Precipitation Behaviors and Strengthening of Carbides in H13 Steel during Annealing

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Deploying optical microscopy, transmission electron microscopy, electron diffraction and energy dispersive spectrometer analysis. This article analyze the categories and shapes of carbides of three different positions in H13 ingot after annealing: upside, middle and bottom of ingot. It is found that the microstructure of H13 after annealing is composed of granular pearlite+ small amounts of ferrite and carbide phase. The categories of carbides mainly include M₇C₃ and MC, precipitation temperatures of which are figured out through thermodynamic calculation. Through the test of mechanical properties, it is found sample at the bottom has the optimal mechanical property. Through statistics of amounts and average sizes of precipitates and calculation of precipitation strengthening, it is found that, from upside to bottom of H13 after annealing, the size of precipitates decreases with increase of precipitation volume fraction, and contributions of precipitates to yield strength enhance gradually. [doi:10.2320/matertrans.M2014452]

(KEYWORDS: precipitates, H13 after annealing, thermodynamic calculation, precipitation strengthening)

1. Introduction

H13(4Cr5MoSiV1), adopted by AISI standard, is regarded as a kind of air-cooling hardening hot work die steel which is widely applied in forging mold, casting mold and hot extrusion mold manufacturing. It has good heat resistance, toughness and hardenability, with the main alloying elements of Cr, Mo and V.¹ Compared with importing H13 steel, there are still many deficiencies in domestic H13 steel: such as serious banded segregation, cracks appeared when using, low impact toughness and so on.² However, spheroidal annealing process can effectively homogenize organization and improve the mechanical properties of steel.

Owing to more alloying elements and sophisticated components in H13, the material organization, especially categories of carbides change obviously during heat treatment. It is usually considered that there exist MC, M₆C, M₇C₃ and M₁₂C₆ carbides during heat treatment. Literature³ reports that there exist M₁₂C₆, M₆C and MC without M₂₃C₆; Liu Shuxun⁴ found M₁₂C₆ rather than M₃C₅ in 5% Cr hot work die steel, while Tsuji⁵ and Mebarki⁶ reported that there exist M₃C₅, MC, M₁₂C₆ and M₆C carbides in 5% hot work die steel. Some scholars⁷⁻⁹ believe that the reason of this difference is related to heat treatment temperatures. M₃C₅ appears below 873 K, and it transforms to M₁₂C₆ when temperature rises above 873 K.

Research on effect of alloying elements on H13 steel is not deep enough. Literature¹₀ regards Cr as the main element to improve hardness and strength of materials. Cr exists in M₈C carbides, improving heat resistance and hardenability of steel.¹¹ V can refine grain and improve high temperature stability of steel, and combine with C to form MC carbides.¹²

This article deploys the methods of carbon membrane extraction replica to make TEM (Transmission Electron Microscopy) sample in order to observe the morphologies and categories of precipitates. Through test and statistics of carbides after annealing, types, particle size distribution, average diameter and the influence of precipitates on mechanical properties are obtained.

2. Experimental Procedure

2.1 Experiment methods

This experiment deploys the methods of H13 smelting process, after tapping from EAF (Electric Arc Furnace) and smelting in LF (Ladle Furnace), VD (Vacuum Degassing) and ESR (Electroslag Remelting), φ440 mm × 3000 mm ingot of 1t is available. Forge the ESR ingot to a diameter of 220 mm bar stock. The forging temperature is 1373 K. Annealing for 15 hours at 1133 K, analyze compositions of nonmetallic elements by using Carbon Sulfur Analyzer and Nitrogen Oxygen Analyzer. The compositions of metallic elements are tested by chemical titration. The result is shown in Table 1.

2.2 Sample, sample preparation and testing equipments

The sampling position is shown in Fig. 1. Sample from upside, middle and bottom of bar stock after annealing, the size of which are φ220 mm × 60 mm respectively. In each position, get impact value samples (charpy V), tensile samples and metallographic samples in 1/2 radius of cross...

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Using carbon extraction replica to make sample preparation, the specific step is, firstly, put the polishing metallographic samples into 8% nitric acid alcohol solution to corrode, then evaporate it with a layer of about 20~30 nm thick carbon film. Finally, extract precipitates by using 10% nitric acid alcohol solution, and the carbon membrane is gained by copper net. Morphologies of precipitates can be observed by using TEM after the copper net is being dried.

