PHASE ANALYSIS OF CARBON–CERAMIC COMPOSITES SYNTHESIZED BY IN-SITU SINTERING

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ABSTRACT

Carbon–ceramic composites with different compositions were sintered by hot-pressing in nitrogen under 1800°C and 1900°C by in-situ synthesis from petroleum coke, carbon fiber, silicon, B4C, SiC, TiC and TiO2. Phase analysis of the composites was performed by XRD. The results of qualitative phase analysis show that the composites consist of C, SiC, TiB2 and Ti(C,N1-x), which illustrates that the starting material Si, B4C and TiO2 or TiC reacted completely to form SiC, TiB2 and Ti(C,N1-x) during the sintering process. The precise measurement of the lattice constant of Ti(C,N1-x) gives the composition of Ti(C,N1-x), in which the value of x is around 0.7. Quantitative analysis gives the phase composition of the composites, therefore, the relationships between the properties and the phase composition were obtained.

1. INTRODUCTION

Carbon–ceramic composites show promise to retain good properties of both carbon and ceramic material, such as high mechanical strength, good resistance for high-temperature, corrosion, oxidation, slag and thermal shock, well electrical and thermal conductivity, self-lubrication. The material is attractive for application at high temperature and in severe environments. Investigation on carbon–ceramic composites, such as C-SiC 1, and C-SiC-B4C 2 have been reported. They were usually prepared by chemical vapour deposition 3, coating 4, and sintering 5 or hot-press sintering 6. The C-SiC-B4C composite prepared by hot-press sintering shows good properties 6. However, the sintering temperature of the carbon–ceramic composite with low porosity should be 2000 °C or higher. The in-situ reaction synthesis method has advantages of simplifying the technique, lowering the sintering temperature, reducing the price of starting materials and achieving the design of special microstructure. This method was successfully used to prepare multiphase ceramic composites 7,8. When the in-situ reaction synthesis method was used to prepare carbon-ceramic composite, the sintering temperature can be lowered and the preparation technique can be simplified. C-SiC-TiC-TiB2 composite synthesized by in-situ hot-press sintering at relative lower temperature is dense and shows very good properties 9.

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understand the mechanism of the densification of in-situ synthesized carbon-ceramic composite and to obtain the relationship between properties and phase composition, X-ray diffraction (XRD) was used to determine the phase composition of C–SiC–TiB₂–Ti(CₓNᵧ₋ₓ) synthesized by in-situ hot-press sintering and the precise lattice constant of the Ti(CₓNᵧ₋ₓ) phase.

2. EXPERIMENTAL METHOD

The samples of carbon–ceramic composite with different content of TiO₂ in the starting materials were synthesized by using in-situ hot-pressing in nitrogen from petroleum coke, carbon fiber, silicon, B₄C, SiC, TiC and TiO₂. The volume content of TiC and TiO₂ was changed in each sample (volume content of the other starting materials was fixed in all samples) so as to investigate the effect of different sources of titanium on the properties of the composites. The starting materials were weighted and mixed in alcohol with a stirring speed of 6000 rpm for 10 min. The well-mixed precursor was put into a graphite die with a dimension of 35×25 mm² and sintered in nitrogen at 1800°C and 1900°C under a constant pressure of 25 MPa for 30 min. The sintered products were cut into beams of 35×5×4 mm³. One of the beams from each sample was ground and sieved through a 20 µm sieve. The sieved small powders were used for quantitative phase analysis and precise measurement of lattice constant. The other bulk beams were ground and used for qualitative phase analysis, the measurement of bulk density, oxidation resistance and bending strength.

The precise measurement of lattice constant of Ti(CₓNᵧ₋ₓ), qualitative and quantitative analysis of phase compositions were performed by Siemens D5000 diffraction system. K factor method was used to do quantitative phase analysis, in which silicon powder was added to be used as the internal standard. Silicon powder was also added as the internal standard to determine the lattice constant.

The bulk density was measured by the water immersion method. Bending strength was obtained from three point bending test with a span of 28mm. The oxidation of the samples was performed in a chamber electric furnace in air for required time at different temperature, then the samples were removed from the furnace and cooled down in air. Oxidation resistance is evaluated based on the weight change of the specimen before and after oxidation.

