

Reaction of TiC with SiCl₄ vapor with formation of SiC–TiC composites

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Abstract

The reaction of TiC grains with SiCl₄ vapor was carried out in Ar at 1000–1600 °C to produce TiC–SiC composite powders. The compositions of these powders were controlled by controlling the conversion to SiC, which depends on the reaction temperature. The phases formed by the solid–gas reaction were identified by X-ray analysis (XRD) and the molar ratio of SiC to TiC in the powder was estimated from the area ratios of the respective XRD peaks. The reaction begins at about 1100 °C and its rate increases with temperature to 1600 °C, at which 92% SiC is formed. The morphology of the TiC–SiC composites was observed by scanning electron microscopy and transmission electron microscopy and a reaction mechanism is deduced from the above results and thermodynamic considerations. TiC–SiC composites were densified by spark plasma sintering at 1750 °C and 40 MPa to the relative density 92–96% and a Vickers hardness of 1700–1900 Hv.

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Keywords: Powder-gas phase reaction; Composites; Hardness; SiC; Structural applications

1. Introduction

Silicon carbide (SiC) has excellent properties such as high temperature strength, high hardness, and high oxidation resistance or chemical inertness. Recently, SiC has been used in wear resistant and structural applications, but its moderate fracture toughness (<4 MPa m^{1/2}) limits its further applications. On the other hand, titanium carbide (TiC) is a high temperature structural material with very high melting point (>3000 °C), high hardness, and high electrical conductivity, but is oxidized at relatively low temperatures <500 °C.¹

Many researchers have attempted to improve the toughness of SiC ceramics by forming dispersions with TiC particles. Wei and Becher have reported improved mechanical properties of SiC ceramics hot-pressed at 2000 °C with dispersed TiC particles containing 1 wt% Al and C.² An, Kim and Lee have investigated the effect of the initial α-SiC content on the microstructure and mechanical properties of hot-pressed SiC–TiC composite ceramics using α- and β-SiC powders containing 30 wt% TiC.³ Processing of composite TiC–SiC ceramics by hot pressing of ball milled particles of SiC and TiC has been investigated with the aim of improving their mechanical properties.⁴

Recently, spark plasma sintering (SPS) has attracted much interest for the densification of poorly sinterable materials such as SiC, ZrB₂, Al₂O₃ and ZrO₂.^{5–10} Using SPS, ceramics can be densified in a very short time (several minutes) at low temperatures with suppression of grain growth. For example, SiC–TiC composites have been fabricated by SPS of a mixture of β-SiC and TiC powders without additive at 1800 °C.⁶

There have also been several studies on in situ fabrication of SiC–TiC composites by chemical vapor deposition (CVD) to produce fine homogeneous composite particles of high purity.^{11–16} For example, Kawai et al. fabricated SiC–TiC ceramics by CVD using a gas mixture of SiCl₄, TiCl₄ and hydrocarbon.¹¹ A French group used SiH₂Cl₂ instead of SiCl₄ as a precursor for the CVD deposition of nanocomposite SiC–TiC–C on carbon substrate.^{14,15} Thus, the CVD method can produce fine particles of SiC and/or TiC from gas mixtures at relatively low temperatures (1000–1600 °C). In addition to the fabrication of SiC–TiC composites, layered SiC/TiC ceramics with graded compositions have been fabricated with good mechanical properties.¹⁶

For SiC–TiC composites to be densified, well-mixed unagglomerated powders of SiC and TiC are required as the starting material. As described above, TiC/SiC composites are usually made from respective mechanically mixed powders. However, mechanical mixing of powders introduces inhomogeneity in the composite. In this respect, it was expected that the gas–solid

