Effect of Dilution on Combustion Synthesis of Ti$_3$AlC$_2$ Powders

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Ternary carbides feature a unique characteristic of coexistence of covalent, metallic and ionic bonds in one crystal cell, resulting in unusual properties which combine the merits of both metals and ceramics. In the present work, single-phase ternary Ti$_3$AlC$_2$ was produced by combustion synthesis using Ti, Al and C powders as the raw materials. The experimental results showed that the addition of TiC and Ti$_3$AlC$_2$ affect the formation of the phases in the final product. Increasing addition of TiC and Ti$_3$AlC$_2$ in the raw mixtures and decreasing combustion temperatures resulted in enhancement of the amount of the produced Ti$_3$AlC$_2$.

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1. Introduction

Titanium aluminum carbide (Ti$_3$AlC$_2$) is a member of ternary carbides, which was first synthesized by Pietzka and Schuster.\textsuperscript{1,2} It was recently found that Ti$_3$AlC$_2$ to possess unusual properties featuring the merits of both metals and ceramics. Like metals, it has high thermal and electrical conductivity, it is easily machinable with conventional tools and resistant to thermal shock; like ceramics, it has high strength, high melting point and thermal stability.\textsuperscript{3} By contrast with conventional brittle ceramics, Ti$_3$AlC$_2$ exhibits an extraordinary compressive plasticity at room-temperature.\textsuperscript{3}

Pietzka and Schuster\textsuperscript{1} synthesized Ti$_3$AlC$_2$ by sintering of cold-compacted powder mixtures of Ti, TiAl, Al$_2$C$_3$, and C under argon atmosphere. Tzenov and Barsoum\textsuperscript{4} synthesized Ti$_3$AlC$_2$ by hot isostatic pressure (HIP) sintering process using Ti, Al$_2$C$_3$, and C as raw materials. Nevertheless, both methods require very rigorous conditions, such as high pressure and long sintering time. Moreover, these methods use Al$_2$C$_3$ as aluminum source in order to avoid loss of Al during the synthesis processing, due to the low melting point and high evaporation pressure.

It has been reported that Ti$_3$AlC$_2$ phase was found in the final product of ignited mixture of Ti, Al and graphite powders, by a processing which has been designated as combustion synthesis (CS).\textsuperscript{5} Combustion synthesis of compositions in the Ti–Al–C system using aluminum, titanium and carbon as raw materials, has attracted the interest of many researchers.\textsuperscript{6,7} However, ternary carbide has been never found in their products.

The present work addresses itself to the fabrication of Ti$_3$AlC$_2$ by combustion synthesis using powders of aluminum, titanium and carbon black as raw materials, primarily aiming to achieve low processing cost.

2. Experimental procedure

There is a big difference between the melting points of the raw materials used in the experiments. Aluminum melts at 933 K, and evaporates at 2790 K under atmospheric pressure. The melting and the evaporation points of titanium are between Al and C, at 1939 K and 3631 K, respectively. The evaporation point of carbon black is the one, 4055 K. In CS, the combustion temperatures are usually higher than 1800 K. Therefore, partial loss of aluminum will inevitably occur during the combustion process due to the evaporation at those high temperatures. Phenomena related to the aluminum loss have been observed occurring during the combustion reaction at the ignition of the raw mixture under vacuum. In those cases, white powder was deposited on the surface of the product and the inner walls of the CS chamber. XRD analysis assigned those white powders to aluminum. The amount of titanium loss is less than that of aluminum due to the higher evaporation point. No carbon is lost during the combustion because of the very high evaporation point. Therefore, aluminum should be in slight excess with respect to the precise stoichiometry anticipated in the formula of the crystal structure of Ti$_3$AlC$_2$. Tzenov and Barsoum\textsuperscript{5} adopted excess amount of aluminum and titanium comparing to the stoichiometry, particularly Ti : Al : C = 3 : 1.1 : 1.8. In the present work, the same ratio of the raw material was used in the mixtures.

Titanium (99% pure, 300 mesh, GRINM, Beijing, P. R. China), aluminum (99% pure, 400 mesh, GRINM, Beijing, P. R. China) and carbon black (Beijing chemical Co., P. R. China) were used as raw materials. The compositions of the samples are shown in Table I. The mixtures of the powders were ball-milled in a plenary mill at 125 rpm for 8 h. Cylindrical samples with dimensions of 50 mm in length and 25 mm in diameter were prepared by uniaxial cold-pressed. The samples were put into the CS reactor, whose description has been already presented in details in a previous paper.\textsuperscript{8} The chamber of the CS reactor was first evacuated to a vacuum of 2.33 Pa and then filled with argon 1 MPa. The combustion reaction was ignited by passing an electric current (30A) through a w-shaped tungsten filament.

