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ORIGINAL ARTICLE

Effect of Nano-Crystalline Boehmite Addition on Sintering and Properties of Alumina Ceramics

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ABSTRACT

In this study, alumina ceramics containing up to 10 wt% of boehmite were sintered at 1550, 1600 and 1650ºC for 1 hour. Water absorption, weight loss, porosity and density values were measured after sintering. Boehmite content caused flocculation during mixing in water suspension. Formation of boehmite agglomerates was clearly seen in SEM examination and also it was observed that there were different shrinkages in alumina matrix and in boehmite agglomerates and this caused gaps around agglomerates. Boehmite addition decreased mechanical properties due to the inhomogeneous dispersion of boehmite in alumina mixtures. Large boehmite agglomerates is sintered and shrank differently compared to alumina matrix. These differences caused large grains (agglomerates) of alumina derived from boehmite and also some large crack around these agglomerates. These structural changes resulted in low densities and low flexural strength as the content of boehmite powder increased in the alumina ceramics. This two phased structure in alumina ceramics resulted in large decreases in flexural strength after sintering at 1650ºC as 210 and 140 MPa for pure alumina and for 10 wt% boehmite added alumina respectively.

Key Words: *Alumina, boehmite, microstructure, strength.*

1. INTRODUCTION

Alumina (Al_2O_3) is one of the most widely used ceramic in various industries such as refractory's, mechanical parts, abrasives, insulators, etc. A great number of papers have been published on various aspects; including sintering of alumina, its enhanced densification by seeding, control of microstructure by additives and the packing and densification of bimodal mixed powders [1].

Bodisova et al.; prepared alumina ceramics by pressure filtration of electrostatically stabilized alumina and alumina–boehmite water suspensions and subsequent pressureless sintering of as-prepared compacts. Nanoparticle boehmite sol was used as a dispersant for alumina suspension, it acted as a lubricant and moreover it enhanced the handling strength of the green compacts and also its sinterability. The kinetic analysis of sintering

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confirmed that the definite boehmite addition (2.7 wt% in green compact) affects the densification positively. The higher amount of boehmite addition has negative influence; it causes the flocculation of the suspensions and decreases the density of sintered bodies [2].

Kwon et al.; fabricated porous α-Al_2O_3 ceramics from a bimodal mixture of seeded boehmite and uniformly sized coarse α-Al_2O_3. The densification behaviour of the mixtures was correlated with shrinkage and micro structural evolution. The mixtures sintered at 1200ºC contained more than %30 porosity and the mechanical strength of the mixtures was increased by 2-4 fold relative to the coarse particles alone with similar porosity (<5 MPa) [3].

Ananthakumar et al.; studied the extrusion of alumina pastes by sol gel assisted colloidal processing involving nano particulate boehmite gel as a binder phase. The analysis of alumina–boehmite paste was compared with the conventional water-soluble HPMC polymer system. The exit pressure for alumina–HPMC system was only 0.2 MPa. The addition of processing aids such as 0.25 wt% of PVA, 3.0 wt% of either PEG or glycerin with alumina–15 wt% boehmite paste exhibited very low exit pressure as equal to that of the HPMC binder. A green density of 65% theoretical was achieved for extruded alumina. The alumina rods attained 98% theoretical sintered density at 1500ºC. The study explained the use of nano particulate boehmite gel as a binder for alumina ceramics as well as the influence of conventional ceramic processing additives on extrusion characteristics of alumina–boehmite pastes [4].

Ananthakumar et al, also studied the effect of nanoparticulate boehmite addition to alumina ceramics for slurry compaction. It was reported that up to 17.24 vol.% (which was around 3.5 to 5 wt%, depends on boehmite density), boehmite addition increased the green and sintered densities. Above 17.24 vol.% boehmite additions, the green and fired densities decreased in both slurry compacted and dry-pressed samples [5].

