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Effects of sodium silicate as liquid phase sintering additives on properties of alumina ceramics

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Abstract

This research focused on the production of high-performance alumina products. The feasibility of using soluble alkali silicate in liquid phase sintering of alumina was studied. Liquid soluble alkali silicate was used to enhance the plastic forming of alumina and formed liquid phase sintering to attain fired alumina products with high strength, high alumina content and low water absorption. The methodology consisted of the mixing of organic binder with sodium silicate (Na_2SiO_3), used as liquid phase sintering additive, of 0-15 wt%. Magnesium carbonate ($MgCO_3$), used as the grain growth inhibitor, of 0-1 wt% were added and followed by alumina powders. The mixtures were kneaded thoroughly creating a dough. Alumina bodies with a diameter sizes of 10 and 35 mm were differently obtained from extrusion and uniaxial pressing techniques. Drying and firing process were carried out at 110°C for 24 h and 1600°C for 2 h. The results demonstrated that the addition of Na_2SiO_3 led to an increase of bulk density, while correspondingly showed a lowering of water absorption. Fired alumina products with water absorption of 0.37% were derived by extrusion with the addition of 1 wt% of $MgCO_3$ and 10 wt% of Na_2SiO_3 solution.

1. Introduction

Alumina is the most well-known fine ceramic material for chemical and physical stability. It has a very high melting point (about 2000°C). Alumina has been generally employed for its high electrical insulation, strength, corrosion and wear-resistance properties in many applications such as electrical components, mechanical parts, refractories, abrasives and filler in some applications [1].

At present, many sintering techniques can be used to improve final density of alumina products up to 98% of theoretical density, for example: spark plasma sintering [2] and microwave sintering [3]. Moreover, starting raw alumina powders usually have sizes in the submicron range. Liquid phase sintering (LPS) is one of many techniques that is used to densify alumina products to obtain high density up to 98.5% of theoretical density without using expensive equipment and starting raw alumina powders in submicron sizes unlike other techniques [4].

LPS is a sintering technique of powder compacts containing more than one component at temperatures above the solidus of the components which allows the presence of a liquid in the system during sintering. It consists of three main processes which are particle rearrangement, solution-precipitation and final densification. LPS is considered faster than conventional sintering because particles can transport and redistribute through the liquid flow in the particle rearrangement process.

In general, sintering additive is usually applied to decrease the sintering temperature of alumina to save on manufacturing cost. Solid additive requires wet milling to give well-dispersed and homogeneous mixing which takes long time to get rid of water or solution before it can be used as raw material. Subbarao [5] studied the diffusibility of alkali ions in alumina structure, results showed that sodium ion moved at the fastest rate followed by lithium ion and potassium ion, respectively. Besides, Louet *et al.* [6] reported that the increasing amount of sodium oxide in alumina affected in a decline of sintered density while silica (SiO_2) had no significant effect.

Apart from determining the sintering technique and additive, controlling the grain size enhances physical properties of alumina products because small grains within the sample can result in dense grain boundaries that delay crack propagation when the sample is damaged [7]. To get small grains, magnesium carbonate is considered as a grain growth inhibitor because at sintering temperature 1600°C, K. Bodisova [8] described that the smallest grain size of alumina can be achieved by using magnesium oxide.

Generally, there are many ceramic processing techniques sorted by moisture content from high to low which are slip casting, plastic forming and dry pressing, respectively [9]. Higher moisture content

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results in higher drying shrinkage and the lowering of solid content in sintered products, and alumina content is proportional to strength and density according to a report by Morrell [10]. Moreover, Lorente-Ayza [11] investigated the difference between dry pressing and extrusion in the application as microfiltration membrane sintered at 1160°C, extruded samples showed higher mechanical strength and lower water absorption than dry pressed samples.

The main purpose of this study is to prepare sintered alumina samples by utilizing the extrusion method which give high production volumes. In this case, this research decided to utilize sodium silicate (Na_2SiO_3) as the sintering additive in liquid form of aqueous solution which can be mixed with alumina more easily than in solid form and saves on processing time by forming liquid phase with alumina at sintering temperature. Since, Na source is used in many works in the form of sodium acetate [12] sodium chloride [13], and sodium carbonate [14], but no previous report has mentioned the use of a sodium silicate solution, a white-to-transparent liquid which contains sodium oxide (Na_2O) and silicon dioxide (SiO_2), as a sintering additive of alumina before. Moreover, magnesium carbonate ($MgCO_3$) was used as the grain growth inhibitor in this research because small grains are preferred in order to increase the mechanical strength. Effects of Na_2SiO_3 amount will be investigated further in terms of bulk density, water absorption, strength, microstructure and existing phase of sintered samples.

