OURNALOF

Ceramic Processing Research

Electrodeposition of an alumina precursor on a silicon carbide surface

Masaru Murao^a, Tomoyuki Maeda^a, Naoki Matsunaga^b, Soichiro Sameshima^a and Yoshihiro Hirata^{a*}

^aDepartment of Advanced Nanostructured Materials Science and Technology, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

^bDepartment of Applied Chemistry and Chemical Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

An electrodeposition method was used to form nanometre-sized alumina particles on a silicon carbide surface. A direct current in the range from 0.15 to 11.8 mA/m² was flowed between a cylindrical carbon cathode and a porous silicon carbide anode in an aqueous solution containing ethylenediaminetetraacetatoaluminium (III) (Al-EDTA⁻) at a pH 6. The current density increased with an increase of the applied voltage and showed a maximum as a function of deposition time. The deposited alumina precursor was estimated to be (OH)Al(OOCH)₂. After calcination at 800 °C in an Ar atmosphere, the uniformly deposited precursor changed to alumina particles with a specific surface area of 44.3 m²/g.

Key words: Electrodeposition, Current density, Alumina precursor, Silicon carbide.

Introduction

A submicrometre-sized silicon carbide (SiC) with a small amount of Al_2O_3 and rare-earth oxide (RE₂O₃) is densified through a dissolution-reprecipitation mechanism in the SiO₂-Al₂O₃-RE₂O₃ liquid. A uniform addition of sintering additives enhances the densification rate and the formation of uniform dense microstructures after sintering. In our previous studies, colloidal dispersion technology and the adsorption of a rare-earth ion were coupled to add 0.2 μ m Al₂O₃ and RE³⁺ ions of a nitrate aqueous solution to 0.8 µm SiC [1-5]. The interaction of the SiC-Al₂O₃-RE³⁺ ion system is controlled by the pH of the suspension, the surface charge of SiC and Al_2O_3 particles and the concentration of the RE³⁺ ion. The consolidated powder compact showed high sinterability and good mechanical properties after hotpressing at 1950°C. In this paper, the electrodeposition of Al₂O₃ on a SiC surface was investigated to coat the SiC surface uniformly in an aqueous solution. The reduction of Al³⁺ ions to Al metal in an aqueous solution is impossible because of the high reduction potential of Al^{3+} ion (E°=-1.66 V). Therefore, the experiment was carried out using an $Al(NO_3)_3$ -ethylenediamine tetra acetic acid disodium salt (EDTA-2Na) solution.

Experimental Procedure

A high purity α -SiC powder (98.9 mass% SiC, 0.66%

SiO₂, 0.37% C, 0.004% Al, 0.013% Fe) of median size 0.8 µm (Yakushima Electric Industry Co., Ltd., Japan) was used as the starting material of the electrode. A 40 vol% SiC suspension stirred for 24 h at pH 5 was consolidated using a gypsum mold. The dried green compact was sintered at 1850°C for 2 h in an Ar atmosphere (FVH-5, Fuji Dempa Kogyo Co., Ltd., Japan). The relative density measured by the Archimedes method with kerosene and the specific resistance at room temperature for the sintered SiC were 60.7% and 2.39 $\times 10^3$ Ωcm, respectively. The specific surface area of the porous SiC was 0.85 m^2/g . The sintered compact was cut with diamond wheel into a $5 \times 4 \times 40$ mm electrode, and then polished with SiC abrasive paper. Aluminium nitrate $(Al(NO_3)_3 \cdot 9H_2O > 98.0 \text{ mass}\%)$, Wako Pure Chemical Industries, Ltd., Japan) and ethylenediamine - N,N,N',N', - tetraacetic acid disodium salt $(C_{10}H_{10}N_2O_8Na_2 \cdot 2H_2O > 99.5 \text{ mass\%}, \text{ Wako Pure}$ Chemical Industries, Ltd., Japan) were dissolved into double distilled water to prepare $0.01 \text{ mol/l Al}(NO_3)_3$ and 0.01 mol/l EDTA-2Na solutions, respectively, and mixed at a molar ratio of 1:1.1 at pH 6 adjusted with 1 mol/l CH₃COONH₄ solution. Figure 1 shows the scheme of the electrodeposition apparatus [6-8]. The porous SiC anode was set at the center of the cylindrical carbon cathode of 30 mm inside diameter, 50 mm outside diameter and 40 mm high. The electrodeposition of ethylenediaminetetraacetato-aluminium(III) (Al-EDTA-) was carried out in the current density range from 0.15 to 11.8 mA/m² for 24-72 h. The corresponding electric field strength was 1.5-7.7 V/cm. After the electrodeposition, the SiC electrode was dried at 100°C for 24 h in air to estimate the deposited species by Fourier transform infrared spectroscopy (FT-IR, IR Report-100,

^{*}Corresponding author:

Tel : +81-99-285-8325 Fax: +81-99-257-4742

E-mail: hirata@apc.kagoshima-u.ac.jp



Fig. 1. Scheme of the electrodeposition apparatus.

