Reaction Mechanism of in Situ TiCp/Fe Composite in (Ti–Fe)–C–Al System


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1. Introduction

During the past decade, considerable researches have been directed to the development of in situ metal matrix composites (MMCs), in which the reinforcements are formed in situ by exothermal reactions among elements or between an element and a compound.1,2) Most of the researches on MMCs are focused on the particulate reinforced lightweight metal-based composites, e.g. Al-based, Ti-based and Mg-based, due to their attractive virtues of low density, low melt point, high specific strength compared with ferrous metals, and especially apply in the concentrated on the particulate reinforced steel- or iron-based composites which produce a combination of excellent toughness and to achieve significant cost reductions with high hardness and thermal stability. Fe–Ti–C system as a model reaction system of steel- or iron-based composites has been extensively studied by number of researchers,13–18) and meantime, Fe–Al–Ti–C and Fe–W–Ti–C system also have been investigated mainly in FeAl- and Fe2Al-based composite.19–21) However, as a novel reaction system, few investigations have been reported on the particulate reinforced steel- or iron-based composites (MMCs), in which the reinforcements are formed in situ by exothermal reactions among elements or between an element and a compound.1,2) Most of the researches on MMCs are focused on the particulate reinforced lightweight metal-based composites, e.g. Al-based, Ti-based and Mg-based, due to their attractive virtues of low density, low melt point, high specific strength compared with ferrous metals, and especially apply in the conditions of lightweight combine with high strength and stiffness.3,4) However, the mechanical properties of these light metals are far below that of steel, iron or their alloys, so their applications are suffered significant limitation. To break through these limits, more and more interests have concentrated on the particulate reinforced steel- or iron-based composites which produce a combination of excellent wear resistance and/or cutting performance with improved toughness and to achieve significant cost reductions over existing materials.5–8) Various carbides (e.g. TiC, VC, Cr3C2, WC, NbC)4–9) and oxid (e.g. Y2O3, Al2O3)10–12) have been reported as the reinforcement particulates for steel- or iron-based composites, and Ramquist’s work13) has shown that TiC particulate is easily wet by iron at high temperatures, and as time progresses, wetting further improves because of chemical wetting; furthermore TiC particulate is a perfect reinforcement for steel- or iron-based composites with high hardness and thermal stability. Fe–Ti–C system as a model reaction system of steel- or iron-based composites has been extensively studied by number of researchers,13–18) and meantime, Fe–Al–Ti–C and Fe–W–Ti–C system also have been investigated mainly in FeAl- and Fe2Al-based composite.19–21) However, as a novel reaction system, few investigations have been reported on (Ti–Fe)–C–Al system.22) The aim of the present work is to investigate the effects of Al in the self-propagating high temperature synthesis reaction in (Ti–Fe)–C–Al reaction system, as well as the possible reactions and the reaction mechanism in this system.

2. Experimental

In the present study, the starting materials were made from commercial available powders of Ti–Fe (a much cheaper substitute material of titanium powder, its composition is shown in Table 1), aluminum (98.0 wt% purity), and carbon (98.0 wt% purity) with particulate size less than 75, 75, 0.5 μm, respectively. Titanium and carbon were at a ratio corresponding to that of stoichiometric TiC, and Al (include the Al composition in the ferrotitanium powder) was at ratios of 0, 10, 20, 30, 40, 50 wt% of the starting materials, respectively. After being mixed in a low-speed ball-grinding mill for 8 h, the 6 kinds of required powders (about 70 mg each) were pressed into an Al2O3 crucible of 130025, P.R. China. E-mail: fangshijie827@sohu.com

Note

2. Experimental

3. Results and Discussion

3.1. DTA Experimental Results

DTA curves of the mixture powder samples with different Al content are shown in Figs. 1(a)–1(f). It can be observed that when the Al content of the mixture powders sample ups to 0, no obvious endothermic or exothermic peaks occurred, as shown in Fig. 1(a). When the Al content increases from 10 to 40 wt%, the exothermic peaks all occur from the start of 650°C, as well as with the increase of Al content, the heights of the exothermic peaks also increase, as shown in Figs. 1(b)–1(e). Figure 1(f) shows that when the Al content reaches to 50 wt%, in addition to the exothermic peak enhancing from the start of 654°C, an endothermic peak occurs from the start of 640°C. Figure 1 reflects a trend that, with the increase of Al content, the exothermic peaks increase accordingly around 660°C, and when the Al content is no less than 30 wt%, the shapes of the exothermic peaks change into a sharp needle shape, which indicates that these reactions are intensive reactions.

