

## Simultaneous synthesis and consolidation of a nanocrystalline TiSi<sub>2</sub>-SiC composite by pulsed current activated combustion

In-Yong Ko<sup>a</sup>, Jeong-Hwan Park<sup>a,b</sup>, Hyun-Kuk Park<sup>a</sup> and In-Jin Shon<sup>a,b\*</sup>

<sup>a</sup>Division of Advanced Materials Engineering, the Research Center of Advanced Materials Development, Chonbuk National University, 664-14 Deokjin-dong 1-ga, Deokjin-gu, Jeonju, Jeonbuk 561-756, Republic of Korea

<sup>b</sup>Department of Hydrogen and Fuel Cells Engineering, Specialized Graduate School, Chonbuk National University, 664-14 Deokjin-dong 1-ga, Deokjin-gu, Jeonju, Jeonbuk 561-756, Republic of Korea

**A dense nanophase TiSi<sub>2</sub>-SiC composite was synthesized by a pulsed current activated combustion synthesis method within 2 minutes in one step from mechanically activated powders of TiC and Si. Simultaneous combustion synthesis and consolidation were accomplished under the combined effects of a pulsed current and mechanical pressure. Highly dense TiSi<sub>2</sub>-SiC with relative density of up to 97% was produced under simultaneous application of a 60 MPa pressure and the pulsed current. The average grain size and mechanical properties of the composite were investigated.**

**Key words:** Pulsed current activated combustion, Composite materials, Nanophase, Mechanical properties, TiSi<sub>2</sub>-SiC.

### Introduction

Nanocrystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties [1, 2]. As nanomaterials possess high strength, high hardness, excellent ductility and toughness, undoubtedly, more attention has been paid to their application of nanomaterials [3, 4]. In recent days, nanocrystalline powders have been developed by thermochemical and thermomechanical processes named as the spray conversion process (SCP), co-precipitation and high energy milling process [5-7]. However, the grain size in sintered materials becomes much larger than that in the pre-sintered powders due to rapid grain growth during the conventional sintering process. Therefore, even though the initial particle size is less than 100 nm, the grain size increases rapidly up to 500 nm or larger during the conventional sintering [8]. So, controlling the grain growth during sintering is one of the keys to the commercial success of nanostructured materials. In this regard, the pulsed current activated sintering method which can make dense materials within 2 minutes, has been shown to be effective in achieving this goal [9, 10]. TiSi<sub>2</sub> has received considerable attention in recent years for its potential application as a high-temperature structure material. Its properties provide a desirable combination of a high melting temperature (1540 °C), high modulus (255.6 GPa at room temperature), high oxidation resistance in air,

and a relatively low density (4.07 g·cm<sup>-3</sup>) [11, 12]. In addition, the thermal and electrical conductivities are relatively high and therefore they are also attractive for electronic interconnections and diffusion barriers [13]. SiC is a very interesting ceramic material due to its properties such as high hardness, low bulk density and high oxidation resistance which make SiC useful for a wide range of industrial applications. Furthermore, the isothermal oxidation resistance of metal silicide-SiC composites in dry air provide to be superior to that of a monolithic metal silicide compact [14]. However, as in the case of many intermetallic compounds, the current concern about these materials focuses on their low fracture toughness below the ductile-brittle transition temperature [15-18]. To improve their mechanical properties, the approach commonly utilized has been the addition of a second phase to form a composite [19-24].

