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## High Pressure Sintering of Nano-Size $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

Nilgun Kuskonmaz

Additional information is available at the end of the chapter

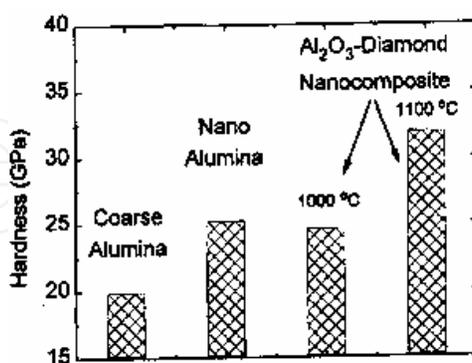
<http://dx.doi.org/10.5772/53324>

### 1. Introduction

In recent years nano crystalline materials have been paid much attention because they have a variety of interesting and novel physical properties.

Research on the sintering of nano crystalline ceramics has focused on the problem of achieving high densities (> 95% of theoretical) without excessive grain growth.

Dense and fine grained alumina ceramics are widely used in practical applications, because of mechanical, electrical and optical properties. The mechanical strength, dielectric properties and transparency are strongly affected by the microstructure of alumina ceramics such as porosity, grain size and their distribution. (Fig.1)

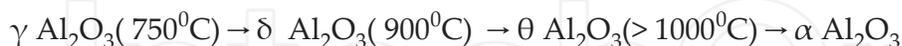


**Figure 1.** The variation of hardness in alumina-diamond nanocomposite with sintering temperature at 1GPa "in [1]"

For example, the transparency and mechanical strength of alumina were improved by decreasing the grain size, and the residual porosity less than 0.05% was required for obtaining a high transmission of light."in [2]"

Alumina ceramics with sub micrometer microstructure obtained by pressureless sintering have been widely studied.

It is difficult to obtain a fully dense ceramic with nanocrystalline grain size. Because phase transformation sequences that occur during the conventional sintering process at atmospheric (ambient ) pressure:

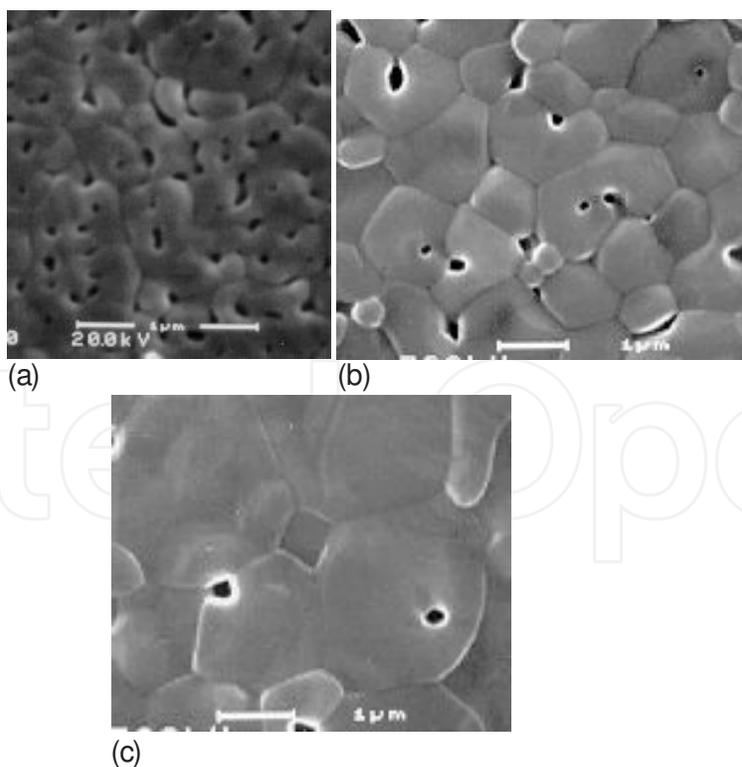


The transition paths and temperatures vary depending on the particle size, chemical homogeneity, heating rate, and water vapor pressure.

