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Manufacture and mechanical properties of magnesium potassium titanate short fiber/glass composite

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Abstract—We generated a composite of short magnesium potassium titanate fibers ($K_2MgTi_7O_{16}$) and glass by calcining hydrated potassium tetratitanate fibers/non-swelling synthetic fluorine mica with a mass ratio of 7 : 3 at calcination temperatures of 1000°C or higher for 1 h. The sintered density and bending strength of the $K_2MgTi_7O_{16}$ obtained was 79% and 27 MPa, respectively, at a calcination temperature of 1100°C. We also isolated magnesium potassium titanate fibers approximately 3 μm in diameter by treatment with a 5% fluoric acid solution for 30 min.

Keywords: Potassium tetratitanate fibers; potassium pridelite; magnesium potassium titanate fibers; KDC method; non-swelling synthetic fluorine mica.

1. INTRODUCTION

Since it is easy to produce short fibers of alkali-metal titanate compounds, they may find use as filling materials for FRP or FRM composites in automobile components. Among the alkaline-metal titanate compounds, potassium hexatitanate ($K_2Ti_6O_{13}$) fibers are being widely used as reinforcing materials for plastics [1]. To date, potassium hexatitanate fibers used for reinforcement have been produced by the conversion of potassium tetratitanate ($K_2Ti_4O_9$) fibers which are converted either by calcination or flux into potassium hexatitanate ($K_2Ti_6O_{13}$) fibers [2]. Potassium tetratitanate fibers are not used as reinforcing materials for ceramics because of their low mechanical strength, but they have advantages because of their low cost and ease of synthesis. However, since potassium hexatitanate fibers contain water-soluble potassium, their applications in polyester resins, in which the effects of dissolved potassium must be avoided, have been restricted.

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Ceramic whiskers consisting of needle-like monocrystals of magnesium potassium titanate [3] short fibers are expected to have characteristics such as high strength, high elasticity, superior wear resistance and heat resistance, and low dissolution of potassium; accordingly, they may be expected to be used as materials having light weight, low energy consumption and high performance.

At present, methods such as the flux method by Fujiki *et al.* are used for the synthesis of magnesium potassium titanate short fibers [4]. However, no studies have been reported regarding the strength of porous sintered bodies of magnesium potassium titanate short fibers.

In this study, we adopted a unique synthetic method in which a mixture of hydrated potassium tetratitanate fibers and non-swelling synthetic fluorine-mica is fired, after which we attempted to synthesize porous ceramics having a whisker frame structure of potassium pridelite fiber without using complex procedures [3, 5–7]. In addition, we measured the mechanical properties of a composite of magnesium potassium titanate fiber and glass, which was obtained during this synthetic procedure. Furthermore, we succeeded in isolating magnesium potassium titanate short fibers.

2. EXPERIMENTAL METHODS

2.1. Agents

Potassium tetratitanate fibers were synthesized using the KDC method [8] and immersed in water to obtain their hydrates ($K_2Ti_4O_9 \cdot 2.2H_2O$). This results in short fibers with diameters of 2–2.5 μm and lengths of 40–100 μm. Non-swelling synthetic fluorine mica (Coop Chemical Co., Ltd.) was used; its composition was Si: 20.86, Mg: 14.91, K: 3.48, Al: 0.08, Fe: 0.04, O: 56.47 and F: 4.16 (mol%), and the mean particle diameter was approximately 10 μm. High purity ethanol was used as a dispersing medium. Figure 1 shows scanning electron microscopy (SEM) images of the hydrated potassium tetratitanate fibers and the synthetic fluorine mica.

2.2. Synthesis

The hydrated potassium tetratitanate fibers and non-swelling synthetic fluorine mica were mixed at mass ratios ranging from 9 : 1 to 5 : 5 using an ultrasonic mixer with ethanol as a dispersing medium for 4 min, then dried at 80°C for 24 h. The resulting powder was formed under a uniaxial pressure of 62.1 MPa, then calcined at 900–1100°C for 1 h. To prevent deformation of specimens, calcination was performed by embedding the specimens into a zirconia ball 1 mm in diameter.

