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Combustion synthesis of TiC_x–TiB_2 composites with hypoeutectic, eutectic and hypereutectic microstructures

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Abstract

Self-propagating high-temperature synthesis (SHS) of compacted blends of Ti, B_4C and/or C powders was used to fabricate in situ TiC_x–TiB_2 composites with different compositions. The microstructures of the resultant products were studied by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM), and the reaction sequence in the SHS reaction process was explored by quenching the combustion wavefront. The results showed that the TiC_x–TiB_2 composites with 27.4, 36.7 and 61.7% TiB_2 in molar fractions display hypoeutectic, eutectic and hypereutectic microstructures, respectively, and TiC_x is the leading phase in formation of the eutectic phase during solidification. Moreover, substoichiometric TiC_x forms prior to TiB_2 in phase formation sequence even for the hypereutectic composition sample.

Keywords: Self-propagating high-temperature synthesis (SHS); Composites; Microstructure-final; TiC; TiB_2

1. Introduction

TiC–TiB_2 composites possess not only high-melting points, high hardness, excellent wear resistance and good thermal stability, but also superior properties such as enhanced fracture toughness and bending strength compared with constituent ceramic components.[1,2] Therefore, TiC–TiB_2 ceramic composites are attractive for application as advanced structural materials, and many methods, such as reactive sintering,[3] reaction hot pressing,[4] spark plasma synthesis,[5] transient plastic phase processing,[6] and self-propagating high-temperature synthesis (SHS), also termed combustion synthesis (CS)[2,7] have been developed for the synthesis of such TiC–TiB_2 ceramic composites.

On the other hand, TiC_x–TiB_2 has been demonstrated to be a eutectic system[8–12] and the eutectic composition and temperature of this system are significantly dependent on the composition of TiC_x.[8,11] According to the Ti–C phase diagram,[13] the value of x in TiC_x ranges from 0.47 to 1.0 and the eutectic point of the TiC_x–TiB_2 system, as indicated in Fig. 1, may shift from e_1 to e_2 as the value of x varies from 0.47 to 1.0. The eutectic points given in Fig. 1 might not be accurate since considerable controversy exists in the reported eutectic composition and temperature for the TiC_x–TiB_2 system in the past years. Some representative values obtained by both experimental measurement and theoretical calculation are shown in Table 1. One possible reason for the large scatter might be the influence of the variable composition of TiC_x with its range of stoichiometry, especially on the eutectic temperature. Another is that it might be rather difficult to accurately determine the eutectic composition in the TiC_x–TiB_2 system regarding the difficulty in measuring the compositions of the light elements (boron and carbon). Therefore, more delicate and powerful measurements need to be carried out in order to clarify this confusion.

In this study, we prepared TiC_x–TiB_2 composites with different compositions using Ti–B_4C and Ti–B_4C–C systems by SHS and examined their microstructures, from which the eutectic composition for the TiC_x–TiB_2 system was suggested. It is worth mentioning that Zhang et al.[2] and Song et al.[7] also fabricated TiC–TiB_2 composites with different compositions by SHS using proper proportions of Ti, B_4C and C powders. However, the relationship between the composition of the products and

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Table 1
The reported eutectic composition and temperature in the TiC_x–TiB_2 system[8–12]

Reaction	Eutectic composition (mol.% TiB_2)	Eutectic temperature (°C)	Method	Reference
$L \leftrightarrow TiC_{0.92} + TiB_2$	43	2620	Experiment	[8]
$L \leftrightarrow TiC_{0.95} + TiB_2$	44	2520	Experiment	[9]
$L \leftrightarrow TiC_{0.68} + TiB_2$	–	2380	Experiment	[9]
$L \leftrightarrow TiC_{0.92} + TiB_2$	35	2600	Experiment	[10]
$L \leftrightarrow TiC_{0.6} + TiB_2$	40.1	2637	Calculation	[11]
$L \leftrightarrow TiC_{0.8} + TiB_2$	40.5	2688	Calculation	[11]
$L \leftrightarrow TiC_{1.0} + TiB_2$	40.2	2663	Calculation	[11]
$L \leftrightarrow TiC + TiB_2$	28	–	Experiment	[12]