The transformation from  $\theta$  - $\text{Al}_2\text{O}_3$  to  $\alpha$  -  $\text{Al}_2\text{O}_3$  involves a change in the oxygen sublattice from cubic close packing to hexagonal close packing and generally requires temperatures above  $1100^\circ\text{C}$ .

There is 10% decrease in specific volume during transformation because the density changes from  $3.56 \text{ g/cm}^3$  ( $\theta \text{ Al}_2\text{O}_3$ ) to  $3.986 \text{ g/cm}^3$  ( $\alpha - \text{Al}_2\text{O}_3$ ).

As a result of the volume reduction and low real nucleation density ( $10^8$ - $10^{11}$  nuclei / $\text{cm}^3$ ) during the transformation, the  $\alpha$  -  $\text{Al}_2\text{O}_3$  colonies recede from the matrix and the microstructure develops into vermicular morphology containing larger scale interconnected porosity. (Fig. 2)



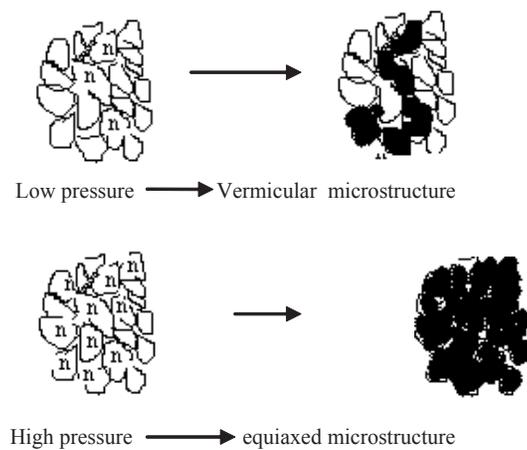
**Figure 2.** SEM images show the microstructure development of  $\alpha - \text{Al}_2\text{O}_3$  specimens pressureless sintered at (a)  $1200^\circ\text{C}$ , (b)  $1400^\circ\text{C}$ , (c)  $1500^\circ\text{C}$  for 5 h. All specimens have fully transformed to  $\alpha - \text{Al}_2\text{O}_3$  at these sintering temperatures "in [3]".

The temperature required for the densification of this vermicular microstructure is over  $1600^\circ\text{C}$ . to obtain dense, fine grained  $\alpha$ - $\text{Al}_2\text{O}_3$  at low temperatures, the scale of the vermicular microstructure must be minimized "in [4]".

Pressure-assisted densification provide to obtain nanometric grains in fully sintered compacts.

The effect of pressure on nucleation and growth of the  $\alpha$ - phase is the critical subject because the final grain size after sintering depends on these factors.

Low pressures create a smaller number of nucleation sites where the transformation begin.. These nuclei grow very fast forming vermicular clusters. The clusters stop growing when they touch on each other.



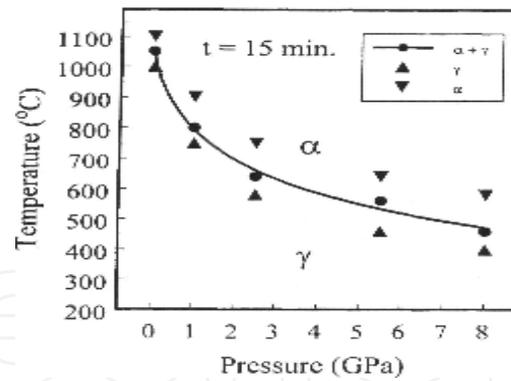
During High pressure each particle can act as an original nucleation site and transformation can occur within each particle, so that avoiding the formation of vermicular structure. In other words, high pressure can create a sufficient number of nucleation sites to prevent the formation of the vermicular structure.

Modifications in the structure, by the application of high pressure, have been investigated by several groups "in [5-7]". They have reported applying pressure decreases the thermodynamic energy barrier and kinetic energy barrier required for nucleation and causes the phase transformation to shift to a lower temperature.

Figure 3 shows that the start of transformation from  $\gamma$ - to  $\alpha$ - $\text{Al}_2\text{O}_3$  temperature decreases from about  $1075^\circ\text{C}$  at 1 atmosphere, to around  $800^\circ\text{C}$  at 1 GPa, and to  $640^\circ\text{C}$  at 2.5 GPa;  $560^\circ\text{C}$  at 5.5 GPa and to  $460^\circ\text{C}$  at 8 GPa.

