Low-temperature synthesis of high-purity Ti_2AlC powder by microwave sintering

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In this work, Ti_2AlC powders of high purity were prepared successfully by a facile microwave sintering technique which can reduce the sintering temperature from 1300 to 850°C obviously. This was probably because of the fact that the microwave field can decrease the activation energy of the particle surface, and improve ionic conductivity and the grain surface migration of charged vacancies. In addition, the purity of Ti_2AlC powders can be controlled by adjusting the molar ratio of Ti/Al/C/TiC as a precursor. It was interestingly found that Ti_2AlC powders with the highest purity of 96.6% were obtained at the molar ratio of Ti/Al/C/TiC = 1.5:1.0:0.5:0.45. This was probably attributed to the addition of TiC which favoured the formation of Ti_2AlC. However, excess TiC would influence the reaction path in the Ti–Al–C system and thus reduce the purity of Ti_2AlC. Therefore, this work can provide a facile method to synthesise other MAX powders.

1. Introduction: Recently, Ti_2AlC, a layered ternary carbide, has attracted much interest due to its combination of unique properties of metals and ceramics [1]. Various methods have been employed to synthesise bulk Ti_2AlC samples although Ti_2AlC was first synthesised and its structure was elucidated in the early 1960s [2]. However, it was very difficult to prepare phase-pure Ti_2AlC due to the narrow phase range in the Ti–Al–C ternary phase diagram [3, 4]. In the late 20th century, Barsoum *et al.* [5, 6] successfully fabricated high-purity Ti_2AlC polycrystals by reactively hot-pressing and high-isostatic pressing a mixture of Ti, graphite and Al_4C_3 powders. Later, Wang *et al.* [7, 8] also synthesised polycrystalline Ti_2AlC by using a solid–liquid reaction and simultaneous densification method. However, these two methods required higher sintering temperatures above 1000°C. Therefore, it was of great importance to synthesise Ti_2AlC powders at lower sintering temperatures.

Recently, the synthesis of Ti_2AlC powder with high purity has become more and more important because the synthesis process was a prerequisite of fabricating complex shape and composite bulk materials [9, 10]. In addition, a new type of 2D material called Mxene exhibited unique morphology and good electrical conductivity, magnetic and thermal properties. Also, it was expected to be applied in a gas sensor, catalysis, and other fields. This material also needed high-purity Ti_2AlC powders as a raw material [11, 12]. Therefore, it was very necessary to prepare high-purity Ti_2AlC powders.

To prepare Ti_2AlC powders of high purity at lower temperatures, microwave sintering was employed here. Since the heating was supported by the microwave resource, the process was thought to save time and energy compared with the conventional sintering process. In addition, the purity of Ti_2AlC powder can be controlled by adjusting molar ratios of Ti/Al/C/TiC and sintering temperatures. The highest purity of 96.6% for Ti_2AlC powder was obtained at the molar ratio of Ti/Al/C/TiC = 1.5:1.0:0.5:0.45 and a lower sintering temperature of 850°C.

2. Experimental

2.1. Materials: Commercial powders of Ti (99.0% pure, 10.6 μm), Al (99.8% pure, 12.8 μm), TiC (99.2% pure, 8.4 μm), and carbon black (99%, 13.2 μm) were purchased from the Institute of Non-Ferrous Metals, Beijing, China. All powers were of chemically pure reagents and were used directly without further purification.

2.2. Preparation: The above powders with different molar ratios were first mixed with ethanol for 24 h. Then it was compacted in a steel mould and uniaxially pressed at 30 MPa to form pellets of 20 mm in diameter and 5 mm in thickness. Microwave sintering of the green compacts was carried out by using a 2.45 GHz, 2 kW single-mode cavity commercial microwave furnace (Model NJZ4-3, Nanjing, China) in flowing Ar gas at ambient pressure. The heating rate was kept at around 100°C/min by controlling the incident microwave power. The heating temperature was controlled at about 850°C for 10 min. The samples were prepared after cooling to room temperature naturally.

2.3. Characterisation: The phase structures of samples were characterised by using a rotating anode X-ray diffractometer (Model D/MAX-RB, RIGAKU Corporation, Japan). The microstructures of the samples were investigated via scanning electron microscopy (SEM; Model JSM-5610LV, JEOL Ltd, Japan), coupled with energy-dispersive spectroscopy (EDS) for chemical analysis (Model Phoenix, EDAX, USA).