Table 1. Chemical composition (wt%) of ferrotitanium.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Ti</th>
<th>S</th>
<th>P</th>
<th>Si</th>
<th>Al</th>
<th>Mn</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt, %)</td>
<td>0.3</td>
<td>65</td>
<td>0.7</td>
<td>0.05</td>
<td>0.7</td>
<td>5</td>
<td>1</td>
<td>0.3</td>
<td>balance</td>
</tr>
</tbody>
</table>
calculation, it can be concluded that the diffraction peaks of Fe has not existed. As the Al content reaches to 30 wt%, the diffraction peaks of Ti continue to weaken, as well as occurs weak TiC peaks. As the Al content increases to 40 wt%, FeAl diffraction peaks weaken, and TiC diffraction peaks enhance, and the Ti phase can not be detected using XRD, as well as the weak Al diffraction peaks occurs.

When the Al content reaches to 50 wt%, the diffraction peaks of Al enhance, as well as that of FeAl continued to weaken, and C diffraction peaks decrease to minimum, and with the increase of Al content, the diffraction peaks of TiC further move to high diffraction angles.

4. Discussion

When the Al content ups to 0 in the sample, no obvious exothermic or endothermic peaks occurr, this phenomenon indicates that no reactions had happened in this sample. The XRD result shows that the DTA products are Fe, C, Fe2Ti and Ti, and Fe2Ti is not the reaction product, but the original phase which comes from the Ti–Fe powder. When

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**Fig. 1.** DTA curves of the samples with different Al contents (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50 wt%.

**Table 2.** XRD analysis results of DTA reaction products.

<table>
<thead>
<tr>
<th>Al Content (wt. %)</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>C+Ti+Fe2Ti+Fe</td>
</tr>
<tr>
<td>10</td>
<td>C+Ti+Fe2Ti+FeAl+FeAl2+Fe</td>
</tr>
<tr>
<td>20</td>
<td>C+Ti+Fe2Ti+FeAl+FeAl2+Fe</td>
</tr>
<tr>
<td>30</td>
<td>C+FeAl+FeAl2+TiC+Ti</td>
</tr>
<tr>
<td>40</td>
<td>C+FeAl+FeAl2+TiC+Al</td>
</tr>
<tr>
<td>50</td>
<td>C+FeAl+FeAl2+TiC+Al</td>
</tr>
</tbody>
</table>

