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Effect of reactant C/Ti ratio on the stoichiometry of Combustion-synthesized TiC_x in Ti–C system

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In this study, self-propagating high-temperature synthesis (SHS) of the powder compact consisting of titanium and graphite was used to synthesize titanium carbide (TiC_x). The relationship between the C/Ti ratio in the reactants and the stoichiometry of the resultant TiC_x phase was investigated. The result showed that when the molar ratio of C to Ti in the reactants increased from 0.6 to 1.2, the stoichiometry of the resultant TiC_x phase first increased and then decreased with the maximum value appearing at C/Ti = 1.0, so did the change in the maximum combustion temperature; Furthermore, with an increase in the particle size of graphite, the maximum combustion temperature and the stoichiometry of the resultant TiC_x phase decreased. Consequently, the maximum combustion temperature might play a dominating role in determining the final composition of the TiC_x phase.

Key-words : Self-propagating high-temperature synthesis (SHS), X-ray diffraction (XRD), Ceramic, Carbide, Defect

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1. Introduction

TiC is an important carbide because of its high melting point, low density, high hardness, good thermal and electrical conductivity and excellent high temperature stability. It has a cubic NaCl-type crystal structure and possesses a wide composition range with C/Ti stoichiometry varying from 0.47–1.0.[1] The property of TiC_x was found to depend strongly on its stoichiometry, e.g, with the decrease in C/Ti stoichiometry (x), the modulus and hardness decrease, while the thermal and electrical conductivity and its wettability by molten metals increase significantly.[2),3)]

It was reported that the stoichiometry of TiC_x was related to the C/Ti ratio in the reactants when TiC_x was produced by self-propagating high-temperature synthesis (SHS).[3)–6)] For instance, Zarrinfar et al.[3)] and Choi et al.,[4)] respectively, reported that the stoichiometry of TiC_x was almost identical to the ratio of C/Ti in the reactants, except for C/Ti = 1.0; whereas, Lee et al.[5)] argued that the stoichiometry of TiC_x synthesized from the Ti + C reactants was essentially less than the reactant C/Ti ratio when the reactant C/Ti ratio is in the range of 0.85–1.1. Adach et al.,[6)] on the other hand, obtained an appreciable amount of free carbon for the C/Ti ratio equaling 0.8 and 1.05 when the carbon fiber (7 μm in diameter and 0.2 mm in length) was used as the carbon source. As indicated, inconsistency exists in the previous studies regarding the dependence of the stoichiometry of TiC_x on the reactant C/Ti ratio and moreover, the nature behind the apparent depending behavior has not yet been disclosed. The objective of this article is thus to provide some insight into this issue based on our recent experimental results.

2. Experimental procedure

The raw materials used were commercial powders of Ti (99% purity, ~50 μm, Institute of Nonferrous Metals, Pekin, China) and graphite (99% purity, Jilin Carbon Ltd., Co., Jilin, China). The graphite powders with particle sizes of ≤ 1 μm, 29–38 μm and 50–74 μm were used (in most runs, the graphite powder with particle size of 29–38 μm was used except for those specifically indicated cases). The reactant powders with C/Ti molar ratios of 0.6, 0.8, 1.0 and 1.2 were homogeneously mixed and then uniaxially pressed into cylindrical compacts of ~22 mm in diameter and ~15 mm in height with green densities of ~65 ± 2% of theoretical. The SHS experiments were conducted in a self-made stainless-steel box, as shown in **Fig. 1**, under an atmosphere of industrial argon (99.9%). The compact was placed on a graphite plate with a thickness 2 mm and ignited from the bottom by an arc heating using a current of 45 A. During the SHS process, the combustion temperature was measured by W–5%Re/W–26%Re thermocouples that were inserted into the compact at a depth about 3 mm beneath the center of the top surface and the signals were recorded and processed by a data acquisition system with a speed of 20 points per second (for temperatures higher than 2573 K, they were determined by extrapolation from the available temperature-electromotive force function). The samples

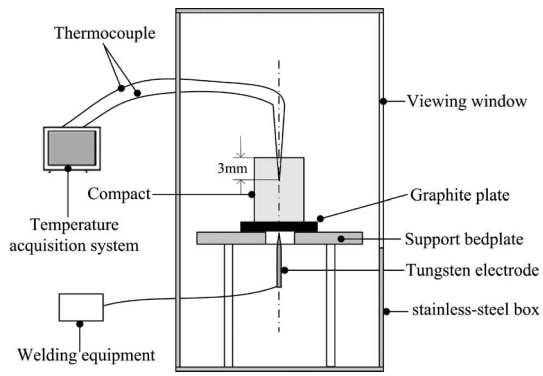

Fig. 1. Experimental schematic diagram of SHS.

