Electrically and thermally conductive SiC ceramics

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Electrically and thermally conductive SiC ceramics were fabricated by hot-pressing β-SiC, 2 or 4 vol % TiN, and 2 vol % Y2O3 powder mixtures in a nitrogen atmosphere. X-ray diffraction data indicated that the specimens consisted mostly of β-SiC grains and traces of α-SiC and Ti2CN clusters. Highly-conductive Ti2CN clusters segregated between SiC grains contributed to reduce the electrical resistivity of the TiN-doped SiC specimens. The high thermal conductivity of the TiN-doped SiC specimens was attributed to the lack of solubility of Ti and V in the SiC lattice and the suppression of a massive β→α phase transformation in SiC. The electrical resistivity and thermal conductivity of the SiC with 2 vol % TiN specimen were 2.4 × 10^{-3} Ω cm and 174.1 W/m·K, respectively.

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1. Introduction

There has been a great deal of attention paid to silicon carbide (SiC) because of its unique combination of chemical, mechanical, thermal, magnetic, and electrical properties. Various industrial applications of SiC ceramics, such as substrate materials for power devices, heater and heater plates for semiconductor processing, capsule materials for nuclear fuel, mirrors for space reflecting telescopes, and gas seal rings in compressor pumps, take advantage of its excellent thermal conductivity and other properties. Most of the above applications require mechanical machining of SiC parts after sintering. Thus, thermally and electrically conductive SiC ceramics are very useful for producing SiC parts with complex shapes by electrodischarge machining. However, there have been no reports examining thermally and electrically conductive SiC ceramics.

Silicon carbide can form various crystal structures having the same chemical composition but a differing number of stacking layers in the unit cell. There is only one crystal structure with cubic symmetry, which is identified as the β-phase or 3C. At high temperature (~2000°C), β-phase transforms to α-phases with hexagonal or rhombohedral symmetry, with 4H, 6H, and 15R being the major polytypes observed in SiC ceramics.

α-SiC (mostly 6H) ceramics sintered with 2 wt % BeO showed a very high thermal conductivity (270 W/m·K) and a very high electrical resistivity (~10^{13} Ω cm). SiC ceramics sintered with 1 wt % B showed a thermal conductivity of 170 W/m·K and an electrical resistivity of 2 × 10^{10} Ω cm, whereas SiC ceramics sintered with 1 wt % Al showed a thermal resistivity of 60 W/m·K and an electrical resistivity of ~10^{12} Ω cm. The thermal conductivity and electrical resistivity of β-SiC ceramics sintered with 7 wt % Y2O3-La2O3 were 165 W/m·K and 3.4 Ω cm, respectively.

Voit et al. reported a thermal conductivity with a range of 55–70 W/m·K and an electrical resistivity with a range of 10^{10}–10^{12} Ω cm in α-SiC ceramics sintered with 10 vol % Al2O3–Y2O3 using packing powder containing VS2. Zhan et al. reported a thermal conductivity of 47 W/m·K and an electrical resistivity of 1.1 × 10^{15} Ω cm in β-SiC ceramics sintered with 10 wt % Y–Al–Si oxyinitride glass. Recently, electrically-conductive β-SiC ceramics have been developed by doping nitrogen into a SiC lattice. However, their thermal conductivity has not been reported. Thus, the reported thermal conductivity and electrical resistivity were 47–270 W/m·K and 10^{9}–10^{14} Ω cm, respectively. The electrical resistivity of ~10^{10} Ω cm is too high to be machined by conventional electrical discharge machining.

Recently, the addition of 1 vol % TiN in β-SiC containing 2 vol % Y2O3 led to a decrease in electrical resistivity and an increase in thermal conductivity of SiC ceramics. The thermal conductivity and electrical resistivity of the SiC ceramic sintered with 2 vol % Y2O3 and 1 vol % TiN were 211 W/m·K and 1.6 × 10^{-2} Ω cm, respectively. Thus, the further addition of TiN into SiC ceramics containing 2 vol % Y2O3 would be of interest.

