Mechanical strength and electrical conductivity of reactively-sintered pseudobrookite-type Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions

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Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions were synthesized by reactive sintering of α-Al$_2$O$_3$, TiO$_2$ anatase and MgCO$_3$ (basic) powders at 1400°C (and at 1300°C for some composition) for 2 h, with changing the MgTi$_2$O$_5$ to form the composition of Al$_{1-x}$Ti$_x$O$_5$–Mg$_{1-y}$O$_5$ (x = 0.0–1.0) and evaluated their properties. With increasing MgTi$_2$O$_5$ molar ratio, the matrix Al$_2$TiO$_5$–MgTi$_2$O$_5$ grains became more anisotropic, and the coefficient of thermal expansion increased due to the decrease of microcracks. Al$_{1.4}$Ti$_{1.5}$Mg$_{0.5}$O$_5$ (x = 0.9) showed the maximum strength of 47.9 MPa. On the other hand, MgTi$_2$O$_5$ (x = 1.0) showed low bending strength of 13.2 MPa due to the grain growth during the sintering at 1400°C. Al$_{1.4}$Ti$_{1.5}$Mg$_{0.5}$O$_5$ (x = 0.7) sintered at 1300°C indicated the highest conductivity. The conductivity of pseudobrookite-type ceramics strongly depends on microcracks.

Key-words : Reactive sintering, Mechanical properties, Electrical conductivity, Thermal expansion, Al$_2$TiO$_5$, MgTi$_2$O$_5$

1. Introduction

Al$_2$TiO$_5$ with pseudobrookite-type structure has been widely studied because of (a) its low coefficients of thermal expansion (CTE), (b) its high melting point and (c) its high thermal shock resistance. Since low thermal expansion materials are necessary under some specific high-temperature applications, such as a thermistor and a heat exchanger, pseudobrookite-type ceramics are widely used for these devices. The low CTE of Al$_2$TiO$_5$, however, is attributed to microcracks caused by anisotropic thermal expansion under cooling from the sintering temperature. Therefore, sintered Al$_2$TiO$_5$, usually not fully dense, generally shows low fracture strength.

Bayer reported that the CTE of pseudobrookite-type Al$_2$TiO$_5$ for each crystalline axis (space grope: Cmcm) were $\beta_a = -3.0 \pm 0.3$, $\beta_b = 11.8 \pm 0.6$, $\beta_c = 21.8 \pm 1.1$ (×10$^{-6}$/°C) in a temperature range of 20–1020°C. The CTE of polycrystalline Al$_2$TiO$_5$ ceramics, however, was rather small as an oxide, typically reported as <2.0 × 10$^{-6}$/°C. Despite the fascinating low thermal expansion behavior, Al$_2$TiO$_5$ is not so thermally stable and decomposes into Al$_2$O$_3$ and TiO$_2$ below the equilibrium temperature of 1280°C, which limits the applications of Al$_2$TiO$_5$, particularly in reducing atmosphere.

Besides Al$_2$TiO$_5$, several ceramics with pseudobrookite-type structure, such as MgTi$_2$O$_5$ and Fe$_2$Ti$_2$O$_7$ were investigated. Solid solutions of pseudobrookite-type structure (e.g. Al$_{1-x}$Fe$_x$Ti$_2$O$_7$) and others have also been synthesized and their CTE, thermal stabilities and microstructures have been reported. MgTi$_2$O$_5$ with pseudobrookite-type structure has potentially good mechanical properties with high thermal shock resistance, because its thermal expansion anisotropy is smaller than Al$_2$TiO$_5$. To date, MgTi$_2$O$_5$ has been investigated for a third-generation diesel particulate filter with low cost, high temperature stability and better mechanical properties than Al$_2$TiO$_5$. MgTi$_2$O$_5$ can be synthesized in an intermediate temperature range of 1000–1200°C because of relatively high temperature stability among pseudobrookite-type ceramics. MgTi$_2$O$_5$ stabilizes the crystal phase of Al$_2$TiO$_5$ by forming an all-proportional solid solution. Therefore MgTi$_2$O$_5$ has been used as a stabilizer of Al$_2$TiO$_5$ in order to restrain the decomposition of Al$_2$TiO$_5$ in a temperature range of 750–1300°C (decomposition temperature of MgTi$_2$O$_5$ is 130–230°C). For these reasons, Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solution with intermediate feature between Al$_2$TiO$_5$ and MgTi$_2$O$_5$ has been studied as low CTE material with relatively high fracture strength.

