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Effect of Al_2O_3 on the microstructure and mechanical properties of Ti_3AlC_2/Al_2O_3 in situ composites synthesized by reactive hot pressing

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Abstract

Ti_3AlC_2/Al_2O_3 in situ composites with different Al_2O_3 contents were successfully synthesized from the powder mixture of Ti, TiC, Al and TiO_2 by a reactive hot-pressing method at 1350 °C. The effect of Al_2O_3 on the microstructure and mechanical properties of the composites was investigated in detail. The results indicate that the as-fabricated products mainly consist of Ti_3AlC_2, Al_2O_3 and a small amount of TiC. With increasing the Al_2O_3 content, the flexural strength of Ti_3AlC_2/Al_2O_3 composites increase gradually, the fracture toughness reaches the peak value of 8.21 MPa $m^{1/2}$ as the Al_2O_3 content increasing to 9 wt%, the hardness attains the maximum value of 10.16 GPa for 12 wt% Al_2O_3. The strengthening mechanism of the composites was also discussed.

Keywords: B. Composites; C. Mechanical properties; D. Al_2O_3; Ti_3AlC_2

1. Introduction

Ti_3AlC_2 is a layered machinable ceramic representative of $M_{n+1}AX_n$ phases (also called MAX), with $n = 1$, 2 or 3, where M is an early transition metal, A is an A-group element and X is C or N [1–4]. It combines both the merits of metals and ceramics. Like metals, it is good electrical and thermal conductive, relatively low hardness, and plastic at the high temperatures, and is easy to be machined by both electrical discharge method and conventional cutting tools. Like ceramics, it possesses high melting point, high modulus, low density, high thermal stability and good antioxidation [5,6]. In addition, Ti_3AlC_2 also has nice self-lubricating property. However, the potential application of Ti_3AlC_2 as a high temperature structural material is limited due to its low hardness and unsatisfactory strength [7,8].

Incorporation of a second phase is an effective way to overcome these weaknesses of MAX carbides [8–14]. Considering the high hardness and modulus, excellent chemical stability and approximate thermal expansion coefficient, Al_2O_3 is chosen as reinforcement to increase the mechanical properties of MAX, such as Ti_3SiC_2 [9,10] and Ti_3AlC_2. Wu et al. [11] reported that the addition of Al_2O_3 into Ti_3AlC_2 matrix was shown to enhance its friction behavior and wear resistance. Chen et al. [12,13] successfully fabricated Ti_3AlC_2/Al_2O_3 directly from the powder mixture of Ti, C, Al and Al_2O_3 by in situ hot pressing/solid–liquid reaction process at 1500 °C, In comparison to monolithic Ti_3AlC_2, the Ti_3AlC_2/Al_2O_3 composites are substantially improved in the hardness, toughness, compressive strength, and flexural strength. However, the large size and inhomogeneous distribution of the Al_2O_3 particles hindered further increase of its mechanical properties. Recently, Yeh et al. [14] successfully prepared the Ti_3AlC_2/Al_2O_3 and Ti_2AlC/Al_2O_3 composites through in situ synthesis in the mode of self-propagating high-temperature synthesis (SHS) in Ti–Al–C–TiO_2 systems, but work on the strengthening Ti_2AlC and Ti_3AlC_2 by incorporation of second phase Al_2O_3 is not reported. However, to our knowledge, the method of in situ reactive hot pressing has not been applied into the synthesis of the Ti_3AlC_2 matrix composites. The reactive hot pressing represents an in situ processing technique for the fabrication of composites, which takes the advantage of low energy requirement, contaminant-free interface.

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So the objective of the present work is to fabricate Ti_3AlC_2/Al_2O_3 composites in the Ti–TiC–Al–TiO_2 system using the in situ reactive hot pressing technique. The effect of the content of in situ formed Al_2O_3 on the phase composition, microstructure, density and room-temperature mechanical properties including hardness, flexural strength, and fracture toughness of the composites were investigated in detail. And the strengthening mechanism of the composites was also discussed.

