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Electrical and thermal properties of SiC-Zr_2CN composites sintered with Y_2O_3-Sc_2O_3 additives

Seung Hoon Jang[a], Young-Wook Kim[a,*], Kwang Joo Kim[b]

[a] Functional Ceramics Laboratory, Department of Materials Science and Engineering, The University of Seoul, Seoul 02504, Republic of Korea
[b] Department of Physics, Konkuk University, Seoul 05029, Republic of Korea

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ABSTRACT

SiC-Zr_2CN composites were fabricated from β-SiC and ZrN powders with 2 vol% equimolar Y_2O_3-Sc_2O_3 additives via conventional hot pressing at 2000 °C for 3 h in a nitrogen atmosphere. The electrical and thermal properties of the SiC-Zr_2CN composites were investigated as a function of initial ZrN content. Relative densities above 98% were obtained for all samples. The electrical conductivity of Zr_2CN composites increased continuously from 3.8×10^3 $(\Omega m)^{-1}$ to 2.3×10^5 $(\Omega m)^{-1}$ with increasing ZrN content from 0 to 35 vol%. In contrast, the thermal conductivity of the composites decreased from 200 W/mK to 81 W/mK with increasing ZrN content from 0 to 35 vol%. Typical electrical and thermal conductivity values of the SiC-Zr_2CN composites fabricated from a SiC-10 vol% ZrN mixture were 2.6×10^4 $(\Omega m)^{-1}$ and 168 W/m K, respectively.

1. Introduction

Recent papers on SiC-nitride composites show that nitrogen in metal nitrides (AlN, BN, Si_3N_4, or TiN) can be a source of N-doping in SiC grains and can increase the electrical conductivity of SiC ceramics significantly by growing N-doped SiC grains in the composites [1–5]. The addition of 2 vol% AlN into α-SiC increased the electrical conductivity from 6.3×10^{-10} Ω^{-1} cm^{-1} for monolithic SiC to 5.3×10^{-7} Ω^{-1} cm^{-1} when the composites were sintered without sintering additives in an argon atmosphere [1]. The addition of 10 vol% BN into α-SiC increased the electrical conductivity from 2.0×10^{-10} Ω^{-1} cm^{-1} for monolithic SiC to 1.1×10^{-6} Ω^{-1} cm^{-1} when the composites were sintered without sintering additives in an argon atmosphere [2]. The addition of 10 vol% Si_3N_4 into β-SiC increased the electrical conductivity from 7.7×10^{-1} Ω^{-1} cm^{-1} for monolithic SiC to 11.1 Ω^{-1} cm^{-1} when the composites were sintered at 1850 °C with 2 vol% Y_2O_3-Sc_2O_3 in a nitrogen atmosphere [3]. The addition of 10 vol% TiN into β-SiC increased the electrical conductivity from 10 Ω^{-1} cm^{-1} for monolithic SiC to 2.4×10^2 Ω^{-1} cm^{-1} when the composites were sintered at 2000 °C with 2 vol% Y_2O_3-Sc_2O_3 in a nitrogen atmosphere [4]. The addition of various nitrides into SiC has resulted in changes in electrical conductivity. The results can be understood as followings:

(1) The addition of Si_3N_4 led to higher electrical conductivity than the addition of AlN and BN because the cations of the latter materials (Al and B) formed p-type acceptors in the composites, and these acceptors compensated for N-derived donors [6,7].
(2) The difference in electrical conductivity between the SiC-AlN composites and SiC-BN composites was attributed to the difference in Al and B solubilities in the SiC lattice [8–10].
(3) The remarkable increase in electrical conductivity for the SiC-TiN composites was attributed to both the growth of N-doped SiC grains and the formation of electrically conductive Ti_2CN in the composites [4,5].