Handling strength of green compacts is mainly achieved by using polymer binders (eg: PVA, PEG). However, polymer additions often influence the suspension rheology negatively, thereby causing its flocculation (agglomerates). Polymer additions can also cause micro structural defects formation during the burning out stage and their residues may have adverse effects on sintering process. Therefore, it may be an advantage to use inorganic binder instead of polymers in ceramics preparation, especially when it changes its composition directly to desired product during sintering (alumina in our case).

As seen from the above studies that boehmite was added to alumina ceramics as binder and plasticizer. Especially in extrusion pastes, boehmite powders act as inorganic lubricant and when added to the ceramics batches, during sintering, it losses the OH groups and transforms to transition alumina (γ- δ-, and θ-Al_2O_3) at lower sintering temperatures and around 1200°C to α-Al_2O_3 [6]. This is important in ceramic production because organic additives have to be removed from the ceramic system during drying and sintering. It is a crucial part and usually creates problems of cracks, porosities, high volume of shrinkages in ceramic production. The use of boehmite can reduce these problems because only the OH groups have to be removed and remaining part is transformed to alumina. The amount of materials which has to be removed during sintering is less and this affects the amount of shrinkages during sintering.

In this study, in order to see the effect of the nano-crystalline boehmite addition to alumina ceramics during sintering, boehmite powders were added in simplest manner by just adding up to 10 wt%, to a mixture of alumina and boehmite powders in a water suspension. Alumina ceramics containing up to 10 wt% boehmite were sintered 1550, 1600 and 1650°C for 1 hour soaking time.

2. EXPERIMENTAL

One of the starting powder is commercial reactive alumina A-16 SG (Alcoa Chemical, Bauxite, AR, USA), with average particle size of 0.5 µm, having specific surface area of 8.5 m^2/g, as typical values declared by the manufacturer. HiQ 40 boehmite (BASF), having surface area of 250 m^2/g, and average particle size of 50 µm was given by the manufacturer.

The particle size of boehmite is also measured with Nano-sizer (Malvern, Nano SZ) in the Laboratory. The result of the particle size and distribution of the boehmite powder is given in Figure 1. The mean particle size was measured as 497.9 nm but as can be seen from the distribution that most of the boehmite powders were smaller than this value. Because of the differences of particle sizes between manufacturer declaration and our measurement, SEM and TEM are also used to determine the real particle size of the boehmite powder.

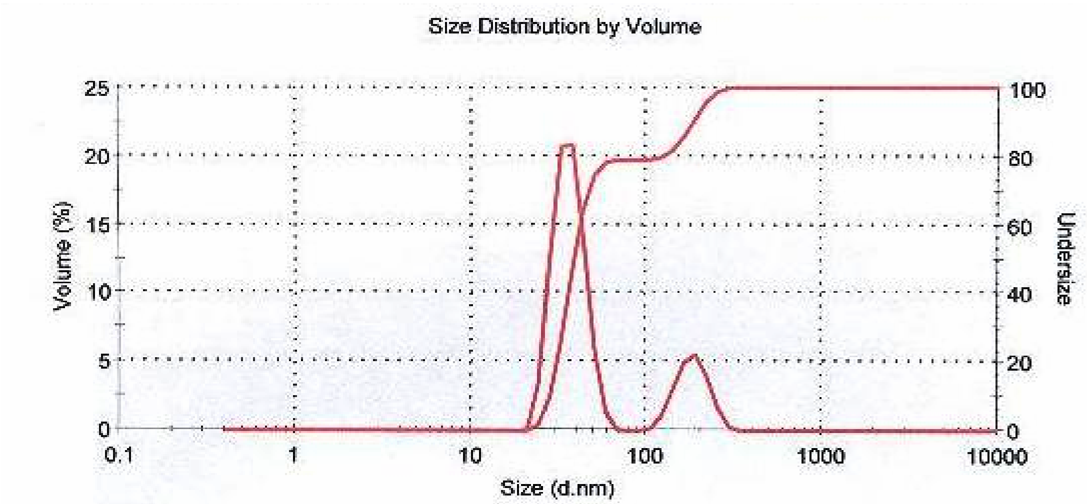
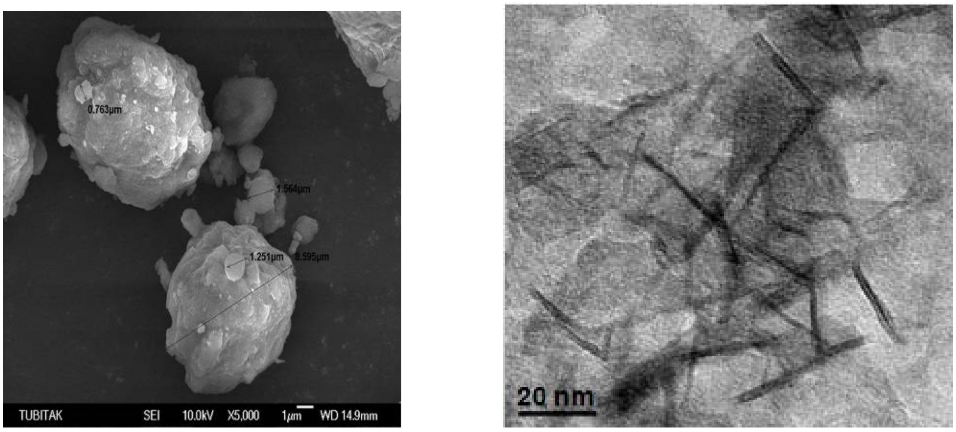


