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Low temperature preparation and machinability of porous ceramics from talc and foamed glass particles

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Abstract

Porous ceramics were prepared by firing mixtures of talc ($Mg_3Si_4O_{10}(OH)_2$) and foamed glass particles (ceramic balloons, CB) with and without LiCl as a sintering acid. The mixing ratios of the starting materials were talc:CB = 7:3, 8:2, 9:1 and 10:0, with additions of LiCl of 0, 2 and 5 mass%. The mixtures were formed into pellets and fired at 600–1000 °C. The pellets without LiCl showed very poor strength even when fired at 1000 °C but those containing LiCl were much stronger, even when fired at only 600 °C. The crystalline phases in these samples changed to enstatite ($MgSiO_3$) at ≥ 700 °C by decomposition of the talc under the fluxing action of the LiCl. The resulting samples were machinable and easily cut and drilled. The cutting rate decreased with increasing bending strength, for example, from 105 mm^2/s and 6.3 MPa to 50 mm^2/s and 16.3 MPa, respectively. The drilling rate of the present sample was found to be only slightly less than Teflon (polytetrafluoroethylene, PTFE) but much faster than graphite, glass ceramics, etc.

Keywords: Machinability; Porosity; Composites; Platelets; Clays

1. Introduction

One of the greatest disadvantages of ceramics is that they are brittle and difficult to machine. Ceramics with machinability are therefore very attractive materials for a variety of applications. Three major processes are known for the preparation of machinable ceramics, i.e. (1) glass crystallization, generating platy crystalline grains in the glassy matrix, (2) sintering with platy particles or crystalline materials with weak cleavage planes and (3) the use of ceramics containing pores in the matrix.

Mica glass ceramics are the best examples of the first preparation method,[1] accomplished by in situ volume crystallization of fine platy mica grains in a matrix by annealing the cast bulk glass. Good machinability is developed by deflection and absorption of cracks at the cleavage planes and the interlocking microstructure of the platy mica grains. Mica glass ceramics are dense, and show good bending strength (70–120 MPa) that can be further enhanced by forming composites with ceramic particles such as alumina, giving strengths of 650 MPa.[2]

Although mica glass ceramics have good machinability and mechanical properties, the possible chemical compositions of glasses for generating mica grains by annealing are limited, restricting their applications. The sintering method for preparing machinable ceramics from mixtures of platy particles has the advantage of producing a variety of chemical compositions and combinations of crystalline phases. Many papers report various composites, including Si_3N_4/BN,[3] AlN/BN,[4] Al_2O_3/BN,[5] Al_2O_3/Ti_3SiC_2,[6] $Al_2O_3/LaPO_4$,[7] Ce-TZP/$CePO_4$,[8] etc. Furthermore, some monophase crystalline compounds such as $CaWO_4$,[9] $LaPO_4$,[10] and γ-$Y_2Si_2O_7$,[11] also show machinability. These ceramics have weakly bonded planes in their structure, allowing them to be easily broken. These are thought to be the source of the low shear deformation resistance, with resulting good machinability.

Porous ceramics containing small pores of controlled size and distribution in the matrix can also be machined. Kawai and Yamakawa[12] prepared porous Si_3N_4 ceramics consisting of interlocking rod-like β-Si_3N_4 grains. The porosity of this ceramic was about 43% and the bending strength was 270 MPa. The pores in the microstructure suppress crack propagation and the materials become machinable. The pores also play an important role in enhancing thermal shock

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resistance, and such ceramics have the added advantage of light weight.

However, the machinable ceramics described above need to be fired at high temperatures. To save energy in the preparation of these materials, it is important to lower the firing temperature. This paper describes the preparation of machinable ceramics from mixtures of talc, a clay mineral with platy particles, and foamed glass particles (ceramic balloons (CB)), which help to lower the density when LiCl is added as a sintering aid. The machinability and mechanical properties of the resulting porous ceramics were investigated and compared with other machinable materials.

