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FEASIBILITY STUDY ON THE FORMING OF ALUMINA BEADS AND PELLETS BY AGAR GELCASTING

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โดยทั่วไปลูกบดอะลูมินาขนาดเล็กขึ้นรูปโดยใช้แพนแกรนนูเรเตอร์ อย่างไรก็ตามเป็นการ ยากที่จะขึ้นรูปลูกบคขนาดเล็กที่มีขนาดเส้นผ่านศูนย์กลาง 1-2 มิลลิเมตร งานกรั้งนี้มุ่งสนใจถึง วิธีการขึ้นรูปแบบใหม่โดยวิธีหล่อจากอาการ์เจล โดยของผสมของสารแขวนลอยอะลูมินาและ สารละลายของอาการ์ที่ 1.5-4% โดยน้ำหนักถูกหยุดโดยปีเปตลงไปในน้ำมันที่ถูกทำให้เย็น ทำให้ ของผสมมีรูปร่างเป็นทรงกลมเนื่องจากแรงตึงผิว หลังจากของผสมเปลี่ยนสถานะกลายเป็นเจล แล้วจะถูกแขกออกจากน้ำมันเข็นและถูกทำให้แห้งโดยการวางทิ้งไว้ที่อุณหภูมิห้อง และเผาซิน เทอร์ที่อุณหภูมิ 1300-1400°C พบว่าน้ำมันเครื่อง Tellus 46 ที่อุณหภูมิ 0°C มีความหนืดที่ เหมาะสมในการขึ้นรูป ที่ความเข้มข้นของสารละลายอาการ์ 1.5% พบว่ารูปร่างของหยุดที่เพิ่งหลุด ออกมาจากปลายปีเปตจะเป็นทรงกลมมากขึ้นเมื่อจำนวนของอาการ์เพิ่มขึ้นจาก 0.25-1.0% โดย น้ำหนัก อย่างไรก็ตามที่ความเข้มข้นของสารละลายอาการ์ ≥ 2%พบว่ารูปร่างของหยุดจะกลายเป็น วงรีมากขึ้นเมื่อจำนวนของอาการ์เพิ่มขึ้น หลังจากการทำให้แห้งพบว่าหยุดที่เปลี่ยนสถานะเป็นเจล จะมีรูปร่างผิดไปจากทรงกลมมากขึ้นเมื่อจำนวนของอาการ์ลดลง ค่าความหนาแน่นสัมพัทธ์สูงสุด ของถูกบดที่ได้รับคือ 99% โดยมีจำนวนของอาการ์ 0.25 และ 1.0%ซึ่งเตรียมจากสารละลาขอาการ์ที่ บีความเข้มข้น 1.5%

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The alumina grinding beads are usually formed by a pan granulator method, however it is difficult to form small size beads (1-2mm diameter). This work is focused on a new forming method which uses agar as gelling agent in gelcasting. The mixtures of alumina suspension and agar solution (concentration 1.5-4wt.%) are dropped into cooled oil using a pipette. The shape of the mixture becomes sphere by its surface tension. After the mixture transformed to gel, it is separated from cooled oil. Later the gelled beads are dried in air and finally sintered at 1300-1400°C. Tellus 46 oil is the cooled oil having the proper viscosity for forming. At 1.5wt.% concentration of agar solution, the shape of drop which is just dropped from the pipette tip is almost sphere. The sphere became better when final agar content increases from 0.25 to 1.0wt.%. However, at concentration \geq 2wt.% the shape of drop became more and more oval with increasing of the agar content. After drying, gelled beads deform more and more when the agar content decreases. The 99% relative density is obtained for the specimen with the final agar content 0.25 and 1.0wt.% prepared from 1.5wt.% concentration of agar solution.

"จุฬาลงกรณมหาวิทยาลย

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CHAPTER I

INTRODUCTION

High hardness, chemical inertness, and respectable strength and fracture toughness combined with relatively low production costs make alumina one of the most widely used ceramics. Alumina ceramics find can be used in a number of abrasive wear environments, such as ball mills, grinders, mixers, containers for abrasive slurries, and cutting tools [1]. Alumina grinding beads have been used for grinding, mixing, and dispersing in fields of ceramics, food, pharmaceutical, ink, pigment and nanomaterials. The features of alumina beads are high density, excellent toughness, and superior hardness.

In the present, alumina beads (1-2 mm diameter) are formed by pan granulator method, however size of the beads can not controlled uniformly. This work is focused on new forming method that uses agar as gelling agent in gelcasting method. We expected that this method can control size uniformly by dropping the mixture of alumina suspension and agar solution into cooled oil. After the mixture sol transforms to gel, the gelled drops become solid by air drying (syneresis). Factors of forming for example type and temperature of oils, optimum composition of the mixture, viscosity of the mixture, and shape of beads after sintering are studied. In addition, forming the pellet type specimen in metal die was also studied.

The objectives of this research are as follows:

- 1. To get alumina beads having the shape close to sphere narrow diameter and the density close to theoretical value by agar gelcasting.
- 2. To get alumina pellets by agar gelcasting.

CHAPTER II

LITERATURE REVIEW

2.1 Structure and properties of agar

The structure of agar that is extracted commercially from a number of red algae species has been studied for decades, primarily by Japanese scientists. Agar extracted comprises of two groups of polysaccharides: agarose, the gelling component, it is an essentially sulfate-free neutral (non-ionic) polysaccharide and agaropectin is the non-gelling ionic (charged) polysaccharide. Agaropectin includes a small amount of sulfate (~2%) but has no commercial value and is largely discarded during the commercial production of agar. Agarose and agaropectin contents vary in different types of commercial agar [2]. Repeat unit of agar is shown in Fig. 2.1.



Fig. 2.1 Repeat unit of agar [17]

The ash content of agar depends first and foremost on its origin (type of seaweed). The metallic and non-metallic constituents are important, especially in the bacteriological grade agars. Theirs compositions are sulfur, 1.0-1.5%: sodium, 0.6-1.2%: calcium, 0.15-0.25%: magnesium, 400-1200ppm: potassium, 100-300ppm: phosphorus, 10-80ppm: iron, 5-20ppm: manganese, 1-5ppm: zinc, 5-20ppm and strontium, 10-50ppm[3].

The physical properties of agar solutions and gels are important to the manufacturer and the scientist. Although agar is soluble in boiling water, when used in forms other than fine powder (i.e. bars strings and flakes), an overnight soak in cold water helps to achieve full dissolution [4]. Soaking agar for a short time (of the order of minutes) helps in reaching quick and good dissolution. The pH during soaking and boiling should be kept neutral.

Setting temperatures were found to increase with agar concentration, as did gelation temperatures of agarose. At a predetermined (constant) temperature, the higher the setting point of the sol, the higher the rigidity coefficient of the gel. The gelling temperature of agarose increases with increasing methoxyl content. The slower cooling rate give the higher the temperature of agarose gelation.

Agar is unique among gelling agents because gelation occurs at temperatures far below the gel's melting temperature. Agar produces rigid gels at concentration of ~1% (w/w). The sol sets to a gel at about $30-40^{\circ}$ C. This gel is rigid and it maintains its shape. Gels with self-supporting shapes can be formed with 0.1% agar (the rest being water). The gel is melted by heating to ~85-95°C. There is a relationship between gel strength and melting point. Both increase in the same direction, although some exceptions can be found.

Agar has thermal reversibility at temperatures over 0°C. Agar is the most typical thermoreversible colloidal substance. The phase change between gel and sol is safely repeated, only if the aqueous medium is maintained at neutral.