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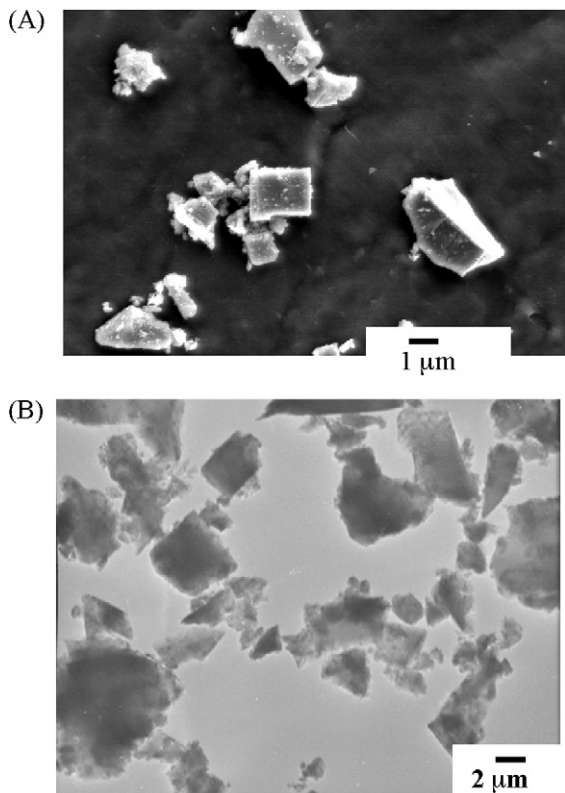


Fig. 1. SEM (A) and TEM (B) images of TiC powder.

reaction of TiC grains with SiCl₄ vapor could produce a homogeneously dispersed composite of TiC–SiC, similarly to CVD. Since the reaction of solid TiC with vapor SiCl₄ has not previously been reported, it was of interest to investigate the production of SiC–TiC composites by this solid–gas reaction. The purpose of this study was therefore to investigate the novel reaction of TiC grains with SiCl₄ vapor to produce TiC–SiC composite particles and to fabricate TiC/SiC ceramics from this powder by SPS. The effect of trace oxygen impurities on the reaction of TiC with SiCl₄ vapor is discussed in terms of the variation in morphology and chemical composition of the product.

2. Experimental procedures

The starting material was TiC powder (99.5 wt% purity with 0.2 wt% Mo and W impurities) (Rare Metallic Co. Ltd. Japan) and liquid SiCl₄ (99.0 vol.% purity) (Wako Pure Chem. Ind. Ltd.,

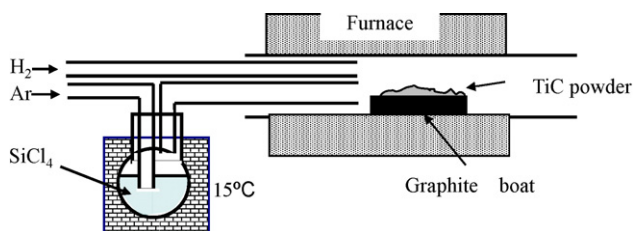


Fig. 2. Schematic representation of the experimental setup for the reaction of TiC with SiCl₄.

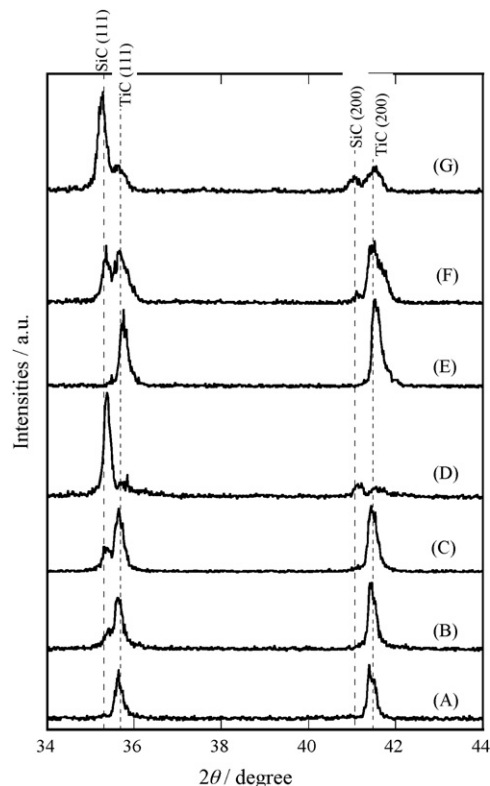


Fig. 3. XRD diffraction patterns of the products obtained after reaction of TiC with SiCl₄. Temperature (°C) without H₂: (A) 1000, (B) 1100, (C) 1300, and (D) 1500. Temperature (°C) with H₂: (E) 1300, (F) 1400, and (G) 1500.

