The Development of an Electroconductive SiC-ZrB₂ Composite through Spark Plasma Sintering under Argon Atmosphere

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Abstract – The SiC-ZrB₂ composites were fabricated by combining 30, 35, 40, 45 and 50 vol. % of zirconium diboride (ZrB₂) powders with silicon carbide (SiC) matrix. The SiC-ZrB₂ composites and the sintered compacts were produced through spark plasma sintering (SPS) under argon atmosphere, and its physical, electrical, and mechanical properties were examined. Also, the thermal image analysis of the SiC-ZrB₂ composites was examined. Reactions between β -SiC and ZrB₂ were not observed via x-ray diffraction (XRD) analysis. The apparent porosity of the SiC+30vol.%ZrB₂, SiC+35vol.%ZrB₂, SiC+40vol.%ZrB₂, SiC+45vol.%ZrB₂ and SiC+50vol.%ZrB₂ composites were 7.2546, 0.8920, 0.6038, 1.0981, and 10.0108%, respectively. The XRD phase analysis of the sintered compacts demonstrated a high phase of SiC and ZrB₂. Among the SiC+ZrB₂ composites, the SiC+50vol. %ZrB₂ composite had the lowest flexural strength, 290.54MPa, the other composites had more than 980MPa flexural strength except the SiC+30vol.%ZrB₂ composite; the SiC+40vol.%ZrB₂ composite had the highest flexural strength, 1011.34MPa, at room temperature. The electrical properties of the SiC-ZrB₂ composites had positive temperature coefficient resistance (PTCR). The V-I characteristics of the SiC-ZrB₂ composites had a linear shape in the temperature range from room to 500°C. The electrical resistivities of the SiC+30vol.%ZrB₂, SiC+35vol.%ZrB₂, SiC+40vol.%ZrB₂, SiC+45vol.%ZrB₂ and SiC+50vol.%ZrB₂ composites were 4.573×10^{-3} , 1.554×10^{-3} , 9.365×10^{-4} , 6.999×10^{-4} , and $6.069 \times 10^{-4} \Omega \cdot \text{cm}$, respectively, at room temperature, and their resistance temperature coefficients were 1.896×10^{-3} , 3.064×10^{-3} , 3.169×10^{-3} , 3.097×10^{-3} , and $3.418 \times 10^{-3} / ^\circ\text{C}$ in the temperature range from room to 500°C, respectively. Therefore, it is considered that among the sintered compacts the SiC+35vol.%ZrB₂, SiC+40vol.%ZrB₂ and SiC+45vol.%ZrB₂ composites containing the most outstanding mechanical properties as well as PTCR and V-I characteristics can be used as an energy friendly ceramic heater or ohmic-contact electrode material through SPS.

Keywords: Spark Plasma Sintering (SPS), Positive Temperature Coefficient Resistance (PTCR), V-I characteristics, Thermal image, Energy friendly ceramic heater, Ohmic-contact electrode material

1. Introduction

SiC, with its high melting point of 2,800°C, is a thermodynamically stable IV-IV-compound semiconductor. In addition, based on its specific features, low thermal expansion coefficient, approximately $4.36 \times 10^{-6} / ^\circ\text{C}$ at 20-1,000°C, heating-conductivity, thermal impact resistivity, strength, and oxidation-resistance, SiC is considered an outstanding semiconductor [1]. However, due to the low efficiency of its diffusion caused by the strong covalent bond between Si and C, without sinter additives, it is difficult to obtain sinter density. Also, below 1,000°C, the electrical resistivity of SiC is considered as negative temperature coefficient resistance (hereafter, NTCR), which causes increases in its temperature and uncontrollable electrical current in it, re-

sulting in its overheating [2]-[3].

