Fabrication, Microstructure, and Microhardness at High Temperature of In Situ Synthesized Ti$_3$Al/Al$_2$O$_3$ Composites

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Abstract: In this study, in situ Al$_2$O$_3$-reinforced Ti$_3$Al composite was fabricated after $8 \ h$ of milling and sintering at 850 $^\circ$C. A mixture of TiO$_2$ and Al powders were mechanically milled in a planetary mill, cold-compacted and sintered under a protected argon atmosphere. The microstructure and microhardness of the Al$_2$O$_3$ embedded in Ti$_3$Al matrix at both room and elevated temperature has been reported. The obtained results showed that the Ti$_3$Al/Al$_2$O$_3$ composite was successfully synthesized via the powder metallurgy method. Ti$_3$Al phase and Al$_2$O$_3$ particles were formed after $8 \ h$ of milling and sintering at 850 $^\circ$C. The microstructure formation of round and uniformly distributed Al$_2$O$_3$ particles in the Ti$_3$Al matrix improved the microhardness of the composite. At normal temperature, the microhardness of the material measured about 11.5 GPa. Meanwhile, at elevated temperatures, from 600 to 800 $^\circ$C, it decreased from 4.18 GPa to 3.15 GPa.

Keywords: Ti-Al composite; nanoparticle Al$_2$O$_3$; mechanical milling

1. Introduction

Ti-Al composite nanomaterials have been receiving considerable interest due to their specific properties, such as relatively high melting point, low density, high specific strength, high elastic modulus, good oxidation resistance, good mechanical properties and high creep resistance at elevated temperatures [1–4]. However, Ti-Al alloys are brittle at room temperature and have low fracture toughness [3,4]. The microhardness of intermetallic alloy was improved using various methods. Skvortsov et al. reported that the hardness of low-alloy steel was increased via the cold metal transfer method under applied external magnetic fields [5]. Zuev et al. showed that the contact potential difference and electric potential were important to affect the microhardness of metals [6]. Taotao et al. reported that the hardness of TiAl intermetallic material increased via the random distribution of Al$_2$O$_3$ particles in the host matrix of Ti-Al compounds [7]. In situ Al$_2$O$_3$-reinforced Ti-Al composites not only maintain the excellent properties of the Ti-Al matrix but also improve other properties due to the hardening property of Al$_2$O$_3$.

There have been quite a few studies on the synthesis of Al$_2$O$_3$-reinforced Ti-Al composites. Binh et al. reported that the Ti$_3$Al/Al$_2$O$_3$ and TiAl$_3$/Al$_2$O$_3$ composites were well-fabricated by using the thermal reaction of oxide TiO$_2$ with metallic Al by using ball milling and sintering at high temperature [8]. Welham et al. showed the possible fabricated TiAl$_3$/Al$_2$O$_3$ composite via the reaction of oxide TiO$_2$ with metallic Al under vacuum [9]. Ying et al. pointed out that the TiAl$_3$ intermetallic phase was formed from the reaction of Al with TiO$_2$ at temperatures above 820 $^\circ$C, while the Al$_2$O$_3$ phase was difficult to form at temperatures below 800 $^\circ$C and the $\alpha$-Ti(Al,O) phase proceeded at temperatures
above 1000 °C [10]. The phase form during the reaction of TiO$_2$ with Al powder was also reported to be dependent on the milling time in the high-energy ball mill method where the formation of TiAl$_3$/Al$_2$O$_3$ was first formed and changed to TiAl/Al$_2$O$_3$ [11]. The TiAl/Ti$_3$Al-Al$_2$O$_3$ composite was synthesized from nanosized TiO$_2$ and micron-sized Al powders by applying high pressure during thermal sintering [12]. Travitzky et al. reported that the dense interpenetrating phase Al$_2$O$_3$-TiAl-Ti$_3$Al composite was fabricated by the pressure-assisted thermal explosion of a TiO$_2$-Al powder blend [13]. The complex Al-Ti-Al$_2$O$_3$ composite was reported to be fabricated by using the spark plasma sintering technique [14]. The results indicated that the complex phase formed as a function of the chemical ratio source between oxide TiO$_2$ and metallic Al powder and also depended on the method of fabrication processing. In addition, during the synthesis process, the reaction between Al and Ti could form intermetallic phases such as TiAl, TiAl$_3$ and Ti$_3$Al compounds. The formation of these intermetallic phases has a great effect on the properties of the composites. Al$_2$O$_3$-reinforced Ti-Al composites synthesized by the mechanical method have been shown to have significantly reduced sintering temperature. Studies also show that the mechanical activation of the milling process lowers the temperature of the synthesizing process of Al$_2$O$_3$ and TiAl$_3$ phases from TiO$_2$ and Al as raw materials, from 1000 °C to 650 °C after 5 h of milling [9].

