PHASE TRANSFORMATIONS IN HAFNIUM-BEARING CAST NICKEL-BASE SUPERALLOYS

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Ni$_3$Hf phase in Hafnium-bearing cast nickel-base superalloy was identified. It was found that following reactions occurred in these alloys during thermal exposure,

\[ \text{Ni}_3\text{Hf} + \gamma(\text{C}) \rightarrow \text{MC}_{(2)} + \gamma \]
\[ \gamma'(\text{Hf}) + \gamma(\text{C}) \rightarrow \text{MC}_{(2)} + \gamma \]

The effects of these reactions on the microstructure stability of the alloys were discussed.

INTRODUCTION

At the end of 60's, a lot of scientific research works on microstructure for Hafnium-bearing alloys has been carried out. Among them, Kotval\(^{(1)}\), Dahl\(^{(2)}\) and Collins\(^{(3)}\) had described the change of the amount of eutectic (\(\gamma + \gamma'\)), the composition and morphology of MC carbide in Hafnium-bearing alloys. Up to date, some problems on Ni$_3$Hf phase and its transformation in thermal exposure have not been revealed. The precipitation character of secondary MC\(_{(2)}\) carbide, the relation between its character and the stability of their microstructure have not been reported. The object of this investigation is to study the phase transformation of three Hafnium-bearing cast alloys, and to pay special attention to transformation of Ni$_3$Hf phase and precipitation of secondary MC\(_{(2)}\).

MATERIALS AND PROCEDURES

Chemical compositions of the superalloys studied are listed in Table 1.
Table 1. Chemical Composition of Studied Alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Cr</th>
<th>Ni</th>
<th>Co</th>
<th>W</th>
<th>Mo</th>
<th>Al</th>
<th>Ti</th>
<th>Nb</th>
<th>Ta</th>
<th>Hf</th>
<th>C</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10.0 base</td>
<td>9.59</td>
<td>4.78</td>
<td>3.57</td>
<td>5.42</td>
<td>2.28</td>
<td>—</td>
<td>—</td>
<td>1.59</td>
<td>0.09</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>5.62</td>
<td>n</td>
<td>11.70</td>
<td>9.49</td>
<td>2.21</td>
<td>0.08</td>
<td>1.35</td>
<td>3.14</td>
<td>1.74</td>
<td>0.110</td>
<td>0.037</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>9.64</td>
<td>n</td>
<td>9.84</td>
<td>10.13</td>
<td>0.57</td>
<td>5.85</td>
<td>1.71</td>
<td>—</td>
<td>2.43</td>
<td>1.68</td>
<td>0.130</td>
<td>0.02</td>
</tr>
</tbody>
</table>

In order to study the effects of temperature and time on phase transformation, specimens were exposed for 1000 hours at 850, 900, 950, 1000 and 1050°C, respectively. In order to study phase transformation at high temperature, the specimens were soaked at a range of 1100—1240°C, at 20°C intervals.

The cast-and exposed-specimens were studied by metallography, electron diffraction, X-ray and chemical phase analysis. Mono-phase revelation method is used. For Ni₅Hf phase, 10ml nitric acid, 20ml hydrofluoric acid, 30ml glycerin solution is used to etch electrolytly. Current density is less than 0.025A/cm², 3~5 seconds. For secondary carbide MC₁₁, Samples are tinted at 380—400°C/30min. In this condition the secondary MC₁₂ appeared as dark-blue, the secondary M₅C and M₂₃C₆ not be revealed either. Carbide extraction is carried out with 50ml hydrochloric acid, 100ml glycerin, 1050ml methyl alcohol solution at −5°C, current density 0.01A cm².

EXPERIMENTAL RESULTS

Cast Microstructure

At as-cast condition, hafnium-bearing nickel-base alloys consist of γ, γ', eutectic (γ+γ'), MC, M₀B₂, M₂SC and Ni₅Hf. The formation process of these phase and their revealing distinguishing technique refer to (4). In this paper two phases related closely to Hafnium (that is MC₁₁, and Ni₅Hf) were examined in detail.

Primary MC₁₂ Carbide. Hf rich primary MC₁₁ was also formed in Hf-bearing alloys, beside Nb⁺, Ta⁺, Ti-rich primary MC₁₁. Generally both carbides are isolated, but sometimes conjugated, i.e. MC₁₁ exists at the centre and Hf-rich MC₁₂ at its edge (Fig.1). Both carbides in three alloys were systematically studied by electron microprobe, quantitative metallography and phase analysis methods. The results were listed in Table 2.
Table 2 Composition and Amount of Both MC in Various Alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Kinds of MC</th>
<th>Formula of MC</th>
<th>MC Amount in Alloys vol%</th>
<th>HF Content in MC wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MC_{(1)} (Ti.75 W.13 Mo.10 Hf.02)C</td>
<td>0.42</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MC_{(2)} (Hf.44 Ti.38 Mo.18 W.05)C</td>
<td>0.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>MC_{(1)} (Nb.52 Ti.21 W.11 Mo.09 Hf.07)C</td>
<td>1.00</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MC_{(2)} (Hf.43 Ti.11 W.08 Mo.02)C</td>
<td>0.09</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>MC_{(1)} (Ti.47 Ta.28 W.17 Hf.08)C</td>
<td>0.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MC_{(2)} (Hf.58 Ta.10 Ti.12 W.11)C</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 shows that even though the content of C and Hf in three alloys is similar, but the tendency of MC_{(2)} formation is different. It is interesting to notice that in the same alloy the change of carbon content in a very wide range has little effects on amount of MC_{(2)}, but it has a significant effect on amount of MC_{(1)}. For example, the amount of MC_{(2)} increased from 0.44% to 0.47 vol% and that of MC_{(1)} increased from 0.42% to 0.63 vol%, as content of carbon in Alloy A increased from 0.09% to 0.15 wt%, respectively.

