

New approach to provide an electrical conductivity to structural ceramics

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New approach to provide an electrical conductivity to insulator structural ceramics was suggested. In this concept, sintering additives form conductive network after sintering and result in a great reduction of amount of conductive phase addition compared with particle dispersion method generally used. Na⁺ ionic-conductive silicon nitride and Na⁺ ionic-conductive magnesia ceramics were successfully fabricated by this method.

Key words: Critical volume, Glassy Grain boundary phase, Ionic conductivity, Silicon nitride, Magnesia.

Introduction

To provide an electrical conductivity to insulator structural ceramics have been actively investigated to expand their applying area by replacement of electronic ceramics or metal products. It is also expected that high electrical conductivity brings them an improvement of machinability, which is one of the problems to be solved for structural ceramics, due to a probability to apply Electrical Discharge Machining (EDM) [1, 2]. In all attempts, conductive secondary phase "particles" were dispersed into the insulating matrix. Generally, TiN [3-6], SiC [7], and MoSi₂ [2] have been used as dispersed phases, where the electrical conductivity of composites increased according to percolation theory [8]. In the case of this method, massive addition, generally over 15 volume percent, is required to express enough conductivity, and it alters and governs the mechanical or physical properties of these ceramics. Here we will suggest the new approach to fabricate electrical-conductive structural ceramics by controlling the grain boundary phase with much less addition than particle dispersion method.

Theory

When conductive particles are dispersed into an insulator matrix and volume of the conductive phase increases from zero up to a critical volume fraction of percolation, one particle contact with neighbors and form finite conductive path in grain boundary, where

entire composite is insulating. Near the critical volume, infinite conductive network is formed and the resistivity of the entire composite abruptly decreases (insulator-conductor transition). To reduce the volume of dispersed phase, an approach by controlling the size of dispersed particles have been generally adopted. It is computationally and experimentally reported that the critical volume fraction changed according to the ratio between a radius of dispersed phase R_m and matrix particles R_p [9, 10]. R. P. Kusy [10] described the critical volume fraction V_c for conductive phase in terms of the particle size ratio as

$$N = N' + N''$$

$$V_c = \frac{1 + (N''/N')}{1 + (N''/N') + (1/N')(R_p/R_m)^3}$$

where N , N' and N'' are total number of dispersed particles, number of particles, which contribute to and which are redundant to forming conductive network, respectively. This indicates that the critical volume fraction of secondary phase can be decreased to a several percent by reducing the size of dispersed particles for constant size of matrix grains as illustrated in Fig. 1(a) and (b). However, at least about 10 vol% of addition was required due to experimental limitation for ceramic composites or nanocomposites until today.

In this research, we focused on grain boundary of ceramic materials, which can be considered as infinite network. Some of structural ceramics fabricated with sintering additives have residual grain boundary phases, which consist of glassy or crystalline phase. By controlling the composition of grain boundary phase to form electrical-conductive glassy grain boundary phase

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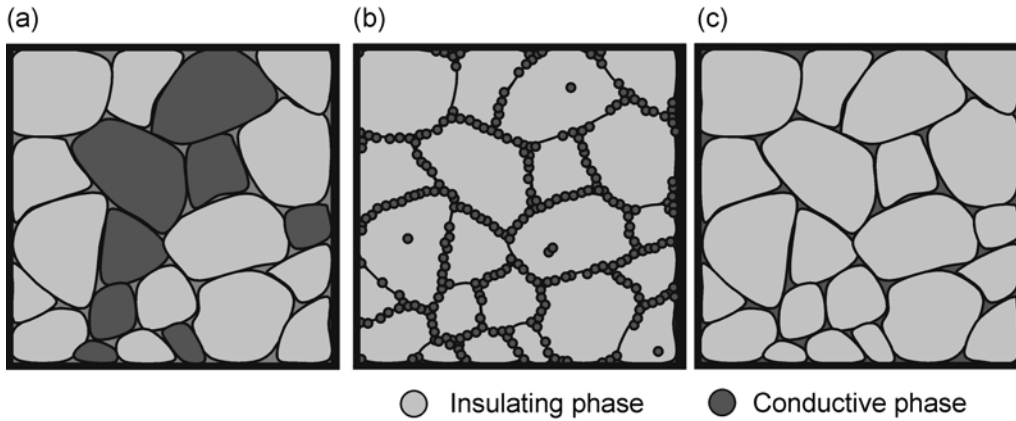


Fig. 1. Illustrations describing an influence of particle size ratio and a difference between conductive particle dispersion and conductive grain boundary phase. (a) Large size conductive particles are dispersed in insulator matrix ($R_m \approx R_p$). (b) Small particles are dispersed ($R_m \ll R_p$). (c) Conductive grain boundary phase is formed.

as shown in Fig. 1(c), it is certainly expected that the radius of conductive phase R_m can be reduced into near zero, resulting in an abrupt decrease of critical volume V_c , since the glassy phase is not aggregation of “particles.” In this concept, only sintering additives, which forms conductive glassy grain boundary phase after sintering, are required instead of conductive particles.