A transition metal boride, ZrB₂, from crystallography of view, the hexagonal closed packed (hereafter, HCP) crystal structure of the AlB₂ type, is composed of an alternating sequence of MBMBMB like metal atoms and graphite-like boron. In this kind of structure, there are strong covalent bonds between boron-boron and metal-boron atoms as well as distinctive bonds containing characteristics of metallic bonds. The strong covalent bond leads its high melting temperature, 3250°C, high hardness, 23GPa, and high strength, 500MPa. And the metallic bond leads its low electrical resistivity, $10^{-5} \Omega \cdot \text{cm}$ and high thermal conductivity, 60W/mK [4]. Hence, with the combination of SiC and ZrB₂, a SiC-ZrB₂ composite containing high electrical conductivity, superior oxidation resistance, and high mechanical strength, which can be used as a conduction material or ohmic-contact electrode at high and low temperature, can be obtained.

In general, a SiC ceramic has been produced via hot press (hereafter, HP), a solid-state sintering process, at approximately 1,950 ~ 2,100°C. And in order to lower HP's temperature below 1,950°C, the production method of the

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Received: February 26, 2010; Accepted: April 27, 2010

liquid-phase sintering process such as $\text{Al}_2\text{O}_3+\text{Y}_2\text{O}_3$ has been employed [5]-[7].

Compared to HP, SPS helps the surface of the molecular particle to access easier activation with the clarification of its surface. In addition, with high speed diffusion, highly efficient heating, fast sintering transformation, and the supply of high energy density, a high quality sintered compact at low temperature within a short time period can be obtained. Moreover, for various sintered compact materials such as metal and ceramics, it is possible to sinter them in a wide range of temperature and pressure, and it is also convenient to control a sintered microstructure with no grain growth through SPS. Although HP is similar to SPS, significant differences of SPS from HP are that electric field is applied to both upper and lower electrodes, and materials are sintered within powders by direct heating only through SPS [8]-[10]. However, according to many experimental studies, the density parameter of sintered compacts is still unclear, which results in a limitation in systematic examinations [11]-[12].

In this experiment, SPS under argon atmosphere was employed to obtain a ceramic composite of SiC-ZrB_2 , a quick sintered and high density sintered compact at 1,500, 450~600°C lower than HP's. In addition, in order to analyze the mechanical, electrical and thermal properties of the SiC-ZrB_2 composite through SPS under argon atmosphere, XRD, relative density, field emission scanning electron microscope (hereafter, FE-SEM), energy dispersive spectroscopy (hereafter, EDS), flexural strength, thermal image, V-1 characteristic, and the electrical resistivity of the SiC-ZrB_2 composite were examined. Based on these examinations, the SiC-ZrB_2 composite was diagnosed to determine whether it is useful as an energy friendly ceramic heater or ohmic-contact electrode material.

2. Experimental Procedure

2.1 Powder Preparation

In this experiment, high-pure $\beta\text{-SiC}$ (H. C. Starck, Germany, Grade BF12) and ZrB_2 (H. C. Starck, Germany, Grade B) were used as the starting materials. $\beta\text{-SiC}$ and ZrB_2 were combined with the ratio of 70:30, 65:35, 60:40, 55:45, and 50:50 vol.%, and then were designated as SZ30, SZ35, SZ40, SZ45 and SZ50 in that order. These designated materials were combined with distilled water within the polyurethane bowl (volume: 1583.4ml) containing acetone (approximately 500 ml). They were then applied to the planetary-ball-mill process with the two high purity SiC balls (10mm Φ , 20mm Φ) with 1:5 ratio of the number of SiC balls for 24 hours. After that, they were completely dehydrated for 12 hours at 100°C, and then the completely dehydrated materials, powders, were sieved by using a 60mesh screen.

2.2 Sintering Process

After the dried powders were put in a graphite die of 15mm Φ inner diameter, enclosed with graphite foil, they were sintered using a Dr. Sinter SPS-515S apparatus (Sumitomo Coal Mining Co. Ltd., Tokyo, Japan) under the following conditions: 1,500°C, argon atmosphere and the uniaxial pressure of 50 MPa. The sintering conditions were: (i) the powders were heated at high speed with 100°C/min up to the final sintering temperature of 1,500°C for 5 minutes; (ii) a pressure of 50 MPa was constantly applied during the entire experiment; (iii) the on/off pulse sequence was 12:2 (one pulse time: 2.78ms), and after the sintering process was completed, the pressure was released, and then the electrical current was shut off. The final specimen of the SiC-ZrB_2 composites was approximately 15 mm in diameter and 5 mm in thickness.