The objective of this research is to investigate the thermal and electrical conductivities of SiC ceramics containing 2 vol % Y2O3 and 2 or 4 vol % TiN.

2. Experimental

In order to prepare SiC specimens, β-SiC (~0.5 μm, 3C polytype, BF-17, H. C. Starck, Berlin, Germany), TiN (~1.0 μm, Grade C, H. C. Starck, Berlin, Germany), and Y2O3 (99.99%, Kojundo Chemical Laboratory Co., Ltd., Sakado-shi, Japan) powders were mixed by ball milling using SiC media in a polypropylene jar for 24 h in ethanol. Two specimens containing 2 vol % (STN2) or 4 vol % TiN (STN4) were prepared while the Y2O3 additive content was fixed at 2 vol % in both specimens (Table 1).

The milled slurry was dried, sieved, and hot-pressed at 2000°C for 3 h under 40 MPa in an atmospheric pressure of N2 gas.

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. The hot-pressed specimens were polished and etched with CF4 plasma containing 10% oxygen. The etched microstructure was observed by scanning electron microscopy (SEM, S4300, Hitachi Ltd., Hitachi, Japan).

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Hall-effect measurements were performed on the specimens (10 × 10 × 1 mm) at room temperature using the van der Pauw technique to obtain the electrical resistivity, carrier density, and carrier mobility. The external magnetic field applied perpendicular to the square-shaped sample plane was 1 T.

Thermal diffusivity was measured using the laser flash method. Differential scanning calorimetry (DSC, Model Q200, TA Instrument, Inc., New Castle, DE) and thermal diffusivity measurement equipment (Model LFA 447, NETZSCH GmbH, Selb, Germany) were used for the heat capacity (C_p) and thermal diffusivity (α) measurements, respectively. The specimens (2.84 × 2.84 × 1 mm for measuring the heat capacity and 10 × 10 × 4 mm for measuring the thermal diffusivity) were obtained by cutting from hot-pressed ingots followed by polishing, with the large surfaces of the specimens oriented perpendicular to the hot-pressing direction. The α and C_p values were measured five times each at room temperature, and the average values were used to calculate the thermal conductivity (κ) from the equation,

$$\kappa = \alpha d C_p$$  \hspace{1cm} (1)

where d is the density of the specimen. The average phonon mean-free path L was estimated from the equation,

$$L = \frac{3\kappa}{C_p \nu}$$  \hspace{1cm} (2)

where ν is the average sound velocity at all temperatures.\(^{21}\)

3. Results and discussion

Both specimens were nearly fully densified without appreciable porosity (99.9% theoretical density) by conventional hot pressing at 2000°C for 3 h under an applied pressure of 40 MPa in flowing nitrogen. During hot pressing of the specimens, the Y_2O_3 additive reacts with SiO_2 and TiO_2, native oxides in SiC and TiN particles, respectively. The reaction forms a Y–Ti–Si oxide melt. With increasing temperature, a Y–Ti–Si oxycarbonitride melt is produced by the dissolution of SiC and nitrogen from the atmosphere.\(^{4,22}\)

The XRD patterns of the specimens are shown in Fig. 1. Both specimens revealed characteristic peaks for 3C-SiC (JCPDS 29-1129) marked by squares, 6H-SiC (JCPDS 72-4531) marked by diamonds, and Ti_3CN (JCPDS 71-6059) marked by triangles. Thus, the XRD patterns of the TiN-doped SiC specimens indicated that TiN particles transform to Ti_3CN clusters during the sintering process by combining with carbon atoms from neighboring β-SiC particles. A possible reaction for the in situ formation of Ti_3CN was suggested in a previous work.\(^{22}\)

\[4\text{TiN} + 2\text{SiC} \rightarrow 2\text{Ti}_2\text{CN} + \text{Si}_{\text{liquid}} + \text{N}_2(\text{gas})\]  \hspace{1cm} (3)

Both the liquid Si and gaseous N\(_2\) in the above reaction are soluble in the liquid phase, Y–Ti–Si oxycarbonitride, during hot pressing. The possibility of the precipitation of the Ti_3CN phase from the Y–Ti–Si oxycarbonitride melt during hot pressing was also suggested in a previous paper.\(^{22}\)

Figure 2 shows typical microstructures of the STN2 and STN4 specimens. The microstructures consisted of equiaxed SiC grains (dark grey grains) and equiaxed or irregular shaped Ti_3CN grains (light grey grains). Most of the Ti_3CN grains were located on grain boundaries or multigrain junctions. The white junction phase in Fig. 2 was a residual liquid-phase after sintering.

