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Preparation of Porous $LiAl_5O_8$ by Reaction bonded sintering

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Abstract

The porous $LiAl_5O_8$ was fabricated by the reaction bonded sintering process. Powders of Al_2O_3 (0.3µm) and Li_2O (1.0 µm) were used as starting materials. They were mixed with ratios of Al_2O_3 and Li_2O in 5:1, 7:3 and 5:5 by mole in the water for 6 hours and were dried at 100^oC for 10 hours. The mixed powder was pressed to form a 10 mm diameter disk specimen. The disk specimens were then sintered at temperatures of 1300^oC for 2 hours. Specimens sintered at 1300^oC for two hours formed two kinds of lithium aluminates, namely $LiAlO_2$, and the $LiAl_5O_8$ in the mixture with the ratios of 7:3 and 5:5. The mixture with the ratio of 5:1 formed only the $LiAl_5O_8$ phase. The specimen mixed by 5:1 molar ratio had a homogeneous grain size and a pore size distribution. The Li_2O reacted completely with the Al_2O_3 even below the evaporation temperature of the Li_2O. In the specimen mixed by 5:5 ratio, the pore of specimens was larger and longer which would be resulted from the evaporation of Li_2O during the sintering process. The thermal expansion coefficient of the specimen mixed by 5:1 molar ratio was lower than that of the specimen with other mixing ration.

Keywords: Porous ceramics, Reaction bonded Sintering, Lithium aluminates, Pore size distribution.

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1. Introduction

Porous materials evoke significant interests for their applications such as catalysis, separation, lightweight structure materials, photonic crystals and nanoelectronic properties [1-5]. Various process techniques have been employed to form different porous structures in ceramic materials [6]. The use of pore former or foaming agents that evolve gases during calcinations is a common method [7, 8]. Partial sintering has been used as an alternative approach to obtain the porous structure [9-11]. A variety of materials that have porous structures have been successfully fabricated, such as Al_2O_3, SiC, TiO_2. However, these processes generally produce macroporous structures with a wide distribution of pore sizes.

The reaction bonded sintering is a method for preparing porous ceramic materials which synthesis new materials and sinter at the same time by controlling particle size of raw materials to control pore size distribution[13]. $LiAl_5O_8$ is the target material to fabricate porous substrate. Because the $LiAl_5O_8$ has a crystal structure of the spinel in which Li^+ can be exchanged with other metallic cations, as the result to improve electrical conductivity. An electrical insulator consisted of some electrical conductivity is the most desirable property as a substrate.

The purpose of this experiment is to fabricate porous $LiAl_5O_8$ using the reaction bonded sintering which controlling of microstructure was examined by changing the molar ratio of Al_2O_3 and Li_2O.

2. Materials and Experiment

The porous $LiAl_5O_8$ was fabricated by reaction bonded sintering. Al_2O_3 (0.3μm) and Li_2O (1.0 μm) powders were used for starting materials. Two types of powders were mixed by molar ratio of Al_2O_3 and Li_2O for 5:1, 7:3, 5:5 in water for 6 hours and were dried for 100°C for 10 hours. The ratio of mixing was selected from phase diagram of Al_2O_3 and Li_2O (Fig.1) at 82 mole% of Al_2O_3 and 18 mole% of Li_2O which corresponds to the following equation (1).

$$5Al_2O_3 + Li_2O \rightarrow 2LiAl_5O_8 \qquad (1)$$

The molar ratio of 5:1 is corresponding to stoichiometric composition. The molar ratio of 7:3 and 5:5, Li_2O was also chosen. Because the melting point and the evaporation temperature of Li_2O is far lower than those of the alumina, it may evaporate and be lost before reaction with Al_2O_3. The mixed powder was pressed to form 2 mm thickness and 10 mm diameter disk specimens. Disk specimens were sintered in air for 2 hours. To obtain an optimum molar ratio of Al_2O_3 and Li_2O, specimens with initial three different molar ratio of Al_2O_3 and Li_2O were sintered at 1300°C. The preparation process of porous $LiAl_5O_8$ is summarized in Fig. 2.

