Difference of graphitization of polymer in the gelcasted bodies using alumina and silica as matrices

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We have been developing a new route in synthesizing conductive alumina through gel casting method and then sintered in an inert environment. In this study, we fabricate a semi-conductive ceramics utilizing silica as the matrix and investigate the effect of this matrix on the basic properties for a semi-conductive ceramic body. The results were then compared to the gelcast alumina body sintered under inert atmosphere. Synthesize gelcast silica body gave a higher relative density and lower conductivity if compared to the gelcast alumina body sintered under inert atmosphere. This is because the gelcast silica during sintering, some silica matrix component attached to nano-carbon network (originating from polymers) form a SiC under inert atmosphere. This carbon-consuming process causes defects which inhibits graphitization and structural disorder onto the gelcast silica body.
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Recently, synthesizing composite materials by adding some functionality to ceramic materials in improving the properties of composite ceramic body has been widely reported.[1)–7)] One typical method in molding/producing a composite materials consist a mixture of filler materials and ceramic oxide particles as matrix and this mixture produced as a ceramic product.[1)–4)] To make the insulating ceramics body be a conductive ceramic material,[4)–7)] metal oxides, and carbon are often added as conductive fillers. Then using carbon nanotubes (CNTs) as fillers to make a conductive ceramic material has been the subject of extensive research for the past decade.[5)–7)] The addition of CNTs to the ceramic body resulted to higher tensile strength and produced semi-conductive property to the composite ceramic body. However, CNTs have high cohesiveness that makes uniform dispersion difficult to achieve. The effect of this cohesion can be resulted into segregation and structural deformity (defects) onto the matrix. If the amount of CNTs added onto the ceramic body was increased which is higher than the amount required to obtain sufficient ceramic semi-conductive, this resulted to the degradation of ceramic material properties. Hence, the anisotropic effects, and countermeasures against these properties are continuously being investigated.[5)–7)]

Our research group has successfully developed a new process in synthesizing conductive alumina by gelcasting method under inert atmosphere.[8)–12)] Basically, gelcasting is a method for forming green body through the polymerization of monomers and gelling agents dissolved in slurry. The resulting polymer with a network structure is used as a precursor that is subsequently carbonized by sintering under inert atmosphere to form a conductive network path. A characteristic of the gel casting method is that the precursor used a uniform polymer network channel formed when monomers dissolved generating as a dispersion medium to the slurry. Hence, this network of carbon atoms (polymer materials as precursor), which is the source of the conductivity, exists uniformly in between the ceramic particles. Studies in the past have shown that this carbon network has a nano-graphite-like structure interconnected within the ceramic particle which known as nano-carbon network (NCN).[10)] The filler materials in this synthesized conductive ceramics using our method is composed of nano-carbon networks derived from the polymers, and this material undergoes only structural changes such as graphitization to make the ceramic body conductive. Thus, we can expect that the physico-chemical properties of conductive ceramics can be varied by replacing the alumina ceramic matrix with other ceramic oxide matrices.

The conductivity of gelcast alumina body gradually increased at higher sintering temperature under inert atmosphere because it promotes more graphitization of carbon present on the gelcast alumina body.[8)–12)] However, even if the NCN graphite structure exists but the ceramic oxide matrix changed, the conductive properties of the material would be different.

So in this study, we used silica as a ceramic matrix, which has a lower sintering temperature than alumina and synthesized a semi-conductive silica ceramics with NCN. Furthermore, we compared silica-matrix and alumina-matrix ceramics and investigate the effect of the matrix material onto the various properties of a semi-conductive ceramic material.

Table 1 shows the composition of the gel-slurry used in this study. Amorphous silica powder (SO-C2, Admatechs Ltd., Japan) was used as the ceramic powder while methacrylamide and N,N,N',N'-tetramethylethylenediamine were used as the gelling agents. A commercially available NH^{4+} salt of poly acrylic acid (PAA) (celuna D305, Chukyo Yushi Co., Ltd., Japan) was used as the dispersant. Distilled water was used as the dispersion medium. The powder vol% of the slurry was adjusted to 50 and mixed for 24 h at 60 rpm by using a ball mill. The obtained slurry was vacuum degassed, and to this slurry, 104 µL of 10 mass% ammonium peroxodisulfate solution was then added as an

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Table 1. Slurry composition of silica slurry (gel cast slurry recipe)

	mass%
Silica	68.8
Distilled water	24.8
Monomer Methacrylamide	4.85
Crosslinker N,N,N',N'-tetramethyletylenediamine	1.60

initiator and mixed for 3 min. Then, 17 µL of *N,N,N′,N′*-tetra-methylethylenediamine was added and mixed for another 3 min. The resulting mixture was then poured into a Teflon mold. The mold was sealed with an acrylic plate to prevent dehydration and kept in a nitrogen atmosphere for 12 h. The samples were demolded after confirming solidification and dried in a humidity-controlled chamber (E-TAC FX-206P, Kusumoto Chemicals Ltd., Japan) at 25°C (humidity was decreased from 95 to 60% at a rate of 5%/day). Sintering temperature was carried out at 1300, 1400, 1500, 1600, and 1700°C for 2 h in a controlled-argon atmosphere furnace with an internal pressure of 0.15 MPa.

