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Ceramics International 36 (2010) 1027–1031
CERAMICS INTERNATIONAL
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Reaction mechanism in Ti–SiC–C powder mixture during pulse discharge sintering

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Received 9 April 2009; received in revised form 29 August 2009; accepted 7 November 2009
Available online 29 November 2009

Abstract

During pulse discharge sintering (PDS) of Ti/SiC/C powder mixture, combustion synthesis reactions occurred at heating rates above 20 °C/min. With an increase in heating rate, combustion synthesis occurred at higher temperatures. The essential of this combustion reaction is the liquid reaction between Ti and formed Ti_5Si_3. The exothermic TiC formation during PDS process promotes this liquid reaction. We have found that the combustion reactions alone did not finish the formation reactions for Ti_3SiC_2, and further heating following the combustion reactions is necessary for the synthesis process of Ti_3SiC_2.

Keywords: Ti_3SiC_2; Combustion synthesis; Pulse discharge sintering

1. Introduction

Ti_3SiC_2 was synthesized firstly by Jeitschko and Nowotny via chemical reaction in 1967 [1]. It is a layered ternary carbide belonging to the "312" family of MAX phases [2]. Ti_3SiC_2 has unusual properties that combine many of the best attributes of metals and ceramics [3–10], which can be attributed to its special crystalline structure, that is, a layered hexagonal structure in which almost close-packed planes of titanium are separated from each other by hexagonal nets of silicon; every fourth layers is a silicon layer, while carbon atoms occupy the octahedral sites between the titanium layers [11,12].

In order to synthesize Ti_3SiC_2, various processes including chemical vapor deposition [13], arc-melting method [14], hot-isostatic-pressing (HIP) or hot-pressing (HP) [6,15–20], pulse discharge sintering (PDS) [20–27] and self-propagating high-temperature synthesis (SHS) [28–33] were employed. Among these synthesis methods, self-propagating high-temperature synthesis, also called combustion synthesis, is a novel technique which opens new perspectives in processing of advanced ceramic materials [28]. However, the preparatory milling treatments for the reactants and the high heating rates are usually necessary when SHS method is used to synthesis Ti_3SiC_2. Recently, Riley et al. reported the SHS of Ti_3SiC_2 starting from 3Ti + SiC + C reactants without the preparatory milling treatments and the heating rate was reduced obviously from 500 °C/min to 30 °C/min [29]. This is believed to be the lowest heating rate for inducing SHS reactions for Ti_3SiC_2 synthesis in the open literature. PDS, also called spark plasma sintering (SPS), is a recent innovation and its versatility allows quick densification to nearly theoretical density in a number of metallic, ceramic and other engineering components [34–36]. In the PDS process, pulse current is applied to the powder compact and the joule heat is utilized for the sintering or synthesis, hence the powder compact can be heated uniformly in a short time, in comparison to conventional furnaces such as in HIP or HP where the heat was transferred from the furnace heating elements to the powder compact by thermal radiation or conduction. Therefore, combustion reaction for Ti_3SiC_2 synthesis could be induced in a lower heating rate if PDS technique is employed as heating source. Moreover, the applied pressure could improve the densification of synthesized product during the PDS sintering process. In this study, we will analyze the effect of heating rate on combustion reaction by recording

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doi:10.1016/j.ceramint.2009.11.018

shrinkage displacement curve, namely the displacement of the ram with sintering temperature, or with time, while the axial pressure applied to the powder compact was kept constant. Another objective of this study is to clarify the reaction mechanism of combustion synthesis for Ti_3SiC_2 from Ti/SiC/C powder mixture. To achieve this, another advantage of PDS technique will be utilized, i.e., the system can be cooled down rapidly in the middle of the sintering stage at a cooling rate of ~250 °C/min. The high cooling rate enabled the "freezing" of the intermediate phases during the sintering process.

