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A novel simple method to stably synthesize Ti_3AlC_2 powder with high purity

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Abstract

In this work, a novel simple method is presented to synthesize highly pure Ti_3AlC_2 powder by heating 2TiC/Ti/Al (molar ratio) powder system between 1300 °C and 1400 °C for 15–30 min in flowing argon atmosphere. 2TiC/Ti/Al is selected as the raw material because of its much lower exothermal quantity than elemental 3Ti/Al/2C powder system in reacting process. The purity of Ti_3AlC_2 is not sensitive to the final temperature, soaking time or raw material scale. Its content is maintained around 97 wt.%, even though the scale of mixed raw materials vary from 5 g to 1000 g. The synthesized samples can be easily ground into powders with a mean particle size of 4.9 μm. Synthesis mechanism shows that both Ti_2AlC and Ti_3AlC_2 will generate from the reaction among TiC, Ti and Al below 1200 °C. Above 1300 °C, Ti_2AlC will continue to react with TiC and generate Ti_3AlC_2. The formation of Al liquid phase above 660 °C is considered as a promoting factor in the reacting process.

Keywords: Ti_3AlC_2; High-purity; Pressureless; Reaction mechanism

1. Introduction

Recently, a family of layered ternary compounds have been widely noticed, which are normally notated as $M_{n+1}AX_n$, 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 [1–6]. They combine both the merits of metals and ceramics. Like metals, they are highly thermal and electrical conductive, easy to be machined with conventional tools without lubrication, and well resistant to thermal shock; like ceramics, they present a high strength, high melting point and thermal stability.

In this family, Ti_3SiC_2 and Ti_3AlC_2 are two representative compounds, which have attracted more and more attentions. Besides having all common properties of this ternary compounds class, Ti_3AlC_2 has better plasticity at room temperature than others. It is also a potential electric contact material because of its high electrical conductivity [2] and low frictional coefficient resulting from its layered graphite-like structure.

Ti_3AlC_2 bulk materials have been first synthesized by Pietzka and Schuster [1], by sintering cold-compacted powder mixtures of titanium, TiAl, Al_4C_3 and carbon in pure hydrogen for 20 h. From then on, a number of researchers successfully prepared Ti_3AlC_2 bulk materials with various methods [2–6].

However, synthesis of Ti_3AlC_2 powder with high purity is becoming more and more important because powder synthesis of a certain ceramic is a prerequisite of fabricating complex shape and composite bulk materials. So far, there are very few reports referred to the Ti_3AlC_2 powder synthesis. Guo et al. [7] synthesized Ti_3AlC_2 using Ti, Al, C and 35 wt.% TiC as starting material by self-propagating high-temperature synthesis (SHS) method, where the TiC played a role of diluent to prevent thermal explosion reaction among the element powders. Wang and Zhou [3] fabricated Ti_3AlC_2 from elemental powders with a little TiC remained by the solid–liquid reaction method. However, the purity of Ti_3AlC_2 was not high enough. Moreover, none of the above methods has studied about the stability and feasibility to synthesize highly pure Ti_3AlC_2 in large scale.

In our previous work, pure Ti_3AlC_2 powder has been synthesized using elemental powders of Ti, Al and C at 1400 °C for 5 min, with a little addition of B_2O_3, which is adopted to decrease the thermal explosion reaction between Ti and C [8]. However, this method was not stable enough to synthesize highly pure Ti_3AlC_2 powder when holding temperature and soaking time fluctuated and raw material weight increased, even though the synthesizing process is easy to operate. Therefore, it is necessary to find a simple stable way for fabricating highly pure Ti_3AlC_2 powder.

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In order to avoid the thermal explosion reaction between Ti and C, in the present work, TiC is chosen as raw material to supply entire carbon during synthesis procedure of Ti_3AlC_2 powder. The effects of holding temperature, soaking time and sample scale on the purity of Ti_3AlC_2 powder are studied.

2. Experimental procedure

TiC (Beijing Fangda ceramic company, 99.0% pure, ~5 μm), Ti (Beijing Research Institute of Nonferrous Metal, 99.4% pure, −500 mesh), Al (Beijing Research Institute of Nonferrous Metal, 99.5% pure, −320 mesh) and activated carbon (Beijing Dali Activated Carbon Factory, 98% pure) powders were used in this work. The starting materials, with stoichiometric molar ratio of 2TiC/Ti/Al, were ball-milled in absolute alcohol for 24 h. After dried in vacuum, the blended powders were sieved with 100-mesh screen.

For comparison, the elemental powders with stoichiometric molar ratio of 3Ti/Al/2C were chosen for parallel research. Differential thermal analysis (DTA) (TGA 92, Setaram, France) was used to detect the differences of endothermal and exothermal changes between these two kinds of blended powders. To keep the same experimental conditions, two samples with the same weight of 82 mg were loaded into corundum crucible and heated to 1250 °C at a heating rate of 15 °C/min in flowing argon atmosphere.