Ni_{3}Hf Phases. Ni_{3}Hf generally occurs in nickel-base alloys containing Hf more than 0.4 wt%. This phase is usually found around eutectic(γ+γ') and appears as small blocks or in cellular form (Fig.2). Results by electron microprobe indicated that Ni_{3}Hf has a composition of (Ni.80 Co.20)_{5} (Hf.69 Cr.29 W.06 Ti.05) in Alloy B. Ni_{3}Hf phase was identified by X-ray diffraction and electron diffraction at extraction replica. Table 3 shows diffraction results of alloyed Ni_{3}Hf.

Table 3 X-ray Diffraction Results of Alloying Ni_{3}Hf Phase

| Observed Value | ASTM 17 | 2θ | hkl | | Observed Value | ASTM 17 | 2θ | hkl |
|---------------|---------|----|-----| |---------------|---------|----|-----|
| d | I/I₀ | d | I/I₀ | | d | I/I₀ | d | I/I₀ |
| 3.82 | 30 | 111 | | 1.26 | 40 | 1.283 | 60 | 533 | 511 |
| 3.31 | 30 | 200 | | 1.18 | 60 | 1.13 | 20 | 440 |
| 2.35 | 30 | 220 | | 1.128 | 20 | 1.113 | 20 | 600 | 442 |
| 2.025 | 100 | 311 | | 1.069 | 60 | 1.055 | 40 | 620 |
| 1.97 | 50 | 222 | | 1.024 | 50 | 1.018 | 50 | 533 |
| 1.528 | 30 | 331 | | 1.007 | 40 | 622 |
| 1.480 | 30 | 420 | | 0.935 | 20 | 711 | 551 |
the amount of Hf. For different alloys even though content of Hf is the same, but the volume percent of Ni$_5$Hf is different. The volume of Ni$_5$Hf is slightly influenced by the variation of carbon concentration. The main factors influenced on volume of Ni$_5$Hf are the alloying element, amount of MC-former and the degree of alloying.

Effects of Thermal Exposure on Microstructure

During above thermal exposure, the following reactions occurred in these alloys:

\[ \text{Ni}_5\text{Hf} + \gamma(\text{C}) \rightarrow \text{MC}_{(2)} + \gamma \] (1)

\[ \gamma'(\text{Hf}) + \gamma(\text{C}) \rightarrow \text{MC}_{(2)} + \gamma \] (2)

In metallic radical of secondary MC$_{(2)}$ precipitated from above reactions, the Hf is predominant. A major source of Hf is either from Ni$_5$Hf or from eutectic $\gamma'$, whereas that of Carbon is the Carbon which liberated by MC$_{(1)}$ decomposition or solutioned in $\gamma$ matrix.

Transformation of Ni$_5$Hf during Thermal Exposure. Ni$_5$Hf is instable above 900°C temperature and easily changed into Hf-rich MC$_{(2)}$.

Time-Temperature Transformation curve of Ni$_5$Hf phase in Alloy B obtained by experiment (Fig. 3) showed that the effect of temperature on transformation of Ni$_5$Hf is more significant than that of the time. The time for complete transformation is about 400 hours.

Fig. 1. Primary MC$_{(1)}$ and MC$_{(2)}$ in as-Cast Alloy A and B.
  a) Alloy A as-Polished;
  b) Alloy C 450°C/30min Heat Tinting.

Fig. 2. Ni$_5$Hf Phase in Alloy B.
at 1050°C and it is only two hours at 1180°C. The incipient melting of Ni₅Hf occurs above 1190°C and this phase precipitated again during subsequent air cooling.

With continuous reaction the amount of Ni₅Hf constantly decreases and the volume percent of MC(2) constantly increases. It can be seen that MC(2) nucleates around Ni₅Hf and grows at the expense of Ni₅Hf (Fig.4). The soaked samples at various temperature and time were analysed by quantitative metallography, as shown in Fig.5.

Formation of Secondary MC(2) Carbide. The secondary MC(2) forms according to reactions(1) and(2). Different reactions occur in different alloys. The reaction(1) is dominant in Alloy B and the reaction(2) is dominant in Alloy A and C. The MC(2) formed by reaction(1) often concentrated in clusters in Ni₅Hf area (Fig.4) and the MC(2) formed by reaction(2) distributed more dispersively in eutectic γ'(Fig.6). It is different from secondary MeC and M₂₃C₆ that this secondary MC(2) is enclosed by γ. This phenomenon itself is an evidence of the reaction(1) and(2).