The phases formed were identified by XRD (Cu target, Ka, Rigaku D/max–RB, Japan). The microstructure of the products was observed and analyzed by SEM (JSM–6, Japan) coupled with facilities of energy dispersive spectroscopy (EDS).

The peak of Ti$_3$AlC$_2$ at 2θ = 9.5° (002) and the peak of TiC at 36.1° (111) were chosen to represent the relative concentration of these two phases because both of them do not overlap with peaks of other phases. F defines the ratio of $I_{\text{Ti$_3$AlC$_2$-002}}/I_{\text{TiC-111}}$, where $I_{\text{Ti$_3$AlC$_2$-002}}$ and $I_{\text{TiC-111}}$ denote the intensity of the XRD peaks which correspond to the (002) lattice plane of Ti$_3$AlC$_2$ and the (111) plane of TiC, respectively. The values of the ratio F are listed in Table 1.
Table 1. Composition of the Raw Materials and the Combustion Characteristics

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Stoichiometry (molar ratio) Ti:Al:C</th>
<th>TIC (wt.%)</th>
<th>Ti₃AlC₂ (wt.%)</th>
<th>Combustion temperature (K)</th>
<th>Resulting phases</th>
<th>F Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAC0</td>
<td>3:1:1.1:1.8</td>
<td>0</td>
<td>0</td>
<td>2276.7</td>
<td>Ti₃C, Ti₃AlC₂</td>
<td>0.14</td>
</tr>
<tr>
<td>TAC2</td>
<td>3:1:1.1:1.8</td>
<td>20.0</td>
<td>0</td>
<td>2146.8</td>
<td>Ti₃AlC₂, TiC</td>
<td>1.99</td>
</tr>
<tr>
<td>TAC3</td>
<td>3:1:1.1:1.8</td>
<td>30.0</td>
<td>0</td>
<td>2002.7</td>
<td>Ti₃AlC₂, Ti₃C</td>
<td>2.96</td>
</tr>
<tr>
<td>TAC3.5</td>
<td>3:1:1.1:1.8</td>
<td>35.0</td>
<td>0</td>
<td>1877.8</td>
<td>Ti₃AlC₂, Ti₃C</td>
<td>3.13</td>
</tr>
<tr>
<td>TAC4</td>
<td>3:1:1:1.8</td>
<td>40.0</td>
<td>-</td>
<td>-</td>
<td>Unignited</td>
<td>-</td>
</tr>
<tr>
<td>TAC2-10</td>
<td>3:1:1:1.8</td>
<td>20.0</td>
<td>10.0**</td>
<td>-</td>
<td>Ti₃AlC₂, TiC</td>
<td>2.64</td>
</tr>
<tr>
<td>TAC3-5</td>
<td>3:1:1:1.8</td>
<td>30.0</td>
<td>5.0***</td>
<td>-</td>
<td>Ti₃AlC₂, TiC</td>
<td>3.55</td>
</tr>
</tbody>
</table>

* F defines the ratio of I₁₁₁₃₋₄₋₀₋₂₂₋₀₋₂₂₋₀₋₂₂ and I₁₁₁₃₋₄₋₀₋₂₂₋₀₋₂₂, where I₁₁₁₃₋₄₋₀₋₂₂ and I₁₁₁₃₋₄₋₀₋₂₂ denote the intensity of the XRD peaks which correspond to the (002) lattice plane of Ti₃AlC₂ and the (111) plane of TiC, respectively. **With added 10 wt.% of the combustion product from the sample TAC2; *** With added 5 wt.% of the combustion product from the sample TAC3.

3. Results and discussions

3.1 Effect of TiC addition

Figure 1 shows the phases formed in the final product for difference additions of TiC in the raw mixture. In the case of no TiC-addition (TAC0, Fig. 1a), XRD analysis showed that TiC was the main phase, while traces of Ti₃AlC₂ were also identified. In the case of addition of TiC in the raw mixtures, the XRD results showed that the main phase in the final products was Ti₃AlC₂ containing also very small amount of TiC (Figs. 1b, c and d). Figures 1e and 1f show the XRD results of the combustion products with both Ti₃AlC₂ and TiC in the raw mixtures. In this case, Ti₃AlC₂ was also the main phase with traces of TiC. These experimental results indicate that the addition of TiC in the raw mixtures have greatly favored the formation of Ti₃AlC₂.