In order to stably fabricate highly pure Ti_3AlC_2 powder in large scale, a pressureless synthesis method was adopted by calcining the blended powders of 2TiC/Ti/Al in flowing argon atmosphere. They were heated at a rate of 30 °C/min to the final temperatures (from 1200 °C to 1500 °C), holding for 15–60 min. To testify the stability of the process, the sample scales were selected from 5 g to 1000 g, respectively.

The loose products were crushed and disk milled, followed by ball-milling with tungsten carbide balls for 48 h. After sieved with 200-mesh screen, the particle size distribution of powders was carried out with particle size analyzer (PSA) (Master Sizer 2000, Malvern Instruments, British). The D50 value was measured as the mean particle size of the powders. The morphology of the samples was observed with scanning electron microscope (SEM) (JSM-6460LV, JEOL, Japan).

X-Ray diffractometer (XRD) (D/max-rB Rigaku Japan) was used to detect the phases of the products. The samples were step scanned with a step size of 0.02° and count time of 2 s/step, with the 2θ ranges from 5° to 50°. After removing background and stripping $K_{\alpha 2}$, the diffraction intensities of (0 0 2) peak of Ti_3AlC_2, (1 1 1) peak of TiC and (0 0 2) peak of Ti_2AlC were measured, respectively. The weight percents of Ti_3AlC_2 were calculated by Eq. (1), which were presented by the present authors in the reference of [9]:

$$\begin{cases} w_a = \dfrac{I_a}{I_a + 0.220 I_b + 0.084 I_c} \\ w_b = \dfrac{I_b}{4.545 I_a + I_b + 0.382 I_c} \\ w_c = \dfrac{I_c}{11.905 I_a + 2.619 I_b + I_c} \end{cases} \quad (1)$$

where, w_a, w_b and w_c are the weight percent of Ti_3AlC_2, Ti_2AlC and TiC. Similarly, the I_a, I_b and I_c stand for the integral intensities of the peaks of Ti_3AlC_2, Ti_2AlC and TiC mentioned above.

In addition, on the top of the products, there is always a thin layer of yellow cotton-like matter, which is proved as Al_4C_3 whiskers, and will be discussed elsewhere.

3. Results and discussion

3.1. DTA analysis

DTA curves for the blended powders of 3Ti/Al/2C system and 2TiC/Ti/Al system are shown in Fig. 1. It is clear that these two material systems show totally different DTA behavior. For 3Ti/Al/2C system (Fig. 1(a)), a very sharp exothermal peak appears around 650 °C, which is considered as the thermal explosive reaction between Ti and C. For 2TiC/Ti/Al system (Fig. 1(b)), however, an endothermal peak around 660 °C and one exothermal peak around 720 °C emerge in turn, which are corresponding to the melting of Al and formation of TiAl alloy, respectively. Because of the extremely high exothermal peak, the gentle endothermal peak in 2TiC/Ti/Al powder might be concealed. Comparing the exothermal peaks in the two systems, the exothermal quantity in 2TiC/Ti/Al sample was much gentler than that in 3Ti/Al/2C sample. The detected voltage related to the heat quantity in 2TiC/Ti/Al sample reached to the maximum of 5.95 μV, compared to the 46.98 μV of elemental sample. According to our previous work [8], when the elemental powder system was used, the thermal explosive reaction between titanium and carbon was very easy to happen and the crucibles with elemental powders often broke into several pieces, especially in the case of large sample size. Thus, due to the much smaller exothermal quantity, the 2TiC/Ti/Al powder system could be a potential starting material for fabricating highly pure Ti_3AlC_2 powders more easily and stably, in that no intense thermal explosion will happen.

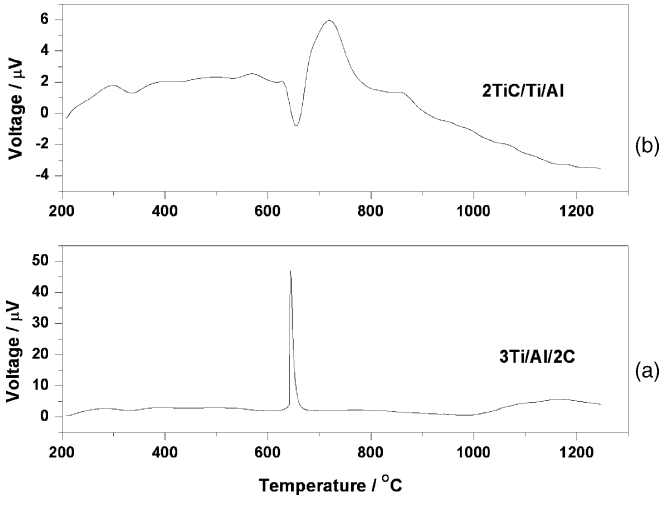

Fig. 1. The DTA curves of: (a) 3Ti/Al/2C and (b) 2TiC/Ti/Al system from 200 °C to 1250 °C.