2.3. Measurement

The crystal phase of the sintered bodies was identified by a powder X-ray diffractometer (RINT-1500, Rigaku Denki). The surface of the sintered bodies was ob-

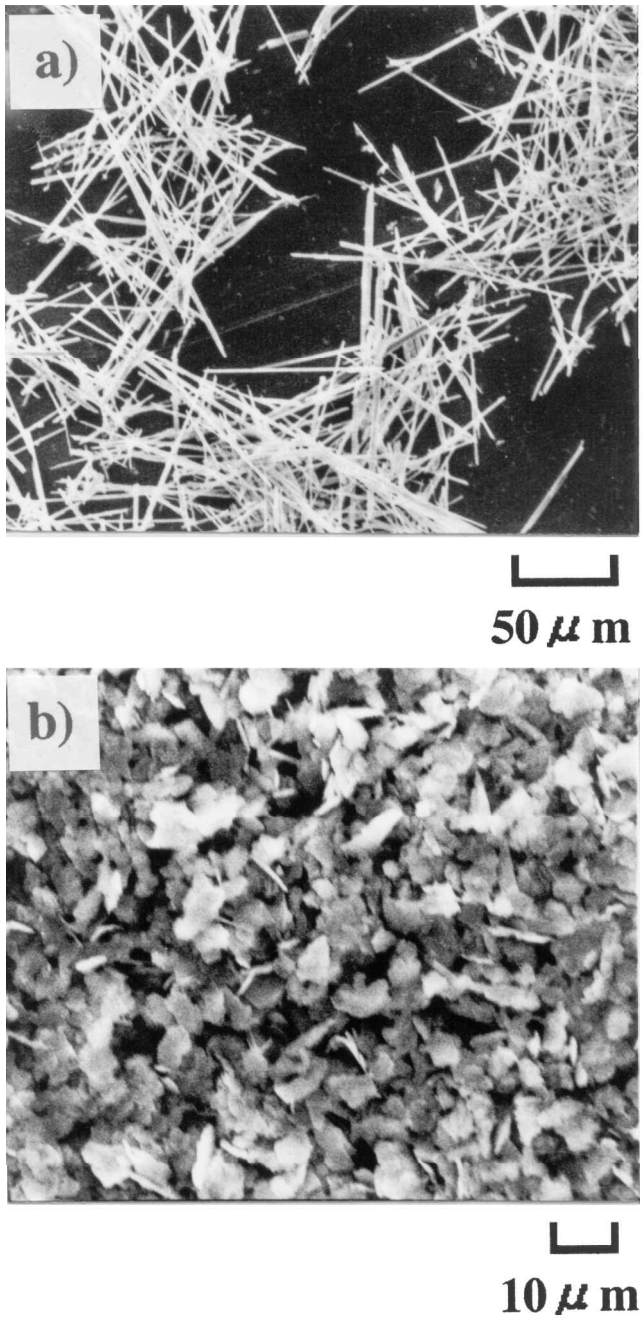

Figure 1. Scanning electron micrographs of the reactants (a) potassium tetratitanate fiber; (b) non-swelling mica.

served using a scanning electron microscope (T-220, Nippon Electronics). The diameter and length of the whiskers were measured using SEM images taken from arbitrary fields. The thermal decomposition process was investigated using an apparatus for thermogravimetry (TG/DTA-2000, MAC SCIENCE).

The bending strength of the sintered bodies was measured using a 3-point bending method, i.e. using three weighted points (cross-head speed: 0.5 mm/min, span: 15 mm). Fifteen specimens were used in the measurement, and the bending strength for each specimen was calculated from the measured breaking load based on JIS R-1601.

3. RESULTS

3.1. Synthesis

Figure 2 shows powder X-ray diffraction patterns of sintered bodies obtained from mixtures of hydrated potassium tetratitanate fibers and synthetic fluorine mica with mass ratios ranging from 9 : 1 to 5 : 5 calcined in air at 1000°C for 1 h. When the mass ratio is 9 : 1 (in terms of molar ratio, K : Mg : Ti = 3.70 : 0.64 : 7.00), the major peaks are attributed to $K_2MgTi_7O_{16}$ (potassium pridelite), and peaks attributed to $K_{0.8}Mg_{0.4}Ti_{1.6}O_4$ and $K_2Ti_6O_{13}$ are also observed. When the mass ratio is 8 : 2 (molar ratio, K : Mg : Ti = 3.80 : 1.42 : 7.00), the main product is $K_2MgTi_7O_{16}$, and a small amount of $K_2Ti_6O_{13}$ is also produced. These by-products are generated due to the lack of MgO. When the mass ratio is 7 : 3 (molar ratio, K : Mg : Ti = 4.06 : 2.44 : 7.00), only crystals of $K_2MgTi_7O_{16}$ are observed. When the mass ratio is 6 : 4 (molar ratio, K : Mg : Ti = 4.32 : 3.80 : 7.00) or 5 : 5 (molar ratio, K : Mg : Ti = 4.84 : 5.23 : 7.00), diffraction peaks from synthetic fluorine mica which has not yet reacted are observed. In addition, the coexistence of a considerable amount of glass phases is suggested from the presence of halo patterns near 30°.

