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Low-temperature Solid-state Synthesis of Nanometer TiB_2-TiC Composite Powder

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Abstract: TiB_2-TiC composite powders were prepared at low temperature in the Ti-B system with the PTFE polytetrafluoroethylene (polytetrafluoroethylene) as a chemical activator. Reaction temperature, phase composition and morphology were measured *via* differential thermal analysis, X-ray diffraction and field emission scanning electron microscopy (FESEM) in order to explore the reaction mechanism, respectively. Actual solid-state reaction synthesis experiments were carried out for the same composition in an argon atmosphere furnace. It was found that TiB_2-TiC composite powder could be synthesized successfully at 550℃ by adding 10wt% PTFE into the initial reactant Ti-B mixture. The FESEM image showed that the average size of the product was smaller than 400 nm. According to differential thermal analysis results, the combustion synthesis mainly includes two reaction processes: firstly, the initial reaction between titanium and PTFE particles resulting in great amounts of heat release; subsequently, the released energy triggers the solid-state reaction between titanium and boron particles to form TiB_2.

Key words: TiB_2-TiC; solid-state synthesis; PTFE; reaction mechanism

It is well known that titanium diboride (TiB_2) based ceramics present series of excellent comprehensive properties such as high melting point, hardness and strength, excellent chemical resistance, electrical conductivities, *etc*[1-2]. This combination of properties has made them very attractive in several areas, including cutting tools, wear resistant parts, metal melting crucibles and electrode materials[2-3].

Normally, TiB_2 based ceramic powders are mainly synthesized by the following methods: direct reaction between titanium and elemental boron, metal-thermal reduction, carbothermal reduction, self-propagating high-temperature synthesis and mechanical chemical synthesis[4-9]. Among these methods, metal-thermal reduction and carbothermal reduction are the most commonly used, yet they are high energy consuming as the results of the synthesis temperatures which are higher than 1000℃, meanwhile, large amounts of carbon oxide emit during carbothermal reduction process[6]. In terms of mechanical chemical synthesis, although it's a powerful method for fabrication of various materials, it also has several disadvantages. For instance, final products are contaminated by grinding media[8]. Recently, for saving energy and getting high purity products, the research on the low-temperature solid-state reaction synthesis routes of ceramics has become more and more environmentally important[10-16]. In these works, polytetrafluoroethylene (PTFE) has been applied as a chemical activator in initiating the solid-state reaction synthesis of the low-caloric systems, *e.g.* Si-C, Mo-Si-C, SiO_2-Al-C. Furthermore, the reaction between titanium and PTFE is highly exothermic[17-18] and generates TiF_3 vapor at its sublimation temperature 1037℃[11, 19], which has been considered by US military for ammunition enhancement[20-21].

The purpose of this study is to investigate the solid-state reaction behaviour of a family of Ti-B-PTFE compositions with the intention of using these solid powders to solid-state reaction synthesis TiB_2-TiC compositions at a low temperature. Here, PTFE is considered not only as a reaction promoter, but also as a carburizing agent to participate in the synthesis process.

1 Experimental

1.1 Sample preparation

Titanium (>99.5wt% purity, particle size between 45 μm and 50 μm), amorphous boron (>99.9wt%, <1 μm) and PTFE (>99.9wt%, <3 μm) powders were used as reactants. Titanium and boron powders were mixed with a molar ratio of 1:2. And PTFE content was designed according to

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the stoichiometry of the following reaction:

$$\begin{aligned}&(1+10x)\text{Ti}+2\text{B}+3x/n(-\text{C}_2\text{F}_4-)_n\\&\rightarrow \text{TiB}_2+6x\text{TiC}+4x\text{TiF}_3\end{aligned} \qquad (1)$$

According to equation (1), the amount of PTFE should be enough to ignite the overall reaction through the highly exothermic pre-reaction between titanium and PTFE, on the other hand, more PTFE would results in less production of TiB_2 and TiC due to the increasing by-product TiF_3. Therefore, the addition of PTFE to the initial Ti-B reactant mixture ranged from 0 to 12wt% in present study.

Mixing of starting powders was performed using a planetary ball milling for 2 h in a plastic jar with zirconia balls. Then, the powder mixtures were pressed into cylindrical green bodies under the pressure of 250 MPa at room temperature.