2. Experimental

2.1. Preparation of porous ceramics

The starting materials were talc from Haicheng, China (Shokozan Mining), CB (Marunaka Clays) and LiCl (Wako Chemicals). The mass ratios of talc to CB were 7:3, 8:2, 9:1 and 10:0 and 0, 2 and 5 mass% of LiCl were added. In the samples without LiCl, talc and CB were dry mixed in a ball mill without the milling media. The samples containing LiCl were mixed wet, dried then lightly mixed again using an agate mortar and pestle to counteract any segregation during drying because of the density difference of the components. After drying at 110 °C overnight, the powders were uniaxially pressed at 20 MPa into pellets (ϕ10 mm) and 50 mm × 5 mm × 2 mm testpieces. The samples without LiCl were fired at 800–1000 °C while those with LiCl were fired at 600–800 °C for 12 h at a heating rate of 1 °C/min. The samples are designated by (firing temperature)–(talc content)–(LiCl content).

2.2. Characterization

The chemical compositions of the starting materials were determined by X-ray fluorescence (RIX2000, Rigaku). X-ray diffraction measurements on the pellets were used to identify the crystalline phases, using monochromated Cu Kα radiation (LaX XRD-6100, Shimadzu). Thermal analysis was carried out using a DTA–TG instrument (Thermoplus, Rigaku) at a heating rate of 10 °C/min. The Hunter whiteness index was measured using a colorimeter (CM-2500d, Konica-Minolta Sensing) and the bulk densities were calculated from weight and volume of the samples. The microstructures of the starting materials and fired samples were observed by SEM (JSM-5310, JEOL) at an accelerating voltage of 15 kV for Pt-sputtered samples. The pore size distribution was measured using a Hg porosimeter (Pore Master 60GT, Quantachrome).

2.3. Machinability and bending strength

The machinability of the samples was evaluated from cutting and drilling rates using a precision diamond cutter (Isomet, Buhler) and electric drill (D10SC, Hitachi Machinery), respectively. The cutting rate (mm^2/min) was calculated from the time needed to cut the sample by applying weight of 25 g at a blade rotation speed of 120 rpm. The diamond blade was dressed with a porous SiC ceramic before the cutting test. The drilling rate (mm/min) was calculated from the time needed to pierce a hole in the sample using a stainless steel drill (ϕ2 mm) with an applied weight of 2.6 kg and a rotation speed of 2500 rpm. Machinable mica glass ceramics (MACOR®, Corning),[13] vermiculite board (MOISS, Mitsubishi Material Kenzai)[14] and medium-density wood board (MDWB) were used as the reference materials.

The four-point bending strengths of the samples were measured on the as-prepared testpieces using a universal testing machine (AUTOGRAPH DCS-R-10TS, Shimadzu) at a cross-head speed of 0.5 mm/min. The sample sizes were 50 mm × 5 mm × 2 mm. The average bending strengths were obtained from measurements of 11 samples.

3. Results and discussion

3.1. Porous ceramics

The chemical compositions of the starting materials are listed in Table 1. The main constituents of talc are MgO and SiO_2, and their contents are very close to the ideal values. The particles are thin platelets several μm in size (Fig. 1) and the Hunter whiteness index is 91.7. The main constituents of the CB are SiO_2 and Al_2O_3, with 2–3 mass% of Na_2O, K_2O and Fe_2O_3. As shown in Fig. 1, the particle shape is spherical, with an average particle size of about 10 μm diameter. The bulk density of CB (0.3 g/cm^3) is much smaller than talc (true density 2.7 g/cm^3), making the volume ratio of CB much higher than the mass ratio.

The DTA–TG curve of the talc sample showed an endothermic peak with an accompanying weight loss of about 4.7 mass% at 870 °C due to dehydroxylation. This value is in very good agreement with the theoretical value (4.75 mass%). By contrast, the DTA–TG curve of the sample of talc with 5 mass% LiCl showed two endothermic peaks with accompanying weight losses of about 6.8 mass% at 80 °C and 11.2 mass% at 600 °C. The first peak is assigned to the dehydration of the adsorbed and hydrated water of LiCl and the second peak is thought to be due to the dehydroxylation of talc and the partial evaporation of LiCl. The lowering of the dehydroxylation temperature by 270 °C may be caused by melting of the LiCl (mp = 614 °C). From these results, the firing temperatures of the porous ceramics were set at 800–1000 °C for the samples without LiCl and at 600–800 °C for the samples containing LiCl.