Figure 3 shows SEM images of a sintered body with the mass ratio of 7 : 3 and the particles after washing using fluoric acid and drying. From these images, we measured the diameter and length of 50 fibers, and calculated a mean fiber diameter and mean fiber length. As a result, the mean diameter of the magnesium potassium titanate fibers was 3 μm. The mean diameter of the hydrated potassium tetratitanate fibers which were obtained from hydrization and synthesis using the KDC method was approximately 2 μm, and their length was 40–100 μm; compared to these values, the fiber length of the magnesium potassium titanate fibers was shorter. This is thought to be due to the breakage of fibers during 4 min of mixing and sintering.

Figure 4 shows powder X-ray diffraction patterns of the sintered bodies under different calcination temperatures, when the mass ratio of hydrated potassium tetratitanate fibers and synthetic fluorine mica was 7 : 3. At a calcination temperature of 900°C, the sintered body consisted of the synthetic fluorine mica, the potassium tetratitanate and the potassium hexatitanate which was prepared from the potassium tetratitanate. Magnesium potassium titanate fibers were produced only in minute

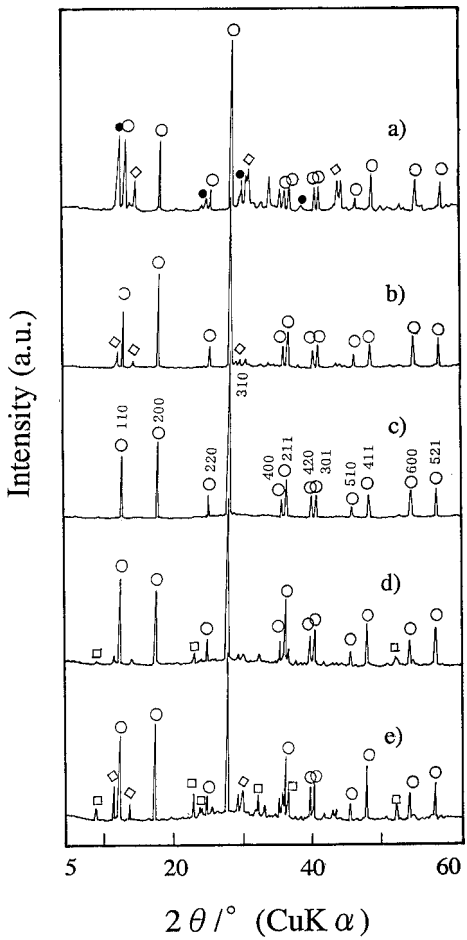

Figure 2. Powder X-ray diffraction patterns of products calcined at 1000°C for 1 h from mixtures of potassium tetratitanate fiber with non-swelling fluorine mica. (a) mass ratio (potassium tetratitanate fiber : non-swelling fluorine mica) 9 : 1; (b) 8 : 2; (c) 7 : 3; (d) 6 : 4; (e) 5 : 5. (●) $K_{0.8}Mg_{0.4}Ti_{1.6}O_4$; (◇) $K_2Ti_6O_{13}$; (○) $K_2MgTi_7O_{16}$; (□) $KMg_{2.5}Si_4O_{10}(OH)_2$.