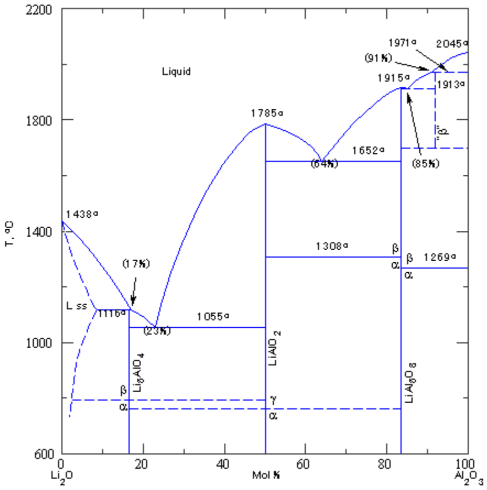


Figure 1 Phase diagram of Al_2O_3 and Li_2O [12]

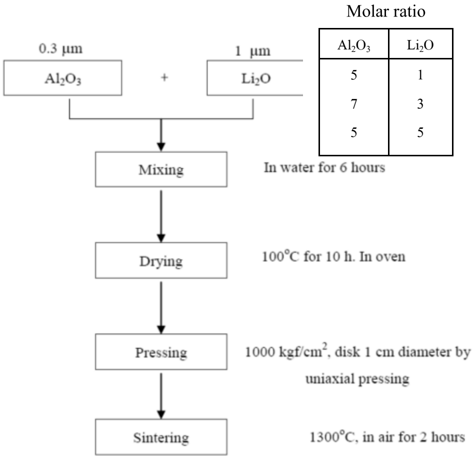


Figure 2 Process of preparation of porous $LiAl_5O_8$

Sintered specimens were observed by SEM (JEOL, JSM 5400, Japan) and their crystallographic phases were characterized by the X-ray diffractrometry (XRD, Rigaku, Japan). Pore size distribution of sintered specimens were measured by a mercury porosimeter (Quantachrom instrument, USA), with a technique of so-called the Archimedes method. The calculated pore size was examined by washburn's equation. Thermal expansion was also measured.

3. Results and Discussion

3.1 Phase analysis by x-ray diffraction;

Fig. 3 shows the x-ray diffraction pattern of specimens sintered at 1300°C for two hours. There found two kinds of aluminate, $LiAlO_2$ (JCPDS No. 73-1338) and $LiAl_5O_8$ (JCPDS No. 71-1736) in the specimens whose initial mixing ratio of 7:3 and 5:5. The amount of $LiAlO_2$ depended on the amount of Li_2O and this phase formed at lower temperature than $LiAl_5O_8$ and some Li_2O was evaporated. As a result, the ratio of Al_2O_3 and Li_2O will be changed and formed $LiAl_5O_8$. In the specimen having the initial mixing ratio of 5:1, there found only $LiAl_5O_8$ which was corresponding to the equation (1). From this result, it was confirmed that the Li_2O did not evaporate nor was lost before their reaction with the Al_2O_3 powders.

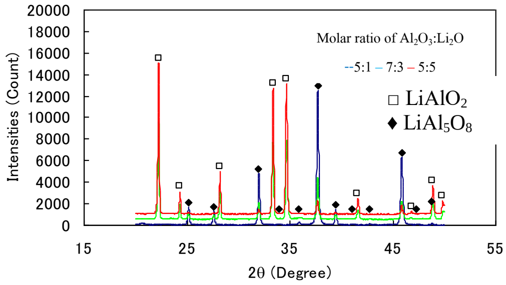
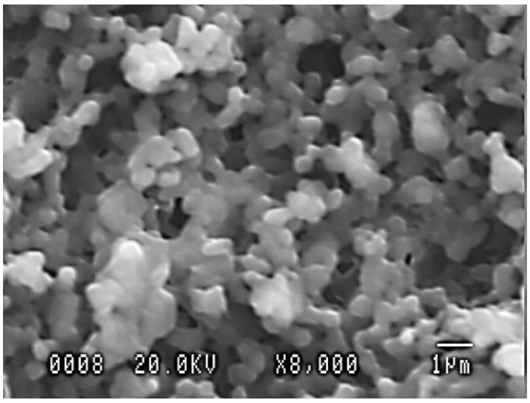


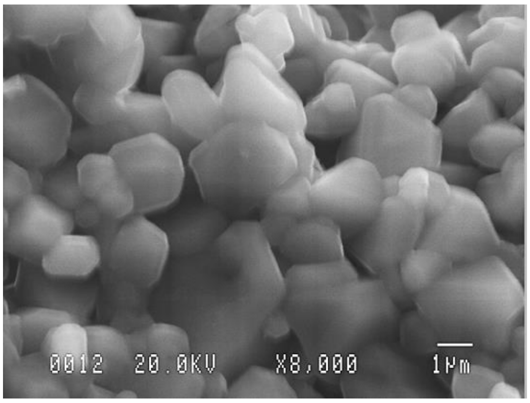
Figure 3 The x-ray diffraction pattern of sintered specimens prepared with varies mixed molar ratio of Al_2O_3 and Li_2O. Sintering temperature as 1300°C