2. Experimental

0, 0.5, and 1 wt% of $MgCO_3$ powder (UNILAB®, Ajax Finechem, Australia) was dispersed in organic binder solution consisting of 13.17 wt% of sodium carboxymethyl cellulose (CMC) (Krungthepchem Co., Ltd., Bangkok, Thailand, 1.88 wt% of polyvinyl alcohol (PVA) (Wako Pure Chemicals Co., Ltd., Osaka, Japan), 0.94 wt% of polyethylene glycol (PEG) (Wako Pure Chemicals Co., Ltd., Osaka, Japan), 1.88 wt% of glycerol (UNILAB®, Ajax Finechem, Australia) and 82.13 wt% of water. This was followed by the adding of Na_2SiO_3 solution (Na_2O 10.10 wt%, SiO_2 31.12 wt%, water 58.78 wt%, C.Thai Chemicals Co., Ltd., Thailand) and Al_2O_3 powders size of 2.5 μm (P122SB, Alteo), respectively. After that, the mixtures were kneaded thoroughly forming a dough.

Since chemical compositions of commercial Na_2SiO_3 solution was fixed, the increase of Na_2SiO_3 solution amount resulted in a higher moisture content of the dough. In order to form the dough with an optimal moisture content for plastic forming by extrusion, compositions of organic binder solution were fixed, and smaller amount of water was added when Na_2SiO_3 solution was increased from 0, 5, 10 to 15 wt%.

At 0 and 5 wt% of Na_2SiO_3 solution, the dough can be formed with the same amount of organic binder solution and water but a lower amount of water was needed for the addition of 10 and 15 wt% of Na_2SiO_3 solution as shown in Table 1.

Alumina bodies with diameter sizes of 10 and 35 mm were shaped differently by uniaxial pressing and extrusion techniques to obtain pellet and cylinder-shaped samples. A drying process was carried out at 110°C for 24 h. After that, samples were placed in alumina crucible and sintered at 1600°C in air for 2 h, then air cooled to room temperature.

Sintered pellet-shaped samples were weighed before and after immersion in water to measure sintered water absorption and bulk density using Archimedes' method.

Sintered cylinder-shaped samples were used to determine flexural strength using the three-point bending test. Consequently, samples were cut into 3 mm-thick pellets by diamond blade and polished using a sequence of 200, 600, 800, and 1200 mesh polishing paper. Then, polished samples were polished again with diamond paste using a sequence of 1 and 3 μm. Finally, microstructures of fracture and polished surface were observed by using a scanning electron microscope (SEM), and existing phases were identified by x-ray diffraction.

Table 1. Amount of each composition at different Na_2SiO_3 and $MgCO_3$ content.

Formular		Na_2SiO_3 (g)	Al_2O_3 (g)	$MgCO_3$ (g)	Organic binder solution (g)	Water added (g)
$MgCO_3$ (wt%)	Na_2SiO_3 (wt%)					
0.5	0	-	125.00	0.625	20	10
	5	6.25	118.75	0.594	20	10
	10	12.50	112.50	0.563	20	5
	15	18.75	106.25	0.531	20	-
1	0	-	125.00	1.250	20	10
	5	6.25	118.75	1.188	20	10
	10	12.50	112.50	1.126	20	5
	15	18.75	106.25	1.062	20	-

3. Results and discussion

The obtained data can be designated that the different amount of $MgCO_3$ in this system did not affect significantly the properties of sintered alumina samples which were formed by uniaxial pressing technique. Therefore, the effect of $MgCO_3$ added at 0.5 and 1 wt% can be neglected reasonably when considered in bulk density and water absorption results.

3.1 Sintered materials' characteristic

As shown in Figure 1, the addition of liquid phase sintering additives or Na_2SiO_3 resulted in an improvement of bulk density. As pores were removed through liquid formed during sintering, the larger amount of liquid caused a rise in bulk density [15].

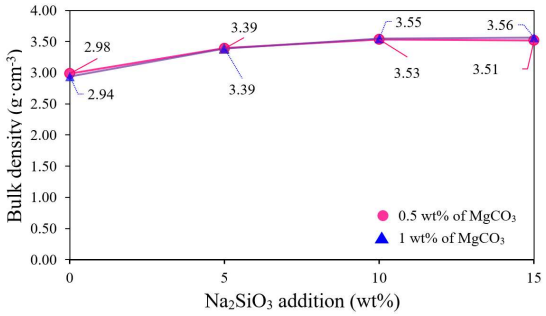

Figure 1. Bulk density of sintered alumina samples at 0, 5, 10 and 15 wt% of Na_2SiO_3 with 0.5 and 1 wt% of $MgCO_3$.

