Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 29 (2009) 2403–2409
www.elsevier.com/locate/jeurceramsoc

Reaction of TiC with $SiCl_4$ vapor with formation of SiC–TiC composites

S. Shimada *, A. Onuma

Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Received 21 August 2008; received in revised form 19 December 2008; accepted 13 January 2009
Available online 10 February 2009

Abstract

The reaction of TiC grains with $SiCl_4$ 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.

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, ZrB_2, Al_2O_3 and ZrO_2.[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 $SiCl_4$, $TiCl_4$ and hydrocarbon.[11] A French group used SiH_2Cl_2 instead of $SiCl_4$ 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

* Corresponding author. Tel.: +81 11 706 6576; fax: +81 11 706 6576.
E-mail address: shimashi@eng.hokudai.ac.jp (S. Shimada).

0955-2219/$ – see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2009.01.010

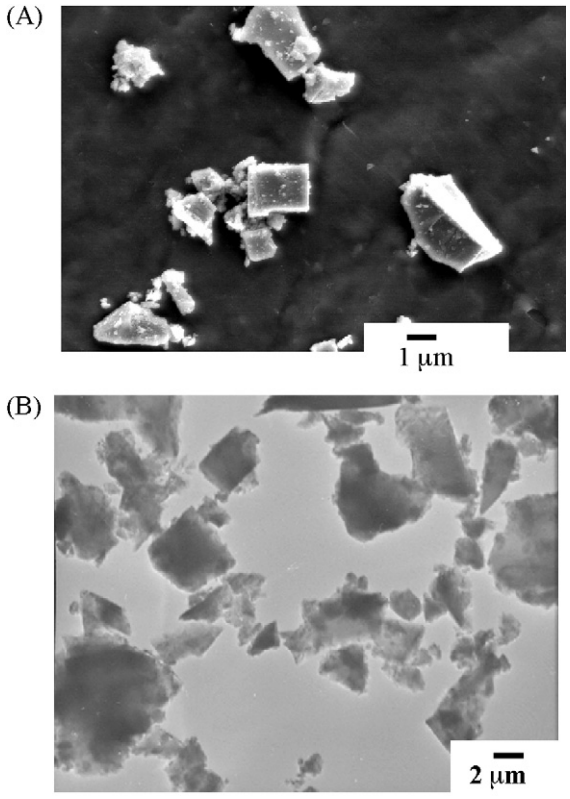

Fig. 1. SEM (A) and TEM (B) images of TiC powder.

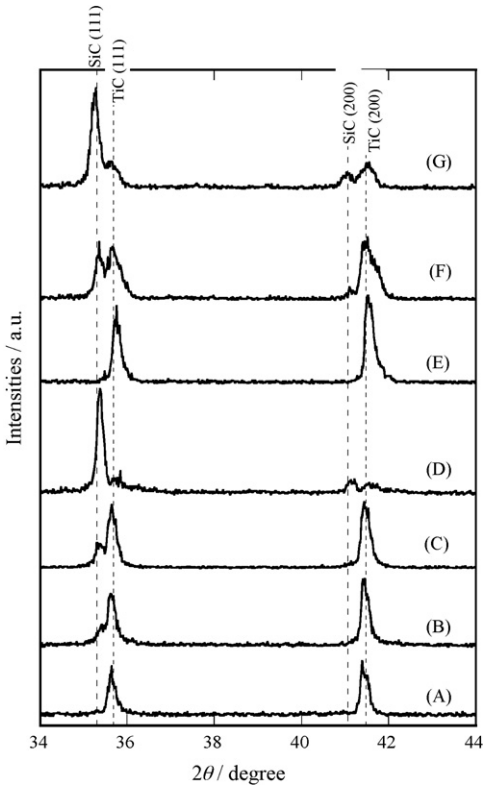

Fig. 3. XRD diffraction patterns of the products obtained after reaction of TiC with $SiCl_4$. Temperature (°C) without H_2: (A) 1000, (B) 1100, (C) 1300, and (D) 1500. Temperature (°C) with H_2: (E) 1300, (F) 1400, and (G) 1500.

reaction of TiC grains with $SiCl_4$ vapor could produce a homogeneously dispersed composite of TiC–SiC, similarly to CVD. Since the reaction of solid TiC with vapor $SiCl_4$ 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 $SiCl_4$ 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 $SiCl_4$ 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 $SiCl_4$ (99.0 vol.% purity) (Wako Pure Chem. Ind. Ltd., 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. $SiCl_4$ vapor was generated and transported by bubbling Ar through liquid $SiCl_4$ kept at 15 °C. Assuming that the vapor–liquid equilibrium of $SiCl_4$ is maintained, the $SiCl_4$ vapor pressure is estimated to be 20 kPa at 15 °C. TiC powder was placed in a graphite boat 10 cm long, over which $SiCl_4$ 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 $SiCl_4$ was carried out at 1000–1600 °C for 60 min, in some cases with the addition of 50 ml min^{-1} of flowing H_2. The time dependency of the formation of SiC was also carried out without H_2 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_{TiC}/I_{SiC}) of the four peaks against the weight ratio (W_{TiC}/W_{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 TiO_2 by oxidation in air at 600 °C and subsequent dissolution in a sulfuric acid.

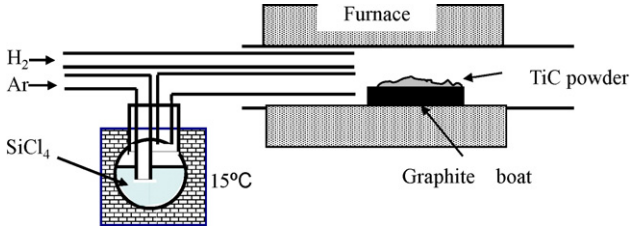

Fig. 2. Schematic representation of the experimental setup for the reaction of TiC with $SiCl_4$.

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