The SiC specimens containing Ti_3CN were n-type semiconductors. The electrical resistivity, carrier density, and carrier mobility obtained by Hall measurements were 2.4 × 10^{-17} Ω·cm, 2.7 × 10^{20} cm^{-3}, and 9.4 cm²/V·s for STN2 and 1.8 × 10^{-14} Ω·cm, 1.2 × 10^{20} cm^{-3}, and 2.9 × 10^{12} cm²/V·s for STN4, respectively (Table 2). The donors in the SiC specimens are created by N substitution of C sites (N_2) in the zincblende SiC lattice, and are known to have a binding energy of ~60 meV.\(^{23}\)

The smaller resistivity of STN4 is due to the larger carrier mobility. The observed mobility enhancement in STN4 is attributed to the increase in density of the conductive Ti_3CN clusters. In a previous study,\(^{20}\) the electrical resistivity, carrier density, and carrier mobility of a base-line material (SiC sintered with 2 vol % Y_2O_3 and no TiN addition) were reported as 1.3 × 10^{-17} Ω·cm,
The thermal conductivities of SiC ceramics sintered with 10 vol% Al2O3 using a packing powder containing VSi2 and SiC ceramics sintered with 10 wt% Y2O3−SiO2 glass during sintering, which stabilizes the massive transformation leads to more phonon scattering at phases in SiC (Fig. 1). The occurrence of the massive phase transformation leads to more phonon scattering at α/β interfaces, resulting in decreased thermal conductivity. In the present specimens, the massive phase transformation was suppressed because of the formation of Y−Ti−Si oxycarbonitride glass during sintering, which stabilizes β-SiC. Recently, a thermal conductivity of 234 W/m·K was reported in SiC ceramics sintered with 10 vol% Y2O3−Sc2O3. However, its electrical resistivity was not reported. The thermal conductivity values of the present specimens (174.1 W/m·K for STN2 and 161.5 W/m·K for STN4) are comparable to that of SiC ceramics sintered with 7 wt% Y2O3−La2O3 (165 W/m·K). However, electrical resistivities (~10−3−10−4 Ω cm) of the STN2 and STN4 specimens were three or four orders of magnitude lower than that (~10−6 Ω cm) of SiC ceramics sintered with 7 wt% Y2O3−La2O3.  

Figure 3 shows the variation of electrical resistivity and thermal conductivity as a function of TiN content in the starting composition. The base-line properties (SiC sintered with 2 vol% Y2O3 and no TiN addition) were obtained from a previous paper. The addition of 2 or 4 vol% TiN in SiC with 2 vol% Y2O3 significantly decreased the electrical resistivity (10−2 or 10−3 times). The thermal conductivity also decreased gradually with increasing TiN content. This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Korea Government (MSIP) (2012R1A2A2A01004284).

4. Conclusions

Electrically and thermally conductive SiC ceramics were fabricated by sintering β-SiC containing TiN (2 and 4 vol%) and 2 vol% Y2O3 by conventional hot pressing at 2000°C for 3 h in a nitrogen atmosphere. X-ray diffraction data indicate that the specimens consist mostly of β-SiC grains and traces of α-SiC and Ti2CN clusters. The electrical resistivity and thermal conductivity of the SiC with 2 vol% TiN specimen were 2.4 × 10−3 Ω·cm and 174.1 W/m·K, respectively. In contrast, those of the SiC with 4 vol% TiN specimen were 1.8 × 10−4 Ω·cm and 161.5 W/m·K, respectively. High-conductive Ti2CN clusters segregated between the SiC grains contribute to reduce the resistivity of the SiC specimens. Alternatively, the thermal conductivity of the SiC specimens showed a decreasing trend with increasing TiN content. The inter-grain Ti2CN clusters are likely to prevent further improvements in the thermal conductivity. The relatively high thermal conductivity of SiC containing TiN is attributed to the lack of solubility of Ti and Y in the SiC lattice and the suppression of a massive β→α phase transformation in SiC.

