Microstructure and evolution of (TiB$_2$+Al$_2$O$_3$)/NiAl composites prepared by self-propagation high-temperature synthesis

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Abstract: (TiB$_2$+Al$_2$O$_3$)/NiAl composites were synthesized by self-propagation high-temperature synthesis, and their phase compositions, microstructures and evolution modes were studied. The microstructures and shapes vary with the TiB$_2$+Al$_2$O$_3$ content in the NiAl matrix. TiB$_2$ particles take a great variety of elementary shapes such as white bars, plates, herringbones, regular cubes and cuboids. These results outline a strategy of self-assembly processes in real time to build diversified microstructures. Some TiB$_2$ grains in sizes of 2−5 μm are embedded in Al$_2$O$_3$ clusters, while a small number of TiB$_2$ particles disperse in the NiAl matrix. It is believed that the higher the TiB$_2$+Al$_2$O$_3$ content is, the more the regular shapes and homogeneous distributions of TiB$_2$ and Al$_2$O$_3$ will be present in the NiAl matrix.

Key words: (TiB$_2$+Al$_2$O$_3$)/NiAl composites; self-propagation high-temperature synthesis; microstructure; evolution mechanism

1 Introduction

Due to its low density (5.59 g/cm$^3$), high melting point (1911 K), good thermal conductivity and good corrosion resistance [1], the NiAl intermetallic compounds have a wide application for components in high-temperature and corrosive environments, such as aero-engines, blades of gas turbine, thermal barrier coatings, and corrosion-resisting coatings. However, the low plasticity at room temperature and low strength at high temperature limit their applications in industry and production [2,3].

Up to now, many publications have involved in improving the room temperature plasticity and high temperature strength of Ni−Al intermetallic compounds. Adding different alloy elements such as Mo [4], Ti [5], Cr [6], and rare-earth metals [7] in NiAl is an efficient way to improve its properties. By adding or forming ceramics particles, such as Al$_2$O$_3$ [8,9], TiB$_2$ [10], NbB$_2$ [11] and TiC [12,13], the strength and creep properties of Ni−Al composite material can also be greatly improved. MICHALSKI et al [14] fabricated a NiAl−Al$_2$O$_3$ composite with different amounts of Al$_2$O$_3$ in NiAl through spark plasma sintering and self-propagation high-temperature synthesis (SHS) of Ni and Al, and the results showed that the hardness of NiAl−Al$_2$O$_3$ increased and the fracture toughness of it was almost twice that of NiAl. The fabrication of NiAl matrix composites was carried out by a variety of novel processes such as combustion synthesis [11,14], mechanical alloying [13] and high pressure reaction sintering. It has been proved that combustion synthesis has significant advantages, such as low energy consumption, inexpensive fabrication equipment, simplicity of operation and in situ synthesis of composite components, compared with other conventional methods. Via combustion synthesis procedure, a series of NiAl matrix composites reinforced by TiB$_2$, NbB$_2$, TiC, Al$_2$O$_3$, ZrB$_2$ [15] and TiN [16] were obtained conveniently.

At present, many researches focus on TiB$_2$ and Al$_2$O$_3$ ceramics as a duplex reinforced phase in different matrices because of their similar thermal expansion coefficient, chemical and physical compatibility [17]. By adding TiB$_2$ into Al$_2$O$_3$ ceramics, the growth of Al$_2$O$_3$ grains and the propagation of cracks in the matrix can be
prevented. Consequently, the fine and well-distributed TiB\textsubscript{2} phase would help to enhance the strength and fracture toughness of the composite material. Thus, it would contribute to improving the abrasion resistance and fracture toughness in cutting tool materials [18,19].

The study on the previous work indicates that the fabrication of TiB\textsubscript{2}\textplus{}Al\textsubscript{2}O\textsubscript{3}/NiAl composite materials through combustion synthesis has not been fully investigated. The fundamental objective of the present study is to investigate the microstructures and their evolution modes when different TiB\textsubscript{2}\textplus{}Al\textsubscript{2}O\textsubscript{3} contents were formed in the NiAl matrix, using Ni, Al, B\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} as raw materials, via combustion synthesis. Also, the correlation between the TiB\textsubscript{2}\textplus{}Al\textsubscript{2}O\textsubscript{3} content, microstructure and properties of the composites was investigated.