Fig. 2 is a field map showing bulk density and good handling strength (shown by the shaded areas), plotted as a function of sample composition and firing temperature. In the samples without LiCl, most of the samples except the talc sample (talc:CB = 10:0) fired at 900 °C were very fragile and had no

Table 1
Chemical compositions of the starting materials (mass% in dry base)

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
Talc	66.5	0.2	0.1	33.1	0.1	0.0	0.0
Ideal value	66.5	–	–	33.5	–	–	–
CB	77.3	12.1	1.8	0.1	1.2	3.0	2.9

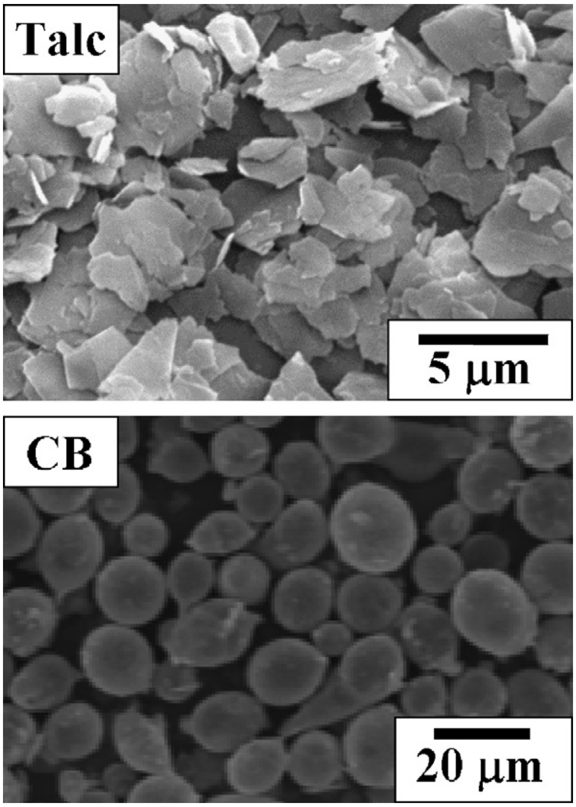

Fig. 1. SEM micrographs of talc and CB used as the starting materials.

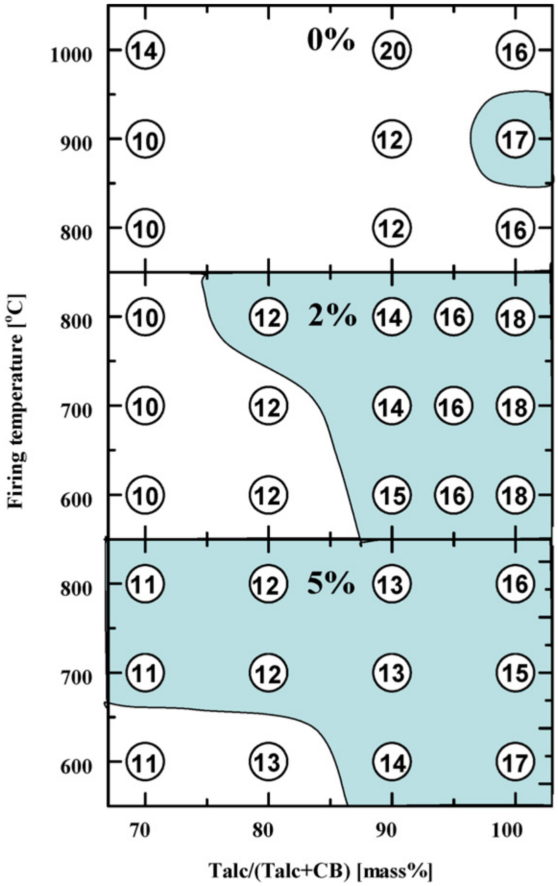

Fig. 2. Field maps for bulk density (g/cm^3) and range of handling strengths as functions of talc content and firing temperature for LiCl = 0, 2 and 5 mass% samples. The numbers in the figure represent the values 10 times of bulk densities.