Figure 1. Particle size and distribution of the boehmite powder.



(a) (b)

Figure 2. Microstructure and particle size of boehmite powder (a.SEM, b.TEM).

As can be seen in Figure 2a, the grain size of boehmite powder which is given by the manufacturer is actually the size the agglomerates when studied under scanning electron microscope (Jeol JSM 6335 F-SEM) and from Figure 2b, the grain size of boehmite powder is around 25 nm and bar shaped under transmission electron microscope (JEOL 2100 LaB_6 HRTEM).

Alumina ceramics, containing boehmite with the ratio of 0, 1, 3, 5, and 10 wt%, were named as AB-0, AB-1, AB-3, AB-5 and AB-10 in this study. Processing of alumina ceramics with boehmite was carried out by the following route. First; 20wt% of water and 0.7 wt% Darvan-C (Polymerdeflocculant, R.T Vanderbilt Company, Inc.) were mixed for 5 minutes, then the required amount of boehmite powders were added to this water solution and stirred for 15 minutes. Second; alumina powders were added to the boehmite solution and stirring was carried out for 5 hours and the pH value was around ~8.5 and viscosity value was around 110 cP for this boehmite-alumina slurry. Third; the mixture was dried in an oven at 100ºC and it was granulated by using 800 µm sieve. Finally; the powders obtained after granulation were pressed with 1 ton/cm^2 pressure in the 37x7x7 mm dimensions using OHC model hydraulic press and sintered at 1550, 1600 and 1650ºC for 1 hour.

The weights and dimensions of specimens were measured and weight loss and shrinkage values were calculated. Apparent density, water absorption and porosity values were determined by the Archimedes water displacement technique. Flexural strength values of all specimens were measured by 3-point bending test with Zwick model tensile/compressive test equipment. Microstructures of the specimens were examined by using Jeol JSM 6335 F model scanning electron microscope (SEM) from the polished surfaces.

3. RESULTS AND DISCUSSION

Changes in the shrinkage values of the sintered boehmite-alumina ceramics at different temperatures were given in Figure 3. It is seen that shrinkage increased with the increasing boehmite content and sintering temperatures. Also it can be seen in the figure that the shrinkage values in length were smaller than in thickness in the bar shaped dry-pressed and sintered alumina-boehmite ceramics. This can be attributed to the alignment of especially boehmite particles perpendicular to pressing directions.