Many similar high-temperature dense composites are usually prepared in a multistep process [25, 26]. However, the method of field-activated and pressure-assisted combustion synthesis has been successfully employed to synthesize and densify materials from the elements in one step in a relatively short period of time. This method has been used to synthesize a variety of ceramics and composites, including MoSi<sub>2</sub>-ZrO<sub>2</sub>, Ti<sub>5</sub>Si<sub>3</sub> and its composites, WSi<sub>2</sub> and its composites, and WC-Co hard materials [27-32]. These materials that are generally characterized by a low adiabatic combustion temperature which cannot be synthesized directly by the self-propagating high-temperature synthesis (SHS) method. It is apparent from Fig. 1 that when the TiC phase is in contact with silicon, the formation of the TiSi<sub>2</sub> and SiC phases can be thermodynamically possible by a solid state displacement reaction

\*Corresponding author:  
Tel : +82 63 270 2381  
Fax: +82 63 270 2386  
E-mail: ijshon@chonbuk.ac.kr

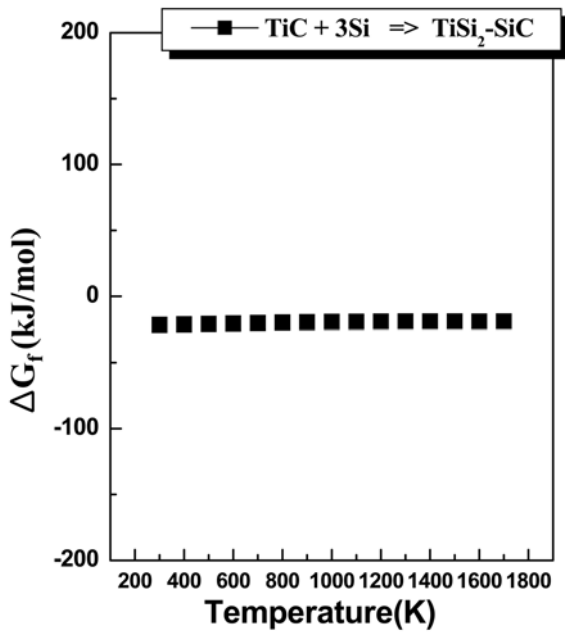


Fig. 1. Temperature dependence of the Gibbs free energy variation by interaction of the Ti-carbide phase (TiC) with silicon.

according to following equation :



The purpose of this study was to produce dense nanocrystalline  $\text{TiSi}_2$ -SiC composite within 2 minutes in one-step from mixtures of mechanically activated TiC and 3Si powders by using the pulsed current activated combustion method and to evaluate its mechanical properties (hardness and fracture toughness).

### Experimental Procedures

Powders of 99.5% titanium carbide (2.5–4  $\mu\text{m}$ , Alfa Products) and 99.5% pure silicon (–325 mesh, Alfa Products) were used as starting materials. Fig. 2 shows the SEM images of the raw materials used. TiC and 3Si powder mixtures were first milled in a high-energy ball mill, (Pulverisette-5 planetary mill) at 250 rpm and for 10 h. Tungsten carbide balls (5 mm in diameter) were used in a sealed cylindrical stainless steel vial under argon atmosphere. The weight ratio of ball-to-powder was 30 : 1. Fig. 3 shows XRD patterns of the raw powders and milled TiC+Si powder. Milling resulted in a significant reduction of grain size. The grain size and internal strain were calculated using Suryanarayana and Grant Norton's formula [33] :

$$B_r(B_{\text{crystalline}} + B_{\text{strain}})\cos\theta = k\lambda/L + \eta\sin\theta \quad (2)$$

where  $B_r$  is the full width at half-maximum (FWHM) of the diffraction peak after an instrumental correction;  $B_{\text{crystalline}}$  and  $B_{\text{strain}}$  are the FWHM caused by the small grain size and internal stress, respectively;  $k$  is a constant (with a value of 0.9);  $\lambda$  is the wavelength of the X-ray