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were crushed into powders and the phases in the powders were identified by X-ray diffraction (XRD, D/Max 2500PC Rigaku Co., Japan) with Cu Kα radiation using a scanning speed of 4°/min and an angle (2θ) step of 0.05°. In order to evaluate the lattice parameter of the synthesized TiC_x phase, a much slower scanning was performed around the main peaks at a scanning speed of 0.05°/min with an angle (2θ) step of 0.002°.

3. Results and discussion

Figures 2 and **3** show the variations in temperature (T) and (dT/dt) with time (t) during the SHS reaction in the different C/Ti ratio samples, respectively. It was observed during the experiments that the samples with high C/Ti ratios were much easier to ignite and the SHS reaction was more violent. The maximum combustion temperature (T_c) and the maximum heating rate (dT/dt) at the combustion front as a function of the C/Ti ratio in the reactants are plotted in **Fig. 4**. As indicated, T_c increases with the increase in the C/Ti ratio, reaches a maximum value at C/Ti = 1.0 and then slightly decreases at C/Ti = 1.2. This variation tendency is consistent with the theoretical prediction for the dependence of adiabatic temperature on the C/Ti stoichiometry,[1] despite the fact that the real experimental temperatures are much lower than the adiabatic ones due to considerable heat loss. The maximum heating rate, derived from the time-temperature curves, also increases with increasing the C/Ti ratio and thus turns to be nearly constant at C/Ti = 1.0 and 1.2.

Figure 5 shows the XRD patterns of the SHS products for the samples with different C/Ti ratios. The reaction products consist mainly of TiC_x phase. However, unreacted Ti or/and C, more or less, were also detected in the samples except for C/Ti = 1.0. The peaks of TiC_x have some angle deviations, corresponding to a variation in its lattice parameter (α_0). The calculated lattice parameter and the corresponding TiC_x stoichiometry as a function of the C/Ti ratio in the reactants are shown in **Fig. 6**.

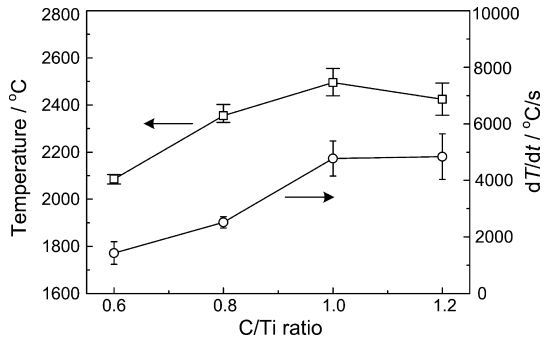

Fig. 4. Variations in maximum combustion temperature, T_c, and maximum heating rate, dT/dt, with the reactant C/Ti ratio.

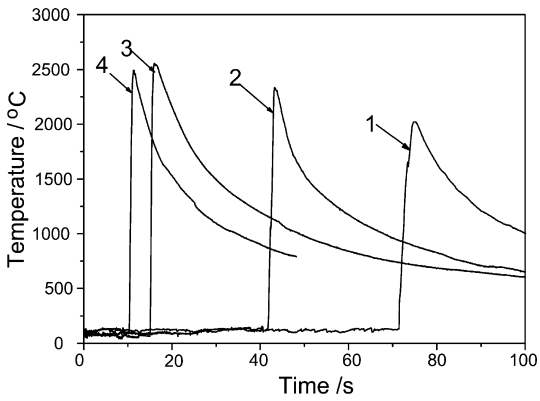

Fig. 2. Typical time–temperature plots during the SHS reaction in the Ti–C samples with different C/Ti ratios: (1) 0.6, (2) 0.8, (3) 1.0 and (4) 1.2.

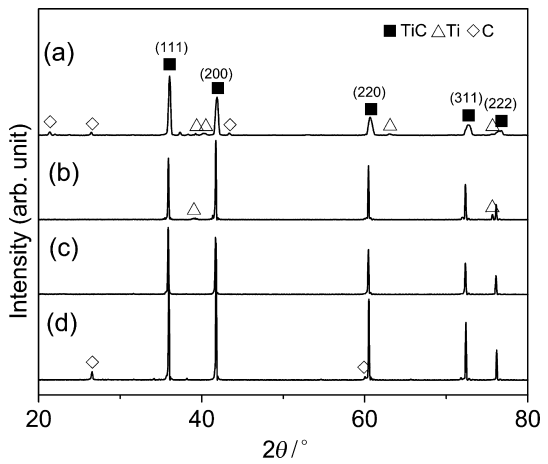

Fig. 5. XRD patterns for the reacted Ti–C samples with different reactant C/Ti ratios: (a) 0.6, (b) 0.8, (c) 1.0 and (d) 1.2.