Deploying ZBC2452-B Pendulum impact testing machine, the impact values of three samples are tested. Deploy CMT4105 electronic universal testing machine to test tensile strength, yield strength, elongation and area reduction rate. DHB-3000 Brinell hardness (HBW2.5/187.5) tester is used to measure hardness of samples. In addition, observe organizations of steel by using 9XP-PC optical microscopy, and observe the morphology of carbides of three samples by using High Resolution Transmission Electron Microscope (F30). Accelerating voltage of TEM is 300 kV.

3. Results and Discussions

3.1 Microstructure observation

The microstructures of H13 after annealing are composed of granular pearlite, small amounts of ferrite and carbide phase. The microstructures of different positions are shown in Fig. 2.

From Fig. 2, it can be seen that microstructures of middle and bottom are more uniform than those of upside, where there exist large eutectic carbides and element segregation and banded carbides. It is also found that there are lots of carbides segregated among dendrites. These carbides become the source of microsegregation during solidification process. The enrichment of large amounts of metallic elements among dendrites is the direct reason of formation of banded segregation after casting. The different degrees of segregation of upside, middle and bottom are owing to different solidification speed during ESR. From upside to bottom of H13 ingot, solidification speed increases so that degree of upside segregation is more serious than that of bottom’s.

3.2 Mechanical properties

From mechanical property of Table 2, it can be seen that the bottom of H13 ingot after annealing has the optimal comprehensive mechanical property. It sets solid foundation on the consequent quenching and tempering process. The change of elongation and hardness show that the middle of H13 has the best ductility. From upside to bottom, the change of property is as follows, tensile strength and yield strength both have tendency of increasing, instructing that strength increases as well as plasticity becomes better. The increase of impact value indicates that the toughness improves severely from upside to bottom of H13 ingot. In conclusion, the bottom of H13 ingot has the best comprehensive mechanical property.

3.3 The morphologies and types of H13 precipitates

Through electron diffraction and EDS (Energy Dispersive Spectrometer) analysis, it can be concluded that precipitate types after annealing are mainly M23C6, V8C7 and VC, the morphologies of which are shown in Fig. 3, Fig. 4 and Fig. 5.
From Fig. 3, 4 and 5, it can be seen that spherical particles are Cr-rich $M_23C_6$ carbides. This kind of carbides are more than 200 nm; The shapes of $V_8C_7$ are 100 $\times$ 50 nm short bar-like. VC is square-like carbides, smaller than 100 nm. Due to short-time stay in $\delta$-Ferrites\(^{15}\) and high speed of solidification during ESR, the author consider that H13 directly enters austenite area after solidification. The austenite area is between solid line 1755 K\(^{17}\) and Ar1 line 1048 K.\(^{18}\)

The solubility product of Cr$_{23}$C$_6$ in austenite is deduced as follows.

Firstly, the Gibbs free energy of formation of Cr$_{23}$C$_6$ in austenite is obtained through following chemical reaction.\(^{19,20}\)

$$23\text{Cr}(s) + 6\text{C}(s) = \text{Cr}_{23}\text{C}_6(s)$$

$$\Delta G^\circ = -309600 - 77.4T$$ \hspace{1cm} (1)

$$\text{Cr}(s) = [\text{Cr}] \hspace{1cm} \Delta G^\circ = 19250 - 46.86T$$ \hspace{1cm} (2)

$$[\text{Cr}]_L = [\text{Cr}]_S \hspace{1cm} \Delta G^\circ \approx 1046 \text{ J/mol}$$ \hspace{1cm} (3)

$$[\text{Cr}]_S = [\text{Cr}]_F \hspace{1cm} \Delta G^\circ \approx -418 \text{ J/mol}$$ \hspace{1cm} (4)

According to formula (2)–(4), the Gibbs free energy of solid Cr dissolved in austenite is obtained as Formula (5).

$$\text{Cr}(s) = [\text{Cr}]_F \hspace{1cm} \Delta G^\circ = 19878 - 46.86T$$ \hspace{1cm} (5)

Then, according to equilibrium solubility product formula of graphite dissolved in austenite,\(^{21}\)

$$\lg[C]_F = 1.595 - \frac{1762}{T}$$ \hspace{1cm} (6)

The Gibbs free energy of graphite dissolved in austenite is obtained as follows.
\[ C(s) = [C]_y \quad \Delta G^\theta = 33735 - 30.532T \]  