As for Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions, there have been several studies on CTE and microstructures. However, relatively few studies have been reported on the functional properties of pseudobrookite-type ceramics, such as dielectric properties, photocatalytic function and electrical properties. In this study, we have synthesized Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions from α-Al$_2$O$_3$, TiO$_2$ anatase and MgCO$_3$ (basic) powders by reactive sintering method, with changing the MgTi$_2$O$_5$ ratio to form the composition of Al$_{1-x}$Ti$_x$O$_5$–Mg$_{1-y}$O$_5$ (x = 0.0–1.0) and evaluated their properties. First, CTE and fracture strength of Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions (7 compositions including end members) were systematically characterized. Second, electrical conductivity of these Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions were also systematically measured by AC impedance method. For the pseudobrookite-type MgTi$_2$O$_5$–O$_5$ (x = 0.2, 0.3, 0.5, 0.8 and 0.9), a systematic analysis of electrical conductivity at 800°C was carried out by Steiner et al. However, such a systematic analysis on the Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions has not yet been reported. Temperature dependence of electrical properties was discussed for a solid solution with the highest conductivity.

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2. Experimental

2.1 Sample preparation

Commercial α-Al2O3 (99.99% purity, Taimei Chemicals Co. Ltd., Saitama, Japan), Ti2O anatase (99% purity, Kojundo Chemical Laboratory Co. Ltd.) and MgCO3 (basic) (99.9% purity, Kojundo Chemical Laboratory Co. Ltd., with actual composition of Mg3(CO3)2(OH)2·4H2O) powders were used as starting materials. MgCO3 (basic) includes hydroxyl groups and hydrated water. Hence, prior to the powder mixing, each starting powder was characterized by thermogravimetry-differential thermal analysis (TG-DTA) to clarify the weight-loss during the heating up to 1000°C. Required powder weight was corrected using the TG-DTA results. α-Al2O3, Ti2O anatase and MgCO3 (basic) powders were weighed according to the final compositions of Al2TiO4–MgTi2O5 solid solutions, expressed as Al2(1–x)Ti1+xMg0.5O5, where x is the molar ratio of MgTi2O5. The powders were mixed by wet ball-milling with ZrO2 media for 2 h using ethanol. The slurries were dried in an evaporator, and then, dried at 80°C in air. The dried powders were dry ball-milled with ZrO2 balls for 2 h, and were sieved through a 150-mesh screen. Cylindrical pellets (diameter of 15 mm) and rectangular bars (4 × 6 × 50 mm) were prepared by the uniaxial press of mixed powders. The slurries were dried in an evaporator, and then, dried at 80°C in air over the frequency range of 5 Hz to 13 MHz. A K-type thermocouple was placed in the tubular furnace to monitor the temperature vicinity to the pellet. Prior to the temperature measurement, the temperature was kept at the target temperature for 20 min to stabilize the sample temperature.

2.2 Phases and microstructure

Constituent phases of sintered Al2TiO4–MgTi2O5 solid solution samples were analyzed by X-ray powder diffraction (MultiFlex, Cu-Kα, 40 kV and 40 mA, Rigaku, Japan). Prior to the powder XRD measurement, the sintered samples were pulverized with an agate mortar using ethanol, and the XRD patterns were collected in the range of 2θ = 10–70°. ICDD-JCPDS database was used for identifying constitution phase and indexing pseudobrookite phase.

Microstructure of the samples was observed by scanning electron microscopy (TM3000 Table Microscope, Hitachi, Japan). The samples were coated with Au by sputtering (SC-701, 3.5 mA for 5 min, Sanyu Electron, Japan). In order to evaluate the size of microcracks, mirror surfaces polished with 9, 3 and 0.5 µm diamond slurries were observed. Energy dispersive X-ray spectrometry (EDS) was carried out for an elemental analysis of the surfaces of the sintered samples.

2.3 Density and mechanical properties

The bulk densities of the sintered samples were measured by mass and dimensions. For CTE measurement, the sintered rectangular bars were machined into the test pieces (the length of measured direction is 10–20 mm) with waterproof abrasive papers. The CTE was evaluated by thermomechanical analysis (Thermo plus EVO II, RIGAKU, Japan) in a temperature range of 50–1000°C.

In order to evaluate fracture strength, sintered rectangular bars were machined into the test specimens. The tensile face and corners of each specimen were polished and chamfered by waterproof abrasive paper. Fracture strength was measured by three-point bending test with a span of 30 mm and crosshead speed of 0.5 mm/min by using a universal testing machine (Autograph AG-20KN, Shimadzu Co. Ltd., Japan). Three to five specimens were used for each measurement.