2. Experimental

Ti (50 μm, 99.3% purity), TiC (75 μm, 99.05% purity), Al (75 μm, 99.5% purity), and TiO_2 (25 μm, 99.5% purity) powders were used as the starting materials. For the preparation of Ti_3AlC_2/Al_2O_3 in situ composites, the powder mixtures containing Al, TiO_2, Ti, and TiC were formulated with stoichiometry given according to the following reaction. Considering the vaporization of Al at high temperatures, the content of TiC was reduced to 90 wt% and the content of Al was increased to 10 wt% in the starting powders. The detailed compositions of the samples were listed in Table 1.

$$x\mathrm{TiC} + (x-3)\mathrm{Ti} + (x+4)\mathrm{Al} + 3\mathrm{TiO_2} \rightarrow x\mathrm{Ti_3AlC_2} + 2\mathrm{Al_2O_3} \quad (1)$$

First, the blend of powders was ball milled in alcohol for 1 h and then dried at 50 °C for several hours. Then the milled powders were compacted uniaxially under 10 MPa in a graphite mold and coated with BN inside. The compacted samples were hot press sintered in vacuum (less than 6.0×10^{-2} Pa) at a rate of 5 °C/min to 1350 °C and held for 2 h under a pressure of 16 MPa. Finally, the samples were cooled down to room temperature in the furnace. The surfaces of samples were ground to remove graphite layer. The phase analysis of the sintered bulks was identified by X-ray diffraction (XRD) using a diffractometer with Cu Kα radiation (D/max-2200PCX). The microstructures of the samples were investigated by scanning electron microscope (SEM, JEOL JSM-6700F) and energy dispersive spectroscopy (EDS).

The measurements of all the mechanical properties were performed at room temperature by averaging 6 individual measurements. The sample densities were measured by Archimedes' method. Hardness measurements were performed on the HXD-1000 tester (Shanghai Second Optical Ltd., China) with a diamond indenter under a 1000 N load for 15 s. The three-point bending flexural strength tests were conducted by the PC-1036PC (Perfect Instrument Co. Ltd., Taiwan, China) material tester with a span of 20 mm at a cross-head speed of 0.5 mm/min with the specimen dimensions of 4 mm × 4 mm × 30 mm. The fracture toughness K_{IC} was measured on the PC-1036PC testing machine by using the single edge pre-cracked beam (SEPB) method with a notch depth of $0.4W$ (W is the width of specimen), at a cross-head speed of 0.05 mm/min, with a loading span of 20 mm. The flexural strength and fracture toughness were calculated with the following equations, respectively.

$$\sigma = \frac{3PL}{2bh^2} \quad (2)$$

$$K_{IC} = Y \times \frac{3PLa^{1/2}}{2BW^2} \quad (3)$$

Table 1
The compositions of the samples (wt%).

Specimens No.	Ti	TiC	Al	TiO_2	Theoretical targeted Al_2O_3 content
YL0[a]	28.49	54.87	15.68	1.17	0
YL5	24.50	52.67	17.39	5.85	5
YL9	20.79	50.61	18.99	10.22	9
YL12	17.95	48.99	20.23	13.61	12
YL15	14.62	47.19	21.64	17.47	15

[a] YLXX refers to the sample number, and XX is the targeted weight percent of Al_2O_3 phase.

3. Results and discussion

The X-ray diffraction patterns of monolithic Ti_3AlC_2 and Ti_3AlC_2/Al_2O_3 composites hot pressed at 1350 °C for 2 h are shown in Fig. 1. It can be clearly seen that the monolithic Ti_3AlC_2 from the sample YL0 of Ti:TiC:Al = 1.2:1.8:1.1 (in mole ratio) is composed of Ti_3AlC_2 and small amount of TiC (Fig. 1(a)). The previous work [15] also revealed that the TiC often existed in the final products as an intermediate phase for synthesis of Ti_2AlC and Ti_3AlC_2 due to the short reaction time and large amounts of reaction heat released from the thermal explosion reaction between the Ti and C. When small amount of 5.85 wt% TiO_2 was incorporated in the initial materials (Fig. 1(b)), a small amount of Al_2O_3 phase was also found in addition to the Ti_3AlC_2 phase. It is worth noting that that the as-sintered sample is composed of dominant Ti_3AlC_2 and a small amount of Al_2O_3 and TiC, and the ratio of Al_2O_3 content to Ti_3AlC_2 content increases with increasing TiO_2 amount in the initial materials (Fig. 1(c)–(e)). Compared with the previous works [4,14], the synthesis temperature of 1350 °C in this work is much lower than that of 1400 °C. The presence of the above-mentioned phases in the composite samples confirms the

