CHAPTER V

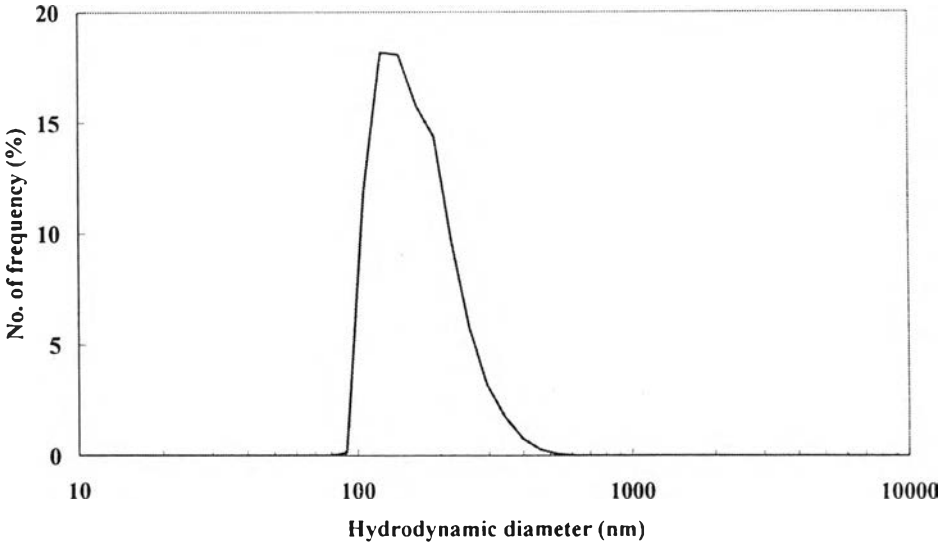
RESULTS AND DISCUSSION

With a promising results revealed by many previous works, this research has set its aim to develop a modified method for preparing transparent poly-crystal alumina by using slip casting technique. Effect of the starting materials and process variable on the properties of specimen obtained in each preparation stage will be thoroughly reported and discussed in this chapter.

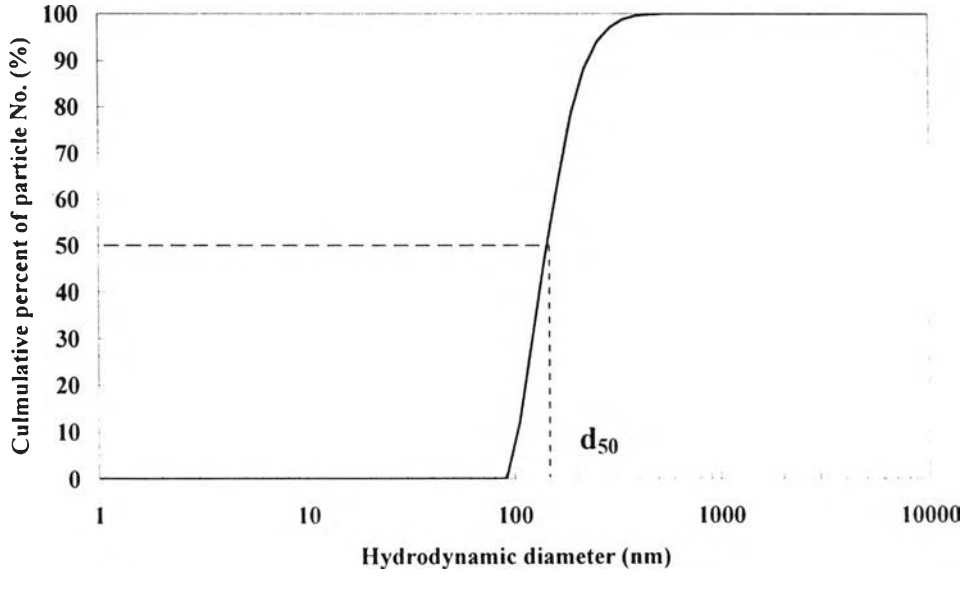
5.1 Characterization of alumina powder as starting material

In order to get alumina sintered body with grain size in nanometer to submicrometer order, the starting raw material must be smaller than the target grain size otherwise growth of grains (or particle) during the sintering process will be hinder light transmission due to multilevel scattering inside the specimen [Apetz, et al. (2003)]. Therefore the particle size distribution (PSD) of starting alumina powder was taken into account as the first factor.

In this work, commercially available TM-DAR alumina powder was used as raw material. The TM-DAR alumina powder is sampled and dispersed in water and then ultrasonicated for 15 minutes in order to give the well-dispersed suspension. The suspension was characterized by the dynamic light-scattering technique to get particle size distribution (PSD), which is shown in Figure 5.1. From the result, alumina powder has an average size of 162 nm and its figure, which could be observed from typical image, is spherical as shown in Figure 5.2.



(a)



(b)

Figure 5.1 Particle size distribution of TM-DAR alumina powder (a) % No. of frequency (b) % culmulative No. of particle

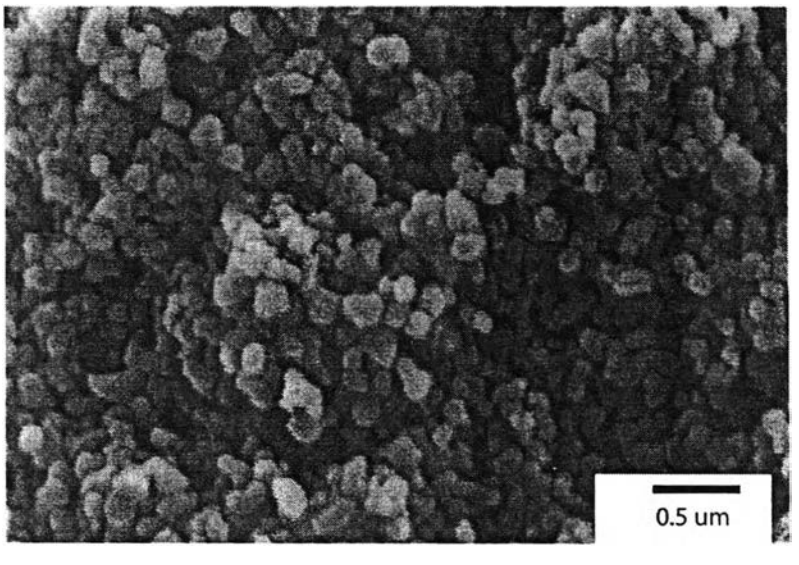


Figure 5.2 SEM image of TM-DAR alumina powder

5.2 Rheological behaviors for preparing of the appropriate alumina slurries

5.2.1 Effect of organic content on the properties of alumina slurries

In wet processes, such as slip casting, preparation of a slip or suspension plays an important role in obtaining green body specimen with high homogeneity and high density. In order to identify suitable conditions for preparation of well-dispersed alumina slurries with high solid content, role of organic additives added to slurries was investigated.

5.2.1.1 Effect of PMAA deflocculant concentration on the viscosity of alumina slurries

Polymethacrylic acid (PMAA) is an effective deflocculants which could provide electrosteric repulsive force due to accumulation of electrical charges and polymer barriers on particle surface, resulting in preventing the agglomeration of alumina particles.

According to the result in Figure 5.3, optimal value of deflocculant concentration to get slurry with minimal apparent viscosity could be observed to rely on percentage of solid loading in slurries with a rotational speed of 100 rpm. It can be clearly seen that effect of deflocculant addition is divided into 2 regions. In the first region, with a low content of deflocculant viscosity of alumina slurries prepared with any solid loading was very high. But with further addition of deflocculant then the slurries viscosity became drastically decreased. The lowest viscosity of alumina slurry with solid loading of 70, 75 and 80 wt% could be achieved with deflocculant concentration of 1.18, 1.25 and 1.50 wt%., respectively. In contrast, a further increase in deflocculant concentration above each optimum point resulted in a significant increase in slurries viscosity. There results lead to implications, which could be schematically depicted in Figure 5.4. When insufficient amount of deflocculant is added into alumina slurry, it is reasonably supposed that there is insignificant repulsive force acting among each suspended particle. Therefore those particles trend to agglomerate as could be depicted in Figure 5.4(a), resulting in slurry with a relatively high viscosity. At the optimal addition of deflocculant, sufficient amount of deflocculant molecules would be attached to the surface of each suspended alumina particle, bringing about equilibrium of repulsive and attractive forces acting among each particle (Figure 5.4 (b)). Therefore a uniform suspension of alumina particles could be prepared with a minimal viscosity regarding to each solid loading. However, with a further increase in deflocculant concentration, an excessive amount of deflocculant molecules could hinder movement of particles and results in agglomeration of dispersed particles as shown in Figure 5.4 (c).

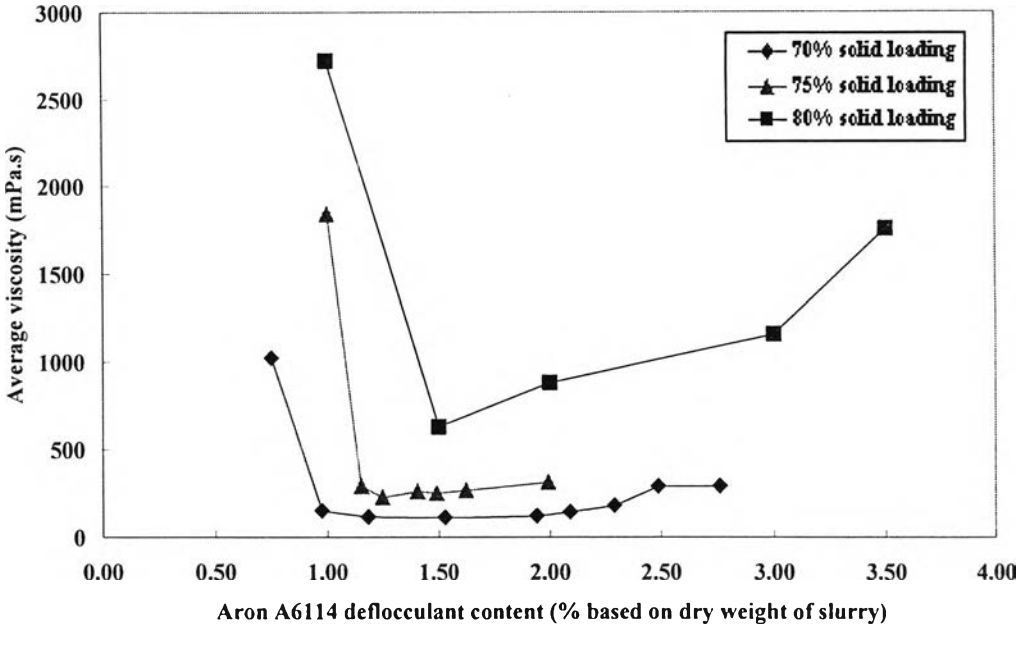
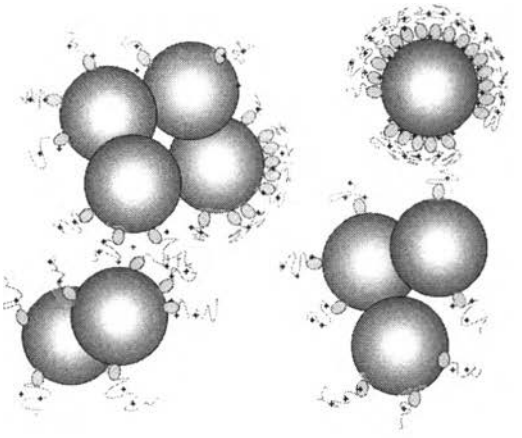
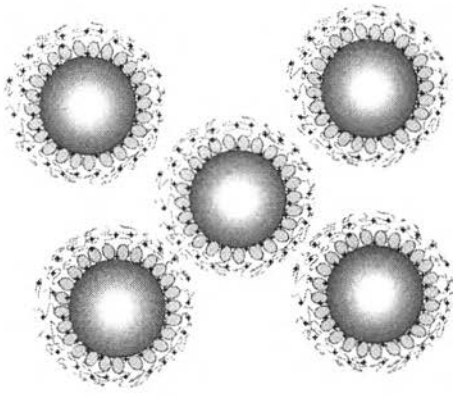


Figure 5.3 The effect of Aron A6114 deflocculant concentration on the viscosity of 70%, 75% and 80% solid loading of alumina slurries.