In this study, in situ Al$_2$O$_3$-reinforced Ti$_3$Al composite was fabricated from aluminum powder and titanium dioxide powder via the powder metallurgy method. The formation of the composite occurred after 8 h of milling and sintering. Microstructure and microhardness at room temperature and elevated temperature were studied and compared with other titanium-based materials.

2. Materials and Methods

Raw materials used in this study were commercial aluminum (Al) and titanium dioxide (TiO$_2$) powder from Merck KGaA (Darmstadt, Germany) and Xilong Chemical Co. Ltd. (Shantou, Guangdong, China), respectively. According to the particle size and chemical composition information provided by the manufacturers, the aluminum powder has a particle size of less than 50 µm and contains less than 1% Fe impurity, and the titanium dioxide powder has a chemical composition of 99.7% TiO$_2$ and its particle size is 2 µm. The mixture of aluminum and titanium dioxide powder was prepared in accordance with the stoichiometry of reaction between Al and TiO$_2$ (Equation (1)):

\[
5 \text{Al} + 3 \text{TiO}_2 \rightarrow \text{Ti}_3\text{Al} + 2 \text{Al}_2\text{O}_3
\] (1)

The powder mixture was weighed, mixed into a ball mill in a closed chamber under argon atmosphere. Samples were then milled for 8 h. The mixture of milled powder and mill ball was fed into a stainless steel mill with the ball-to-powder ratio of 10:1. The mechanical mill used was a vertical planetary ball mill NQM-4 of Yangzhou Nuoya Machinery Co., Ltd. In order to prevent the powder mixture from oxidizing during the milling process, the ball-milling tank was filled with argon. The milling parameters were set as follows: the rotation speed was 300 rpm, the zirconia milling-balls diameter was 10 mm and the milling time was 8 h. The milled sample was compressed with pressure at 100 MPa. The pressed sample was sintered at 650, 750 and 850 °C in a resistance furnace (EF 11/8B, Lenton, Hope Valley, United Kingdom) under argon atmosphere for 30 min. The sample disk was polished using sandpaper, increasing in roughness from 80 to 2000 CC-Cw and finally, using Al$_2$O$_3$ powder. A sketch of sample fabrication processing is shown in Figure 1.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) was performed on milled powder using a sample weighing 10,852 mg, using a Setaram Labsys Evo S60 instrument, Lyon, France. The sample was heated to 1000 °C at a rate of 10 °C/min. All analyses were performed under high-purity argon atmosphere at a flow rate of 150 mL/min.
The phase composition and microstructure of the sintered products were characterized by employing X-Ray diffraction (XRD) (Smart Lab, Rigaku, Tokyo, Japan) and scanning electron microscopy (SEM) (JSM7001FD, JEOL, Kyoto, Japan). Microhardness was measured with the Vickers HMV-1 tester (Shimadzu Corporation, Kyoto, Japan), tested under 245.2 mN and 15 s. The microhardness of samples was measured in at least three positions.