2 Experimental

The raw materials are commercial pure Ni powder (99.9%, 38−50 \(\mu\)m), Al powder (99.9%, 75 \(\mu\)m), B\textsubscript{2}O\textsubscript{3} powder (98%, 75 \(\mu\)m), and TiO\textsubscript{2} powder (98%, 45 \(\mu\)m). The powder mixtures were considered as two parts: one was Ni+Al in which the mole ratio was fixed to \(n(\text{Ni}):n(\text{Al})\)=1:1, the other was Al+TiO\textsubscript{2}+B\textsubscript{2}O\textsubscript{3} in which the mole ratio was fixed to \(n(\text{Al}):n(\text{TiO}_2):n(\text{B}_2\text{O}_3)=10:3:3\), and the latter was added into the former in mass fractions of 0, 5%, 10%, 15%, 20%, 25% and 30%, respectively. In order to produce a homogeneous mixture, all the powders were mixed in a three−dimension blender for about 6 h. Then, the mixtures were poured into metal molds with dimensions of \(d20 \text{ mm} \times 20 \text{ mm}\) and pressed at a pressure of 150 MPa into cylindrical compacts. Seven typical green compacts were fabricated with different contents of Al+TiO\textsubscript{2}+B\textsubscript{2}O\textsubscript{3}. In order to make the reactants react completely, the green compacts were preheated in an electric furnace at 300 \(^\circ\text{C}\) for 30 min. After that, the compacts together with the molds were taken out and a small amount of Mg powders was poured onto the surface as the initiating combustion agent. At last the compacts were ignited by live tungsten wire immediately. The reactions between powders in raw materials were as follows:

\[
\begin{align*}
\text{Ni}+\text{Al} & \Rightarrow \text{NiAl} \\
10\text{Al}+3\text{TiO}_2+3\text{B}_2\text{O}_3 & \Rightarrow 3\text{TiB}_2+5\text{Al}_2\text{O}_3
\end{align*}
\]

Under the present condition, the reaction in green compact could self-sustain due to its high exothermic heat (SHS), the process is shown in Fig. 1.

The crystalline phases of the products were characterized by X-ray diffraction (XRD, Model D/Max 2500PC Rigaku, Japan). The morphologies of the fracture and microstructure were observed by scanning electron microscopy (SEM, Model KYKY2800B) and field emission scanning electron microscopy (FESEM, NOVA NANOSEM 450, FEI). The compositions of samples were analyzed using electron probe microanalysis (EPMA, JXA−8230). The microhardness was measured by FM−700 with the load of 1 N and sustaining for 10 s. For each compound, five indentations were taken in the microhardness test and made an average of these points with a consideration of relative errors.

3 Results

In the sample without Al+TiO\textsubscript{2}+B\textsubscript{2}O\textsubscript{3}, the Ni+Al reaction wave propagated steadily, and the speed was about 25 mm/s. When adding Al+TiO\textsubscript{2}+B\textsubscript{2}O\textsubscript{3} into Ni+Al, the igniting delay time prolonged. Once the reaction was initiated, the reaction wave spread rapidly. When the content of Al+TiO\textsubscript{2}+B\textsubscript{2}O\textsubscript{3} increased to 15%, the spreading speed reached up to 40 mm/s. Thus, the whole reaction in the compacts almost took place at the same time, similar to thermal explosion. After the reactions finishing, the samples were slowly cooled down.

3.1 Phase analysis

Figure 2 shows the XRD pattern of the raw materials. It illustrates that the powder mixture is composed of Ni, Al, TiO\textsubscript{2} and B\textsubscript{2}O\textsubscript{3}. Figure 3 shows the XRD patterns of products obtained by adding different contents of Al+TiO\textsubscript{2}+B\textsubscript{2}O\textsubscript{3}.
The reaction products simply consist of NiAl when the mixture contains only Ni and Al, which is in accordance with Reaction (1). After adding Al+TiO$_2$+B$_2$O$_3$, TiB$_2$ and Al$_2$O$_3$ ceramic phases appear besides NiAl phase. The higher the reactant content of Al+TiO$_2$+B$_2$O$_3$ is, the more the TiB$_2$ and Al$_2$O$_3$ ceramic phases can be generated. Moreover, there are hardly any unreacted raw materials. Thus, it can be deduced that the reactions were completely carried out, and the phases which are expected according to Reaction (2) are obtained.