2.3 Physical Characteristics Measurement

The theoretical densities of the SiC-ZrB_2 composites were calculated based on the rule of mixture (3.217g/cm³ for $\beta\text{-SiC}$, 6.085g/cm³ for ZrB_2), and the apparent densities of each SiC-ZrB_2 composite was measured 10 times based on the Archimedes method.

After graphite was burnt out by maintaining the sintered SiC-ZrB_2 composites at 900°C for 5 minutes, the external surface of it was analyzed by XPS (K-Alpha ESKA SYSTEM, Thermo Electron Corp, England), EDS (S-4800, horiba, Japan), XRD (X'Pert PRO MRD, PANalytical B.V., Nederland) with $\text{CuK}\alpha$ radiation, phase identification. The microstructures of an external surface, cross-sectional layer, and fracture surface tested by flexural strength were observed through FE-SEM (S-4800, Hitachi, Japan).

The final SiC-ZrB_2 composites, the sintered compacts, were ground by a diamond wheel, and the disks were machined to produce approximately 1.0-0.7-10 mm³ dimension bars. The surfaces of the bars were then polished using 1 μm diamond paste and were beveled at 45 degrees for mechanical testing (ASTM F394-78). The three-point flexural strength of each sintered compact was measured 5~6 times at room temperature using a material test apparatus (Instron, Model 4204, USA) under the following conditions: 10 mm outer span, 8 mm inner span, and 0.07 mm/min cross head speed. The sintered compacts were cut using wire-EDM (Electrical Discharge Machining, Genspark 340, Taiwan) in order to produce specimens eventually to measure their electrical resistivity.

The electrical resistivity of each specimen processed with EDM by Genspark 340 was measured 200 times between room to 500°C based on the Pauw method [13]; the V-1 characteristics of them naturally appeared. Lastly, 5 spots were randomly pointed on each specimen, and they were measured using the thermal image camera (TVS-100E, Nipon Avionics Co. Ltd., Japan). Fig. 1 shows the shape and dimension of specimen, and circuit diagram to measure the thermal image.

Fig. 1. Shape and dimension of specimen (a), and circuit diagram to measure the thermal image (b).

3. Experimental Results and Discussion

3.1 Apparent Density

As shown in Fig. 2, an addition of ZrB₂ increased by 30, 35, 40, 45, and 50 vol.% to which corresponding theory densities were 4.0774, 4.2208, 4.3642, 4.5076, and 4.6510 g/cm³, respectively, according to the rule of mixture, and experimental apparent densities were 3.7816, 4.1831, 4.3379, 4.4581, and 4.1854 g/cm³, respectively. Because the obtained apparent densities of SZ35, SZ40, and SZ45 were closed to the theory density, their densifications were well established. Among them, the densification of SZ40 was established the best because it demonstrates the smallest apparent porosity, 0.6038%.

Table 1 demonstrated a mass and volume variation of before and after sintering the SiC-ZrB₂ composites. The symbols ▼ and ▲ shown in Table 1 illustrate decreases and increases, respectively, after sintering the SiC-ZrB₂

composites. In the case of the specimen, SZ30, after sintering the SiC-ZrB₂ composites, as its mass variation decreased at the same time its volume variation significantly increased. This result is considered that under argon atmosphere, although the SiC-ZrB₂ composites have been sintered, SiC always contains SiO₂ and SZ30 contains the greatest amount of SiC, 70%. This resulted in a specific sintering process caused by electrical discharge. According to Eqs. 2 and 4 in Table 2 [14]-[15], through the specific sintering process, SiO₂ amorphous glass phase and porosity have formed, which may cause high apparent porosity. Moreover, due to the fact the remaining vol.% of SiC that always contains SiO₂ decreases as the addition of ZrB₂ increases, a mass variation decreases according to Eqs. 2 and 4 in Table 2. A mass variation of SZ50 decreased the least, whereas its volume variation increased the most, which results in the highest apparent porosity, 10.0108%. Although an oxidation degree of SiC and ZrB₂ dependent on temperature in the air for 5 minute burn-out at 900 °C has not been clarified, due to the fact ZrB₂ is easily oxidized in the air, leading to the formation of vapor species, it is considered that the layer of SiO₂ became higher.

