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Electrical conductivity of gelcast alumina sintered under inert atmosphere

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Abstract

Electrically conductive alumina ceramic has been successfully fabricated by sintering of dried gelcast alumina in an inert atmosphere. The process was developed similar to the conventional gelcasting method except for varying the amount of monomer in the premix solution. The sintering treatment was carried out in argon gas from 1100 °C to 1700 °C. Van der Pauw's method was used to measure the electrical resistivity. The results showed that increasing monomer addition and sintering treatment were significantly affecting in lowering electrical resistance. Using the lowest monomer addition and increased sintering treatment, the measured electrical resistivities were in the range from 1.94 Ω-cm to 0.37 Ω-cm. The material exhibited ohmic behavior and rendered two regimes of Arrhenius profile in the plot of electrical conductivity against increasing temperature from 20 °C to 600 °C. All conduction processes were governed by the presence of carbon that caused the alumina grains in polygonal morphology typical of densification. Furthermore, physical tests were conducted to describe the electrical conduction behavior of the material.

Keywords: Gelcasting; Electrical conductivity; Electrically conductive alumina; Inert gas

1. Introduction

Virtually any electrically insulating ceramic materials can be made electrically conductive if sufficient conductive phase, particularly carbon, is added to their compositions. Then, they are classified as carbon-based materials[1] which have many potential applications including dense honeycomb filter with heating capability, electromagnetic wave absorber, high thermal conductor, and aerospace.[2] However, the introduction of the conductive phase in the form of powder into insulating powder causes a serious problem during mechanical mixing that leads to nonuniformity of physical properties.

Alternatively, through gelcasting process, the non-homogeneities in physical properties could be minimized. This is because the freshly gelcast part consists of a well-distributed three component system comprising the ceramic particles, gel matrix, and the polymer strands that cross-link throughout the entire inter-particle spaces.[3] As the part dries, the gel matrix ruptures and coats on individual ceramic particles. During the progress of drying, the gel-matrix continues to rupture creating several interconnected voids and interstices which may be empty spaces within the gelcast part, but they are more likely occupied by the polymer strands. As the gel matrix coats on the particles, it keeps shrinking until complete drying and remains in encapsulating the individual ceramic particles to render effective binding performance. The dried gel coating and polymer strands are attractive precursors for pyrolysis into continuous interlink pathways of carbon.[4,5]

Currently, the pyrolysis of the gelcasting polymer gel into carbon has been utilized for ceramics, such as silicon carbide and boron carbide, which functions as sintering aid and carbon supplement.[6] This is practically achieved by performing the binder burn-out in a neutral or reducing environment that leaves about 15% carbon residue[4] relative to the original polymer mass in the gelcast part. However, to the best of our knowledge, the electrical conductivity of gelcast part sintered in oxygen-free atmosphere is not well studied. In our previous study, we tried to sinter the gelcast part in nitrogen atmosphere, but the host alumina reacted with nitrogen in the presence of carbon to form aluminum nitride[4] and CO/CO_2 gas, thereby reducing the carbon network concentration. It is, therefore, suggested that a proper choice of sintering gas is the key point to avoid reactions; and hence, it improves essentially the electrical conductivity.

The present work, therefore, is undertaken to investigate the electrical conductivity of dense gelcast alumina ceramic that was sintered under inert atmosphere. This process could possibly change the gel polymer network in gelcasted sample into carbon network without reaction with the host alumina

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particles. This carbon network is expected to provide a well-continuous electrical conductive pathway through the alumina matrix in a small carbon concentration. To carry out the study, alumina-based slurries were gelcasted in a controlled *in situ* solidification process at room temperature. The resulting samples were carefully dried and sintered in argon gas. Physical characterizations were conducted to describe the observed electrical behavior.