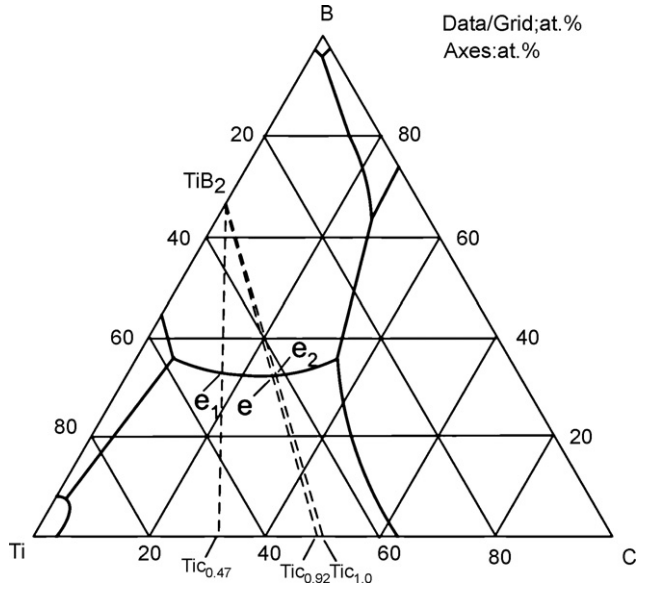

Fig. 1. A schematic projection of liquidus surface of the Ti–B–C ternary phase diagram (after Rudy and Windisch[8]).

their microstructures was not reported therein. Also, the formation mechanism of TiC_x and TiB_2 in the SHS reaction was proposed in the present paper. Such understandings are expected to promote the development of the TiC_x–TiB_2 composites with tailored microstructures.

2. Experimental procedure

The characteristics of the starting powders with their sources are presented in Table 2. The theoretical molar ratios of TiC:TiB_2 in the products were predetermined to be 2.33:1, 1.47:1 and 1:2, based on the following reactions:

$$3.33Ti + 0.5B_4C + 1.83C \rightarrow 2.33TiC + TiB_2 \quad (1)$$

$$2.47Ti + 0.5B_4C + 0.97C \rightarrow 1.47TiC + TiB_2 \quad (2)$$

$$3Ti + B_4C \rightarrow TiC + 2TiB_2 \quad (3)$$

Powder blends with proper proportions were dry-mixed in a stainless-steel container using stainless-steel balls at a low speed (~35 rpm) for 8 h to ensure homogeneity. The mixtures were uniaxially pressed into cylindrical compacts of 22 mm in diameter and 15 mm in height at pressure ~60 MPa with green densities of 65 ± 2% of theoretical, as determined from weight and geometric measurements.

The SHS experiments were conducted in a self-made stainless-steel vessel. The compact was placed on a graphite-flat with a thickness of ~2 mm, below which a tungsten electrode was set up as the reaction ignition source. The vessel was first evacuated and then filled with industrial argon (99.9%) at 1 atm. The reaction was initiated by arc heating, which was generated by passing a strong current between the tungsten electrode and the graphite-flat. As soon as the SHS reaction was initiated, the power was switched off. Phase analysis and microstructure of

Table 2
The characteristics of the powder reactants used in this study

Reactant	Source	Purity (wt.%)	Particle size (μm)
Ti	Institute of Nonferrous Metals, Pekin, China	99.5	~50
B_4C	Abrasive Ltd. Co., Dunhua, China	≥95[a]	~3.5
Graphite	Graphite Ltd. Co., Jilin, China	99.5	~1

[a] The main impurities are dissociative boron and carbon together with <1 wt.% Fe_2O_3.

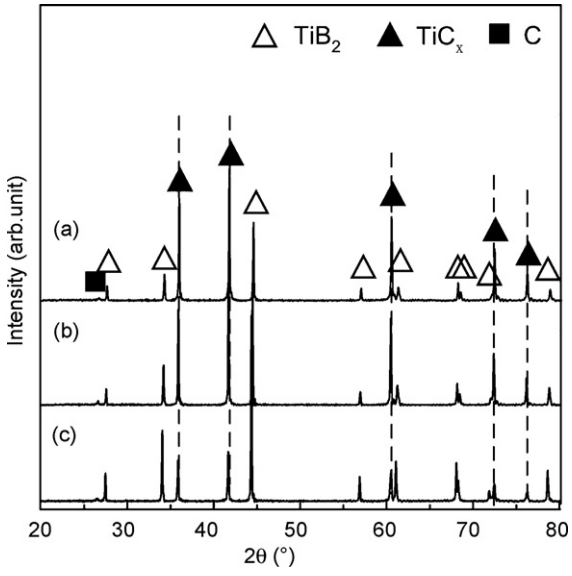

Fig. 2. XRD patterns of the SHS reaction products with (a) 27.4 mol.% TiB_2, (b) 36.7 mol.% TiB_2 and (c) 61.7 mol.% TiB_2, respectively.