Fabrication and Mechanical Properties of Al₂O₃/TiAl in Situ Composites Doped With Nb₂O₅

F. Wang, N. Fan*, J. Zhu, H. Jiang
Key Laboratory of Auxiliary Chemistry & Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science & Technology, Xi'an, Shaanxi 710021, China

Abstract:
Al₂O₃/TiAl composites were successfully fabricated from powder mixtures of Ti, Al, TiO₂, Cr₂O₃ and Nb₂O₅ by a hot-press-assisted exothermic dispersion method. The effect of the Cr₂O₃ and Nb₂O₅ addition on the microstructures and mechanical properties of Al₂O₃/TiAl composites was characterized. The results showed that the specimens are mainly composed of TiAl, Ti₃Al, Al₂O₃, NbAl₃ and Cr₂Al. The Vicker-hardness and density of Al₂O₃/TiAl composites increase gradually with the increase of Nb₂O₅ content. When the Nb₂O₅ content was 6.54 wt %, the flexural strength and fracture toughness of the composites have a maximum values of 789.79 MPa and 9.69 MPa·m¹/₂, respectively. The improvement of mechanical properties is discussed in detail.

Keywords: Al₂O₃/TiAl Composites; In-situ Reaction; Microstructure Characterization; Mechanical Properties; Micro-alloying

1. Introduction

TiAl based intermetallic compound has been considered to be one of the best candidate materials for elevated temperature applications due to its excellent properties such as low density, high hardness and attractive oxidation resistance at high temperature [1-4]. However, such composites suffer from limited ductility and fracture toughness at room temperature.

Recent research has demonstrated that the low temperature ductility can be greatly improved through the methods of composition optimization and microstructure control [5-8]. By alloying with substitutional elements such as Nb, Cr, Mn, Fe, Ni and Cu, modification of the chemical composition may result in higher ductility and fracture toughness [9-14]. On the other hand, the development of TiAl matrix composites is another promising way to improve the mechanical properties of TiAl intermetallics.

The existence of second-phase particles can prevent the movement of the grain boundaries, restrain the growth of grains, and improve the heat-resistance stability. Al₂O₃ has been chosen as a ceramic reinforcement because of its advantageous thermo-mechanical behavior, inclusive of wear resistance, environmental stability, high temperature strength, and so on. Therefore, there arises a requirement to investigate the TiAl intermetallic matrix composites (IMCs) reinforced by Al₂O₃ particles [15-18].

In this work, the idea of both micro-alloying and composite strengthening by Al₂O₃ has been considered. Al₂O₃/TiAl composites were produced by hot-press-assisted in situ
reaction synthesis method with elemental powder mixtures of Ti, Al, TiO₂, Cr₂O₃ and Nb₂O₅. The phase composition of the as-synthesized composites was identified by the XRD analysis, and the effect of the Nb₂O₅ addition on microstructure and mechanical properties were investigated in detail.

2. Experimental

Ti (280 mesh, 99.3 % purity), Al (200 mesh, 99.5 % purity), TiO₂ (0.5 μm, 99% purity), Nb₂O₅ (500 mesh, 99.5% purity), and Cr₂O₃ (320 mesh, 99% purity) powders were used as raw materials. The following mixtures were prepared according to Tab. I. The mixture powders were ball milled in alcohol for 1 h. Further processes included drying under 40 ºC for several hour, Then the milled powders were compacted uniaxially under 10 MPa in a graphite mold coated with BN inside and firstly slowly heated to 900 ºC in vacuum (~10⁻² Pa) for 1 h. And then the compact was heated to 1300 ºC at a rate of 5 ºC /min under a pressure of 17.6 MPa and held for 2h with the pressure maintained. Finally, the sample was cooled down to room temperature. The surface layer of the samples was machined off to remove contaminants prior to characterization.

<table>
<thead>
<tr>
<th>Specimens No.</th>
<th>Ti</th>
<th>Al</th>
<th>TiO₂</th>
<th>Cr₂O₃</th>
<th>Nb₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>55.94</td>
<td>36.08</td>
<td>3.98</td>
<td>4.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1</td>
<td>54.08</td>
<td>34.88</td>
<td>3.84</td>
<td>3.87</td>
<td>3.34</td>
</tr>
<tr>
<td>2</td>
<td>52.28</td>
<td>33.72</td>
<td>3.72</td>
<td>3.74</td>
<td>6.54</td>
</tr>
<tr>
<td>3</td>
<td>50.65</td>
<td>32.67</td>
<td>3.60</td>
<td>3.62</td>
<td>9.46</td>
</tr>
<tr>
<td>4</td>
<td>49.07</td>
<td>31.65</td>
<td>3.49</td>
<td>3.51</td>
<td>12.29</td>
</tr>
</tbody>
</table>