Experimental

Very fine α - Si_3N_4 (SN-E10, Ube Industries Co., Ltd., Ube, Japan) and MgO powder (500A, Ube Material Industry Ltd., Ube, Japan) with high purity were used as matrices. $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass, which is known as Na^+ -ion conductive glass [11, 12], was selected both to form liquid phase as sintering aids and to easily vitrify in Si_3N_4 and MgO ceramics. α - Al_2O_3 (>99.99% pure, Taimicron TM-DAR, Taimei Chemicals Co. Ltd., Nagano, Japan), Na_2CO_3 (>99% pure, KOJUNDO Chemical Laboratory, Saitama, Japan), which is a source of Na_2O , and SiO_2 (>99.9% pure, KOJUNDO Chemical Laboratory, Saitama, Japan) were used as sintering additives. These components were weight into a composition 90 Si_3N_4 (or MgO)/10 (40 Na_2O - 30 Al_2O_3 - 30 SiO_2 [mol%]) [wt%]. They were mixed by wet ball-milling in a polyethylene pot with ethanol for 24 hours. Then, the mixed powders were dried and crushed by dry ball-milling in the polyethylene pot for 24 hours to eliminate the agglomerates. These powders were packed into carbon mold with 20 mm in inside-diameter and sintered by a Pulsed Electric Current Sintering (PECS) (Dr. SINTERTM, SPS-2040, IZUMI TECHNOLOGY Co., Ltd., Hokkaido, Japan). The Si_3N_4 ceramics were sintered at 1600°C for 3 minutes under an applied pressure of 50 MPa in N_2 atmosphere. The MgO ceramics were sintered at 1300°C for 3 minutes under 30 MPa in Ar. The heating rate for all sintering was 100°C/min. As-sintered samples were ground by diamond

wheels and polished with diamond pastes to less than 1 mm in thickness.

Crystalline phases of sintered specimens were determined by XRD analysis.

The electrical conductivity was calculated from the resistance measured by two-terminal A.C. method between 100 and 1000°C at frequency of 10 kHz in air atmosphere by using LCR meter (HP-4284A, Hewlett Packard Co., USA). Before the measuring, platinum electrodes were pasted at the center of both side of specimens with 15 mm diameter and heat-treated at 700°C for 1 minute.

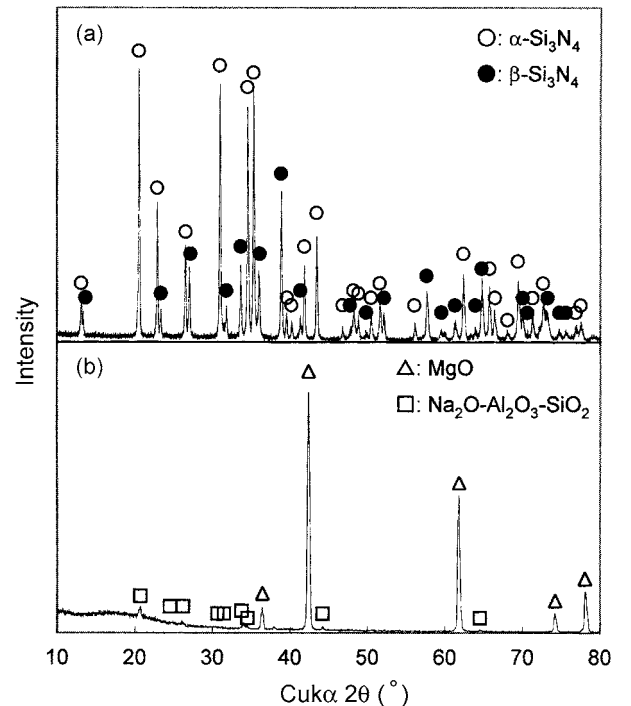


Fig. 2. XRD data for (a) $\text{Si}_3\text{N}_4/\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ceramics with 87:13 of α : β phase ratio and (b) $\text{MgO}/\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ceramics.