The thermal conductivity of SiC-nitride (AlN, BN, Si_3N_4) composites shows a decreasing trend with increased nitride content. Specifically, the thermal conductivity of SiC-AlN composites decreased from 104 to 35 W/mK when the AlN content was increased from 2 to 35 vol%; this was due to the increased formation of 2H solid solution in the composites [1]. The thermal conductivity of SiC-BN composites decreased from 100 to 32 W/mK when BN content was increased from 2 to 35 vol%; this was due to the formation of various defects (N_C and B_{Si} or interstitial B in the SiC lattice) caused by the dissolution of BN into the SiC lattice [2]. These defects hindered efficient phonon transport via increased phonon scattering at the defects. In both composites, the thermal conductivity of monolithic SiC (83.9 W/mK) was slightly lower than those of the composites containing 2 vol% AlN or 2 vol% BN. The lower thermal conductivity of the base-line material was due to the large

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* Corresponding author.
E-mail address: ywkim@uos.ac.kr (Y.-W. Kim).

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amount of residual porosity (18.2%), because those materials were hot-pressed without sintering additives [1,2]. The thermal conductivity of the SiC-Si_3N_4 composites decreased from 93 to 57 W/mK with increased Si_3N_4 content from 0 to 35 vol% when the composites were hot-pressed with 2 vol% Y_2O_3-Sc_2O_3 as a sintering additive [3]. The tendency for thermal conductivity to decrease with additional amounts of Si_3N_4 is due to increased phonon-grain boundary scattering in the SiC lattice, because Si_3N_4 acts as a grain growth inhibitor for SiC grains. In contrast, upon the addition of TiN into SiC, the thermal conductivity showed a maximum at 2 vol% TiN and a decreasing tendency as the TiN content was increased to 35 vol%. Specifically, the addition of 2 vol% TiN into SiC (designated as STN2) led to an increase in thermal conductivity from 200 W/mK to 224 W/mK [11]. The higher thermal conductivity of STN2 compared to monolithic SiC could be understood in light of the oxygen scavenging of TiN from the SiC lattice [11,12]. The added TiN formed Ti_2CN in the composites by reacting with SiC during sintering. The thermal conductivity of SiC-Ti_2CN composites decreased from 224 to 90 W/mK with increased TiN content from 2 to 35 vol%. This was caused by the lower thermal conductivity of Ti_2CN as compared to SiC and the decreased grain size of SiC from 4.7 to 1.9 μm, which increased phonon-grain boundary scattering in the composites [11].

Zirconium nitride (ZrN) is an important nitride ceramic with various structural and functional applications because of its unique combination of properties including high melting point, high electrical conductivity, excellent chemical stability, low neutron capture capability, and resistance to corrosion against molten iron/steel [13–17]. Thus, ZrN is a potential candidate as an inert matrix fuel for the transmutation of actinides and as accident-tolerant fuel particle coatings [16,18,19]. Silicon carbide (SiC) also has attractive properties such as high thermal conductivity, excellent mechanical properties, and resistance to heat, oxidation, corrosion, and wear [20–24]. Thus, the incorporation of electrically-conductive ZrN into N-doped semiconducting β-SiC is an area of interest. Several researchers have investigated the mechanical and electrical properties of ternary composites containing SiC and ZrN, such as Si_3N_4-SiC-ZrN [25], ZrB_2-SiC-ZrN [26–28], and $(Zr,Hf)B_2$-SiC-ZrN [26]; however, there are no reports on SiC-ZrN binary composites.

In this work, SiC-Zr_2CN composites were fabricated by hot-pressing powder mixtures consisting of SiC, ZrN, and Y_2O_3-Sc_2O_3. The Y_2O_3-Sc_2O_3 additive system was selected as a sintering additive because of its potential for high thermal conductivity. Monolithic SiC ceramics sintered with 1 vol% Y_2O_3-Sc_2O_3 showed a high thermal conductivity of 234 W/mK in a previous work [24]. The effect of initial ZrN content on the electrical and thermal properties of SiC-Zr_2CN composites was investigated.

2. Experimental procedure

Commercially available β-SiC (~0.5 μm, Grade BF-17, H.C. Starck, Berlin, Germany), ZrN (Kojundo Chemical Laboratory Co., Ltd., Sakado-shi, Japan), Y_2O_3 (99.99%, Kojundo Chemical Laboratory Co., Ltd.), and Sc_2O_3 (99.9%, Kojundo Chemical Laboratory Co., Ltd.) powders were used as the starting materials. Five batches of powder mixtures were mixed in ethanol for 24 h using SiC balls and a polypropylene jar (Table 1). The ZrN contents in the batches were 0, 4, 10, 20, and 35 vol%. The additive content was fixed at 2 vol% and the Sc_2O_3:Y_2O_3 molar ratio was 1:1 in all batches. The milled slurry was dried, sieved (60 mesh), and hot-pressed at 2000 °C for 3 h under an applied pressure of 40 MPa in a nitrogen atmosphere.