The XRD spectra shown in Figs. 1b, 1c and 1d shed light on the influence of the amount of TiC addition in the raw mixtures on the phases formed in the combustion products. The phases formed in the combustion product of the sample TAC2 were primarily Ti₃AlC₂ and traces of TiC. The intensity of the peak assigned to Ti₃AlC₂ in the X-ray spectra became gradually stronger with increasing the amount of TiC addition, from 20 wt.%, to 30 wt.%, and finally to 35 wt.%. Figure 2 shows the dependence of F value on the amount of TiC addition. Evidently, TiC positively influences the formation of Ti₃AlC₂. These experimental results would also potentially assure that TiC can sufficiently react with liquid Ti-Al melt to form Ti₃AlC₂ crystals, coming in accordance with the results reported in the literature.⁹

With regards to the influence of TiC additives on the mechanism of the formation of Ti₃AlC₂, which is related to the thermodynamics of the system, the experimental results showed the followings. The combustion were gradually decreased temperatures over increasing amount of TiC addition, as shown in Fig. 3. Thus, in the case of 40 wt.% TiC addition, the raw mixture could not ignite at all. Figure 4 aims to correlate the combustion temperature with the amount of the produced Ti₃AlC₂. Evidently, the amount of Ti₃AlC₂ was reduced with increasing the combustion temperature, which agrees fairly well with the dependence of the amount Ti₃AlC₂ on TiC addition, mentioned earlier in this article. The decom-
position temperature of Ti$_3$AlC$_2$ is approximately between 1633 K$^{11}$ and 1673 K$^{11}$. Therefore, the increase of the amount of TiC addition could effectively reduce the decomposition of Ti$_3$AlC$_2$ because the combustion temperature considerably decreases with increasing amount of TiC addition, which subsequently favors Ti$_3$AlC$_2$ formation. These results agreed well with the explanation given for the mechanism of the formation of Ti$_3$AlC$_2$ presented by Tomoshige and Matsushita.$^9$

As far as the kinetics of the CS process is concerned, in our previous work, we have shown that TiC is an intermediate product formed during the combustion synthesis of Ti$_3$AlC$_2$. In the Ti-Al-C system with TiC additions, the first step is the exothermic reaction between Ti and C to form TiC. The combustion reaction is instantly completed. The combustion temperature is reduced very rapidly. As the combustion temperature descends in order to approach the required temperature to form Ti$_3$AlC$_2$, the formation reaction of Ti$_3$AlC$_2$ would cease. Therefore, formation of Ti$_3$AlC$_2$ requires enough prompt TiC supply. Otherwise, TiC would be the main phase in the final product. Addition of TiC provides adequate TiC for advancing the reaction to form Ti$_3$AlC$_2$. Increasing concentration of TiC results in increasing velocity of Ti$_3$AlC$_2$ formation and consequently to larger amount of Ti$_3$AlC$_2$ in the final product.

3.2 Effect of Ti$_3$AlC$_2$ addition

Sample TAC2-10 corresponds to the raw composition of sample TAC2 with 10 wt. % addition of combustion product of the TAC2. Similarly, 5 wt. % combustion product of the TAC3 was added to the raw mixture of TAC3, and the resulting sample was denoted as TAC3-5. The XRD spectra are illustrated in Fig. 1. The results of XRD in conjunction with the F values listed in Table 1, indicate that the addition of Ti$_3$AlC$_2$ favors the formation of Ti$_3$AlC$_2$ since it likely provides crystal seeds and decreases the combustion temperature.

3.3 Microstructure of the final products

**Figure 5** shows the microstructure of the combustion products observed by SEM. The product of the sample TAC0 comprised equal-axed particles (Fig. 5a). On the other hand, the products of the samples TAC2, TAC3, TAC35, TAC2-10 and TAC3-5 consisted of two-dimensional layered plates, whose chemical composition, determined by EDS, corresponds to Ti$_3$AlC$_2$.

4. Conclusions

(a) Addition of TiC and/or Ti$_3$AlC$_2$ is absolutely necessary in the production of Ti$_3$AlC$_2$ by combustion synthesis using Ti, Al and C as the raw materials.

(b) Additions of TiC and Ti$_3$AlC$_2$ favor the formation of Ti$_3$AlC$_2$. Increasing amount of TiC additions increases the amount of Ti$_3$AlC$_2$ in the final combustion product.

(c) Low combustion temperature also favors the formation of Ti$_3$AlC$_2$.

(d) TiC is an intermediate product in combustion synthe-

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![Fig. 4. Effect of combustion temperature on F values.](image)

![Fig. 5. Microstructures of the combustion products: (a) TAC0, (b) TAC3, (c) TAC2-10, (d) TAC3-5.](images)
sis of Ti$_2$AlC$_2$.

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References