The compact density was determined using the Archimedes method in accordance with JIS R 1634. The carbon structure of the sintered gelcast body was analyzed by Raman spectroscopy. Measurements were performed using a laser micro-Raman spectrometer (NRS-3100, JASCO Japan Corp., Japan) (wavelength: 532 nm; output power: 11 mW). Wavenumbers between 1000 and 2000 cm^{-1} were measured at 1.86 cm^{-1} intervals with an exposure time of 10 s. The carbon structure was estimated by peak deconvolution and curve fitting of the D-band (1350 cm^{-1}) and G-band (1580 cm^{-1}), which are unique to carbon.

Conductivity of the gelcast ceramic body was measured using the four-terminal method in which samples cut to dimensions 3 mm × 3 mm × 40 mm were used. In this method, a current and voltage generator (R6243, Advantest Japan Corp., Japan) with an applied current of 0.1 mA was used.

The carbon content of the compacts was measured by thermogravimetric–differential thermal analysis (TG–DTA) from room temperature to 1400°C with the heating rate of 10°C/min.

Figure 1 shows the change in density of the sintered gelcast ceramic body with increasing sintering temperature. The results of the sintered gelcast alumina-matrix were obtained from our previous study as shown in Fig. 1.[11] For both sintered gelcast silica- and alumina-matrix, the relative density was about 60% at 1300°C, indicating that densification and sintering did not occur at this temperature. For sintered gelcast silica-matrix compacts, the relative density increased at the temperature range between 1400–1500°C approximately around 98%. But the relative density of the sintered gelcast silica decrease at 1700°C. The slight decrease was due to the formation of bubbles (macroholes) visually observed in **Fig. 2**. Above 1500°C, the silica and carbon content are identified to form silicon carbide (SiC) according to the following reaction:[13],[14]

$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g) \qquad (1)$$
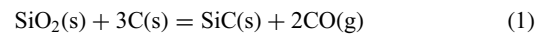
Hence, the presence of macroholes (bubble formation) may attribute to the formation of CO gas bubbles which eventually decrease the relative density of the sintered gelcast silica material.

The conductive properties of the sintered gelcast silica and gelcast alumina matrix[11] upon increasing firing temperature were shown in **Fig. 3**. The sintered gelcast silica matrix showed semi-conductive property when the firing temperature reached 1400°C but beyond 1500°C imply no significant value in terms of the conductive. Wherein, the semi-conductivity of sintered silica-matrix was about 1/100 times of that sintered gelcast alumina-matrix. TG–DTA of the sample fired at 1700°C showed an exothermic weight decrease of 0.75 wt% between 600 and 660°C, possibly due to the combustion of carbon. For alumina-matrix compacts, the carbon content was about 0.8 wt%. So,
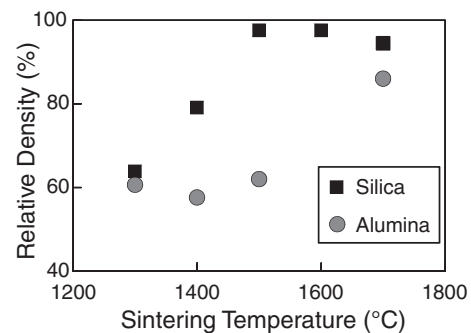

