Electrical characterizations of Al$_2$O$_3$/ITO grain boundary composites

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ABSTRACT
To retain the advantageous properties of Al$_2$O$_3$ ceramics, their electrical conductivity must be controlled using a small amount of the conducting phase by pressure-less sintering in an air atmosphere. In this study, the electrical conductivity of Al$_2$O$_3$ ceramics was successfully increased from $10^{-16}$ to over $10^0$ S/cm by precipitating a small amount of indium tin oxide (ITO) grain boundary phase. An ITO phase of only 3-mol% (4.45 vol.%) was propagated three-dimensionally in pressure-less sintered Al$_2$O$_3$. Electric discharge machining (EDM) showed the machinability of electrically conductive Al$_2$O$_3$/3-mole% ITO grain boundary composites. Furthermore, the temperature dependency of the electrical conductivity was identified as metallic, exhibiting an electrical conductivity that decreases slightly with increases in measurement temperature, as observed in metals and ITO. The temperature dependence of the electrical conductivity of ITO was maintained in the Al$_2$O$_3$/ITO grain boundary composites.

1. Introduction
Sintered Al$_2$O$_3$ ceramics have been widely used in machine and electronic parts, such as mechanical sealings, crucibles, abrasives, and substrates, because of their excellent properties of high strength and hardness, high heat resistance, high insulating, and low material cost [1–8]. Low processing cost is also achieved as densification of the product is attained by pressure-less sintering in an air atmosphere. Recently, due to their good fluorine plasma resistance, Al$_2$O$_3$ ceramics have attracted attention as materials for electronic devices and semiconductor manufacturing equipment. To further expand their applications in the field of semiconductor manufacturing equipment, such as focus rings and shower plates, the conductivity of insulating Al$_2$O$_3$ ceramics must be increased from $10^{-16}$ S/cm to over $10^0$ S/cm.

In conventional particle-dispersed composites (Figure 1(a)), secondary conductive particles in excess of 12 vol% are required to provide electrical conductivity to insulating ceramics [9–14]. The addition of substantial numbers of the second-phase particles, however, has a negative impact on the excellent properties of matrix ceramics. Imparting electrical conductivity to insulating materials by adding a small conductive second-phase has recently been investigated. For insulating ceramics, it has been reported that a small amount of carbon nanotube (CNT) or graphene with an extremely anisotropic shape can create a conductive pathway [15–18]. Although a few volume% of graphite-derived materials can increase electrical conductivity, their composites must be sintered under uniaxial pressure in an inert atmosphere, which is a necessary process for sintering Al$_2$O$_3$ ceramics. A conductive oxide material should be selected as a secondary conductive phase to remove unnecessary processes. Conductive nonoxide materials, such as carbon nanotubes, graphene, SiC, and transition metal nonoxides [9–18], usually require an inert gas atmosphere for sintering.

Indium tin oxide (ITO) is one of the most widely used candidates for use in the conductive second phase, because it has a high conductivity of more than 10S/cm and can be sintered in an air atmosphere [19,20]. It has been reported, however, that a large amount (> 20 vol%) of the ITO phase is necessary to make insulating Al$_2$O$_3$ electrically conductive [21].

Our group recently reported that increasing the conductivity of a sintered body is achievable by transforming a small volume of the grain boundary phase from an insulating material to an electrically conductive material [22,23]. In our previous study [24], we successfully increased the electrical conductivity of insulating Al$_2$O$_3$ by sintering Al$_2$O$_3$/ITO composites at a relatively higher temperature than the sintering temperature of 1500°C commonly used for Al$_2$O$_3$, because it was found to be possible to penetrate the ITO liquid-phase at the grain boundaries between Al$_2$O$_3$ grains due to the lower melting point of ITO as compared to Al$_2$O$_3$, as shown in Figure 1(b). However, the electrical conductivity of $10^{-1}$ S/cm, achieved in the previous
research, is not sufficient for application to semiconductor processes because of the extremely low ITO content of <1.5 mol% (2.24 vol%).

In this study, improvement of the electrical conductivity of Al₂O₃/ITO composites was investigated by controlling the content of ITO and the composition of SnO₂ in ITO. The conducting pathways at the grain boundaries were identified by surface current distribution images obtained from scanning probe microscopy (SPM) and scanning electron microscopy (SEM) observations. Additionally, the influences of a small amount of the conductive ITO grain boundary phase on EDM and the temperature dependence of electrical conductivity were examined. Besides these electrical characterizations, fracture strength was also evaluated.