2.4 Electrical properties

The surfaces of the sintered pellets were polished by waterproof abrasive paper to enhance electrode adhesion. Platinum paste electrodes and platinum wires were attached to the surfaces of sintered pellets and heated up to 1200°C for 1 h. The pellet was positioned in the center of a tubular furnace. Impedance spectra were measured at 750–1000°C in air over the frequency range of 5 Hz to 13 MHz. A K-type thermocouple was placed in the tubular furnace to monitor the temperature vicinity to the pellet. Prior to the temperature measurement, the temperature was kept at the target temperature for 20 min to stabilize the sample temperature.

3. Results and discussion

3.1 Phases and microstructure

Figure 1 shows XRD patterns of the samples with the composition of Al2(1–x)Ti1+xMg0.5O5, where x is the molar ratio of MgTi2O5, obtained by reactive sintering at 1400°C for 2 h. By using the calibrated starting powder, XRD data of all samples sintered at 1400°C represented single Al2TiO4–MgTi2O5 solid solution [pseudobrookite-type phase, space group: Cmcn(63)]. The Al2(1–x)Ti1+xMg0.5O5 (x = 1.0, i.e. MgTi2O5) sample was composed of only pseudobrookite-type phase. The Al2(1–x)Ti1+xMg0.5O5 (x = 0.0, i.e. Al2TiO3) sample was composed mainly of pseudobrookite-type phase with trace of Al2O3 and Ti2O3 phase. The easier formation of pseudobrookite-type MgTi2O5 (formable at 920°C) can be attributed to the smaller size-difference between Mg2+ ion and Ti4+ ion than the size-difference between Al3+ ion and Ti4+ ion. The Al2(1–x)Ti1+xMg0.5O5 (x = 0.1) sample, despite low molar ratio of MgTi2O5, was composed of only pseudobrookite-type phase, because of the decrease in distortion of MgO octahedra, due to the substitution of metal ions (2Al3+→Mg2++Ti4+).15

Figure 2 exhibits typical SEM images of the surfaces of Al2(1–x)Ti1+xMg0.5O5 (x = 0.1, 0.3, 0.7 and 1.0) samples with Au coating. The increases of grain size and densifications with increasing MgTi2O5 molar ratio were confirmed. With increasing MgTi2O5 molar ratio, the matrix Al2TiO4–MgTi2O5 grains became more anisotropic. The grain size and anisotropy depended on the molar ratio of Al2TiO3: MgTi2O5. MgTi2O5 solid solution [pseudobrookite-type phase, space group: Cmcm(56)] showed XRD patterns of the samples with the composition of Al2(1–x)Ti1+xMg0.5O5, obtained by reactive sintering at 1400°C for 2 h. By using the calibrated starting powder, XRD data of all samples sintered at 1400°C represented single Al2TiO4–MgTi2O5 solid solution [pseudobrookite-type phase, space group: Cmcn(63)]. The Al2(1–x)Ti1+xMg0.5O5 (x = 1.0, i.e. MgTi2O5) sample was composed of only pseudobrookite-type phase. The Al2(1–x)Ti1+xMg0.5O5 (x = 0.0, i.e. Al2TiO3) sample was composed mainly of pseudobrookite-type phase with trace of Al2O3 and Ti2O3 phase. The easier formation of pseudobrookite-type MgTi2O5 (formable at 920°C) can be attributed to the smaller size-difference between Mg2+ ion and Ti4+ ion than the size-difference between Al3+ ion and Ti4+ ion. The Al2(1–x)Ti1+xMg0.5O5 (x = 0.1) sample, despite low molar ratio of MgTi2O5, was composed of only pseudobrookite-type phase, because of the decrease in distortion of MgO octahedra, due to the substitution of metal ions (2Al3+→Mg2++Ti4+).15

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temperature, pseudobrookite-type structure became more stable for solid-solutions, resulting more rapid and more anisotropic grain growth with increasing MgTi2O5 content.

EDS elemental analysis was carried out on the surface of uncoated samples. Table 1 summarizes atomic percent of Al2(1−x)Ti1+xMg0.9O5 (x = 0.1−1.0) solid solutions sintered at 1400°C for 2 h. The full density of each composition was calculated by the Vegard’s law.

### 3.2 Density and mechanical properties

Figure 3 shows relative density as a function of composition [Al2(1−x)Ti1+xMgO5 (x = 0.0−1.0)] obtained by reactive sintering at 1400°C for 2 h. The relative densities of Al2(1−x)Ti1+xMgO5 (x = 0.1−1.0) were much higher than that of Al2(1−x)Ti1+xMgO5 (x = 0.0). Al2(1−x)Ti1+xMg0.9O5 (x = 0.9) sintered at 1400°C showed the highest relative density, 92.6%.