2. Experimental procedure

Starting powders of coarse Ti (−150 μm, 99%), SiC (2–3 μm, 99.9%), and C (5 μm, 99.7%) were used in this study. The stoichiometric molar ratio for Ti_3SiC_2 with Ti:SiC:C = 3:1:1 were selected for this study. These powders were mixed in a Turbula shaker mixer in Ar atmosphere for 24 h. The powder mixture was filled in a graphite mold (20 mm in diameter) and sintered in vacuum by using PDS technique (PAS-V, Sodick Co. Ltd.). The sintering temperature was monitored and controlled through an infrared camera. A hole of 3 mm in diameter and 10 mm in depth was drilled from the outside of the 15 mm thick wall of the graphite mold, and the IR camera was focused at the bottom of this hole for temperature monitoring. Confirmation experiments with thermal couples inserted into the powder compact inside the mold indicated that the temperature monitored with IR camera is about 50–100 °C lower. The heating rates were selected to be 10 °C/min, 20 °C/min, 30 °C/min, 40 °C/min and 50 °C/min, respectively. And the sintering temperature was selected in the range of 1200–1500 °C and held for 0–20 min. Sintering temperature, axial pressure as well as the ram displacement were recorded to monitor the shrinkage of the powder compact during sintering process. The powder compact was kept under a constant axial pressure of 50 MPa during sintering. After sintering, the samples were ground to remove the surface layer for 1 mm in order to eliminate the effect of reaction layer, if any. Then the samples were analyzed to identify the phase constitution by X-ray diffractometry (XRD) with CuKα radiation at 30 kV and 40 mA. The microstructure of the synthesized samples were observed and analyzed by using scanning electron microscopy (SEM) equipped with an energy-dispersive spectroscopy (EDS) system.

3. Results and discussion

Fig. 1 shows the shrinkage displacement as a function of sintering time during heating Ti/SiC/C powder mixture at various heating rates. At 10 °C/min, no abrupt shrinkage was observed, whereas abrupt shrinkage displacements were observed in all the curves at heating rates at 20 °C/min or above. Meanwhile, intensive exothermic phenomena were observed, as shown in the temperature variation with sintering time at different heating rates in Fig. 2. Note that the temperature is regulated by the competitive effect of joule heating and water cooling. The temperature curve of heating rate at 10 °C/min is steady, while the curves at heating rates of 20 °C/min or above show sharp spikes during the heating process. Though the programmed temperature schedule is the controlled parameter during sintering, the abrupt release of the exothermic reaction heat exceeded the regulating ability of the system even though a water cooling system was employed, leaving sharp spikes in the temperature record. Not surprisingly, corresponding to the temperature spikes, abrupt dips in applied voltage, and hence the electric current were observed (not shown). Compared with sintering curve of PDS Ti/Si/TiC [37], we can find that the shrinkage is abrupt in this study. This means rapid reaction with strong exothermic effect had occurred when heating rates were at 20 °C/min or above. This instant exothermic reaction indicates combustion reaction. The abrupt shrinkage was caused by the liquid product of combustion reaction; the liquid phase immediately filled the gaps in the powder or mold under applied pressure. In fact, we observed liquid phase formed and squeezed out along the inner surface of graphite mould, after cooling. It is also found in Fig. 2 that the combustion reaction shifted to higher temperature with increasing heating rate. This increased reaction temperature with heating rate is attributed to that

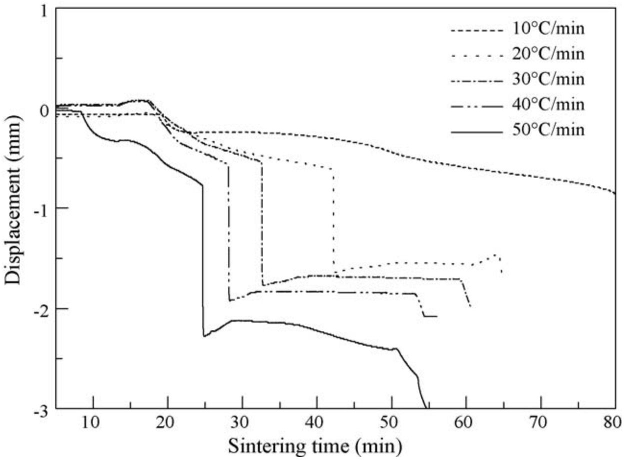

Fig. 1. The shrinkage curves of samples sintered at heating rates of 10 °C/min, 20 °C/min, 30 °C/min, 40 °C/min and 50 °C/min, respectively.