The three-point bending flexural strength test of the specimens was conducted by the PT-1036PC material tester (Perfect Instrument Co. Ltd, Taiwan, China) with a span of 20 mm at a cross-head speed of 0.5 mm/min. The fracture toughness test of the specimens was carried out by the single edge notched beam (SENB) method, at a cross-head speed of 0.05 mm/min, with a loading span of 20 mm. The hardness of the samples was tested by using a Vickers hardness testing machine (HXD-1000, Shanghai second optical Ltd, China) using a load of 100 kg applied for 15 s. The bulk density of the as-synthesized composites was measured by the Archimedes method. The flexural strength and fracture toughness were determined with the following formulas, respectively, \( \sigma = \frac{3PL}{2bh^2} \), \( K_c = Y \times \frac{3PLa^{1/2}}{2bh^2} \), where P is the breaking load of the specimen, and h, b, L, α, and Y are the height, width, span, notch depth, and form factor of the specimen, respectively. The flexural strength and fracture toughness were calculated by averaging five individual measurements. The phase composition of the composite was identified by the X-ray diffraction analysis (XRD, D/max 2200PC, Rigaku, Japan) with Cu Ka radiation operating at 40 kV. Microstructure analyses of the samples were conducted in a scanning electron microscope (SEM, JSM-6700, JEOL Ltd, Japan).

3. Results and discussion

3.1 Phase composition

Fig. 1 shows the XRD patterns of the Al₂O₃/TiAl in-situ composites by hot pressed at 1300 ºC with different contents of Nb₂O₅. With the increase of Nb₂O₅ content, the as-synthesized composites consist of \( \gamma \)-TiAl, \( \alpha_2 \)-Ti₃Al, and Al₂O₃ as three major phases together.
with a significantly smaller amount of Cr$_2$Al, NbAl$_3$ phase, and no any peaks of the unreacted Ti, Al, TiO$_2$, Cr$_2$O$_3$ or Nb$_2$O$_5$ can be detected. Moreover, it can be seen that the $\alpha_2$-Ti$_3$Al /$\gamma$-TiAl ratio increases obviously with increasing Nb$_2$O$_5$ content. The presence of the above mentioned phases in the composite samples confirms the feasibility of the following in situ reactions. Moreover, formation of the reinforcement Al$_2$O$_3$ is also identified, which confirms the contribution of the displacement reaction of Al with Nb$_2$O$_5$, Cr$_2$O$_3$ and TiO$_2$. So the reaction mechanism could be shown as follows:

$$4\text{Al} + 3\text{TiO}_2 \rightarrow 3\text{Ti} + 2\text{Al}_2\text{O}_3$$

$$3\text{Al} + \text{Cr}_2\text{O}_3 \rightarrow \text{Cr}_2\text{Al} + \text{Al}_2\text{O}_3$$

$$28\text{Al} + 3\text{Nb}_2\text{O}_5 \rightarrow 6\text{NbAl}_3 + 5\text{Al}_2\text{O}_3$$

$$4\text{Ti} + 2\text{Al} \rightarrow \text{TiAl} + \text{Ti}_3\text{Al}$$

Fig. 1. XRD patterns of in situ Al$_2$O$_3$/TiAl composites hot pressed at 1300$^\circ$C with different contents of Nb$_2$O$_5$ (a) 0 wt %; (b) 3.34 wt %; (c) 6.54 wt %; (d) 9.46 wt %; (e) 12.29 wt %

3.2 Microstructurues

Fig. 2 represents the fracture surface of product morphology and EDX analysis results in point of the Al$_2$O$_3$/TiAl in situ composites with Nb$_2$O$_5$ content of 6.54 wt %. According to the atom ratio and the XRD (Fig. 1) results, the dark regions represent $\gamma$-TiAl, $\alpha_2$-Ti$_3$Al matrix and Cr$_2$Al, NbAl$_3$ phase which form a lamellar structure. Meanwhile, the bright phase contains mainly Al and O and has an atomic composition of 43.64% and 51.91%, respectively, which is close to stoichiometric ratio of Al$_2$O$_3$.

Fig. 3 shows the SEM micrographs of the fracture surface of the Al$_2$O$_3$/TiAl in situ composites with various Nb$_2$O$_5$ contents synthesized by hot pressing. It is clearly from Fig. 3(a) and Fig. 3(b) that with the Nb$_2$O$_5$ content increase, the structure of the as-sintered composites becomes refine with Al$_2$O$_3$ particles remaining on the grain boundaries. The Al$_2$O$_3$ particles change from an agglomerating state to an interpenetrating network structure, which is beneficial for the toughening effect in the composite material. However, when the Nb$_2$O$_5$ content reaches 12.29wt % (Fig. 3d), the Al$_2$O$_3$ particles tend to agglomerate again, which are
detrimental to the mechanical properties and reduce uniformity of the $\text{Al}_2\text{O}_3$/TiAl in situ composites.

![Fig. 2. EDS analysis of fracture surface of product (with Nb$_2$O$_5$ of 6.54 wt %).](image)

**Fig. 2.** EDS analysis of fracture surface of product (with Nb$_2$O$_5$ of 6.54 wt %).

![Fig. 3. SEM images of fracture surface of products with different contents of Nb$_2$O$_5$](image)

(a) 0 wt %; (b) 3.34 wt %; (c) 6.54 wt %; (d) 12.29 wt %.