Figure 4 represents CTE as a function of composition [Al2(1−x)Ti1+xMgO5 (x = 0.0−1.0)]. Al2(1−x)Ti1+xMgO5 (x = 0.1−0.3) exhibits relatively low thermal expansion values and Al2(1−x)Ti1+xMgO5 (x = 0.0−0.1) showed negative thermal expansion behavior up to 950°C. Thermal expansion increased with increasing MgTi2O5 ratio due to decrease of microcracks. Al2(1−x)Ti1+xMgO5 (x = 0.0), however, did not represent the lowest thermal expansion. In our previous work,30 we revealed that secondary phase dispersion is effective to reduce the Al2TiO5 matrix grain size and to reduce the strong anisotropy of Al2TiO5, which resulted in fewer microcracks. In the XRD result, Al2(1−x)Ti1+xMg0.9O5 (x = 0.9) was mainly composed of pseudobrookite-type phase with some Al2O3 and TiO2 phases. Therefore, coexisted Al2O3 and TiO2 grains probably inhibited the anisotropic grain growth of Al2TiO5.

Figure 5 shows bending strength as a function of composition [Al2(1−x)Ti1+xMgO5 (x = 0.0−1.0)]. Al2(1−x)Ti1+xMgO5 (x = 0.0) indicated 8.1 MPa. Bending strength of Al2(1−x)Ti1+xMgO5 (x = 0.0−0.9) increased with increasing MgTi2O5 ratio due to the decrease of microcracks. Al2(1−x)Ti1+xMg0.9O5 (x = 0.9) showed the maximum strength of 47.9 MPa. On the other hand, MgTi2O5
In this work, Al1.8Ti1.1Mg0.1O5 \((x = 0.9, 1.0)\) solid solutions sintered at 1400°C for 2 h: (a) \(x = 0.9\) and (b) \(x = 1.0\).

\((x = 1.0)\) showed very low bending strength of 13.2 MPa due to the grain growth during the sintering at 1400°C, despite its high relative density and high CTE. The low strength of MgTi2O5 is attributable to the crack growth accompanied by the grain growth, as shown in Fig. 6, which shows mirror surfaces of Al2(1-x)Ti1-xMg0.7O5 \((x = 0.9, 1.0)\) solid solutions sintered at 1400°C.

### 3.3 Electrical properties

Figure 7 shows the electrical conductivity as a function of composition \([\text{Al}_{x} \text{Ti}_{1-x} \text{Mg}_{0.7} \text{O}_{5}] (x = 0.0–1.0)\) at 1000°C in air. In this work, Al1.8Ti1.1Mg0.1O5 \((x = 0.1)\) indicated the lowest conductivity, and Al0.6Ti1.7Mg0.7O5 \((x = 0.7)\) indicated the highest conductivity. This complicated conductivity dependence is attributable to (1) grain size, (2) secondary phases \((x = 0, \text{i.e.} \text{Al}_{2} \text{O}_{3} \text{and TiO}_{2} \text{dispersion})\), (3) large microcracks for small grains \((x = 0.9\) and 1.0), and (4) density change (Fig. 3).

Since the composition of Al0.6Ti1.7Mg0.7O5 \((x = 0.7)\) showed the highest conductivity, we focused on this composition in the following part. In order to examine the effect of sintering temperature on the conductivity, the sample was also sintered at 1300°C as well as 1400°C. By lowering the sintering temperature (from 1400 to 1300°C), the sample had smaller grain size and hence smaller microcracks, as well as somewhat smaller density.

Figure 8 shows typical surface SEM images of Al0.6Ti1.7Mg0.7O5 \((x = 0.7)\) samples sintered at (a) 1400°C and (b) 1300°C. XRD (not shown) confirmed that the Al0.6Ti1.7Mg0.7O5 \((x = 0.7)\) sample sintered at 1300°C was also composed of single pseudobrookite-type phase. The sample sintered at 1300°C had a bi-modal structure, i.e., anisotropic large grains and anisotropic small grains (shown in the inset). The relative density of Al2(1-x)Ti1-xMg0.7O5 \((x = 0.7)\) samples sintered at (a) 1400°C and (b) 1300°C were 90.7 and 88.6%, respectively.