At elevated temperatures, agarose exists as a disordered random coil, but on cooling, it forms strong gels at a low polymer concentration. The gelation process involves the adoption of the ordered double-helix state [5-8]. The double helix structure formed on cooling is shown in Fig. 2.2.



4

Fig. 2.2 Schematic representation of the double helix structure formed on cooling [17]

Agar gel shrinkage results in syneresis. The amount of syneresed water is inversely proportional to the square of concentration of agar solution. Agar gel syneresis is influenced by the concentration of the gel, holding time, apparent gel strength, rigidity coefficient, pressurization, and total sulfate content [9].

The effect of inorganic salts on the time required to set agar sols has been thoroughly covered in the literature. Potassium sulfate has been shown to accelerate gelation the most, whereas iodine is the least effective. Ferric and ferrous salts (at 1ppm) have been reported to reduce the transparency of a 1% agar gel. Sodium chloride (table salt) slightly increases gel strength [10]. The addition of sugar (up to 60%) contributed to agar strength. The effects of sugars (sucrose, glucose, fructose, maltose, galactose, mannose and ribose) on the gel-sol transition of agarose and **k**-carrageenan have been studied [11]. The effects of sugar were ascribed to hydrogen bonding between hydroxyl groups in polymers and sugars and/or structural changes in the solvent water.

2.2 Gel casting of alumina ceramics

Polysaccharide gel casting is based on the gelation of polysaccharide on cooling to create a three-dimensional network [12]. The amount and nature of agar in solution have effect on the gel strength at room temperature. However, the amount of polysaccharides in ceramic suspension should be as low as possible because of the inherent increase in slip viscosity, shrinkage of bodies, and drawbacks related to burn out of organics.

In 1999, Z.P. Xie et al. [13] developed a cast forming process for ceramic based on agarose gelation. For the casting of alumina, an agarose addition of ~1wt% and a solid loading of ~54vol% were found to be a homogeneous density distribution, and a green strength > 3MPa. Green parts can be sintered directly without special binder burn out procedures, and without deformation of cracking in the sintered parts. This was attributed to its uniform distribution of composition in the green state.

S.M. Olhero et al. [14] (1999) studied the synergetic effect of mixture of agar and galactomannan (80/20) to consolidate alumina suspensions by gelcasting. Polysaccharide solutions were prepared at 60°C and added to alumina suspensions maintained at the same temperature. These alumina/polysaccharides slurries were then poured into non-porous moulds. Sintered bodies always give lower density compared with slip casting method. This was attributed to the hypothesis of the occurrence of bridging flocculation in the presence of polysaccharides. In addition, they showed that optimal processing conditions require the use of high solid loading suspensions.

A.J. Millán et al. [15] (2000) compared two different routes for improving the consolidation of alumina by agarose gelation as shown in Fig 2.3. The first was agarose addition as a solid powder and then heating the slurry, and the second was independent preparation of the slurry and the agarose solution and further mixing at a temperature higher than 60°C. The first route showed that the addition as a powder limits the solid loading because viscosity increases abruptly. The slip starts to flocculate at temperatures around 60°C, where the agarose can not fully dissolve. A green density of 54% theoretical was obtained by this route and the sintered density was 94% of theoretical because of the presence of agarose agglomerates undissolved. The second

route demonstrates to be suitable for obtaining reliable alumina parts with a green density of 58% theoretical and a sintered density of 98.7% theoretical. The other advantage of this mixing route was that, when all additives were dissolved the quantity necessary to promote gelation can be significantly reduced.



Fig. 2.3 Flow chart of the two processing routes [15]

In 2001, A.J. Millán et al. [16] used carrageenan as gelling agent in gel casting. Within the studied range (1-3wt%) the carrageenan was dissolved completely below 65°C, and the gel was completely formed at 30°C. These were advantages with respect to other additives that need higher temperature to dissolve completely (usually more than 80°C). A commercial alumina powder was used (Condea HPA05, Germany) with a mean particle size of 0.35µm. Alumina slips were prepared at solid loading of 80wt% by adding final carrageenan at 0.25wt%. The green density of the formed body was higher than 58% of theoretical and the sintered density was higher than 98%. The SEM microstructure of polished sintered surface is shown in Fig. 2.4.



Fig. 2.4 SEM microstructure of sintered gel cast alumina samples [16]

A.J. Millán et al. [17] (2001) studied rheological properties of three polysaccharides solution, agar, agarose, and carrageenan for gel casting. The viscosity of solutions of the three additives was measured at a temperature of 65°C as a function of the solution concentration as shown in Fig. 2.5. The lowest viscosity was obtained for agarose. The maximum viscosity was obtained for carrageenan solution.



Fig. 2.5 Viscosity at 65°C of the three additive solutions prepared at different concentrations [17]

A.J. Millán et al. [18] (2001) investigated the influence of the addition of solution of agar, agarose and carrageenan on the rheological properties of alumina slurries. These gelling additives had been successfully used for ceramic suspensions providing a high consistency on cooling. The concentration of polysaccharide solution has a key role in the variation of viscosity. On the other hand, for the same final polysaccharide content, the concentration of polysaccharides solution has a significant influence on drying shrinkage. The increasing viscosity of the slurries with gelling agents on cooling (above the T_d) can be associated to the formation of coil helices.

A.J. Millán et al. [19] (2001) studied the green density and the mechanical behavior at room temperature of gel casting alumina bodies using agar, agarose and carrageenan as gelling additives. A commercial α -Al₂O₃ was used (Condea HPA05, USA) with a mean particle size of 0.35µm. Values of the bending strength up to 4MPa were higher than those of slip cast alumina without gelling additives (0.5±0.2MPa), and they increase with the final concentration of polysaccharides. Young's modulus values were mainly influenced by concentration of the polysaccharide solution which their values decreased with increasing viscosities.

In 2004, I. Santacruz et al. [20] reported the preparation of agarose solutions to concentrations of 3.0 and 5.6wt% by simply heating at 65°C and by overpressure heating (>110 °C) added into alumina suspensions. The greater efficiency of the dissolution process made the viscosity of the solution to be one order of magnitude lower than that of a solution with one half of agarose concentration prepared by direct

heating. Green density as high as 63%TD were obtained, similar to those obtained by slip casting. Sintering at 1500° C/2h leads to relative density > 99% of theoretical, similar to those obtained by slip casting.



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CHAPTER III

EXPERIMENTAL PROCEDURE

3.1 Raw materials

A list of the raw materials which were used in the experiment and their suppliers are shown in Table 3.1.

Raw materials	Purity (%)	suppliers	
Alumina powder (A-21)	> 99.00	Sumitomo chemical Co.,Ltd.	
Alumina powder (TMDA)	> 99.99	Taimei chemical Co.,Ltd.	
MgO powder (MJ-30)	> 99.98	Ube materials Co., Ltd.	
Agar powder (M7)	≥ 99.00	Ina-shokuhin Kogyo Co.,Ltd.	
Dispersants			
(NH ₄ salt of PMAA, Aron,	าหยบวก	5	
A6114)		Toagousei Co., Ltd.	
(NH ₄ salt of PAA, Dispex, A-40)	Conc. 40wt.%, pH 8	Loxey (Thailand) Co., Ltd.	