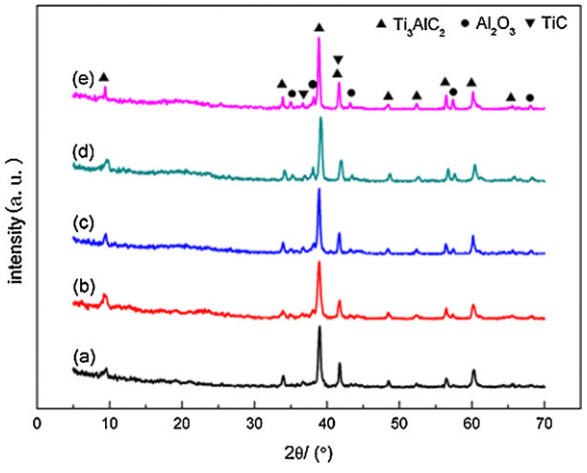

Fig. 1. X-ray diffraction patterns of the Ti_3AlC_2/Al_2O_3 composites with various Al_2O_3 contents. (a) 0 wt%; (b) 5 wt%; (c) 9 wt%; (d) 12 wt%; and (e) 15 wt%.

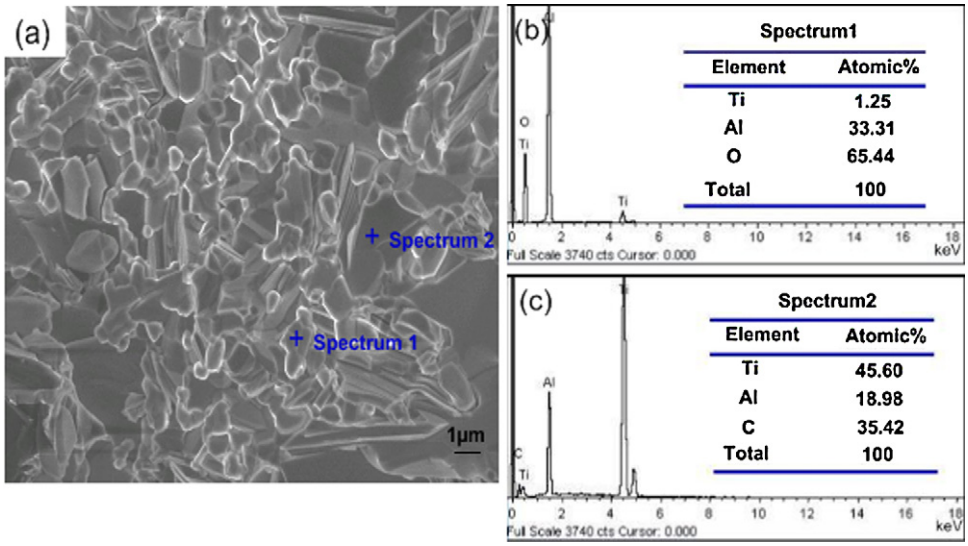

Fig. 2. (a) SEM micrographs and (b) and (c) EDS analysis results of the fracture surface of the Ti_3AlC_2/Al_2O_3 with 9 wt% Al_2O_3 composites sintered at 1350 °C.