(a)



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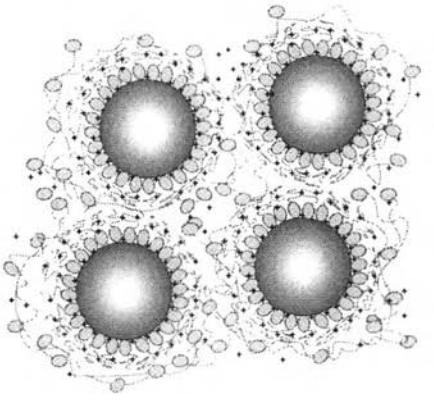


(c)

Figure 5.4 The model of PMMA deflocculant quantity on the submicron-alumina slurries with high solid content in case of (a) insufficient deflocculant (b) appropriate deflocculant in well-dispersed slurries (c) excess of deflocculant

5.2.1.2 Effect of CMC binder concentration on the viscosity of well-dispersed alumina slurries

The relationships between viscosity and binder concentration for alumina slurries with solid content of 70% and 75% are shown in Figure 5.5. It can be clearly seen that apparent viscosity of alumina slurry drastically increased when a few amount of CMC binder is added. This event causes the presence of absorbed binder molecules results in the hindering of particle movement. Practically, slurries with over 1200 MPa.s were too viscous for casting it in gypsum mold. Hence, the available content of binder employed for further process should in the range of 0 - 0.1 wt% for 75 % solid loading and less than 0.2 wt% for 70 % solid loading.

According to the results in Figure 5.3 and 5.5, the compositions of slurries to be studied further are decided as shown in Table 5.1.

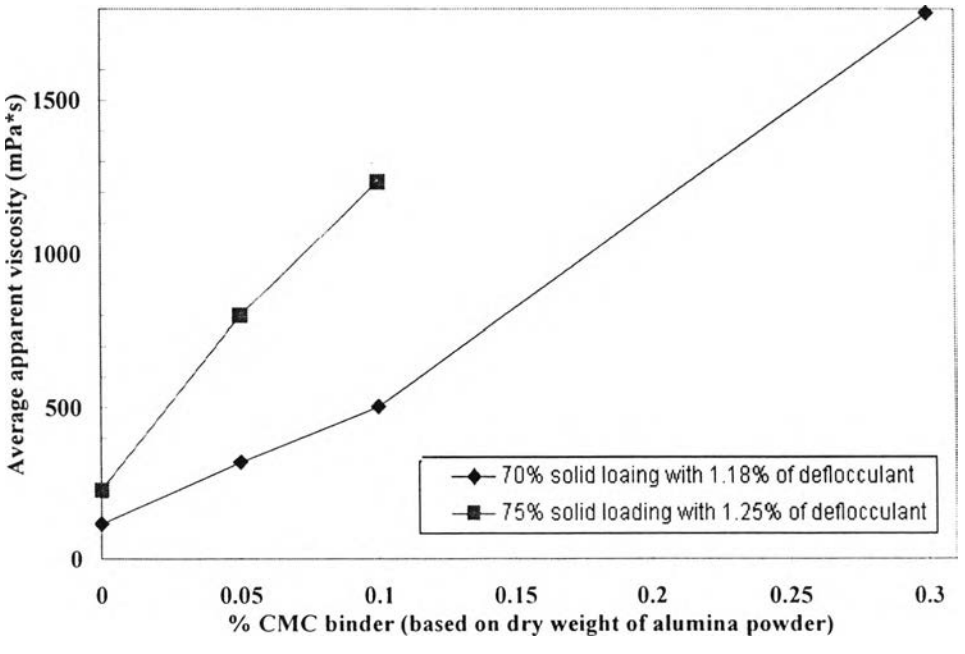


Figure 5.5 The effect of binder concentration on the viscosity of 70%, 75% and 80% solid loading of well-dispersed alumina slurries

Table 5.1 The composition of slurries

Sample ID.	Composition (wt.%)			
	Alumina	Water	*Deflocculant	*Binder
A	70	30	1.18	-
B	75	25	1.25	-
C	80	20	1.5	-
D	70	30	1.18	0.05
E	70	30	1.18	0.1
G	75	25	1.25	0.05
H	75	25	1.25	0.1

* Based on the dry alumina powder

5.2.2 Effect of spindle speed on the viscosity of the alumina slurries

The viscosity of slurries generally decreases with increasing the spindle speed due to the rearrangement of additive molecules and alumina particles. Figure 5.6 - 5.8, show the results for the slurries with deflocculant and Figure 5.9 – 5.10 show the slurries with deflocculant and binder. This kind of behavior conformed to the shear thinning flow model which viscosity varies on time and shear force acting on slurries during mixing.

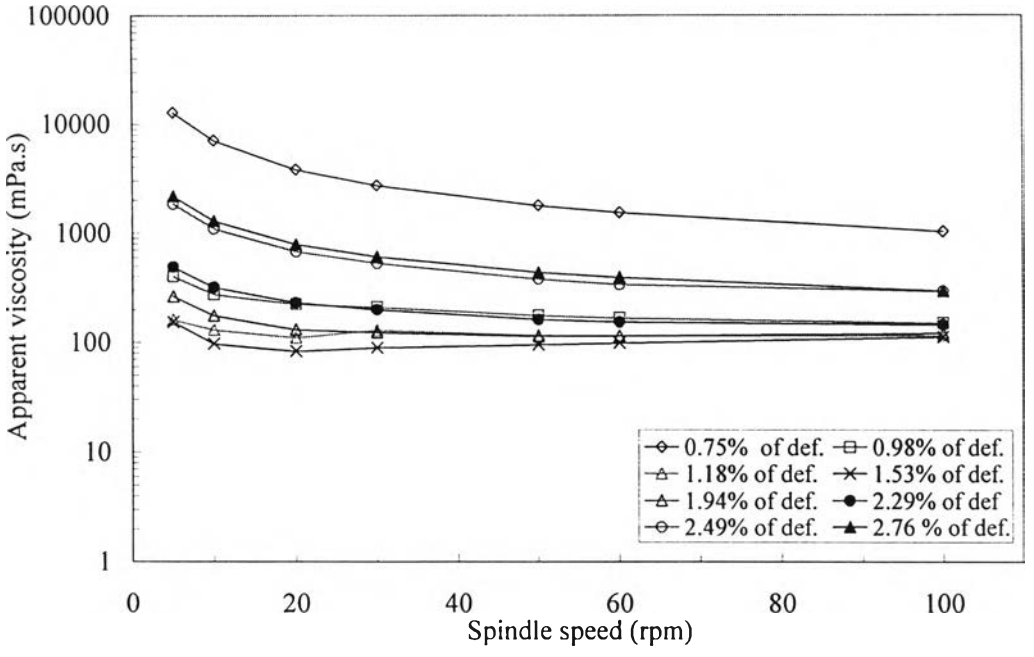


Figure 5.6 The effect of spindle speed on the viscosity of the alumina slurries with 70% solid content at various concentrations of deflocculant

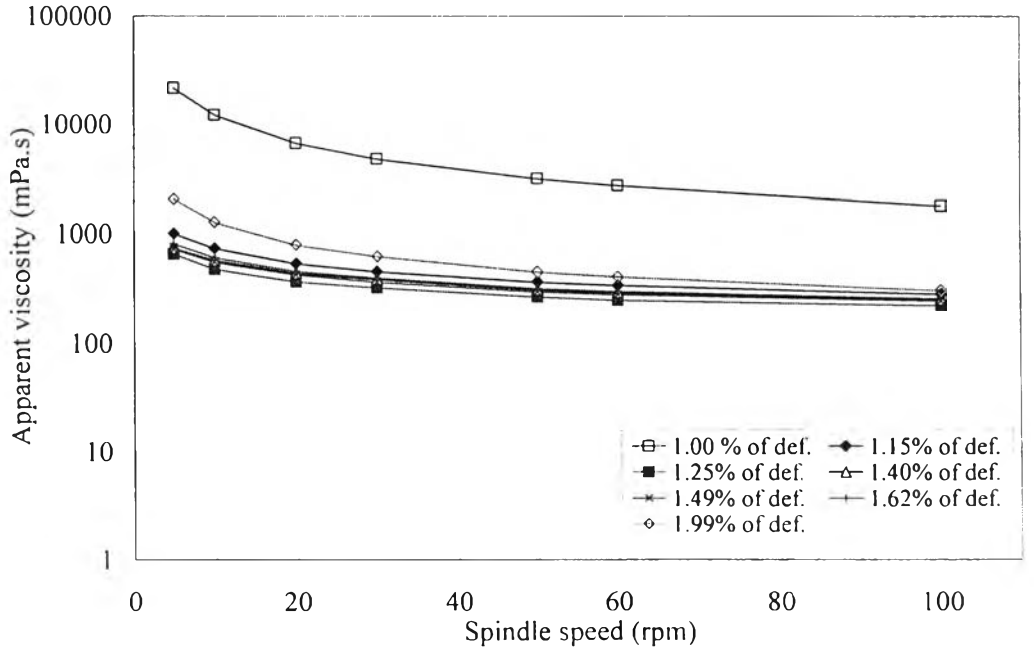


Figure 5.7 The effect of spindle speed on the viscosity of the alumina slurries with 75% solid content at various concentrations of deflocculant

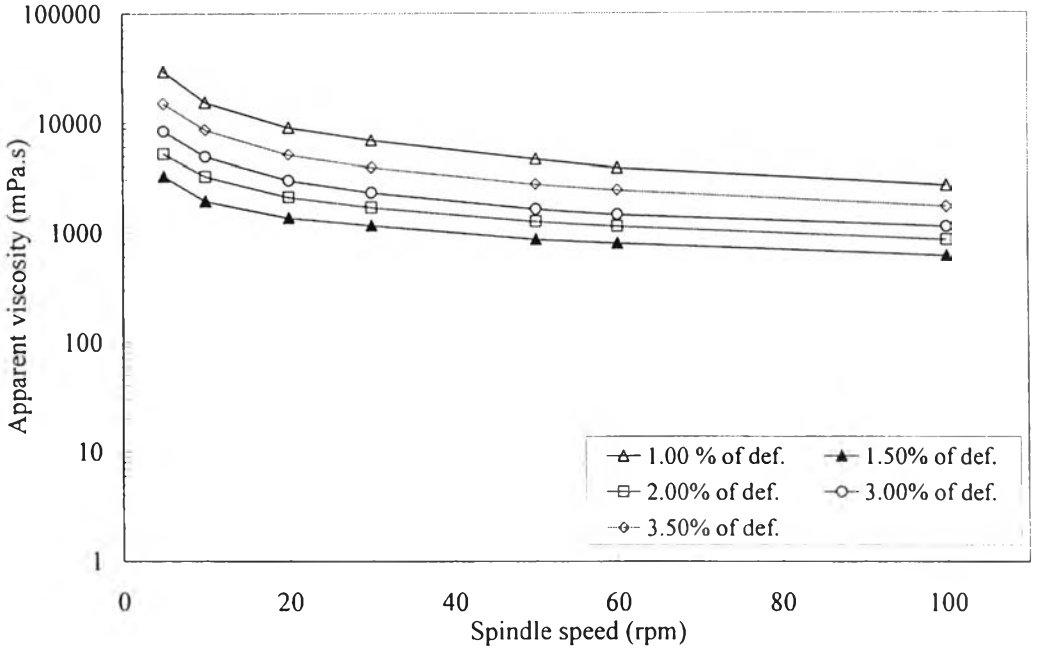


Figure 5.8 The effect of spindle speed on the viscosity of the alumina slurries with 80% solid content at various concentrations of deflocculant