Table 3.1 Raw materials used in the experiment

3.2 Process flow chart for alumina beads

3.2.1 Viscosity measurement of oil

The four-kind of oils including Tellus 46, 100 (machine oil), soybean oil, and silicon oil were measured using a rotary viscometer (Brookfield RVDE). The oil was poured into 250ml beaker, then put the beaker in a cooler at the temperatures of 30, 10, 0°C respectively. The evolution of viscosity on cooling temperature was studied at a constant shear stress of 60 rpm.

3.2.2 Viscosity of the mixture with temperature

The flow chart of this experiment is similar to Fig. 3.1. A commercial alumina powder (TMDA, Taimei chemical Co., Ltd., Japan) with a mean particle size of 0.4µm was used. Alumina suspension was prepared by ball milling for 16h with HDPE bottle and alumina balls. The ammonium salt of poly(methacrylic) acid (Aron, A6114) was used As deflocculant at an optimum concentration of 1.6 wt% referred to dry solid [21]. The suspension was prepared to a solid loading of 75wt%. MgO powder was used as the sintering aid at a fixed amount of 0.03wt% referred to dry solids. Agar solution was prepared to the concentration of 2wt%. The final concentration of agar at the amount of 0.75wt% was added to the suspension on the basis of dry solid (composition of mixture A3 shown in Table 3.2). The viscosity evolution of the mixture was measured by a rotary viscometer (Brookfield RVDE) with cooling temperature at a constant shear rate of 100rpm .



Fig. 3.1 The flow chart of forming alumina beads



Fig. 3.2 Picture of pipette and oil in glass cylinder used for forming

Final agar content	Concentration of agar solution (wt%)			
(wt%)	1.5	2.0	3.0	4.0
0.25	A1	B1	C1	D1
0.50	A2	B2	C2	D2
0.75	A3	B3	C3	D3
1.00	A4	B4	6	-

Table 3.2 Nomenclature of the mixtures

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3.2.3 Falling time of the mixture drop in oil

The two-kind oils including Tellus 46 and soybean oil were used in this experiment. The oil was filled in a 1000ml beaker that has the height of 30cm then the beaker was put in a cooler at the temperatures of 30, 10 and 0°C, respectively. The picture of the beaker filled with oil and pipette used are shown in Fig 3.2. The mixture of alumina suspension and agar solution for composition A3 shown in Table 3.2 was dropped into the oil by a pipette at each temperature, meanwhile the falling time of drops in oil was recorded. After that, the gelled drops were separated from oil and dried in air (syneresis) at room temperature for 24h. The shapes after syneresis were observed by naked eye.

3.2.4 Types of pipette on the weight of the mixtures after dropping

The mixture of alumina suspension and agar solution A1 (Table 3.2) was prepared according to the flow chart shown in Fig. 3.1. Types of pipette are shown in Table 3.3. The drop shape just separated from the tip of dropper was observed by naked eye.



Fig. 3.3 Picture of tip of pipette made of glass, plastic, and metal

Materials	Diameter at tip of needle (mm)	Shape at tip of needle
	0.45	
	0.50	
motol	0.70	Cylinder and tip is inclined
metai	0.80	
4	0.90	
	1.20	
Glass	1.20	Cylinder
plastic	0.85	Cone

Table 3.3 Types and characteristics of pipette

สถาบันวิทยบริการ จุฬาลงกรณ์มหาวิทยาลัย The various conditions of forming and drying of alumina beads of the mixture A2 are shown in Table 3.4.

Condition No.	oil	Syneresis technique
1	Tellus 46, 30cm height, 0°C	Soak in PEG-400
2	Tellus 46, 70cm height, 0°C	Air dried at RT
3	Tellus 46, 30cm height, 0°C	Vacuum at 0°C
4	Tellus 46, 30cm height, 0°C	Cooled at 0°C
5	Tellus 46, 30cm height, 0°C	Cooled at 5°C
6	Tellus 46, 30cm height, 0°C	Fan dried at RT
7	Tellus 46, 15cm height + PEG-400, 15cm height, 0°C	Air dried at RT
8	Tellus 46, 30cm height, 0°C	Soak in glycerin

Table 3.4 Various conditions for forming and drying of alumina beads using mixture A2

RT = Room Temperature

3.2.6 Variation of the concentration of agar solution and final agar content on viscosity

The mixtures of various content of alumina suspension and agar solution were prepared with the same condition of 3.2.2. The variation of concentration of agar solution and final agar content are shown in Table 3.2. The viscosity of the mixtures was measured at a constant temperature of 50°C. The mixtures were heated in an ultrasonic water bath. The mixtures were mechanically stirred for 1 min, before measuring viscosity at a constant shear rate of 100rpm.

3.2.7 Shape of alumina beads after sintering

After measuring the viscosity of the mixtures, the mixtures were dropped into Tellus 46 oil at a temperature of 0°C and kept for 10 min to make sure that the mixtures transform to gel completely. The gelled drops were separated from the cooled oil, then dried in air (syneresis) at room temperature for 24h. The green beads were sintered at the temperatures of 1300, 1350 and 1400°C. The shape of alumina beads were observed by scanning electron microscope at low magnification.

3.2.8 Bulk density and water absorption

The bulk density and water absorption of sintered beads were measured according to Archimedes' method (ASTM standard: C830-93) and calculated by equation (3.1) and (3.2)

Bulk density =
$$\frac{W_d}{W_{ext} - W_{exc}}\rho$$
 (3.1)

% Water absorption =
$$\frac{W_{sat} - W_d}{W_d} \times 100$$
 (3.2)

Where (W_d) is dry weight, (W_{sat}) is saturated weight, (W_{sus}) is suspended weight and ρ is water density at measurement temperature which was referred from reference [22].

Note: This measurement has little difference from ASTM standard: C830.93. In the case of ASTM, the measurement is done for only one sample, but in the case of this measurement alumina beads in the range between 5-15 beads was measured at one time. Because the size of alumina beads was so small (diameter about 1mm) that it may make inaccuracy in the measurement. Therefore, a number of alumina beads were used to reduce inaccuracy.

3.2.9 Microstructural observation

The microstructure of sintered beads was examined by optical microscope and scanning electron microscope (SEM). The alumina beads were mounted on resin and polished with silicon carbide abrasive paper following by the fineness of paper No. 600, 1200 and 1500, respectively. Cross section of the polished specimens was observed by optical microscope. Finally, the alumina beads were polished with 3 and 1µm diamond paste, respectively. After that the polished specimens were taken out of resin by soldering iron gun (see Fig. 3.4). The polished specimens were thermally etched at the temperature of 50°C lower than the sintering temperature for 1h. The etched specimens were coated with gold by sputtering for 3min before the SEM observation.



Fig. 3.4 Picture of soldering iron gun

3.3 Preliminary experiment using alumina powder A-21

Process flow chart of making alumina beads is shown in Fig.3.1. A commercial alumina powder A-21 (Sumitomo, Japan) with a mean particle size of 10µm was used. The alumina powder was milled by an attritor mill for 10h prior to be used for making alumina suspension. The mean particle size after milling was about 1µm (measured by particle size analyzer as shown in appendix A). Various suspensions with different solid loading (70, 75 and 80wt.%) and dispersant concentration were prepared for measuring viscosity. Two-kind of dispersants, A6114 (PMAA) and A-40 (PAA), were compared at the same solid loading by measuring viscosity. All suspensions were prepared by ball milling for 16 h with HDPE bottle and alumina balls. The viscosity of suspension was measured using a rotary viscometer at 100rpm.