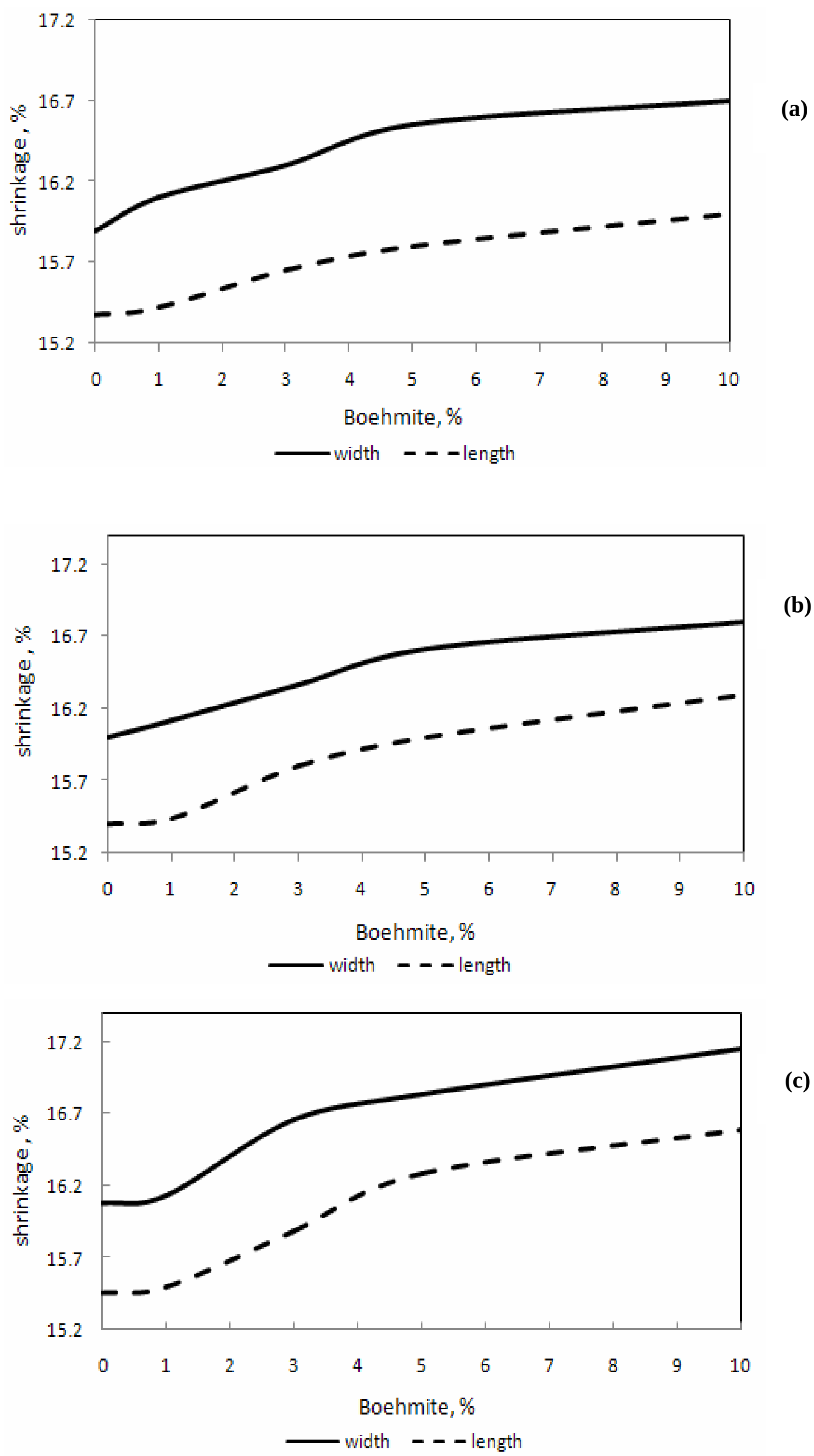


Figure 3. Shrinkage% of boehmite-alumina ceramics with increasing boehmite content at different sintering temperatures (a) 1550ºC (b) 1600ºC (c) 1650ºC.

