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Temperature fluctuation/hot pressing synthesis of Ti_3SiC_2

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A novel temperature fluctuation synthesis and simultaneous densification process for the preparation of Ti_3SiC_2 was developed. The advantages of this novel method include low synthesis temperature, short reaction time and simultaneous densification. The microstructure and room temperature mechanical properties of the Ti_3SiC_2 synthesized using this method were investigated. The result demonstrated that the Ti_3SiC_2 ceramic consisted of mainly laminated grains. It was found, with the aid of computer simulated crystallite shape, that the laminated Ti_3SiC_2 grains were composed of thin hexagonal plates. These laminated grains characterized the Ti_3SiC_2, and were responsible for the mechanical properties of the polycrystalline Ti_3SiC_2 ceramic. The measured flexural strength and the fracture toughness were 470 ± 26 MPa and 7.0 ± 0.2 MPa·m$^{1/2}$, respectively. The high toughness was attributed to the contribution of crack deflection, crack bridging, delaminating and grain pull-out of laminated Ti_3SiC_2.

1. Introduction

Titanium silicon carbide (Ti_3SiC_2) is a material which shows a unique combination of the merits of both metals and ceramics. Like metals, it is a good thermal and electrical conductor, not susceptible to thermal shock, and easy to machine with conventional tools. Like ceramics, it is oxidation-resistant and extremely refractory. Ti_3SiC_2 crystallizes in a hexagonal structure with the space group $P6_3/mmc$ [1]. The lattice constants are $a = 0.3068$ nm and $c = 1.7645$ nm [2–4]. The melting point of Ti_3SiC_2 is 3200°C and the theoretical density is 4.52 g/cm^3. The Young's modulus and hardness are 320 GPa and 4 GPa, respectively [5]. The electrical conductivity is $9.6 \times 10^6\ \Omega^{-1}\cdot m^{-1}$ and increases with the decrease of temperature [6].

Despite the excellent properties, Ti_3SiC_2 is difficult to synthesize. A number of methods including HIP-SHS [7], arc-melting followed by annealing [8], and reactive hot pressing [5] were developed recently to synthesize Ti_3SiC_2 and its composites. Although some of the methods are quite successful [5, 7] for the preparation of relatively pure Ti_3SiC_2, these methods are either complex or need long reaction time. Novel methods thus need to be developed for the synthesis of Ti_3SiC_2. In the present paper, we describe a novel temperature fluctuation/hot pressing process for the synthesis and simultaneous densification of polycrystalline Ti_3SiC_2. The microstructure and room temperature mechanical properties of Ti_3SiC_2 were also investigated.

The idea of the temperature fluctuation/hot pressing synthesis is based on the following facts. First, the previous work [9] demonstrated that the presence of liquid phase enhanced the formation of Ti_3SiC_2. Second, the reaction for the formation of Ti_3SiC_2 from elemental Ti, Si, and graphite is exothermic [10, 11]. Third, silicon melts at 1420°C and the melting of Si is endothermic. Finally, besides assisting the synthesis of Ti_3SiC_2, the presence of liquid silicon can act as an *in situ* liquid additive for the densification of Ti_3SiC_2. So, if the compacted Ti, Si, and graphite powder mixture is rapidly heated to the temperature above 1420°C, silicon will melt and a small amount of Ti_3SiC_2 will form. Then we reduce the temperature of the compacted powder mixture to 1200°C, which is a suitable temperature for the formation of Ti_3SiC_2 [8], to synthesize and densify bulk Ti_3SiC_2. Since the reaction for the formation of Ti_3SiC_2 from elemental Ti, Si, C is exothermic, the reaction-released heat will keep silicon as a liquid phase [10, 11]. Thus the synthesis and densification can be conducted at relatively low temperature. Liquid silicon acts as an *in situ* liquid phase for the synthesis of Ti_3SiC_2, as well as an additive for the densification of Ti_3SiC_2. In this paper, we describe in detail the temperature fluctuation/hot pressing synthesis and simultaneous densification process for the preparation of polycrystalline Ti_3SiC_2. The microstructure and fracture behaviour were also investigated.