Japan). The TiC had a mean particle size of about 3.5 μm and consists of angular plate-like grains, as shown by SEM and TEM (Fig. 1A and B). The experimental arrangement for preparing TiC/SiC composite powder is shown in Fig. 2. SiCl₄ vapor was generated and transported by bubbling Ar through liquid SiCl₄ kept at 15 °C. Assuming that the vapor–liquid equilibrium of SiCl₄ is maintained, the SiCl₄ vapor pressure is estimated to be 20 kPa at 15 °C. TiC powder was placed in a graphite boat 10 cm long, over which SiCl₄ vapor was passed in flowing Ar carrier gas (100 ml min^{−1}). It is reported by the gas supplier that the Ar contained an oxygen impurity of several tens ppm. The solid–vapor reaction of TiC with SiCl₄ was carried out at 1000–1600 °C for 60 min, in some cases with the addition of 50 ml min^{−1} of flowing H₂. The time dependency of the formation of SiC was also carried out without H₂ at 1300 °C for 0–60 min. The weight ratio of TiC to SiC in the composites was semi-quantitatively determined from the calibration curve using their peaks (1 1 1), (2 0 0), (2 2 0), and (3 1 1). The curve was constructed from a plot of the intensity ratio ($I_{\text{TiC}}/I_{\text{SiC}}$) of the four peaks against the weight ratio ($W_{\text{TiC}}/W_{\text{SiC}}$) for previously mixed powder of TiC and SiC; the SiC was obtained from the samples formed at 1600 °C, from which TiC was removed as TiO₂ by oxidation in air at 600 °C and subsequent dissolution in a sulfuric acid.

An SPS apparatus (SPS-501L, Sumitomo Coal Mining Co. Japan) was used to sinter the TiC/SiC composites. 0.25 g of the composite powder was pressed to a compact of 6 mm diameter by cold uniaxial pressing (100 MPa) and sintered at 1750 °C for

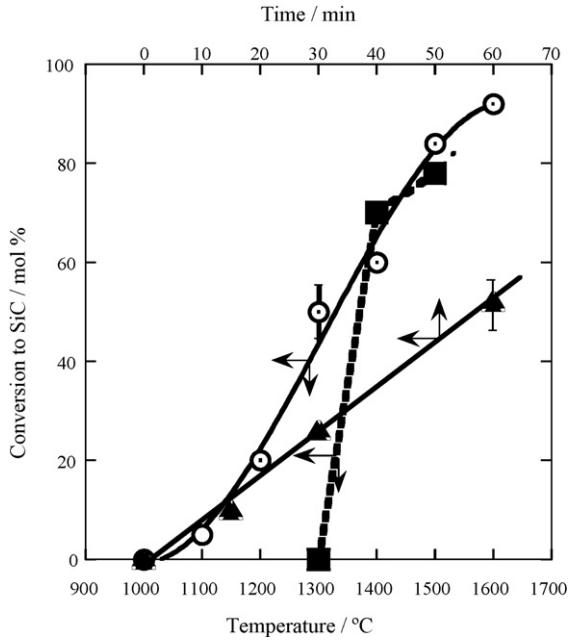


Fig. 4. Relationship between degree of conversion to SiC and temperature or time. Temperature, 1000–1600 °C for 60 min; time, 0–60 min at 1300 °C. Marks: circle and cubic, α value against temperature with and without H_2 , respectively; triangle, α value against time.