2. Materials and methods

2.1. Fabrication of samples

The ITO content (%) was increased from 0.5 to 3 mol%, while the weight ratios of SnO₂ in ITO were set at 0, 1, 2.5, 5, and 10%, corresponding to In₂O₃:0%Sn, In₂O₃:1%Sn, In₂O₃:2.5%Sn, In₂O₃:5%Sn, and In₂O₃:10%.
Sn in Figure 2, respectively. Al₂O₃ powder (L30, 4 N nano alumina, Anhui Junjing International Co., Ltd., China), In₂O₃ powder (INO02PB, Kojundo Chemical Laboratory Co., Ltd., Japan), and SnO₂ powder (SNO03PB, Kojundo Chemical Laboratory Co., Ltd., Japan) were dispersed in ethanol using an ultrasonic homogenizer (U200 controls, IKA, Germany) to mix these powders homogeneously without contamination. The dried mixture was uniaxially compacted into φ15 × 3 mm³ disks for electrical characterisation or into 47 × 36 × 6 mm³ rectangular bars for fracture strength measurement, and was cold pressed isostatically at 200 MPa. The powder compacts were put on an Al₂O₃ powder bed in an alumina crucible and sintered in an air atmosphere at from 1650°C to 1800°C for 5 min in an electric resistance furnace (Super Boy, Maruho Denki Co., Ltd., Japan).

2.2. Measurements

The crystalline phases of the sintered samples were identified by X-ray diffractometry (XRD) (Shimadzu Co., XRD-6100, Japan). SEM (JSM-7001 F, JEOL Ltd., Tokyo, Japan) and energy-dispersive X-ray (EDX) analyses were used to observe their microstructures and conduct a microchemical examination. At 25°C, the electrical conductivity of a sample with a conductivity of over 10⁻³ S/cm was measured using a four-pin method resistivity meter (Loresta-GP, Mitsubishi Chemical Analytech Co., Ltd., Japan). The DC electrical conductivity of an Al₂O₃/ITO composite with a conductivity of less than 10⁻³ S/cm was measured using an electrometer (Model 6517, Keithley, Ohio). At up to 200 V of applied voltage, a modified die-sinker EDM test was conducted on small holes drilled with a 1 mm diameter. The electrical resistivity distributions on the sample surface were visualized using a surface current image in the contact mode in conjunction with an SPM (SPM-9700, Shimadzu Co., Japan). The sample size for SPM observation was 2 mm × 3 mm × 1.5 mm. The sample surface was polished using diamond slurry with a particle diameter of 0.5 μm. In the SPM measurement, a conductive probe scanned the sample surface, and the current flowing through the probe to the sample mount stage was measured at a fixed DC bias of −10 V. Fracture strength was evaluated using a three-point bending test (Model Autograph AG-10TC, Shimadzu Co., Ltd., Japan). The specimen thickness, span length, and crosshead speed were 3 mm, 30 mm, and 0.5 mm/min, respectively. Their relative density was measured by the Archimedes method via immersion in toluene. The theoretical density was calculated using specific gravities of 3.97 for Al₂O₃ and 7.18 for ITO.

3. Results and discussion

3.1. Determination of sintering temperature for conductive Al₂O₃/ITO

For conductive Al₂O₃/ITO, the sintering temperature must be optimized. Figure 2(a) shows the XRD patterns of Al₂O₃/2 mol% In₂O₃ doped with 5 wt% SnO₂ (2 mol% In₂O₃:5%Sn) pressure-less sintered at 1650°C–1800°C for 5 min in air. Al₂O₃ and In₂O₃ were identified as crystalline phases in all Al₂O₃ sintered with In₂O₃ and SnO₂ at 1650°C–1800°C (Figure S1). SnO₂ forms an ITO solid solution with In₂O₃ [25]. The reduction of the peak intensity of ITO in Al₂O₃/ITO sintered at 1800°C is attributed to the high sintering temperature due to the volatilization of In₂O₃. Figure 2(b) indicates the relationships among the electrical conductivity, sintering temperature, and SnO₂ composition of Al₂O₃/2 mol% ITO composites. Al₂O₃/ITO composites sintered at temperatures below 1650°C remained insulators, but sintering at 1700°C enhanced their electrical conductivity. Thereafter, a small decrease in conductivity was recognized at a sintering temperature of 1800°C. As shown in the XRD profile of Al₂O₃/ITO sintered at 1800°C, it is thought that the conductivity was decreased by volatilization of In₂O₃ phase. Notably, the conductivity of Al₂O₃/2 mol% In₂O₃ without SnO₂ decreased from the sintering temperature of 1750°C to a greater extent than that of Al₂O₃/2 mol% In₂O₃ with SnO₂.