Later, the alumina suspension of 75wt.% solid loading was used for forming beads. The ammonium salt of polyacrylic acid (Dispex, A-40) was used as deflocculant at an optimum concentration of 1.1wt% referred to dry solid. Agar solution was prepared by mixing agar powder with distilled water to total concentration of 2wt% and then by boiling. This solution was added to alumina suspension maintaining a temperature of both ceramic suspension and agar solution at 50°C. The final concentration of gelling matter added to the suspension was 0.2wt% on the basis of dry solids. The mixture of alumina suspension and agar solution was dropped into cooled oil (soybean oil), which is 30cm depth at a temperature of 0°C then gelled drops were

separated from the cooled oil. The gel beads were dried in air at room temperature for 24h. The green beads were sintered at a temperature of 1630°C for 2h. The shape of the sintered beads was observed by eye.

3.4 Process flow chart for alumina pellets

The flow chart of forming alumina pellets by gel casting in metal die is shown in Fig. 3.6. The composition A4 in Table 3.2 was used for the experiment according to the flow chart of Fig. 3.1. Metal die with dimensions of diameter 25mm x thickness 3mm (see Fig. 3.5) was warmed to 50°C in water bath before casting. When the mixture was poured into metal die at room temperature, the mixture can not be filled into the metal die because the mixture changes to gel right away. Composition A2, A4, B1, B2 and C2 in Table 3.2 were also formed. After casting, the metal die was put in cooled water at 10°C. Gelled sample was removed from die and dried in a closed vessel for 3 days. After casting and drying, samples were calcined at 800°C for 2h with the heating rate of 10°/min. The calcined samples were sintered at 1300, 1350 and 1400°C for 2h. The shape of sintered sample was observed by the naked eye. The bulk density and water absorption of sintered sample were measured according to Archimedes' method.



Fig. 3.5 Picture of metal die used for forming the disk shape



Fig. 3.6 Flow chart of forming alumina disks by gelcasting in metal die

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Basic properties of agar and oils

4.1.1 Viscosity of the oils

Viscosity of four-kind of oils with temperature in the range of 0 to 30°C is shown in Fig. 4.1. The viscosity of oil increased at low temperature. When temperature decreased to 0°C the viscosity of silicon oil and Tellus 46 sharply increased. On the other hand, the viscosity of soybean oil and Tellus 100 slightly increased. The two-type of oils, Tellus 46 and soybean oils, were chosen for performing the following experiments, because the viscosity of silicon oil was too high and that of Tellus 100 was very close to that of soybean oil.



Fig. 4.1 Viscosity of four-kind of oils with temperature

4.1.2 Viscosity of the mixtures with temperature

The viscosity of the mixture A3 as a function of the temperature is shown in Fig. 4.2. When the temperature was decreased from 55 to 37° C the viscosity of the mixtures slightly increased from 700 to 1000mPa.s. At the temperature of 36° C, the viscosity sharply increased which is attributed to gelling temperature (T_g) of agar. The optimum temperature for dropping should be higher than gelling temperature. The viscosity of suspension must be as low as possible. Otherwise, slurry does not fall easily from the tip of the pipette. Therefore, the temperature of mixture was kept at 50° C before the mixture is dropped from the pipette.



Fig. 4.2 Viscosity of the mixture A3 as a function of temperature

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4.2 Effect of process conditions

4.2.1 Diameter of the pipette tip

The slurry was dropped using pipette. It is easily expected that the size of the drop depends on the diameter of the pipette tip. Fig. 4.3 shows weight of a drop of mixture A1 (Table 3.2) as a function of the diameter at the tip of pipette. The weight of drops increased with increasing the size of diameter. Therefore, the size of drop is determined by the diameter of the pipette tip. In addition, 1.2mm tip of glass pipette provided the weight of drop about 22mg and the weight of drop from 0.85mm tip of plastic pipette was about 13mg. When compared at the same diameter, the glass pipette provided the largest drop size and the metal pipette provided the least one. In this experiment, 0.85mm tip of plastic pipette was used for the rest of the experiment.



Fig. 4.3 Relationship between the diameter at the tip of metal pipette and weight of mixture drop of A1
4.2.2 Falling time of suspension drops in oil

Fig. 4.4 shows the relationship between the falling time of the mixture drop, temperature of oils and figure of the beads at the bottom of the glass cylinder. When the viscosity of oil is high, it takes long time until the drop falls down to the bottom and vice versa. And when the falling time is short, the drop deformed more because the drop is not still transformed to gel completely. Tellus 46 oil at 0°C is the optimum condition in forming because the almost spherical gel beads were obtained by this condition. On the other hand, soybean oil is not suitable for use in forming due to its low viscosity. The type and temperature of oil and the depth of oil are the key factors to obtain sphere gel. After this experiment, the condition for forming is Tellus 46 oil at 0°C.



Fig. 4.4 Relationship between falling time, temperature of oil, and shape of the beads at the bottom of the glass cylinder

4.2.3 Drying conditions

The viscosity of the slurry increases when temperature decreased as shown in Fig.4.1. However, the strength to maintain the figure of the gelled drop in spherical shape is not enough. When water in the drop was decreased by evaporating or syneresis, then the strength increases. Therefore, several drying conditions were tested.

From Fig. 4.5 in condition 1, the shape of green beads was flat-oval because PEG-400 quickly absorbs water that is inside of gelled beads. In condition 2, the shape of green beads was almost sphere. Green beads can not be obtained by condition 3 because water can not be evaporated off from the gelled beads at so low temperature as 0° C. The water in the formed sphere changes to ice quickly and do not evaporate at condition 4. The shape of green beads obtained by condition 5 and 6 were the same with condition 2. However, condition 5 takes longer time of drying than condition 6 due to low evaporation rate of water at lower temperature. Tellus 46 and PEG-400 were filled in the 1000cc cylinder in condition 7. Since the density of PEG-400 is larger than that of Tellus 46, the top half in the cylinder was Tellus 46 and bottom half was PEG-400. During forming at this condition the shape of drops is changed to oval at the junction between PEG-400 and Tellus 46. The shape of green beads was irregularoval with center-pit. The shape of green beads was almost sphere for condition 8. However, glycerin was absorbed in the surface of gelled beads. So in this condition, it took long time for evaporating glycerin. PEG (Polyethylene Glycol) and glycerin can absorb water. Due to the very quick syneresis, however, the figure of drop changed to irregular from sphere. As a result, we selected condition 2 as the drying condition after this.

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Condition 1: Tellus 46, 30cm height,	Condition 2: Tellus 46, 30cm height,
0°C,soak in PEG-400	0°C, air dried at room temperature
Can not be dried	Can not be dried
Condition 3: Tellus 46, 30cm height,	Condition 4: Tellus 46, 30cm height,
0°C, put in vacuum pump at 0°C	0°C, cooled at 0°C
Condition 5: Tellus 46, 30cm height,	Condition 6: Tellus 46, 30cm height,
0°C, cooled at 5°C	0°C, blown by fan at room temperature
Condition 7: Tellus 46 + PEG-400,	Condition 8: Tellus 46, 30cm height,
15+15cm height, 0°C, soak in PEG-400	0°C,soak in glycerin

Fig. 4.5 Shape of green beads after drying in various drying conditions

4.3 Preliminary experiment to form beads using alumina A-21

4.3.1 Viscosity of high solid loading slurry

Fig. 4.7 shows the viscosity of 70, 75 and 80 wt.% A-21 alumina slurry as a function of the amount of PMAA and PAA. For each sample, the viscosity was recorded at 30s at a shear rate of 100 rpm. From Fig. 4.7 as the weight percent of solid increases, the viscosity also increased. The alumina slurry using PAA as dispersant had lower viscosity than one using PMAA. This might be attributed to the molecular weight of the dispersants which the molecular weight of PAA (72) less than that of PMAA (86). Joseph C. III and Ilhan A. A. [23] found that as the molecular weight increases, the viscosity of the slurry drastically increases. From the curves, the viscosity of slurry decreases when the amount of PMAA and PAA increases. In the beginning, the high viscosity was obtained due to incomplete adsorption of negative charge of polymer (COO) on the particle surface. When the amount of dispersant increases, viscosity decreases to 100mPa.s and the stable slurry was obtained due to complete adsorption of COO. In all cases, the minimum viscosity and the stable slurry were obtained at about 1.1wt.% of both PMAA and PAA. Curiously, 80wt.% alumina slurry with PAA should has the high viscosity but it had the low viscosity. This might be attributed to decreasing of pH value [23, 24] as shown in Fig. 4.8.