The formation reaction of Cr$_{23}$C$_6$ in austenite is calculated by using Formula (1)–(7). The metallic elements and Carbon are deployed 1% solution as standard state.

\[ 23[Cr]_y + 6[C]_y = Cr_{23}C_6(s) \quad \Delta G^\theta = -969204 + 1183.512T \]  

Finally, the solubility product of Cr$_{23}$C$_6$ dissolved in austenite is obtained as follows according to Formula (8).

\[ \ln([Cr]_y^{23} \cdot [C]_y^6) = 142.35 - \frac{116574.93}{T} \]  

Formula (9) can be converted to Formula (10).

\[ \lg([Cr]_y^{23} \cdot [C]_y^6) = 61.81 - \frac{50618.73}{T} \]  

According to literature, the solubility products of VC dissolved in austenite and V$_8$C$_7$ dissolved in ferrite are as follows,

\[ \lg([V]_y^{12} \cdot [C]_y^6)_y = 6.72 - \frac{9500}{T} \]  

\[ \lg([V]_y^{12} \cdot [C]_y^{0.875})_y = 5.65 - \frac{9340}{T} \]  

Put \( [Cr]_y = 5.13 \), \( [V]_y = 0.99 \), \( [C]_y = 0.39 \) into formula (10), (11) and (12), and the precipitation temperatures of V$_8$C$_7$, VC and Cr$_{23}$C$_6$ are calculated as 1553.8 K, 1331.8 K and 1056.0 K respectively.

From Fig. 6, when lowering H13 from austenite temperature to room temperature, the solubility product of Cr$_{23}$C$_6$ decreases rapidly. Although precipitation temperature of Cr$_{23}$C$_6$ is lower than that of VC and V$_8$C$_7$, its precipitation amount is more than that of V$_8$C$_7$ and VC.

The precipitation sequence of three types of carbides is V$_8$C$_7$ > VC > Cr$_{23}$C$_6$. It can be concluded that V$_8$C$_7$ starts to precipitate during ESR process before forging, while VC and Cr$_{23}$C$_6$ start to precipitate during forging process and annealing. As annealing for 15 hours at 1133 K, it can be seen that V carbides do not have obvious tendency of growing up, while Cr carbides grow up obviously during annealing.

3.4 The statistics of precipitate amounts and calculation of precipitation strengthening

Figure 7 shows the precipitate morphologies of three positions in H13. It can be seen that the sizes of precipitate particles are large, and distribute unevenly. The amounts of precipitates become larger from upside to bottom of ingot. The distribution and size of precipitates have main effect on final mechanical properties of H13.

In order to obtain precipitate distribution accurately, 45 pieces of pictures of 58.8 µm$^2$ (large visual field) and 45 pieces of pictures of 14.5 µm$^2$ (small visual field) are taken into statistics in this experiment. The result is shown in Table 3.

From Fig. 7 and Table 3, it can be seen that the amount of precipitates increases and average particle size becomes smaller from upside to bottom of H13 ingot. The main reason lies in the different solidification speed during ESR process. The bottom of ingot has the highest solidification speed. Combined with Fig. 2, it can be concluded that the more rapid the solidification is, the microstructures of steel are more even, and the precipitates distribute more dispersively. Therefore, the comprehensive mechanical property is greatly improved.

This article deploys the methods of McCall-Boyd to measure volume fraction of dispersive second phase. This method is required to measure diameter of each precipitate in a certain area of photos taken by TEM. Then, the equivalent average diameters are available. In addition, the number of precipitates must be calculated.

The volume fraction of precipitates can be calculated as follows

\[ f = \left( \frac{1.4\pi}{6} \right) \cdot \left( \frac{N D_{\text{mean}}^2}{A} \right) \]  

Where A is area of measured photos; $D_{\text{mean}}$ is equivalent average diameter. According to Theory of Gladman, this
The article adopts following formula (14) to calculate increment of precipitation strengthening of H13 after annealing.

$$\Delta \sigma_p = 0.8995 \times 10^4 \frac{f_i}{d} \ln(2.417d)$$  (14)

Where $d$ is equivalent average diameter of precipitates, nm; $f_i$ represents volume fraction of precipitates.

According to increment of precipitation strengthening of different size ranges proposed by Yong Qilong (23), the total increment of precipitation strengthening can be summed up by increment of precipitation strengthening of different size ranges. The result is shown in Table 4.

