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Synthesis and mechanical properties of (Ti, Mo)$_2$AlC/Al$_2$O$_3$ composite by a reaction hot pressing method

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Abstract

A dense (Ti, Mo)$_2$A1C/10 wt% Al$_2$O$_3$ in-situ composite was successfully fabricated from powder mixtures of Ti, Al, TiC and MoO$_3$ by reactive hot pressing sintering, and the reaction path was investigated in detail. It was found that the production of the (Ti, Mo)$_2$A1C/10 wt% Al$_2$O$_3$ was composed of a series of intermediate reactions: i.e., first reaction between Ti and Al forms Ti–Al intermetallics, and the thermite reaction between Al and MoO$_3$ producing Al$_2$O$_3$ and Mo. Then the intermetallics and the residual Ti and Al transformed to TiAl equilibrium phase. Finally, the (Ti, Mo)$_2$A1C/Al$_2$O$_3$ composite was formed by the reaction of TiAl TiC, and Mo. The Vickers hardness, flexural strength, compressive strength and fracture toughness of the composite were 4.75 GPa, 458 MPa, 971 MPa, and 6.03 MPa m$^{1/2}$, which are improved by 25%, 69%, 48%, and 146%, respectively, compared to the single-phase Ti$_2$AlC. The reinforcing mechanism was also discussed.

Keywords: Composites; Mechanical properties; Al$_2$O$_3$; (Ti, Mo)$_2$AlC

1. Introduction

Ti$_2$A1C is one of the M$_n$AX$_{n+1}$ phases, where M is an early transition metal, A is an A-group element (mostly III A and IV A), X is carbon and/or nitrogen, and $n=1$, 2 or 3 [1]. It has received considerable attention due to its combination of the merits for both the metals and ceramics [2–4], which has good electrical and thermal conductivity, easy machinability, and damage tolerance, high melting point, low density and has a thermal stability. However, its low hardness and low creep strength limit its application as structural components. Strengthening by solid solution or incorporation of a second reinforcement is effective way to overcome these weaknesses [5,6].

Recently, solid solution strengthening effects were investigated by both theoretical calculation and experimental results [7–9]. For example, Meng et al. [5] synthesized the (Ti, V)$_2$AlC solid solution and the strengthening mechanism was discussed. The Vickers hardness, flexural strength and shear strength of the (Ti$_{0.8}$, V$_{0.2}$)$_2$AlC were enhanced by 29%, 36% and 45%, respectively. Gupta and Barsoum [7] synthesized V$_2$AlC and (Ti$_{0.5}$, V$_{0.5}$)$_2$AlC solid solution using a hot isostatic pressing procedure, and a solid solution strengthening effect was exhibited. For the other hand, the synthesizing of composite seems to be another promising approach to improve the hardness and strength for the M$_n$AX$_{n+1}$ phases [10,11]. Among the second phase reinforcement, Al$_2$O$_3$ has been chosen as a candidate owing to its high temperature strength, excellent mechanical properties, wear resistance and high hardness [12,13]. The main problems for synthesizing Al$_2$O$_3$ reinforced M$_n$AX$_{n+1}$ composites are the compatibility between the two phases and the distribution of Al$_2$O$_3$.

In-situ synthesis of Al$_2$O$_3$ reinforced TiAl-based composites has received more and more attention worldwide due to the fine grain size and uncontaminated interfaces of the Al$_2$O$_3$ reinforcement [14,15]. Moreover, the previous reports [16,17] revealed that Mo can also improve the wettability between ceramic phase and metallic phase, which would prevent the ceramic grains from aggregating,

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and consequently modify the microstructure of the resultant materials. Hence, considering the combination effect of solid solution with Mo and incorporation of Al_2O_3 on the mechanical properties of Ti_2AlC, in the present work, MoO_3 together with Ti, Al, TiC was adopted to synthesize and optimize the (Ti, Mo)$_2$A1C/Al_2O_3 composites. The reaction mechanism of (Ti, Mo)$_2$A1C/Al_2O_3 in-situ composites was studied in detail and the microstructure and mechanical properties of (Ti, Mo)$_2$A1C/Al_2O_3 were investigated.