Grain growth is limited by the low sintering temperature and variation of nucleation events in the  $\gamma$  phase at high pressure creates a nanoscale  $\alpha$  grain size "in [7]".

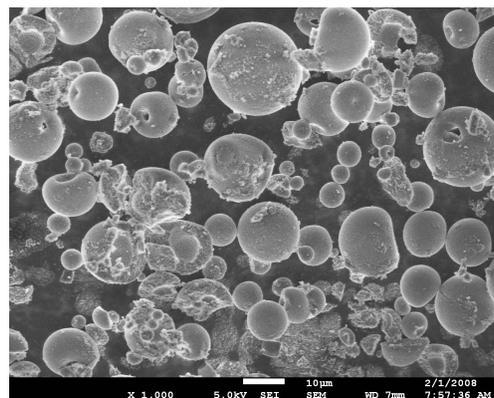
In this work the required conditions were examined to produce high- density nano-  $\text{Al}_2\text{O}_3$  ceramics using high pressure and different sintering temperatures. The effect of various sintering conditions on the properties of sintered sample such as microstructure and relative density were discussed.



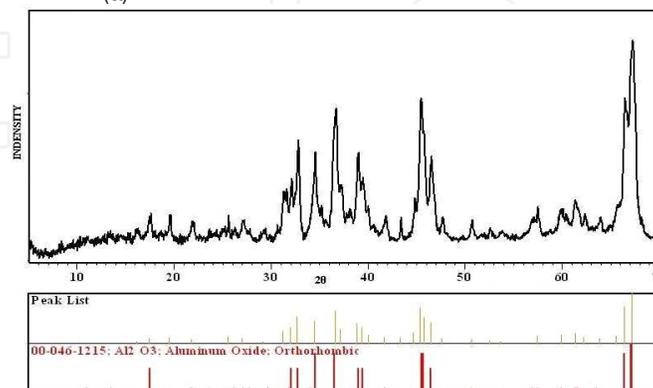
**Figure 3.** Pressure – Temperature phase diagram of  $\alpha$  and  $\gamma$  phases of  $\text{Al}_2\text{O}_3$  "in [ 7 ]".

## 2. Experimental procedure

The starting powder used consists of spherical  $\gamma$ -  $\text{Al}_2\text{O}_3$  phase with an average particle size of 20 nm (Plasma & Ceramic Technologies Ltd.-Latvia) and specific surface area of  $50 \text{ m}^2/\text{g}$  in the granulated state. ( Fig.4)



(a)



(b)

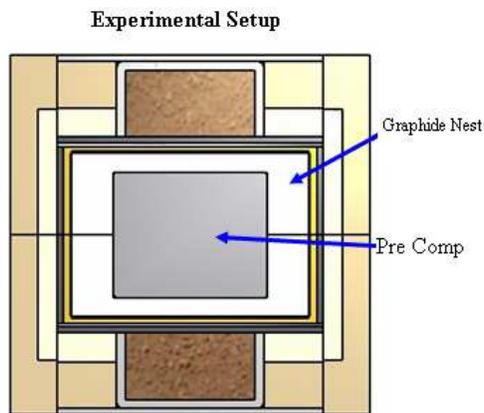
**Figure 4.** a) SEM micrograph of the starting granulated  $\gamma$ - $\text{Al}_2\text{O}_3$  powder. (b) XRD spectrum of the starting  $\gamma$ - $\text{Al}_2\text{O}_3$  powder (JSPDS Card No: 00-046-1215).

The impurity content of the initial powder was given in Table 1, in accordance with the analytical certificate supplied.

Chemical impurities: (ppm)	Fe	Si	Na
According to supplier's analytical certificate:	<1000	<200	< 1000

**Table 1.** The chemical composition of the starting  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder.

The powder was first preheated in the air at 700 °C for 3 h for the removal of the binder. After preheating, the pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder containing no additives was uniaxially cold pressed at 20 MPa into cylinders 20mm in diameter and 10mm in height. All the green compacts were pellets of 4 g. Green compact was encapsulated in a cube die made of pyrophyllite.