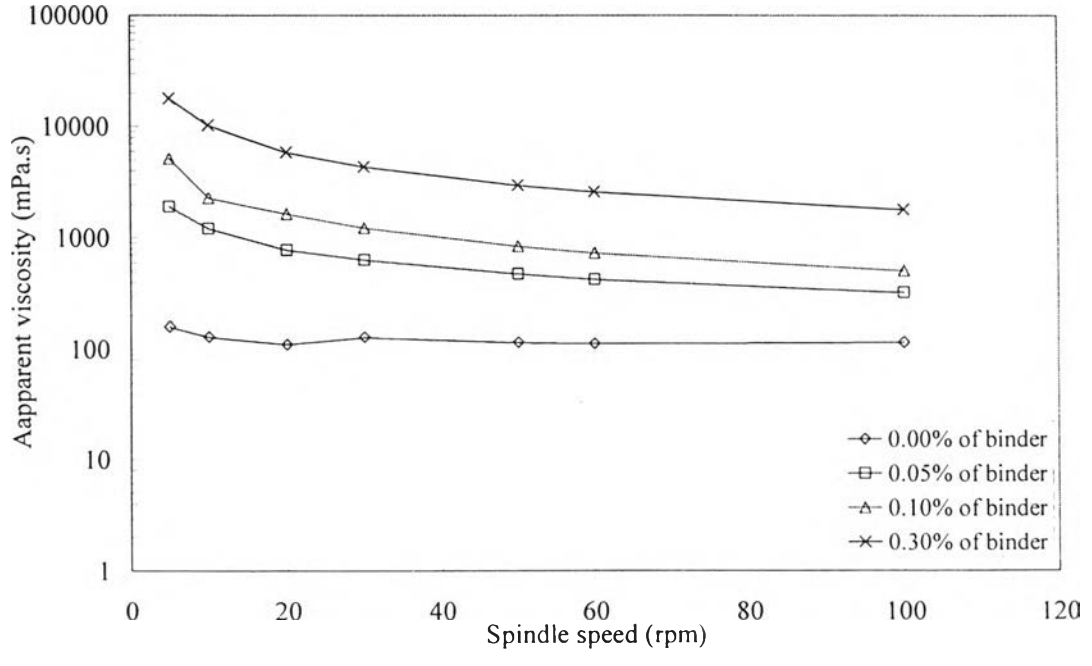


Figure 5.9 The effect of spindle speed on the viscosity of the alumina slurries with 70% solid content and 1.18 wt% deflocculant at various concentrations of binder

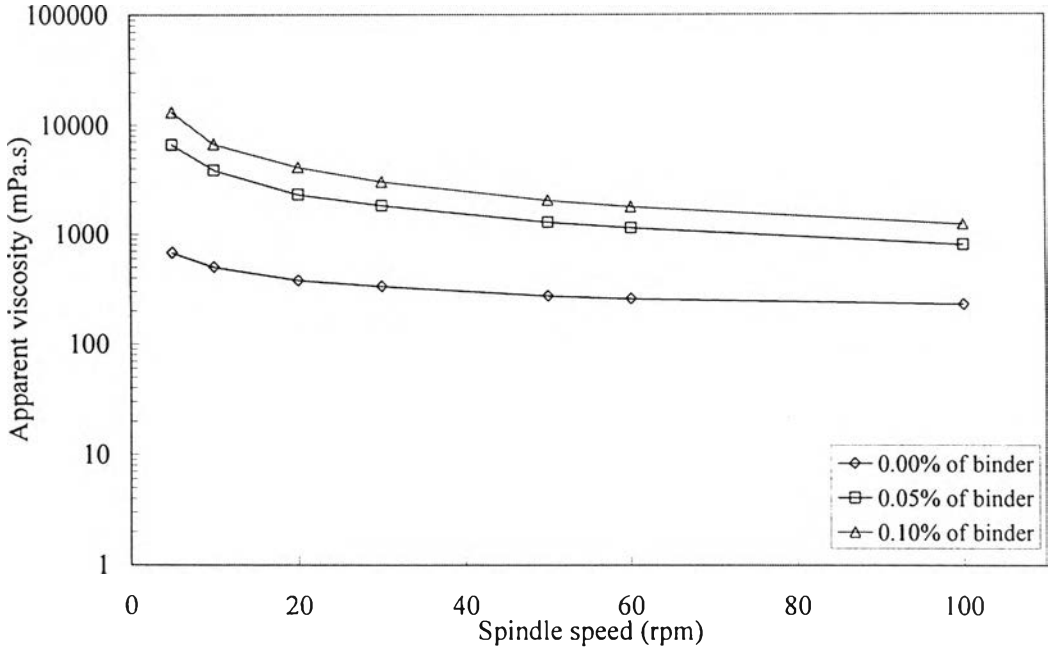


Figure 5.10 The effect of spindle speed on the viscosity of the alumina slurries with 75% solid content and 1.25 wt% deflocculant at various concentrations of binder

5.3 Effects of deflocculant and binder on the properties of alumina green body prepared by slip casting technique

From the previous results, the available slurries with various concentrations of the alumina powder and CMC binder were decided as shown in the Table 5.1. The density and strength of the green bodies were characterized.

5.3.1 Effects of solid loading concentrations

5.3.1.1 Density of the alumina green body

The relative density of alumina green body with various solid concentrations is shown in Figure 5.11. It can be obviously seen that well-dispersed slurries with 70, 75 and 80 wt% of alumina powder can provide green body with density of 56.5%, 60.4% and 61.7%, respectively. It is understood that the compaction of higher solid loading slurry provides the lower interparticle voids occurred due to vaporization of moisture in specimen during consolidation and drying process.

Therefore, it can be indicated that slurries with higher solid fraction can promote green body with higher density.

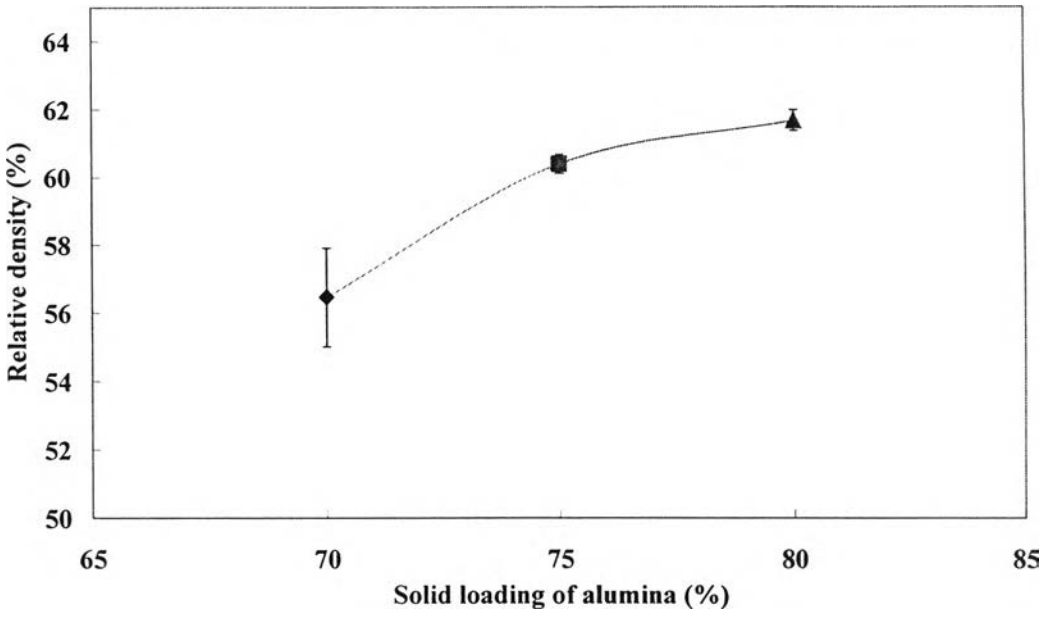


Figure 5.11 The effect of solid content of slurries on the relative density of the alumina green body

5.3.1.2 Strength of the alumina green body

Mechanical strength of green body is another factor for evaluation of handling. The strength of alumina green body as a function of solid content of slurries is shown in Figure 5.12. The flexural strength of 1.67, 1.81 and 2.15 MPa were obtained for 70%, 75% and 80% solid content of slurries, respectively. It should be noted that the green body with 80% solid slurry promotes the highest flexural strength because amount of interparticle contacts in high concentrated suspension is much more than that of low-concentrated suspension. The interparticle contacts play an important role to support weight and force that acting on specimen.

From these results, it can be summarized that the higher flexural strength of green body specimen can be obtained when the suspension with high solid content is employed.

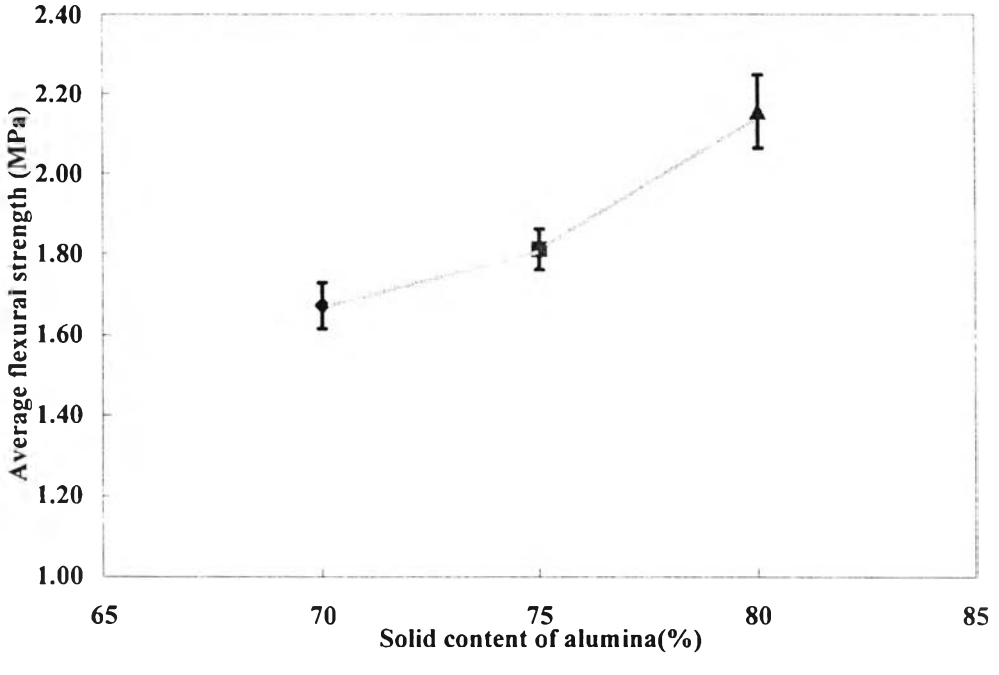


Figure 5.12 The effect of solid content of slurries on the strength of the alumina green body

5.3.2 Effects of CMC binder concentration

5.3.2.1 Density of alumina green body

Figure 5.13 show the effect of CMC binder on the density of green bodies with well-dispersed suspension. It should be noted that augmentation of binder concentration caused diminution of green body density, particularly in the 75% well-dispersed slurry, because binder molecules provide excessive barriers around each particles which caused increment of the distances and vacancy among particles. This kind of phenomenon leads to the reduction of the green-compact density.