2. Experimental

Commercial powders of Ti (200 mesh, 99.5% purity), Al (200 mesh, 99.5% purity), TiC (98.0% purity) and MoO_3 (99.5% purity) were used as the starting constituents for preparing (Ti, Mo)$_2$AlC/Al_2O_3 by hot pressing sintering in this work. The mass ratio of Ti, Al, TiC and MoO_3 was 1:1:1.5:0.6, which were designed according to the stoichiometric composition of (Ti, Mo)$_2$AlC/10 wt% Al_2O_3, with an excess of Al as the modification according to the previous experiences of synthesizing Ti_2AlC.

The powders were mixed by ball milling in ethanol for 1 h and then were dried for several hours. The powder mixture were compacted uniaxially under 10 MPa in a graphite mold pre-coated with BN. The compacted samples were sintered by hot pressing at different temperatures for 2 h under a pressure of 15 MPa in vacuum ($\sim 10^{-2}$ Pa). After sintering, the samples were cooled down to ambient temperature in furnace. The surface layers of the samples containing contaminants were removed by grinding prior to characterization.

Phase constitution of the obtained samples were identified by X-ray diffraction (XRD, D/max-2200 PC X, Cu target, K_α radiation (40 kV and 30 mA)), with a scanning step of 0.02° and scanning rate of 8°/min. The polished surface of (Ti, Mo)$_2$AlC/Al_2O_3 sample was etched in an acid solution consisting of HF, HNO_3, and H_2O mixed at an equal volume fraction. The microstructures were studied using scanning electron microscopy (SEM, JEOLJSM-6700F) equipped with energy dispersive spectroscopy (EDS).

The density of composites was determined by the Archimedes method. The Vickers hardness was conducted using a HXD-1000 tester at a load of 10 N with a dwell time of 15 s. The flexural strength was measured by three-point bending method with a 30 mm span at a cross-head speed of 0.5 mm/min at room temperature. The fracture toughness was determined by single edge-notched-beam (SENB) method at room temperature with 20 mm span at a crosshead speed of 0.05 mm/min. The compressive tests were conducted using specimens with a dimension of $4 \times 4 \times 8$ mm^3 with the crosshead speed of 0.05 mm/min. The height direction of the specimen is parallel to the direction of hot pressing. Each final value was averaged over five measurements.

3. Results and discussion

The X-ray diffraction patterns of the (Ti, Mo)$_2$A1C/10 wt% Al_2O_3 composite hot pressed at different temperatures for 2 h are summarized in Fig. 1. The phase compositions in the specimens prepared at different temperatures are also listed in Table 1. When the powder was heated at 500 °C, there was no much pronounced change, and the main phases were to the same as the starting powders. When the temperature was increased to 700 °C, Ti–Al intermetallics, such as $TiAl_3$ and Ti_3Al were detected by XRD. When the temperature was further increased to 900 °C, the peak of TiAl was detected. This suggests that molten Al first reacted with Ti to produce $TiAl_3$ and Ti_3Al, and then transformed to TiAl equilibrium phase. These results are similar to the previous results in synthesis of Ti_2AlC or Ti_3AlC_2 [18,19]. At the same time, the thermite reaction between the molten MoO_3 (melting point 795 °C) and Al (melting point 660.8 °C) formed Al_2O_3 and Mo at 900 °C. And the reaction path in this range could be expressed as follows:

$$Al(s) \rightarrow Al(1) \quad (1)$$

$$Ti + 3Al(1) \rightarrow TiAl_3 \quad (2)$$

$$3Ti + Al(1) \rightarrow Ti_3Al \quad (3)$$

$$TiAl_3 + 2Ti \rightarrow 3TiAl \quad (4)$$

$$Ti_3Al + 2Al \rightarrow 3TiAl \quad (5)$$

$$2Al + MoO_3 \rightarrow Al_2O_3 + Mo \quad (6)$$

Ti_2AlC was appeared at 1100 °C and its content was dramatically increased with increasing the temperature,