From Table 5, it can be concluded that the size of precipitates decreases and volume fraction increases from upside to bottom of ingot. The contributions to yield strength of different positions are also improved gradually. Combined with experiment results of Table 2, it can be seen that the strength and toughness of H13 are both improved as precipitates are getting finer and dispersive. The middle of ingot has the best ductility, but the bottom of ingot has the worst. It is explained that excessive precipitates are not benefit for ductility of H13. Therefore, in the actual production process, through adjusting ESR, forging and

<table>
<thead>
<tr>
<th>Sample</th>
<th>Visual field area, $A/\mu m^2$</th>
<th>The amount of photos</th>
<th>The amount of precipitates</th>
<th>The total amount of precipitates</th>
<th>The amount of precipitates per area/ $\mu m^2$</th>
<th>Average size, $D/\mu m$</th>
<th>Total average size, $D/\mu m$</th>
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<tbody>
<tr>
<td>1/2 radius of upside</td>
<td>58.8</td>
<td>15</td>
<td>841</td>
<td>1142</td>
<td>1.04</td>
<td>278.83</td>
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<tr>
<td>1/2 radius of middle</td>
<td>14.5</td>
<td>15</td>
<td>301</td>
<td>452</td>
<td>1.38</td>
<td>229.80</td>
<td>225.88</td>
</tr>
<tr>
<td>1/2 radius of bottom</td>
<td>58.8</td>
<td>15</td>
<td>1366</td>
<td>2140</td>
<td>1.95</td>
<td>253.47</td>
<td>225.88</td>
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</table>

<table>
<thead>
<tr>
<th>Size, $D/\mu m$</th>
<th>Amount</th>
<th>Average diameter, $D/\mu m$</th>
<th>Volume fraction, $f_i$</th>
<th>Yield strength increment, $\Delta \sigma_p /MPa$</th>
</tr>
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<tbody>
<tr>
<td>Sample position</td>
<td>upside</td>
<td>middle</td>
<td>bottom</td>
<td>upside</td>
</tr>
<tr>
<td>Average size, $D/\mu m$</td>
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<td>230.42</td>
<td>225.88</td>
<td></td>
</tr>
<tr>
<td>Volume fraction, $f_i/%$</td>
<td>8.11</td>
<td>11.90</td>
<td>12.26</td>
<td></td>
</tr>
<tr>
<td>Yield strength increment, $\Delta \sigma_p /MPa$</td>
<td>191.77</td>
<td>218.99</td>
<td>244.20</td>
<td></td>
</tr>
<tr>
<td>Actual yield strength, $\sigma_y/MPa$</td>
<td>302.62</td>
<td>317.53</td>
<td>316.01</td>
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<tr>
<td>Proportion of precipitation strengthening accounted for actual yield strength/%</td>
<td>63.37</td>
<td>68.97</td>
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</table>

<p>| Table 3 | The statistics of amounts and average sizes of upside, middle and bottom of H13. |
|----------------|----------------------------------|---------------------|---------------------------|-----------------------------|</p>
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<p>| Table 4 | Contribution of precipitate strengthening to size and volume fraction of precipitates. |
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annealing processes, i.e. adjusting cooling rate or ratio of alloying elements, based on obtaining uniform organization, control the amounts of precipitates in order to obtain H13 steel with optimal property.

4. Conclusion

(1) The types of precipitates of H13 are mainly Cr-rich $\text{M}_2\text{C}_6$ and V-rich MC, the size of which are about 200 nm and 100 nm. The shapes are sphere-like and square-like. The precipitation temperatures of $\text{V}_8\text{C}_7$, VC and $\text{Cr}_2\text{C}_6$ are 1553.8 K, 1331.8 K and 1056.0 K respectively through thermodynamic calculations.

(2) From upside to bottom of H13 ingot after annealing, precipitates are getting finer, volume fraction increases and contribution to yield strength is improved.

(3) The contribution to yield strength of precipitates is $291 \pm 344$ MPa, which takes up $63 \pm 77\%$. As precipitate amount increases and particle size becomes finer, the comprehensive mechanical properties are improved. The bottom of H13 ingot has optimal mechanical property. As large size and amount of carbides precipitating during annealing, too many precipitates are not benefit for ductility of H13, but has little effect on toughness and strength.

Acknowledgments

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