feasibility of the overall reaction expressed as Eq. (1). The in situ formation of Al_2O_3 along with Ti_3AlC_2 is resulted from the thermite reaction of Al and TiO_2. It should be noted that the thermite reaction between Al and TiO_2 is a highly exothermic reaction, which releases large amounts of reaction heat. The increasing temperature facilitates faster and more complete diffusion of the reactants during reactive hot pressing, leading to a more uniform distribution of the second phase, Al_2O_3, and lower synthesis temperature of 1350 °C. The presence of TiC in the final product has often been observed in the formation of Ti_3AlC_2 and Ti_2AlC as an intermediate phase. So the reaction (1) could be divided into following reactions:

$$Ti + Al \rightarrow TiAl \quad (4)$$

$$3TiO_2 + 4Al \rightarrow 2Al_2O_3 + 3Ti \quad (5)$$

$$TiAl + 2TiC \rightarrow Ti_3AlC_2 \quad (6)$$

Fig. 2 displays the SEM micrograph of the fracture surface and the EDS analysis of Ti_3AlC_2/9 wt% Al_2O_3 composite. It is obvious that the material consists of the lamellar matrix phase and the particle-like second phase. The size of particles is about 1 μm, the platelike matrix grains are closely packed into a laminated configuration, which is characteristic of the layered ternary carbides, Ti_3AlC_2. Combined with the EDS analysis, the chemical composition indicates that the particle phase is enriched with Al, O and a small amount of Ti, and the atomic compositions of Al and O are 33.41% and 65.44% in mole ratio, respectively, which is close to stoichiometric Al_2O_3. From Fig. 1(c), for the lamellar matrix phase the quantitative atomic ratio of Ti:Al:C is 45.60:19.89:35.42, which is quite consistent with the predicted one of 3:1:2 for Ti_3AlC_2. Therefore, the composite is mainly composed of the matrix Ti_3AlC_2 and the second reinforcement phase, Al_2O_3. The latter one disperses at the grain boundaries of the matrix phase.

Fig. 3 displays the SEM micrographs of the in situ reactive hot pressed Ti_3AlC_2/Al_2O_3 composites with different Al_2O_3 contents. When the Al_2O_3 content is 5 wt%, the matrix Ti_3AlC_2 are coarse with a grain size of 10–15 μm (Fig. 2(a)). When increasing the Al_2O_3 content to 9 wt%, the size of the matrix grain decreases significantly to 5–10 μm, and Al_2O_3 grains disperses uniformly in the matrix (Fig. 2(b)). With further increasing the Al_2O_3 content to 15 wt%, surface pores and local agglomeration of Al_2O_3 grains tend to occur at the grain boundaries (Fig. 2(c)). It seems that too many Al_2O_3 grains would hinder the densification process of the composites.

Fig. 4 shows that the density and hardness of Ti_3AlC_2/Al_2O_3 composites with different Al_2O_3 contents. With increasing Al_2O_3 contents, the density of the Ti_3AlC_2/Al_2O_3 composites gradually decreases, due to the fact that the density of Al_2O_3 is smaller than that of Ti_3AlC_2. It is worth noting that the measured densities of all synthesized Ti_3AlC_2/Al_2O_3 composites are 99–99.7% of the theoretical density, which indicates that the as fabricated samples are nearly full dense. From Fig. 4, it can also be seen that with increasing Al_2O_3 content, the Vickers hardness of Ti_3AlC_2/Al_2O_3 gradually increases. It is reported that the hardness of monolithic Ti_3AlC_2 is about 3.5–4.7 GPa [4]. In this study, the maximum value of hardness reaches 10.16 GPa as the Al_2O_3 content increases to 12 wt%, which is almost 3 times of that of the monolithic Ti_3AlC_2. This partially derives from the higher hardness of the reinforcing Al_2O_3 phase, and partially from the refined grain size of the composites resulted from the second phase of Al_2O_3. However, when the Al_2O_3 content is high enough (15 wt%), the hardness decreases, which is attributed to the loose microstructure caused by too many Al_2O_3 content, which is consistent with the above SEM results.