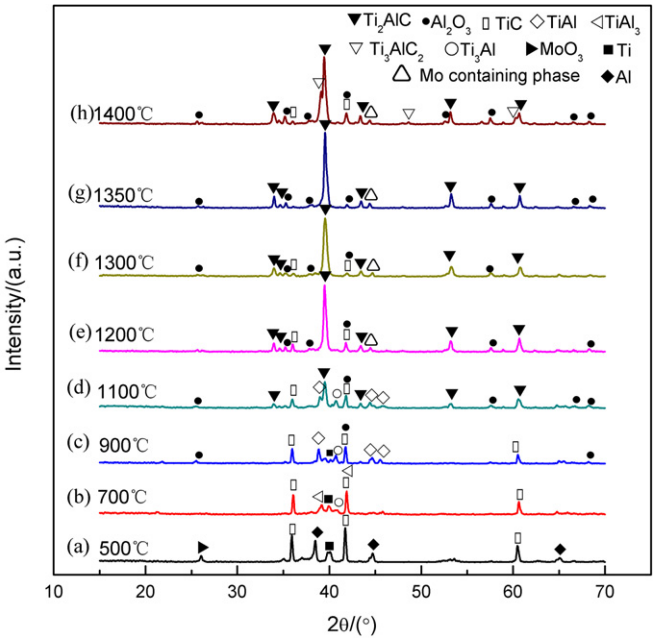

Fig. 1. XRD patterns of in-situ (Ti, Mo)$_2$A1C/10 wt% Al_2O_3 composite hot pressed at different temperatures.

while the content of Ti–Al intermetallics decreased gradually. When the temperature was increased to 1350 °C, only the Ti_2AlC and Al_2O_3 could be detected, without Ti–Al intermetallics and TiC phase remained, implying that the product possessed a high purity. However, when the temperature was further increased to 1400 °C, Ti_2AlC began to decompose to Ti_3AlC_2 and TiC. It was indicated that the optimal temperature to synthesize (Ti, Mo)$_2$AlC/10 wt% Al_2O_3 composites was 1350 °C, which was much lower than that in the previous investigation [20]. It is worth noting that, although the main phase was Ti_2AlC indexed by the JCPD card No. 29-0095, its reflection peaks shift to large angles evidently, which was attributed to the decrease of lattice parameters due to the formation of (Ti, Mo)$_2$AlC solid solution by replacement of Ti with smaller sized Mo. So the formation of (Ti, Mo)$_2$AlC could be as follows:

$$TiC + TiAl + Mo \rightarrow (Ti, Mo)_2AlC \quad (7)$$

Table 1
Summary of phase constitution of the prepared specimens in the temperature range of 500 °C – 1400 °C for 2 h.

Temperatures (°C)	Phase composites in the samples
The starting materials	Ti, Al, TiC, MoO_3
500	Ti, Al, TiC, MoO_3
700	$TiAl_3$, Ti_3Al, Ti, TiC
900	Al_2O_3, TiAl, Ti_3Al, Ti, TiC
1100	Ti_2AlC, Al_2O_3, TiAl, Ti_3Al, TiC
1200	Ti_2AlC, Al_2O_3, TiC, the Mo containing phase
1300	Ti_2AlC, Al_2O_3, TiC, the Mo containing phase
1350	Ti_2AlC, Al_2O_3, the Mo containing phase
1400	Ti_3AlC_2, Ti_2AlC, Al_2O_3, the Mo containing phase

Fig. 2 shows the SEM micrograph of the polished surface and the EDS analysis of the (Ti, Mo)$_2$A1C/10 wt% Al_2O_3 composite hot pressed at 1350 °C. The material mainly consists of a grey laminar matrix, minor fine granular grains (spectrum 2) and dendritic grains (with white color, spectrum 3). Although the content of each phase in the sample was hard to indentify accurately, the EDS analysis results indicated that the grey layered phase was composed of Ti, Al, C and Mo elements (spectrum 1), and the atomic ratio of Ti and Al was quite close to stoichiometric proportion of 2:1, which indicated that the grey laminar grains were (Ti, Mo)$_2$A1C. The content of C in the EDS was much higher than that of the theoretical value in Ti_2AlC because the C was too light to be detected precisely. The existence of some small amount of Mo in the matrix phase further confirmed the solid solution of Mo in Ti_2AlC, which was in agreement well with the XRD results given in Fig. 1.

The granular grains consist of Al and O, and their atomic ratio is very close to the stoichiometric composition of 2:3 for Al_2O_3. The dendritic grains are enriched with Mo and Al with an atomic ratio of 26.07:27.52, which is consistent with the result in the previous work [17]. The previous work revealed that the Ti–Al dendritic phase would be formed when the content of addition of Mo was high in the TiC/Al composites.