handling strength, though some degree of densification resulted from firing at 1000 °C. Fig. 3 shows the XRD patterns of the samples without LiCl with compositions of talc:CB = 7:3 and 10:0 fired at 800–1000 °C. As expected from the DTA–TG results, the samples fired at 900 °C and 1000 °C showed decomposition of the talc with the formation of enstatite ($MgSiO_3$). Since densification of enstatite requires temperatures >1000 °C,[15] the use of a sintering aid is needed for low temperature sintering of the present samples; for this reason LiCl was added. The samples containing LiCl showed adequate handling strength even when fired at ≤800 °C. This trend becomes more apparent with increasing content of LiCl, talc, and firing temperature. Since the bulk densities did not change with firing temperature, the improved strength is thought to arise from the bonding effect of molten LiCl, which also accelerates the talc decomposition and its reaction with CB to form Li-containing crystalline phases (Fig. 4). These Li-phases have not yet been fully identified. The amount of enstatite formed by decomposition of the original talc under various conditions is listed in Table 2. The reaction of CB can be inferred from observation of the fracture surfaces of samples with and without LiCl, fired at 800 °C (Fig. 5). CB particles can clearly be seen in the sample without LiCl, reflecting a poor degree of reaction, whereas in the sample containing LiCl, pores formed by the balloons have replaced the CB particles due to the reaction of the CB with LiCl.

The porous ceramic products were lightly colored by the Fe_2O_3 impurity in the CB. Thus, the Hunter whiteness decreased from 91.7 in sample 800–100–0 (talc) to 76.4 in sample 800–70–0 with increasing CB content. The addition of LiCl enhanced the Hunter whiteness from 76.4 in sample 800–70–0 (without LiCl) to 81.2 by the addition of 2 mass% of LiCl (sample 800–70–2), and further to 89.3 by the addition of 5 mass% LiCl in sample 800–70–5.

The pore size distributions (PSDs) of selected samples are shown in Fig. 6. The total pore volumes were the smallest in sample 600–90–2 (0.28 ml/g) and the largest in sample 800–90–5 (0.56 ml/g). The peak positions of their PSDs were 0.24 μm in sample 600–90–2, 0.49 μm in sample 800–90–2, 0.89 μm in

Table 2
Formation amount of enstatite in the samples

Talc:CB	LiCl (mass%)	Firing temperature (°C)				
		600	700	800	900	1000
100:0	0			–	++	++
90:10	0			–	++	++
70:30	0			tr	+	+
100:0	2	tr	+	+++		
90:10	2	tr	+	+++		
80:20	2	–	tr	++		
70:30	2	–	tr	++		
100:0	5	–	+++	+++		
90:10	5	–	++	+++		
80:20	5	–	++	++		
70:30	5	–	++	++		