Table 1. Mass and volume variation of before and after sintering SiC-ZrB₂ composites

Specimen	mass before sintering[g]	mass after sintering[g]	mass variation[%]	volume before sintering[cm ³]	volume after sintering[cm ³]	volume variation[%]
SZ30	3.6028	3.482	▼ 3.3529	0.8836	0.921	▲ 4.2100
SZ35	3.7295	3.605	▼ 3.3382	0.8836	0.862	▼ 2.4731
SZ40	3.8562	3.735	▼ 3.1430	0.8836	0.861	▼ 2.5547
SZ45	3.9829	3.861	▼ 3.0606	0.8836	0.866	▼ 1.9955
SZ50	4.1096	4.050	▼ 1.4503	0.8836	0.968	▲ 9.4989

Fig. 2. Density and apparent porosity of SiC-ZrB₂ composite.

Table 2. Reaction equations

Number of equation	Reaction Equations
1	$ZrB_2 + SiC + 4O_2(g) \rightarrow ZrO_2(s) + B_2O_3(g) + SiO_2(g) + CO(g)$
2	$SiC + \frac{3}{2}O_2 = SiO_2(s,l) + CO(g)$
3	$ZrB_2 + \frac{5}{2}O_2 = ZrO_2(s) + B_2O_3(l)$
4	$SiO_2 + CO = SiO(g) + CO_2(g)$
5	$B_2O_3(l) = B_2O_3(g)$

3.1 Phase Analysis and Microstructure

As shown in Table 3, Si, C and O atoms in an external surface layer of all specimens of the SiC-ZrB₂ composites were obtained. In order to analyze atoms bonds, the external surface of the SiC-ZrB₂ composites was examined through x-ray photoelectron spectroscopy (XPS). As a result, equal to the analysis of energy dispersive spectroscopy (EDS), Si, C and O atoms were obtained from all the specimens shown in Fig. 3; Si 2p peak is considered SiO₂ and C 1s peak is considered graphite. It is considered that graphite was obtained because it has not completely removed although it was burnt out for 5 minutes at 900 °C. In addition, it is considered amorphous phase has been formed in the external surface layer when sintering the SiC-ZrB₂ composites because SiC always contains SiO₂.

Table 3. EDS analysis of an external surfaces of the SiC-ZrB₂ composites

Specimen atom	SZ30	SZ35	SZ40	SZ45	SZ50	Remarks
Si	53.75	47.36	40.38	43.69	32.51	atom%
C	36.57	47.43	44.44	45.70	25.82	
O	9.67	5.21	15.18	10.61	41.66	
Total	100.00	100.00	100.00	100.00	100.00

Fig. 3. X-ray photoelectron spectroscopy of an external surfaces of the SiC-ZrB₂ composites.

SEM pictures of an external surface and fracture surface tested through a flexural strength experiment of specimens are shown in Fig. 4. SZ30 and SZ50 contained the greatest porosity in its both external and fracture surfaces. Although it is difficult to observe porosity in an external surface of other specimens SZ35, SZ40 and SZ45, in their fracture surfaces, their porosity follows the aspect of apparent porosity shown in Fig. 2.

The analysis result of the SiC-ZrB₂ composites through XRD is shown in Fig. 5. All peak values appear on an International Centre for Diffraction Data (ICDD) card and code numbers, 01-089-3843 (SiC), 01-089-2223 (SiC), and 01-075-1050 (ZrB₂). Although SiO₂ and graphite phases were observed at an external surface of the SiC-ZrB₂ composites via EDS and XPS analyses, only SiC and ZrB₂ phases were observed via XRD analysis. Due to different properties of analysis apparatuses, thickness is measured in μm

Fig. 4. FE-SEM of a fracture surface of the SiC-ZrB₂ composites.