**Figure 5.** The sample assembly for Al<sub>2</sub>O<sub>3</sub> ceramics sintered at high pressure.

All the high-pressure sintering experiments were carried out in a cubic anvil apparatus. High mechanical pressure was applied on all six faces of the die concurrently.

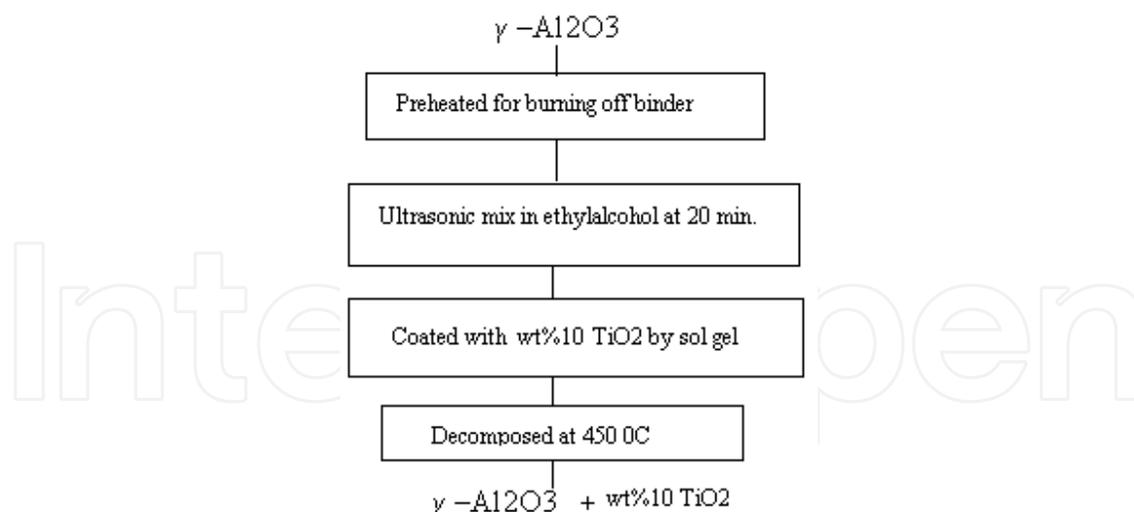
Additionally 10 wt% TiO<sub>2</sub> was added by sol-gel to inhibited the grain growth.

TiO<sub>2</sub> doped alumina were prepared by adding titanium –isopropoxide (Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) into alumina.

The TIP was hydrolyzed by addition of water. The ethanol was removed in a rotating evaporator at 65 °C and powders were dried in a furnace at 90 °C for 24 hour. After drying powder mixture was decomposed into oxide at 400 °C.

The Al<sub>2</sub>O<sub>3</sub> bodies were fabricated in cubic anvil high pressure (2- 7 GPa) and varying temperature ( 600-1200 °C) for 1- 15 minutes.

Phase analysis of the sintered samples was carried out by X-ray diffraction (XRD). Grain sizes were estimated from high-resolution scanning electron micrographs taken from fracture surfaces and micro hardness was determined on the polished surfaces using an applied load of 500 g.

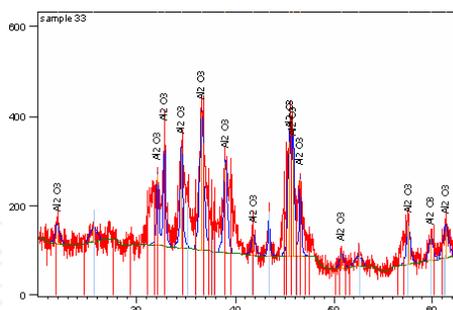


**Figure 6.** Processing flow chart for coating  $\gamma$ - $\text{Al}_2\text{O}_3$  particle with 10 wt % $\text{TiO}_2$  by sol-gel.