2. Experimental procedure

2.1. Materials and chemicals

The starting powder was alumina (AL 160SG-4) with a mean particle size (D_{50}) of 0.60 μm. This was dispersed in a premix solution that was prepared by dissolving organic components in distilled water. A commercial ammonium salt of polycarboxylate (D-305, MW = 8000–10,000 g/mol) was used as a dispersant. This was supplied by Chukyo Yushi, Nagoya, Japan. The organic components were methacrylamide (MAM) as a monomer, and *N,N′*-methylenebisacrylamide (MBAM) as a cross-linker. The polymerization reaction was initiated using ammonium peroxodisulfate and catalyzed by *N,N,N′,N′*-tetramethylethylenediamine. All of the gelcasting chemicals were supplied by Wako Chemical, Osaka, Japan. The premix solutions in varying monomer content were prepared at 18.01 wt.%, 30.01 wt.%, and 38.98 wt.% relative to the mass of the solution. Then, the corresponding three slurries were prepared with identifying codes of S1, S2, and S3, which represent the increasing monomer content, the gelled, dried and sintered samples. Accordingly, the cross-linker was added at 20:1, 40:1, and 60:1 ratio relative to the monomer (MAM:MBAM), and the dispersant was about 0.30 wt.% based on powder mass. These premix compositions were employed since they were previously determined to give increased carbon yield without noticeable forming defects.[4]

2.2. Gelcasting procedure

Gelcasting slurries were prepared by adding alumina powder into polyethylene bottle with manual hand mixing. The solid loadings of about 52–55 vol.% were reached depending on the amount of monomer in the premix solutions. Further milling was conducted for at least 12 h in order to break down agglomerates and to improve the fluidity of the slurry. This was followed by vacuuming for 10 min, so that the trapped air bubbles were removed. The resulting slurries were added with initiator in 10% solution (1.03 μL/g) and catalyst (0.17 μL/g). The final slurry was poured into a Teflon mold with 10 rectangular cavities, so that it gelled into several test bars. The slurry was allowed to gel in the mould for 3 h at 25 °C under nitrogen atmosphere. The freshly gelled body was demolded and subjected to a controlled humidity drying for 4 days from 90% to 60% with 10% decrease per day. The dried bodies were sintered at 1100 °C, 1200 °C, 1300 °C and 1700 °C in argon atmosphere for 2 h. The heating rates were 1 °C/min until 600 °C and 4 °C/min until the desired high temperatures. Representative samples were re-sintered in an air at 1550 °C for 2 h for comparative evaluation.

2.3. Characterizations of physical properties

Electrical resistivity measurements were done using the van der Pauw's method with a square plate (6 mm × 6 mm × 2 mm) sample that was cut out from sintered test bar samples. Thin copper wires were used as an electrodes connected to four corners of the plate using silver paste. The contacts were adhered properly by heating at 150 °C for 4 h. Afterwards, two of the four electrodes were connected to a current source (Advantest, R6243) with a preset dc current of 0.5 mA. The other two electrodes were connected to a digital voltmeter (Advantest, R6551) so that the voltage was obtained manually. In this method, two consecutive measurements were performed by applying the current to two adjacent sides of the sample and the voltage was measured at each opposite side of the current contacts. These gave R_A and R_B from which the resistivity (ρ) of the sample was approximately calculated by the following equations[7,8]:

$$\rho = \left(\frac{\pi d}{\ln 2}\right)\left[\frac{R_\mathrm{A}+R_\mathrm{B}}{2}\right] f(R_\mathrm{A}, R_\mathrm{B}) \qquad (1)$$

$$f(R_\mathrm{A}, R_\mathrm{B}) \cong 1 - \left[\frac{(R_\mathrm{A}-R_\mathrm{B})}{(R_\mathrm{A}+R_\mathrm{B})}\right]^2 \left(\frac{\ln 2}{2}\right) - \left[\frac{(R_\mathrm{A}-R_\mathrm{B})}{(R_\mathrm{A}+R_\mathrm{B})}\right]^4 \times \left[\frac{(\ln 2)^2}{4} - \frac{(\ln 2)^3}{12}\right], \quad R_\mathrm{A} \geq R_\mathrm{B} \qquad (2)$$

where d thickness of the plate, R_A and R_B surface resistances, and the geometric factor $f(R_\mathrm{A}, R_\mathrm{B})$. The electrical conductivity change with respect to increasing temperature was determined in argon atmosphere using a heating rate of 5 °C/min until 600 °C. The current and voltage plot (*I–V* plot) was also conducted in order to observe the ohmic behavior of the material at room temperature. X-ray diffraction (Model RINT 1000, Rigaku, Cu Kα, 30 kV) was conducted to determine the phases responsible for the electrical conductivity. Scanning electron microscopy (JSM-6100, JEOL, Japan) was performed on sintered and re-sintered samples in order to gain insight on the conductive path due to carbon network. Bulk density was determined following the Archimedes principle. The flexural strength was carried out in three-point mode (span = 40 mm, cross-head speed = 0.5 mm/min). Furthermore, TGA/DTA analysis of sintered samples was conducted until 1400 °C at a rate of 10 °C/min with 100 ml/min flow of oxygen.