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**Fig. 2.** X-ray patterns of reaction products of the samples with (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50 wt% Al contents.
the Al content is 10 wt%, Al reacts with Fe to form a small quantity of FeAl and FeAl\textsubscript{2}, as well as due to the little Al content, there is still the non-reactive Fe phase remained in the reaction products. Since FeAl\textsubscript{1} and FeAl\textsubscript{2} are intermetallic compound, and intermetallic compound has both metalloid bond and covalent-bond, the bond-energy of that is higher, so the exothermic quantity of heat of forming FeAl\textsubscript{1} and FeAl\textsubscript{2} are higher, and meantime, the partial Al reacts with Fe\textsubscript{2}Ti to form Ti, FeAl\textsubscript{1} or/and FeAl\textsubscript{2}, so the diffraction peaks of Fe\textsubscript{2}Ti decrease. Since the reaction between Al and Fe\textsubscript{2}Ti belongs to thermit reaction, the reaction also emits high exothermic quantity of heat. As the Al content reaches to 20 wt%, FeAl\textsubscript{1} and FeAl\textsubscript{2} increase in the reaction products, the exothermic quantity of heat of the reactions also increase accordingly. When the Al content up to 30 wt%, due to Al reacts with Fe\textsubscript{2}Ti to form more FeAl\textsubscript{1} or/and FeAl\textsubscript{2} and Ti, as well as Al directly reacts with Fe to form more FeAl\textsubscript{1} and FeAl\textsubscript{2}, and these reactions emit higher exothermic quantity of heat which further ignites the reaction between Ti and C to form TiC. Although the TiC content is less, due to the reaction of forming TiC is a high exothermic reaction, the reactive exothermic peak continues to increases sharply. Jiang et al.\textsuperscript{23} investigated the solid-state mechanism of Al–Ti–C mixture powder preforms, they suggested that solid-state Al reacts with solid-state Ti to form TiAl\textsubscript{x}, (x=1, 3) firstly, then TiAl\textsubscript{x} will react with C to form a more thermodynamically stable TiC. In the present investigation, no any trace of TiAl\textsubscript{x} is detected, so the reaction mechanism of (Ti–Fe)–C–Al system should be as follow:

\[
\begin{align*}
\text{Al} + \text{Fe}_{2}\text{Ti} &\rightarrow \text{Ti} + \text{FeAl}_{x} \quad (x=1, 2) \\
\text{Al} + \text{Fe} &\rightarrow \text{FeAl}_{x} \quad (x=1, 2) \\
\text{Ti} + \text{C} &\rightarrow \text{TiC} 
\end{align*}
\]

That is, Al reacts with Fe\textsubscript{2}Ti to form FeAl\textsubscript{1} or/and FeAl\textsubscript{2} and Ti, as well as Al reacts with Fe to form FeAl\textsubscript{1} (x=1, 2), and the two reactions emit higher exothermic quantity of heat which further ignited the reaction between Ti and C to form thermodynamically stable TiC. As Al content reaches to 40 wt%, due to the higher Al content, Fe content is relative lower, so the diffraction peaks of FeAl weaken. Due to the excess of Al in the sample, the more liquid-state Al phase is produced (Since the exothermic peaks cover up the endothermic peaks of Al melting, no exothermic peaks appear around 660°C in the DTA curve.), which leads to the increase of more osculant odds between Ti and C, further fastened the reaction between Ti and C, as well as the higher exothermic quantity of heat. As the Al content reaches to 50 wt%, due to the more Al content, the endothermic peaks of Al melting are not covered, and the excessive liquid-state Al leads to the ascendant kinetic conditions between Ti and C to form TiC. Although the excessive Al leads to the decrease of Ti and C, however the reaction of producing TiC is more completeness, which results in the much higher exothermic quantity of heat. Such viewpoint can be proved that, with the increase of Al content in the samples, the diffraction peaks of TiC continually move to the high diffraction angles, which indicated the crystal lattice constant of TiC \textsubscript{1} is closing to that of stoichiometric TiC. It is need to explain that, although there were some tiny reaction peaks at the range from 1 100 to 1 200°C, no other reaction products were detected using DTA, so such reactions will not be discussed in the present investigation.

5. Conclusions

(1) Al is contributed to the forming of TiC in the (Ti–Fe)–C–Al system, and Al reacts with Fe\textsubscript{2}Ti to form FeAl\textsubscript{1} or/and FeAl\textsubscript{2} and Ti, as well as Al reacts with Fe to form FeAl\textsubscript{x}, (x=1, 2), then the two reactions emit high exothermic quantity of heat which further ignites the reaction between Ti and C to form thermodynamically stable TiC.

(2) Under DTA conditions, due to the high heating rate, TiC phase of the reaction products lacks of C, which lead to the partial C does not react and remains. With the increase of Al content, the reaction of producing TiC is more completeness. The excessive Al increases the liquid Al in the reactions, which lead to the increase of more osculant odds between Ti and C, further fastened the reaction between Ti and C.

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REFERENCES