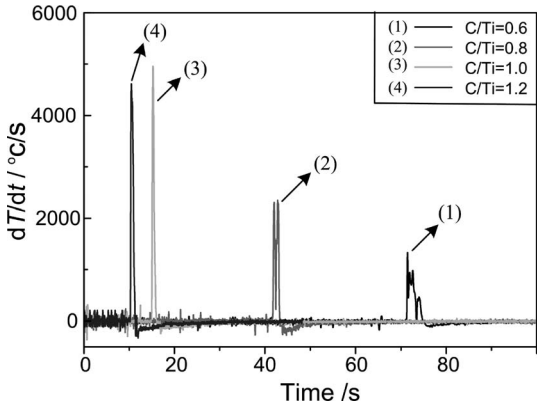

Fig. 3. Typical plots of dT/dt vs time during the SHS reaction in the samples with different C/Ti ratios.

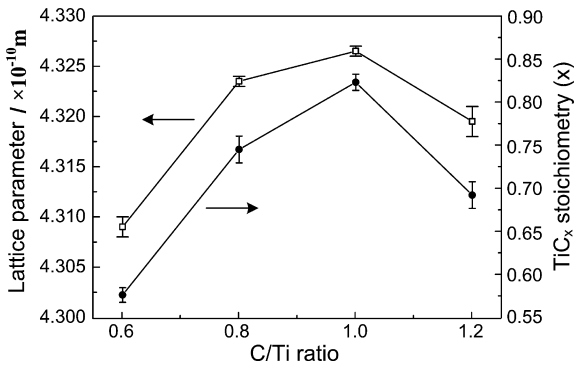

Fig. 6. Variations in the lattice parameter (α_0) and the stoichiometry (x) of TiC_x with the reactant C/Ti ratio.

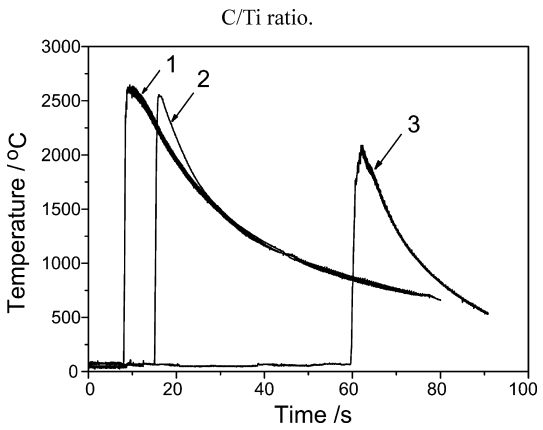

Fig. 7. Typical time–temperature plots during the SHS reaction in the Ti–C samples (C/Ti = 1.0) with the particle sizes of graphite (1) ≤ 1 μm, (2) 29–38 μm and (3) 50–74 μm.

As indicated, the lattice parameter first increases with the C/Ti ratio increase, reaches a maximum value of (4.327 ± 0.001) × 10^{-10} m at C/Ti = 1.0 and then decreases with a further increase in C/Ti. In comparison, the value of α_0 does not differ significantly for the reactant C/Ti ratio between 0.8 and 1.2, but significantly decreases to (4.308 ± 0.002) × 10^{-10} m for C/Ti = 0.6. This result is somewhat different from that reported by Zarrinfar et al.,[3] in which a maximum lattice parameter of 4.330 × 10^{-10} m was obtained for the reactant C/Ti ~0.8. On the other hand, the C/Ti stoichiometry in the synthesized TiC_x was estimated from the available relationship between the lattice parameter of TiC_x and its stoichiometry, as given in Ref. 1). Clearly, the synthesized TiC_x phases in all the samples are substoichiometric (i.e., $x < 1$) with the maximum stoichiometry (x) of 0.82 ± 0.01 appearing at C/Ti = 1.0 in the reactants, and the stoichiometry in the products deviates considerably from that in the reactants. It has been reported that the SHS reaction to form TiC_x from Ti and C is controlled by carbon diffusion through liquid or solid TiC_x,[7] and the formation of substoichiometric TiC_x is more favorable than a stoichiometric one.[8] Because of the large temperature gradient (10^2–10^3°C/mm) and short reaction time (on the order of a few seconds) of the Ti–C combustion reaction, the stoichiometric TiC was difficult to form. This fact has been manifested by many researchers.[3),4),8] On the other hand, the loss of reactant C in the form of carbon oxide may be possible during the SHS process. Holt and Munir reported that substantial gases such as carbon monoxide were evolved when the Ti–C compact was combusted in a vacuum chamber.[1] In this sense, it is the substoichimetric TiC rather than the stoichimetric TiC that was developed.