Fig. 5 shows the flexural strength and fracture toughness of the Ti_3AlC_2/Al_2O_3 composites with different Al_2O_3 contents. It can be clearly seen that the flexural strength increases from 497 to 720 MPa as increasing Al_2O_3 content from 0 to 15 wt%. However, the K_{IC} increases with increasing the Al_2O_3 content, and reach a maximum value of 8.2 MPa $m^{1/2}$ at 9 wt% Al_2O_3 content, and then decreases dramatically. Combined with the SEM analysis results (Fig. 3), the fracture toughness of the Ti_3AlC_2/Al_2O_3 composites begins to

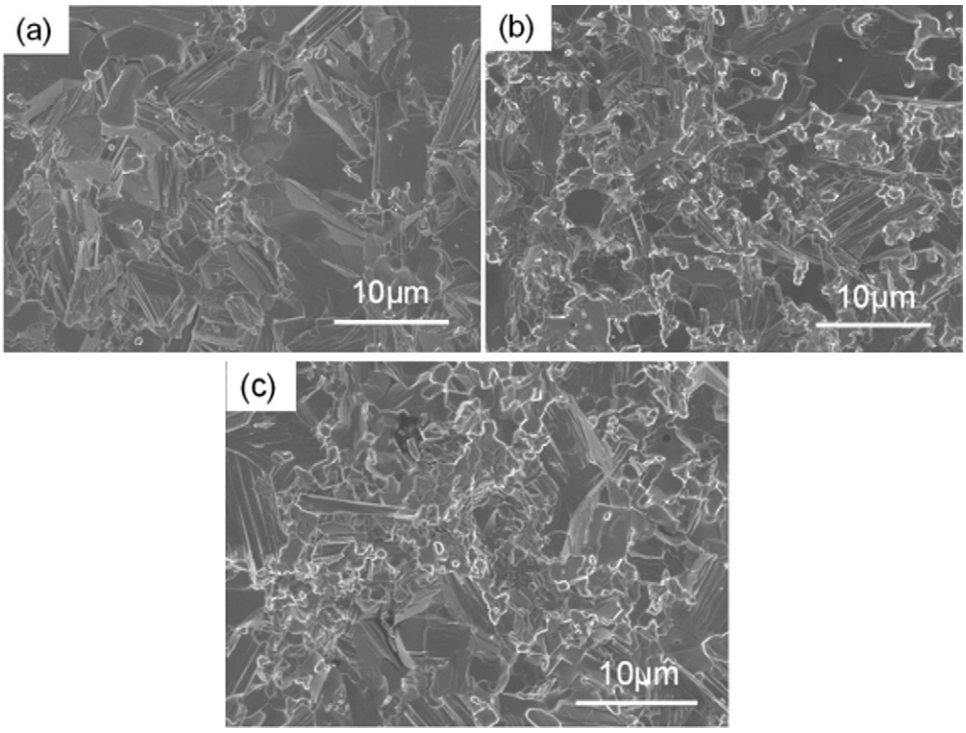

Fig. 3. SEM microstructures of the Ti_3AlC_2/Al_2O_3 composites with different Al_2O_3 contents. (a) 5 wt%; (b) 9 wt%; and (c) 15 wt%.

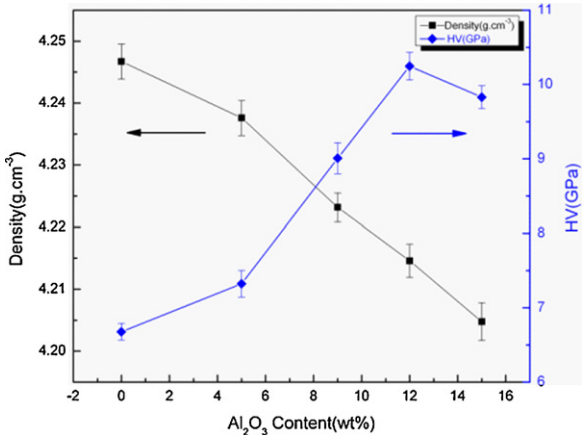

Fig. 4. Density and hardness of the Ti_3AlC_2/Al_2O_3 composites with different Al_2O_3 contents.