2. Experimental procedures

The starting materials for the temperature fluctuation/hot pressing synthesis of Ti_3SiC_2 were Ti powders

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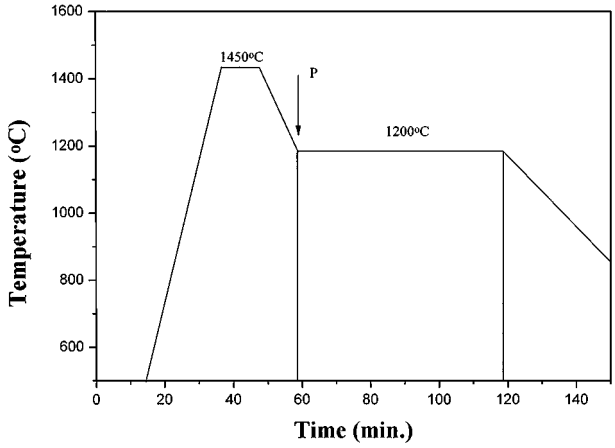


Figure 1 Temperature-time schedule for the temperature fluctuation/hot pressing synthesis of bulk Ti_3SiC_2.

with average particle size of 40 μm (from Institute of non-ferrous metals, Beijing, China), Si powders with average particle size of 80 μm , and graphite powders with average particle size of 10 μm (both from China's No. 4 grinding wheel Inc., Shangdong, China). Powders with Ti: Si: C ratios near the stoichiometric composition were dry-mixed in a polypropylene jar for ten hours. After mixing, the powders were cold-pressed into discs of 50 mm in diameter and 15 mm in thickness under a pressure of 5 MPa, and then put in a graphite die. The temperature fluctuation/hot pressing synthesis was performed via the temperature vs. time diagram shown in Fig. 1. The powder compact was first heated to 1450 °C and kept for 10 min., and then the temperature was reduced to 1200°C and kept for 60 minute. A uniaxial pressure of 40 MPa was applied for densification when the temperature was reduced to 1200°C.

The phase composition and microstructure of the Ti_3SiC_2 were analyzed by X-ray diffraction and scanning electron microscopy. The X-ray diffraction data were collected by a step-scanning diffractometer (Rigaku D/max-A) using Cu K_α radiation. The quantitative phase analysis for the synthesized Ti_3SiC_2 was done using the Rietveld method [12], and the DBWS program [13] in Cerius^2 3.8 computational program for material research (Molecular Simulation Inc., USA). The microstructure of the Ti_3SiC_2 was examined with an S-360 scanning electron microscope (Cambridge Instrument, Ltd.). To understand the microstructural features of polycrystalline Ti_3SiC_2, the crystallite shape of Ti_3SiC_2 was generated using the *Morphology* program based on Donnay-Harker theory [14–16] in Cerius^2 3.8.

The fracture toughness and the flexural strength of the material were determined at room temperature. The temperature fluctuation/hot pressing prepared slab was electrical discharge machined into rectangular bars with dimensions of $3 \times 6 \times 36$ mm^3 for fracture toughness measurement and $3 \times 4 \times 40$ mm^3 for flexural strength testing. Single-edge-notched-beam (SENB) specimens with the notch width of 0.1 mm were used for fracture toughness measurement. The fracture toughness measurement was performed on Shenck universal-testing machine (Shenck Treble Inc., Germany) in three-point bending. The crosshead displacement rate was selected to be 0.05 mm/min. The flexural strength was tested also in three-point bending with the crosshead speed of 0.5 mm/min. The fracture surfaces and the crack propagation path were examined in scanning electron microscopy.

3. Result and discussion

3.1. Synthesis and densification of Ti_3SiC_2

The formation of Ti_3SiC_2 using the temperature fluctuation/hot pressing process from elemental Ti, Si, and graphite powders can be described in the following equations:

$$\mathrm{Si\,(s)} \rightarrow \mathrm{Si\,(l)} \tag{1}$$

$$3\mathrm{Ti\,(s)} + \mathrm{Si\,(l)} + 2\mathrm{C\,(s)} \xrightarrow{\mathrm{Si\,(l)}} \mathrm{Ti_3SiC_2\,(s)} \tag{2}$$