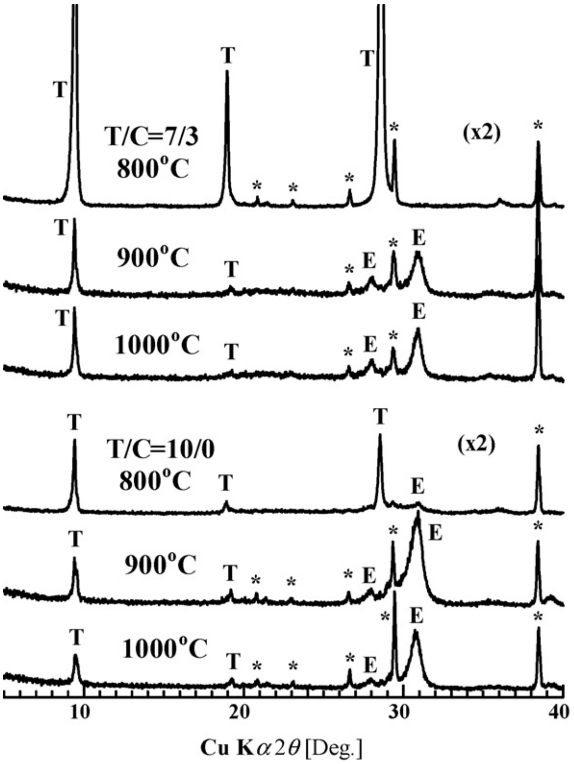

Fig. 3. XRD patterns of samples containing talc:CB = 7:3 and 10:0 without LiCl, fired at 800–1000 °C. Key: T = talc, E = enstatite, * = sample holder.

sample 800–70–5 and 0.24 and 0.73 μm in sample 800–90–5. These pore sizes are thought to correspond to the necks of bottle-shaped pores because the diameters of the original CB are much larger than these pore sizes. Comparison of samples 600–90–2 and 800–90–2 shows that the pore size and volume are greater in the sample fired at 800 °C than in that fired at 600 °C because of the difference in the microstructures before and after liquid phase sintering. Comparison of samples 800–90–2 and 800–90–5 shows that the pore size and volume increases with increasing LiCl content. This may be due to the acceleration of reaction among molten LiCl, talc and CB.

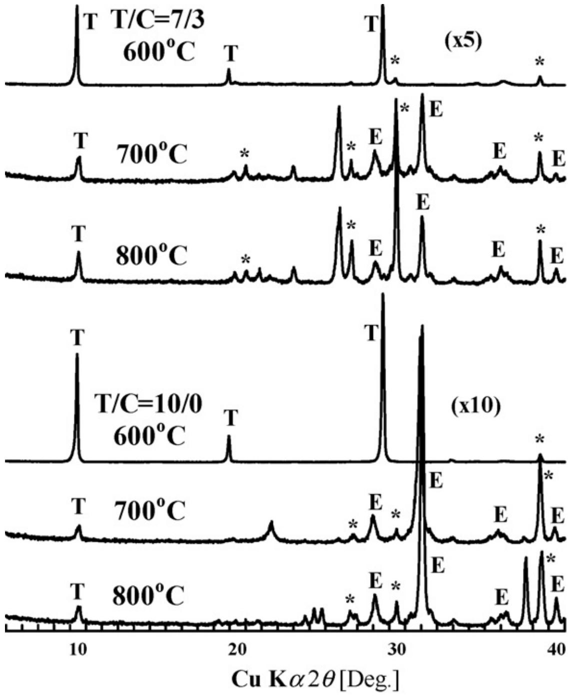

Fig. 4. XRD patterns of samples containing talc:CB = 7:3 and 10:0 with LiCl = 5 mass%, fired at 600–800 °C.