Fig. 5. X-ray diffraction of an external surface of the SiC-ZrB₂ composites.

via XRD but it is measured in nm via XPS, the oxidized thickness by SiO₂ is considered to be in nm. The SEM pictures of a cross-sectional surface of the SiC-ZrB₂ composites were taken with 400 magnifications shown in Fig. 6 because it is difficult to distinguish the difference between external surface layers with cross-sectional surface layers with higher magnification. Therefore, it is considered the thickness of oxidation layers would be formed in nm.

Fig. 6 illustrated a disk-like specimen cut by 2 mm at a right angle to the external surface; internal layers of an external surface were pictured by SEM and then EDS mapping was performed on that same part. Si, C, Zr, B and O atoms can be obtained through EDS mapping but in this study oxidation condition was examined only with Si, Zr and O atoms, because it is difficult to obtain an exact value

Fig. 6. FE-SEM (i) of a cross-sectional layer and EDS maps showing the distribution of (ii) Si, (iii) Zr and (iv) O of an external surface layer of the SiC-ZrB₂ composites.

for B and C atoms due to low sensitivity of EDS to light atoms like B and C [16]-[17]. As shown in the EDS map, layers have formed only for Si and Zr but not for O.

3.3 Mechanical Properties

As shown in Fig. 7, the flexural strengths of the SiC-ZrB₂ composites, 290.54~1011.34MPa, at room temperature were twice as high as the flexural strength of SiC or ZrB₂ single crystal without porosity, 350~500 MPa and 512~618 MPa, respectively, except SZ30 and SZ50 [18]-[19]. In general, the flexural strength is closely related to the grain growth of annealed ceramic. In addition, as the ceramic microstructure becomes a coarse phase-shaped ceramic microstructure through ceramic annealing, the fracture toughness of the ceramic microstructure increases, but its flexural strength decreases [20]-[22]. However, with the second phase composition and proper annealing, the ceramic microstructure becomes more stable, and can prevent decreases in flexural strength.

The factor that gives an effect on mechanical strength of ceramic composites is $\sigma = \sigma_0 \exp(-k\alpha)$ (σ_0 is the flexural strength of the material with no defect, α is residual porosity, and k is a constant) [23]. Therefore, flexural strength is highly dependent on the existence of porosity. However, it is difficult to accurately examine specific analysis regarding porosity due to the effects of grain growth, phase-shaped, and grain boundary caused by annealing and debonding by the combination of liquid phase.

Because mechanical strength shown in Fig. 7 is dependent on the porosity shown in Fig. 2, as porosity increases flexural strength decreases. On the other hand, as porosity decreases, flexural strength increases. Porosity can be re-confirmed with the FE-SEM picture of a fracture surface of the SiC-ZrB₂ composites shown in Fig. 4.

Fig. 7. Three-point flexural strength of the SiC-ZrB₂ composites.

3.4 Electrical Resistivity

The electrical resistivity of SiC single crystal at room temperature is approximately 0.13 $\Omega \cdot \text{cm}$. However, due to the NTCR characteristic, the resistivity drops to 0.1 $\Omega \cdot \text{cm}$ up to 250°C, and when it reaches 900°C due to the PTCR characteristic, the resistivity increases to approximately 0.16 $\Omega \cdot \text{cm}$. The electrical resistivity of SiC polycrystalline is 0.1~0.3 $\Omega \cdot \text{cm}$ at room temperature. However, due to the NTCR characteristic, the resistivity drops to one-third up to 800°C, and it gradually increases over 800°C due to the PTCR characteristic. The difference between SiC single crystal and polycrystalline comes from the fact that the grain of SiC polycrystalline is smaller than SiC single crystal and it also contains a greater amount of grain boundaries than SiC single crystal; grains in SiC polycrystalline grow as the sintering temperature increases up to 800°C, causing its electrical resistivity to decrease [24]. The electrical conduction mechanism of SiC polycrystalline has been explained as the band model having electric potential barriers at grain boundaries. It has been stated that it goes over the electric potential barriers with the high thermal excitation at high temperature, and passes through the electric potential barriers with the tunnel and bulk conduction at low temperature [24].