amounts due to the low synthesis temperature. At a calcination temperature of 950°C, the peaks observed were attributed mostly to potassium pridelite, but diffraction peaks of unreacted $K_2Ti_6O_{13}$ were also observed. At calcination temperatures of 1000°C or higher, only the diffraction peaks of potassium pridelite were observed. Thus, it is demonstrated that the synthesis of potassium pridelite requires calcination temperatures of 1000°C or higher. The lattice constant of the magnesium potassium titanate fibers along the a-axis length was 1.0155 nm and that along the c-axis length was 0.2973 nm; these values are almost identical to the a-axis length of 1.0157 nm and c-axis length of 0.2974 nm for $K_2MgTi_7O_{16}$ on JCPDS card No. 18-1032 [3]. These results demonstrate that the current method can pro-

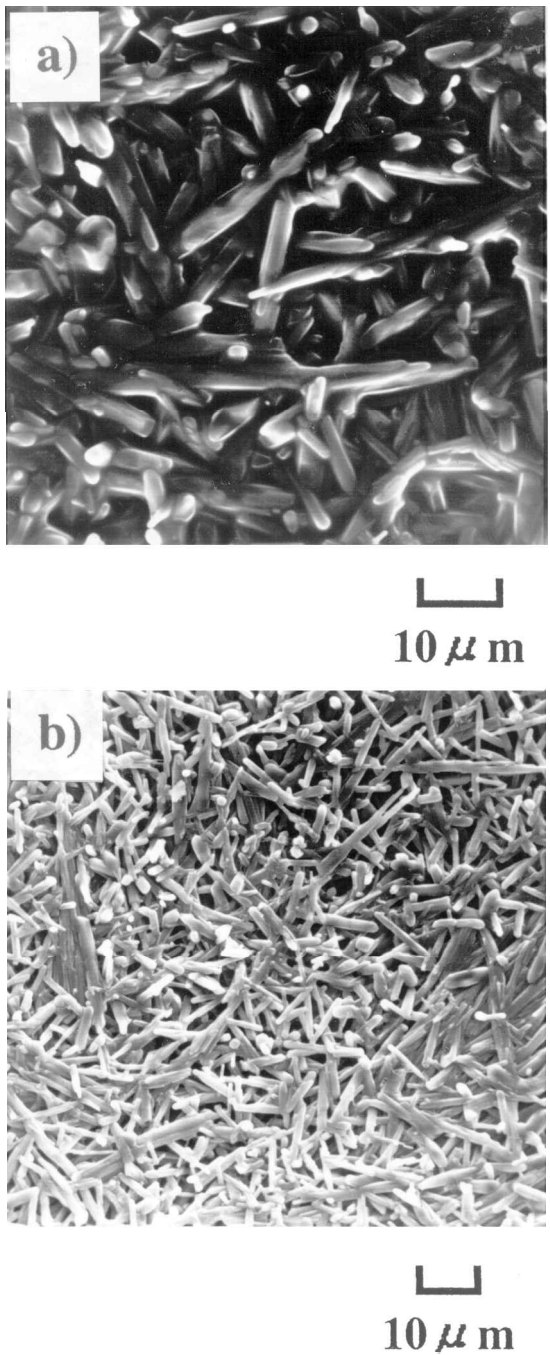

Figure 3. Scanning electron micrographs of potassium tetratitanate fiber, mica calcined at 1000°C for 1 h and magnesium potassium titanate fiber. (a) surface; (b) after the isolation.