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References

1) L. S. Sigl, J. Eur. Ceram. Soc., 23, 1115–1122 (2003).
2) K. Krnel, D. Sciti and A. Bellosi, J. Eur. Ceram. Soc., 23,
3135–3146 (2003).

3) Y. Zhou, K. Hirao, Y. Yamauchi and S. Kanzaki, J. Mater. Res., 18, 1854–1862 (2003).

4) Y.-W. Kim, S.-H. Lee, T. Nishimura and M. Mitomo, Acta Mater., 53, 4701–4708 (2005).

5) Y. Hirata, N. Suzue, N. Matsunaga and S. Sameshima, J. Eur. Ceram. Soc., 30, 1945–1954 (2010).

6) M. Hotta, H. Kita and J. Hojo, J. Ceram. Soc. Japan, 119, 129–132 (2011).

7) Y.-W. Kim, K. J. Kim, H. C. Kim, N.-H. Cho and K.-Y. Lim, J. Am. Ceram. Soc., 94, 991–993 (2011).

8) F. Frajkorova, M. Hnatko, Z. Lences and P. Sajgalik, J. Eur. Ceram. Soc., 32, 2513–2518 (2012).

9) A. L. Ortiz, O. Borrero-Lopez, M. Z. Quadir and F. Guiberteau, J. Eur. Ceram. Soc., 32, 965–973 (2012).

10) K. J. Kim and Y.-W. Kim, J. Eur. Ceram. Soc., 32, 1149–1155 (2012).

11) U. Sydow, K. Sempf, M. Herrmann, M. Schneider, H.-J. Kleebe and A. Michaelis, Mater. Corrosion, 64, 218–224 (2013).

12) M. Fukushima, J. Ceram. Soc. Japan, 121, 162–168 (2013).

13) M. Herrmann, K. Sempf, M. Schneider, U. Sydow, K. Kremmer and A. Michaelis, J. Eur. Ceram. Soc., 34, 229–235 (2014).

14) Y.-W. Kim, K.-Y. Lim and W. S. Seo, J. Am. Ceram. Soc., 97, 923–928 (2014).

15) Y. Takeda, Ceram. Bull., 67, 1961–1963 (1988).

16) Y. Takeda, K. Nakamura, K. Maeda and Y. Matsushita, J. Am. Ceram. Soc., 70, C-266–C-267 (1987).

17) G. D. Zhan, M. Mitomo, R. J. Xie and A. K. Mukherjee, J. Am. Ceram. Soc., 84, 2448–2450 (2001).

18) E. Volz, A. Roosen, W. Hartung and A. Winnacker, J. Eur. Ceram. Soc., 21, 2089–2093 (2001).

19) G. D. Zhan, M. Mitomo and A. K. Mukherjee, J. Mater. Res., 17, 2327–2333 (2002).

20) K. J. Kim, K.-Y. Lim and Y.-W. Kim, J. Am. Ceram. Soc., 97, 2943–2949 (2014).

21) K. Watari, H. Nakano, K. Sato, K. Urabe, K. Ishizaki, S. Cao and K. Mori, J. Am. Ceram. Soc., 86, 1812–1814 (2003).

22) K. J. Kim, J. M. Kim and Y.-W. Kim, J. Eur. Ceram. Soc., 34, 1149–1154 (2014).

23) K. J. Kim, K.-Y. Lim and Y.-W. Kim, J. Am. Ceram. Soc., 96, 3463–3469 (2013).