20 min in vacuum (6 kPa) under a uniaxial pressure of 40 MPa. The temperature on the graphite die surface was measured by optical pyrometer. For comparison, mechanically mixed TiC and SiC powders (99.9 wt% purity β -SiC) (Wako Pure Chem. Ind. Ltd., Japan) were also processed by SPS to obtain composite ceramics. The phases in composite powder and on the polished surfaces of the ceramics formed by SPS were identified by X-ray diffraction analysis (XRD). The powder obtained by reaction of TiC with $SiCl_4$ was observed by field emission scanning electron microscopy (FE-SEM) (JSM-35CF, JEOL Japan) and transmission electron microscopy (TEM) (JEM-2000EX, JEOL Japan) equipped with energy-dispersive X-ray analysis (EDX) for semi-quantitative determination of the elements. The microstructure of polished surfaces of composite ceramics formed by SPS was observed by SEM. The Vickers hardness (Hv) of the SiC–TiC composite ceramics was measured using a load of 1000 g for 10 s.

3. Results and discussion

3.1. Reaction of TiC with $SiCl_4$ without H_2

Fig. 3(A)–(D) shows the XRD patterns of the TiC–SiC composite powders produced by reaction of TiC grains with $SiCl_4$ vapor at 1000–1500 °C without H_2 . No reaction occurs at 1000 °C, but a very slight formation of SiC is detected at 1100 °C. The amount of SiC increases at 1300 °C and becomes predominant with only a trace of TiC at 1500 °C. As shown in

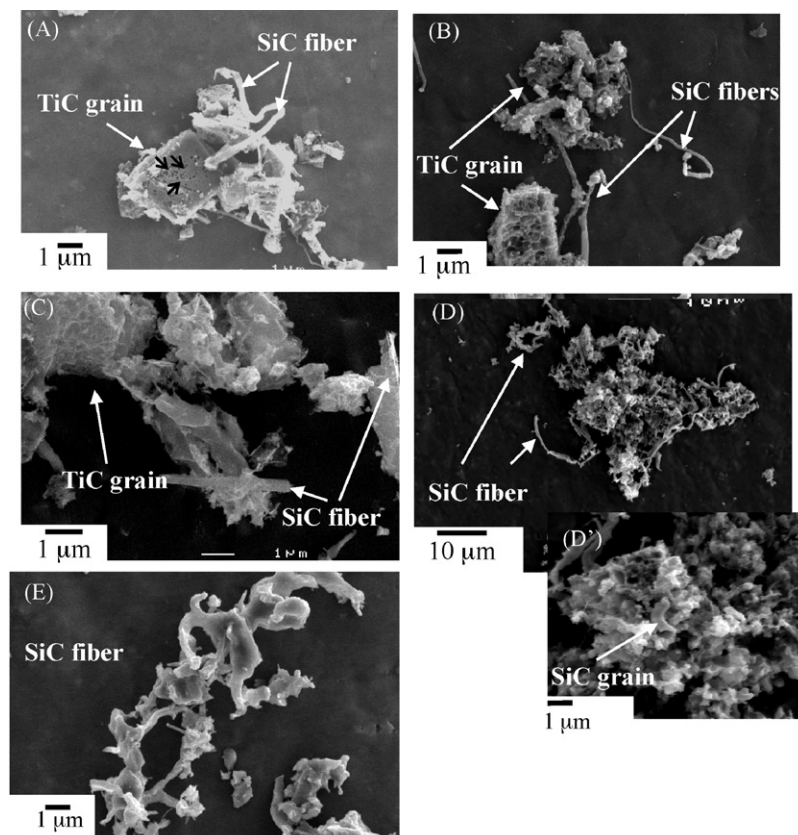


Fig. 5. SEM images of the products obtained after reaction of TiC with $SiCl_4$ without H_2 . Temperature (°C): (A) 1200, (B) 1300, (C) 1400, (D) 1500, and (E) 1600.