Fig. 3(b) shows the fracture microstructure of the (Ti, Mo)$_2$A1C/10 wt% Al_2O_3 composite. For comparison,

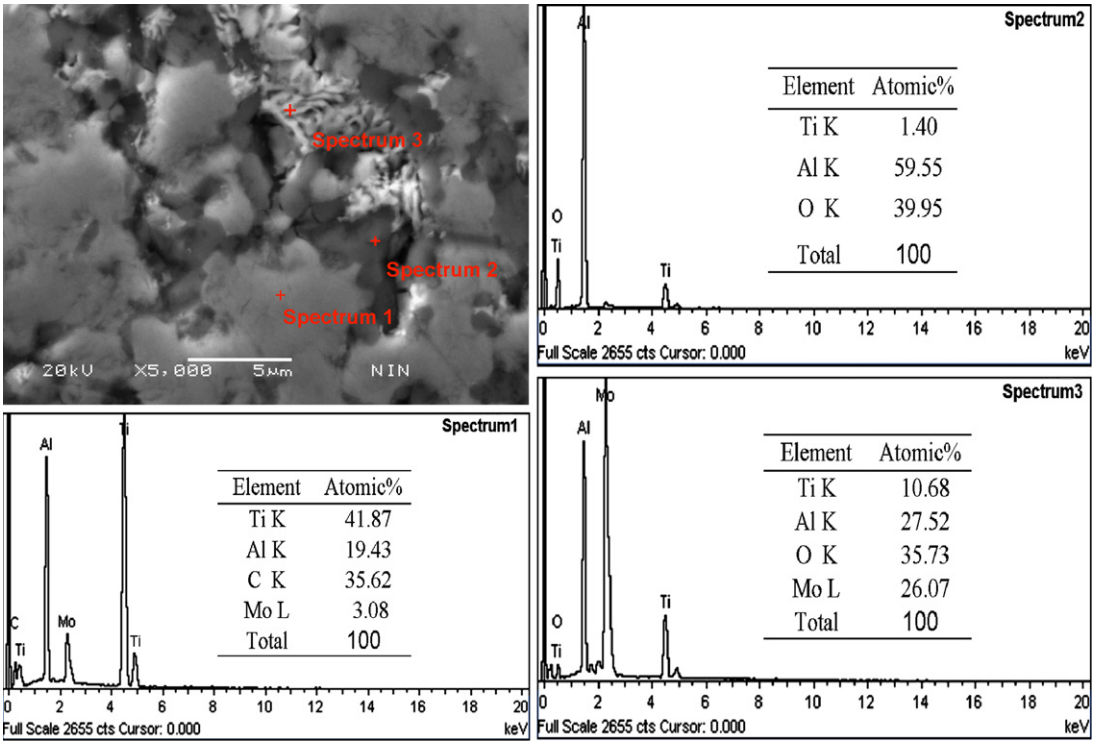

Fig. 2. Microstructure and EDS spectra of the etched (Ti, Mo)$_2$A1C/10 wt% Al_2O_3 composite hot pressed at 1350 °C for 2 h.

the microstructure of the monolithic Ti_2AlC fabricated by the same method was also presented (Fig. 3(a)). They are both fully dense and possess a laminal characteristic of Ti_2AlC grains. However, the grain sizes of Ti_2AlC and (Ti, Mo)$_2$AlC are 10 ± 2 μm, 5 ± 3 μm in diameter and 5 ± 2 μm, 3 ± 1 μm in thickness, respectively. The incorporation of Al_2O_3 in the composites leads to a significant reduction of the matrix grain size. It could conclude that the in-situ formed Al_2O_3 (1–3 μm) has an obvious hindering effect on growing the grain size of the matrix, and it agrees well with the experimental phenomena of Meng et al. [5], who reported that solid solution has no evident effect on microstructure.

The mechanical properties of the (Ti, Mo)$_2$AlC/10 wt% Al_2O_3 in-situ composite, comparing with those of the monolithic Ti_2AlC, Ti_2AlC/Al_2O_3 composite, as well as the (Ti, V)$_2$AlC solid solution from the previous works are shown in Table 2. It can be clearly seen that the Vickers hardness, flexural strength and compressive strength of the (Ti, Mo)$_2$AlC/10 wt% Al_2O_3 in-situ composite are higher than those of the monolithic Ti_2AlC, (Ti, V)$_2$AlC solid solution and Ti_2AlC/Al_2O_3 composite. However, the fracture toughness of (Ti, Mo)$_2$AlC/10 wt% Al_2O_3 in-situ composite are lower than those of samples in the previous studies [20,6], the reason is not very clear at the present.