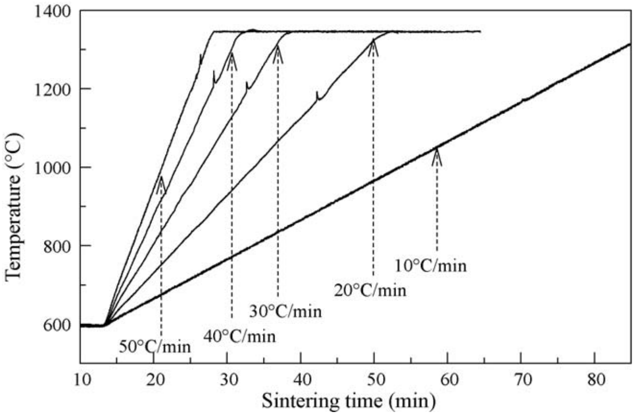

Fig. 2. The temperature curves of samples sintered at heating rates of 10 °C/min, 20 °C/min, 30 °C/min, 40 °C/min and 50 °C/min, respectively.

the combustion reaction requires energy accumulation to achieve a critical condition; at higher heating rate the reaction did not take place until the system is heated to a higher temperature to accomplish this accumulation.

In order to understand the mechanism of this combustion synthesis reaction during sintering Ti/SiC/C process, samples of the powder mixture were heated to some intermediate temperatures following the same heating and loading procedures as in the aforementioned experiments, and cooled down immediately when the programmed temperature was reached, in order to "freeze" the intermediate phases during the sintering process. Intermediate temperatures of 1200 °C and 1240 °C were selected when the heating rate was 40 °C/min. It is worth noting that the monitoring temperature is about 50–100 °C lower than the sample temperature inside the graphite mold according to the verifying results. Therefore, sintering temperatures of the samples were higher than the recorded. But for the convenience of discussion, we still use the recording temperature to describe the reaction temperature. The 1200 °C corresponds to the temperature before combustion synthesis reaction, and 1240 °C corresponds to the temperature after combustion synthesis reaction. Fig. 3 shows the X-ray diffraction patterns of such processed two samples. When the sample was heated to 1200 °C, the peaks of new intermediate phase Ti_5Si_3 and TiC peaks were observed. However, the main peak of Ti_3SiC_2 at about $2\theta = 39.5°$ was not detected. When the sample was heated for one more minute to 1240 °C and cooled down immediately, large amount of Ti_3SiC_2 formation was confirmed on the XRD patterns. In other words, the formation process of Ti_3SiC_2 occurred mainly within this 1 min time span or in the 40 °C temperature range.

By comparing the XRD patterns of the synthesized product before and after combustion as in Fig. 3, we can assume the mechanism of the reactions during heating Ti/SiC/C powder mixture. Upon heating, Ti reacted with C and SiC to form TiC and Ti_5Si_3. In our previous study [38], the formation of TiC and Ti_5SiC_3 at about 1000 °C were detected during PDS TiH_2/C/SiC mixture powders. But the results of energy-dispersive spectroscopy (EDS) showed that these intermediate Ti_5Si_3 phase was not pure, but containing some carbon, and hence should be designated as $Ti_5Si_3C_x$. The peaks of $Ti_5Si_3C_x$ shift to lower angle than those of Ti_5Si_3. Similar results were also reported in Ti/SiC/C system during hot-isostatic-pressing [16]. Therefore, after the formation of $Ti_5Si_3C_x$, un-reacted Ti coexisted locally with $Ti_5Si_3C_x$. Once the local temperature at the interface of $Ti_5Si_3C_x$ and Ti exceeds 1330 °C, Ti–Si liquid phase will be formed at the composition of eutectic Ti–Ti_5Si_3. The reason why local temperature may quickly increase to above 1330 °C could be attributed to the following: (1) as aforementioned, the sample temperature inside the mold is higher for around 50–100 °C, (2) the formation of TiC from Ti and C is an exothermic reaction; we previously reported that TiC starts to form when sintering temperature is higher 900 °C, and this may increase the local temperature to above the average sample temperature; (3) at the powder contacts the electrical resistance is locally high which leads to more joule heat during sintering which inevitably increases the local temperature. The formation of Ti–Si liquid phase immediately filled the gaps in the powder compact under the applied pressure. The un-reacted powder particles were immersed into the liquid phase, and further reaction (such as the formation of more TiC, Ti_5Si_3 and Ti_3SiC_2) was greatly assisted. This showed an abrupt shrinkage in the displacement–time curve. As direct evidence of liquid reaction, solidified morphology micrographs of liquid phase can be observed on the fracture surface. Fig. 4 shows the fracture morphology of the sample which was heated to 1240 °C and cooled down immediately. The isolated particles are integrated by the liquid phase. Moreover, the dendrites solidified from liquid phase can be observed obviously, as marked by circles in Fig. 4. The dendrites were identified to be the $Ti_5Si_3C_x$ phase according to the EDS analysis.