Fig. 1. The relative density of the gelcast ceramics with increasing sintering temperature under inert atmosphere.
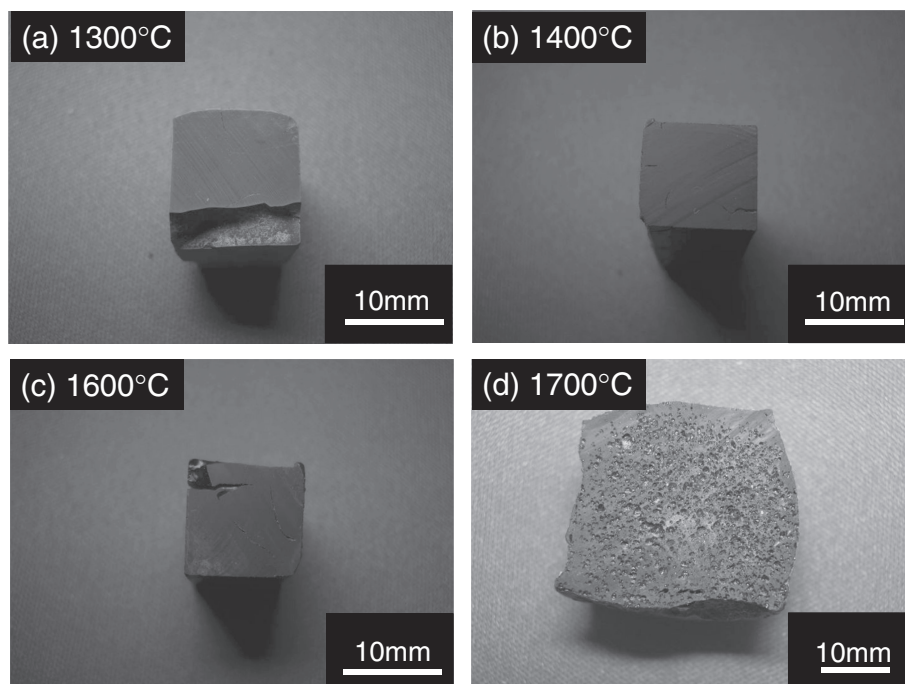

Fig. 2. Digital images of the gelcast silica matrix with increasing sintering temperature under inert atmosphere.

the difference in the conductivity could not be attributed to the difference of the carbon content.

The Raman spectroscopy results are shown in **Fig. 4**. The D-band (1350 cm^{-1}) and G-band (1580 cm^{-1}) were observed, as in the case of alumina-matrix compacts[11] at increasing sintering temperature. For sinteried gelcast alumina matrix, relatively sharp G-band peak was observed and the D-band intensity decreased upon increasing the sintering temperature.[11] While, upon increasing the firing temperature for sintered gelcast silica-matrix
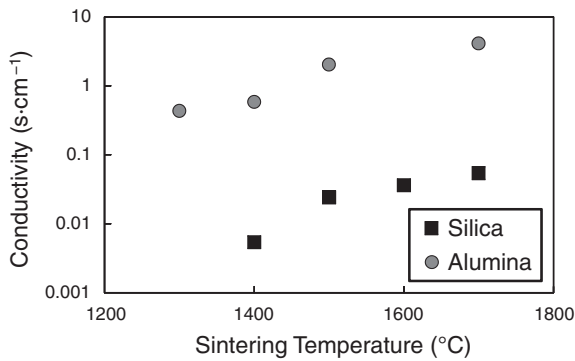

Fig. 3. The conductive properties of the gelcast silica and gelcast alumina upon increasing sintering temperature under inert atmosphere.
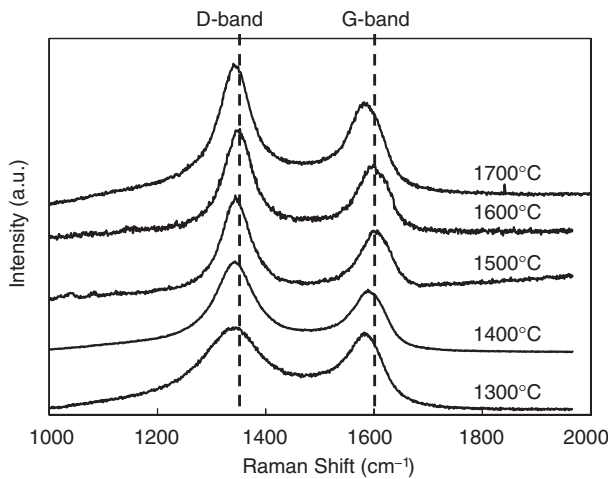

Fig. 4. The Raman spectra of the gelcast silica matrix upon increasing sintering temperature under inert atmosphere.

compacts, the D-band intensity increased and the G-band intensity did not change significantly but a broad G-band peak was observed. **Figure 5** shows the half-width of the G-band ($\Delta \nu_{1580}$) and the G-band to D-band intensity ratio (I_{1350}/I_{1580}). The results for sintered gelcast alumina-matrix were also shown based on our previous studies.[11] The values of both $\Delta \nu_{1580}$ and I_{1350}/I_{1580} decreased for sintered gelcast alumina-matrix. This indicates that graphitization progressed upon increasing the sintering temperature for these gelcast alumina compacts.[11] On the other hand, no increase in graphitization was observed for sintered gelcast silica-matrix compacts. In this case, the value of $\Delta \nu_{1580}$ decreased and that of I_{1350}/I_{1580} increased from 1300 to 1400°C. But, the trend was reversed at higher temperatures. On the other hand, all values were close to the sintered gelcast alumina-matrix compact sintered at 1300°C which showed almost no graphitization had occurred.