3. Results and discussion: Fig. 1 shows the X-ray diffraction (XRD) patterns of these samples with different molar ratios of precursors [(a) Ti/Al/C = 2:1:1, (b) Ti/Al/C/TiC = 1.7:1.0:0.7:0.3, (c) Ti/Al/C/TiC = 1.5:1.0:0.5:0.5, (d) Ti/Al/C/TiC = 1.2:1.0:0.2:0.8]. It can be seen that most diffraction peaks corresponded to the structures of Ti_2AlC (JCPDF29-0095), a few diffraction peaks belonged to the structures of TiC (JCPDF89-3828), Ti_3AlC_2 (JCPDF52-0875) and $TiAl_2$ (JCPDF42-1136). This indicated that the main phases in samples (a) and (b) were Ti_2AlC and TiC, but it contained quite a large amount of $TiAl_2$. When the TiC content was increased in the precursor mixture, only Ti_2AlC and TiC existed in sample (c) with a molar ratio of Ti/Al/C/TiC = 1.5:1.0:0.5:0.5. According to the formula in the previous work [13] and XRD results, the weight percentage of Ti_2AlC content can be calculated as 95.8%, which was a very high value compared with other previous work. When further increasing the

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TiC content, the Ti_3AlC_2 appeared in the samples. This was because Ti_2AlC would react with redundant TiC to produce Ti_3AlC_2. The results confirmed that proper addition of TiC would favour the formation of Ti_2AlC. In this sense, the purity of Ti_2AlC powder can be controlled by adjusting the molar ratio of Ti/Al/C/TiC as precursors.

Based on the above results, the high-purity Ti_2AlC material can be obtained by this facile microwave sintering technique. The main reasons are presented as follows: firstly, the activation energy of the particle surface would decrease the influence of the microwave field. Meanwhile, a microwave field can improve ionic conductivity and a high-frequency electric field, and then it can contribute to the grain surface migration of charged vacancies [14, 15]. Secondly, at 850°C, aluminium was dissolved in a liquid phase, meanwhile, carbon black and titanium carbide were excellent absorbing materials so that other three precursors can absorb microwave heat to make microwave sintering reaction more quick and homogeneous. In this sense, the formation of Ti_2AlC can be obtained at low temperatures and in a short time. The formation mechanism was different from that in the previous work [16] and the reaction process can be expressed as follows:

$$1.5Ti + Al + 0.5TiC + 0.5C \rightarrow Ti_2AlC. \quad (1)$$

Fig. 2 shows the SEM images of the obtained samples. In Fig. 2*a* for sample (a), it can be seen that grains were integrated to each other due to the high $TiAl_2$ content. For samples (b) and (c), the nature of the tabular structure can be observed in Figs. 2*b* and *c*. The results of EDS analysis are shown in Figs. 2*e* and *f*, indicating that grains were composed of C, Al, and Ti elements, and their atomic ratio was about 1:1:2.5. In this sense, the grains were probably Ti_2AlC, which was in good agreement with the above XRD results. It can be seen that the addition of TiC usually favoured the formation of Ti_2AlC. In addition, the grains showed platelets with 2–5 μm in thickness and 5 μm in length. For sample (d) in Fig. 2*d*, the grains of Ti_2AlC decreased in size because Ti_3AlC_2 exhibited a new phase. The results indicated that excess TiC would influence the reaction path in the Ti–Al–C system and thus reduced the purity of Ti_2AlC. In this sense, the TiC content could have very important effects on the purity of the obtained samples.