X-ray diffraction results showed that diffraction lines of MC(2) after 1050°C/100 hours was clearer than that of cast condition. The lattice parameters of MC(1) and MC(2) measured are about 4.40 and 4.50 Å, respectively.

The secondary MC(2) precipitated from reactions(1) and(2) was analysed by electron microprobe. The composition of secondary MC(2) for Alloy A, B and C may be expressed by following formula: (Hf₀.₉₁Ti₀.₀₉)C, (Hf₀.₅₉Nb₀.₃₇Ti₀.₀₄)C and (Hf₀.₈₁Ta₁.₁₁Ti₀.₀₅W₀.₀₃)C, respectively.

It can be seen that the major former of secondary MC(2) is Hf, Nb and Ta, the Ti enters slightly secondary MC(2). In view of composition the substantial different between secondary MC(2) and primary MC(2) is that the former contains more Hf. For Nb-, Ta-free alloys, secondary MC(2) is substantially HfC.

For long-time exposed samples at various temperature, the phase analysis was performed and results summarized in Fig.7. This figure also shows that MC(1) progressively decomposed and secondary MC(2) progressively precipitated with the increase of temperature.

If alloys were different, the tendency to precipitate secondary MC(2) would be different. The volume percent of precipitated MC(2) in Alloy A, B and C after 1050°C 200hr exposure is 0.08, 0.28 and 0.05 vol. %, respectively. It may be seen that Alloy B with highest
Fig. 3. Time-Temperature-Transformation (TTT) Curve of \( \text{Ni}_5\text{Hf} \) Phase in Alloy B.

Fig. 4. \( \text{Ni}_5\text{Hf} \) Partially Changed into \( \text{MC}_{(2)} \) after 950°C/2000hr Exposure in Alloy B.

Fig. 5. The Relation between the Volume Percent of \( \text{Ni}_5\text{Hf} \), \( \text{MC}_{(2)} \) and the Time at Various Temperature in Alloy B.

Fig. 6. Dispersive Secondary \( \text{MC}_{(2)} \) Precipitated in Eutectic \( \gamma' \) in Alloy C after 1050°C/1000hr Exposure.

Fig. 7. The Change of Content of Hf, Nb and Ti in MC after 1000hr Exposure at Various Temperature for Alloy B.
content of Ni₃Hf will precipitate secondary MC₂ most easily.

In Hf-bearing alloys, because of existing the primary and secondary MC₂ carbide, the formation of M₆C and M₂₃C₆ Carbide is strongly restricted, so that the total amount of minor phase only change slightly. In Alloy A with and without Hf, even though both are exposed at 900°C/1000hr, total amount of minor phase increased by 1.22 time in Hf-free alloy and only increased by 63% in Hf-bearing alloy.

DISCUSSION OF RESULTS

In Sims's work(3), there is a preferred order for MC-former, determined to be Ta, Nb, Ti and V. In view of our results the preferred order is Hf, Nb, Ta and Ti. The reasons are as follows; 1. not only Hf entered into MC₁, but alone form Hf-rich MC₂ in all as-cast Hf-bearing alloy; 2. MC₁ is predominately Ti-rich in the alloys which contained Ti alone (Alloy A) and its major composition is Nb in the alloy contained simultaneously Nb and Ti; 3. Hf in secondary MC₂ is the richest one, Nb is the second, Ta is the third, Ti entered slightly into secondary MC₂. In addition, Hf-free Alloy B precipitates secondary NbC at high temperature exposure and Hf-free Alloy C does not precipitate secondary TaC.

It can be seen from the above that Nb has stronger affinity with Carbon and is inferior to Hf. It was proved by systematic research works of Restall and Toulson(6) that Nb forms MC more easily than Ta.

In a word, primary and secondary Hf-rich MC₂ is very stable at high-temperature, this part of Carbon which was got by MC₂ does not take part in the reactions of M₆C and M₂₃C₆ precipitation. However, the secondary MC₂ can be formed by the Carbon which is liberated by decomposition of MC₁ at high-temperature exposure and the residual Carbon in the matrix. These two reactions restrict the formation of secondary M₆C and M₂₃C₆, however for majority of Hf-bearing alloys the concentration of Cr, Mo, and W is much higher than that of Hf, degree of the segregation of various elements are different, so that completely repressing precipitation of M₆C and M₂₃C₆ is rather difficult.

CONCLUSIONS

1. An intermetallic phase Ni₃Hf occurs in Hf-bearing cast nickel-base superalloys with high degree of alloying.
During long time thermal exposure above 900°C, the following reactions may occur in Hf-bearing cast nickel-base superalloys:

\[ \text{Ni}_5\text{Hf} + \gamma (\text{C}) \rightarrow \text{MC}_{(2)} + \gamma \]

\[ \gamma' (\text{Hf}) + \gamma (\text{C}) \rightarrow \text{MC}_{(2)} + \gamma \]

Because of the above two reactions, the formation of \( \text{M}_6\text{C} \) and \( \text{M}_{23}\text{C}_6 \) is restricted.

**REFERENCE**