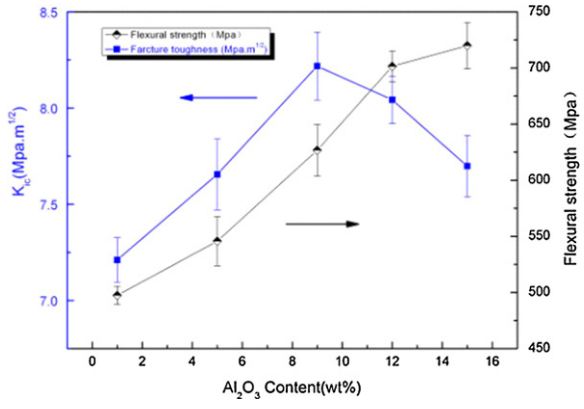

Fig. 5. Flexural strength and fracture toughness of the Ti_3AlC_2/Al_2O_3 composites with different Al_2O_3 contents.

decrease when the Al_2O_3 content is exceeded to 9 wt%, due to the agglomeration of the Al_2O_3 phase. So the optimum Al_2O_3 concentration is 9 wt%, at which the flexural strength and the fracture toughness are increased by 25.95% and 13.86%, respectively. The typical properties of the composite with 9 wt% Al_2O_3 are summarized in Table 2. For comparison, the results of the monolithic Ti_3AlC_2 fabricated by the solid–liquid reaction synthesis and simultaneous in situ hot pressing process in Ref. [4], Ti_3AlC_2/Al_2O_3 composite fabricated from the powder mixture of Ti, C, Al and Al_2O_3 by in situ hot pressing process in Ref. [12] and Ti_3AlC_2/TiC–Al_2O_3 composites obtained by in situ synthesis in the mode of thermal explosion from $3TiO_2$–5Al–2C system in Ref. [16] are also included. It can be seen that flexural strength and fracture toughness of the present sample are much higher than those of the monolithic Ti_3AlC_2 and Ti_3AlC_2/TiC–Al_2O_3 reported in Refs. [4] and [16], respectively. The fracture toughness is similar to that of the Ti_3AlC_2/Al_2O_3 composite reported in Ref. [12], and the hardness and flexural strength are much higher, which are resulted from the finer microstructure with uniform distribution. Compared with Ref. [16], the hardness of the present samples are much lower than Ti_3AlC_2/TiC–Al_2O_3 due to the higher content of Al_2O_3 in the latter.

The modification of the strength and fracture toughness is mainly attributed to the in situ formed Al_2O_3. The previous work [10,12] revealed that the addition of Al_2O_3 would improve the mechanical properties due to its high hardness, 18 GPa, and high Young's modulus, 386 GPa. The fine grain size controlled by the presence of dispersed fine Al_2O_3 grains and sintering at relatively low temperature of 1350 °C is another important reason to strengthen the Ti_3AlC_2/Al_2O_3 composites.

Table 2
Summary of typical properties of the as-prepared Ti_3AlC_2/Al_2O_3 composite (with ~9 wt% Al_2O_3), together with monolithic Ti_3AlC_2 [4], Ti3AlC_2/TiC–Al_2O_3 [16] and Ti_3AlC_2/Al_2O_3 composite [12] for comparison.

Properties	Flexural strength (MPa)	Fracture toughness (MPa $m^{1/2}$)	Density (g cm^{-3})	Hardness (GPa)	References
Ti_3AlC_2	340	7.2	4.24	3.5–4.7	[4]
Ti_3AlC_2/Al_2O_3	500	8.8	–	5.5	[12]
Ti_3AlC_2/TiC–Al_2O_3	466 ± 39	5.8 ± 0.3	–	13.3 ± 1.1	[16]
Ti_3AlC_2/Al_2O_3	626 ± 30	8.2 ± 0.2	4.224	8.9 ± 0.2	In this work

4. Conclusions

The Ti_3AlC_2/Al_2O_3 composites were synthesized by the in situ hot pressing method under a pressure of 16 MPa at 1350 °C for 2 h based on the Ti–TiC–Al–TiO_2 system. The phases of the as-sintered samples are mainly made of small sized Ti_3AlC_2 and Al_2O_3. The introduction of Al_2O_3 improves the hardness, fracture toughness and flexural strength of the composites. When the Al_2O_3 content is 9 wt%, the hardness, flexural strength and fracture toughness of the in situ composites increase by 62.18%, 25.95% and 13.86%, respectively.

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