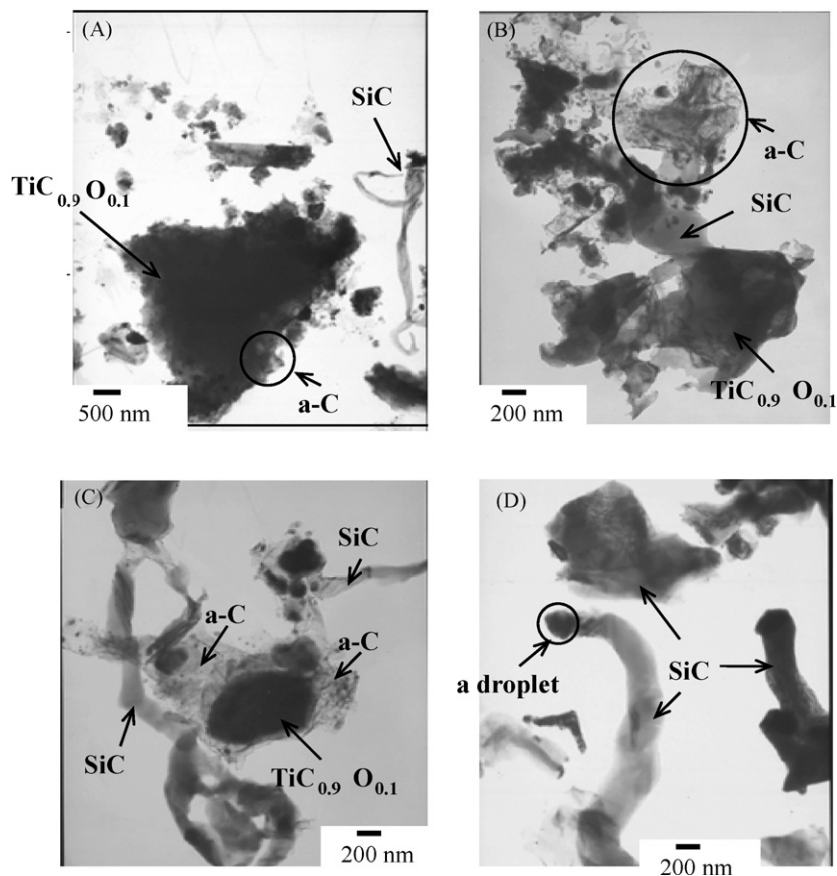


Fig. 6. TEM images of the products obtained after reaction of TiC with SiCl₄ without H₂. Temperature (°C): (A) 1200, (B) 1400, (C) 1500, and (D) 1600.

Fig. 4, the conversion to SiC was plotted as a function of temperature (1000–1600 °C) (circles) and time (0–60 min at 1300 °C) (triangles). It is found that the reaction of TiC with SiCl₄ is initiated at 1000–1100 °C, proceeds to an extent of 40–80 at 1300–1500 °C and is 92% complete at 1600 °C.

Typical SEM images of the samples obtained after the vapor–solid reaction of TiC with SiCl₄ at various temperatures are shown in Fig. 5. The TiC and SiC fibers/grains were identified by EDX. The reaction at 1200 °C (Fig. 5A) results in the appearance of corroded TiC grains containing many 0.1–0.3 μm holes (see black arrows) with SiC fibers growing from the edges of TiC grains. At 1300 °C (Fig. 5B), the TiC grains become porous or collapsed into fine grains because of severe corrosion by SiCl₄, leaving SiC grains/fibers growing from the TiC. Some discrete SiC fibers are also seen. With increasing temperature to 1400 and 1500 °C (Fig. 5C and D/D'), the TiC particles completely lost their original shape and SiC fibers or plates are formed from or on these collapsed TiC grains. At 1600 °C (Fig. 5E), the TiC granular structure has virtually disappeared, but worm-like SiC fibers 1–10 μm thick and several hundred microns long predominate.