PMAA (Aron, A6114)

PAA (Dispex, A-40)



Fig. 4.6 Schematic of PMAA and PAA polymer segment [23]



Fig. 4.7 Viscosity of alumina slurry (A-21) at the solid loading of 70, 75 and 80% as a function of dispersant of PMAA and PAA



Fig. 4.8 The pH of alumina slurry (A-21) at the solid loading of 70, 75 and 80% as a function of dispersant of PMAA and PAA

4.3.2 Sintered alumina beads

Fig. 4.9 shows alumina beads after sintering. The shape of alumina beads is close to sphere and the mean diameter is about 1mm. The microstructure is not yet studied.



Fig. 4.9 Figure of alumina beads after sintering



4.4 Alumina beads made of submicron powder TMDA

4.4.1 Effect of the concentration of agar solution and the final agar content on the viscosity of mixtures

Fig. 4.10 shows the relationship between the viscosity of the mixture at 50° C and the concentration of the agar solution (1.5 - 4wt.%) and the final agar content (0.25 - 1wt.%). The different trend was observed [18] for the agar concentration of 1.5 wt% and that of ≥ 2 wt%. The viscosity of mixtures made from 1.5wt% agar solution decreased with increasing final agar content. This is in agreement with the reduction in the solid content in the final mixtures as shown in Table 4.1. On the other hand, the viscosity increased with increasing the final agar content in the mixtures when the agar solution was ≥ 2 wt% of concentration. The final solid content also decreases with decreasing the final agar content but the decrease is slightly. Therefore, the evolution of viscosity must be now related to the rheological behavior of the agar solution itself, where viscosity strongly increases with concentration.



Fig. 4.10 Relationship between concentrations of agar solution and final agar content on the viscosity of mixtures

Concentration of agar	Final agar content (wt.%)					
solution (wt.%)	0.25	0.5	0.75	1.0		
1.5	66.0	59.4	54.1	49.6		
2.0	67.8	62.5	58.0	54.1		
3.0	69.8	66.0	62.5	-		
4.0	70.8	67.8	65.1	-		

Table 4.1 Final alumina content (%) in the mixtures A1-D3



4.4.2 Figure of alumina beads after sintering

The figure of drop when it was removed from the tip of the pipette was almost sphere and became sphere during falling down in the cooled oil due to its surface tension for the agar concentration of 1.5wt% solution. On the other hand, the figure was oval for ≥ 2 wt% of agar concentration and kept oval during falling in the cool oil due to the high viscosity (> 750cP) of the mixtures. The possibility to get oval shape increased with increasing the concentration of agar solution and the final agar content. The deformation rate after sintering was a little different. The final deformation rate is shown in Fig. 4.11. The deformation (%) in the figure means the deformation rate from the curved surface changing to the flat surface because the gel strength is not enough to support the weight of alumina suspension. The percentage is not exactly quantitative based on the mathematical definition, but semi quantitative from naked eye observation. As shown in the figure, deformation of sintered specimen was large when the agar content in agar solution was low and the deformation decreases with increasing the final agar content for all agar solution. Real shape of alumina beads is shown in Fig. 4.12. The size of alumina beads made is in the range of 1 - 2 mm. The surface of alumina beads was smooth and no crack, but the figure was not perfect sphere.



Fig. 4.11 Deformation of alumina beads preparing from the mixtures A1 - D3

A1	A2	A3	A4
1 mm	1 mm	1 mm	
B1	B2	B3	В4
1 mm	mm	1 mm	1 mm
C1	C2	C3	
1 mm	1 mm	1 mm	-
D1	D2	D3	
1 mm		1 mm	- 2 2 ย

Fig. 4.12 Figure of alumina beads prepared from the mixtures A1-D3

4.4.3 Bulk density and water absorption

Fig. 4.13 shows the relative density of the sintered beads (mixtures A1-A4) as a function of the final alumina content. The relative density increased with sintering temperature in all mixtures. The relative density was higher for the composition with fewer amount of final agar content. However, the tendency was not so consistent. This might be attributed to the inhomogeneous and pores in the mixture as seen in Fig. 4.15. The relative density reached to 98% T.D. (referred to 3.98 g/cm³) when sintered at 1400°C. The water absorption shown in Fig. 4.14 was 3-7% when sintered at 1300°C and almost 0% when sintered at 1400°C. Alumina powder TMDA can sinter to full density at 1300°C when it is formed by mechanical press followed by CIP [21]. Therefore, the gel cast forming is inferior in getting high density at low sintering temperature. The relative density of the specimen B-D series (as shown in appendix B) did not reach to full density even sintered at 1400°C.



Fig. 4.13 Relative density of the mixtures A1-A4 at the sintering temperatures of 1300, 1350 and 1400° C



Fig. 4.14 Water absorption of the mixtures A1-A4 at the sintering temperatures of 1300, 1350 and 1400°C

4.4.4 Microstructure of alumina beads

Fig. 4.15 shows cross section of alumina beads after polishing. Small pores having size about 50µm still remained in the sintered beads. These pores are uniformly distributed in these specimens, although their viscosities are different. This is attributed to the amount of final solid loading is almost the same [25]. However, air bubbles are inevitably introduced during mixtures preparation.

Fig. 4.16 shows SEM microstructure of sintered beads A1 and A3. There are many small pores having the size about 1 - 2µm. The residual pores decrease with increasing the sintering temperature. However, it still remains at 1400°C in good agreement with the relative density results. These pore size is thought to correspond to pores generated by burned out of gelled agar. Increasing sintering temperature from 1300 to 1400 resulted in pore shrinkage and elimination of some pores.

The SEM microstructure of specimens A1 and A3 after polishing and thermal etching is shown in Fig. 4.17. Both samples show dense, homogeneous microstructures with small residual porosity located at triple points. The average grain size of specimens A1 and A3 at 1400° C, which were measured by intercept method, are 0.5 and 0.53µm, respectively.



Fig 4.15 Cross section of alumina beads obtaining from optical microscope





A3 (1300°C)

-- 10µm

Fig. 4.16 Microstructure at low magnification of specimens A1 and A3 sintered at $1300^\circ C$ and $1400^\circ C$



Fig. 4.17 Microstructure at high magnification of specimens A1 and A3 sintered at 1400°C

4.4.5 Discussion on the process making alumina beads of TMDA by agar gelcasting

Alumina beads can be formed by agar gelcasting with dropping technique. However, its shape was not completely sphere due to deformation after drying. The key factors affect on the shape of alumina beads are (1) the figure of suspension dropping out of the pipette tip, (2) the figure of the drop falling down in oil and (3) the drying process. In addition, the proper temperature of dropping should be around 50°C so that the low suspension viscosity is maintained (\leq 800mPa.s). Concentration of agar solution and final agar content had strong effect on the shape and relative density of alumina beads. Also, the high final alumina content was required to get the high relative density. For the proper composition, the concentration of agar solution and the final agar content should be as low as possible but gel strength must high enough for maintaining the bead shape. In addition, the suspension must be stirred before dropping to reduce air bubble in the drops.