3.2 Microstructure and hardness

The microstructures on polished surface of samples with different contents of ceramics are shown in Fig. 4. In the samples only containing Ni+Al, the NiAl grains are coarse with a lot of needles and parallel plates, as shown in Figs. 4(a) and (b), and this is in accordance with Ref. [20]. After adding Al+TiO$_2$+B$_2$O$_3$, some white bars and plates (~5 μm) distributed along the boundary of the matrix appear, and the grains of NiAl matrix are refined remarkably, as shown in Figs. 4(c) and (d). Furthermore, some plates (10−15 μm) are alternatively distributed with a kind of grey phase, and their distributional patterns are very similar to herringbone
structure. When the content of Al$^+$TiO$_2$+$B_2$O$_3$ increases to 20%, the white phase turns to be fine regular particles (smaller than 5 μm), mainly in the shape of cubes or cuboids gathering together as clusters on an irregular dark grey conglomerations, as shown in Fig. 4(e). Also the aggregation (60–70 μm) of white particle clusters on the irregular conglomerations and some white particles still distribute along the grains boundary of the matrix. The white particles seem to be inlaid in the dark grey conglomerations. With further increasing the content of Al$^+$TiO$_2$+$B_2$O$_3$, the amount of white particles increases significantly. But the size of aggregations of white particles, becomes smaller. In addition, some white particles disappear in the matrix, as shown in Fig. 4(f).

The microhardness test results are listed in Table 1. The average microhardness of the matrix in NiAl products without and with 10% (Al$^+$TiO$_2$+$B_2$O$_3$) are HV$_{100}$ 398 and HV$_{500}$ 501, respectively, which are close to the hardness of pure NiAl [20]. The microhardness of herringbone structure in the product with 10% (Al$^+$TiO$_2$+$B_2$O$_3$) is HV$_{100}$ (1160–1730), which fluctuates remarkably. Compared with the product with 10% (Al$^+$TiO$_2$+$B_2$O$_3$), the hardness of white cube or cuboids gathering clusters in the products with 20% and 30% (Al$^+$TiO$_2$+$B_2$O$_3$) is higher, and the highest hardness is up to HV$_{100}$ 2700. The hardness of dark grey irregular conglomerations which look like being pinned under the cube or cuboid particles is HV$_{100}$ (1260–1480). The hardness of the products with 20% and 30% (Al$^+$TiO$_2$+$B_2$O$_3$) also varies from HV$_{100}$ 570 to HV$_{100}$ 1420, and the highest hardness is close to that of dark grey conglomerations.

### Table 1 Microhardness and adiabatic temperature of samples with different contents of Al$^+$TiO$_2$+$B_2$O$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Microhardness (HV)</th>
<th>Adiabatic temperature/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure NiAl</td>
<td>398±19</td>
<td>1911</td>
</tr>
<tr>
<td>NiAl–5% (TiB$_2$–Al$_2$O$_3$)</td>
<td>410±21</td>
<td>1938</td>
</tr>
<tr>
<td>NiAl–10% (TiB$_2$–Al$_2$O$_3$)</td>
<td>501±25</td>
<td>1965</td>
</tr>
<tr>
<td>NiAl–15% (TiB$_2$–Al$_2$O$_3$)</td>
<td>567±28</td>
<td>1992</td>
</tr>
<tr>
<td>NiAl–20% (TiB$_2$–Al$_2$O$_3$)</td>
<td>595±29</td>
<td>2018</td>
</tr>
<tr>
<td>NiAl–25% (TiB$_2$–Al$_2$O$_3$)</td>
<td>608±31</td>
<td>2045</td>
</tr>
<tr>
<td>NiAl–30% (TiB$_2$–Al$_2$O$_3$)</td>
<td>596±30</td>
<td>2072</td>
</tr>
<tr>
<td>Pure (TiB$_2$–Al$_2$O$_3$)</td>
<td>–</td>
<td>2448</td>
</tr>
</tbody>
</table>

### 3.3 Composition

The SEM images of typical samples and the results of EDS composition analysis are shown in Fig. 5 and Tables 2 and 3, respectively. Combining the results of XRD analysis, microhardness test and EDS composition analysis, we can deduce that the white bars and plates which distribute along the boundary of the matrix or in herringbone structure at Spectrum 1 in Fig. 5(a) and the white particles in regular cube or cuboids shapes shown in Figs. 4(e) and (f) and Spectrum 3 in Fig. 5(b) are all TiB$_2$ grains. The gray matrix shown in Figs. 4(a) and (c) and Spectrum 2 in Figs. 5(a) and (b) is NiAl intermetallic compound. The irregular dark grey clusters which are around or under the cube or cuboids particles in Figs. 4(e) and (f) and Spectrum 3 in Figs. 5(a) and (b) are Al$_2$O$_3$.