1.2 Methods

In order to determine ignition temperatures of the reactions, differential thermal analysis (DTA) experiments were carried out with green bodies (approximately 50 mg) from room temperature to 1300℃ at the heating rate of 10 ℃/min in argon atmosphere using a NETZSCH STA409PC thermal analyser. Meanwhile, to illustrate the reaction mechanism, the DTA experiments of PTFE, B-PTFE and Ti-PTFE were also carried out in the same way, respectively. Furthermore, the solid-state reaction synthesis experiments were carried out with the ϕ6 mm×5 mm cylindrical green body in an argon atmosphere furnace at 550℃, which was determined according to DTA results. Meanwhile, the solid-state reaction synthesis experiments also were carried out at 1300℃. The obtained products were reduced to powder form and identified by X-ray diffraction (XRD) using a Bruker D8-ADVANCE X-ray diffractometer with Cu Kα radiation in the 2θ ranging from 15° to 85°. The morphologies of products were observed using a LEO model 1550 field emission scanning electron microscope (FESEM) with energy dispersive spectroscopy (EDS).

2 Results and discussion

2.1 Thermal analysis

In the DTA trace for the Ti-B powder mixture at a heating rate of 10℃/min (Fig. 1(a)), a broad exothermic peak is appeared in the temperatare range of 896-1077℃, of which the peak temperature is 952℃. The exothermic peak could be related to the solid-state reaction between titanium and boron[22-23], which generates titanium borides. In Ti-B mixture with 1wt% PTFE, the DTA trace shows another small exothermic peak in the temperatare range of 510–570℃, corresponding to the reaction between titanium and PTFE[17-18, 24], in addition to the exothermic peak at 955℃ for the formation of titanium borides (Fig. 1(b)). When the addition amount of PTFE reaches up to 5wt% and 8wt%, the exothermic peaks related to the reaction between titanium and PTFE are much sharper, as shown in Fig. 1(d) and (e). However, the wide exothermic peaks corresponding to the solid-state reaction between titanium and boron are still observed in the DTA traces for the samples with 1wt%, 3wt%, 5wt% and 8wt% PTFE, meaning PTFE addition which is no more than 8wt% is not enough to induce the reaction between titanium and boron by the pre-reaction between titanium and PTFE.

Figure 1(f) and (g) show the DTA curves of Ti-B system with 10wt% and 12wt% PTFE, in which only an extremely sharp exothermic reaction peak is observed in the temperature range of 518–538℃, representing a fast energy release process. Noticeably, the peak temperature is 522℃ in the temperatare DTA curve of Ti-B system with 10wt% PTFE, 430℃ lower than that of Ti-B system without PTFE. Reasonably, this peak must be a combination of two exothermic reaction processes: Firstly, titanium reacts with PTFE[17-18], releasing large amounts of heat; subsequently, the released energy triggers the solid-state reaction between titanium and boron particles to form TiB_2. Importantly, there is no other exothermic peak from 550℃ to the end of DTA measurement, which means the reaction between titanium and boron has accomplished in the temperature range of 518–538℃.

2.2 Phase analysis (XRD)

Obviously, by adding 10wt% PTFE, the reaction between titanium and boron can be initiated below 550℃ by utilizing the energy released in the exothermic reaction between titanium and PTFE, with TiC as a by-product. To further validate this mechanism, solid-state reaction

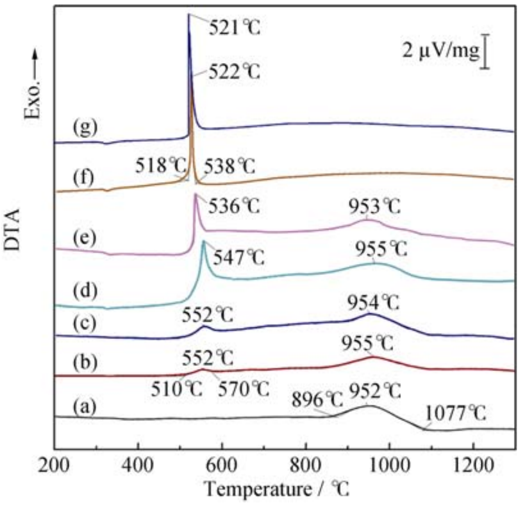

Fig. 1 DTA curves of the Ti-B mixtures with (a) 0wt%, (b) 1wt%, (c) 3wt%, (d) 5wt%, (e) 8wt%, (f) 10wt%, and (g) 12wt% PTFE

