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Rapid synthesis and consolidation of $TiSi_2$ by pulsed current activated combustion

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Dense $TiSi_2$ was synthesized by a pulsed current activated combustion synthesis method within 1 minute in a one step from mechanically activated powders of Ti and Si. Simultaneous combustion synthesis and consolidation were accomplished under the combined effects of a pulsed current and mechanical pressure. Highly dense $TiSi_2$ with a relative density of up to 96% was produced under simultaneous application of 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, Sintering, High temperature material, Mechanical properties, $TiSi_2$.

Introduction

An increase in operating temperature of a gas turbine engine will bring us reductions in both fuel consumption and CO_2 emissions. It requires ultra-high temperature structural materials which overwhelm the performance of nickel-based superalloys commercially used as turbine blade and rotors. Among candidate materials, titanium silicides are very attractive for applied temperatures up to 1,300 °C and higher. $TiSi_2$ exhibits low density, high temperature strength, high modulus (255.6 GPa at room temperature) and excellent oxidation resistance in air [1, 2]. In addition, the silicide has found wide applications as thin films in microelectronics ; for example, as ohmic contacts, Schottky barriers, gates and interconnects in very largy scale intergrated circuits [3-5]. This is primarily because of their large silicon content, high electrical conductivity, high-temperature stability, and good corrosion resistance.

The $TiSi_2$ compound is a face centered ordered orthorhombic C54 type of structure with lattice constants a = 0.8275, b = 0.4799, c = 0.8547 nm, and with a density of 4.07 g/cm^3. The congruent melting temperature is 1,540 °C.

Many similar high-temperature dense composites are usually prepared in a multistep process [6, 7]. 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 $MoSi_2$-ZrO_2, Ti_5Si_3 and its composites, WSi_2 and its composites, and WC-Co hard materials [8-13]. These materials, that are generally characterized by a low adiabatic combustion temperature, cannot be synthesized directly by the self-propagating high-temperature synthesis (SHS) method. It is apparent from Fig. 1 that when the Ti

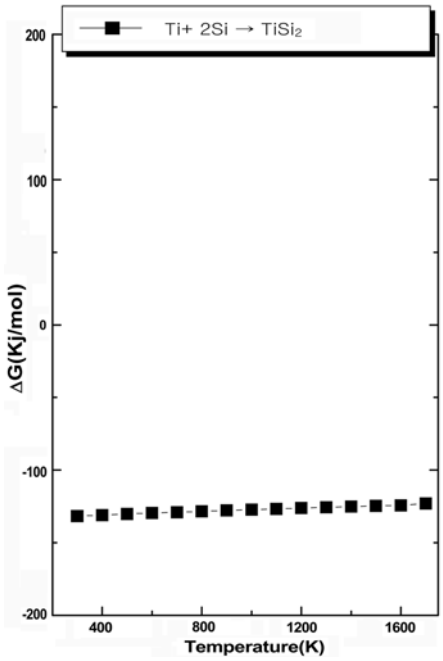

Fig. 1. Temperature dependence of the Gibbs free energy variation by interaction of Ti phase with Si.

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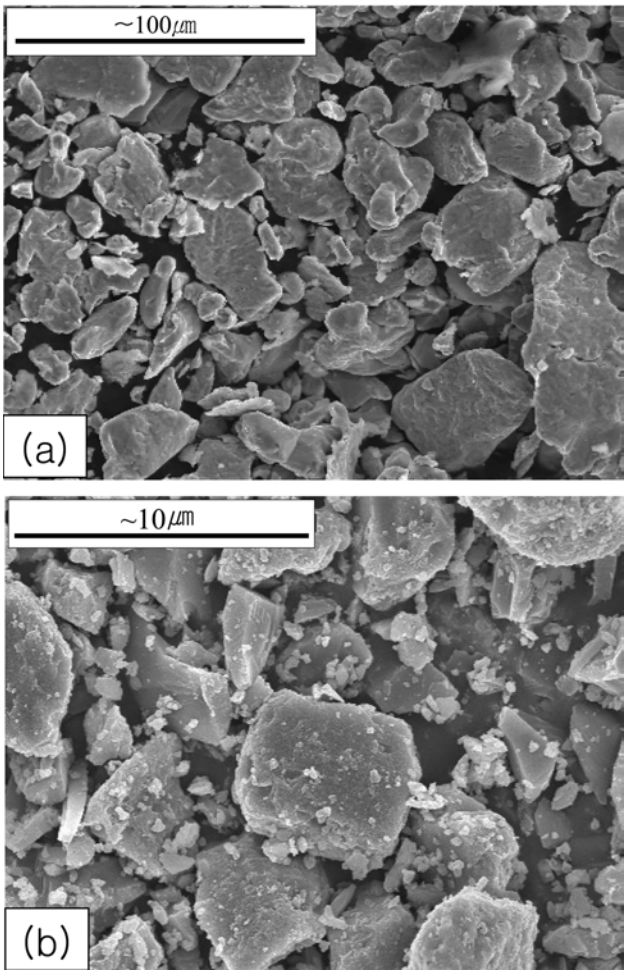