The morphologies and compositions of the products obtained by the solid–vapor reaction at 1200–1600 °C were determined by TEM with EDX (Fig. 6). These images of the products are typical. The TiC grains reacted at 1200 °C (Fig. 6A) have the composition TiC_{0.9}O_{0.1} with the formation of amorphous carbon (a-C) (circled) on the grain edges. SiC fibers with the atomic

ratio of about 1:1 (56 at.% Si and 44 at.% C) are formed separately from the TiC. The products obtained at 1300 °C were similar to those at 1200 °C. At 1400 °C (Fig. 6B), the TiC converts to TiC_{0.9}O_{0.1}, together with plate-like SiC grains (arrowed) and film-like a-C (circled). Fibrous SiC (not seen here) was also formed. At 1500 °C (Fig. 6C), several SiC fibers stretch from the a-C film surrounding a TiC grain. At 1600 °C, the amount of fibrous and platy SiC increases, with droplets of composition 60Si, 20O, 5Ti, 5W and 5Mo wt% at fiber tips (Fig. 6D). These droplets should be formed by enrichment of W and Mo, acting as a catalyst for the formation of SiC fibers through vapor–liquid–solid process (VLS).¹⁷

3.2. Reaction of TiC with SiCl₄ and H₂

The XRD patterns obtained when H₂ was introduced into the reaction system are shown in Fig. 3(E)–(G). SiC peaks were not detected at 1300 °C, but increase greatly at 1400–1500 °C. The conversion to SiC is rapidly increased from 1300 °C, reaching 70–80% at 1400–1500 °C (cubic, Fig. 4), as in the reaction without H₂. The SEM and TEM images of the products formed at 1500 °C are shown in Fig. 7. In contrast to the reaction without H₂, blocky or platy SiC is formed with a small amount of fibers (Fig. 7A). SiC/TiC grains containing 12 Si, 34 Ti, 52 C and 2 O wt% exist close to the SiC blocky grains (Fig. 7B). SiC fibers containing a droplet (Fig. 7C) with the composition 34Si, 2Ti, 52C, 7O, 2Mo and 2W wt% grow from SiC grains. It should be

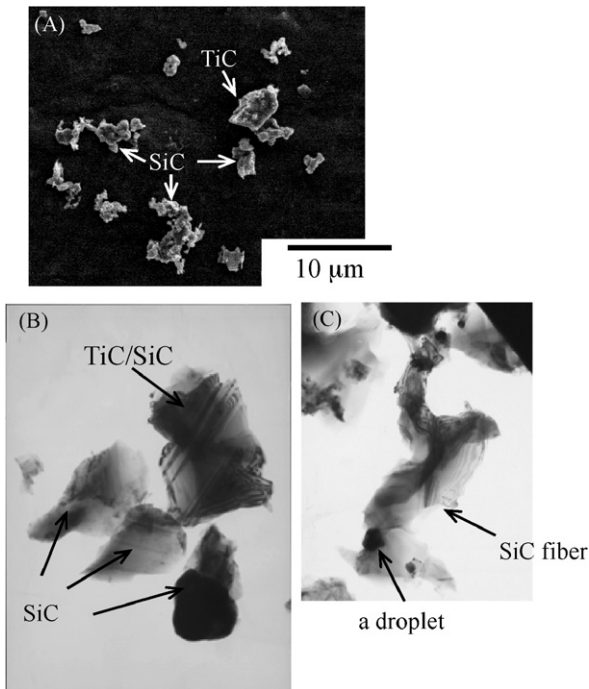


Fig. 7. SEM and TEM images of the products obtained after reaction of TiC with SiCl₄ with H₂ at 1500 °C.

noted that 2–9 at.% oxygen is always present in the SiC formed in both with and without H₂. Some SiC fibers grew from droplets containing Mo and W (1300 and 1600 °C in Figs. 6D and 7B), similarly to the reaction without H₂.

3.3. Mechanism of reaction of SiCl₄ with TiC

The time-dependency of the formation of SiC by reaction of TiC with SiCl₄ at 1300 °C for up to 60 min without H₂ (triangles, Fig. 4) clearly shows that the reaction proceeds linearly with time, suggesting that the vapor–solid reaction is controlled by the surface reaction of TiC with SiCl₄. This surface reaction aggressively attacks the TiC grains, leaving many holes on their surfaces (Fig. 5A and B), from which gaseous products emanate. It is interesting that a-C always forms on the edges of the TiC grains or their relics, accompanied by the formation of SiC fibers adjacent to the a-C (Fig. 6A–C). As mentioned above, 2–9 at.% oxygen always is present in the SiC or TiC, probably originating from the ppm trace of O₂ in the Ar as reported from supplier.