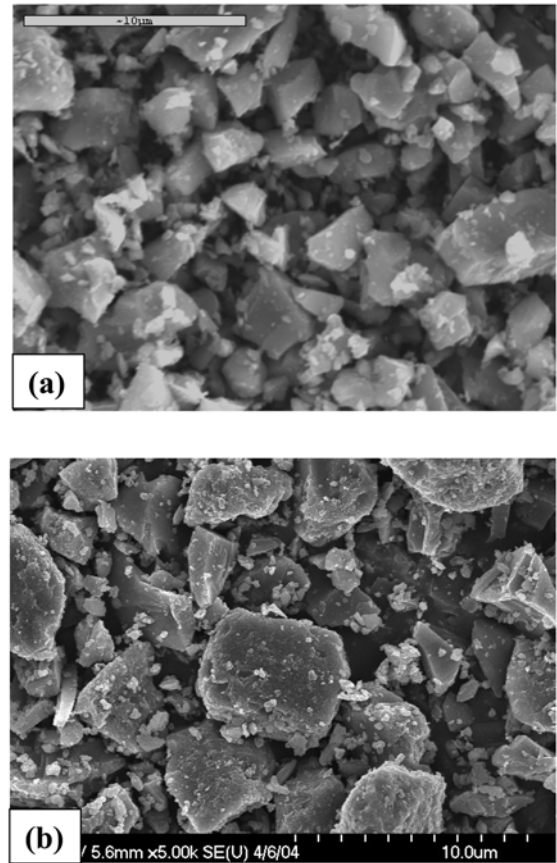
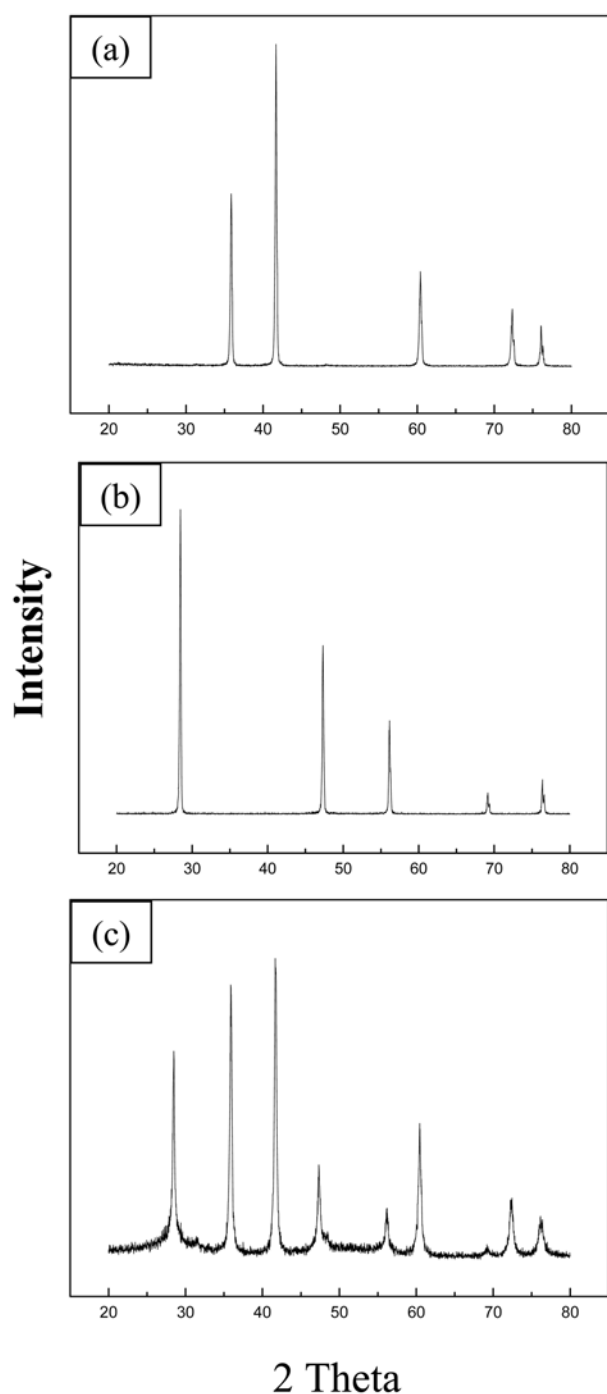