3. Results and Discussion

3.1. Microstructure

Figure 2 shows the DTA curve of samples using a planetary ball mill after 8h-milled. It can be seen that, during the heating phase, a clear exothermic peak appeared at 580.1 °C, which is below the melting point of aluminum. This is the possible reaction temperature between TiO$_2$ and Al powder; the energy then continued to climb as temperature increased up to 850 °C, beyond which no other energetic events were found. Experiments of Shi et al. indicated an exothermic peak at 891.3 °C when the mixture was not mechanically milled [15]. The results of this study show that the process of milling the sintered mixture is necessary to reduce the onset temperature to around the melting temperature of aluminum, which is also consistent with the study results of the previous reports [3,6].

Figure 3 exhibits the XRD patterns of the in situ composite samples sintered at 850 °C. As can be seen, titanium aluminide (Ti$_3$Al) was formed in the reacted sample. The main peak of intermetallic phase Ti$_3$Al was detected at 2θ angle of 39.92°; the remaining peaks mainly corresponded to Al$_2$O$_3$ detected in the reacted sample. On the basis of Figure 3, there is also a small amount of Ti$_2$Al$_5$ phase, but no peak indicates the presence of residual Ti, Al or TiO$_2$. The above results suggest that the synthesis process occurred completely.
The presence of these intermetallic phases in the mixed sample confirms the feasibility of the following in situ reactions:

\[
4 \text{ Al} + 3 \text{ TiO}_2 \rightarrow 3 \text{ Ti} + 2 \text{ Al}_2\text{O}_3 \quad (2)
\]

\[
\text{Al} + 3 \text{ Ti} \rightarrow \text{Ti}_3\text{Al} \quad (3)
\]

Figure 2. Differential thermal analysis curve of samples using a planetary ball mill after 8h-milled.

Figure 3. X-ray diffraction patterns of reacted sample after sintering at 850 °C.

The microstructure of the obtained composite after 8 h of milling and sintering at 850 °C was studied. As shown in Figure 4, lighter particles are dispersed \( \text{Al}_2\text{O}_3 \) on the \( \text{Ti}_3\text{Al} \) matrix as the darker region. Most \( \text{Al}_2\text{O}_3 \) (corundum) particles have a grain size of 0.2 ÷ 1.0 µm and a round and uniform shape in the composite, which increases the mechanical properties [16]. Figure 5a show the COMPO-SEM images of samples after being sintered at 850 °C. The contrasting dark and bright regions in COMPO-SEM images were related to the \( \text{Al}_2\text{O}_3 \) and \( \text{Ti}_3\text{Al} \) matrix, respectively. Our results were consistent with recent reports on the microstructure of \((\gamma + \alpha_2)\)-\( \text{TiAl/\text{Ti}_3\text{Al/Al}_2\text{O}_3} \) composites or \( \text{TiAl}_3/\text{Al}_2\text{O}_3 \) composites [3,17]. The darker and lighter regions in contrast, in COMPO-SEM images, originated from the higher atomic number values of the \( \text{Ti}_3\text{Al} \) phase than that of the \( \text{Al}_2\text{O}_3 \) phase [17]. The EDS mapping for Ti, Al and O elements for \( \text{Ti}_3\text{Al/Al}_2\text{O}_3 \) samples are
shown in Figure 5b–d, respectively. The results show that the Ti and Al elements were present everywhere in the samples but were inhomogeneously distributed in the samples as shown in Figure 5b,c, which is believed to relate to the contributions of Ti$_3$Al or Al$_2$O$_3$ phases. The oxygen was found to contribute in all samples where the brighter image was related to Al$_2$O$_3$ regions and the darker image corresponded to Ti$_3$Al regions [3,17]. The inhomogeneous distribution of Ti, Al and O in our samples further suggested that the Al$_2$O$_3$ phase was randomly distributed in the intermetallic Ti$_3$Al matrix during the reaction of Al metal with oxide TiO$_2$. This result agrees with the above XRD result that, when the milling time lasts up to 8 h, the reaction between oxide TiO$_2$ and metallic Al occurred completely, which formed Ti$_3$Al and Al$_2$O$_3$ phases under sintering processing.

Figure 4. SEM image of Al$_2$O$_3$/Ti$_3$Al composite after 8 h of milling and sintering at 850 °C.