The relationships between ΔG° and temperature (T)¹⁸ for direct reactions of TiC with SiCl₄ to form a-C with SiCl_{4-x} and TiCl_x ($x=1-3$) and that of TiC with SiCl₄ to form TiCl₄ are plotted in Fig. 8, showing that these reactions are ruled out because of their positive values or near zero of ΔG° , although there is a possibility of these reactions to go forward, since TiCl_x gas ($x=1-4$) is continuously removed from the open reaction system.

To account for the existence of a-C, the reaction of TiC with SiCl₄ to form a-C requires the participation of O₂ [18]

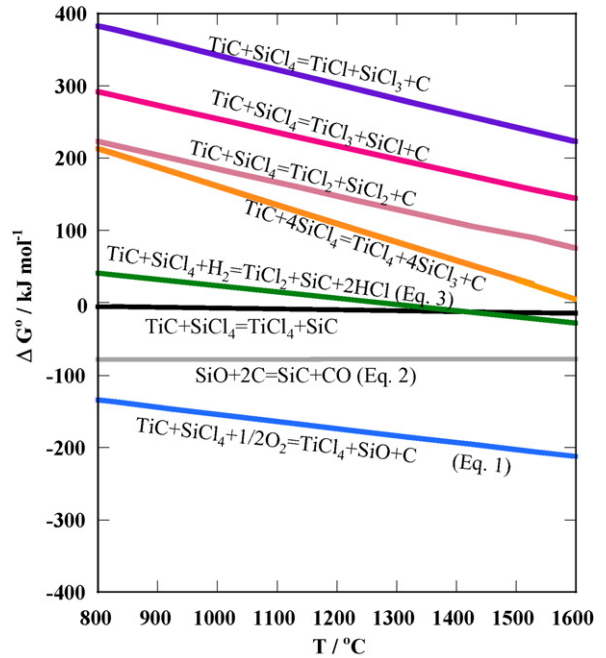
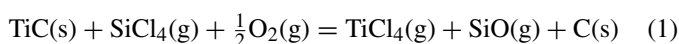


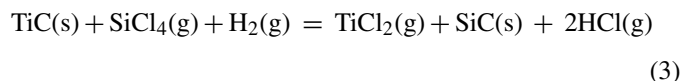
Fig. 8. ΔG° for the various possible reactions as a function of temperature.

The O₂ in Eq. (1) is probably supplied as the Ar gas impurity. The formation of a-C on oxidation of TiC at low oxygen pressures also is explained by several reports.^{19,20} Once the a-C is formed on the TiC, SiO reacts with this C, forming SiC with a negative value of ΔG



The reaction of Eq. (2) is consistent with the fact that SiC fibers grow from a-C formed, reflecting a participation of gas phase SiO, on the edges or relics of TiC grains (Fig. 6B and C).

When H₂ gas is introduced into the reaction system, the trace of O₂ in the Ar is removed and thus the reaction of Eq. (1) is suppressed. Instead, the reaction represented by Eq. (3) produces SiC in the presence of H₂



Reaction Eq. (3) is plausible, since the initial temperature of about 1400 °C for the formation of SiC in the presence of H₂ is close to 1430 °C, at which ΔG for reaction (3) becomes negative (Fig. 8).