Figures 2(c,d) show how sintering temperature affects the morphology of the ITO phase. The ITO phase in Al₂O₃/ITO sintered at 1650°C was localized in the Al₂O₃ matrix, whereas, upon sintering at 1700°C, ITO penetrated between the Al₂O₃ grains to form a grain boundary phase. It is thought that molten ITO infiltrated into the grain boundaries at 1700°C by capillary force. Furthermore, EDX analysis of Al₂O₃ grains and grain boundary phases reveal that all trace amounts of SnO₂ were doped into In₂O₃ without any reaction with Al₂O₃ (Figure 2(e–g)). The ITO grain boundary phase of Al₂O₃/1 mol% ITO was mainly observed at the interfaces of the facial boundary [24], whereas the ITO phase in the Al₂O₃/2 mol% ITO grew at triple points rather than at two facial boundaries, as shown in the schematic of Figure 1(c). It can be considered that the fabricated conductive Al₂O₃ composite, including the ITO grain boundary phase, can be distinguished from conventional particle-dispersed composites as Al₂O₃/ITO grain boundary composites. Considering these results, a sintering temperature between 1700°C and 1750°C is appropriate to make Al₂O₃ electrically conductive using the ITO grain boundary phase. In this study, a sintering temperature of 1700°C was adopted to attain high conductivity in Al₂O₃/ITO composites with various SnO₂ compositions.
3.2. Effect of ITO composition on conductivity of Al₂O₃/ITO

Figure 3(a) plots the electrical conductivity of Al₂O₃/ITO composites with different compositions and ITO contents. The electrical conductivity increased with increases in ITO content. The Al₂O₃/3 mol% In₂O₃ doped with 5 wt% SnO₂ (3 mol% In₂O₃:5%Sn) indicated a high conductivity of 2 × 10⁹ S/cm, which was about one digit higher than that achieved in our previous work [24]. Doping with SnO₂ was more effective in enhancing conductivity than withholding doping. However, the optimal SnO₂ doping content for achieving high conductivity varied depending on the ITO content. At low ITO contents, doping with low wt% of SnO₂ increased the conductivity. Doping with 1 wt% SnO₂ enhanced the conductivity of Al₂O₃/1 mol% ITO which was not increased by doping with 2.5 wt% or above. In the Al₂O₃/3 mol% ITO, however, conductivity increased with increases in the doping content of SnO₂. As regards composites containing less than 1.5 mol% ITO, the effects of the ITO composition and microstructure on conductivity have been reported in our previous work [24].

Highly conductive materials with conductivities of about 1 × 10⁹ S/cm are considered capable of to be characterization by EDM [26]. As shown in Figure 3(b), it was possible to use EDM to produce an elaborate pattern of 51 holes measuring 1 mm in diameter in Al₂O₃/3 mol% In₂O₃:5%Sn containing 2.0 × 10⁹ S/cm. These penetration holes demonstrate that the ITO grain boundary phase propagates three-dimensionally in Al₂O₃ composites as thick as 1.5 mm. Although conventional insulating ceramics require a conducting particle content of above 17.5 vol% for EDM [27,28], a conducting grain boundary phase of only 4.45 vol% enabled the EDM of Al₂O₃.

3.3. Electrically conductive pathway

Figure 4 shows an atomic force microscopy (AFM) image, current distribution image, and superposition image for the electrically conductive Al₂O₃/2 mol% In₂O₃:10%Sn. The conducting pathway in the insulating Al₂O₃ matrix is visualized in Figure 4. Contact mode measurements were used to obtain the surface current distribution image because ITO has a high conductivity of 10⁹ S/cm. The current flowing between the upper and lower surfaces of the sample was measured using the three-dimensionally propagated ITO conductive pathways (Figure 4(d)). In the AFM height image (Figure 4(a)), Al₂O₃ grains and ITO grain boundaries
correspond to bright and dark areas, because portions of the ITO were more worn than Al₂O₃ by surface polishing. The current distribution image (Figure 4(b)) shows the surfaces of the low and high electrically conductive materials, corresponding to the blue and red areas, respectively. Analysis of the superposed image (Figure 4(c)) of the AFM height and current distribution images demonstrated that the ITO grain boundary phase acted as a conductive pathway in the insulating Al₂O₃ because of higher electrical conductivity of the ITO grain boundary phase as compared to that of the Al₂O₃ matrix. These results showed that three-dimensionally ITO conductive pathways were formed at the grain boundaries in the Al₂O₃ matrix by sintering Al₂O₃ with a small amount of In₂O₃ and SnO₂.

The electrical conductivity of ITO has a metallic temperature dependence that causes it to decrease with increases in the measurement temperature. The electrical conductivities of semiconductors and insulators such as Al₂O₃, however, increase with increasing measurement temperature. In conductive Al₂O₃/ITO grain boundary composites, the temperature dependence of conductivity can be expected to be metallic. Figure 5 shows the electrical conductivity of monolithic ITO and its composite and Si as a semiconductor in the range of 25°C to 500°C. The electrical conductivity of Si largely increased with increases in measurement temperature, whereas the conductivity of Al₂O₃/ITO composite and monolithic ITO slightly decreased, indicating metallic conductivity. It was found that the temperature dependence of ITO was maintained in a small amount of the grain boundary phase as a conductive pathway.