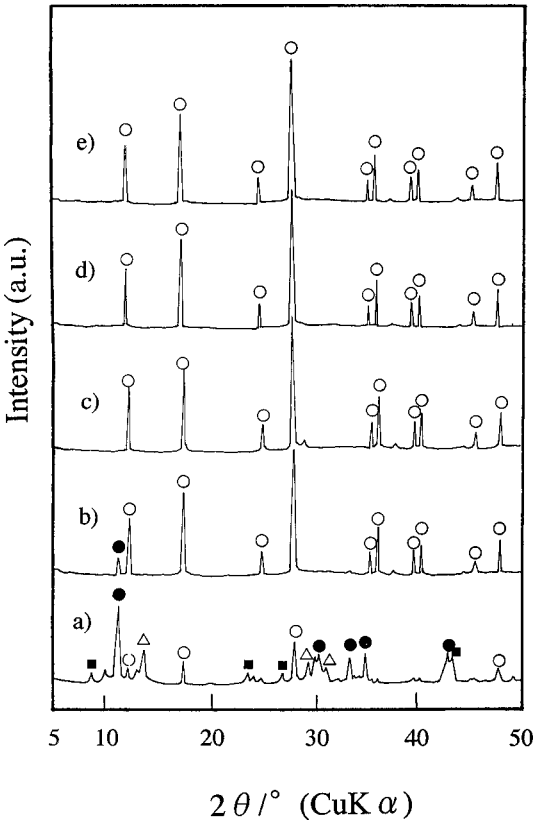

Figure 4. Powder X-ray diffraction patterns of products calcined at 900 to 1100°C for 1 h from potassium tetratitanate fiber and mica (mass ratio 7 : 3). (a) 900°C; (b) 950°C; (c) 1000°C; (d) 1050°C; (e) 1100°C; (△) $K_3Ti_8O_{17}$, (●) $K_2Ti_6O_{13}$, (■) $K_2Ti_4O_9$, (○) $K_2MgTi_7O_{16}$.

duce magnesium potassium titanate in a short period of time in a simple operation compared with other synthetic methods [3, 5–7].

To investigate the generation of the composite of magnesium potassium titanate short fibers/glass, thermogravimetric analysis was carried out for (a) synthetic fluorine mica, (b) hydrated potassium tetratitanate fibers, (c) a mixture of hydrated potassium tetratitanate fibers with synthetic fluorine mica with a mass ratio of 7 : 3, and (d) a composite of potassium tetratitanate fibers and glass; Fig. 5 shows the results. The TG curve for (a), mica, shows a reduction of mass at temperatures of 1000°C or higher; this is due to the vaporization of K_2O. The reduction of mass for (b), potassium tetratitanate fibers, at temperatures of 500°C or lower is due to the release of H_2O [8]. For (c), a mixture of hydrated potassium tetratitanate fibers with synthetic fluorine mica with a mass ratio of 7 : 3, the reduction of mass due to the dehydration of potassium tetratitanate was observed at temperatures of 500°C or lower; then the potassium tetratitanate was converted to potassium hexatitanate ($K_2Ti_6O_{13}$) around 950°C, and then to potassium octatitanate ($K_2Ti_8O_{16}$) around

1000°C. In the course of this reaction, a portion of K_2O is released and reacts with a component of the fluorine mica to induce glassification. In addition, magnesium ions contained in the synthetic fluorine mica are replaced by some of the titanium ions contained in the potassium octotitanate, to generate potassium pridelite ($K_2MgTi_7O_{16}$). These reactions are supported by the powder X-ray diffraction patterns of calcined bodies of hydrated potassium tetratitanate fibers and synthetic fluorine mica with a mass ratio of 7 : 3 at calcination temperatures ranging from 900°C to 1100°C, as shown in Fig. 4.

Characteristics and structures of the potassium titanate compounds are variations of chains of TiO_6 octahedra [10], which are roughly classified into layered structures [11] and tunnel structures [12]. In the layered structure, K^+ ions existing between the layers are easily eluted by hydration or acid treatment. To reduce the elution rate of potassium, increasing the heating temperature is known to form a tunnel structure. Therefore, we synthesized magnesium potassium titanate having a tunnel structure.

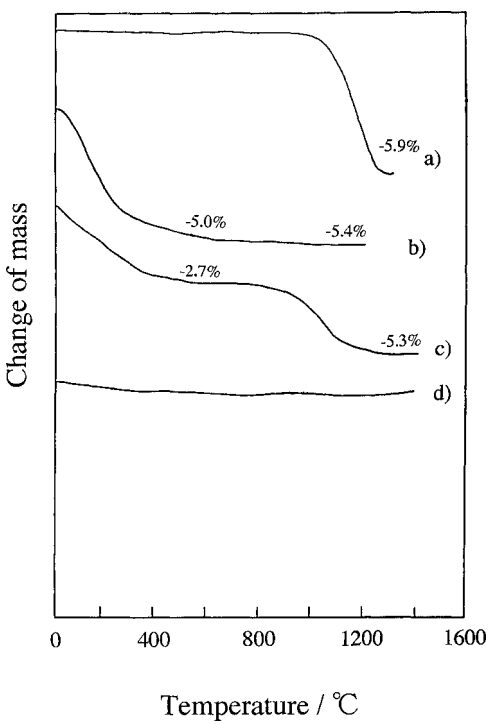

Figure 5. TG curves of mica (a), potassium tetratitanate fiber (b), potassium tetratitanate fiber with mica mixed 7 : 3 (c), potassium tetratitanate fiber with mica (mass ratio 7 : 3) calcined at1000°C for 1 h (d).