Therefore, the aforementioned liquid reaction induced by PDS is mainly Ti–Si reaction, and the formed liquid phase further reacted with the un-reacted particles and accelerated the formation of TiC, Ti_5Si_3 and Ti_3SiC_2. However, the effect of

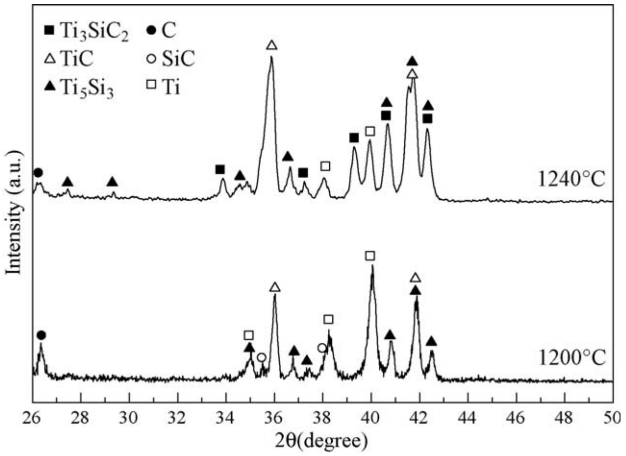

Fig. 3. XRD patterns of the Ti/SiC/C powder compacts heated to 1200 °C and 1240 °C with heating rate at 40 °C/min, and cooled down immediately.

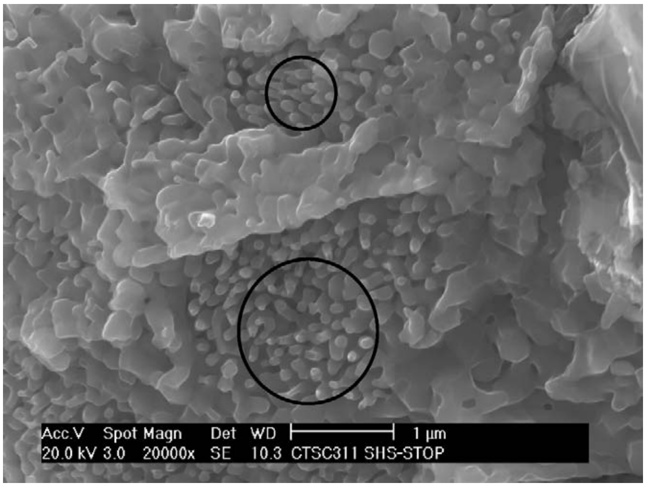

Fig. 4. Scanning electron micrograph showing the fracture surface morphology of the powder compact heated to 1240 °C and cooled down immediately.