3. Results and discussion

3.1. Carbon content of sintered samples

The sintered gelcast part in argon atmosphere is considered as a composite of conductive carbon and alumina. The presence of pyrolyzed carbon serves as the continuous conductive path for allowing the current to flow, and the electrical conductivity depends solely on its concentration after successful

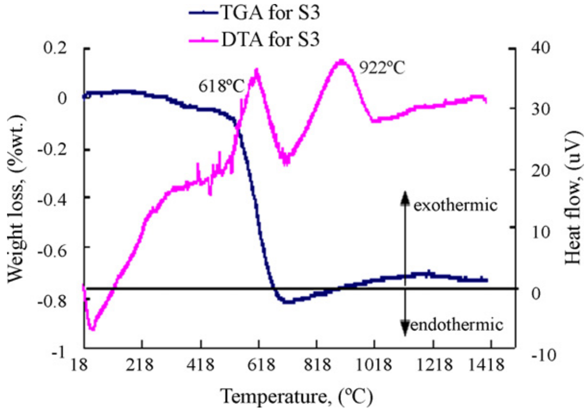

Fig. 1. TGA/DTA analysis of argon-sintered sample S3 conducted in oxygen atmosphere.

sintering. Thus, it is very important to determine the approximate amount of the pyrolyzed carbon using simultaneous TGA/DTA analysis[2,9] as typically shown in Fig. 1, using sample S3. It can be noted that there are two observable exothermic thermal events at 618 °C and 922 °C. The first event is due to the oxidation of surface carbon that is directly exposed to the oxidizing gas at above 600 °C, leaving a protective bed of aluminum oxide particles. Further heating at higher temperature with combination of gas diffusion process through the bed, the carbon at the bottom is completely oxidized above 900 °C.

The oxidation is depicted by a single weight loss in the temperature range of 200–700 °C, as can be seen in Fig. 1. From 700 °C to 1400 °C, the weight loss has gone approximately constant indicating that the oxidation happens at lower temperature. Accordingly, at 1400 °C with increasing monomer content, the pyrolyzed carbon, relative to the initial mass of the sintered samples for S1, S2, and S3, was about 0.34 wt.%, 0.58 wt.%, and 0.84 wt.%, respectively. These results suggest that only a very minute amount is required to effect a good electrical conduction using the current process as compared to introducing metallic component by mechanical mixing process.

Since the pyrolyzed carbon in the sintered gelcast sample is minimal, a proper selection of sintering gas is a necessity to avoid the reduction of carbon by chemical reaction. Takahashi[4] et al. reported that the use of nitrogen atmosphere caused the reaction of alumina with nitrogen in the presence of carbon to form AlN and CO/CO_2 gas, which led to a significant reduction of carbon. Thus, electrical resistivity was seriously increased to a more insulating material (about 10^6 Ω-cm). Therefore, with the use of appropriate sintering gas or the mixture of inert gases could possibly tailor the electrical conductivity from low to higher magnitude. In this study, the argon atmosphere is promising since it renders no reaction between the pyrolyzed carbon and the host alumina particles. This was confirmed using XRD analysis of sample S1, as shown in Fig. 2. All peaks pattern of argon-sintered samples were compared to identical sample sintered in air atmosphere. The comparison revealed that there was no difference in peaks of samples sintered from both gases, indicating that the carbon phase is an amorphous type.[10] Moreover, Fig. 2 gives us information that there are no other phase exists that may entail consumption of carbon in the form of gas; and thus, the continuous carbon network is preserved even at higher temperature, which is necessary for electrical conduction. This is supported with the lowest measured electrical resistivity (<1 Ω-cm) as shown in the following section.