**Fig. 3.** SEM images of fracture surface of products with different contents of Nb$_2$O$_5$

### 3.3 Mechanical properties

Fig. 4 shows that the density and Vicker hardness of the $\text{Al}_2\text{O}_3$/TiAl in situ composites. A linear increase in density and Vickers hardness with increasing Nb$_2$O$_5$ content is evidently observed. The density increase from 3.73 to 4.01 g/cm$^3$, and the hardness value increase from 2.87 to 5.10 GPa. These are likely because the fact that when the Nb$_2$O$_5$ content
increased, the amount of Ti$_2$Al, NbAl$_3$ increased and which have much higher density and hardness than TiAl. The increase of hardness is also attributed to the higher hardness of the in situ formed Al$_2$O$_3$. In addition, with increasing the Nb$_2$O$_5$ content, the microstructures of the composites are finer and have uniform distribution between the reinforcement phase of Al$_2$O$_3$ and TiAl matrix (Fig. 3), which is another important aspect for increasing the density and hardness.

Fig. 4. Vickers hardness and density of products as a function of Nb$_2$O$_5$ content.

Fig. 5. Flexural strength and fracture toughness of products as a function of Nb$_2$O$_5$.

Fig. 5 shows the flexural strength and fracture toughness of Al$_2$O$_3$/TiAl in situ composites as a function of Nb$_2$O$_5$ content. The values of the flexural strength and fracture toughness increase as the increasing Nb$_2$O$_5$ content until 6.54 wt %, at which point both of them reach the highest values of 789.79 MPa and 9.69 MPa·m$^{1/2}$, respectively. Previous investigations revealed that doping with both Nb and Cr could improve the mechanical properties of Al$_2$O$_3$/TiAl composites more than those doped with single Nb [19]. These results indicate that the introduction of a certain amount of Nb$_2$O$_5$ can improve the mechanical properties effectively due to the dispersion of Al$_2$O$_3$ ceramics particles. However, when the
Nb$_2$O$_5$ content increase up to 6.54 wt%, the agglomeration of the Al$_2$O$_3$ particles has a negative effect to the mechanical properties of the composite, which can be seen clearly from Fig. 3 (c) and (d). In addition, when Nb and Cr were added to the composites, some Nb and Cr substituted Ti atoms in the crystal lattice of the Ti–Al intermetallic compound. The difference in bond energy between Nb, Cr and Ti could change the crystal lattice of the Ti–Al intermetallic compound and make the bond stronger. In other words, double elements doped can increase the strength of the composites than one element [19].

4. Conclusions

Al$_2$O$_3$/TiAl in situ composites were fabricated by the hot-press-assisted exothermic dispersion method with elemental powder mixtures of Ti, Al, TiO$_2$, Cr$_2$O$_3$ and Nb$_2$O$_5$. The as-sintered products consist of $\gamma$-TiAl, $\alpha_2$-Ti$_3$Al, Al$_2$O$_3$, and Cr$_2$Al, NbAl$_3$ phases. Al$_2$O$_3$ particles tend to disperse on the grain boundaries forming a lamellar $\gamma+\alpha_2$ structure and the composites consist of an interpenetrating network of fine Al$_2$O$_3$ particles. With the Nb$_2$O$_5$ content increasing, the grains of the composites are remarkably refined and the dispersion of Al$_2$O$_3$ particles becomes more uniform. So that the density and Vickers hardness of the samples increase with the Nb$_2$O$_5$ content increased from 0 to 12.29 wt%. The density increase from 3.73 to 4.01 g/cm$^3$ and the hardness value increase from 2.87 to 5.10 GPa. When increasing the Nb$_2$O$_5$ content until 6.54 wt %, the flexural strength and fracture toughness reach the highest values of 789.79 MPa and 9.69 MPa·m$^{1/2}$, which are increased by 16.6% and 17.0%, respectively.

Acknowledgements

This work was supported by the National Foundation of Natural Science, China (51272145, 51171096), and the Graduate Innovation Fund of Shaanxi University of Science and Technology.

5. References


Садржај: Al$_2$O$_3$/TiAl композити су успешно добијени из смеше прахова Ti, Al, TiO$_2$, Cr$_2$O$_3$ и Nb$_2$O$_5$ егзотермном дисперзионом методом уз помоћ топлог пресовања. Карактерисани су додаці Cr$_2$O$_3$ и Nb$_2$O$_5$ на микроструктуру и механичка својства композита Al$_2$O$_3$/TiAl. Резултати указују да се узорци углавном сastoје из TiAl, Ti$_3$Al, Al$_2$O$_3$, Nb$_3$Al$_3$ и Cr$_2$Al. Тврдоћа по Викерсу и густина Al$_2$O$_3$/TiAl композита расте линеарно са повећавањем удела Nb$_2$O$_5$. Када је садржај Nb$_2$O$_5$ 6.54 wt %, отпорност на савијање и жилачност имају максималне вредности од 789.79 MPa и 9.69 MPa·m$^{1/2}$, истим редом. Детаљно је описано побољшање механичких својстава.

Кључне речи: Al$_2$O$_3$/TiAl композити; реакција in-situ; микроструктура; механичка својства; микро-легирање