To further investigate the effects of the TiC content in the precursor on the purity of Ti_2AlC, the samples were obtained with different TiC contents of 0.4 and 0.45. The two samples were subjected to XRD characterisation and the results are shown in Fig. 3. It can be seen that the main phases were Ti_2AlC and TiC in the samples. According to the quantitative phase analysis based on the XRD patterns, the sample with a precursor ratio of Ti/Al/C/TiC = 1.5:1.0:0.5:0.4 showed ratios of 89.9% for Ti_2AlC and 10.1% for TiC. The sample with a precursor ratio of

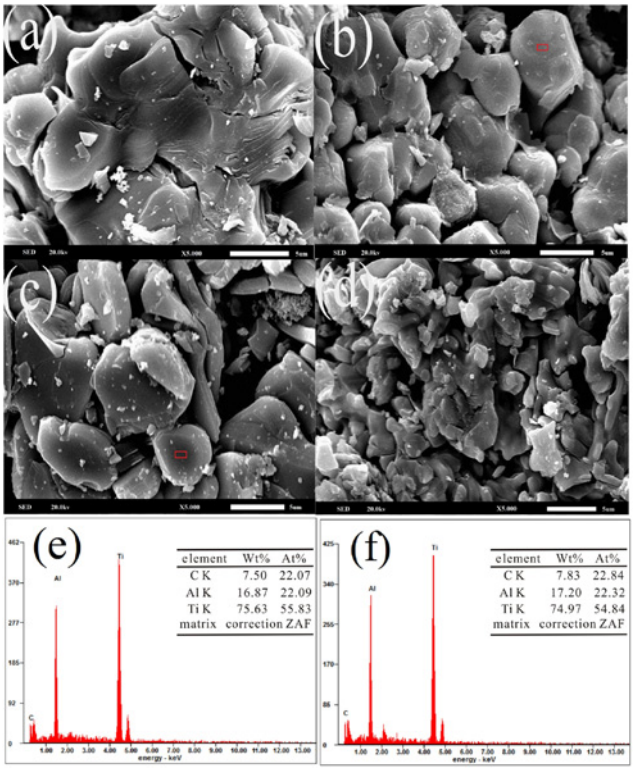

Fig. 2 *SEM images of Ti_2AlC powder synthesised from different precursors*
a Ti/Al/C = 2:1:1
b Ti/Al/C/TiC = 1.7:1.0:0.7:0.3
c Ti/Al/C/TiC = 1.5:1.0:0.5:0.5
d Ti/Al/C/TiC = 1.2:1.0:0.2:0.8
e EDS of sample (b)
f EDS of sample (c)

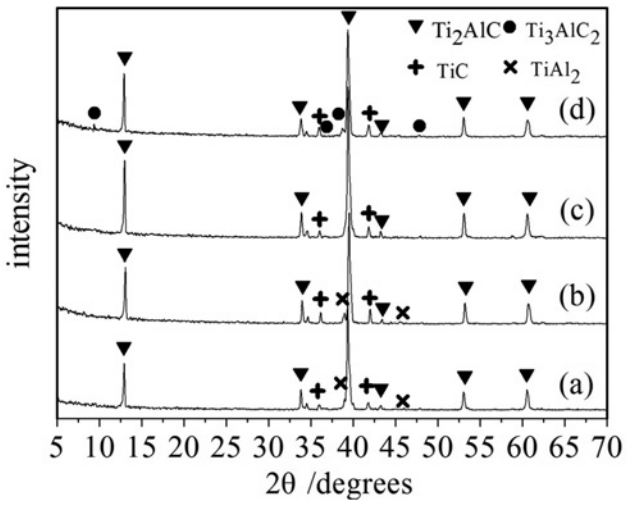

Fig. 1 *XRD patterns of samples*
a Ti/Al/C = 2:1:1
b Ti/Al/C/TiC = 1.7:1.0:0.7:0.3
c Ti/Al/C/TiC = 1.5:1.0:0.5:0.5
d Ti/Al/C/TiC = 1.2:1.0:0.2:0.8

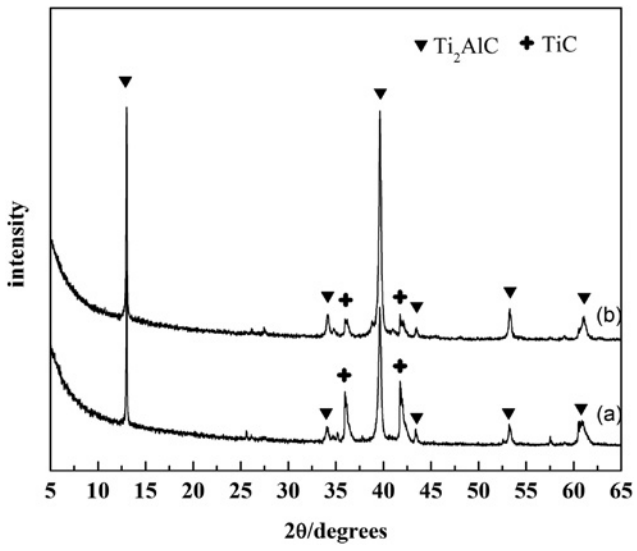

Fig. 3 *XRD patterns of samples with different contents of TiC*
a Ti/Al/C/TiC = 1.5:1.0:0.5:0.4
b Ti/Al/C/TiC = 1.5:1.0:0.5:0.45