Carbon consumption in the SiC-formation could be one of the reasons that no increase in graphitization during the gradual increase of the sintering temperature for the gelcast silica-matrix fabrication. **Figure 6** shows the Raman spectroscopy results for the low-wavenumber regime. Peaks corresponding to SiC are visible near 1000 cm^{-1}, which also corresponds to the amorphous silica that confirms the formation of SiC. These results may be one of the reasons that the conductivity of gelcast silica-matrix compacts is lower if compared to gelcast alumina-matrix. This occurred when the carbon from the polymers in the gelcast silica
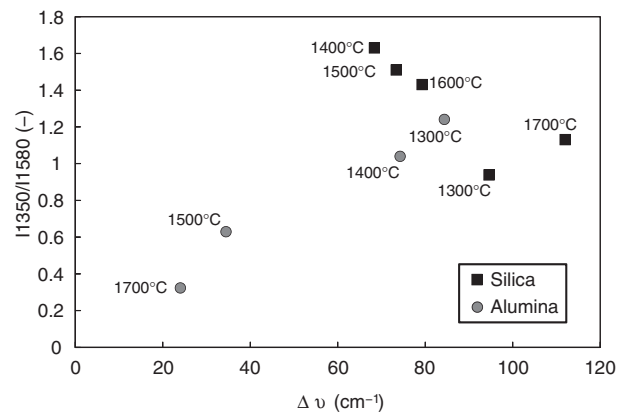

Fig. 5. Correlation plot between the $\Delta \nu_{1580}$ and I_{1360}/I_{1580} of gelcast silica and gelcast alumina matrix composite. ($\Delta \nu_{1580}$; half band width of the peak at 1580 cm^{-1}, I_{1360}/I_{1580}; intensity ratio of peaks at 1350 and 1580 cm^{-1}).
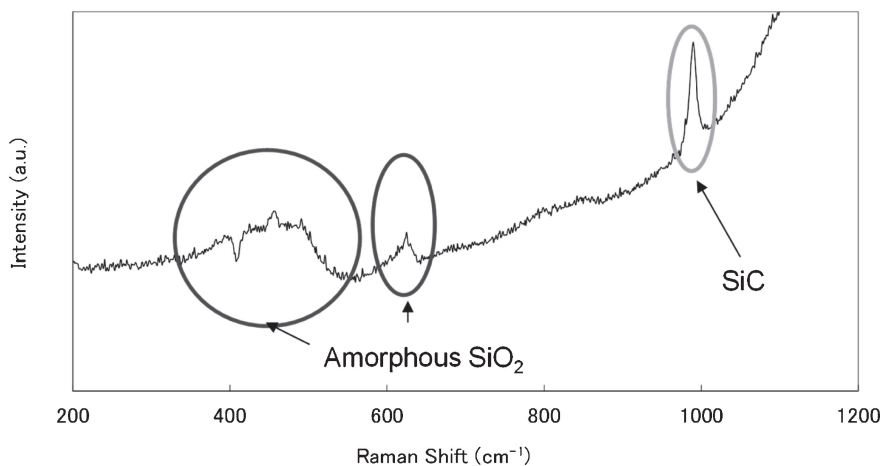

Fig. 6. Raman spectrum of gelcast silica matrix composite sintered at 1300°C under inert atmosphere.

reacted with the silica matrix to form SiC. Eventually, this carbon-consuming reaction caused defects and structural disorder in the matrix and inhibited graphitization.

In summary, we synthesized semi-conductive ceramics using silica has a lower sintering temperature compared to gelcast alumina body. But, the conductive property of this synthesized gelcast silica body was lower if compared to gelcast alumina sintered under inert atmosphere. This is because carbon originating from polymers in a fired compact reacts with the silica matrix to form SiC, and this carbon-consuming process causes defects and structural disorder and inhibits graphitization. In conclusion, we found that the proposed method for synthesizing a semi-conductive ceramics by gel casting sintered under inert atmosphere can enhanced the conductive property of various ceramic oxide materials (ceramic matrix). However, the ceramic matrix material must be carefully selected in order to achieve structural stability of the ceramic body and unwavering during the graphitization of the carbon (sintering the carbon), which is necessary to further increase the conductivity of the ceramic body.

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