3. RESULTS AND DISCUSSION

Fig.1 shows the XRD patterns of some sintered samples. The results show that all the sintered samples are composed of SiC, TiB₂, Ti(CₓNᵧ₋ₓ) and carbon (there is a little SiO₂ in sample No.1 sintered at 1800°C), illustrating that the starting material Si, B₄C, TiO₂ and TiC reacted completely to form SiC, TiB₂ and Ti(CₓNᵧ₋ₓ) during the sintering process. The in-situ synthesis of SiC, TiB₂ and Ti(CₓNᵧ₋ₓ) occurred during the process of sintering. The synthesis reactions can be summarized as follows:
### Table 1 Phase Compositions and Characteristics of the Composites

<table>
<thead>
<tr>
<th>SAMPLE NO</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂(TiC+TiO₂) in the starting materials (vol. %)</td>
<td>100</td>
<td>75</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Sintering temperature (°C)</td>
<td>1800</td>
<td>1900</td>
<td>1800</td>
<td>1900</td>
<td>1800</td>
</tr>
<tr>
<td>Phase composition TiB₂</td>
<td>54</td>
<td>44</td>
<td>45</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td>Ti(C₃N₁ₓ)</td>
<td>17</td>
<td>26</td>
<td>25</td>
<td>27</td>
<td>27</td>
</tr>
<tr>
<td>SiC</td>
<td>19</td>
<td>18</td>
<td>18</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Lattice constant a of Ti(C₃N₁ₓ)</td>
<td>0.42982</td>
<td>0.43062</td>
<td>0.42984</td>
<td>0.43034</td>
<td>0.43004</td>
</tr>
<tr>
<td>Value of x in Ti(C₃N₁ₓ)</td>
<td>0.68</td>
<td>0.76</td>
<td>0.68</td>
<td>0.73</td>
<td>0.70</td>
</tr>
<tr>
<td>Theoretical density (g/cm³)</td>
<td>3.80</td>
<td>3.76</td>
<td>3.75</td>
<td>3.68</td>
<td>3.68</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>3.67</td>
<td>3.51</td>
<td>3.63</td>
<td>3.32</td>
<td>3.45</td>
</tr>
<tr>
<td>Relative density (%)</td>
<td>97</td>
<td>93</td>
<td>97</td>
<td>90</td>
<td>94</td>
</tr>
<tr>
<td>Bending strength (MPa)</td>
<td>425</td>
<td>395</td>
<td>420</td>
<td>295</td>
<td>330</td>
</tr>
</tbody>
</table>

Fig. 1 XRD Patterns of Carbon-Ceramic Composites with Different Compositions

Fig. 2 Relative Density of the Composites versus the Relative Content of TiO₂

Fig. 3 Bending Strength of the Composites versus the Relative Contents of TiO₂
\[
\begin{align*}
2\text{TiO}_2 + \text{B}_4\text{C} + 3\text{C} & \rightarrow 2\text{TiB}_2 + 4\text{CO} \\
2\text{TiO}_2 + 2(2+x)\text{C} + (1-x)\text{N}_2 & \rightarrow 2\text{Ti}(\text{C}_x\text{N}_{1-x}) + 4\text{CO} \\
2\text{TiC} + (1-x)\text{N}_2 & \rightarrow 2\text{Ti}(\text{C}_x\text{N}_{1-x}) + 2(1-x)\text{C} \\
2\text{TiC} + \text{B}_4\text{C} & \rightarrow 2\text{TiB}_2 + 3\text{C} \\
\text{Si} + \text{C} & \rightarrow \text{SiC}
\end{align*}
\]

The lattice constant of \( \text{Ti}(\text{C}_x\text{N}_{1-x}) \) and quantitative analysis results of the samples by XRD were listed in Table 1. From the value of the lattice constant of \( \text{Ti}(\text{C}_x\text{N}_{1-x}) \), the ratio \( x \) of C to C+N in the phase can be calculated according to the equation

\[
a = 0.42392 + 0.00874 x
\]

where the unit of lattice constant \( a \) is nanometer.

![Graph of XRD patterns](image1)

![Graph of phase volume composition](image2)

**Fig.4** Phase Volume Composition of the Composites

**Fig.5** XRD Patterns of Surface and Interior of Sample 3 at Different Oxidation Temperatures for 12 hours

**Fig.6** Weight Change of Sample 3 vs Time Oxidized at 1200 °C
The calculated value of $x$, bulk density, theoretical density, relative density (the ratio of bulk density to theoretical density) and bending strength of the samples are listed in Table 1 also. The value of $x$, which is around 0.7, has no obvious relationship with the relative content of TiO$_2$.