3.2. Effect of sintering treatment on electrical conductivity

Four levels of sintering treatment on the gelcast samples were conducted using sample S1 at 1100 °C, 1200 °C, 1300 °C, and 1700 °C. Correspondingly, the measured electrical resistivities, at room temperature, were 1.94 Ω-cm, 0.73 Ω-cm, 0.51 Ω-cm, and 0.37 Ω-cm. It can be observed that the electrical resistivity decreases with sintering temperature. Thus, the sample S2 and S3 were sintered at 1700 °C, which both yielded the measured electrical resistivities of 0.23 Ω-cm and 0.18 Ω-cm.

It is evident above that increasing sintering treatment and monomer concentration decreases the measured electrical resistivity. This is attributed to the structural evolution of amorphous carbon,[12,13] which typically started at low temperature (about 500 °C) to a material having a continuously increasing fraction of graphite like structure at higher temperature. Associated with this evolution, the electrical conductivity increases because graphite is highly conductive compared to its amorphous phase.[5,10] The graphite phase appeared as precipitated region and depended on the available concentration of amorphous carbon. Hence, in this study, regardless of sintering condition, at increasing monomer dosages, the electrical conductivity increases due to a more precipitation of graphitic region. This region is known as graphene that was developed from the nucleation of free carbon within amorphous char in the form of small stacks of 2–3 polyaromatic layers with 1 nm in lateral extension piled up as plates in turbostratic order.[10,11] The increased concentration of the graphitic region is likely to occur above 1400 °C and strongly influences the rise in electrical conductivity. This is because of the fact that the localized states existing in the π bands as well as in the defect band inherent for noncrystalline phase disappear. This stage of disappearance is the so called non-metal–metal transition[12] that occurs at about 900 °C.

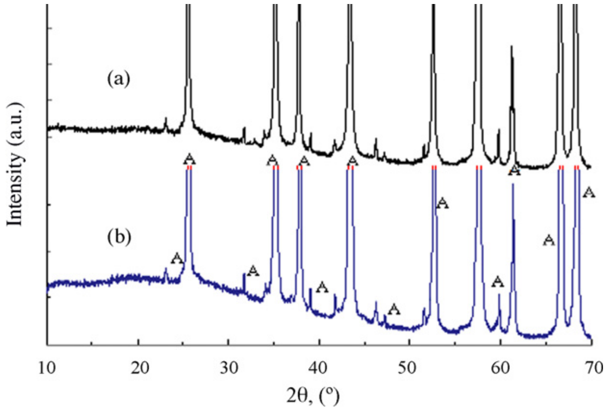

Fig. 2. XRD analysis of sample S1 sintered under different conditions for 2 h: (a) sintered directly in argon at 1700 °C and (b) sintered directly in air at 1550 °C (A=alumina).

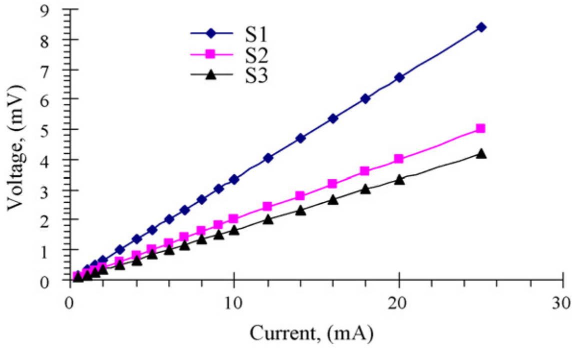

Fig. 3. The *I–V* characteristic of argon-sintered gelcast alumina at room temperature.

In the present study, it is believed that the above phenomenon has existed and contributed much to the increase in electrical conductivity. It is, therefore, suggested that further sintering of the sample above 1700 °C could convert the entire amorphous phase to graphite; and hence, the electrical conductivity will be improved.

3.3. Current and voltage behavior

The current and voltage characteristic was evaluated at room temperature for samples sintered at 1700 °C, as illustrated in Fig. 3. It can be observed that a linear relationship exists among all samples, which indicates a good contact between the electrodes and the tested materials. The linear trend is also an indicative of ohmic behavior for all samples tested in the current range from 0.5 mA to 25 mA. Moreover, there is a sensible deviation in the electrical resistance of sample S1 from S2 and S3. This might be attributed to the difference in concentration of conductive carbon networks as substantiated by the TGA analysis above.