Fig. 2. Scanning electron microscope images of raw materials: (a) Titanium, (b) Silicon powder.

phase is in contact with silicon, the formation of the $TiSi_2$ phase can be thermodynamically possible by a solid state displacement reaction according to following equation:

$$Ti + 2Si \rightarrow TiSi_2 \quad (1)$$

The purpose of this study is to produce dense $TiSi_2$ within 1 minute in one-step from mixtures of mechanically activated Ti and Si powders using this pulsed current activated combustion method and to evaluate its mechanical properties (hardness and fracture toughness).

Experimental Procedure

Powders of 99.5% titanium (-325 mesh, Cerac Company) and 99% pure silicon (-325 mesh, Aldrich Products) were used as the starting materials. Fig. 2 shows the SEM images of the raw materials used. Ti and Si powder mixtures were first milled in a high-energy ball mill, a 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 an argon atmosphere. The weight ratio of ball-to-powder was 30:1. Milling resulted in a significant reduction of grain size.

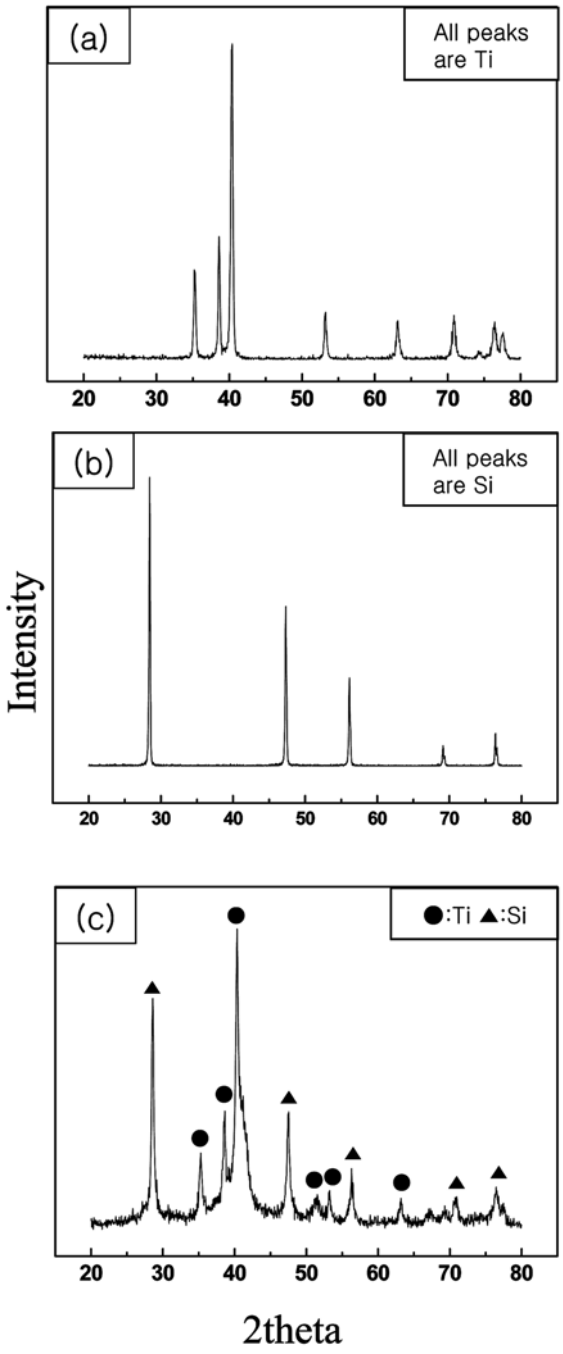

Fig. 3. XRD patterns of the raw materials: (a) Ti, (b) Si and (c) milled Ti+Si.