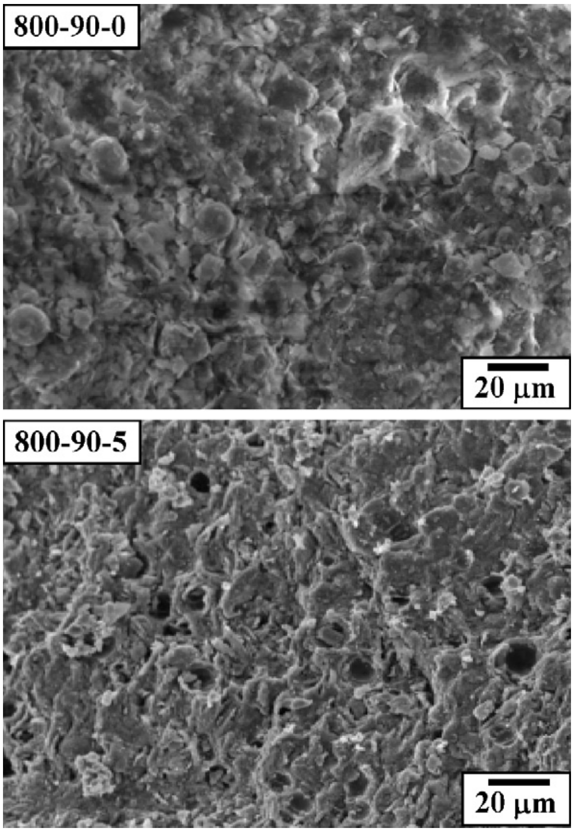

Fig. 5. SEM micrographs of fractured surfaces of the samples with talc:CB = 9:1 fired at 800 °C with LiCl additions of 0 and 5 mass%.

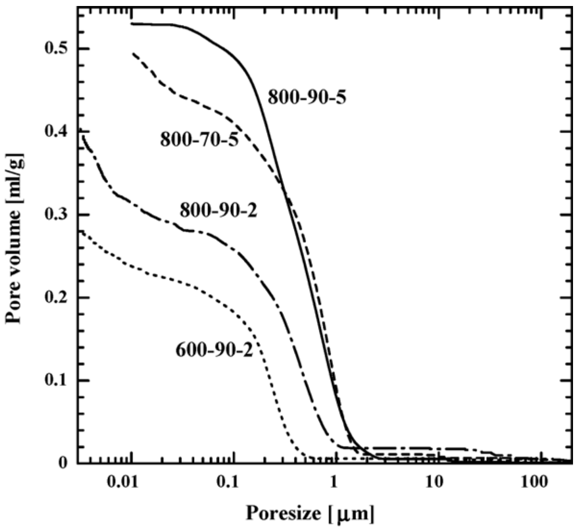

Fig. 6. Pore size distributions of the various samples.

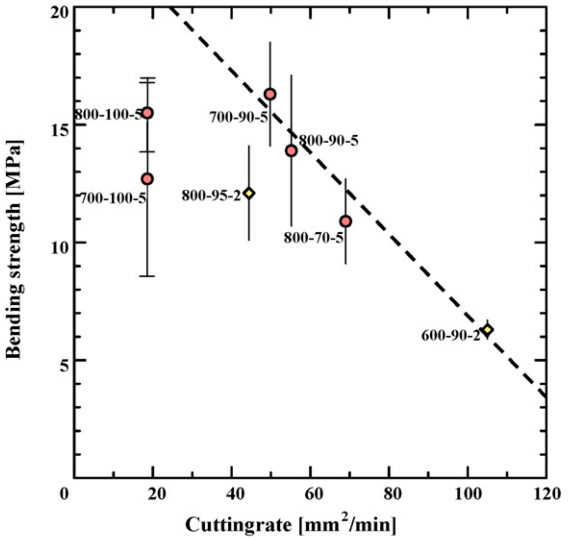

Fig. 7. Relationship between cutting rate and bending strength of the various samples.

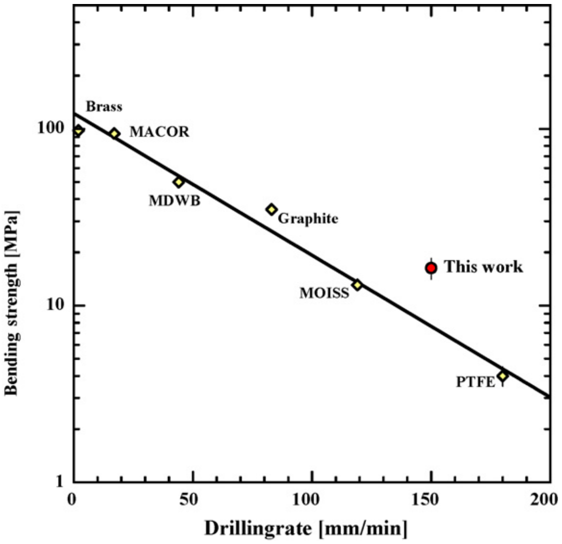

Fig. 9. Relationship between the drilling rate and bending strength of sample 800–90–5 and the reference materials MDWB, MACOR and MOISS, and the reported data[13] for brass, graphite, MACOR and PTFE.