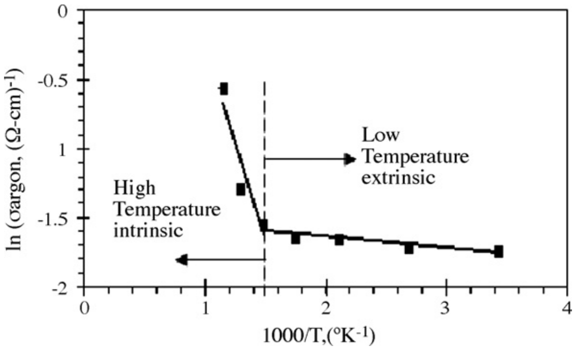

Fig. 4. Arrhenius plot of electrical conductivity of sample S1 from 25 °C to 600 °C in argon atmosphere.

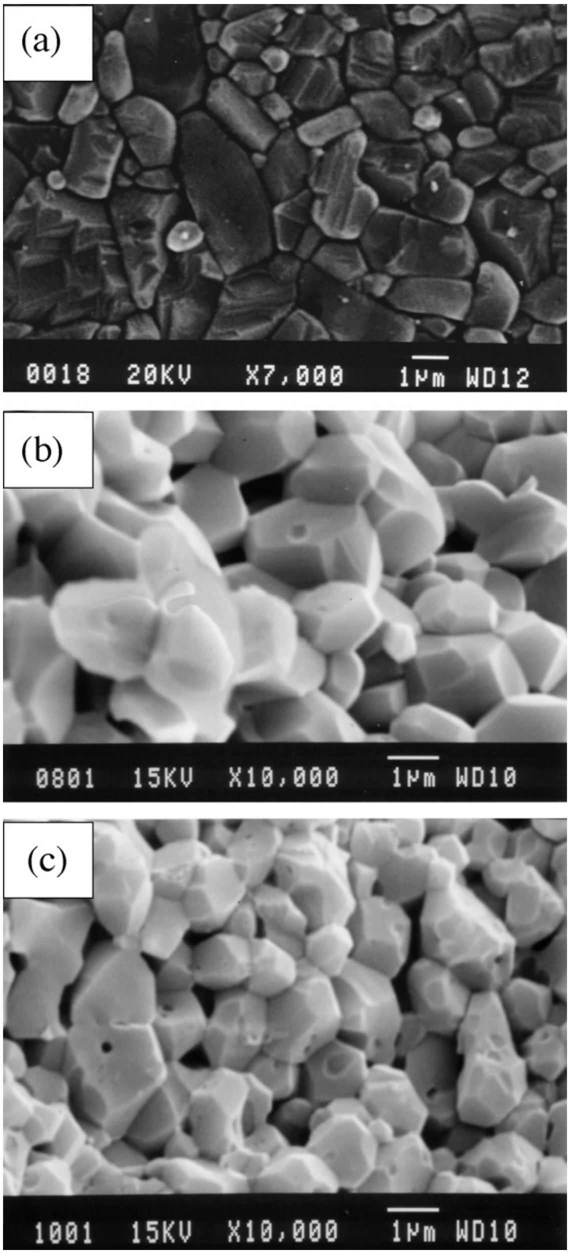

Fig. 5. SEM micrographs of sample S1 sintered under different conditions for 2 h: (a) sintered directly in air at 1550 °C; (b) sintered directly in argon at 1700 °C; (c) re-sintered in air at 1500 °C.