### 3.4. Fracture strength of conductive Al₂O₃/ITO composites

Mechanical properties, including fracture strength, are important for the use of electrically conductive Al₂O₃ in industrial equipment. Table 1 lists relative density, fracture strength, and electrical conductivities of monolithic Al₂O₃ and electrically conductive Al₂O₃/ITO composites fabricated by pressure-less sintering at 1700°C in air. The fracture strength of conductive Al₂O₃/ITO was slightly low compared with the general strength of 350 MPa determined for pressure-less sintered monolithic Al₂O₃ in air. Despite the addition of ITO with its low fracture strength, however, these conductive materials containing 2 mol% ITO or more maintained a high fracture strength close to that of monolithic Al₂O₃ made from L30 powder.

The 90.2% relative density of monolithic Al₂O₃ made from L30 powder was lower than the 99.8% of monolithic Al₂O₃ made from TM-DAR powder (TM-DAR grade, Taimei Chemical Co., Ltd., Tokyo, Japan), because L30 Al₂O₃ powder has poor sinterability. Pores in sintered bodies with low relative density decrease the influence of fracture strength and thus act as a fracture origin. Therefore, it is thought that Al₂O₃ made from L30 powder exhibits a slightly lower fracture strength than Al₂O₃ made from TM-DAR powder. For common brittle ceramics such as Al₂O₃, fracture strength can be estimated by the Griffith theory [29]. In this theory, increases in the size of initial flaws, such as cracks and pores, may decrease fracture strength. Additionally, in densified ceramic materials, the initial flaw size is also related to grain size. It is well known that a high sintering temperature introduces remarkable grain growth such as abnormal grain growth in sintered ceramics, decreasing fracture strength [30]. To maintain the high fracture strength in the electrically conductive Al₂O₃, it is necessary to inhibit grain growth of Al₂O₃ by sintering it at a temperature that can densify polycrystalline Al₂O₃ without excess heating. To form ITO grain boundary phase, however, a sintering temperature of 1700°C, which is higher than the conventional sintering temperature of

| Sample | Relative density (%) | Fracture strength (MPa) | Electrical conductivity (S/cm) |
|--------|----------------------|------------------------|------------------------------|
| 0 mol.%ITO | 90.2 | 301 ± 14 | 1.4 x 10⁻⁶ |
| 1 mol.%In₂O₃:1%Sn | 94.3 | 239 ± 8 | 3.3 x 10⁻³ |
| 2 mol.%In₂O₃:5%Sn | 92.4 | 271 ± 11 | 4.2 x 10⁻³ |
| 3 mol.%In₂O₃:10%Sn | 90.7 | 285 ± 5 | 2.0 x 10⁻⁴ |
| Al₂O₃, TM-DAR | 99.8 | 324 ± 15 | - |

(1) Monolithic Al₂O₃ made from Al₂O₃ powder (TM-DAR grade, Taimei Chemical Co., Ltd., Tokyo, Japan)
1500°C is needed. Therefore, the decrease in the fracture strength of Al₂O₃/ITO can be attributed to the increase in grain growth.

As shown in the observations of the fractured surfaces in Figure 6, monolithic Al₂O₃ with 0 mol% ITO consisted of fine grains, whereas the Al₂O₃/ITO composites exhibited large grain growth. The conductive composite monolithic ITO of less than 1 mol% was composed of large Al₂O₃ grains. Because trace amounts of In₂O₃ can react with Al₂O₃ [31], it is thought that a trace amount of In₂O₃ promotes grain growth in Al₂O₃. The residual In₂O₃, however, inhibits grain growth by Zener’s pinning effect [32]. It was expected that Al₂O₃ composites containing 1 mol% of weak ITO would attain high fracture strength. However, it was found that Al₂O₃ composites containing 3 mol% of ITO exhibited high fracture strength near to that of monolithic Al₂O₃. Because of the inhibition of grain growth of Al₂O₃ by the residual ITO phase the decrease in Al₂O₃ matrix grain size can reduce the size can reduce the size of initial flaws and prevent weak ITO phases from localization.

4. Conclusion

The Al₂O₃ with an ITO phase of only 3-mol% (4.45 vol. %), exhibited high electrical conductivity of more than 10⁸ S/cm, measured using holes drilled by EDM. Current flow analysis conducted by SPM showed that the conductive pathways in Al₂O₃ correspond to the ITO grain boundary phases. Although the amount of ITO in the composite is small, the metallic temperature dependence of the electric conductivity of ITO was maintained due to the conductive pathways of ITO. The fracture strength of the grain boundary composites decreased slightly, however, with the addition of ITO.

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No potential conflict of interest was reported by the author(s).

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