JASCO Co, Japan) and thermogravimetry-differential thermal analysis (TG-DTA, Thermo Plus TG 8120, Rigaku, Japan). The electrodeposited SiC was calcined at 800°C in an Ar atmosphere to observe the Al distribution by an electron probe X-ray microanalyzer (EPMA, JXA-8600S/M, Japan Electron Optics Lab. Co., Ltd., Japan) and to measure the specific surface area by the BET method (Flow Sorb II 2300, Shimazu, Japan).

Results and Discussion

Figure 2 shows the time dependence of the current density at 2-10 V applied voltage. The current density at 2 and 4 V was independent of the deposition time and 0.2 and 2 mA/m², respectively. On the other hand, the current density at 7 and 10 V showed a maximum value within 10 h deposition time, and then the current density decreased with deposition time. As discussed later, 59% of the starting Al³⁺ ions remained in the solution after 72 h deposition time at 10 V when (OH)Al(OOCH)₂ was assumed to be the deposited Al precursor. That is, the decrease of the current density at a longer deposition time is not due to a lack of the



Fig. 2. Current density as a function of deposition time at 2-10 V applied voltage.



Fig. 3. Weight of alumina precursor as a function of deposition time at 2-10 V applied voltage.

amount of Al-EDTA⁻ ions. The above result suggests that an alumina precursor of a low electrical conductivity is deposited to coat the SiC surfaces and this prevents further deposition at a longer time. Figure 3 shows the weight of deposited alumina precursor as a function of deposition time. It is clearly seen that the weight of the deposited precursor increases at a longer deposition time. The current density shown in Fig. 2 is closely related to the deposition behavior of the alumina precursor. Figure 4 shows the TG-DTA curves of the porous SiC immersed in the Al-EDTA solution (a) and the SiC electrode treated for 72 h at 10 V applied voltage. Both of the SiC compacts were dried at 100 °C for 24 h before the TG-DTA measurements. The DTA curves show a small exothermic peak at 450°C. The result in Fig. 4(a) suggests that the negativelycharged Al-EDTA is electrostatically adsorbed on the positive sites (Si-OH $_2^+$) of the slightly oxidized SiC surfaces. The exothermic reaction is explained by the oxidation of the EDTA-related organic compound. From the difference of weight loss between the two TG curves at 1000°C, it was calculated that the electrodeposited



Fig. 4. TG-DTA curves for (a) a porous SiC compact immersed in Al-EDTA solution and (b) a SiC compact electrodeposited for 72 h at 10 V. Both of the SiC compacts were dried at 100°C for 24 h before the TG-DTA measurements.



Fig. 5. FT-IR spectra of (a) as-prepared SiC compact and (b) SiC compact electrodeposited for 72 h at 10 V.

alumina precursor lost 60.95% of its initial weight in changing to alumina. The weight loss for possible precursors was compared with the experimental result. Equations (1)-(3) represent the thermal decomposition of possible precursors. The weight loss for AlOOH or Al(OH)₃ is significantly smaller than the experimental result. On the other hand, the weight loss for the (OH)Al(OOCH)₂ precursor is close to the experimental result.

$$AIOOH \rightarrow 1/2Al_2O_3 + 1/2H_2O$$
(weight loss: 15.0%) (1)

 $Al(OH)_3 \rightarrow 1/2Al_2O_3 + 3/2H_2O$ (weight loss : 34.6%) (2)

$$(OH)Al(OOCH)_2 \rightarrow 1/2Al_2O_3 + 2CO + 3/2H_2O$$

(weight loss : 61.9%) (3)