From the addition of 0 to 10 wt% of Na_2SiO_3, bulk density grew steadily proportional to the amount of Na_2SiO_3 solution added. After that, there was an indistinguishable bulk density value, approximately 3.5 $g \cdot cm^{-3}$, between 10 and 15 wt% of Na_2SiO_3 which means the addition of Na_2SiO_3 solution of more than 10 wt% did not cause any further changes in bulk density of samples. Since, bulk density is not an intrinsic property, it is defined as the mass per unit volume including pores and voids that is related to the microstructure of samples in Figure 4 which is described below. This differed from the work of Louet [5] which described that the increase in sodium oxide caused a decline in density, because this work is concerned about density in terms of bulk density of the samples.

Water absorption was well-concerned in this work because it directly affected the quality and durability of products. It was observed in Figure 2 that water absorption of all samples decreased sharply starting from roughly above 7% at 0 wt% of Na_2SiO_3 to 2.4% and 0.4% at 5 wt% and 10 wt% of Na_2SiO_3. At 10 wt% of Na_2SiO_3, the lowest water absorption value achieved was as low as 0.38% and 0.40% from the addition of $MgCO_3$ at 0.5 and 1 wt%, respectively. This corresponded with bulk density of samples described above due to an elimination of pores through liquid [16] and made the composition with the addition of Na_2SiO_3 at 10 wt% interesting for any applications requiring its low water absorption. For example, lining materials and refractory.

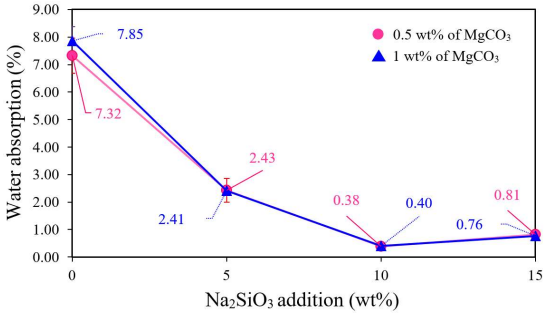

Figure 2. Water absorption of sintered alumina samples at 0, 5, 10 and 15 wt% of Na_2SiO_3 with 0.5 and 1 wt% of $MgCO_3$.

3.2 Mechanism of material system

At sintering temperature, liquid occurred in the system after the additive melted and reacted with alumina. From XRD analysis of pellet-shaped samples containing 10 wt% of Na_2SiO_3 in Figure 3, corundum (Al_2O_3) occurred as main phase followed by the presence of sodium aluminosilicate ($NaAlSiO_4$) which formed after liquid was cooled. No Mg-containing phase found in this case due to a very small amount of $MgCO_3$ amount added in this experiment.

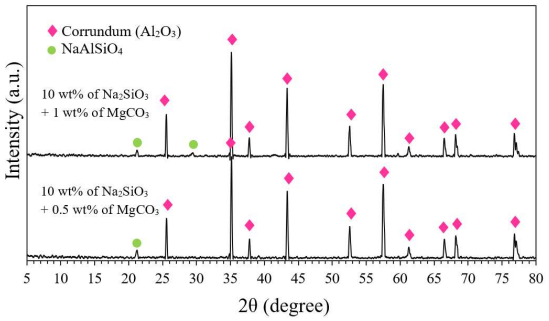

Figure 3. X-ray diffraction analysis of sintered alumina samples at 10 wt% of Na_2SiO_3 with 0.5 and 1 wt% of $MgCO_3$.

Furthermore, scanning electron micrographs in Figure 4 showed that all alumina samples sintered at 1600°C with the 10 wt% of Na_2SiO_3 had similar results in the coexistence of small grains and pores in bulk of samples. Grain sizes is approximately 2.5 µm. It cannot be exactly measured because of unclear grain boundaries. Spherical pores at 0.5 wt% of $MgCO_3$ might have an influence from unexpected inhomogeneous organic components from organic binder solution. Samples containing 1 wt% of $MgCO_3$

showed narrowed pores distributed all over the polished surface. This kind of defect was likely created when the extrusion was conducted. Note that the extruder used in this experimental procedure had no vacuum system which might lead to the trapping of gas in extruded samples.