Figure 5. (a) COMPO-SEM microphotograph of Al$_2$O$_3$/Ti$_3$Al composite with EDS mapping photos of corresponding areas, (b) titanium (Ti), (c) aluminum (Al), (d) oxygen (O) of samples sintered at 850 °C.
3.2. Microhardness

Figure 6 shows that the microhardness of the sintered sample at 850 °C is considerably higher than that of the sample at 650 and 750 °C. This can result from the increased sintering temperature. Al₂O₃ particles formed by in situ synthesis have a finer grain size and are more uniformly dispersed into the Ti₃Al matrix. In addition, a large number of dislocations were formed in the Ti₃Al matrix, leading to the enhanced dispersion of the reinforcement particles, therefore increasing the microhardness of the material. The Vickers hardness value for the sample in this study reached 11.57 GPa at the condition of milling for 8 h. The microhardness of Ti₃Al/Al₂O₃ composite samples at room temperature is compared with the results of Ti₃Al₃/Al₂O₃ composites in previously reported works [3,8].

![Figure 6. Microhardness value of the Ti₃Al/Al₂O₃ composite with selected sintering temperature.](image)

Figure 7 shows that, as the temperature increased, the microhardness of the material decreased. This phenomenon occurs due to the fact that, at elevated temperatures, the Al-Ti intermetallic phase softened, leading to a reduction in interfacial adherence between the matrix and reinforcement particles. At the working temperature of the exhaust valve of a car engine (600–800 °C), the microhardness of the Ti₃Al/Al₂O₃ material decreased from 4.18 to 3.15 GPa (around 35–45 in Rockwell C scale hardness (HRC) units). The observation of microhardness in our samples results at high temperature was comparable with the current used in martensitic heat-resistant steel (name JIS-SUH3, hardness of 30 HRC) and austenitic heat-resistant steel (name JIS-SUH35, hardness of 35 HRC) [18]. Therefore, we expected that our materials were valid replacements able to withstand more extreme conditions than the common materials being used. For a more general assessment of the microhardness of the Ti₃Al/Al₂O₃ composite, the results of previous studies for the Ti₃Al₃/Al₂O₃ composite, Ti metal and Ti-48Al alloy were compared [8]. The results indicate that, with the presence of the reinforcement particles and the intermetallic matrix Ti₃Al, the hardness of the material is significantly improved even at elevated working temperatures. With the appearance of the reinforcement particles and titanium-rich intermetallic, the material produced in this study has the best mechanical properties. When the temperature is higher than 600 °C, we begin to see that the hardness of Ti₃Al/Al₂O₃ composite decreases faster than that of Ti-48Al (a material that has been applied to the automobile engine exhaust valves of Mitsubishi cars) [19]. This illustrates that, at high temperature, the TiAl matrix has lower softening temperature than that of Ti₃Al and Ti-48Al, causing interfacial adherence to decrease rapidly and mechanical properties at this time to depend greatly on the properties of the matrix material. Therefore, in this temperature range, the Ti-48Al
alloy has better mechanical properties than the TiAl/Al$_2$O$_3$ composite. Meanwhile, the hardness of the TiAl$_3$/Al$_2$O$_3$ in situ composite decreases as temperature increases.

![Figure 7](image)

**Figure 7.** Vickers hardness of the sample that was ball milled for 8 h and sintered at 850 °C at different temperatures.

4. Conclusions

In situ Al$_2$O$_3$-reinforced Ti$_3$Al composite was successfully fabricated from aluminum and titanium dioxide powder after 8 h of grinding and sintering at 850 °C. The appearance of Al$_2$O$_3$ reinforcement particles increases the hardness of the Ti$_3$Al matrix where the microhardness value is 4.20 GPa (430 Hv) at 600°C. Compared to other titanium-based materials, the Ti$_3$Al/Al$_2$O$_3$ composite has the highest hardness. Under elevated working-temperature conditions, the hardness of the Ti$_3$Al/Al$_2$O$_3$ composite material is superior. We expect that our observation of high microhardness at high temperatures of the Ti$_3$Al/Al$_2$O$_3$ composite will be applied in car engine exhaust valves.

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