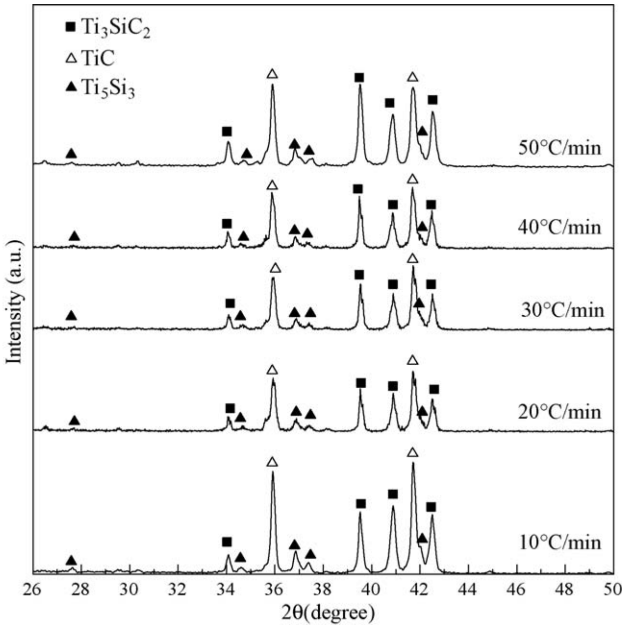

Fig. 5. XRD patterns of samples sintered at 1350 °C for 20 min at heating rates of 10 °C/min, 20 °C/min, 30 °C/min, 40 °C/min and 50 °C/min, respectively.

combustion synthesis reaction on further formation of Ti_3SiC_2 is unknown. Fig. 5 shows the X-ray diffraction profiles of the samples sintered at 1350 °C for 20 min with heating rate at 10 °C/min, 20 °C/min, 30 °C/min, 40 °C/min and 50 °C/min, respectively. The final products in all samples include three phases, i.e., Ti_3SiC_2, Ti_5Si_3 and TiC, and the content of Ti_3SiC_2 did not show obvious variation with the heating rate. Fig. 6 shows the X-ray diffraction profiles of the samples sintered for 20 min at 1400 °C, 1450 °C and 1500 °C, respectively, with the heating rate at 50 °C/min. The contents of TiC and Ti_5Si_3 decreased obviously with an increase in sintering temperature, as can be found in the variation of the relative peak intensities of the two phases in the diffraction patterns. In other words, the phase content of Ti_3SiC_2 in the synthesized products was increased by increasing sintering temperature, indicating that the synthesis reaction of Ti_3SiC_2 cannot be thoroughly finished by the combustion synthesis reaction alone. The formation of more Ti_3SiC_2 depends on the external energy (PDS heat). The results that combustion reactions, or otherwise terminated SHS, is not a sufficient process for the synthesis of Ti_3SiC_2 are well consistent with the literature, where usually the resultant products contain fairly low fraction of Ti_3SiC_2 in the synthesized products [29].

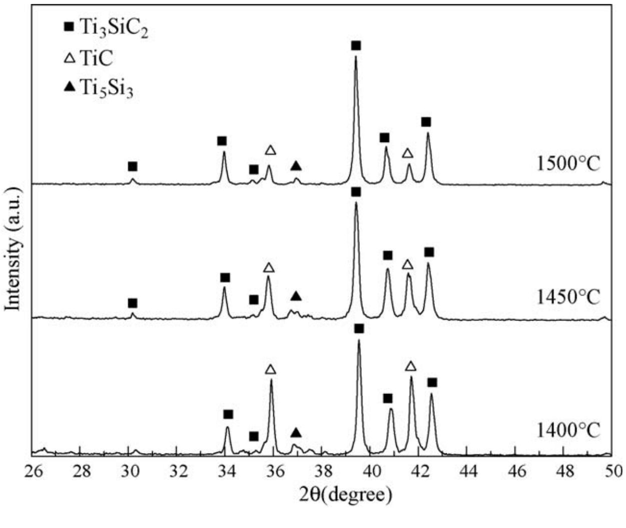

Fig. 6. XRD patterns of samples sintered at 1400 °C, 1450 °C and 1500 °C for 20 min with heating rate at 50 °C/min, respectively.

4. Conclusion

The combustion synthesis reaction was induced through pulse discharge sintering (PDS) Ti/SiC/C powder mixture. The lowest inducing heating rate was found to be 20 °C/min and this low heating rate was made possible by the direct joule heating in PDS process. The essential of this combustion synthesis reaction is Ti–Ti_5Si_3 eutectic reaction and the exothermic reaction of TiC formation during PDS process promotes this eutectic reaction. This combustion synthesis reaction cannot thoroughly finish the whole synthesis reaction of Ti_3SiC_2. Further formation of Ti_3SiC_2 phase depends on increasing the sintering temperature.

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