In contrast, specimens formed with 70% solid content of slurry showed the different behavior. In the first region (0-0.5 wt% of binder concentration), green body density was increased from 56.5 to 58.8% because the binder will aid to make the particles come closer. Meanwhile, CMC addition over 0.05 wt% promoted slightly lower density due to the same effect in case of 75 wt% slurry. Excess binder caused so viscous bubbles in slurries which were difficult to remove, and provided some

defects in green body. Whereas, slurry with 80 wt% solid content was not taken into account for characterizing the green body since its viscosity was too viscous for casting.

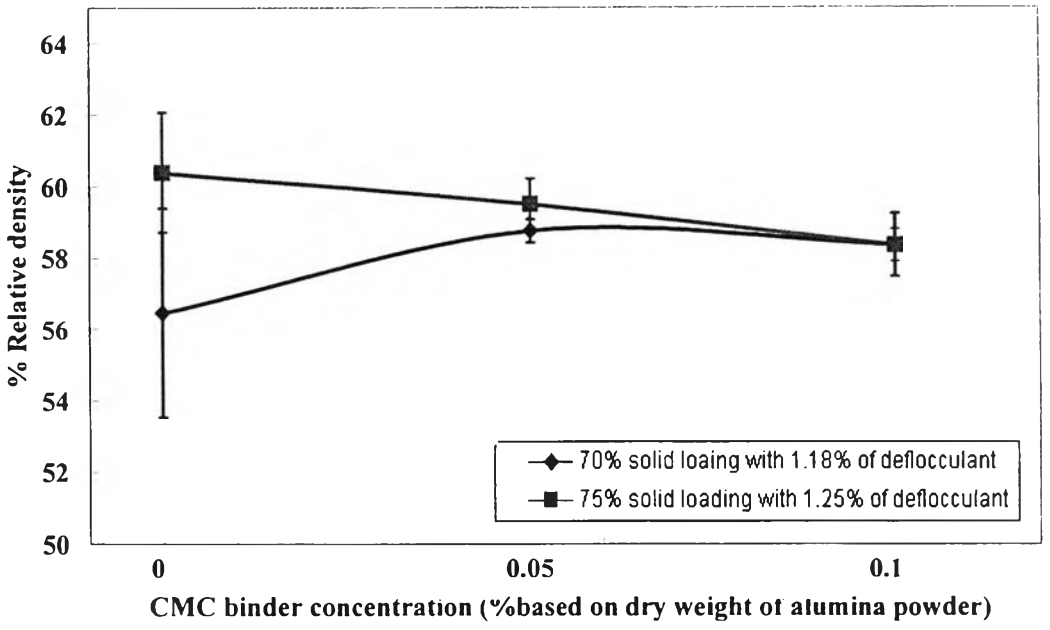


Figure 5.13 The effect of binder concentration in slurries on the relative density of the alumina green body

5.3.2.2 Strength of alumina green body

The average flexural strength of alumina green body depended on binder concentration as shown in Figure 5.14. It can be clearly seen that binder adding up to 0.1 wt% in slurries with 70 wt% solid content improved the average strength from 1.67 MPa to 2.13 MPa. As well as 75 wt% solid content specimen, adding of binder to 0.05 wt% also increase strength up from 1.70 to 2.18 MPa. On the other hand, strength of specimen with 75 wt% solid loading and 0.10 wt% CMC decreased to 1.43 MPa due to the voids from bubbles in slurry.

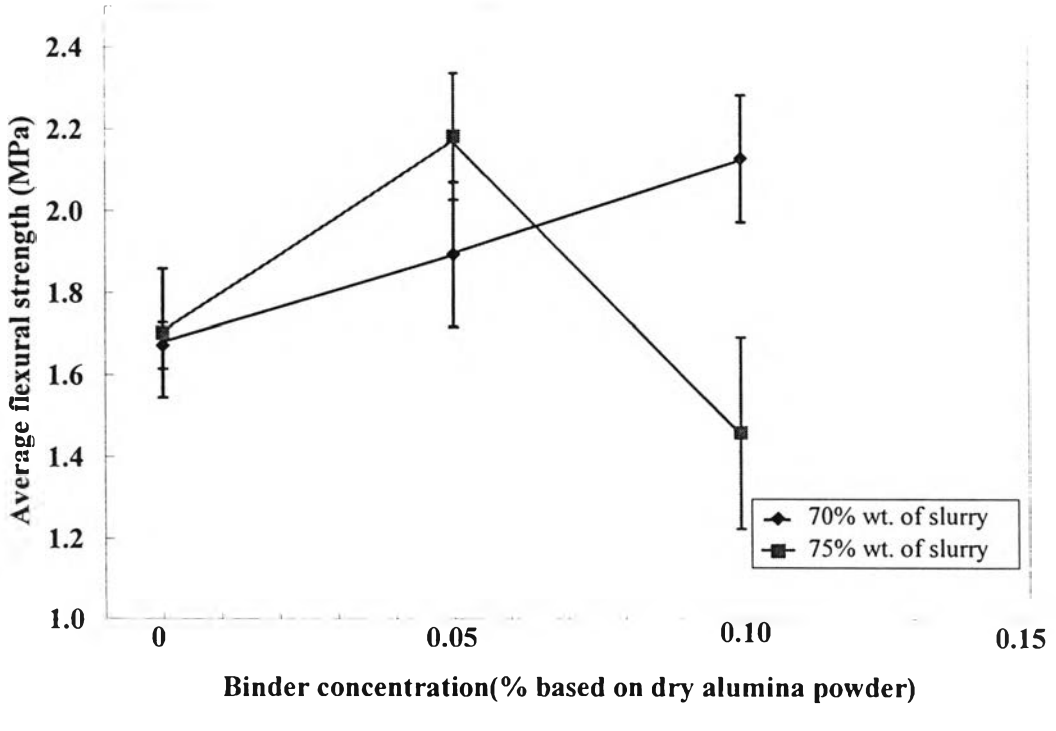


Figure 5.14 The effect of binder concentration in slurries on the strength of alumina green body

5.4 Effect of acid treatment on the properties of alumina calcined body

From the previous experiment, the results of green body density and strength were obtained to justify what kind of specimen should conduct to further process. B and G specimen were selected to investigate for further experiment considering former data, such as density and strength of green body and viscosity of slurry.

In order to decompose the organic composition in the green body specimen, B and G were fired at 800 ^{0}C for 2 h in air atmosphere with the heating and cooling rate of 10 ^{0}C / min. After that specimens are called calcined body. Their densities were slightly increased from green body as shown in Figure5.15.

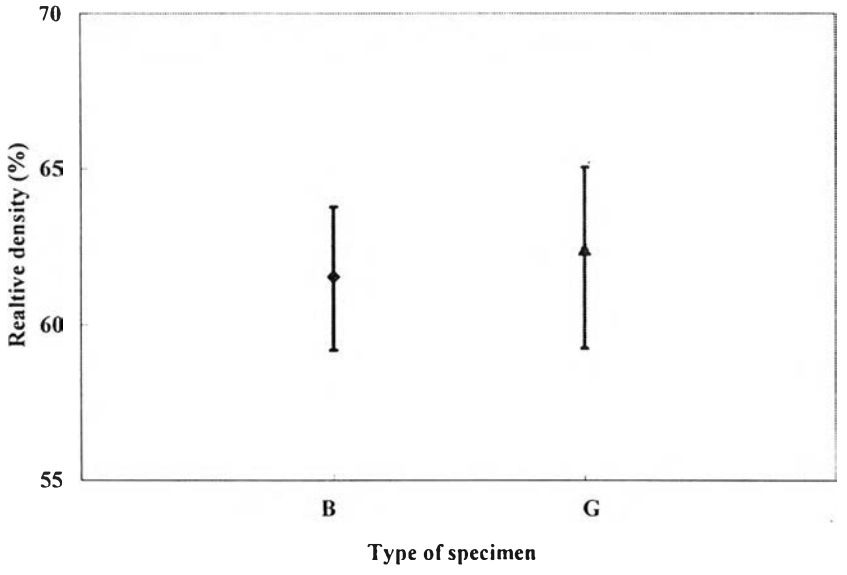


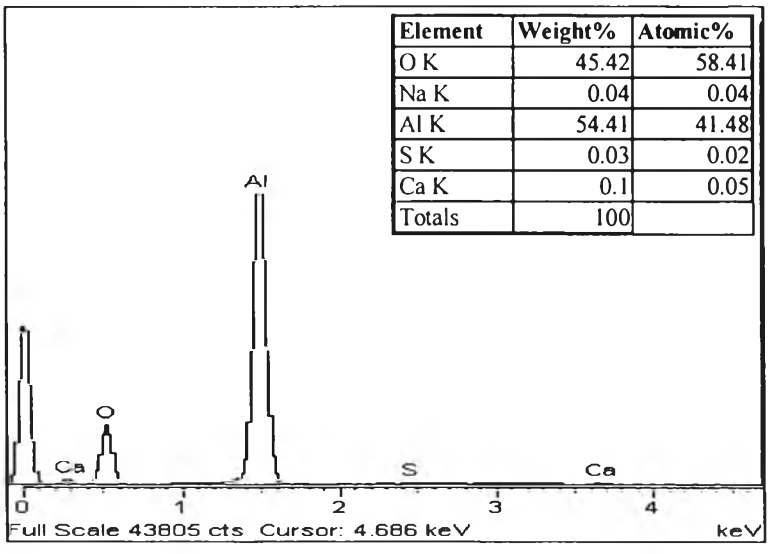
Figure 5.15 The calcined body density of B and G specimens

Remarks:

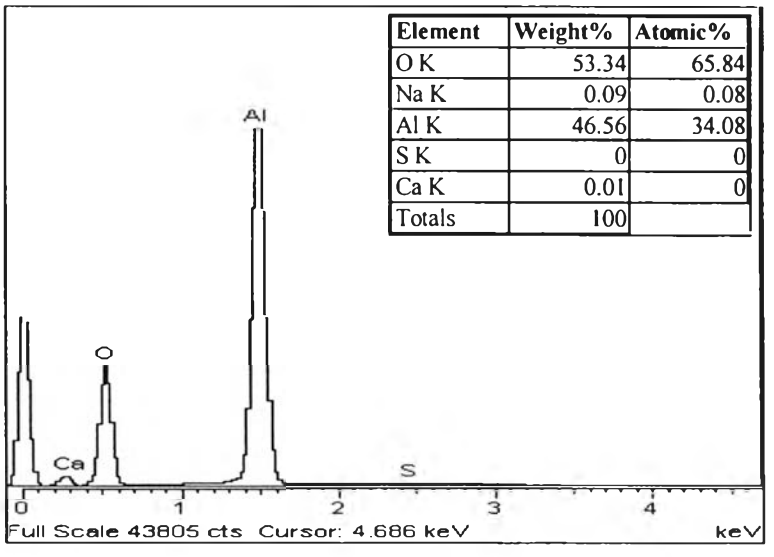
B specimen is fabricated by using 75% solid loading with 1.25 wt% def.locculant

G specimen is fabricated by using 75% solid loading with 1.25 wt % deflocculant and 0.05 wt% binder

Some of calcined bodies of B and G specimen were immersed 1 M HCl solution for 1h in order to investigate the efficiency of acid on elimination of impurities remained in calcined specimen. The energy dispersive X-ray (EDX) spectroscopic analysis has been performed for elemental analysis as shown in Figure 5.16. It is found that calcined specimen with acid treatment shown the lower concentration of calcium compare with untreated condition.