3.2 Surface morphology:

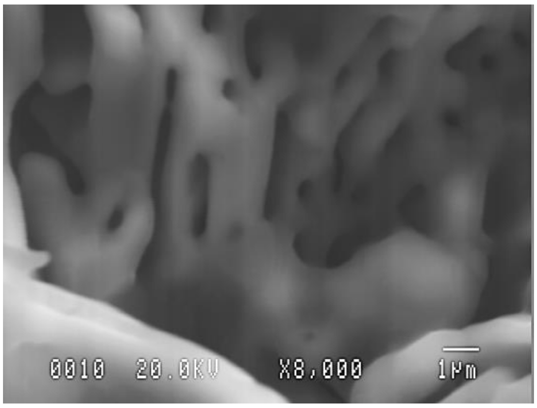
Fig. 4 show SEM photographs of the surface morphology of the specimens sintered at 1300°C with different molar ratios of Al_2O_3 and Li_2O. The ratio of 5:1 (Fig. 4 (a)) showed a homogeneous grain size and pore size distribution because the Li_2O did not evaporate in this ratio. Li_2O completely reacted with the Al_2O_3. The particles of $LiAl_5O_8$ were connected with grain to grain, which could be interpreted that the surface energy of the $LiAl_5O_8$ was high enough for sintering and there was no need for sintering aids. Or, the Li_2O did act as a sintering aid in the process. The ratio of 7:3 showed large grain size and glassy surface structures, because Li_2O went into a liquid phase and reacted with the Al_2O_3 by the liquid-solid reaction which made the growth of grains easy. The ratio of 5:5, pore size of specimens is larger and longer, which would be resulted from or enhanced by the liquidation and evaporation of the Li_2O.



(a)



(b)



(c)

Figure 4 Scanning electron photographs of sintered specimens. Sintering temperature as 1300^{O}C for 2 h in air, (a) mixed ratio 5:1, (b) mixed ratio 7:3 and (c) mixed ratio 5:5.

3.3 Pore size distribution by mercury porosimetry,

Pore size distribution was measure by the mercury porosimetry method. The calculated pore size was examined by washburn's equation. The ratio of 7:3 and 5:5 shows non-homogeneous large pore size in range of 0.08-700 μm which is consistent with the results of scanning electron photograph described above. The homogeneous pore size distribution which calculated by Washburn equation (2) was obtained in the specimen whose initial mixing ratio was 5:1(Fig. 3).

$$Pr = 2\gamma\cos\theta \qquad (2)$$

Where

P is pressure.

r is radius of pores.

γ is surface tension of liquid.

θ is contact angle between liquid and solid.

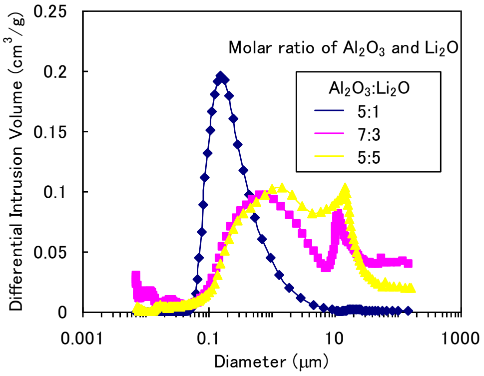


Figure 5 Pore size distribution of sintered specimens for different molar ratio of Al_2O_3 and Li_2O obtained by mercury porosimetry.

3.4 Thermal expansion;

Linear thermal expansion and thermal expansion coefficient of sintered specimens were shown in Fig. 6 and 7 respectively. A thermal expansion coefficient of the specimen, whose initial mixing ratio was 5:1, was lower than that of other two ratios, because the covalent bonding in the 5:1 specimens was higher than the ionic bonding. Here, it is assumed that stronger nature of the ionic bonding will result in the larger thermal expansion coefficient. The specimens of the ratio of 7:3 and 5:5 contain much more lithium cations, which result in the stronger ionic natures. The thermal expansion coefficient of $LiAl_5O_8$ is near to that of the alpha Al_2O_3 ($8x10^{-6}K^{-1}$), which -will be good for use in high temperature applications such as hot gas filter, catalytic support. There, major structural components will be made of the alumina, the most popular industrial refractory ceramics. The $LiAl_5O_8$ has a higher electrical conductivity than Al_2O_3.