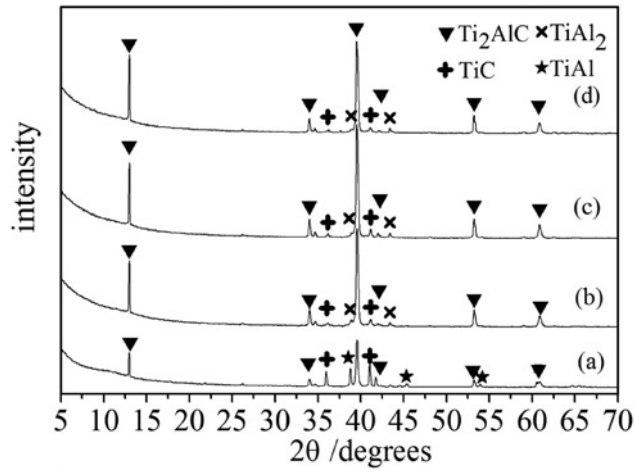

Fig. 4 *XRD patterns of samples at different sintering temperatures*
a 1300°C
b 1400°C
c 1450°C
d 1500°C

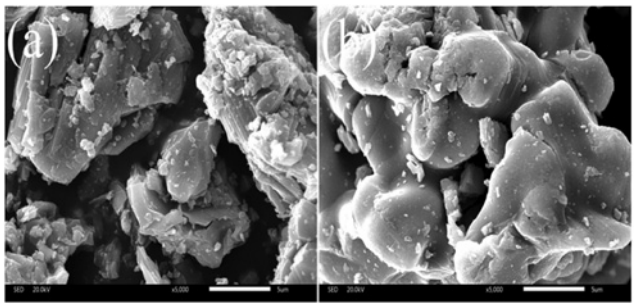

Fig. 5 *SEM images of Ti_2AlC powder material obtained by conventional method at different temperatures*
a 1400°C
b 1450°C

Ti/Al/C/TiC = 1.5:1.0:0.5:0.45 exhibited the highest purity of 96.6% for Ti_2AlC, which was the highest value reported by pressure-less sintering technique. Therefore, the optimal molar ratio of Ti/Al/C/TiC as precursors was 1.5:1.0:0.5:0.45.

To highlight the advantages of the microwave sintering technique, Ti_2AlC was also obtained by a conventional method with Ti/Al/C/TiC = 1.5:1.0:0.5:0.5 as a comparison. The sintering temperature was controlled between 1300°C and 1500°C in argon gas for 2 h. Fig. 4 shows the XRD patterns of these products. The main phases in sample (a) were Ti_2AlC and TiC, but it contained quite a large amount of TiAl. When the sintering temperature was increased, Ti_2AlC, TiC, and $TiAl_2$ in samples (b) and (c) were also identified by XRD. As shown in Fig. 4, the Ti_2AlC content in samples obviously decreased when the sintering temperature was increased accordingly. This was mainly because Ti_2AlC began to decompose when sintered at 1500°C. In addition, Ti_2AlC powders with higher purity obtained at 1400 and 1450°C were not uniform obviously in SEM images of Fig. 5. Therefore, compared with the conventional method, the microwave sintering technique can prepare more uniform Ti_2AlC powders with higher purity at lower temperatures.

4. Conclusion: High-purity Ti_2AlC (96.6 wt%) powder was successfully synthesised by microwave sintering technique with the molar ratio of Ti/Al/C/TiC = 1.5:1.0:0.5:0.45 at a lower sintering temperature of 850°C for 10 min. This demonstrated that the microwave sintering technique can offer lower sintering energy and much shorter time than the conventional sintering techniques. Therefore, this method can be applied in the synthesis of other MAX powders.

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6 References

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