Fig. 2. Scanning electron microscope images of the raw materials: (a) Titanium Carbide, (b) Silicon powder.

radiation;  $L$  and  $\eta$  are the grain size and internal strain, respectively; and  $\theta$  is the Bragg angle. The parameters,  $B$  and  $B_r$ , follow Cauchy's form with the relationship:  $B = B_r + B_s$ , where  $B$  and  $B_s$  are the FWHM of the broadened Bragg peaks and the standard Bragg peaks of the samples, respectively. The FWHM of the milled powder is wider than that of the raw powder due to the internal strain and a reduction of the grain size. The average grain size of the TiC and Si measured by Suryanarayana and Grant Norton's equation were about 59 nm and 74 nm, respectively.

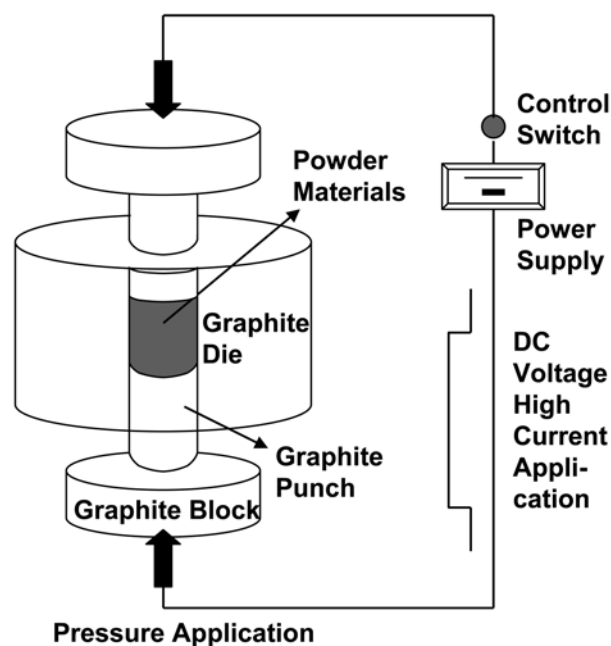
After milling, the mixed powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the pulsed current activated combustion system made by Eltek in South Korea, shown schematically in Fig. 4. The four major stages in the synthesis are as follows. The system was evacuated (stage 1), and a uniaxial pressure of 60 MPa was applied (stage 2). A pulsed current was then activated and maintained until densification was attained as indicated by a linear gauge measuring the shrinkage of the sample (stage 3). The temperature was measured by a pyrometer focused on the surface of the graphite die. At the end of the process, the sample was cooled to room temperature (stage 4). The process was carried out under a vacuum of 40 mtorr (5.33 Pa).