Apparent density, water absorption and porosity values of alumina ceramics that contain different amounts of boehmite were shown in Figure 4.

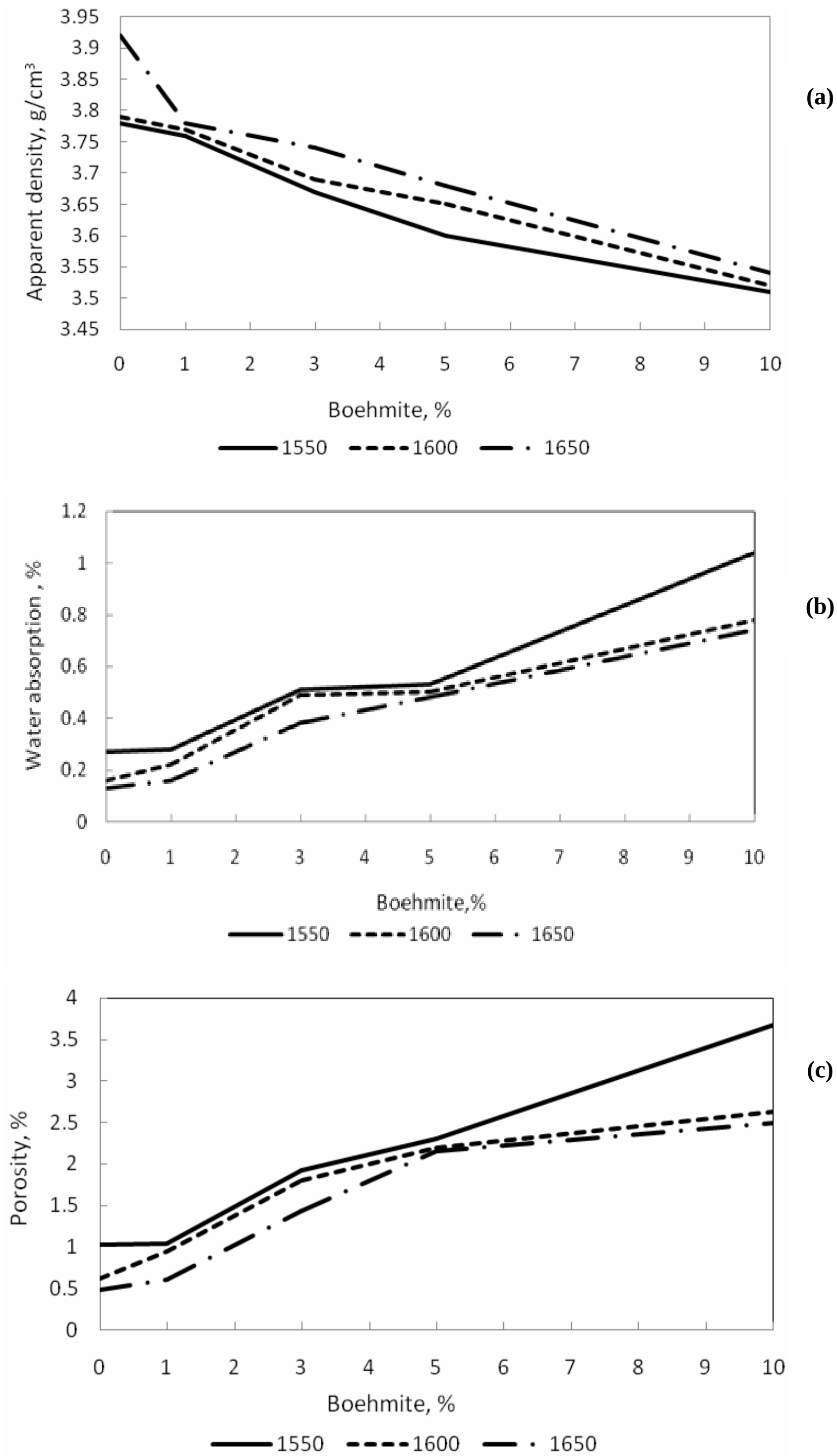


Figure 4. Changes of (a) apparent density (b) water absorption and (c) porosity as a function of increasing boehmite content.