where Ti (s), Si (l), C (s) and Ti_3SiC_2 (s) represent solid Ti, liquid Si, solid C and solid Ti_3SiC_2, respectively. Liquid Si played the most important role in this process. It was formed when the initial powder compact was heated to the temperature above 1420°C. The presence of liquid Si changed the solid-solid reaction into the solid-liquid reaction in the Ti-Si-C mixture. The presence of liquid phase enhanced the formation of Ti_3SiC_2 was shown in the previous work [9]. In addition, liquid Si was also an effective additive for the densification of bulk Ti_3SiC_2. When the temperature was reduced to 1200°C, the reaction-released heat would keep Si in the liquid form. The rapid increase in internal temperature in Ti-Si-C system was previously investigated by Pampuch *et al.* [10]. In their work, two pellets of the Ti, Si, and C powder mixtures were heated at different heating rate. For the pellet rapidly heated at a rate of 500°C/min. to 1050–1200°C, ignition of the reactant mixtures took place, followed by a rapid increase in the temperature of the system, i.e., conditions typical of the thermal explosion regime of solid combustion were realized. For the pellet heated at a rate of 10°C/min. to 1300°C, no ignition and no temperature increase above 1300°C were observed. The work of Pampuch *et al.* [10] demonstrated that both the heating rate and the temperature controlled the ignition and the temperature increase in the Ti-Si-C system. In the present work, powder mixtures of Ti, C, and graphite were heated at a rate of 30°C/min. to 1450°C to make sure that Si was melt and ignition for the formation of Ti_3SiC_2 took place. Although the internal increase in temperature due to the reaction released heat from reaction (2) is difficult to measure, the theoretical calculations [10] supported the hypothesis of this work. The calculated adiabatic temperatures in powder mixtures of Ti, Si, and C by Pampuch *et al.* [10] were in the range of 2550–3290 K. And the estimated peak temperature in regime of solid combustion were 50–300 K lower than the calculated adiabatic temperatures. The difference between the present work and that of Pampuch *et al.* [10] is that instead of solid combustion synthesis, a solid-liquid reaction process was used in this work. And the heating rate (30°C/min.) was much lower than that (500°C/min.) used by Pampuch *et al.* [10]. So the internal temperature increase in the Ti-Si-C system in

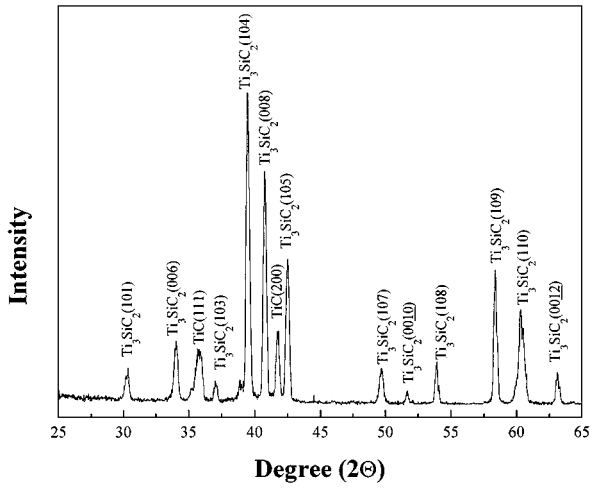


Figure 2 X-ray diffraction pattern of Ti_3SiC_2 prepared through the temperature fluctuation/hot pressing process.

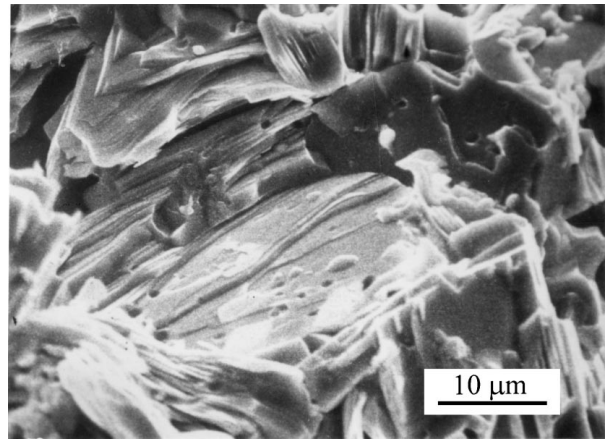


Figure 3 Scanning electron micrograph of Ti_3SiC_2, the laminated Ti_3SiC_2 grains can be seen in the figure.