The relative densities of the synthesized samples were

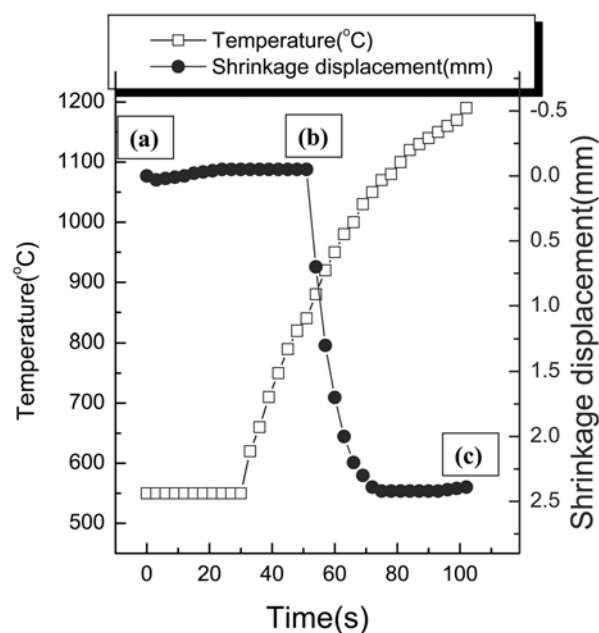


**Fig. 3.** XRD patterns of the raw materials: (a) TiC, (b) Si and (c) milled TiC + 3Si.

measured by the Archimedes method. Microstructural information was obtained from product samples which were polished and etched using a solution of HF (30 vol.%),  $\text{HNO}_3$  (30 vol.%) and  $\text{H}_2\text{O}$  (40 vol.%) for 10 s at room temperature. Compositional and microstructural analyses of the products were made through X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). Vickers hardness was measured by performing indentations at a load of 20 kg with a dwell time of 15 s on the synthesized samples.



**Fig. 4.** Schematic diagram of the apparatus for pulsed current activated combustion synthesis.

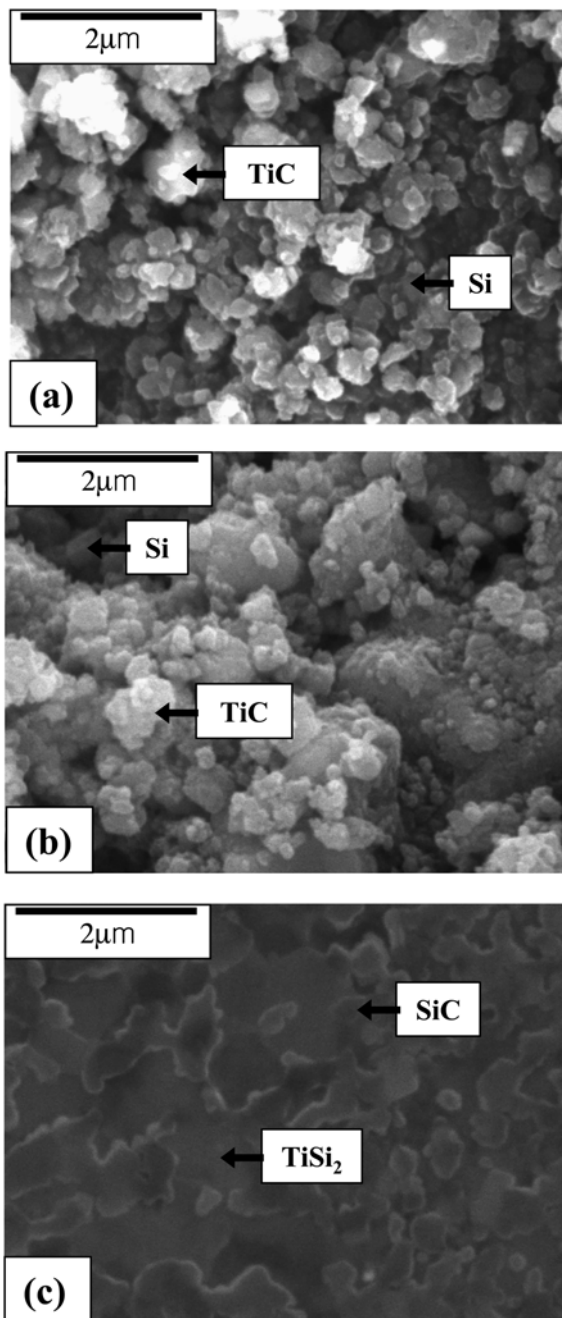


**Fig. 5.** Variations of the temperature and shrinkage displacement with heating time during pulsed current activated combustion synthesis and densification of the  $\text{TiSi}_2\text{-SiC}$  composite (under 60 MPa, 2800A).