As seen in the Figure 4a that apparent densities were decreased with increasing boehmite content at all sintering temperatures for example the apparent density of AB-0 was around 3.92 g/cm^3 after sintering at 1650°C but at the same temperatures the apparent density of AB-10 was around 3.57 g/cm^3. Similar behaviour was observed at all sintering temperatures for boehmite-alumina ceramics. The water absorption and porosity increased with increasing boehmite content again at all sintering temperatures (Figure 4b and c). The typical values of water absorption were around 0.2% for AB-O and around 1% for AB-10. Similar behaviour was observed in porosity values which were around 0.5 to 1% for AB-O and around 2 to 3.5% for AB-10 at various sintering temperatures.

Flexural strength of the boehmite-alumina ceramics with increasing boehmite content were measured by Zwick model tensile/compressive test equipment. It was observed that, as the boehmite content increased, the strength of boehmite-alumina ceramics decreased at all sintering temperatures, as shown in Figure 5 and Table 1.

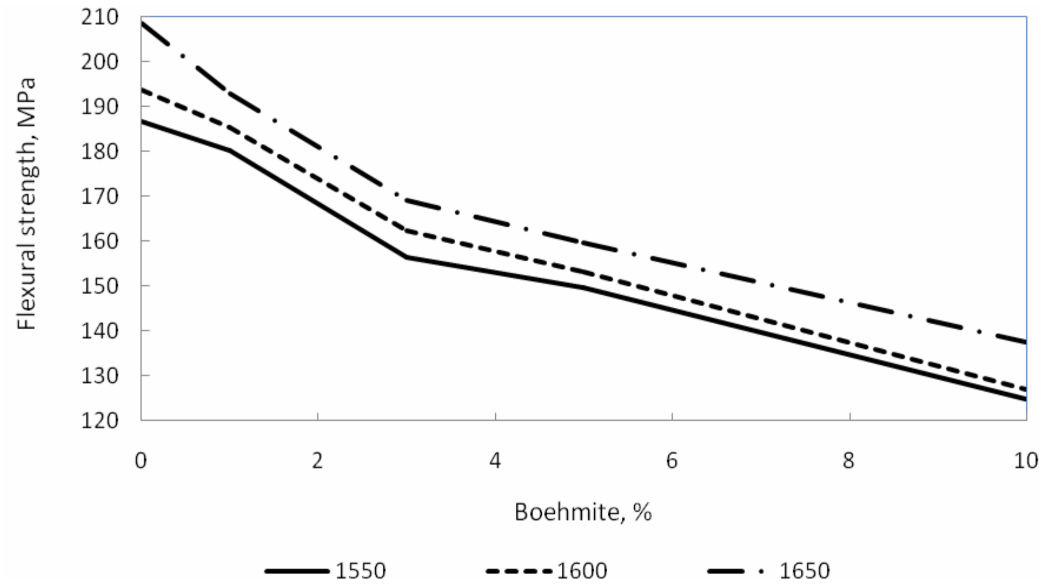


Figure 5. Flexural strength of the boehmite-alumina ceramics with increasing boehmite content sintered at 1550ºC, 1600ºC and 1650ºC.

Table 1. Flexural strength values of boehmite-alumina ceramics by three-point bending test.