### Table 2 EDS compositions of composite with 5% (Al$^+$TiO$_2$+$B_2$O$_3$)

<table>
<thead>
<tr>
<th>Element</th>
<th>Spectrum 1</th>
<th>Spectrum 2</th>
<th>Spectrum 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0</td>
<td>46.27</td>
<td>6.47</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>50.34</td>
<td>39.17</td>
</tr>
<tr>
<td>Ti</td>
<td>33.43</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>66.56</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>3.39</td>
<td>54.36</td>
</tr>
</tbody>
</table>

### Table 3 EDS compositions of composite with 15% (Al$^+$TiO$_2$+$B_2$O$_3$)

<table>
<thead>
<tr>
<th>Element</th>
<th>Spectrum 1</th>
<th>Spectrum 2</th>
<th>Spectrum 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0</td>
<td>41.33</td>
<td>5.23</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>52.36</td>
<td>37.27</td>
</tr>
<tr>
<td>Ti</td>
<td>30.75</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>69.24</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>6.31</td>
<td>57.50</td>
</tr>
</tbody>
</table>
4 Discussion

The mixture of reactants could be considered as two parts: one is Ni+Al which follows Reaction (1), the other is Al+TiO$_2$+B$_2$O$_3$ which follows Reaction (2). If the reaction systems are initiated at room temperature, the adiabatic temperature of Reaction (1) would be $T_{ad} = T_{mNiAl} = 1911$ K [21], while the adiabatic temperature of Reaction (2) would be $T_{ad} = 2448$ K [22]. When preheating the samples at 300 °C, the adiabatic temperatures of Reactions (1) and (2) at 300 °C are much higher than their $T_{ad}$ at room temperature. The $T_{ad}$ of Ni+Al+TiO$_2$+B$_2$O$_3$ hybrid system can be calculated according to the thermodynamic data provided in Ref. [23]. With the increase of Al+TiO$_2$+B$_2$O$_3$ content, the $T_{ad}$ of the mixtures rises to above 1911 K. The adiabatic temperatures of samples with different mass fractions of Al+TiO$_2$+B$_2$O$_3$ are listed in Table 1.

The reaction processes and microstructure evolution mechanisms of the system are shown in Fig. 6. As the melting points of Al and B$_2$O$_3$ are 660 and 445 °C, respectively, Al and B$_2$O$_3$ in the green powder (Fig. 6(a)) melt firstly during the reaction process. The melted Al contacts with liquid B$_2$O$_3$ and infiltrates into the surface of TiO$_2$ particles, as shown in Fig. 6(b). Thus, B and Ti elements are displaced from B$_2$O$_3$ and TiO$_2$, respectively [24,25]. At the same time, Al$_2$O$_3$ and TiB$_2$ are produced rapidly through Reaction (2). Moreover, the surplus molten Al and solid Ni react to form liquid NiAl, as the melting point of NiAl is lower than the adiabatic temperature of reaction system, as shown in Fig. 6(c). The sequences of the whole reaction are as follows:

\[
\begin{align*}
\text{Ni} + \text{Al} & \rightarrow \text{NiAl} \\
2\text{Al} + \text{B}_2\text{O}_3 & \rightarrow \text{Al}_2\text{O}_3 + 2\text{B} \\
4\text{Al} + 3\text{TiO}_2 & \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Ti} \\
\text{Ti} + 2\text{B} & \rightarrow \text{TiB}_2
\end{align*}
\]

\[ (3) \quad (4) \quad (5) \quad (6) \]

**Fig. 6** Sketch of reaction processes and structure evolution modes: (a) Mixed initial powders; (b) Al and B$_2$O$_3$ begin to melt; (c) Grains of NiAl, TiB$_2$ and Al$_2$O$_3$ formatting; (d–f) Morphologies of products with 10%, 20% and 30% (Al+TiO$_2$+B$_2$O$_3$), respectively
When the content of $\text{Al}+\text{TiO}_2+\text{B}_2\text{O}_3$ is less than 10%, both the amounts of $\text{TiB}_2$ and $\text{Al}_2\text{O}_3$, and the temperature of the reaction system are not sufficient. Therefore, the $\text{TiB}_2$ grains grow as irregular bars and plates [26,27] (Figs. 4(d) and 6(d)). $\text{TiB}_2$ and $\text{Al}_2\text{O}_3$ grow into herringbone alternative structure through “self-assembly” mode. When the reaction system cools down below the NiAl melting point, NiAl grains begin to nucleate and grow to form the matrix of composite gradually.