This new forming method had the limit of the narrow proper composition area. However, the onward research is expected to get the superior properties and perfect shape of beads.

4.5 Alumina pellets formed by gelcasting

4.5.1 Final agar content on the figure of alumina pellets

Slurries with various concentrations of agar solution and final agar content were poured into the metal die. Then the metal die was cooled in water at 0°C or room temperature. The shape of specimens formed by agar gelcasting in metal die is shown in Fig. 4.18. The average sintering shrinkage of all specimens was approximately 24%. The relationship between the final alumina content, the concentration of agar solution and the final agar content are shown in Fig. 4.19.

The gelled mixture A1 could not be demolded due to its too low gel strength. Mixture A2 could be formed well. Mixture A4 could be formed well, but it had very high shrinkage after drying due to its low final alumina content. Therefore, mixture A4 was not optimum for forming. Mixture B1 changed to gelled-state with enough strength for handling by putting die in cooled water at 0°C. But mixture B1 at room temperature does not have enough strength for demolding. Mixture B2 could be formed but it had several pits on the surface of specimen. This is attributed to its high viscosity and much amount of water in the mixture. Mixture C2 had the incomplete-pellet shape due to its very high viscosity. In this case, the slurry can not flow into die completely. As a result, two-key factors having effect on the forming of alumina disks were the final alumina content and viscosity of the alumina slurry. The region where these two properties are satisfied is in narrow area as shown in Fig. 4.20.

If the vibration is applied to the metal die when pouring the slurry in the die, the slurry with high viscosity may fill into the die. If so, A3 and B2 may be successfully formed. However, I could not do such experiment because I do not have such idea when I was performing the experiment.



Fig. 4.18 Photograph of specimens after forming by agar gelcasting in metal die



Fig. 4.19 Final alumina content as a function of the concentration of agar





Fig. 4.20 The region where sound figure of pellet can be formed

4.5.2 Final agar content on bulk density and water absorption

The relative density after calcining and sintering of various mixtures is shown in Fig. 4.21 and 4.22, respectively. The relative density of calcined specimen (Fig. 4.21) is in proportion to the final alumina content. The too low relative density value of C2 is the result of air bubble due to the high viscosity of the slurry. The relative density of sintered specimen is also roughly related to the final alumina content as shown in Fig. 4.22.

Fig. 4.23 shows the water absorption of various specimens as a function of sintering temperature. The water absorption is in good agreement with the relative density. The water absorption decreases with increasing sintering temperature. However, the water absorption of A2 should be less than the water absorption of C2. This may be attributed to the much amount of open pores in the specimen made of mixture A2.

From the results, when we consider the forming and the relative density, only mixture B1 is proper composition.



Fig. 4.21 Relative density of various mixtures after calcining at 800°C/2 h



Fig. 4.22 Relative density of various mixtures with sintering temperature



Fig. 4.23 Water absorption of various mixtures with sintering temperature

4.5.3 Discussion on the forming alumina pellets by gelcasting

Using the metal die, alumina pellte was formed to sound figure. However, the region was rather narrow as seen in Fig. 4.20. The region corresponds to the final alumina content 60 - 70wt% and the final agar content 0.25 - 0.50wt%. And same with the result of beads, the relative density of the pellte formed by agar solution did not become high at the sintering temperature lower than 1400°C. Considering all facts mentioned above, the gelcasting process using agar as sol-gel material is not so attractive process.

To make the process attractive, we have to find such an agar or some other materials that give low slurry viscosity less than 800mPa.s and formed high strength at less than 0.20 wt% final agar content for the alumina content over 65 wt% slurry.

CHAPTER V

CONCLUSIONS

The aim of this study was to get alumina beads having the shape close to sphere and the density close to theoretical value with submicron size grain. The conclusions are as follows:

- The spherical alumina beads with about 1mm diameter were formed through gelcasting method using agar as the gelling agent. Concentration of agar solution and final agar content in the mixtures affected seriously on the forming and properties of the sintered beads.
- 2. The perfect spherical beads was not made in this experiment. However, there is some possibility to get the spherical figure and properties by improving the process condition.
- 3. The alumina pellets with very good shape can be obtained by gelcasting method using agar as the gelling agent. The concentration of agar solution and final agar content in the mixtures affected on the forming and properties of the sintered pellets.
- 4. The optimum amount of ammonium salt of PMAA and PAA as dispersant for 70, 75 and 80wt.% of A-21 alumina powder (having mean particle size 1µm after milling in attritor for 10h) were almost the same for the alumina content and about 1.1wt.% to dry-weight basis.

CHAPTER VI

FUTURE WORKS

In this work, the spherical and high density alumina beads could be made. However, syneresis or drying technique should be studied more and more to obtain the alumina beads with higher spherical shape and density. The future works are recommended as follows:

- 1. To obtain higher density, the following process shall be researched that the amount of agar content in the suspension should be decreased but alumina beads still can be formed.
- 2. To obtain perfectly spherical shape, syneresis or drying technique should be studied more and more. In this case, a chemical substance may be added for increasing gel strength.

REFERENCES

- [1]. C. P. Dogan and J. A. Hawk. Role of composition and microstructure in the abrasive wear of high-alumina ceramics. <u>WEAR</u>, 225-229 (1999): 1050-1058.
- [2]. C. Araki. Seaweed polysaccharide. <u>In Proc. 4th Int. Cong. Biochem.</u>, Vienna, Pergamon press, London, (1958): 15-30.
- [3]. W. F. Seip. Specifications and experience in the use of bacterial grade agaragar by a leading manufacturer of dehydrated media. <u>In Proc. 8th Int.</u> <u>Seaweed Symp.</u>, Bangor, Wales, August (1974): 17-24.
- [4]. A. Nussinovitch. <u>Hydrocolloid Applications: Gum technology in the food other</u> <u>industries.</u> Blackie Academic & Professional, an imprint of Chapman & Hall, London, (1997): 8.
- [5]. E. R. Morris and I. T. Norton. Polysaccharide aggregration in solutions and gels, <u>Aggregation Processes in Solution (E. Wyn-Jones and J. Gormally,</u> <u>eds.</u>), Elsevier, Amsterdam, (1983).
- [6]. S. Ablett, P. J. Lillford, S. M. A. Baghdadi, and W. J. Derbyshire. Nuclear magnetic resonance investigations of polysaccharide films, sol, and gels.
 1. Agarose, J. Colloid Inter. Sci., 67(1978): 355.
- [7]. I. C. M. Dea, A. A. Mckinnon, and D. A. Reese. Tertiary and quaternary structure in aqueous polysaccharide systems which model cell wall cohesion: Reversible change in conformation and association of agarose, carrageenan and galactomannans, <u>J. Molec. Biol.</u>, 68(1972): 153.
- [8]. A. Hayashi, K. Kinoshita, M. Kuwano, and A. Nose. Studies of the agarise gelling systems by the fluorescence polarization method II, <u>Polym. J.</u>, 10(1978): 5.
- [9]. T. Matsuhashi. <u>Agar, in Food Gels (ed. P. Harris)</u>, Elsvier Applied Science, London, (1990): 1-53.
- [10]. O. Takegawa. <u>Strength of Agar Gels</u>, Nippon Kaiso-Kogio Res. Lab. Report, No.2, (1963).