SAMPLE CODES	**FLEXURAL STRENGTH (MPa)**		
	1550ºC	**1600ºC**	**1650ºC**
AB-0	186.59	193.65	209.00
AB-1	180.17	185.27	192.87
AB-3	156.37	162.40	169.03
AB-5	149.62	153.32	160.00
AB-10	124.76	127.11	137.59

The first observation was that flexural strength values of all boehmite-alumina ceramics increased with increasing sintering temperature such as the flexural strength values of AB-3 were around 156 and 169 MPa at 1550 and 1650°C, respectively. The addition of boehmite caused decreases in flexural strength of ceramics. This decrease in flexural strength values were getting higher with increasing boehmite content, such as after sintering at 1650°C; the flexural strength values of AB-0 and AB-10 were around 210 and 140 MPa, respectively.

In order to explain this behaviour, micro structural examination of all boehmite-alumina ceramics were carried out. The microstructures of the boehmite-alumina ceramics were shown in Figure 6. Increasing boehmite content in alumina ceramics, resulted with the increased number of agglomerates in the structure as can be seen in the figure. At the same time, with increasing sintering temperatures growth in the size of agglomerates was also observed in all samples. It can be seen that there were cracks or separation between alumina matrix and agglomerates resulted from boehmite. The reason was thought that, the amount of shrinkage in alumina matrix and boehmite agglomerates were different during sintering. Particle sizes of agglomerates were much smaller than alumina particles in the matrix. These observations were similar to that of reported by Bodisova et al. As they explained that higher boehmite content (more than 3 wt%) causes flocculation of the suspension and decreases the density of the sintered body and decreased flexural strength values of the sintered ceramics at all sintering temperatures. According to the result of kinetic analysis in the literature, small amount of boehmite affects the densification positively. The addition of boehmite nanoparticles to alumina suspension results in lower energy barriers [2]. Following these considerations the higher amount of boehmite in system should also positively affect the sintering. However, the sintered densities of boehmite-alumina samples prepared by dry-pressing decreased with increasing boehmite content. Flocculation of probably both alumina and boehmite particles occurs, this means that the suspension consist of weakly aggregates. Due to these aggregate formations in suspension, enhanced flaw formation can occur during calcinations and sintering of dry-pressed compacts [7, 8].

At sintering, the densification of the particles in agglomerates is preferred, then the later densification of the agglomerates requires more energy, which result in lower sintered density at the same sintering conditions comparing to the compacts without boehmite or with lower boehmite content. This means that the boehmite nanoparticles influence the sintering positively only within the agglomerates, which decreases the overall sinterability of the compact. Similar results were obtained in the present study and the agglomerates formation was observed in the microstructure and also the preferred densification of boehmite particles within the agglomerates were obvious in the micro structural examinations.