## Results and Discussion

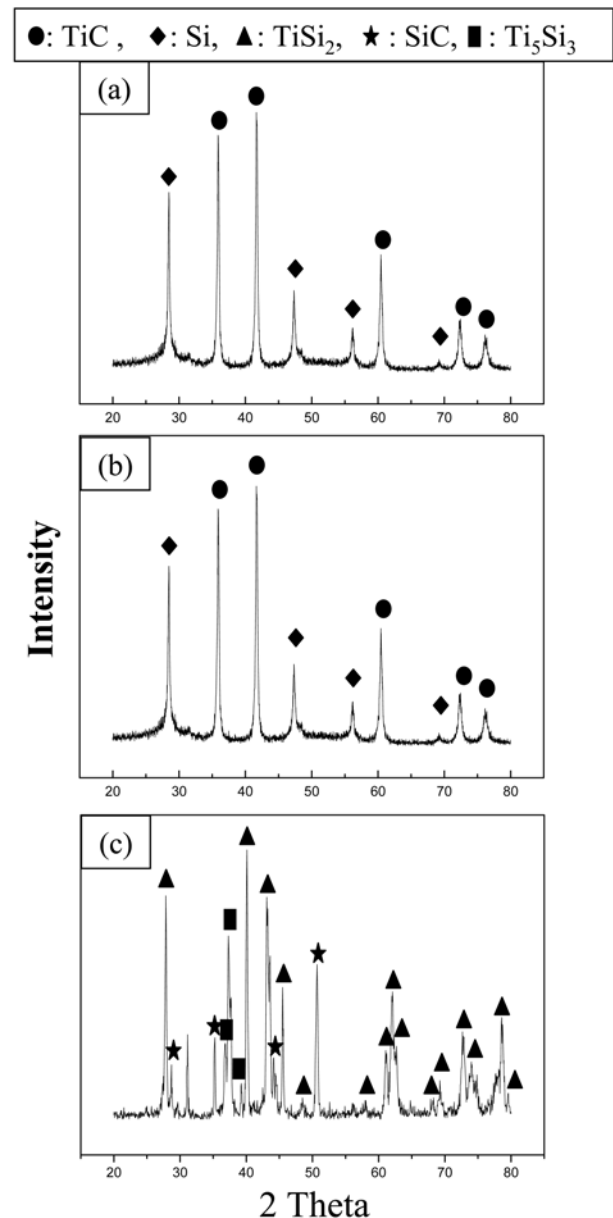
The variations in shrinkage displacement and temperature of the surface of the graphite die with heating time during the processing of the TiC + 3Si system are shown Fig. 5. As the induced current was applied the specimen showed initially a small (thermal) expansion and the shrinkage displacement increased gradually with temperature up to about 850  $^\circ\text{C}$ , but then abruptly increased at about 900  $^\circ\text{C}$ . When the reactant mixture of TiC + 3Si was

heated under 60 MPa pressure to 850 °C, no reaction took place and there was no significant shrinkage displacement as judged by subsequent XRD and SEM analyses. Fig. 6 shows the SEM (scanning electron microscope) images of a powder (a) after milling, a specimen (b) heated to 850 °C and (c) heated to 1200 °C, respectively. Fig. 6(a) and (b) indicate the presence of the reactants as separate phases. X-ray diffraction results, shown in Fig. 7(a) and Fig. 7(b) exhibit only peaks pertaining to the reactants TiC and Si. However, when the temperature was raised to 1200 °C, the starting powders reacted producing highly dense products. An SEM image of an etched surface of a



**Fig. 6.** Scanning electron microscope images of the TiC + 3Si system: (a) after milling, (b) before combustion synthesis, (c) after combustion synthesis.

sample heated to 1200 °C under a pressure of 60 MPa is shown in Fig. 6(c). A complete reaction between these elements (TiC and Si) has taken place under these conditions. These conclusions were supported by X-ray diffraction analysis with peaks of the product phases, TiSi<sub>2</sub> and SiC, as indicated in Fig. 7(c). In addition a minor phase (Ti<sub>5</sub>Si<sub>3</sub>) also existed. The presence of Ti<sub>5</sub>Si<sub>3</sub> in the sample suggests a deficiency of Si. It is considered that this observation is related to oxygen entrapped in the pores of the interior portion of the sample during pressing and may be due to a small amount of oxidation of the Si during the heating. The abrupt increase in the shrinkage displacement at the ignition temperature is due to the increase in density as a result of the molar volume change associated with the formation of TiSi<sub>2</sub>-SiC from The



**Fig. 7.** XRD patterns of the TiC + 3Si system: (a) after milling, (b) before combustion synthesis, (c) after combustion synthesis.