The relative densities of the hot-pressed specimens were determined using the Archimedes method. The theoretical densities of each specimen were calculated according to the rule of mixtures, as shown in Table 1. The crystalline phases of the hot-pressed specimens were analyzed via X-ray diffraction (XRD, D8 Discover, Bruker AXS GmbH, Karlsruhe, Germany) using Cu Kα radiation. The XRD data was analyzed using the Rietveld refinement method for quantitative phase analysis of the Zr_2CN phase. The hot-pressed specimens were cut, polished, and etched with CF_4 plasma containing 10% oxygen. The plasma-etched microstructures were observed with scanning electron microscopy (SEM, S4300, Hitachi Ltd., Hitachi, Japan). One (SZN35) of the samples without a conducting layer coating was analyzed via energy dispersive spectroscopy (EDS, JSM-6010PLUS/LA, JEOL, Tokyo, Japan) at 20 kV.

Hall-effect measurements were carried out on the specimens (10 mm × 10 mm × 0.5 mm) at room temperature using the van der Pauw technique to obtain electrical properties such as carrier density, carrier mobility, and electrical resistivity. An external magnetic field of 1 T was applied perpendicular to the square-shaped specimen plane in the Hall-effect measurements.

Thermal diffusivity (α) and heat capacity (C_P) were measured using the laser flash method with two different equipment: LFA 447 (NETZSCH GmbH, Selb, Germany) and LFA 467 (NETZSCH GmbH, Selb, Germany) for thermal diffusivity and heat capacity measurements, respectively. Samples (10 mm × 10 mm × 2 mm for measuring heat capacity and 10 mm × 10 mm × 3 mm for measuring thermal diffusivity) were prepared by cutting and polishing the hot-pressed specimens where the large surfaces for the samples were oriented perpendicular to the hot-pressing direction. The thermal conductivity (κ) was calculated according to the following equation,

$$\kappa = \alpha\rho C_p \tag{1}$$

where ρ is the density of the sample. The average phonon mean free path (ι) was calculated according to the following equation,

$$\iota = 3\kappa/\nu\rho C_p \tag{2}$$

where ν is the average sound velocity in the composites. The sound velocities in SiC and ZrN are 11820 m/s [29] and 7554 m/s [30] at room temperature, respectively. Since the velocity of sound in Zr_2CN is not available from the literature, the velocity of sound in ZrN was used in the calculation of the phonon mean free path. The sound velocity in the composites was calculated using a rule of mixtures; thus, the mean free path calculated here is not the exact value, but a rough approximation.

3. Results and discussion

3.1. Microstructure and phase analysis

The relative density of a monolithic SiC sample (SZN0) fabricated from a SiC-2 vol% Y_2O_3-Sc_2O_3 mixture via conventional hot-pressing is 98.9%. All of the composite samples containing ZrN can be densified to ≥98.5% when hot-pressed at 2000 °C for 3 h under 40 MPa in a nitrogen atmosphere (Table 1). This result suggests that the addition of ZrN in the 4–35 vol% range is not detrimental in the densification of SiC-Zr_2CN composites. In the monolithic SiC sample, Y_2O_3-Sc_2O_3 additives react with SiO_2, which is always located on the surface of the SiC particles, to form a Y-Sc-Si oxide melt during heating; a Y-Sc-Si oxycarbonitride (OCN) melt is formed with increasing temperature via the dissolution of SiC and nitrogen from the sintering atmosphere [24]. The Y-Sc-Si-OCN melt could enhance densification of the specimen via liquid-phase sintering. Likewise, Y_2O_3-Sc_2O_3 additives react with SiO_2 and ZrO_2, native oxide films of SiC and ZrN, respectively, to form a Y-Sc-Zr-Si oxide melt during heating in SiC-Zr_2CN composites. With increasing temperature, a Y-Sc-Zr-Si-OCN melt is formed via the dissolution of SiC, ZrN, and nitrogen from the sintering

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