3.4. Electrical conductivity behavior with increasing temperature

The dependency of electrical conductivity on temperature was conducted in argon atmosphere using sintered sample S1, at a temperature range of 20–600 °C. This is illustrated in Fig. 4 exhibiting two regimes of Arrhenius behavior with distinctly different temperature dependency.[14] The observed Arrhenius behavior is typical for any amorphous conductive materials,[15,16] and this was corroborated with XRD analysis as discussed above. Experimental result like Fig. 4 can be described qualitatively well by[12]

$$\sigma = \sigma_o \exp\left[\frac{-E_o}{kT}\right] + \sigma_2 \exp\left[\frac{-\Delta W_2}{kT}\right] \quad (3)$$

where the coefficients σ_o, σ_2, E_o, and ΔW_2 are constants independent of temperature, and k Boltzmann constant. According to the Eq. (3), it can be assumed that, for amorphous phase, there are regions of energy in the lower and upper π bands where the localized states lie in the bands and are due to lack of long range order. In Fig. 4, at low temperature, there is an extrinsic regime that is governed by the presence of carbon as impurity of alumina. The conduction of electricity in this regime is may be due to the hole excitation that is modeled by the first term in Eq. (3) with an equivalent activation energy of about 0.17 kcal. At higher temperature, an intrinsic regime appears in a steeper temperature dependency since the activation energy includes both carrier hopping between the nearest neighbor of carbon and activation of charge carrier of alumina. This conduction process is best described by the second term in the Eq. (3), which involves carrier hopping between localized states near the Fermi energy. The hopping energy, ΔW_2, is equal to the order of half the width of the defect band that is about 5.57 kcal.

3.5. SEM analyses and physical properties

The effect of the presence of carbon on alumina microstructure was verified by SEM analysis of sintered S1 as shown in Fig. 5b. It can be observed that the grains of alumina are in polygonal morphology[17] along with few pores as compared with sample directly sintered in air (Fig. 5a). SEM analysis like Fig. 5a is typical for insulating alumina rendering better physical properties. Meanwhile, Fig. 5b shows clear evidence that the pyrolyzed carbon is residing along the grain boundaries and encapsulating every grain of alumina leading to the formation of the continuous conductive network. Encapsulation done by pyrolyzed carbon prevents the alumina grains in close approach, but it promotes densification process. This is because of the fact that carbon is a good inhibitor of grain growth by increasing the surface energy while reducing the grain boundary energy.[18] Although the densification process has occurred in our samples, the sintered density and strength are lower as compared with gelcast alumina sintered directly in air. The observed bulk densities for S1, S2, and S3 were 3.3 g/cm^3, 3.1 g/cm^3, and 3.0 g/cm^3, respectively. Accordingly, the measured strengths, corresponding to S1, S2, and S3, were 210.2 MPa, 174.7 MPa, and 124.7 MPa, respectively. The decrease in density and strength is simply attributed to the increasing concentration of carbon encapsulating the grain of alumina and the existence of pores that may be developed during processing stage. Nevertheless, the observed strength is strong enough for electrical applications and mechanical machining, which is much better than those of reported flexural strengths concerning carbon-based materials.[2,15,19]

In contrast, the sample S1 was re-sintered in air in order to gain insight into the conductive path due to carbon network. Virtually all spaces between grains are more open due to the oxidation of carbon as revealed in the SEM (Fig. 5c). The oxidation process kept the grains in polygonal morphology and left more interconnected open channels that were previously occupied by carbon. This further confirmed that the continuous carbon network was formed from the linkage of alumina grains that were completely encapsulated by pyrolyzed carbon, resulting to the continuous conduction path.[5]

4. Conclusion

Electrically conductive dense alumina has been successfully fabricated by inert sintering of dried gelcast dense body. The increase in monomer addition and sintering treatment significantly decrease the measured electrical resistivity. Using sample S1, the measured electrical resistivity is in the range from 1.94 Ω-cm to 0.37 Ω-cm, for sintering treatment from 1100 °C to 1700 °C. At 1700 °C with varying monomer addition, the measured electrical resistivity is about 0.37 Ω-cm to 0.18 Ω-cm. The material displayed ohmic characteristic in the tested current from 0.5 mA to 25 mA. Two regimes in Arrhenius plot were observed in the temperature range from 20 °C to 600 °C, which was conducted in argon atmosphere. All conduction processes in the temperature range tested were highly dominated by the presence of carbon. Moreover, the pyrolyzed carbon has caused the microstructure of alumina in polygonal morphology both in sintered and re-sintered state. This showed evidence of densification process while, at the same time, it confirms the existence of the continuous conductive paths in alumina matrix.

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