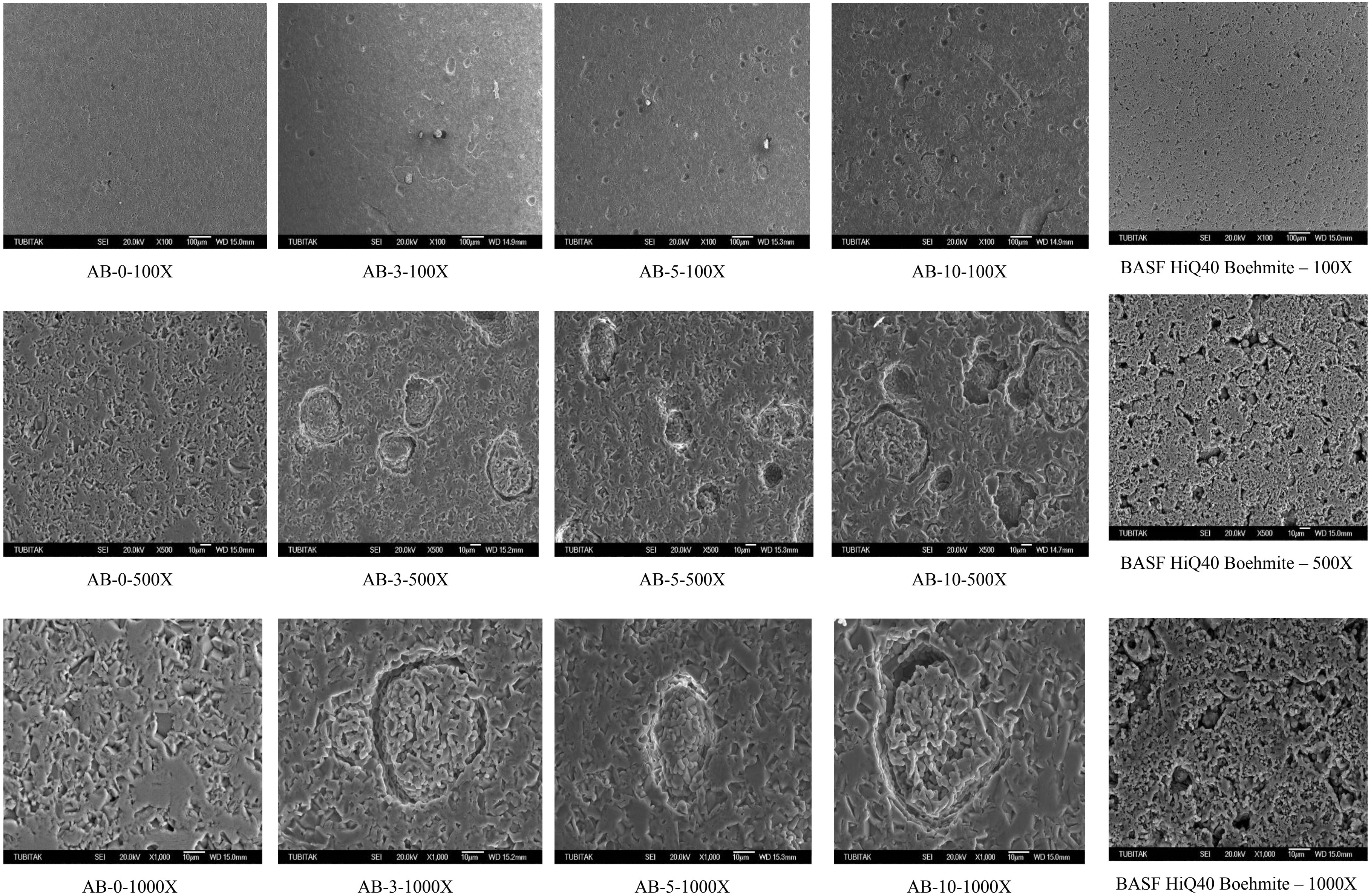


Figure 6. Samples sintered at 1650°C and thermal etched at 1400°C.

4. CONCLUSION

Nano-particle boehmite addition to the alumina ceramics resulted with the decreases in densities and in mechanical properties due to the formation of large boehmite agglomerates in the alumina ceramics. The inhomogeneous mixing of boehmite and alumina powders probably resulted from the flocculation of especially nano-particle bohmite during mixing. The sintering behaviours of the alumina matrix and boehmite agglomerates were different and due to this difference, there were large gaps around boehmite agglomerates. Also, the particle sizes of the boehmite derived agglomerates were smaller than that of alumina. This two phased structure in alumina ceramics resulted in large decreases in flexural strength after sintering at 1650ºC as 210 and 140 MPa for pure alumina and for 10 wt% boehmite added alumina respectively. As reported in the literature the addition of boehmite during the processing of alumina ceramics are beneficial especially in extrusion. Present study showed that the mixing of boehmite to alumina is important but difficult, due to the agglomeration tendencies of nano-sized boehmite powders. Also the sintering behaviors of alumina and boehmite powders are different and this caused different shrinkages. Inhomogeneous mixing of boehmite in alumina ceramics resulted in decreases in all properties of the sintered alumina compared to the alumina without boehmite addition.

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