- [11].K. Nishinari, M. Watase, E. Miyoshi, et al. Effects of sugar on the gel-sol transituin of agarose and κ-carrageenan. <u>Food Technol</u>. Chicago, 49(1995): 10, 90, 92, 96.
- [12].A. J. Fanelli, R. D. silvers, W. S. Frei, J. V. Burlew, and G. B. Marsh. New aqueous injection moulding process for ceramic powders. <u>J. Am. Ceram</u>. Soc., 72(1989): 1833-1836.
- [13].Z. P. Xie, J. L. Yang, D. Huang, Y. L. Chen, and Y. Huang. Gelation forming of ceramic compacts using agarose. <u>Br. Ceram. Trans.</u>, 98(2), (1999): 58-61.
- [14].S. M. Olhero, G. Tari, M. A. Coimbra, and J. M. F. Ferreira. Synergy of polysaccharide mixture in gelcasting of alumina. <u>J. Eur. Ceram. Soc.</u>, 20(2000): 423-429.
- [15].A. J. Millän, R. Moreno, and M. I. Nieto. Improved consolidation of alumina by agarose gelation. <u>J. Eur. Ceram. Soc.</u>, 20(2000)2527-2533.
- [16].A. J. Millän, , M. I. Nieto and R. Moreno. Near-net shaping of aqueous alumina slurries using carrageenan. <u>J. Eur. Ceram. Soc.</u>, 22(2002): 297-303.
- [17].A. J. Millän, R. Moreno, and M. I. Nieto. Thermogelling polysaccharide for aqueous geleasting --- part I: a comparative study of gelling additives. <u>J.</u> <u>Eur. Ceram. Soc.</u>, 22(2002): 2209-2215.
- [18].A. J. Millän, M. I. Nieto, C. Baudin, and R. Moreno. Thermogelling polysaccharide for aqueous gelcasting --- part II:influence of gelling additives on rheological properties and gelcasting of alumina. <u>J. Eur.</u> <u>Ceram. Soc.</u>, 22(2002): 2217-2222.
- [19].A. J. Millän, M. I. Nieto, R. Moreno, and C. Baudin. Thermogelling polysaccharide for aqueous gelcasting --- part III: mechanical and microstructural characterization of green alumina beads. <u>J. Eur. Ceram.</u> <u>Soc.</u>, 22(2002): 2223-2230.
- [20].I. Santacruz, M. I. Nieto, and R. Moreno. Alumina bodies with near-to-theoretical density by aqueous gelcasting using concentrated agarose solutions. <u>Ceramics International</u>, 31(2005): 439-445.

- [21].Soontorn Tansungnoen. <u>Development of transparent nano-crystalline alumina</u> <u>ceramic effects of forming and sintering conditions</u>. (Master's Thesis, Ceramic technology, materials science, Faculty of science, Chulalongkorn University), 2005.
- [22].James S. Reed. <u>Principles of ceramics processing</u>. John wiley & Sons, Inc, 2nd edition, (1995).
- [23].J. Cesarano III and I. A. Aksay. Processing of highly concentrated aqueous α alumina suspensions stabilized with polyelectrolytes. <u>J. Am. Ceram</u>. Soc., 71(12), (1988): 1062-1067.
- [24].J. Cesarano III and I. A. Aksay. Stability of aqueous *α* alumina suspensions with poly(methacrylic acid) polyelectrolyte. <u>J. Am. Ceram</u>. Soc., 71(4), (1988): 250-255.
- [25].S. W. Jiang, T. Matsukawa, S. Tanaka, and K. Uermatsu. Effects of powder characteristics, solid loading and dispersant on bubble content in aqueous alumina slurries. <u>J. Eur. Ceram. Soc.</u>, (2006).

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APPENDICES



Appendix A Particle size of alumina A-21 after milling by attritor for 10h

Appendix B Bulk density, relative density and water absorption of sintered beads of mixture A1-A4

1300°C

Mixture	$W_{d}\left(g ight)$	$W_{_{sat}}(g)$	$W_{_{sus}}\left(\mathrm{g} ight)$	B.D.(g/cc)	R.D.(g/cc)	W.A.(%)
A1	0.2775	0.2868	0.2055	3.40	85.5	3.35
A2	0.2230	0.2302	0.1683	3.59	90.1	3.23
A3	0.0390	0.0290	0.0405	3.38	84.9	3.85
A4	0.4322	0.4601	0.3312	3.34	83.9	6.46

1350°C

Mixture	$W_{d}^{}(g)$	$W_{sat}(g)$	W _{sus} (g)	B.D.(g/cc)	R.D.(g/cc)	W.A.(%)
A1	0.2791	0.2797	0.2060	3.77	94.8	0.21
A2	0.1150	0.1165	0.0856	3.70	93.1	1.30
A3	0.0725	0.0737	0.0541	3.68	92.5	1.66
A4	0.2775	0.2858	0.2076	3.54	88.9	2.99

1400°C

Mixture	<i>W_d</i> (g)	$W_{sat}(g)$	$W_{_{sus}}\left(\mathrm{g} ight)$	B.D.(g/cc)	R.D.(g/cc)	W.A.(%)
A1	0.2932	0.2934	0.2192	3.85	98.9	0.07
A2	0.9580	0.0961	0.0715	3.88	97.4	0.31
A3	0.0693	0.0694	0.0512	3.79	95.3	0.14
A4	0.1290	0.1313	0.0986	3.93	98.8	0.02

Appendix C Bulk density, relative density and water absorption of sintered beads making of B-D series



Relative density of mixture B1-D3 with sintering temperature







1300°C

Mixture	W_{d} (g)	$W_{_{sat}}(g)$	$W_{_{sus}}\left(\mathrm{g} ight)$	B.D.(g/cc)	R.D.(g/cc)	W.A.(%)
B1	0.2640	0.2172	0.1973	3.56	89.5	2.73
B2	0.3252	0.3322	0.2428	3.62	91.0	0.02
B3	0.4424	0.4670	0.3322	3.27	82.1	0.06
B4	0.3295	0.3448	0.2494	3.44	86.4	0.05
C1	0.7611	0.7694	0.5610	3.64	91.5	1.09
C2	0.4458	0.4640	0.3358	3.46	87.0	0.04
C3	0.1427	0.1495	0.1080	3.43	86.1	0.05
D1	0.3429	0.3519	0.2555	3.55	89.1	2.62
D2	0.2159	0.2209	0.1566	3.34	84.0	0.02
D3	0.1314	0.1381	0.1010	3.53	88.7	0.05

1350°C

Mixture	$W_{d}^{}\left(\mathrm{g} ight)$	$W_{_{sat}}(g)$	$W_{_{sus}}\left(\mathrm{g} ight)$	B.D.(g/cc)	R.D.(g/cc)	W.A.(%)
B1	0.2198	0.2199	0.1605	3.69	92.6	0.05
B2	0.2126	0.2160	0.1577	3.63	91.3	0.02
B3	0.2017	0.2068	0.1506	3.58	89.9	0.03
B4	0.2575	0.2645	0.1950	3.69	92.8	0.03
C1	0.3103	0.3103	0.2281	3.76	94.5	0.00
C2	0.2271	0.2320	0.1691	3.60	90.4	0.02
C3	0.1308	0.1353	0.0989	3.58	90.0	0.03
D1	0.2836	0.2879	0.2106	3.66	91.9	1.52
D2	0.1352	0.1402	0.1053	3.86	97.0	0.04
D3	0.1327	0.1379	0.1008	3.56	89.6	0.04