### 3. Results and discussion

#### 3.1. X-ray diffraction profile of sintered samples

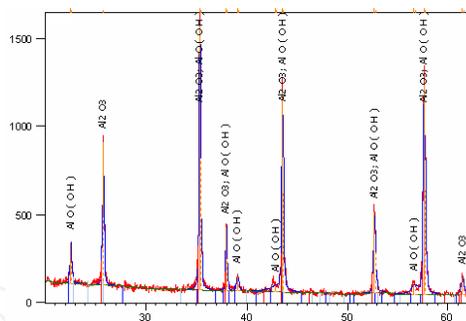
Fig.7-8-9 clearly shows the significant effect of applied pressure time on phase content with the exception of the sample sintered at 5GPa and 500°C for only 5 min.(Fig a). All the sintered samples showed the presence of the  $\alpha$  phase, with no evidence of any remaining  $\gamma$  phase. Because of pressure decreases the transformation temperature of  $\gamma$  to  $\alpha$  phase of  $\text{Al}_2\text{O}_3$



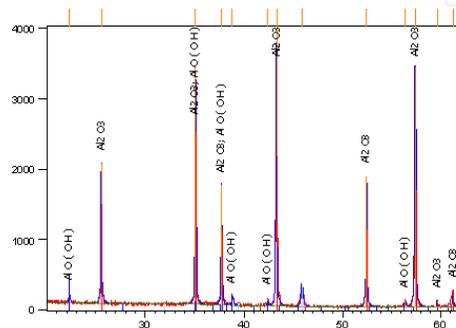
**Figure 7.** XRD patterns of  $\text{Al}_2\text{O}_3$  sintered at 5GPa and 500 °C for 5 min.

Fig. 7-8 also shows that under the same applied pressure (5 GPa) and temperature (500 °C), the sintering time have a significant effect on the phase content, as the sintering time of 5 min. is not adequate for phase transformation from gamma to alpha alumina although both samples are translucent.

An alumina hydrate,  $\text{AlO}(\text{OH})$ , phase ( Fig. 8-9) was found in the samples sintered at 5 and 7 GPa and 500 °C. This phase is caused by trapped water or surface OH groups which forms the hydrate phase during low temperature sintering.



**Figure 8.** XRD patterns of  $\text{Al}_2\text{O}_3$  sintered at 5 GPa and 500 °C for 15 min.



**Figure 9.** XRD patterns of  $\text{Al}_2\text{O}_3$  sintered at 7 GPa and 500 °C for 15 min.

### 3.2. Effect of temperature on the microstructure and density at 5 GPa

As can be seen in Fig 10, the morphology of the sintered samples at high temperatures were different from those sintered at lower temperatures.

The grain size of sintered sample increases with increasing sintering temperature and the grain size distribution was fairly wide at especially high sintering temperature.

Samples sintered at a low sintering temperature (500 °C-700 °C) showed fine (about 200 nm) equiaxed grains under 5 GPa pressures as shown in Fig. 10 ( a ), ( b ).

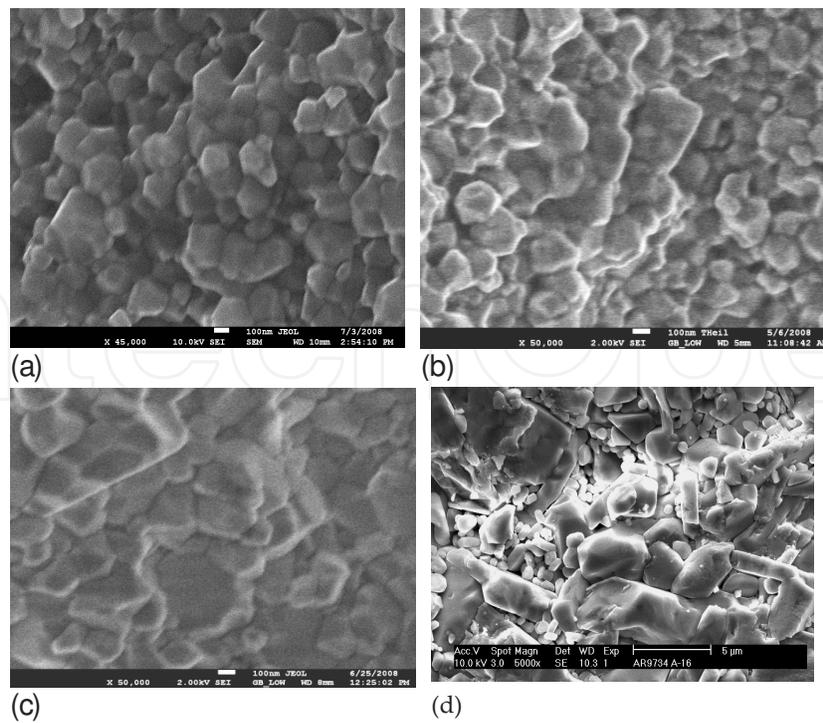
Grain Growth was started at 900 °C and abnormal grain growth was observed at the higher sintering temperature (1200 °C) as shown in Fig. 10 ( c ), ( d ).