The relationships of relative density and bending strength of the composites versus the relative content of TiO$_2$ are shown in Fig.2 and Fig.3. The Figures show that the relative density of all the samples is higher than 90%, which indicates that the composites sintered at 1800 °C or 1900 °C are compact. The sintering temperature was lowered by using in-situ synthesis method. Both the density and the strength of the composites with same compositions sintered at 1900 °C are higher than that at 1800°C, and they increase with the increase of relative content of TiO$_2$. However, the relative density of sample No.1 sintered at 1800 °C is higher than that of other samples sintered at 1900 °C. This means that TiO$_2$ can improve the densification of the composites more effectively than TiC.

Fig.4 gives the relationship of the phase composition in volume percent of the composites versus the relative content of TiO$_2$. The carbon volume content of the composites, which is between 19% and 35%, decreases with the increase of the relative content of TiO$_2$. Although both TiO$_2$ and TiC can react with B$_4$C to form TiB$_2$, TiO$_2$ consumes carbon in the reaction. Consequently, the relative content of carbon in the composites decreases with the increase of TiO$_2$. Fig.3 and Fig.4 together show that the bending strength of the composites goes down with the increase of carbon content and increases with the rise of the content of total ceramic phase TiB$_2$, Ti(C$_x$N$_{1-x}$) and SiC.

Fig. 5 shows the XRD patterns of the surface of sample No.3 after oxidized at different temperatures for 12 h. At 600 °C, the pattern is similar to that of the sintered sample (Fig. 1). There is only one oxide peak appearing, but the peak of carbon disappeared, illustrating that the ceramic phases on the surface of the composite were hardly oxidized; only carbon phase on the surface is oxidized. At 800 °C and above, oxidation of the composite surface is evident. TiB$_2$ began to be oxidized to form TiO$_2$ at 800 °C by comparing the relative intensity of the diffraction peaks. With the increase of temperature, the intensity of the diffraction peaks of TiB$_2$, Ti(C$_x$N$_{1-x}$) and SiC decreases, accompanying the increase of the intensity of diffraction peaks of oxides. At 1200 °C, all the peaks of sintered phases in the surface disappeared, only the peaks of TiO$_2$ was observed, illustrating that the surface of the composite is completely oxidized. However, when the sample surface of the composite oxidized at 1200 °C was ground for a while, the XRD pattern of the sample (topmost pattern in Fig.5) is similar to that of the sample before oxidation, illustrating that only the surface of the composite is oxidized, which coincides with the results of weight analysis (shown in Fig.6) during the process of oxidation. The weight of the composite lost quickly at the first several hours of oxidation and kept constant after 12 hours of oxidation. The results verify that the oxides formed on the surface can protect the inner material from further oxidation.
4. SUMMARY

(1) Compact C-SiC-TiB$_2$-TiC$_x$N$_{1-x}$ composites were in-situ synthesized by hot-pressing from petroleum coke, carbon fiber, silicon, B$_4$C, SiC, TiC, and TiO$_2$ at 1800 °C and 1900 °C. The densification of the composites is improved and the sintering temperature is lowered by using in-situ synthesis method.

(2) XRD qualitative phase analysis shows that the composites consist of C, SiC, TiB$_2$ and Ti(C$_x$N$_{1-x}$), which illustrated that the starting material Si, B$_4$C and TiO$_2$ or TiC reacted completely to form SiC, TiB$_2$ and Ti(C$_x$N$_{1-x}$) during the sintering process.

(3) The precise measurement of the lattice constant of Ti(C$_x$N$_{1-x}$) by XRD gives the composition of Ti(C$_x$N$_{1-x}$), in which the value of x is around 0.7.

(4) XRD quantitative analysis gives the phase composition of the composites. Therefore, the relationships between the properties and the phase composition were obtained. The bending strength of the composites goes down with the increase of carbon content and increases with the rise of the content of total ceramic phase.

(5) XRD patterns and weight changes of the composite after oxidation show that only the surface of the composite was oxidized at high temperature and the oxides formed on the surface can protect the inner composite from further oxidation.

REFERENCE