synthesis experiments were carried out for the same compositions in an argon atmosphere furnace at the heating rate of 10 ℃/min to 550℃. Fig. 2 is the XRD patterns of the Ti-B system without and with different amounts of PTFE additions after solid-state reaction synthesis in argon atmosphere after heating to 550℃.

In Fig. 2(a), there are only titanium peaks, no XRD peak can be related to boron or titanium borides. The absence of boron XRD peaks could be attributed to amorphous nature of the boron powder[14]. The XRD result indicates that no reaction occurrs between titanium and boron. Fig. 2(b) shows the existence of titanium in the XRD pattern of the specimen with 1wt% PTFE, which suggests that no solid-state reaction occurr during the heating process to 550℃ in argon atmosphere. In Fig. 2(c), (d) and (e), the XRD patterns for the specimen with 3wt%, 5wt% and 8wt% PTFE, several weak TiC peaks, as the result of the pre-reaction between titanium and PTFE, are identified, unfortunately no titanium boride peaks can be found. In the XRD patterns for the specimens with 10wt% and 12wt% PTFE (Fig. 2(f) and (g)), both TiB_2 and TiC phases are observed, which means the reaction between titanium and boron was induced when the amount of PTFE is above 10wt%.

Figure 3 presents the XRD patterns of the Ti-B system with different PTFE additions after solid-state reaction in argon atmosphere at 1300℃. Noticeably, it indicates TiB_2 phase is formed in all systems after solid-state reaction. It is due to the temperature is high enough to induce the reaction between titanium and boron. In Fig. 3(a)-(c), the XRD patterns of specimens with 0wt%, 1wt% and 3wt% PTFE addition, several TiB_2 and TiB peaks can be found, unfortunately without TiC peaks. In the XRD patterns for the specimens with 5wt%, 8wt%, 10wt% and 12wt% PTFE (Fig. 3(d)-(g)), there are only TiB_2 and TiC peaks, which means the sufficient heat produced by the early reaction between titanium and PTFE is enough to induce the reaction between titanium and boron.

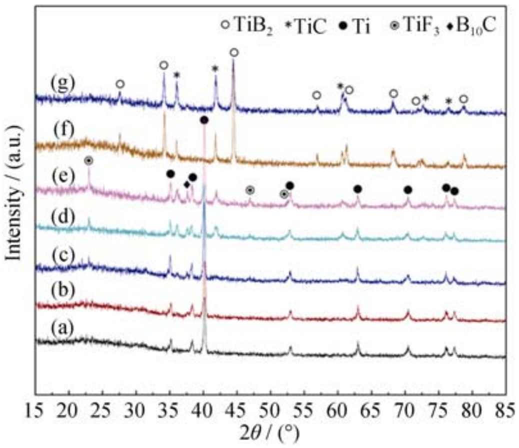

Fig. 2 XRD patterns of the Ti-B mixtures with (a) 0wt%, (b) 1wt%, (c) 3wt%, (d) 5wt%, (e) 8wt%, (f) 10wt%, and (g) 12wt% PTFE after reactions in argon atmosphere at 550℃

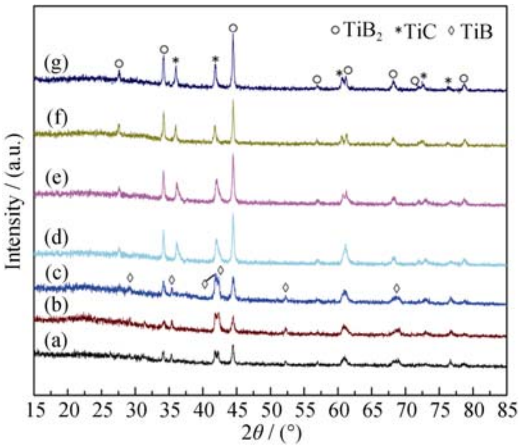

Fig. 3 XRD patterns of the Ti-B mixtures with (a) 0wt%, (b) 1wt%, (c) 3wt%, (d) 5wt%, (e) 8wt%, (f) 10wt%, and (g) 12wt% PTFE after reactions in argon atmosphere at 1300℃