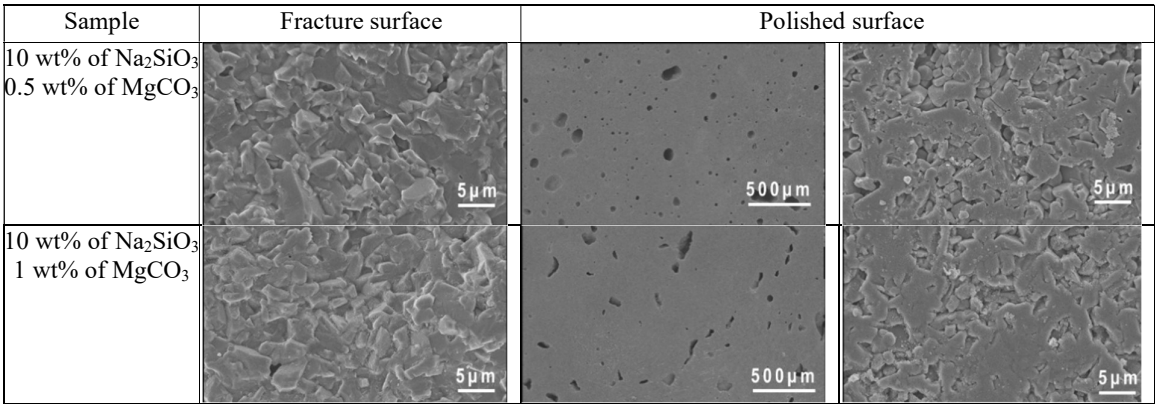

Figure 4. Scanning electron micrographs of fracture and polished surface of alumina samples formed by extrusion at 10 wt% of Na_2SiO_3 sintered at 1600°C, (a) 0.5 wt% 50x, (b) 0.5 wt% 3000x, (c) 1 wt% 50x, and (d) 1 wt% 3000x.

3.3 Mechanical properties

The presence of grain size after sintering in Figure 4 showed that no abnormal grain growth was observed in both 0.5 and 1 wt% of $MgCO_3$ and grains remained small and similar to the starting alumina powders size of 2.3 µm. This is consistent with the work of Bodisova [6], which described that the smallest grain size of alumina can be achieved by using magnesium oxide. Higher content of pores affected in the reduction of grain-grain interface, known as grain boundary, and directly enhanced crack propagation through samples. The presence of large spherical and narrowed pores all over the samples should be the main factor that directly causes the fluctuation in flexural strength of extruded samples as shown in Figure 5.

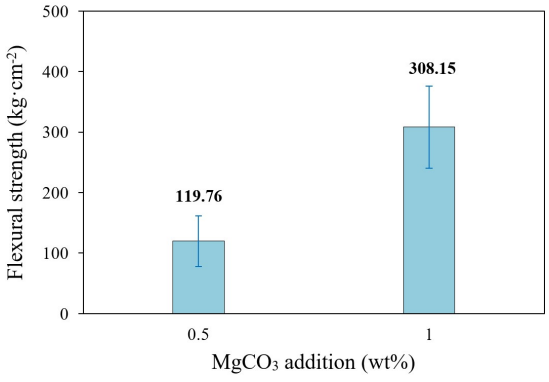

Figure 5. Flexural strength of sintered alumina samples at 10 wt% of Na_2SiO_3 with 0.5 and 1 wt% of $MgCO_3$.

4. Conclusions

The occurrence of liquid phase sintering of Al_2O_3 was confirmed by the existence of the new $NaAlSiO_4$ phase. The addition of Na_2SiO_3 resulted in a decrease of water absorption of sintered alumina samples. The lowest water absorption could reached at 0.38%, in samples containing 10 wt% of Na_2SiO_3, which was very low and desirable for many applications.

Furthermore, bulk density of samples presented stable trends after 10 wt% of Na_2SiO_3 because it directly related to pore volume and pore size of samples which is not an intrinsic property. As seen in SEM images, two main reasons could be identified as;

1. The type of extruder used in this work has no de-airing system that affect the presence of narrowed pores.
2. Organic binder solution used affected this work was not homogeneous enough because round pores showed all over bulk of samples.

At these composition, the addition of 0.5 and 1 wt% of $MgCO_3$ showed almost indistinguishable properties both in water absorption and bulk density. This was because the amount of $MgCO_3$ added in the system was very small as seen in XRD analysis that no Mg-containing phase occurred at any conditions.

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