(a)

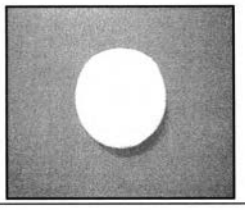
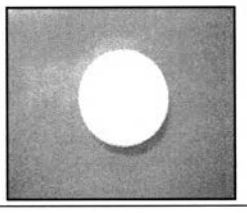
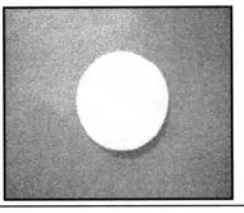
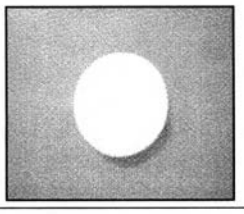
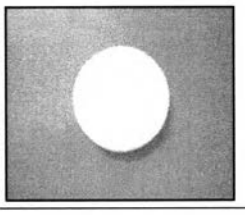
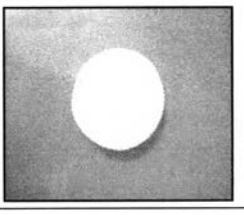
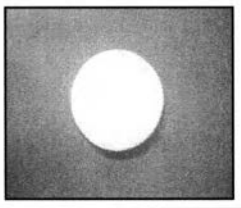
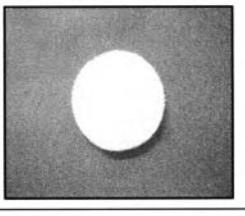
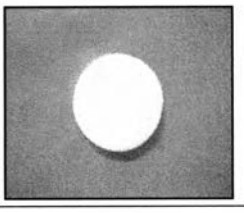
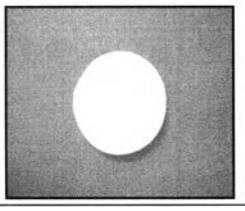
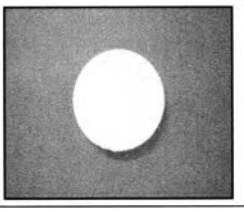
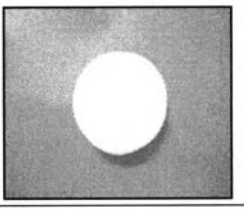


(b)

Figure 5.16 EDX analysis of the calcined body of (a) B specimen without acid treatment (b) B specimen with acid treatement

5.5 Effects of temperature and acid treatment on the properties of the alumina sintered body

5.5.1 Appearance of alumina sintered body

Specimen	Temperature (°C)		
	1250	1300	1350
BU			
BT			
GU			
GT			

Remark: BU: B specimen without acid treatment
BT: B specimen with acid treatment
GU: G specimen without acid treatment
GT: G specimen with acid treatment

Figure 5.17 Appearance of alumina sintered body at various sintered temperature

The appearance of pellet specimens sintered in air at various sintering temperature are shown in Figure 5.17. It was been clearly seen that the color of h B and G specimen without treatment were white at 1250 ^{0}C and changed into yellowish ivory at 1350 ^{0}C. On the other hand, color of acid treatment specimens did not change from white. The color kept white even at 1350 ^{0}C, only with a few yellow spot at 1250 ^{0}C.

5.5.2 Density of alumina sintered body

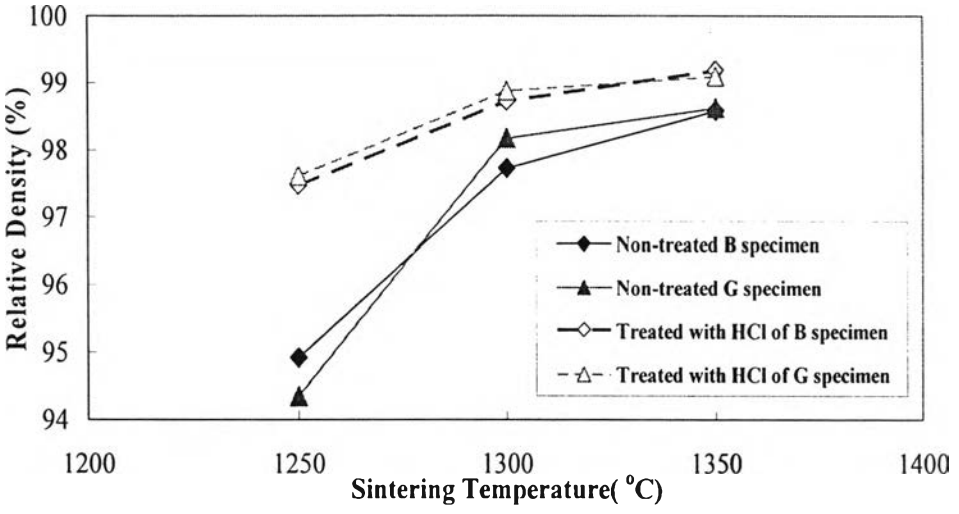


Figure 5.18 The effect of sintering temperature in air atmosphere for 2h on the relative density of B and G specimens

In the sintering process, temperature and atmosphere are also significant factors that must be controlled to give the product with high density and smaller growth of grains. Figure 5.18 illustrated the effect of sintering temperature on the density of sintered specimen. It should be noted that densities of sintered B and G specimen were slightly different at all temperatures since B and G specimen have slightly different in composition. The specimens with acid treatment promoted the higher density than untreated specimen. This must be come from an effect of impurity in specimen. In the previous papers, many researchers reveal that some kinds of impurities such as calcium suppress densification of sintered specimen. Moreover,

presence of calcium in alumina causes abnormal grain growth of sintered body which leads to give specimen with non-uniform microstructure, and high porosity. It should be supposed that acid treatment aids to increase the densification of sintered specimen by eliminating calcium penetrated into specimen during casting in gypsum mold.

5.5.3 Microstructure and grain size

Besides sintering temperature and acid treatment process have an impact on the appearance and density of sintered specimens, they also take an effect on the grain size and microstructure. The results of sintered grain size at various sintered temperature are shown in Figure 5.19 and Table 5.2. Their microstructures observed by SEM for specimen sintered at 1250 ^{0}C, 1300 ^{0}C and 1350 ^{0}C are shown in Figure 5.20, 5.21 and 5.22, respectively.

For comparison B and G specimen, it can be clearly seen that G specimens provide the bigger grains than B specimen. This should be a consequence of impurity. From the manufacturing specification, CMC binder included 7 wt% Na which was in the range of 35-44.5 ppm. in G specimen. At this sintering temperature, Na (boiling temperature, 880 ^{0}C) might be melted and reacted into Na_2O simultaneously. The Na_2O must be reacted with Al_2O_3 and produce small amount of liquid phase which may suppress densification and conduct to the abnormal grain growth.

Acid treatment was contributed to get higher density at lower temperature as shown in Figure 5.18. On the other hand, specimen treated with acid showed bigger gain size as seen in Figure 5.19. It should be noted that small amount of Na strongly contributed to control the size of sintered grain, especially at high temperature as 1350 ^{0}C.

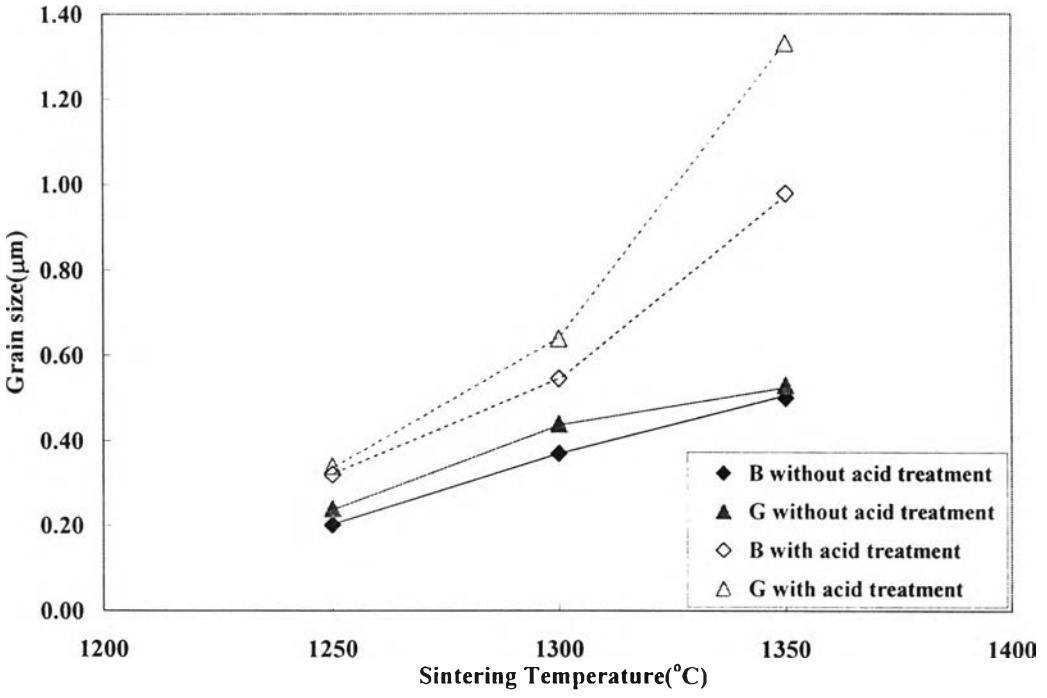


Figure 5.19 The effect of sintering temperature in air atmosphere for 2h on the grain size of B and G sintered specimens

Table5.2 Ratio of particle size of starting materials: sintered grain sizes at various sintering temperature

T	**Ratio of intered grain size : starting material size**			
(°C)	BU	BT	GU	GT
1250	1.2	2.0	1.5	2.1
1300	2.3	3.4	2.7	3.9
1350	3.1	6.0	3.3	8.2