3.2. Mechanical characteristics

Figure 6 shows the bulk density of the calcined bodies obtained from calcination of the hydrated potassium tetratitanate fibers and synthetic fluorine mica with various mass ratios at calcination temperatures ranging from 900°C to 1100°C. The bulk density of the synthetic fluorine mica was 1.5 g/cm^3, which did not change even after calcination at 1050°C. However, the bulk densities of the hydrated potassium tetratitanate fibers and the composites obtained at various mass ratios increased as the calcination temperature was increased. In particular, the bulk density of the composite of the magnesium potassium titanate fibers and glass obtained with a mass ratio of 7 : 3 was the highest. Using 3.70 g/cm^3 as the density of the monocrystal of the magnesium potassium titanate [7], we calculated the degree of sintering at each calcination temperature; it was 54% at a calcination temperature of 1000°C, and 79% at 1100°C.

Figure 7 shows the bending strength at various calcination temperatures of calcined bodies obtained from calcination of the materials at a mass ratio of 7 : 3, at which the bulk density was the highest. The bending strength increased with increasing calcination temperature. In particular, the bending strength significantly increased with the generation of magnesium potassium titanate; when the composite of magnesium potassium titanate fibers and glass was produced, the bending strength was 22 MPa at a calcination temperature of 1000°C, and 27 MPa at 1100°C; these values were twice the bending strength before the generation of the composite. Figure 8 shows the bending strength of the composites obtained with various mass ratios of the hydrated potassium tetratitanate fibers and synthetic fluorine mica calcined at 1050°C.

When the hydrated potassium tetratitanate fibers are calcined at 1000°C or higher, they are converted into potassium hexatitanate. The bending strength of the potassium hexatitanate without synthetic fluorine mica is 4 MPa, that of the

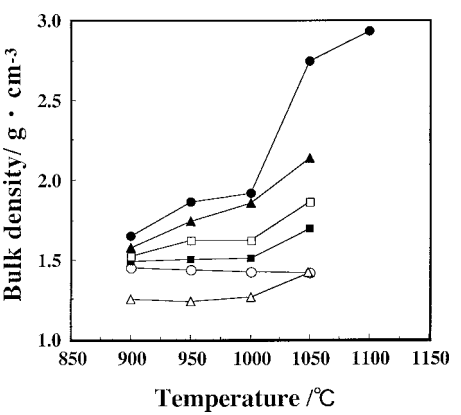

Figure 6. Bulk density of the composite fired at 900 to 1100°C for 1 h. (■) potassium tetratitanate fiber; (○) non-swelling fluorine mica; (▲) weight ratio 9 : 1; (●) weight ratio 7 : 3; (□) weight ratio 5 : 5; (△) weight ratio 3 : 7.

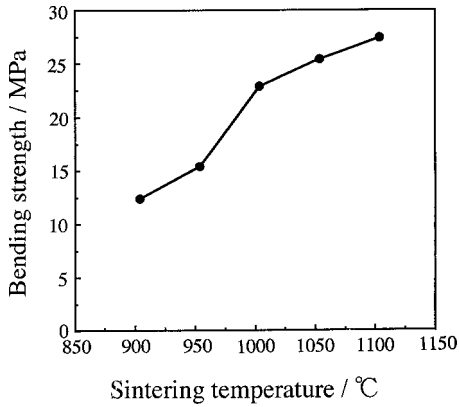

Figure 7. Bending strength of the composite obtained by calcination at 900 to 1100°C for 1 h (weight ratio 7 : 3).