Table 1. Parameters describing the electrical conductivities.

Specimen	Electrical conductivity [$S \cdot cm^{-1}$]		Activation energy [$kJmol^{-1}$]
	100°C	1000°C	
$Si_3N_4/Na_2O-Al_2O_3-SiO_2$	2.6×10^{-8}	3.5×10^{-3}	57.2 (100-1000°C)
$Si_3N_4/Y_2O_3-Al_2O_3$ ^{a)}	3.3×10^{-10}	2.2×10^{-7}	21.4 (100-575°C) 81.6 (575-1000°C)
$MgO/Na_2O-Al_2O_3-SiO_2$	1.7×10^{-7}	1.8×10^{-3}	46.0 (100-1000°C)
MgO	^{-b)}	8.2×10^{-7}	70.1 (350-1000°C) ^{c)}

^{a)} 91 $Si_3N_4/6Y_2O_3-3Al_2O_3$ [mol%]

^{b)} An electrical conductivity at 100°C for MgO couldn't measure, since the conductivity was out of a measurement range of HP-4284A.

^{c)} Only one value was calculated for MgO, because it was difficult to decide whether the variation of electrical conductivity has flexion point or not.

Results and Discussions

Sufficiently densified materials are successfully fabricated by PECS for both Si_3N_4 and MgO ceramics. From XRD result for Si_3N_4 ceramics, only α - and β - Si_3N_4 were identified and no crystalline phase in grain boundary was determined as shown in Fig. 2(a). A broad bulge in the lower 2θ angle area of XRD data for MgO ceramics (see Fig. 2(b)) obviously indicates an existence of glassy grain boundary phase. In the case of MgO ceramics, some extent of glassy phase crystallized to $Na_2O-Al_2O_3-SiO_2$. It can be thought that a fast cooling of the PECS assisted to form these glassy grain boundary phases. The presences of ionic-conductive grain boundary phase in the $Si_3N_4/Na_2O-Al_2O_3-SiO_2$ ceramics were also confirmed by Transmission Electron Microscope (TEM) with Energy Dispersive X-ray Spectroscopy (EDS) [13].

The electrical conductivity and activation energy for both ceramics were indicated in Table 1. The data for $Si_3N_4/Al_2O_3-Y_2O_3$ and monolithic MgO were also listed for comparison. The values for $Si_3N_4/Na_2O-Al_2O_3-SiO_2$ ceramics were two orders of magnitude higher at 100°C and four orders of magnitude higher at 1000°C than those of $Si_3N_4/Y_2O_3-Al_2O_3$, respectively. And that for $MgO/Na_2O-Al_2O_3-SiO_2$ was about three orders of magnitude higher than monolithic MgO at 1000°C. This dramatic improvement suggests that the $Na_2O-Al_2O_3-SiO_2$ glassy phases were constructed as their grain boundary phases and Na^+ cation could carry charge through the glass network [13, 14]. In the variation of electrical conductivity for $Si_3N_4/Y_2O_3-Al_2O_3$ ceramics, activation energy in high temperature range was higher than that in low temperature range as well as the former report by Ohno, *et al.* [15]. On the other hand, the Si_3N_4 and MgO ceramics with $Na_2O-Al_2O_3-SiO_2$ additives showed no flexion point in the variation of conductivity, similarly to the $Na_2O_3-Al_2O_3-SiO_2$ glass [11]. The similarity of variation and values between these ceramics and pure glass clearly indicates that electrical properties of glassy phases, which formed in grain boundary, dominates those of entire materials fabricated by this method.

Summary

The Si_3N_4 and the MgO ceramics with Na^+ -ionic conductivity were successfully fabricated by controlling the composition of grain boundary phase. They showed much higher electrical conductivity compared with conventional Si_3N_4 and MgO ceramics. The advantage of this concept is a facility of the processing and that much lower addition is required to express the electric conductivity than the particle dispersion method.

As Si_3N_4 ceramic is generally sintered by using oxide additives due to its low sinterability and has residual glassy phase in the grain boundary, it was expected that it is relatively easy to form ionic-conductive glassy phase as the grain boundary. On the other hand, MgO ceramic can be easily fabricated without additives. The present result for $MgO/Na_2O-Al_2O_3-SiO_2$ ceramics indicates certain possibility that this concept can be applied to a number of matrices whether the matrices require sintering additives or not.

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