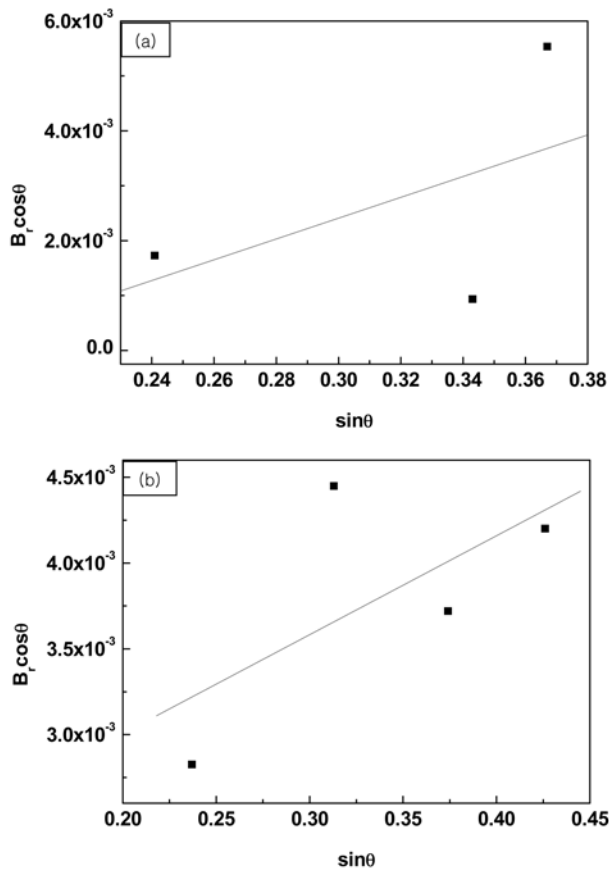


Fig. 8. Plots of  $B_r \cos\theta$  versus  $\sin\theta$  for (a) TiSi<sub>2</sub>, (b) SiC.

ic + 3Si reactants and the consolidation of the product.

The structural parameter, i.e. the average grain size of the TiSi<sub>2</sub> and SiC was estimated using Suryanarayana and Grant Norton's formula [33]. Fig. 8 shows plots of  $B_r \sin\theta$  as a function of  $\cos\theta$ . The intercept ( $k\lambda/L$ ) can be used to calculate the crystallite size ( $L$ ). The average grain sizes of TiSi<sub>2</sub> and SiC prepared using this method were approximately 120 nm and 80 nm, respectively and the SiC particles were well distributed in the matrix, as ascertained by the SEM image of shown in Fig. 6(c).

Vickers hardness measurements were made on polished sections of the TiSi<sub>2</sub>-SiC composite using a 20 kg<sub>f</sub> load and 15 s dwell time. The calculated hardness value of the TiSi<sub>2</sub>-SiC composite was 1050 Kg/mm<sup>2</sup>. This value represents an average of five measurements. The hardness of TiSi<sub>2</sub>-SiC composite is higher than that of monolithic TiSi<sub>2</sub> reported as 964 kg/mm<sup>2</sup> [34] due to the addition of SiC. Indentations with large enough loads produced median cracks around the indent. The length of these cracks permits an estimation of the fracture toughness of the material by means of the Anstis et al. expression [35]:

$$K_{IC} = 0.016(E/H)^{1/2}P/C^{3/2} \quad (3)$$

where  $E$  is Young's modulus,  $H$  the indentation hardness,  $P$  the indentation load, and  $C$  the trace length of the crack measured from the center of the indentation. The modulus