Based on the effective medium theory of R. Landauer [25]-[26] and the Pauw method, electrical resistivities of SZ30, SZ35, SZ40, SZ45, and SZ50 were measured 50 times by the Pauw method at room temperature, 100, 300, and 500°C, respectively. The average value for each temperature is shown in Fig. 8. The electrical resistivities of SZ30, SZ35, SZ40, SZ45, and SZ50 at room temperature were 4.573×10^{-3} , 1.554×10^{-3} , 9.365×10^{-4} , 6.999×10^{-4} , and $6.069 \times 10^{-4} \Omega \cdot \text{cm}$, respectively, and those for 500°C were 8.692×10^{-3} , 3.815×10^{-3} , 2.346×10^{-3} , 1.730×10^{-3} , and $1.592 \times 10^{-3} \Omega \cdot \text{cm}$, respectively. Because the electrical resistivity of a transition metal ZrB₂, $1.5 \times 10^{-5} \sim 4.5 \times 10^{-5} \Omega \cdot \text{cm}$, is lower than the electrical resistivity of semiconductor SiC, 0.1~1.8 $\Omega \cdot \text{cm}$, by approximately 10^{-5} , if the additional amount of a transition metal is over 30 vol.%, the effective medium theory of R. Landauer is no longer applied and its electrical resistivity would be dependent on the chain formation of ZrB₂ grain with its good electrical conductivity.

As shown in Fig. 9, the temperature coefficients of resistance of the SiC and ZrB₂ were calculated by using the rule of mixture, and the experiment values were measured based on the Pauw method. The temperature coefficients of the resistance of SZ30, SZ35, SZ40, SZ45 and SZ50 were 1.896×10^{-3} , 3.064×10^{-3} , 3.169×10^{-3} , 3.097×10^{-3} , and $3.418 \times 10^{-3} / ^\circ\text{C}$, respectively, which demonstrated that they all show the characteristics of PTCR. It can be confirmed that the experiment values of the temperature coefficient of resistance are not dependent on the rule of mixture because electrical current flows dominantly by the chain formation of ZrB₂ with its low electrical resistivity.

Fig. 8. Electrical resistivity of the SiC-ZrB₂ composites by the R. Landauer's effective medium theory and by the Pauw method.

Fig. 9. Temperature coefficient of resistance of the SiC-ZrB₂ composites.

3.5 V-I Characteristics and Thermal Images

The V-I specific slopes of SZ30, SZ35, SZ40, SZ45 and SZ50 at room temperature were 1.96×10^{-1} , 6.27×10^{-2} , 4.34×10^{-2} , 3.18×10^{-2} , and 2.49×10^{-2} respectively, and were 3.72×10^{-1} , 1.53×10^{-1} , 1.09×10^{-1} , 7.92×10^{-2} , and 6.59×10^{-2} respectively at 500 °C. As shown in Fig. 10, the slope increases as temperature increases or the addition of ZrB₂ at constant temperature decreases. Because the fact the slope increases as temperature increases explains specific resistivity increases, it causes electrical resistivity to increase, which eventually demonstrates the characteristics of PTCR. Moreover, the fact that the addition of ZrB₂ decreases the slope increases confirms that the specific resistivity of a transition metal ZrB₂ increases due to the decreased conductivity per volume of ZrB₂.

As shown in Figs. 8, 9, and 10, SZ30, SZ35, SZ40, SZ45 and SZ50 composites are PTCR characteristics, demonstrating V-I characteristics, and because their relative densities are over 97%, except SZ30 and SZ50, it is considered that the SiC-ZrB₂ composite can be used as a resistivity heater or ohmic-contact electrode material.

Table 4 shows the point temperature of the SiC-ZrB₂ composites measured by thermal image. As shown in Table 4, the temperature of SZ30, SZ35, SZ40, SZ45 and SZ50

increased by 29.74, 12.47, 12.12, 10.14, and 6.57 °C, respectively, because they are resistive heaters so they are dependent on electrical resistivity.

Fig. 10. V-I characteristics of the SiC-ZrB₂ composites.