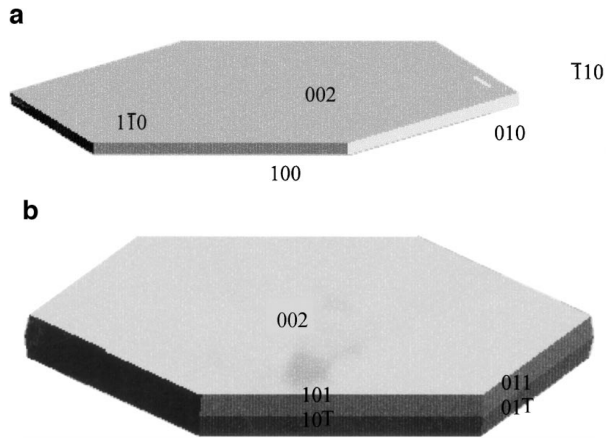


Figure 4 Computer simulated crystallite shape based on Donnay-Harker theory. The top surfaces are {002}, the side faces are either {100}(Fig. 4a) or {101}(Fig. 4b).

the present work would be lower than that calculated by Pampuch *et al.* [10], but it is probably high enough to prevent the solidification of Si. Other support for the hypothesis of this temperature fluctuation method would be the exothermic heat of reaction (2) calculated by Du *et al.* [11]. It is for sure that both theoretical and experimental works are needed to understand the real reaction happened in the temperature fluctuation/hot pressing process.

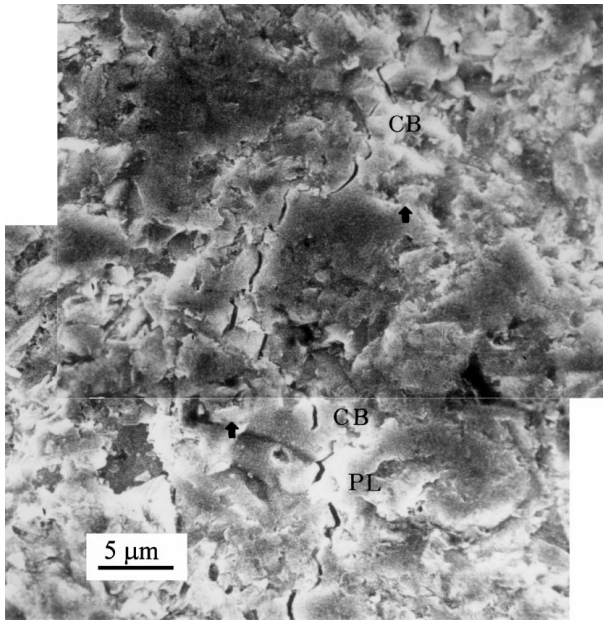
The density measured by Archimedes method was 4.51 g/cm^3, which is close to the theoretical true density of Ti_3SiC_2. Fig. 2 shows the X-ray diffraction pattern of the synthesized bulk material. The X-ray diffraction data encompass the diffraction angles 2θ ranging from 25° to 80°. No peaks of unreacted Si can be seen from the X-ray diffraction pattern. The main phase was Ti_3SiC_2 as indexed in the pattern. Beside Ti_3SiC_2, a small amount of TiC was detected. To determine the amount of TiC, a quantitative X-ray analysis was performed using the Rietveld method [12, 13]. The calculated amount of TiC was 12 wt%. Although the amount of TiC is not insignificant, it may be reduced if the initial composition and the processing parameters are optimized. The above results demonstrate that the temperature fluctuation/hot pressing synthesis is an effective and simple method for the preparation of bulk Ti_3SiC_2 with several advantages of the low synthesis temperature, short reaction time, and simultaneous densification.