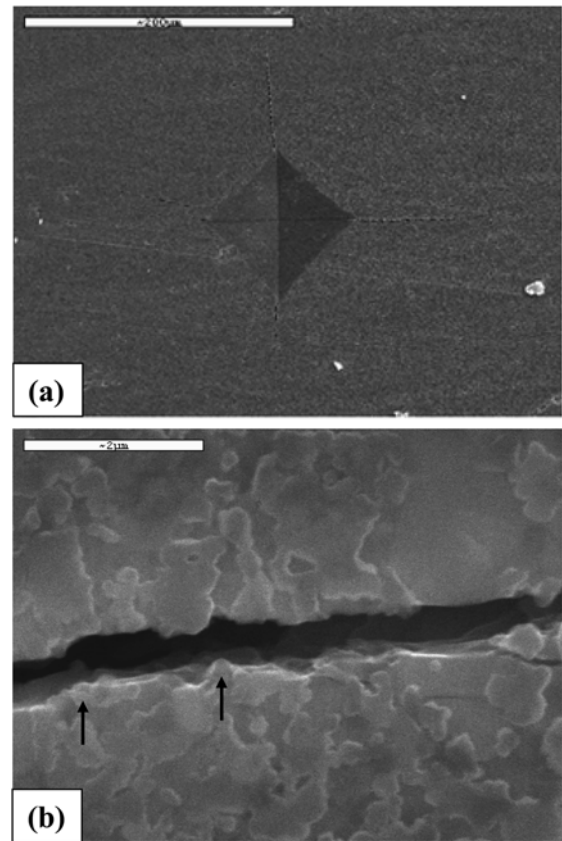


Fig. 9. (a) Vickers hardness indentation and (b) median crack propagating in the TiSi<sub>2</sub>-SiC composite.

was estimated by the rule mixtures for the 0.342 volume fraction of SiC and the 0.658 volume fraction of TiSi<sub>2</sub> using  $E(\text{SiC}) = 448 \text{ GPa}$  [36] and  $E(\text{TiSi}_2) = 255.6 \text{ GPa}$  [12]. The calculated fracture toughness value of the TiSi<sub>2</sub>-SiC composite is about  $5.3 \text{ MPa}\cdot\text{m}^{1/2}$ . The fracture toughness is higher than that of the SiC phases and TiSi<sub>2</sub> phase reported as  $1.8 \text{ MPa}\cdot\text{m}^{1/2}$  and  $1.9 \text{ MPa}\cdot\text{m}^{1/2}$ , respectively [2, 18]. As in the case of the hardness value, the toughness value is the average of measurements on five measurements.

A typical indentation pattern for the TiSi<sub>2</sub>-SiC composite is shown in Fig. 9(a). Typically, one to three additional cracks were observed to propagate from the indentation corner. A higher magnification view of the indentation median crack in the composite is shown in Fig. 9(b). The figure shows crack deflections ( $\uparrow$ ).

## Summary

Using the pulsed current activated combustion method, the simultaneous synthesis and densification of a nano-structured TiSi<sub>2</sub>-SiC composite was accomplished from mechanically activated powders of TiC and Si. Complete synthesis and densification can be achieved in one step within a duration of 2 minutes. The relative density of the composite was 97% for an applied pressure of 60 MPa and with the pulsed current. The average grain sizes of TiSi<sub>2</sub> and SiC prepared by PCACS were about 120 nm

and 80 nm, respectively. The average hardness and fracture toughness values obtained were 1050 kg/mm<sup>2</sup> and 5.3 MPa·m<sup>1/2</sup>, respectively. The present fracture toughness and hardness are higher than those of monolithic TiSi<sub>2</sub>.

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