Figure 9 represents Cole–Cole plots of Al0.6Ti1.7Mg0.7O5 \((x = 0.7)\) sintered at (a) 1400°C and (b) 1300°C, measured over the frequency range 5 Hz to 13 MHz at temperature between 750–900°C in air. Two semicircular arcs, one with high frequency and another with low frequency, can be observed. The one with high frequency and the other one with low frequency corresponds to grain and grain boundary, respectively. The total resistivity of the sample sintered at 1400°C was higher than that of sintered at 1300°C at each measuring temperature, and each semicircular arc (grain and grain boundary) showed decrease in resistivity with increasing measuring temperature. The grain-boundary resistivity of the sample sintered at 1400°C was higher in spite of less grain boundaries than that of sample sintered at 1300°C.

The results in Fig. 9 suggest that conductivity of pseudo-brookite-type ceramics strongly depends on microcracks. Several researchers reported that microcracks show crack healing at high temperature. The decrease of grain-boundary resistivity at high measuring temperatures is attributed to microcrack-healing behavior. For example, the grain boundary resistivity of the sample sintered at 1300°C had little effect on total resistivity at 900°C [see the insert of Fig. 9(b)]. The reason of small grain-boundary resistivity at 900°C can be explained as follows. According to the Bayer’s report, the average CTE \((20–1020°C)\) of Al2TiO5 single crystal and MgTi2O5 single crystal were calculated as 10.2 × 10⁻⁶ and 9.67 × 10⁻⁶/K, respectively. While in this study, the measured CTE at 900–1000°C of the samples sintered at 1400 and 1300°C were 5.23 × 10⁻⁶ and 8.90 × 10⁻⁶/K, respectively. The value of 5.23 × 10⁻⁶/K for the sample sintered at 1400°C is clearly smaller than that of the calculated values of ~10 × 10⁻⁶/K and that of the sample sintered at 1300°C. Thus, the sample sintered at 1400°C still contained open microcracks at 900°C, while a plenty of microcracks of the sample sintered at 1300°C seem to be closed at 900°C.

Arrhenius plots of the conductivity and electrical properties of Al0.6Ti1.7Mg0.7O5 \((x = 0.7)\) sintered at (a) 1400°C and (b)
1300°C are shown in Fig. 10 and Table 2. The activation energy (eV) in grain of samples sintered at 1400 and 1300°C were 3.9 and 3.6, respectively, while the activation energy in grain boundary of samples sintered at 1400 and 1300°C were 4.9 and 4.5, respectively. The sample sintered at 1400°C hence showed somewhat stronger temperature dependence than that at 1300°C. This result also suggested the increase of the amount of microcracks with increasing sintering temperature. In this study, the activation energy in grain boundary was higher than that in grain. Since the microcracks were mainly formed at grain boundaries, temperature dependence of the conductivity became more sensitive at grain boundary than in grain. These results are in good agreement with the microcrack-healing behavior explained for Fig. 9.

4. Conclusions

In this work, the properties of Al₂TiO₅–MgTi₂O₅ solid solutions can be summarized as follows:

1. Except Al₂(1–x)Ti₁+xMgₓO₅ (x = 0.0, i.e. Al₂TiO₅), all samples sintered at 1300–1400°C were composed of single pseudobrookite-type phase. For Al₂TiO₅, a small amount of unreacted Al₂O₃ and TiO₂ were detected.

2. The increases of grain size and densifications with increasing MgTi₂O₅ molar ratio were confirmed. Also thermal expansion increased with increasing MgTi₂O₅ ratio.

3. Al₁₀.₂Ti₉.₈Mg₀.₉O₅ (x = 0.9) showed 47.9 MPa as maximum strength. On the other hand, MgTi₂O₅ (x = 1.0) showed low bending strength (13.2 MPa) despite its high relative density and high CTE.

4. Al₁₀.₆Ti₇.₇Mg₀.₇O₅ (x = 0.7) sintered at 1300°C indicated the highest conductivity. The conductivity of pseudobrookite-type ceramics strongly depend on microcracks.

Table 2. Electrical properties of Al₁₀.₆Ti₁.₇Mg₀.₇O₅ solid solutions sintered at 1400 and 1300°C

| Sintering temperature (°C) | Relative density (%) | Conductivity σ₁⁰⁰₀×10⁻¹ S/cm | Conductivity σ₁⁰⁰₀×10⁻⁹ S/cm | Eₐ(eV) |
|---------------------------|----------------------|-----------------------------|-----------------------------|-------|
| 1400                      | 90.7                 | 42.1                        | 8.9                         | 3.9   |
| 1300                      | 88.6                 | 46.5                        | 10.3                        | 3.6   |

Eₐ: activation energy (G: grain, GB: grain boundary).
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