100 metallurgical microscope, and the grain grade measurement of the microstructure was operated by means of a PL-A600 digital video system and a DT-2000 image analysis software. An HB-3000 Brinell tester was used to measure the hardness of 3 identical specimens and each specimen was tested for 5 times. For mechanical properties measurement, 5 identical specimens were prepared for each individual event, and average values were calculated. AZ1200H universal materials testing machine (Zwick GmbH & Co. KG, Germany) was employed to accomplish the tensile test of the alloy specimens with standard dimension. The broken specimens

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Nb</th>
<th>N</th>
<th>W</th>
<th>Co</th>
<th>Al</th>
<th>Ti</th>
<th>B</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mod. HP</td>
<td>0.06</td>
<td>0.8</td>
<td>0.6</td>
<td>&lt;0.03</td>
<td>&lt;0.02</td>
<td>35</td>
<td>25</td>
<td>1.8</td>
<td>0.8</td>
<td>0.24</td>
<td>1.8</td>
<td>2.2</td>
<td>0.4</td>
<td>0.10</td>
<td>0.01</td>
<td>≤31</td>
</tr>
<tr>
<td>HP</td>
<td>0.35-0.75</td>
<td>≤2.0</td>
<td>≤2.5</td>
<td>≤0.03</td>
<td>≤0.03</td>
<td>33-37</td>
<td>24-28</td>
<td>≤0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>bal</td>
</tr>
</tbody>
</table>
were end-to-end jointed tightly to measure the corresponding parameters and to calculate the percentage elongation and reduction of area after fracture. Charpy impact test was conducted using a JBN-300 pendulum impact testing machine. The specimens were machined with the dimension of $10 \times 10 \times 55$ mm and a notch depth of 2 mm. The fractographies of specimens after tensile and impact tests were characterized by an EVO MA 15 scanning electron microscope (SEM) (Carl Zeiss AG, Germany) operated at 20 kV. A CSS-2900 electronic creep relaxation testing machine (Changchun institute of testing machine, China) was supplied to characterize the high-temperature creep-rupture strength of the designed alloy. The specimens were loaded by a stress of 45 MPa at 900°C, and by a stress of 18 MPa at 982°C, respectively.

**RESULTS AND DISCUSSION**

Figure 1 shows the microstructure of the modified HP-type heat-resistant alloy at room temperature. It can be seen that the austenite grains distribute closely and tightly, a large numbers of which are equiaxed grains. As well known, the austenitic alloys all have much greater creep-rupture strength than the ferritics, and are more ductile and generally easier to fabricate at room temperature. A large amount of small, hard carbide particles exist in the austenite matrix in the vicinity of grain boundaries. These are chemical compounds of carbon with Cr, Mo, W, Ti, or Nb. A good combination of strength and creep-rupture resistance at high temperature can be certainly predicted from the fine mixture of equiaxed grains of austenite and dispersed particles of carbides.

TABLE 2 presents the mechanical properties of the modified HP-type heat-resistant alloy at room temperature. Obviously, the yield strength of the modified alloy is observably higher than that of the normal HP alloy at room temperature, and the tensile strength is similarly higher than that of the normal HP alloy. The strength has been largely improved on account of addition of alloying elements such as Nb, Ti, which result in precipitation of $M_23C_6$ and MC-type carbides. For instance, NbC carbide plays a significant role in improving the mechanical properties. Hardness in excess of 200 HBW is achieved, primarily as a result of the fine scale of the microstructure. Meanwhile, due to decreasing sharply the carbon content, plasticity has been largely improved.

Due to a very subtle carbide distribution, niobium carbides mixed with chromium carbides along the grain boundaries, titanium and other carbides mainly dispersed in the matrix, not only has the strength been increased but also the ductility. Elongation and reduction of area after fracture of the designed alloy characterize excellent ductility and toughness as shown in TABLE 2, as well as in Figure 2 and 3. The abundant, tiny dimples in the fractography show that the tensile failure and the impact break are both taken effect by mechanism of gliding fracture. In fact, it is the decrease in the carbon content that potentially leads to an improvement in impact property.

TABLE 3 expresses the mechanical properties of the modified HP-type heat-resistant alloy at elevated temperatures. Dispersion of fine-particled carbides or intermetallics in the austenite matrix can result in high creep

**TABLE 2 : Mechanical properties of the modified HP-type heat-resistant alloy at room temperature.**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Yield strength / Mpa</th>
<th>Tensile strength / Mpa</th>
<th>Elongation / %</th>
<th>Hardness / HBW</th>
<th>Impact energy / J</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mod. HP</td>
<td>335</td>
<td>725</td>
<td>52</td>
<td>205</td>
<td>53</td>
</tr>
<tr>
<td>HP</td>
<td>270</td>
<td>550</td>
<td>&lt;15</td>
<td>190</td>
<td>—</td>
</tr>
</tbody>
</table>
strength. Nb and Ti are present in form of carbides and nitrides to optimize the structure of grain boundary\cite{15}, and the rare-earth element boron can suppress silicon trapped at the grain boundary and oxygen segregation. In this designed alloy, solubility of carbon in austenite is lowered by the large amount of Cr and Ni. In that way, the secondary carbides growth slowly and σ phase formation becomes difficult on account of the low carbon concentration. Apart from the advantages above, appropriate Nb addition can also improve the creep-rupture strength. Previous study\cite{16,17} also showed that larger amounts of carbide typically result in improved creep properties, and that the presence of both $M_{23}C_6$ and MC carbides are beneficial for high-temperature creep properties.

**CONCLUSIONS**

It is concluded that in the present study, a new modified HP-type heat-resistant alloy with optimized com-
bination of tensile strength, ductility, toughness, hardness at room temperature and creep-rupture strength at elevated temperatures, can be successfully designed by adding Nb, Co and W, reducing C, Mn, Si and Fe, and increasing Mo. The modified HP-type heat-resistant alloy can provide favourable performance parameters for furnace tubes in the chemical and petrochemical industries.

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REFERENCES