Figure 5 shows the FT-IR spectra of the as-prepared SiC compact and the SiC treated for 72 h at 10 V of applied voltage. The adsorption peaks for the electrodeposited SiC electrode were measured at 850, 1110, 1220, 1400, 1620 and 3450 cm⁻¹ wave lengths. The peak at 850 cm⁻¹ is assigned to the stretching vibration of Si-C [9]. On the other hand, the peaks at 1110, 1220 and 1620 cm⁻¹ correspond to the stretching vibration of C=O, C-O and C=O bonds, respectively [10]. The peaks at 1400 and 3450 cm⁻¹ represent the bending and stretching vibration of the OH group, respectively [11-13]. Lopez et al. report the formation of (OH)Al-(OOCH)₂ from Al(OOCH)₃ upon heating to 85°C [14]. They observed the IR peaks of (OH)Al(OOCH)₂ at 775, 800, 1080, 1120, 1390, 1400, 1417, 1428, 1605, 1630, 2930 and 3500 cm⁻¹. Their relatively strong peaks were in accordance with the IR spectrum shown in Fig. 5(b). According to Lopez et al., (OH)Al(OOCH)₂ transforms to amorphous alumina above 355°C and subsequently crystallizes to n-alumina at 945°C. However, no exthothermic peak associated with the crystallization of alumina was measured at 900-1000°C in this experiment because of the small amount of the deposited precursor. The above results in Figs. 4 and 5 suggest that $(OH)Al(OOCH)_2$ is electrodeposited from the Al-EDTA solution. A possible reaction is proposed as follows: Al-EDTA⁻ + OH⁻ \rightarrow (OH)Al(OOCH)₂ + $H_2C_2N(CH_2)_2N(CH_2COO)_2 + 2e^-$. Figure 6 shows the EPMA image of the cross section of the SiC electrodeposited for 72 h at 7 V and calcined at 800°C in an Ar atmosphere. The white spots represent the distributions of Al and O atoms on the SiC particles. As seen in Fig. 6, the precursor-derived alumina was uniformly deposited. The specific surface areas of the as-prepared SiC compact and the electrodeposited SiC electrode were 0.85 and 1.74 m^2/g , respectively. From the above two specific surface areas, it was calculated that the specific surface area of the amorphous alumina was 44.3 m²/g. When the density for η -alumina (3.65 g/ cm³) is used, the particle size corresponding to the specific surface area is calculated to be 37 nm.

Conclusions

An alumina precursor was electrodeposited from the Al-EDTA solution on the surfaces of a porous silicon carbide compact at a current density of 0.15 to 11.8 mA/m². The weight of aluminum precursor increased at a longer deposition time. From the analysis with FT-IR and TG-DTA, the aluminum precursor was estimated to be (OH)Al(OOCH)₂. This precursor changed to amorphous alumina with a specific surface area of 44



Fig. 6. Microstructure (a) and EPMA images of Al (b) and O (c) of a cross section of the SiC electrodeposited for 72 h at 7 V and calcined at 800°C in an Ar atmosphere.

 m^2/g upon heating to 800°C. The derived alumina was uniformly formed on the SiC surfaces.

References

- 1. N. Hidaka and Y. Hirata, Ceram. Trans. 152 (2004) 109-118.
- 2. S. Tabata and Y. Hirata, Ceram. Trans. 152 (2004) 119-128.
- 3. Y. Hirata, S. Tabata, and J. Ideue, J. Am. Ceram. Soc. 86[1] (2003) 5-11.
- N. Hidaka and Y. Hirata, J. Ceram. Soc. Japan 113[7] (2005) 466-472.
- 5. S. Tabata, Y. Hirata, S. Sameshima, N. Matsunaga, and K. Ijichi, J. Ceram. Soc. Japan 114[3] (2006) 239-244.
- Y. Hirata, H. Hatano, H. Kyoda, and K. Hamasaki, J. Mater. Res. 10[11] (1996) 2697-2699.

- 7. Y. Hirata, H. Kyoda, T. Iwamoto, and K. Hamasaki, J. Ceram. Soc. Japan 103[5] (1995) 460-463.
- 8. Y. Hirata. H. Kyoda, T. Iwamoto, H. Hatano and K. Hamasaki, Ceram. Trans. 51 (1995) 237-241.
- G. Ramis, P. Quintard, M. Cauchetier, G. Busca, V. Lorenzelli, J. Am. Ceram. Soc. 72[9] (1989) 1692-1697.
- J. Hou, L. Shi, and Q. Zhu, J. Solid State Chem. 179[6] (2006) 1874-1878.
- A. Szorcsik, L. Nagy, M. Scopelliti, A. Deák, L. Pellerito, G. Galbács, and M. Hered, J. Organometallic Chem. 691[8] (2006) 1622-1630.
- 12. S. Ashihara, N. Huse, A. Espagne, E.T.J. Nibbering, and T. Elsaesser, Chem. Phys. Letters 424[1-3] (2006) 66-70.
- N. Huse, S. Ashihara, E.T.J. Nibbering, and T. Elsaesser, Chem. Phys. Letters 404[4-6] (2005) 389-393.
- 14. S.Y.R. Lopez, J.S. Rodriguez, and S.S. Sueyoshi, Adv. in Tech. of Mat. and Mat. Proc. J. 8[1] (2006) 55-62.