3.2. Machinabilities of the porous ceramics

Fig. 7 shows the relationship between the bending strengths of the samples and their cutting rate. The composite samples containing ≥10 mass% of CB show a tendency towards increased bending strength with decreased cutting rate. Sample 600–90–2 has the lowest bending strength of 6.3(4) MPa and the highest cutting rate of 105 mm^2/s while sample 700–90–5 has the highest bending strength of 16.3(22) MPa and the lowest cutting rate of 50 mm^2/s. The numbers in parentheses represent the standard deviation in the last decimal place. By contrast, the samples containing <10 mass% of CB show deviations from the above trend, towards lower bending strength or lower cutting rate. The inclusion of CB in the samples is therefore found to enhance the strength and machinability by acceleration of the reaction with LiCl and the introduction of small pores in the composite microstructure.

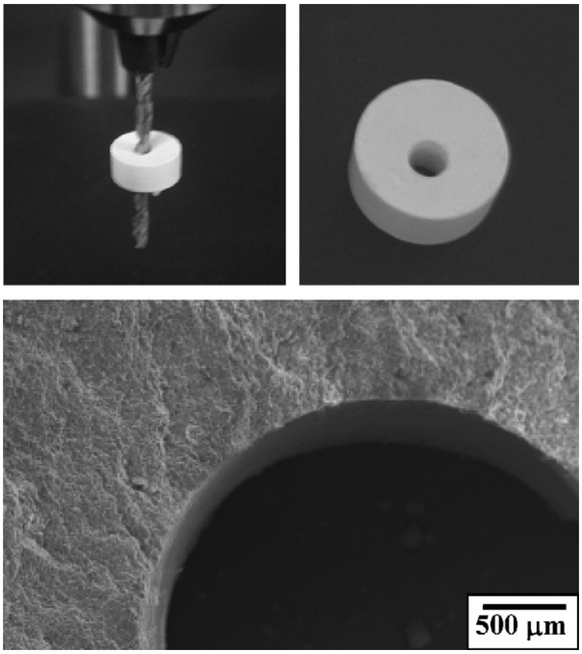

Fig. 8. Photograph of the drilling test and the surface of drilled hole.

The machinability was evaluated further by drilling tests. The drilling test being carried out on sample 800–90–5 and the resulting drilled hole are shown in Fig. 8. Drilling of this sample was very easy and the surface was smooth. The drilling rate of sample 800–90–5 is plotted as a function of bending strength in Fig. 9, which also includes data for reference materials[14] and other reported machinable materials.[13] A clear relationship is observed in these materials, showing increasing drilling rate with decreasing bending strength. The data for the present sample clearly deviates to higher strength and/or higher drilling rate compared with the other machinable materials. Thus, the present material is seen to have an excellent machinability and significant bending strength.

4. Conclusions

Porous ceramics were prepared using thin platy particles of talc ($Mg_3Si_4O_{10}(OH)_2$) and hollow spherical glass particles (CB) using LiCl as a sintering aid. The machinabilities and bending strengths of the products were investigated, with the following results:

(1) Porous ceramics with significant strength could be prepared by firing at 600–800 °C with LiCl, but could not be produced without LiCl even if fired at 1000 °C. The talc component of these samples converted to enstatite ($MgSiO_3$) under the influence of liquid phase sintering by molten LiCl.
(2) The bending strengths (σ) of the resulting samples ranged from 6.3 MPa to 16.3 MPa. The maximum σ value was obtained for the sample with talc:CB = 9:1 fired at 800 °C with the addition of 5 mass% of LiCl.

(3) The cutting rate of the samples was enhanced by the introduction of CB. The sample with the highest strength could readily be drilled, with a smooth resulting hole. This sample showed a high strength and excellent machinability by comparison with other reported reference machinable materials.

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