3.2. Microstructure of Ti_3SiC_2

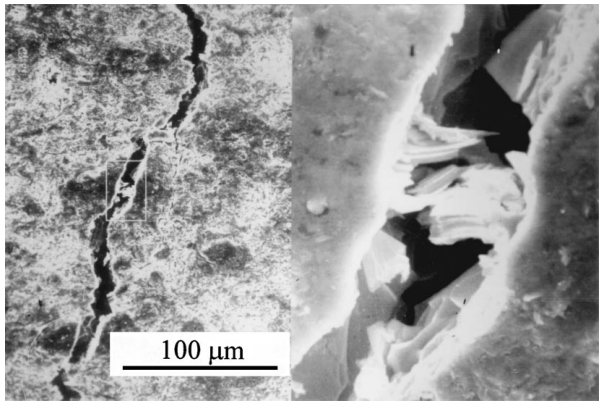
The microstructure of the Ti_3SiC_2 is shown in Fig. 3. Laminated Ti_3SiC_2 grains with dimensions of 20–25 μm in diameter and 5–8 μm in thickness are seen in the figure. These laminated grains are considered as a characteristic of Ti_3SiC_2 which has a layered crystal structure. The laminated grains in Fig. 3 are composed of a number of thin plates. To understand the microstructural feature of the laminated Ti_3SiC_2 grains, the crystallite shape of Ti_3SiC_2 was simulated using the *Morphology* program based on the Donnay-Harker theory [14–16]. The Donnay-Harker method defines the surface F, which will grow at the slowest growth rate and hence will be of the highest morphological importance in crystal morphology. Ti_3SiC_2 crystallizes in a hexagonal structure with the space group of $P6_3/mmc$. According to Donnay-Harker theory [14–16], the crystallite shape of Ti_3SiC_2 is determined by the relative growth rate on (002), (100) and (101) planes. If the growth rates on (002) planes are the slowest, the crystallite shape is a hexagonal plate as is shown in Fig. 4. The top faces are {002} and the side faces are either {100} (Fig. 4a) or {101}(Fig. 4b) faces. From the computer simulated crystallite shape, we see that the thin plates are characteristics of the crystallite shape of Ti_3SiC_2. The observed Ti_3SiC_2 laminates are composed of a number of thin hexagonal plates. These laminated Ti_3SiC_2 grains will be responsible for the mechanical properties of polycrystalline Ti_3SiC_2 ceramics which we will discuss in the next section.

3.3. Mechanical properties

The measured flexural strength and fracture toughness for the polycrystalline Ti_3SiC_2 was 470 ± 26 MPa and 7.0 ± 0.2 MPa·m$^{1/2}$, respectively. The data were the averages of at least five test specimens. The flexural



(a)



(b)

Figure 5 (a) Crack propagation path near the crack tip of a SENB specimen after unloading, the arrow in the figure indicates the direction of the crack propagation. (b) Crack propagation path of a SENB specimen after unloading. The left-hand part is a low magnification micrograph and the right-hand part is its high magnification micrograph taken at rectangular area marked in low magnification.

strength and fracture toughness data are high for a carbide and must be related to the microstructure features. To understand them, the crack propagation path was examined in scanning electron microscopy. Fig. 5a shows the crack propagation path near the crack tip of a SENB specimen after complete unloading. The arrow in the figure indicates the direction of the crack propagation. Unlike brittle ceramics with fine microstructure, the crack propagation of the Ti_3SiC_2 is strongly deflected, which is a characteristic of tough materials. Besides crack deflection, crack bridging (as marked CB in Fig. 5a) and pull-out of laminated Ti_3SiC_2 grains (as marked PL in Fig. 5a) can be identified in the figure. Fig. 5b also shows a crack propagation path of a SENB specimen after unloading. The left-hand part is a low magnification micrograph and the right-hand part is its high magnification micrograph taken at the rectangular area marked in the low magnification. In this figure, the delamination, pull-out of the laminated Ti_3SiC_2 grains, and the grain bridging are clearly shown (see the right-hand part of Fig. 5b). The frequently observed delamination and pull-out of laminated Ti_3SiC_2 grains indicate the weakly bonded interface between the thin plates in the Ti_3SiC_2 grains. From the above analysis, we can make the conclusion that crack bridging, crack deflection, pull-out and delamination of laminated Ti_3SiC_2 grains contribute to the high fracture toughness of Ti_3SiC_2. It is apparent that theoretical work is needed to quantitatively describe each of the contributions.

4. Conclusions

This work demonstrated that temperature fluctuation/hot pressing process was a novel method for the simultaneous synthesis and densification of polycrystalline Ti_3SiC_2, providing relatively low synthesis temperature, short reaction time, and simultaneous synthesis densification. The microstructure analysis revealed that the laminated Ti_3SiC_2 grains consisted of thin hexagonal plates, which are the characteristic crystallite shape for Ti_3SiC_2. The flexural strength and the fracture toughness of Ti_3SiC_2 prepared using the temperature fluctuation/hot pressing method were 470 ± 26 MPa and 7.0 ± 0.2 MPa·$m^{1/2}$, respectively. The high toughness was attributed to the contribution of crack deflection, crack bridging, delaminating and grain pull-out of laminated Ti_3SiC_2.

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