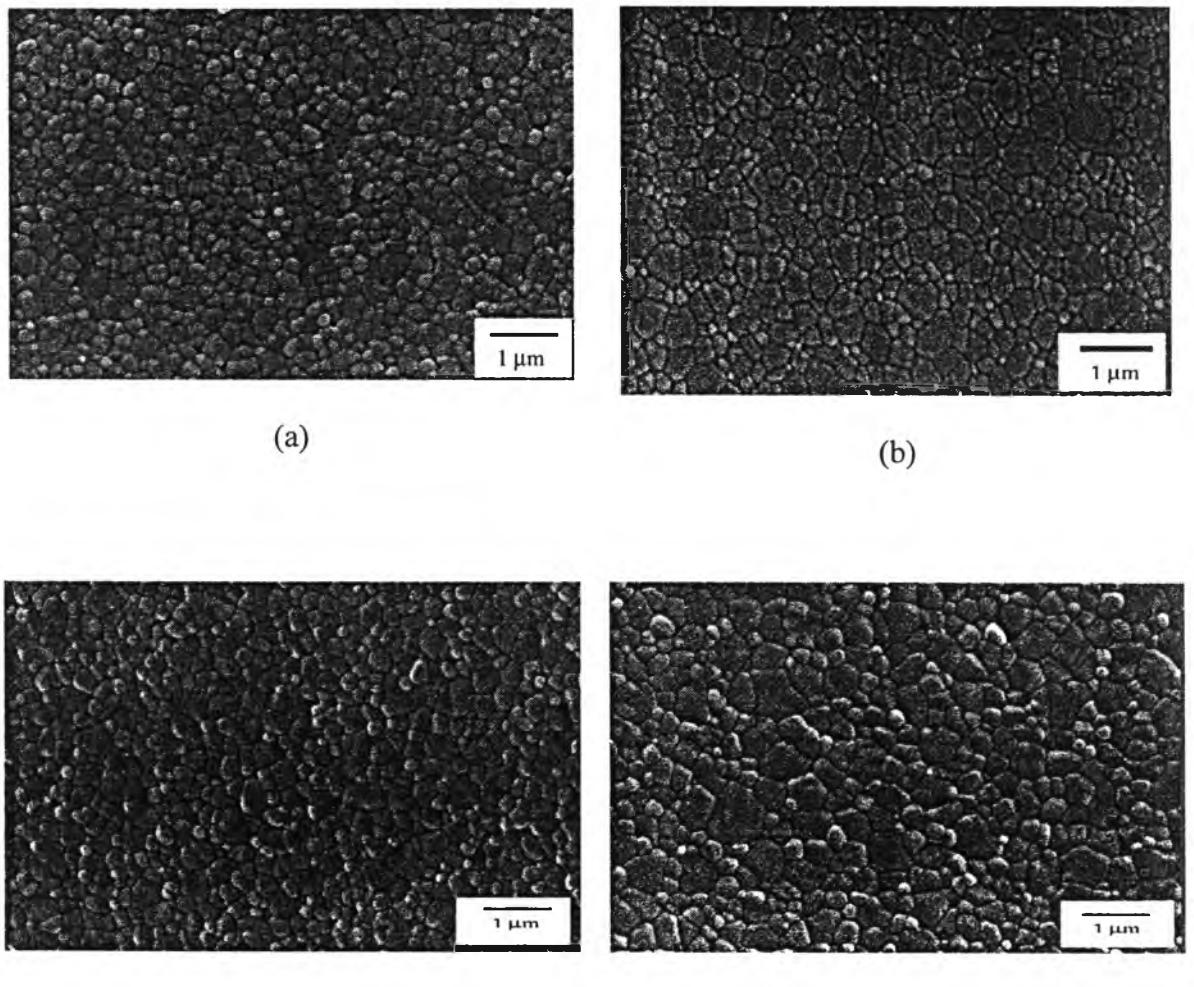


Figure 5.20 SEM micrograph of alumina specimen sintered at 1250 ^{0}C in air atmosphere (a) specimen B without acid treatment (b) specimen G without acid treatment (c) specimen B with acid treatment (d) specimen G with acid treatment

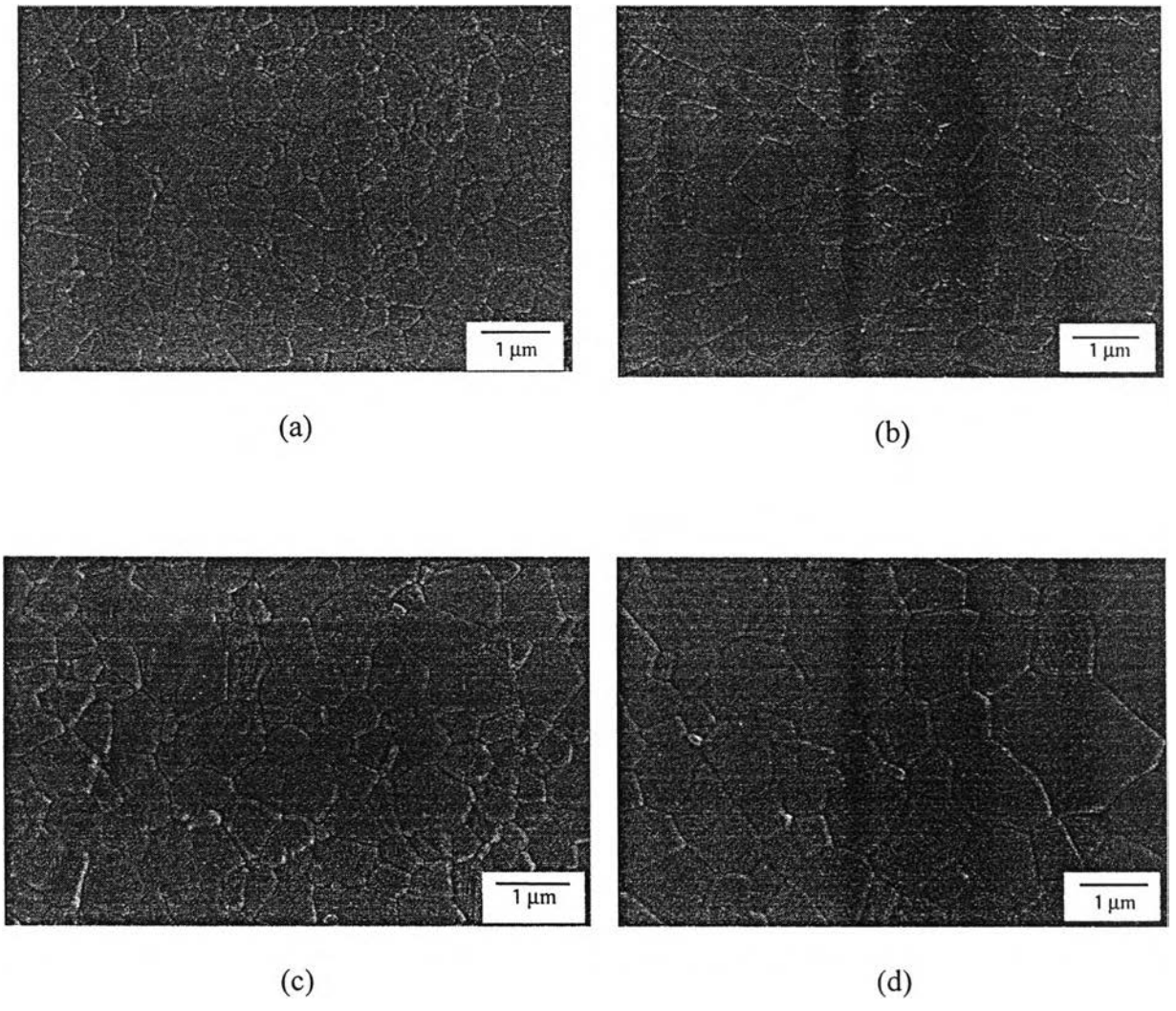


Figure 5.21 SEM micrograph of alumina specimen sintered at 1300 ^{0}C in air atmosphere (a) specimen B without acid treatment (b) specimen G without acid treatment (c) specimen B with acid treatment (d) specimen G with acid treatment

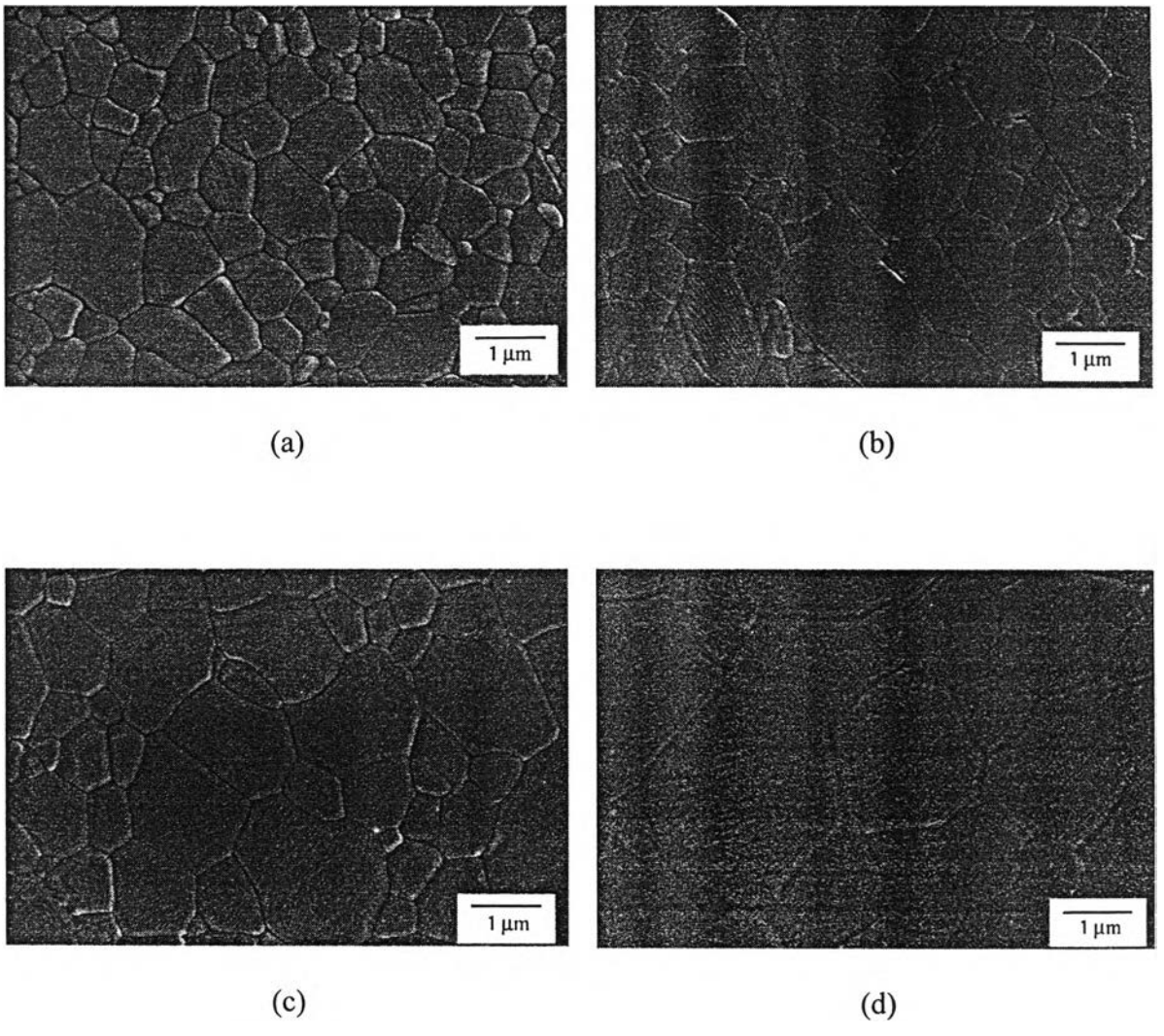


Figure 5.22 SEM micrograph of alumina specimen sintered at 1350 ^{0}C in air atmosphere (a) specimen B without acid treatment (b) specimen G without acid treatment (c) specimen B with acid treatment (d) specimen G with acid treatment.

5.5.4 Shrinkage

In order to give the sintered specimen with the desired size and shape, the shrinkage profile must be concerned. The shrinkage of specimen was speculated from the measurement of the dimension in both before and after sintering by vernier caliper. For the pellet shape, the shrinkage in diameter, thickness and volume were investigated as shown in Figure 5.23, 5.24 and 5.25, respectively. It can clearly seen elevation of sintering temperature conduct to increase the shrinkage in both diametrical and thickness direction. Moreover, It can also be noted that specimen with acid treatment provided more shrink than untreated one which correlated with the density of specimen.