1400°C

Mixture	$W_{d}^{}\left(\mathrm{g} ight)$	W _{sat} (g)	W _{sus} (g)	B.D.(g/cc)	R.D.(g/cc)	W.A.(%)
B1	0.1270	0.2186	0.1624	3.76	94.4	0.01
B2	0.0987	0.0989	0.0739	3.94	99.0	0.00
B3	0.1515	0.1542	0.1161	3.69	99.6	0.02
B4	0.1686	0.1729	0.1286	3.79	95.3	0.03
C1	0.2933	0.2932	0.2160	3.79	95.2	0.00
C2	0.2635	0.2655	0.1941	3.68	92.5	0.00
C3	0.1401	0.1425	0.1309	3.62	90.9	0.02
D19	0.2170	0.2186	0.1624	3.85	96.7	0.00
D2	0.1609	0.1629	0.1223	3.95	99.3	0.01
D3	0.1152	0.1163	0.0873	3.96	99.5	0.00

Mixture	$W_{_{d}}\left(\mathrm{g} ight)$	W_{sat} (g)	W_{sus} (g)	B.D.(g/cc)	R.D.(g/cc)
A4-1	1.2224	1.4916	0.9110	2.10	52.7
A4-2	1.2209	1.4240	0.9088	2.09	52.4
A4-3	1.2456	1.5201	0.9281	2.10	52.7
	Av	/g.		2.10	52.6
	S.	D.		0.01	0.14
A2-1	1.5 <mark>016</mark>	1.8191	1.1208	2.14	53.8
A2-2	1.5994	1.9319	1.1936	2.16	54.2
A2-3	1.5927	1.9229	1.1889	2.16	54.3
A2-4	1. <mark>5854</mark>	1.9177	1.1834	2.15	54.1
	A	vg		2.15	54.1
	S.	D.		0.01	0.2
B2-1	1.7635	2.1452	1.3165	2.12	53.3
B2-2	1.7715	2.1347	1.3222	2.17	54.6
B2-3	1.7698	2.1510	1.3212	2.13	53.4
	A	vg	Ê	2.14	53.8
	S.	D.		0.02	0.6
C2-1	1.9713	2.4091	1.4720	2.10	52.7
	ลถาบ	ב			
B1(RT)-1	1.7653	2.25	56.6		
B1(RT)-2	1.9922	1.4876	2.24	56.3	
Ч	A	2.25	56.5		
	S.	D.		0.01	0.1

Appendix D Bulk density and relative density of calcined pellets at the temperature of 800° C/2h

Mixture	$W_{d}\left(\mathrm{g} ight)$	$W_{_{sat}}(g)$	W _{sus} (g)	B.D.(g/cc)	R.D.(g/cc)
B1(0°C)-1	1.7285	2.0748	1.2911	2.20	55.2
B1(0°C)-2	2.0233	2.4338	1.5111	2.19	54.9
B1(0°C)-3	2.0495	2.4596	1.5309	2.20	55.3
B1(0°C)-4	1.9977	2.3845	1.4917	2.23	56.0
B1(0°C)-5	1.9795	2.3720	1.4780	2.21	55.6
	Av	2.21	55.4		
	S.	0.02	0.4		

Appendix D (Cont.) Bulk density and relative density of calcined pellets at the temperature of 800° C/2h



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1	2	0	\sim	0	\sim
	3	U	U		U

Mixture	$W_{d}\left(\mathrm{g} ight)$	$W_{_{sat}}(g)$	W _{sus} (g)	B.D.(g/cc)	R.D.(g/cc)	W.A.(%)
A4-1	1.2147	1.2771	0.9098	3.30	82.8	5.14
A4-2	1.2418	1.3047	09152	3.58	82.9	5.07
	Av	′g.	3.44	82.9	5.11	
	S.	D.	0.14	0.00	0.04	
A2-1	1.5841	1.6596	1.1865	3.33	83.8	4.77
B2-1	1.7541	1.8322	1.3135	3.37	84.6	4.45
		1118				
C2	-	/ - 8	-	-	-	-
B1(RT)	-		22	-	-	-
B1(0°C)-1	1.7201	1.7767	1.2865	3.49	87.8	3.29
B1(0°C)-2	2.0133	2.0879	1.5069	3.45	86.7	3.71
	Av	′g.	3.47	87.2	3.50	
	S.	D.	0.02	0.6	0.21	

Mixture	$W_{d}\left(\mathrm{g} ight)$	$W_{sat}\left(\mathrm{g} ight)$	W_{sus} (g)	B.D.(g/cc)	R.D.(g/cc)	W.A.(%)
A4-1	1.2125	1.2420	0.9055	3.59	90.2	2.43
A4-2	1.2255	1.2562	0.9152	3.58	90.0	2.53
	Av	′g.	3.59	90.1	2.48	
	S.	D.	0.01	0.1	0.05	
A2-1	1.5759	1.6160	1.7774	3.58	89.9	2.54
B2-1	1.7612	1.7891	1.3092	3.65	91.8	1.58
			IO A			
C2-1	1.9613	2.0007	1.4457	3.52	88.4	2.01
			NAKA			
B1(RT)-1	1.7552	1.7710	1.3041	3.74	94.0	0.90
		13-9-14U				
B1(0°C)-1	2.0382	2.0673	1.5173	3.69	92.7	1.43

Appendix E (Cont.) Bulk density, relative density and water absorption of sintered beads

1350°C

60
Mixture	$W_{d}\left(g ight)$	$W_{sat}(g)$	$W_{sus}\left(g ight)$	B.D.(g/cc)	R.D.(g/cc)	W.A.(%)
A4-1	1.2365	1.2430	0.9137	3.74	94.0	0.53
A4-2	1.2349	1.2448	0.9142	3.72	93.5	0.99
Avg.				3.73	93.8	0.76
S.D.				0.01	0.3	0.23
A2-1	1.4921	1.5028	1.1077	3.76	94.5	0.72
A2-2	1.5894	1.6025	1.1776	3.72	93.6	0.82
Avg.				3.74	94.0	0.77
S.D.				0.02	0.5	0.05
B2-1	1.7589	1.7708	1.3010	3.73	93.7	0.68
12/2/2/2/2						
C2	-	1.56	1201-1771)	-	-	-
1999 19 19 19 19 19 19 19 19 19 19 19 19						
B1(RT)-1	1.9805	1.9849	1.4749	3.87	97.1	0.22
B1(0°C)-1	1.985 <mark>9</mark>	1.9917	1.4774	3.84	96.6	0.29
B1(0°C)-2	1.9674	1.9757	1.4623	3.82	95.9	0.42
Avg.				3.83	96.2	0.36
S.D.				0.00	0.4	0.07

Appendix E (Cont.) Bulk density, relative density and water absorption of sintered beads

1400°C

BIOGRAPHY

Mr. Kowit Lertwittayanon was born in Nakornsrithammarat on 23th February 1976. He received a bachelor's degree in ceramic engineering from school of engineering, Suranaree University of Technology in 1999. He jointed at 1999 and worked for 5 years to Amarin Ceramic Corporation Co., Ltd. He continued a further study in Master's degree in the field of ceramic technology at Chulalongkorn University from June 2004 and graduated at the end of September 2006.



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