Fabrication of laminated Ti/Al₂O₃ composite by vacuum hot-pressing sintering

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Laminated Ti/Al₂O₃ composite was fabricated by tape casting with close control of thickness (about 200 μm) of Al₂O₃ and titanium layers. The green tapes of titanium and Al₂O₃ were prepared at room temperature due to high flexibility and strength. In order to improve the density of green layers, the binder removal temperature range of titanium and Al₂O₃ layers was investigated by differential scanning calorimeter (DSC/TG). The compact laminated Ti/Al₂O₃ composite sintered by vacuum hot-pressing at 1450°C for 60 min under pressure of 25 MPa was researched by X-ray diffraction and scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (EDX). The results showed an obvious diffusion region between Al and Ti layers, and the interfacial phases were composed mostly of Ti and Al₂O₃, together with a little amount of Ti₃Al, TiAl and Al₃Ti₂, and solid solution of O (AlTiO₂). Diffusion line of EDX spectrum indicated that the diffusion distance of dissociated Al³⁺ in Ti layers was about 5 μm.

Key-words: Laminated ceramic composite, Ti/Al₂O₃, Tape casting, Interfacial reaction

1. Introduction

Ti/Al₂O₃ composite is identified as promising materials for biology, aerospace, cutter and many other applications.¹⁻³ In recent years, Ti/Al₂O₃ have triggered tremendous interests among researchers in various preparation methods, which includes vacuum normal-pressure sintering, vacuum hot pressed sintering, self-propagating high-temperature synthesis (SHS), spark plasma sintering (SPS) and laser sintering (LS). Because of well physical and chemical compatibility between Ti and Al₂O₃, the most of properties of Ti/Al₂O₃ composite are superior to monolithic Ti and Al₂O₃ materials. However, the lack of damage tolerance ability constrains the application of Ti/Al₂O₃ composite.⁴⁻⁶ As it is reported, in sintering process, Al³⁺ tends to diffuse from Al₂O₃ to Ti and react with Ti to form inter-metallic compounds, which is the main reason leading to decrease of strength.⁷⁻⁸ Accordingly, the discussion of interfacial reaction and products between Ti and Al₂O₃ is key point.

Laminated structural material has been reported in metal, polymer and ceramic fields, such as laminated SiC, Si₃N₄ and Al₂O₃.⁹⁻¹³ According to the descriptions of many reports, laminated structure improved mechanical properties of materials due to deflect crack to consume more fracture energy.¹⁴⁻¹⁶ Chen obtained Ni/Al₂O₃ successfully and tested its toughness and strength by different sintering methods.¹⁷ At present, laminated Ti/Al₂O₃ composite prepared by tape casting has been rarely investigated. In the present work, alcohol-based tape casting method was used to produce green layers of Ti and Al₂O₃, Laminated Ti/Al₂O₃ composite was obtained by vacuum hot-pressing sintering technology. The interfacial reaction products and diffusion distance of interfacial elements were investigated by X-ray diffraction (XRD) and energy dispersive spectrometer (EDX).

2. Experimental procedure

Figure 1 shows the preparation of laminated Ti/Al₂O₃ composite. Firstly, the sol of 5 wt% PVB (Polyvinyl Butyral) dissolved by ethanol, and plasticizing agent of 5 wt% PEG2000 (Polyethylene Glycol) and powders of 20 wt% Ti (or Al₂O₃) were mixed in the sol and dispersed by ultrasonic for 2 h, respectively. Secondly, the mixed sol was put on tape casting mould at room temperature for 6 h. Then, the green gels were cut into slices and stacked separately to remove binder at 650°C for 2 h. Finally, the laminated sample was sintered by vacuum hot-pressing furnace (VVPgr-80-2300, China) at 1450°C for 60 min under an applied pressure of 25 MPa.

In order to determine the removal temperature range of PVB, TG/DSC (METTER TOLEDO TGA/DSC 1, Switzerland) was performed.

![Fig. 1. Schematic diagram of preparation of laminated Ti/Al₂O₃ composite.](http://dx.doi.org/10.2109/jcersj2.122.222)
utilized. The laminated structure of Ti and Al$_2$O$_3$ was observed by optical metalloscope (BA310MET, China). The phases and compositions of interfaces were identified by X-ray diffraction (D8-ADVANCE, Germany). The microstructure and diffusion distance of adjacent layers were analyzed by a scanning electron microscopy (SEM) (FEI QUANTA FEG 250, United States) equipped with energy dispersive X-ray analysis (EDX).