3.4. SPS of TiC–SiC composites

Composite TiC–SiC powders with various compositions were processed by SPS at 1750 °C and 40 MPa for 20 min in vacuum. Fig. 9(A) and (B) shows the polished surfaces of their ceramics with the molar ratio TiC:SiC = 60:40 and 20:80 prepared from the powders obtained at 1300 and 1500 °C without H₂, respectively. The difference in the backscattering property of the lighter and heavier atoms shows up as gray and white regions corresponding to SiC and TiC, respectively. Table 1 lists the relative densities and Vickers hardness of these ceramics. The

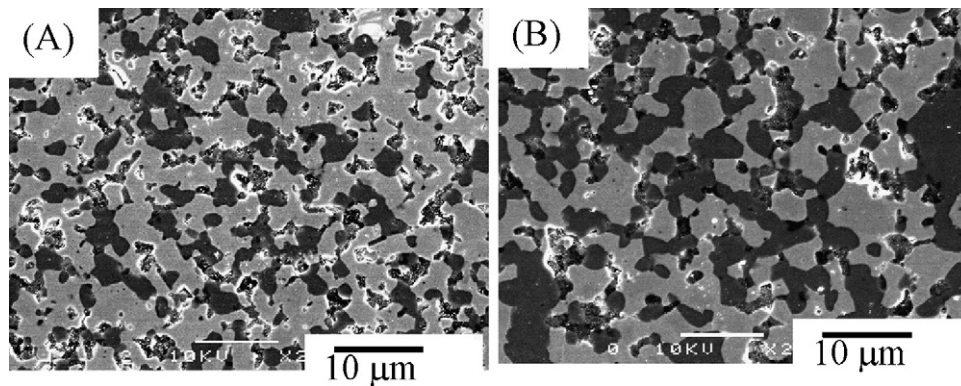


Fig. 9. SEM images of polished surfaces of TiC–SiC ceramics formed processed by SPS at 1750 °C using powders produced at (A) 1300 °C and (B) 1500 °C without H₂.

Table 1
Relative density and Vickers hardness of SPSed bodies.

TiC/SiC/mol%	Relative density/%	Hardness/Hv
60/40 ^a	96	1800
40/60 ^b	92	1700
20/80 ^c	96	2100

All samples were formed without H₂.

^a Reaction temperature of 1300 °C.

^b Reaction temperature of 1400 °C.

^c Reaction temperature of 1500 °C.

sample prepared from composite powder with TiC:SiC = 60:40 possessed a relative density of 96% and Vickers hardness of about 1800 Hv. The microstructure shows aggregated gray 2–5 μm SiC grains separated by successive white TiC layers 2–8 μm thick, with 2–5 μm surface pores. The 40:60 ceramics had a relatively low density ($\leq 92\%$) and were correspondingly less hard (about 1700 Hv). The SiC layers in these samples are continuous, with large 2–10 μm TiC grains isolated. The 20:80 composite ceramics possessed a relative density of 96% with a slightly higher hardness (2100 Hv). Compared with the Vickers hardness of TiC–SiC composite ceramics from mechanically mixed TiC/SiC powder, the hardness of the composite ceramics obtained by solid–vapor reaction is rather small, probably because of their lower relative density. It seems that the formation of fibrous SiC retards the densification of the SiC–TiC composites.

4. Conclusion

TiC–SiC composite powders with various compositions were produced by reaction of TiC grains with SiCl₄ vapor at 1000–1600 °C. In the absence of H₂, the conversion to SiC began at about 1100 °C and rapidly increased with increasing temperature to 92% conversion at 1600 °C. The TiC grains were severely attacked by SiCl₄ vapor, resulting in the formation of SiC fibers or plates together with amorphous carbon (a-C). It was inferred that the presence of a trace O₂ impurity in the Ar carrier gas contributes to the formation of SiC and a-C via the formation of SiO vapor. This mechanism is supported by the temperature dependence of ΔG° for these reactions. The presence of H₂ con-

tributes to the removal of O₂ and directly assists the formation of SiC at relatively high temperatures (>1300 °C).

The resulting TiC–SiC composite powder was densified by spark plasma sintering at 1750 °C. The microstructure consists of aggregated 2–5 μm SiC grains separated by successive TiC layers 2–8 μm thick, with 2–5 μm pores on the surface. The relative density of the ceramics ranged from 92 to 96% with Vickers hardness of 1700–2100 Hv.

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