The grain size and the internal strain were calculated by Suryanarayana and Grant Norton's formula [14] :

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

where B_r is the full width at half-maximum (FWHM) of the diffraction peak after instrument correction; $B_{crystalline}$ and B_{strain} are the FWHM caused by the small grain size and internal stress, respectively; k is a constant (with a value of 0.9); λ is the wavelength of the X-ray radiation; L and η are grain size and internal strain, respectively; and θ is the Bragg angle. The parameters B and B_r follow

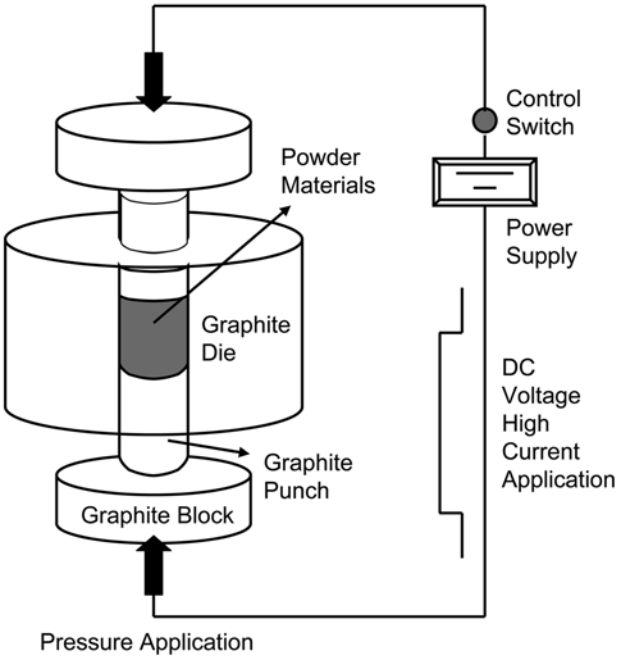

Fig. 4. Schematic diagram of apparatus for pulsed current activated sintering.

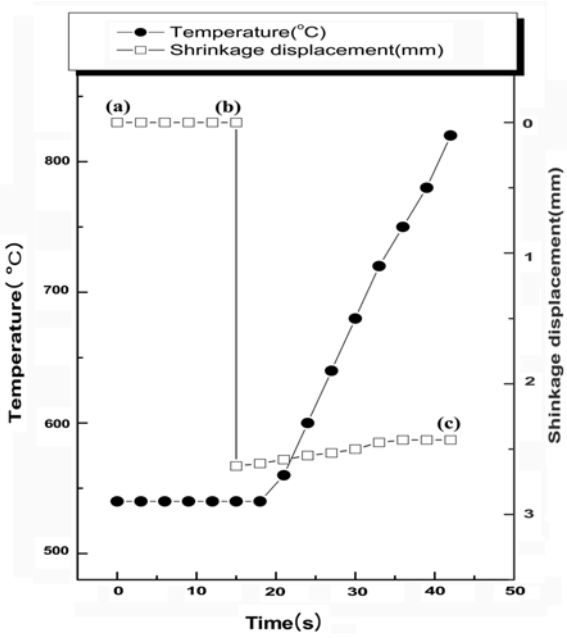

Fig. 5. Variations of temperature and shrinkage displacement with heating time during high-frequency induction heated combustion synthesis and densification of $TiSi_2$ (under 60 MPa, 90% output of total power capacity).

a Cauchy form with the relationship: $B = B_r + B_s$, where B and B_s are FWHM of the broadened Bragg peaks and the Bragg peaks of a standard sample, respectively. Fig. 3 shows XRD patterns of the raw powders and the milled Ti + Si powder mixture. The FWHM of the milled powder is greater than that of the raw powders, due to the internal strain and reduction in the grain size. The average grain sizes of the milled Ti and Si powders were determined to be 70 and 116 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). An induced current (frequency of about 50 kHz) 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 sample were measured by the Archimedes method. Microstructural information was obtained from product samples which were polished and etched using a solution of HF (10 vol.%), HNO_3 (20 vol.%) and H_2O (70 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 10 kg with a dwell time of 15 s on the synthesized samples.