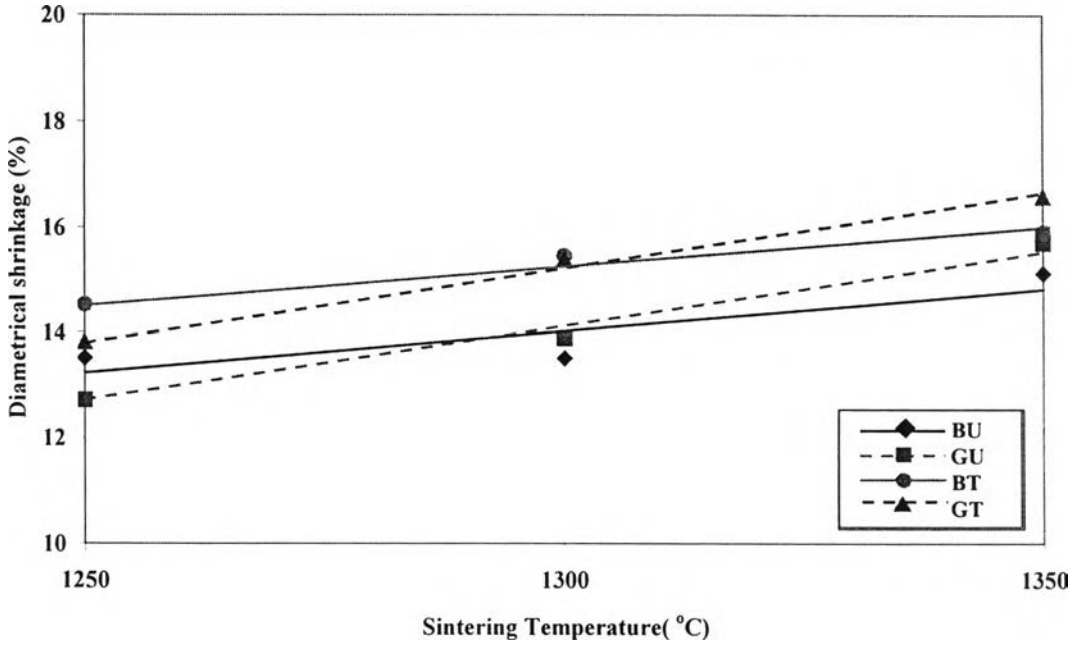


Figure 5.23 The diametrical shrinkage of specimen with pellet shape at various sintering temperature.

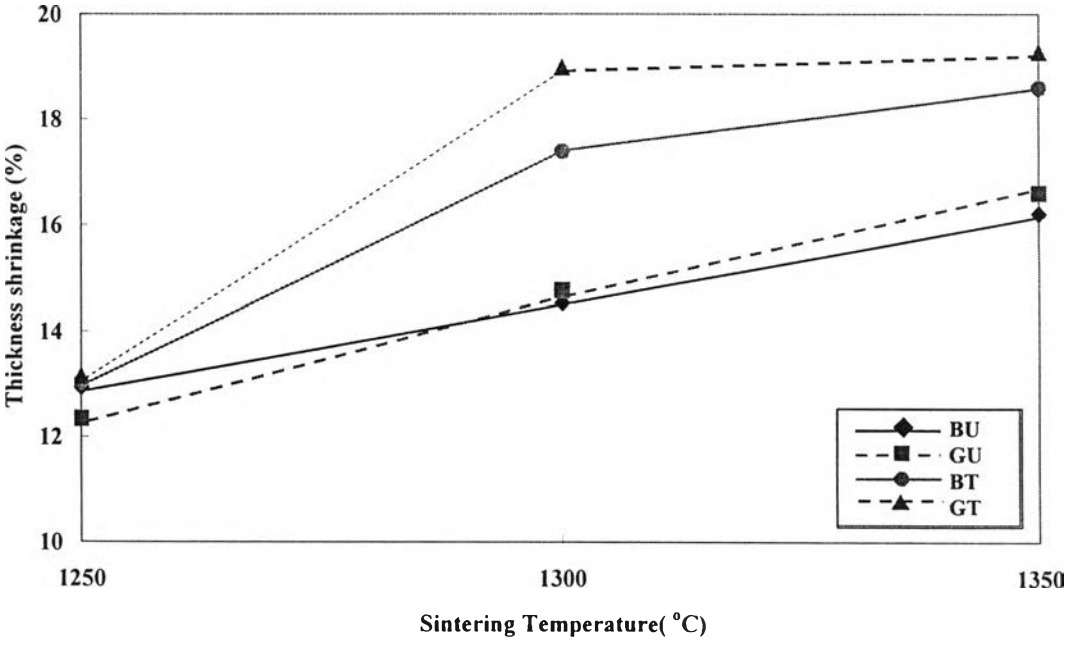


Figure 5.24 The thickness shrinkage of specimen with pellet shape at various sintering temperature.

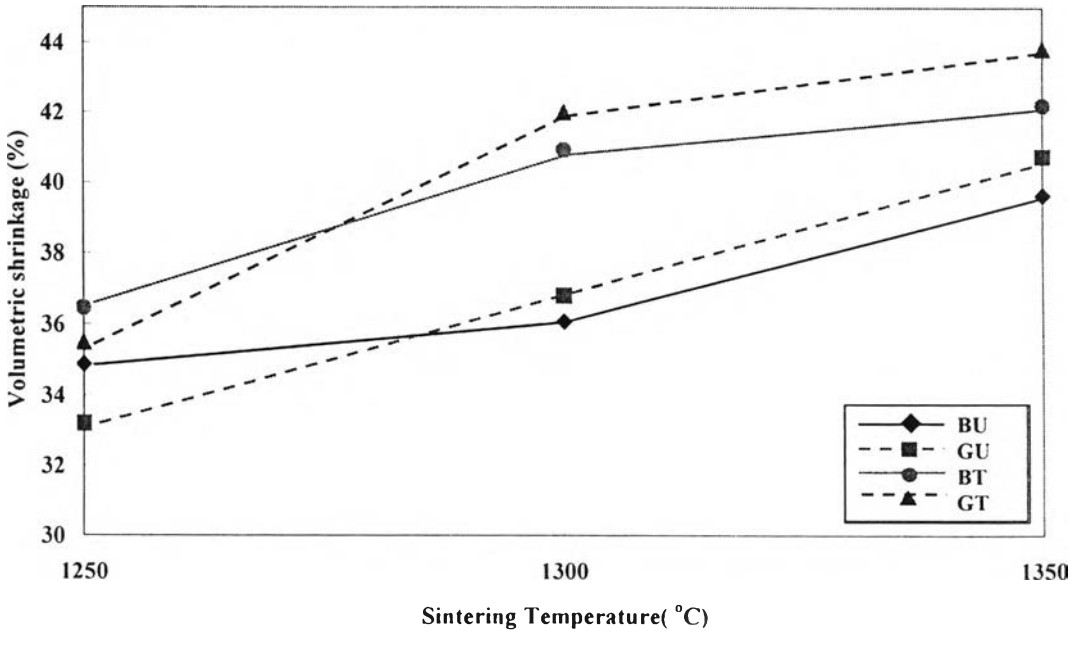


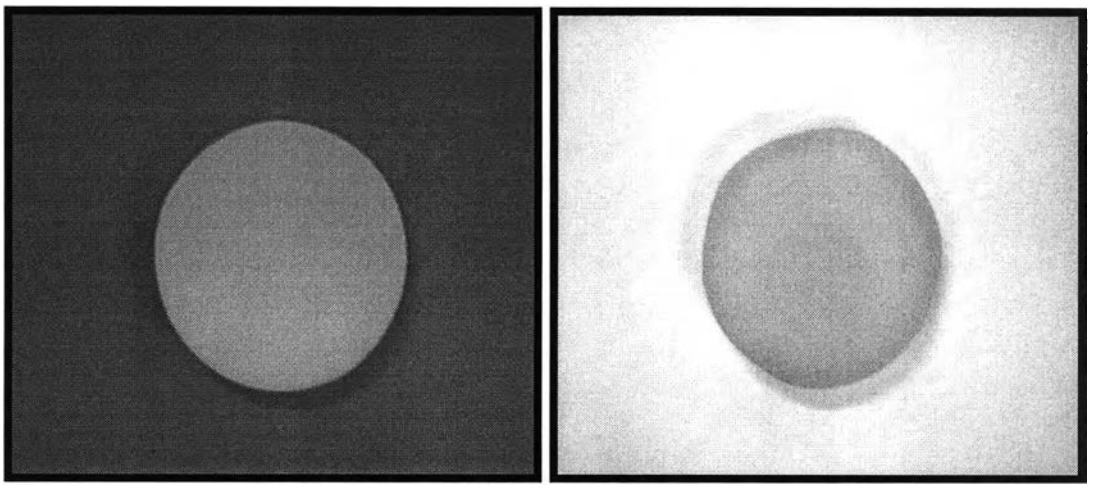
Figure 5.25 The volumetrical shrinkage of specimen with pellet shape at various sintering temperature

5.6 The Effect of HIP on the properties of alumina sintered body

The sintered specimens with the over 95% relative density were selected to sinter in the HIP furnace. Hot Isostatic Press (HIP) was employed to eliminate both the remained pore within the grain and the grain boundaries in order to give the fully dense specimen. From the previous results, sintering in air at 1300 ^{0}C is the low sintering temperature to give both untreated and treated specimen with over 95% relative density. Therefore, Both of B and G specimens with same sintering temperature were adopted to HIP in order to investigate the HIP effect on its property changes.

5.6.1 Appearance of alumina sintered body

The appearance of sintered specimen before and after hipping is shown in Figure 5.26. Appearance of B and G specimen were changed from white or ivory into translucent after HIPing at 1300 ^{0}C and 130 MPa in argon atmosphere. When HIPed specimens were ground to 0.8 mm and polished on both sides, it changed to transparency as shown in Figure 5.27.



(a) **(b)**

Figure 5.26 The appearance of alumina ceramic specimen (a) before hipping and (b) after hipping at 1300 ^{0}C 130 MPa in argon atmosphere

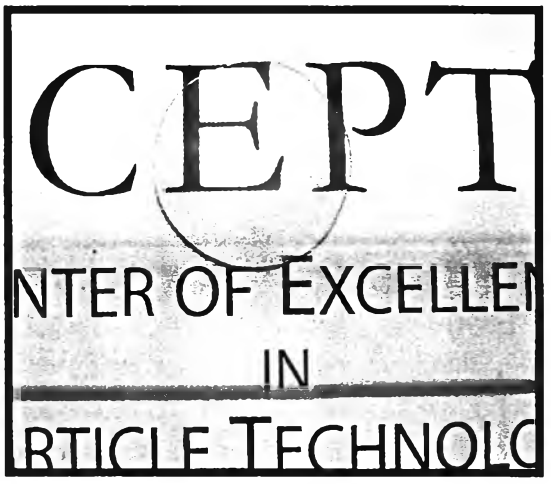


Figure 5.27 HIPed specimen that sintered at 1300 ^{0}C in air followed by HIPing at 1300 ^{0}C, 130MPa in argon atmosphere for 2 h after grinding to 0.8 mm thickness and polishing on its both sides

5.6.2 Density of sintered body

As shown in Figure 5.27 and 5.28, it can be indicate that HIP process is an effective method to give not only transparent appearance, but also fully density.