Table 4. Point temperature of the SiC-ZrB₂ composites

Specimen	SZ30		SZ35		SZ40		SZ45		SZ50	
Time(sec)	Start	60	Start	60	Start	60	Start	60	Start	60
P1	28.00	56.23	28.19	39.58	27.91	39.33	28.09	37.74	28.82	34.85
P2	27.91	56.30	28.00	41.47	27.82	41.06	28.09	39.74	28.73	36.05
P3	28.09	57.88	28.00	40.08	27.82	39.25	27.91	37.66	28.55	34.76
P4	28.09	59.15	27.91	41.30	27.73	40.40	28.00	38.00	28.55	35.28
P5	28.02	59.22	28.03	40.08	27.82	39.66	28.02	37.66	28.66	35.19
Average of point[°C]	28.02	57.76	28.03	40.50	27.82	39.94	28.02	38.16	28.66	35.23
Standard deviation	0.07	1.31	0.09	0.75	0.06	0.69	0.07	0.80	0.10	0.46
Average increase temperature[°C]	29.74		12.47		12.12		10.14		6.57	

4. Conclusion

The characteristics of the SiC-ZrB₂ composites, the sintered compacts, β -SiC and ZrB₂ were combined with the ratio of 70:30 vol.%, 65:35 vol.%, 60:40 vol.%, 55:45 vol.%, 50:50 vol.% through SPS are as follows:

1. The changes of the apparent porosity of the sintered compacts were 7.2546, 0.8920, 0.6038, 1.0981, 10.0108 %, respectively. The relative density of the SiC+40 vol.% ZrB₂ composite was the highest, 99.40 %, and that of the SiC+50 vol.% ZrB₂ composite was the lowest, 89.99 %.
2. According to XPS and EDS analyses, the condensed ZrO₂ phase did not appear in the external surfaces of the SiC-ZrB₂ composites, but SiO₂ amorphous phase appeared. According to XRD analysis, only SiC and ZrB₂ phases appeared in external surfaces of the SiC-ZrB₂ composites, therefore, it is considered that the thickness of the SiO₂ amorphous phase of the SiC-ZrB₂ composites would be in nm.
3. The flexural strength of the SiC-ZrB₂ composites was in accordance with the relative density of them; it can be reconfirmed with the SEM picture of porosity in fracture surfaces. The flexural strength of the SiC+50 vol.% ZrB₂ composite was the weakest, 290.54 MPa, those of the SiC+35 vol.% ZrB₂, SiC+40 vol.% ZrB₂, and SiC+45 vol.% ZrB₂ composites were close to a strong flexural strength, approximate 1000 Mpa, and that of the SiC+40 vol.% ZrB₂ composite was the strongest, 1011.34 MPa.
4. The electrical resistivities of the SiC+30 vol.% ZrB₂, SiC+35 vol.% ZrB₂, SiC+40 vol.% ZrB₂, SiC+45 vol.% ZrB₂ and SiC+50 vol.% ZrB₂ composites were 4.573×10^{-3} , 1.554×10^{-3} , 9.365×10^{-4} , 6.999×10^{-4} , and 6.069×10^{-4} $\Omega \cdot \text{cm}$, respectively, at room temperature, and they demonstrate the characteristics of PTCR in the temperature range of room to 500°C.
5. The V-I characteristic of all the SiC-ZrB₂ composites indicated a linear shape in the temperature range of room to 500°C, and the increasing temperature of the SiC-ZrB₂ composites is in accordance with the aspect of electrical resistivity of them.

In conclusion, it is considered that the most suitable condition to develop an energy friendly ceramic heater or ohmic-contact electrode material of the SiC-ZrB₂ composite through SPS, among the sintered compacts, is to apply the SiC+35 vol.% ZrB₂, SiC+40 vol.% ZrB₂ and SiC+45 vol.% ZrB₂ composites containing the most outstanding mechanical properties, approximate 1000MPa, the highest relative density, 97% and the linear V-I and PTCR characteristics.

Acknowledgement

This work was supported by Wonkwang University Research Grant in 2010.

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