Results and Discussion

The variations in shrinkage displacement and temperature of the surface of the graphite die with heating time during the processing of Ti+Si system are shown Fig. 5 As the induced current was applied the shrinkage displacement abruptly increased at below 550 °C. When the reactant mixture of Ti+Si was heated under a 60 MPa pressure to point (b), no reaction took place and no significant shrinkage displacement as judged by subsequent XRD and SEM analyses. Fig. 6 shows the SEM (scanning electron microscope) images of powders (a) after milling, a specimen (b) heated to (b) point in Fig. 5 and (c) heated to 820 °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 Ti and Si. However, when the temperature was raised to 820 °C, the starting powders reacted producing highly dense products. SEM image of an etched surface of the samples heated to 820 °C under a pressure of 60 MPa is shown in Fig. 6(c). A complete reaction between these elements (Ti and Si) has taken place under these conditions. These conclusions were supported by X-ray diffraction analyses with peaks of the product phase, $TiSi_2$ phase, as indicated in Fig. 7(c). In addition a minor phase (Ti_5Si_3) existed. The presence of Ti_5Si_3 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

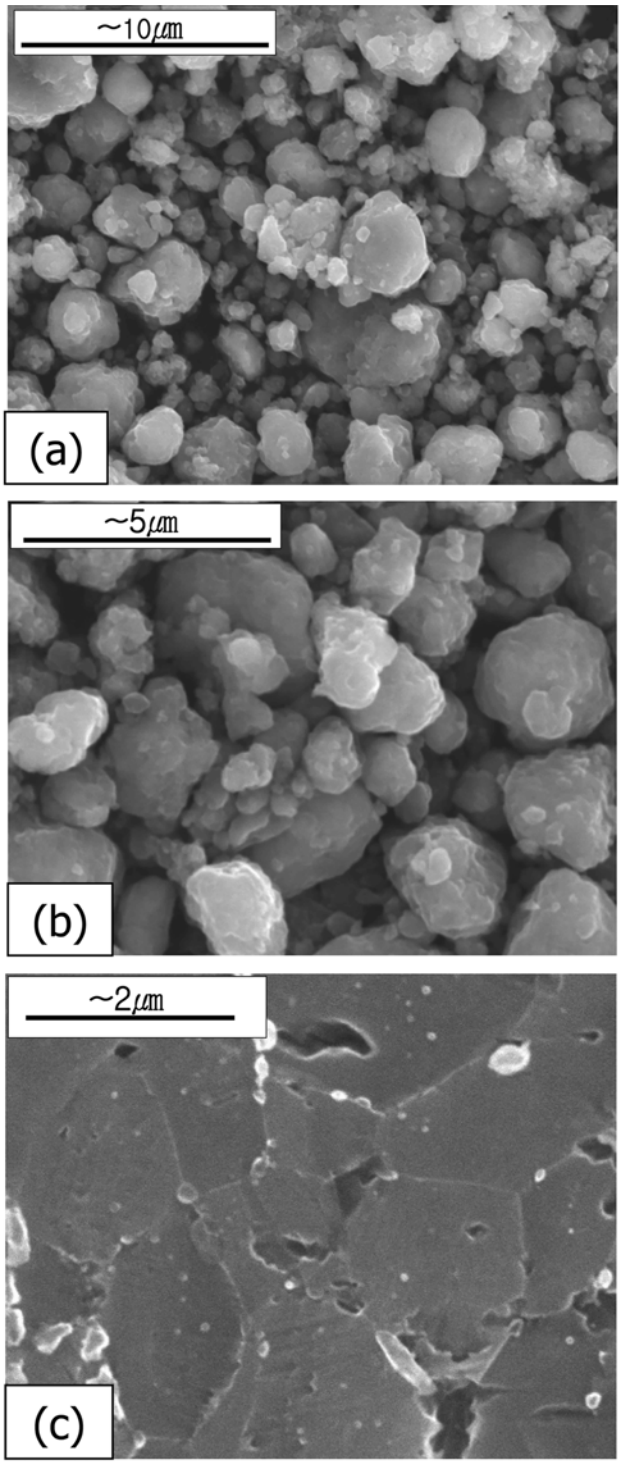

Fig. 6. Scanning electron microscope images of Ti+Si system: (a) after milling, (b) before combustion synthesis, (c) after combustion synthesis.

during pressing and may be due to a small amount of oxidation of 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 $TiSi_2$ from Ti+Si reactants and the consolidation of the product. In this study, the ignition