3. Results and discussions

The DSC (Differential Scanning Calorimeter) and TG (Thermo Gravimetric Analysis) results of Al$_2$O$_3$ green layers in binder removal process were shown in Fig. 2. An obvious weight loss of sample was indicated by the curve of TG from 290 to 433°C. Meanwhile, the curve of DSC showed a prominent endothermic peak at this temperature range. It means that the majority of binder removed from Al$_2$O$_3$ layers during this process, and the DSC/TG result for Ti layers also showed the similar tendency as Al$_2$O$_3$ layers. The tendency of weight loss from 433 to 650°C was gradually moderated, and it turned to be stable after 650°C. Consequently, the binder removal temperature range of Ti and Al$_2$O$_3$ was determined from 209 to 650°C, and slower heating rate as well as longer soaking time greatly affects the binder removal process.

The fracture surface in fracture experiment of Ti/Al$_2$O$_3$ composite was showed in Fig. 3. It can be clearly observed the laminated structure (Ti layers have a brighter metallic luster than Al$_2$O$_3$ layers) and the thickness of each of layers was about 200–250 μm. Figure 4 shows the microstructure of cracks propagating paths and crack deflections after fracture experiment. The clear crack deflections along Ti-Al$_2$O$_3$ interfaces form the step-like cracks, which is effective to extend crack length and absorb more fracture energy. Moreover, the crack branches and deflections appearing in laminated Ti/Al$_2$O$_3$ ceramic composite absorb more fracture energy than monolithic ceramic, which also improve the bending strength and fracture toughness.$^{16,17}$

SEM micrographs of interface between Al$_2$O$_3$ and Ti layers are shown in Fig. 5. The well-grown grain of Al$_2$O$_3$ and Ti spreading either side of the interface (the left area is Al$_2$O$_3$ and the right area is Ti) were observed. Structurally, close bonding of interface made the laminated Ti/Al$_2$O$_3$ reaches to a great bonding strength between Ti and Al$_2$O$_3$ layers. The characterization results of metalloscope and SEM both indicated that the laminated Ti/Al$_2$O$_3$ composite was sintered full density at 1450°C for 60 min under an applied pressure of 25 MPa.

The fracture surface of sample was detected by XRD and the result was shown in Fig. 6. The well-defined peaks of Ti, Al$_2$O$_3$ and inter-metallic compounds between Ti and Al were found, which meant that Ti/Al$_2$O$_3$ laminated composite was mostly composed of Al$_2$O$_3$ and Ti phases, together with little Ti$_3$Al, TiAl, TiAl$_2$ and AlTiO$_2$. To investigate clearly the diffusion phenomena in interfaces, laminated Ti/Al$_2$O$_3$ sample was characterized by EDX, as shown in Fig. 7. Al, Ti and O element diffusion lines exhibit a different gradual trend, it is suggesting that Al element spans the interface and diffuses to Ti layers, whereas Ti and O elements are kept in place. Based on estimation, the diffusion distance, which is the same as the reaction region, is about 5 μm. The results of XRD and EDX confirm that Al element of Al$_2$O$_3$ layers diffused to Ti layers and react with Ti to form inter-metallic compounds in the diffusion region (Fig. 7).

As it is reported,$^{7,8}$ in the process of sintering, Al$^{3+}$ dissociated by Al$_2$O$_3$ diffused to Ti layers and reacted with Ti to form Ti–Al inter-metallic compounds, Ti$_3$Al was the most influential phase to the mechanical properties of composites. In addition, the solid solution of dissociated O is always dispersed in Ti–Al inter-metallic compounds, such as AlTiO$_2$ in XRD patterns of Fig. 6.

Finally, according to the calculation of theoretical analysis of the thermodynamics, the possibility of interfacial reaction products Ti$_3$Al and TiAl were verified. Because of the melting...
point of Al and Ti are 657 and 1670°C, Al will be molten at 1450°C, while Ti remains solid. Therefore, the binary system was appropriated to Raoult’s law and Henry’s law. Due to the interfacial reaction, Ti + Al → Ti₃Al, existing in the binary system, the Gibbs free energy of Ti₃Al was expressed by \( \Delta G_{\text{Ti₃Al}} = \Delta G_{\text{Ti₃Al,0}} + 3RT \ln \alpha_{\text{Ti}} + RT \ln \alpha_{\text{Al}} \). By the above equation, it can be obtained that the Gibbs free energy of Ti₃Al and TiAl were -117.56 KJ/mol and -74.32 KJ/mol, separately. The results showed that Ti₃Al and TiAl could spontaneously react, and it was easier to generate Ti₃Al than TiAl.

4. Conclusions

Ti and Al₂O₃ green layers were prepared by tape casting with close control of thickness. As is shown in SEM micrograph, the laminated Ti/Al₂O₃ composite was sintered compactly by vacuum hot-pressing sintering with great combination of different layers. Crack branches and deflections of interfaces prolong crack length and absorb more fracture strength. The dissociated Al³⁺ diffuses to Ti layers (about 5 μm) and reacts with Ti to form an inter-phase region composed of Al₂O₃, Ti, Ti₃Al, TiAl and AlTi₂ phases.

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