Figure 7 shows the typical time–temperature plots during SHS in the Ti–C samples (C/Ti = 1.0) with different graphite particle sizes and **Table 1** gives the maximum combustion temperatures of the Ti–C samples with different graphite particle sizes and C/Ti ratios. As indicated, an increase in the graphite particle size obviously decreases the maximum combustion temperature. **Figure 8** shows the XRD patterns for the reacted Ti–C samples with different graphite particle sizes and C/Ti ratios. It can be seen that the product in the samples with graphite particle size of ≤ 1 μm only consists of TiC_x phase, while that in the sample with graphite particle size of 50–74 μm consists of C and TiC_x phases, indicating that the resultant TiC_x phase was substoichiometric. On the other hand, the peaks of TiC_x phase have some shifts of diffraction line when the C/Ti ratio increases from 0.6 to 1.0 (see Fig. 8(a–b)) or the graphite particle size increases from ≤ 1 μm to 50–74 μm (see Fig. 8(b–c)). The calculated lattice parameter (α_0) and the corresponding TiC_x stoichiometry (x) were also given in Table 1. Clearly, the stoichiometry (x) of the TiC_x phase decreases with the increase in the graphite particle size, especially for the samples with reactant C/Ti = 1.0. The coarse graphite particles lead to a significant decrease in the maximum combustion temperature and an insufficient diffusion of the carbon atoms, and consequently, the TiC_x phase should be more deficient in carbon when it nucleates and grows.

Table 1. Maximum Combustion Temperature and Lattice Parameter and Stoichiometry of the Resultant TiC_x Phase for the Ti–C Samples with Different C/Ti Ratios and Graphite Particle Sizes

C/Ti ratios	Graphite particle sizes (μm)	Maximum combustion temperatures (°C)	Lattice parameters (× 10^{-10} m)	Stoichiometries (x) in TiC_x
0.6	≤ 1	2230	4.312	0.59
0.6	29–38	2082	4.308	0.57
1.0	≤ 1	2646	4.329	0.89
1.0	29–38	2495	4.327	0.82
1.0	50–74	2086	4.321	0.69

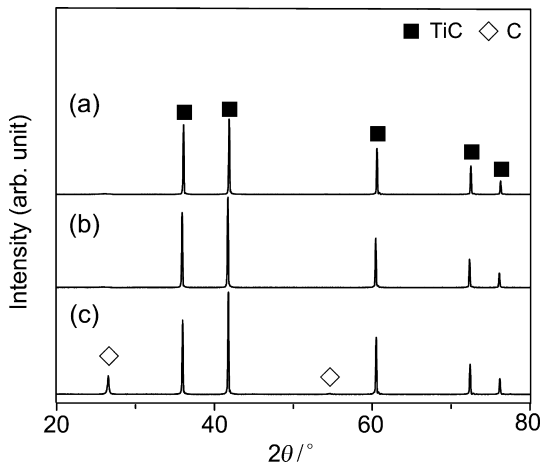

Fig. 8. XRD patterns for the reacted Ti–C samples with (a) C/Ti = 0.6 and graphite particle size of ≤ 1 μm, (b) C/Ti = 1.0 and graphite particle size of ≤ 1 μm, and (c) C/Ti = 1.0 and graphite particle size of 50–74 μm.

It is worth noting that the dependence of the stoichiometry of the yielded TiC_x phase on the C/Ti reactant ratio and the graphite particle size is generally consistent with the behavior of the maximum combustion temperature (see Figs. 2, 4 and Table 1), implying that the temperature might play a crucial role in determining the final composition of the synthesized TiC_x phase. A higher temperature facilitates the atomic diffusion and thus significantly promotes the compositional homogenization.

4. Conclusion

In summary, we have investigated the relationship between the C/Ti ratio in the reactants and the stoichiometry of the resultant TiC_x phase. They do not fit exactly since the nature of TiC_x is highly substoichiometric and the SHS process is very rapid and far from equilibrium. Using coarse graphite particles may enlarge this deviation. The maximum combustion temperature is

speculated to play a dominating role in determining the final composition of the TiC_x phase.

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