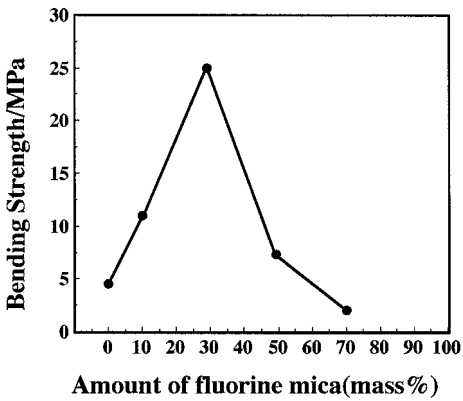

Figure 8. Bending strength of the each composite fired at 1050°C for 1 h.

magnesium potassium titanate fibers generated from potassium hexatitanate with a mass ratio of 9 : 1 is 11 MPa, and that of the composite of the magnesium potassium titanate fibers and glass generated with a mass ratio of 7 : 3 is the highest at 25 MPa. When the mass ratio is 5 : 5, at which level excess synthetic fluorine mica is added, the calcined body is composed of a mixture of magnesium potassium titanate fibers, and glass and fluorine mica, for which the bending strength is low. When the mass ratio is 3 : 7, the bending strength (2 MPa) is significantly lower than the bending strength of calcined bodies of fluorine mica (7 MPa). Similar tendencies are observed for the bulk density.

Figure 9 shows the SEM image of broken surfaces of the composites of magnesium potassium titanate fibers and glass after bending tests. As is known from the results of bending strength shown in Fig. 8, the bending strength is increased by generating magnesium potassium titanate from the potassium hexatitanate and is further increased by the formation of the glass composite. As shown in the image

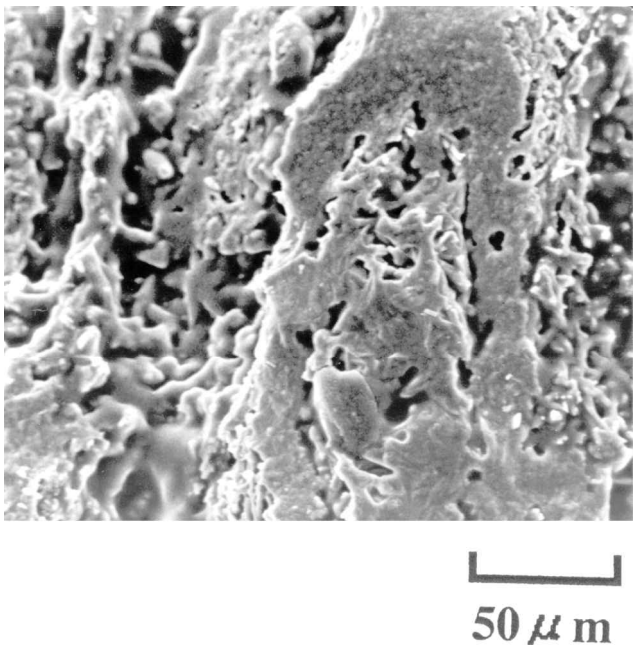

Figure 9. Scanning electron micrographs of composite of magnesium potassium titanate fiber and glass.

in Fig. 9, this result is supported by the formation of bodies by binding magnesium potassium titanate fibers to glasses.

4. DISCUSSION

Comparing bulk density in Fig. 6 and strength concerning sintering temperature of 1050°C, the sample of 7 : 3 has the highest density and strength. It is realized that there is a correlation between them in a high degree. The density depends mainly on the extent to which glass is packed among fibers.

Although the line of 7 : 3 in Fig. 6 shows the bulk density scarcely increases from the sintering temperature of 950°C to 1000°C, bending strength increases rapidly. In the region of this temperature, magnesium potassium titanate becomes the only phase according to the XRD pattern (Fig. 4). Therefore, it is another factor that affects the strength.

5. CONCLUSIONS

We generated sintered bodies using potassium tetratitanate fibers with addition of synthetic fluorine mica as the magnesium source and obtained the following results.

(1) We generated a composite of magnesium potassium titanate fibers/glass by sintering a mixture of hydrated potassium tetratitanate fibers and synthetic

fluorine mica with a mass ratio of 7 : 3 at a calcination temperature of 1000°C for 1 h.

(2) The magnesium potassium titanate fibers can be isolated by treating the mixture of potassium tetratitanate fibers and glass with 5% fluoric acid solution.

(3) The mean fiber diameter of the magnesium potassium titanate fibers was 3 μm, the lattice constant along the a-axis length was 1.015 nm, and that along the c-axis length was 0.2973 nm; these values are almost identical to those of JCPDS card No. 18-1032.

(4) The bending strength of the composite of magnesium potassium titanate fibers/glass was 27 MPa at a calcination temperature of 1100°C, which was significantly higher than that of the starting materials, the hydrated potassium tetratitanate fibers and fluorine mica.

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