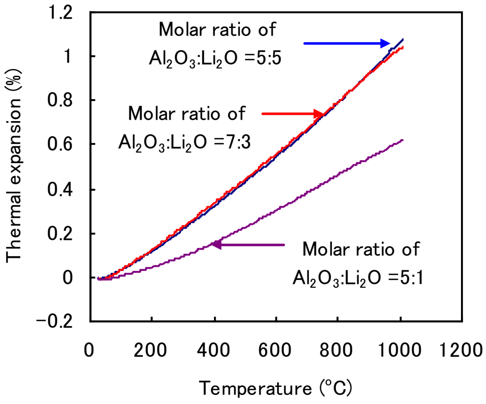


Figure 6 Thermal expansion of sintered specimens. Sintering temperature as $1300^{O}C$.

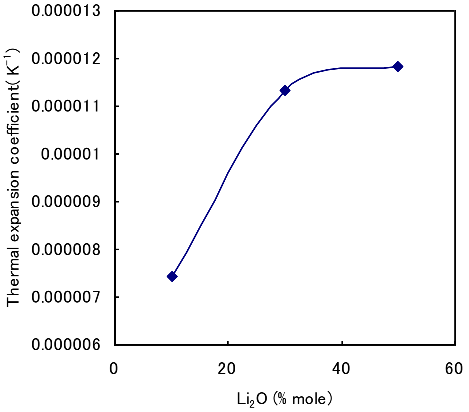


Figure 7 Thermal expansion coefficient of sintered specimens plotted as a function of molar ratio of Al_2O_3 and Li_2O. Sintering temperature as $1300^{O}C$

4. Conclusions

The Porous $LiAl_5O_8$ were prepared by the simple reaction bonding technique with Li_2O and Al_2O_3 powders as starting materials. The optimum chemical mixing ratio of Li_2O and Al_2O_3, and the optimum sintering temperature was systematically surveyed. The obtained conclusions were as follows;

1. The stoichiometric mixture of Li_2O and Al_2O_3, namely the mixing ratio of 5:1 resulted in the best endproducts.

2. The pore size of the sintered porous $LiAl_5O_8$ depended on the amount of accesed Li_2O

3. The formation of a glassy plase would help the sintering, but caused undesirable grain growth.

5. References

[1] Corbin S., Apte P. Engineered porosity via tape casting, lamination and the percolation of pyrolyzable particulates, J. Am. Ceram. Soc. 82 (1999) 693-701.

[2] Chandrappa G., Steunou N, Livage J. Macroporous crystalline vanadium oxide foam, Nature (2002) 702.

[3] Sakka Y., Tang F., Fudouzi H., Uchikoshi T. Fabrication of porous ceramics with controlled pore size by colloidal processing, Sci. Tech. Ad. Mats. (2005) 915-920. 547

[4] Holland B., Blanford C, Stein A. Synthesis of macroporous minerals with highly ordered three-dimensional arrays of spheroidal voids, Science 281 (1998) 538-540.

[5] Davis M. Ordered porous materials for emerging applications, Nature 417 (2002) 813-821.

[6] Tang F., Uchikoshi T., Sakka Y. A practical technique for the fabrication of highly ordered macroporous structures of inorganic oxides. Mats. Res. Bull. 41 (2006) 268-273.

[7] Engin N., Tas A. manufacture of macroporous calcium hydroxyapatite bioceramics J. Eur. Ceram. Soc. 19 (1999) 2569-2572.

[8] Roncari E., Galassi C., Craciun F., Capiani C., Piancastelli A.,microstructural study of porous piezoelectric ceramic s obtained by different technique, J. Eur. Ceram. Soc. 21 (2001) 409-417.

[9.] Yang J., Zhang G., Ohji T. Porosity and Microstructure Control of Porous Ceramics by Partial Hot Pressing, J. Mater. Res. 16 (2001) 1916-1918.

[10] Deng Z., Tanaka Y., Liu Y., Liu Z, Sakka Y., Processing of Silicon Carbide-Mullite-Alumina Nanocomposites J. Ceram. Soc. Jpn. 112 (Suppl.) (2004)s203- s204.

[11] Deng Z., Tanaka Y., Sakka Y., kagawa Y. Modification Al particle surfaces by gamma-Al2O3 and its effect on corrosion behavior of Al, J. Mater. Res. 20 (2005) 672-679.

[12] The AcerS and NIST, Phase equilibra diagrams database versions 3.1

[13] Shuqiang Ding, Yu-Ping Zeng, Dongliang Jiang “In-situ reaction bonding of porous SiC ceramics” Mats. Charac. 59 (2008) 140–143