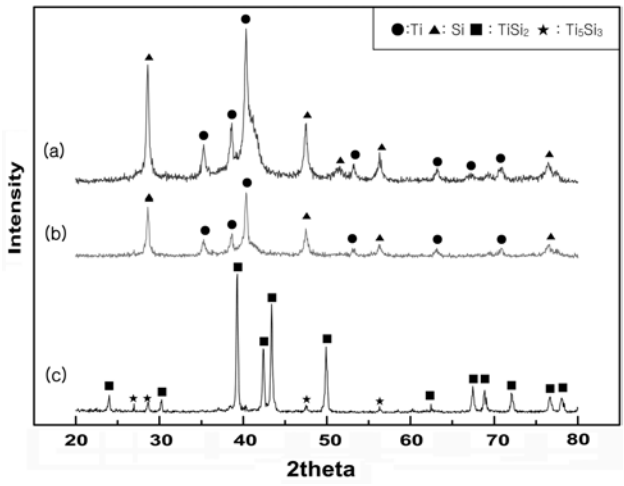

Fig. 7. XRD patterns of the Ti+Si system: (a) after milling, (b) before combustion synthesis, (c) after combustion synthesis.

temperature of $TiSi_2$ was below 550 °C. This temperature is lower than that of the metal silicide reported as about 1,200 °C [15]. It is considered that the mechanically activated reactant powders from high energy ball milling can reacted rapidly and at a lower temperature.

The structural parameter, *i.e.* the average grain size of $TiSi_2$ obtained from the linear intercept method was about 1.2 um. Vickers hardness measurements were made on polished sections of the $TiSi_2$ using a 10 kg_f load and 15 s dwell time. The calculated hardness value of $TiSi_2$ was 964 Kg/mm^2. This value represents an average of five measurements. 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 [16]:

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

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 of $TiSi_2$ was $E(TiSi_2) = 255.6$ Gpa [17]. The calculated fracture toughness value of $TiSi_2$ is about 2.5 $MPa{\cdot}m^{1/2}$. As in the case of the hardness value, the toughness value is the average of five measurements. A typical indentation pattern for $TiSi_2$ is shown in Fig. 8(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 compound is shown in Fig. 8(b). This shows the crack propagates linearly.

Summary

Using the pulsed current activated combustion method, the simultaneous synthesis and densification of $TiSi_2$ was accomplished from powders of Ti and Si. Complete synthesis and densification can be achieved in one step within duration of 1minute. The relative density of the composite was 96% for an applied pressure of 60 MPa

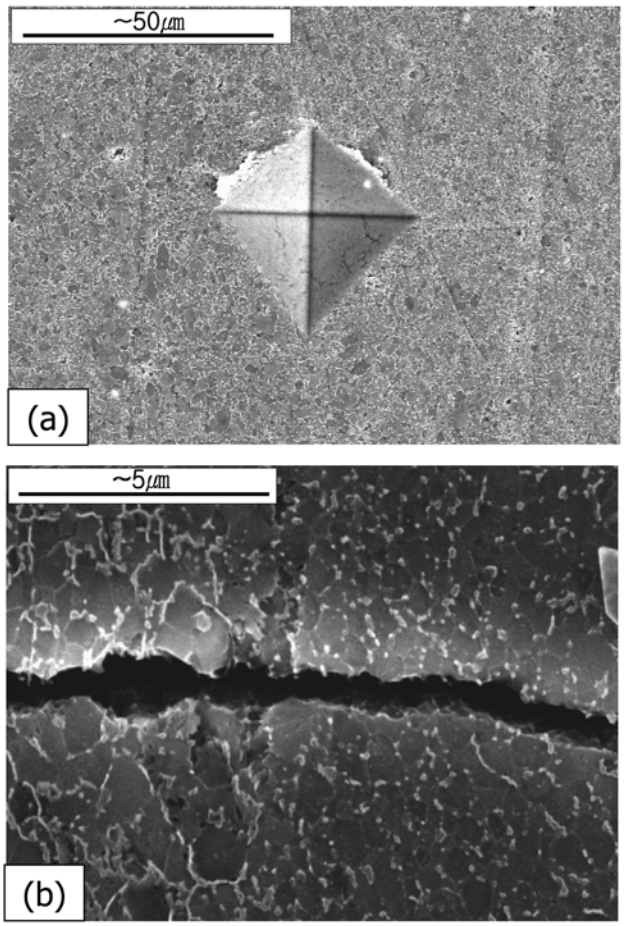

Fig. 8. (a) Vickers hardness indentation and (b) median crack propagating of $TiSi_2$.

using the pulsed current. The average grain size of $TiSi_2$ prepared by PCAC was about 1.2 um. The average hardness and fracture toughness values obtained were 964 kg/mm^2 and 2.9 MPa·m$^{1/2}$, respectively.

Acknowledgement

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