With increasing the content of $\text{Al}+\text{TiO}_2+\text{B}_2\text{O}_3$, the $T_{ad}$ of reaction system increases and a great amount of $\text{TiB}_2$ and $\text{Al}_2\text{O}_3$ is produced. The abundant $\text{TiB}_2$ resources and higher temperature are better for the regularization of $\text{TiB}_2$ [26]. Thus, $\text{TiB}_2$ particles grow freely, develop fully and take shapes of cube or cuboids finally. As $\text{Al}_2\text{O}_3$ grains form around the $\text{TiB}_2$ grains almost simultaneously, it is possible for them to attach together to form large irregular conglomerations, as shown in Figs. 4(e) and (f) and 6(e) and (f). During the grow process of NiAl grains, the conglomerations are pushed to the corner of grains or distribute along the boundaries. Also, this kind of distribution impedes the boundary’s movement and restricts the grain’s growth of NiAl matrix.

When the $\text{Al}+\text{TiO}_2+\text{B}_2\text{O}_3$ content increases to 30%, much higher $T_{ad}$ can be reached and more $\text{TiB}_2$ and $\text{Al}_2\text{O}_3$ are produced. All the above contribute a lot to $\text{TiB}_2$ grains to grow as regular cubes cuboids or hexagons, as shown in Figs. 4(e) and (f) and 7(a). In addition, a large amount of $\text{Al}_2\text{O}_3$ adheres to $\text{TiB}_2$ grains to nuclear, as shown in Fig. 7(b), and grows around them. Because there are no plates to subdivide the spaces between $\text{TiB}_2$ grains, as shown in Fig. 4(b), the $\text{Al}_2\text{O}_3$ grains develop more freely until touching each other to form conglomerations, as shown in Figs. 4(c) and (d). In the meantime, there are also some single $\text{TiB}_2$ cubes or cuboids dispersed in the NiAl liquid and some $\text{Al}_2\text{O}_3$ grains adhere to the impurities in NiAl liquid to nuclear. Finally, when NiAl begins to solidify, almost all the above solid phases that form before NiAl will be pushed to the grain boundaries in the similar way shown in Figs. 4(b) and 6(c), which makes contribution to the formation of refine NiAl grains. What is more, the $\text{Al}_2\text{O}_3$ grains which nucleate on the impurities may remain in the NiAl matrix to help to improve the hardness. These $\text{Al}_2\text{O}_3$ grains may flock together and become big conglomerations because of the self-diffusion of $\text{Al}_2\text{O}_3$. Therefore, the hardness of matrix in Fig. 4(c) varies greatly, and the highest hardness is close to that of pure conglomerations.

5 Conclusions

1) ($\text{TiB}_2+\text{Al}_2\text{O}_3$)/NiAl composites were synthesized by combustion synthesis using Ni, Al, $\text{TiO}_2$ and $\text{B}_2\text{O}_3$ mixed powders. With increasing the content of $\text{Al}+\text{TiO}_2+\text{B}_2\text{O}_3$, more $\text{TiB}_2$ and $\text{Al}_2\text{O}_3$ ceramic phases are generated in the NiAl matrix. When the reactant content of $\text{Al}+\text{TiO}_2+\text{B}_2\text{O}_3$ is less than 10%, $\text{TiB}_2$ and $\text{Al}_2\text{O}_3$ grow into herringbone alternative structure through self-assembly mode.

2) When more $\text{TiB}_2+\text{Al}_2\text{O}_3$ form, $\text{TiB}_2$ particles would grow freely and develop fully and take shapes of cube, cuboids or hexagons finally. At the same time, more $\text{Al}_2\text{O}_3$ which forms around $\text{TiB}_2$ grains tends to attach together to form large irregular conglomerations.

3) The microhardness of NiAl matrix composite increases by 50% from HV (398±19) to HV (608±31), due to grain refining with increasing the content of $\text{TiB}_2+\text{Al}_2\text{O}_3$ to 25%.

References


自蔓延高温合成($\text{TiB}_2 + \text{Al}_2\text{O}_3$)/NiAl
复合材料的显微组织及演化机制

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摘 要：采用自蔓延高温合成技术制备($\text{TiB}_2 + \text{Al}_2\text{O}_3$)增强NiAl基复合材料，并研究其相组成、显微组织和演化机制。结果表明：复合材料的组织及陶瓷相的形貌随添加剂($\text{TiB}_2 + \text{Al}_2\text{O}_3$)含量的不同而变化，TiB$_2$在短时间内以自组装的模式形成长条状、片状、鱼骨状以及规则的四方体和六棱柱等不同形态。TiB$_2$的尺寸在2～5 μm之间，与不规则的Al$_2$O$_3$伴生存在，少量TiB$_2$分布于NiAl基体中。随着陶瓷相含量的增多，TiB$_2$的形状趋于规则，且在NiAl基体中的分布更加均匀。

关键词：($\text{TiB}_2 + \text{Al}_2\text{O}_3$)/NiAl 复合材料；自蔓延高温合成；显微组织；演化机制

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