The hardening and strengthening effects could be attributed to the following reasons. First, the modification in mechanical properties was due to the solid solution of Mo for the Ti_2AlC matrix. According to the theoretical calculation [5], Ti_2AlC would be strengthened as substituting Ti with Mo to form (Ti, Mo)$_2$AlC solid solutions. Since Mo was smaller and had one more valence electron than Ti, the weak Ti–Al bonds were reinforced. Second, the finer microstructure resulted from the inhibiting effect of Al_2O_3 particles was responsible for the improvement of the hardness and strength. Third, the distribution of the reinforcement and the bonding between the matrix and reinforcement grains were modified by the in-situ reaction process and the in-situ formed Mo. The in situ formed Mo could improve the wettability between ceramic phase and metallic phase, which prevents the ceramic grains from aggregating, and consequently the size of reinforcement was reduced and its dispersion was more homogenous [21].

4. Conclusions

A dense (Ti, Mo)$_2$AlC/10 wt% Al_2O_3 in-situ composite with high purity was successfully fabricated by the method of reaction hot pressing using Ti, Al, TiC and MoO_3 as starting powders. The reaction path investigation showed that the reinforcement Al_2O_3 was formed from the thermite reaction of Al and MoO_3, and the matrix of (Ti, Mo)$_2$AlC was produced by the reaction between TiAl, TiC and Mo. The composite possessed the Vickers hardness, flexural strength, compressive strength of 4.75 GPa, 458 MPa, 971 MPa, which are improve by 25%, 69% and 48%, respectively, comparing to the single-phase Ti_2AlC

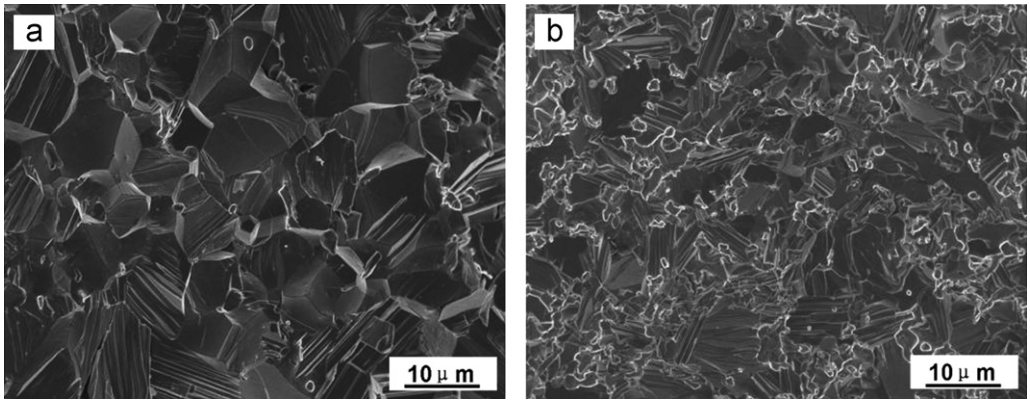

Fig. 3. SEM micrographs of fracture surfaces: (a) the monolithic Ti_2AlC and (b) (Ti, Mo)$_2$A1C/10 wt% Al_2O_3 composite.

Table 2
Summarizes the typical mechanical properties of the (Ti,Mo)$_2$AlC/10 wt% Al_2O_3 in-situ composite, Ti_3AlC_2/10 vol% Al_2O_3, V_2AlC and $(Ti_{0.85},V_{0.15})_2AlC$.

Properties	Density (g/cm^3)	Vickers hardness (GPa)	Flexural strength (MPa)	Fracture toughness (MPa m$^{1/2}$)	Compressive strength (MPa)	Reference
Ti_2AlC	4.10	4.2	384	7.0	670	[20]
Ti_2AlC	4.10 ± 0.02	3.79 ± 0.21	270 ± 20	2.45 ± 0.22	655 ± 32	This work
(Ti,Mo)$_2$AlC/10 wt% Al_2O_3	4.27 ± 0.02	4.75 ± 0.46	458 ± 28	6.03 ± 0.34	971 ± 40	This work
Ti_3AlC_2/10 vol% Al_2O_3	–	4.5	400	8.8	900	[6]
$(Ti_{0.8},V_{0.2})_2AlC$	4.2	4.5	356	6.0	–	[5]

ceramics. It was attributed to the combination reinforcing effects of the in-situ formed reinforcement Al_2O_3 and solid solution of Mo into Ti_2AlC matrix grains.

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