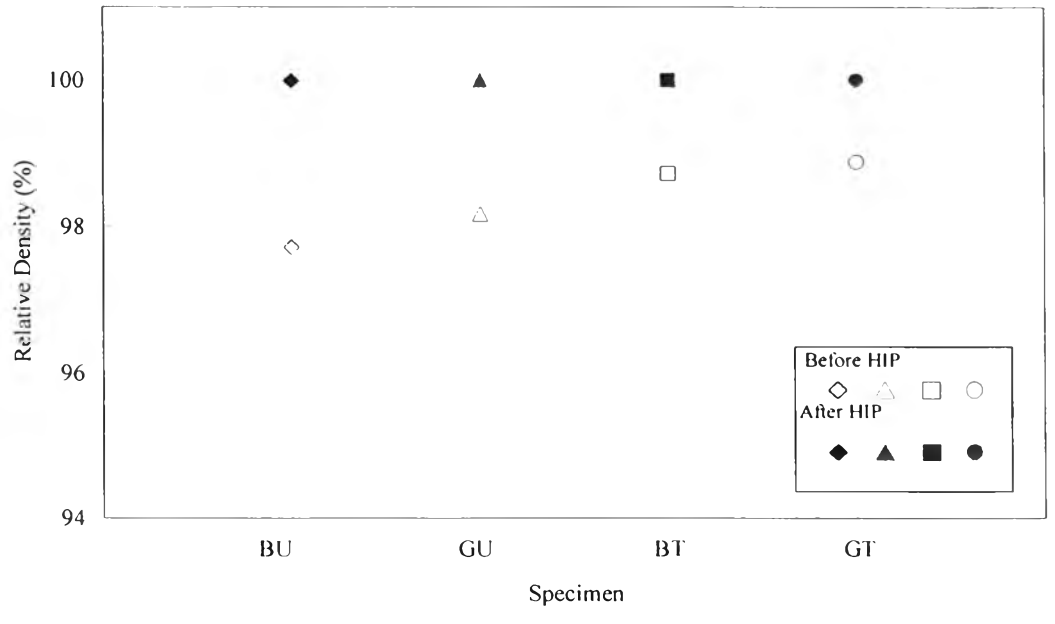


Figure 5.28 The influence of HIP on the relative density of alumina specimens

5.6.3 Average grain size and microstructure of HIPed body

The average grain size of HIPed is shown in Figure 5.29. It can be clearly seen that specimens with acid treatment have a bigger average grain size than untreated one due to effect of impurity elimination and uniformity of grains.

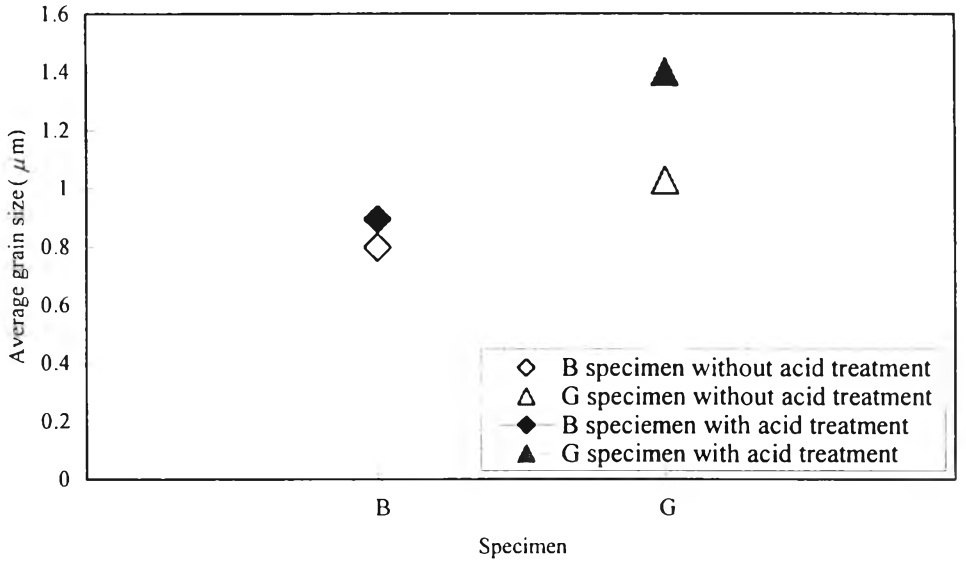
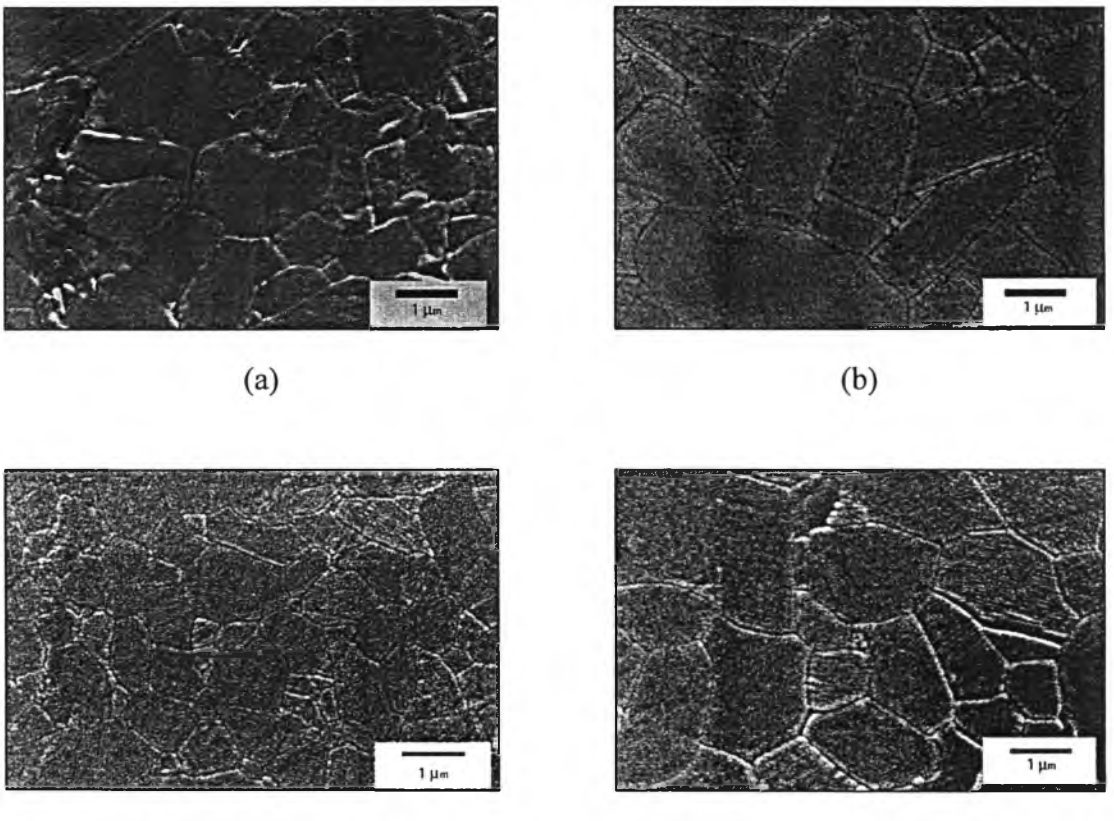


Figure 5.29 Grain size of HIPed specimens

Based on Figure 5.29, the microstructure of different HIPed specimens are shown. Photograph (a) shows larger grain than before HIPing and broad grain size distribution. Photograph (b) shows a larger grain than (a) and elongated grain size. Photograph (c) shows smallest grain size and rather uniform grain. Photograph (d) shows large grain size and rather uniform figure. These differences of microstructure between untreated and treated specimen is due to the existence of Ca from gypsum mold. Ca takes an effect on grain growth with abnormal behavior, for example, elongated grain and non-uniform grain. In addition, Na existence in specimen takes also an effect to give the bigger and broader grain than normal.



(a) (b)

(c) (d)

Figure 5.30 SEM micrograph of alumina specimens HIPed at 1300 ^{0}C, 130 MPa in argon atmosphere for 2 h (a) specimen B without treatment (b) specimen G without acid treatment (c) specimen B with acid treatment (d) specimen G with acid treatment

5.6.4 Transmittance of alumina sintered body

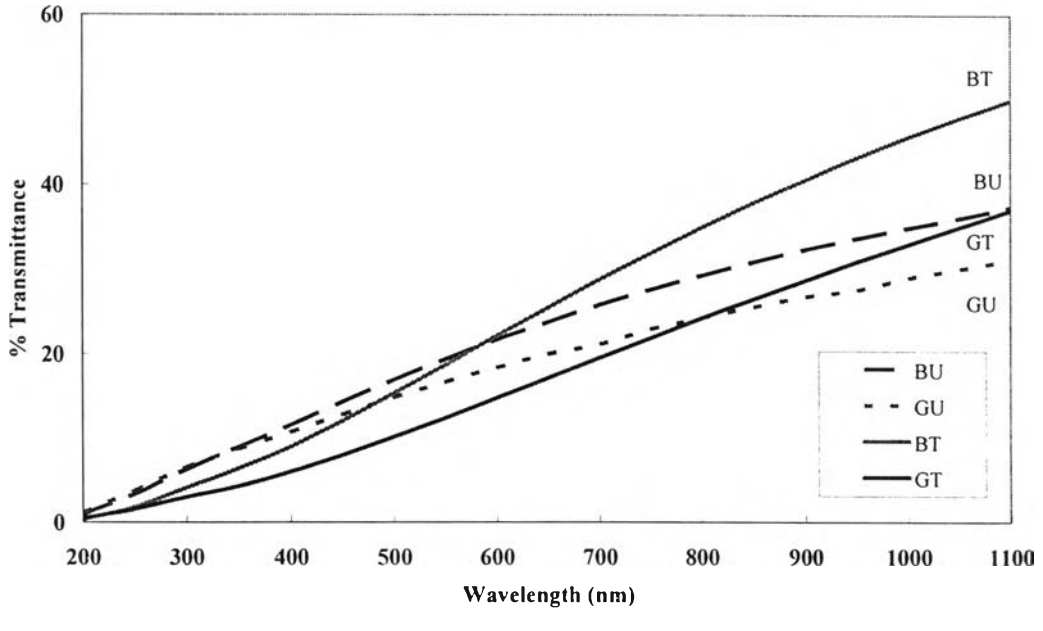


Figure 5.31 Transmittance of HIPed specimens in range of 200-1100 nm with thickness of 0.8 mm.

From the previous results, there is no difference in the density between four specimens as seen in Figure 5.28. However, other properties such as appearance, grain size, microstructure and transmittance are quite different. The transmittance of different specimens with the thickness of 0.8 mm is shown in Figure 5.31. The transmittance of B specimen is higher than G because grain size of B specimen is smaller than G as shown in Table 5.3.

For comparison the influence of acid treatment on the transmittance of alumina specimen, it should be noted that acid treatment help increase the transmittance of B from 37% to 50% and that of G specimen from 31% to 37% at 1100 nm (near IR). This may cause uniformity of grain pattern of acid treatment specimen is better than untreated specimens. On the other hand, at lower than 600 nm for B specimen and lower than 800 nm for G specimen, transmittance of specimen with acid treatment is lower than without acid treatment. This may causes the

specimens without acid treatment have much amount of grains with smaller than average compare with acid treatment specimens.

Table 5.3 Summary of HIPed specimen characteristic

Characteristic	BU	BT	GU	GT
Relative density (%)	100	100	100	100
Average grain size (μm)	0.80	0.89	1.01	1.4
Maximum transmittance (% at 1100 nm)	37	50	31	37
Grain pattern	Elongated and broad	Uniform and broad	Elongated and broad	Uniform and broad