2.3 Morphology analysis

Figure 4 shows the FESEM images and EDS spectrum of the products of Ti-B system with (a) 10wt% and (b) 12wt% PTFE addition after heating to 550℃ in argon atmosphere. It is clearly seen that the obtained composite material consists of agglomerated particles made of a mixture of TiB_2 (bigger and clubbed) and TiC (finer and equiaxed or irregular) phases. Specifically, it can be

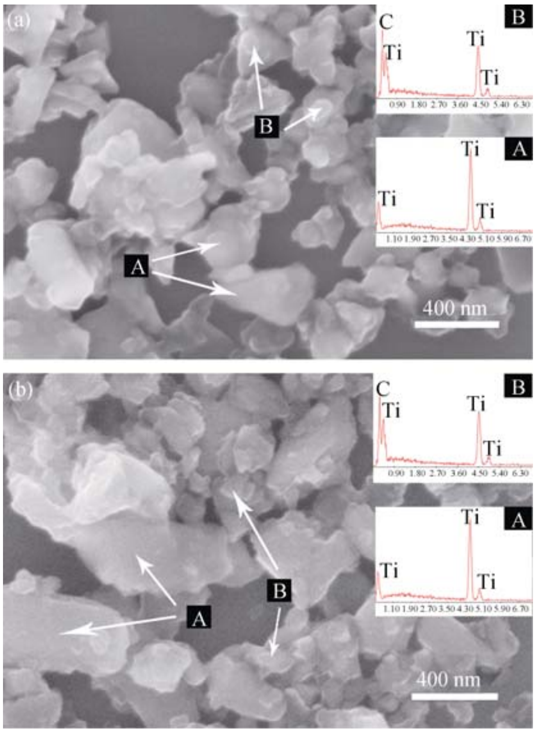

Fig. 4 Morphologies and EDS results of the product of Ti-B system with (a) 10wt% PTFE and (b) 12wt% after reactions in argon atmosphere at 550℃

observed that grains of each phase are in general submicrometer size (<400 nm), which indicates that the peculiar characteristics of combustion synthesis, *i.e.* rapidity and high heating and cooling rates, limit their growth.

2.4 Mechanism analysis

According to the DTA and XRD results, TiB_2-TiC can be synthesized at 550℃ in Ti-B elemental powder compact with 10wt% PTFE addition. It is obvious that the addition of PTFE transforms the slow solid-state reaction of Ti+2B→TiB_2 into an instantaneous exothermic reaction. The possible PTFE-inducing mechanism could be attributed to the exothermic pre-reaction between PTFE and titanium, which releases enough energy to trigger the reaction of Ti+2B→TiB_2 at 518℃ in the compact Ti-B mixture with 10wt% PTFE addition. Once the ignition of Ti-B reacting system is accomplished, the TiB_2-TiC phase is formed, which is different from the result in the literature[14]. When PTFE was the carbon source in the Ti-B system, only TiB_2 and B_4C phases were formed and it contributed to the fact that PTFE is able to selectively carburize amorphous boron to form boron carbide in the report[14]. In our opinion, this is mainly due to the less amount and larger grain size of titanium, leading to the larger contact area between PTFE and boron which causes the formation of B_4C.

In addition, in order to illustrate the reaction mechanism further, the DTA curves of the samples PTFE (Fig. 5(a)), B-PTFE (Fig. 5(b)) and Ti-PTFE (Fig. 5(c)) were obtained in argon atmosphere at a heating rate of 10℃/min from 30℃ to 800℃. The curves reveal that the exothermal reaction peak between titanium and PTFE is earlier and sharper than that of boron and PTFE.

According to the reports[11, 17, 19, 23-26], the possible reaction equations and enthalpies in present Ti-B-PTFE system are summarized systematically as follows:

$$4\mathrm{Ti}+3/n(-\mathrm{C_2F_4}-)_n \rightarrow 4\mathrm{TiF_3(g)}+6\mathrm{C(s)}$$
$$\Delta H_f^0=-3766\ \mathrm{kJ/mol} \quad (2)$$

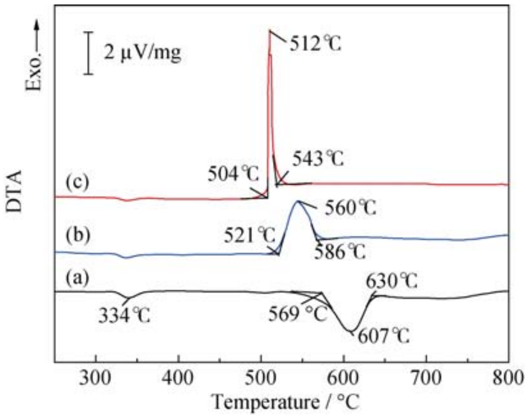

Fig. 5 DTA curves of (a) PTFE, (b) B-PTFE and (c) Ti-PTFE at a heating rate of 10℃/min in argon atmosphere

$$\mathrm{Ti}+\mathrm{C}\rightarrow \mathrm{TiC(s)} \quad \Delta H_f^0=-184\ \mathrm{kJ/mol} \quad (3)$$

$$\mathrm{Ti}+2\mathrm{B}\rightarrow \mathrm{TiB_2(s)} \quad \Delta H_f^0=-323\ \mathrm{kJ/mol} \quad (4)$$

Here, the required carbon in the reaction (3) is provided by PTFE. Before the decomposition of PTFE, the exothermic reaction (2) between PTFE and titanium occurs at about 510℃[17] with an abrupt energy release, 3766 kJ/mol[19] and the maximum theoretical adiabatic flame temperature is 3508℃[18], which is high enough to initiate the reactions Ti+C and Ti+2B, since the activation energies of Ti+C→TiC and Ti+2B→TiB_2 were reported around 364 kJ/mol[27] and 539 kJ/mol[28], respectively, when the reactions occur in solid state. Meanwhile, the heat of solid-state reaction of the mixture is sufficient to convert TiF_3 to vapor.

Moreover, regarding as a highly reactive intermediate product, TiF_3 can interact with other reactants in a relatively easier way, thus facilitating the occurrence of the solid-state reaction synthesis process[11]. SiF_4 was also found to be responsible for the PTFE activated solid-state reaction synthesis of $MoSi_2$-SiC composites[12]. In this regard, it should also be noted that the formation of TiF_3 was clearly observed in the literature[24, 26], which specifically contributed to the investigation of the reaction between metallic titanium and PTFE-based polymers.

In conclusion, the results described above clearly indicate that PTFE is feasible to be the promoter and carbon source in the present work, specifically when added properly, the residue of intermediate TiF_3 could be overcame.

3 Conclusions

TiB_2-TiC composite powder could be synthesized at the temperature as low as 550℃ through the solid-state reaction synthesis of the Ti-B system with 10wt% PTFE. The grain size of the TiB_2-TiC composite powder is smaller than 400 nm. The addition of PTFE into Ti-B system can greatly lower the starting temperature of Ti+B→TiB_2 reaction, due to the large amounts of heat released from the pre-reaction between titanium and PTFE.

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低温固相反应合成纳米级 TiB_2-TiC 复合粉体

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摘 要: 在 Ti-B 体系中引入 PTFE 作为反应促进剂, 实现了 TiB_2-TiC 粉体的低温固相合成。分别采用热分析仪、X 射线衍射仪和场发射扫描电子显微镜, 测定了体系的反应温度, 表征了生成物的物相和微观形貌, 并对其反应过程和反应机理进行了分析。合成实验在氩气炉中进行, 结果表明: 当添加 10wt% PTFE 时, 能够在 550℃通过固相反应制备出平均粒径小于 400 nm 的 TiB_2-TiC 复合陶瓷粉体。DTA 测试表明固相反应合成过程主要包括两步: 首先, 在低温下 PTFE 和 Ti 发生反应并释放出大量的热, 然后, 诱发 Ti 和 B 的固相反应生成 TiB_2。

关 键 词: TiB_2-TiC; 固相合成; PTFE; 反应机理

中图分类号: TQ174 **文献标识码:** A