Previous experimental results indicate that abnormal grain growth in commercially pure alumina is strongly correlated with presence of impurities. The minimum concentration for AGG over 300 ppm silicon or 30 ppm calcium. “in [8]”

This impurities are believed to form glassy films in the grain boundaries and somehow to catalyze AGG.

The sintered density generally increases with the sintering temperature for all samples.

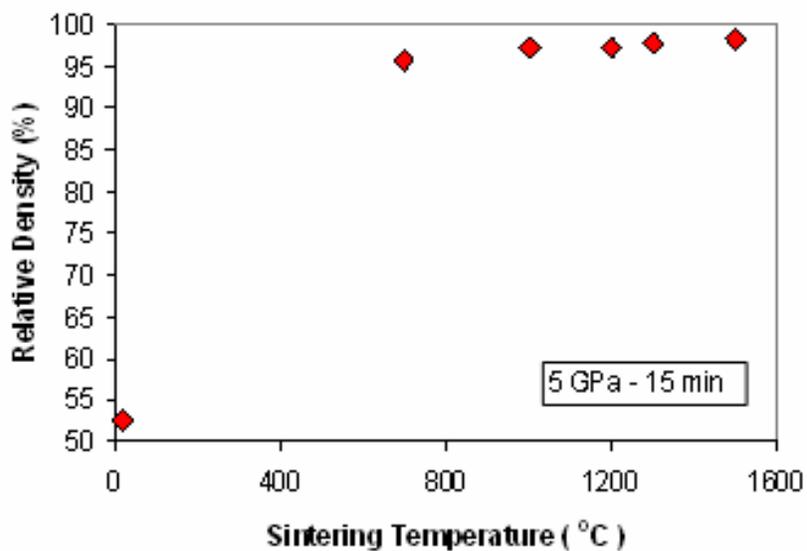
From Figure 11, it is noted that the relative density first increased rapidly, than climbed slowly from 1000 to 1500 °C.



**Figure 10.** The fracture surfaces of  $\text{Al}_2\text{O}_3$  samples sintered at different temperature ( a ) 500 °C - ( b ) 700 °C – ( c ) 900 °C - ( d ) 1200 °C at 5 GPa for 15 min. sintering time.

At 1500 °C. the relative density of sintered sample is reached a highest value of 98.1% when the pressure is 5GPa.

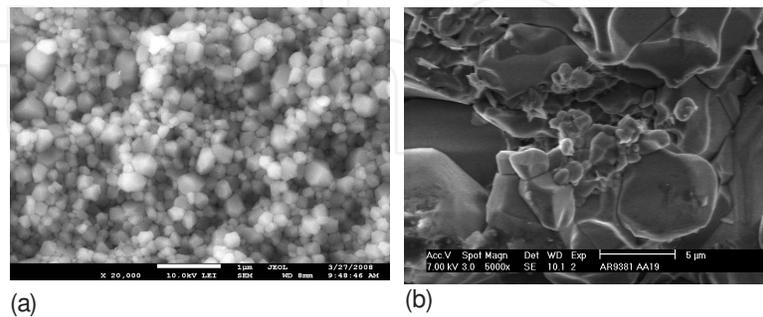
Due to significant grain growth, no complete densification could be reached with initial  $\gamma$ - $\text{Al}_2\text{O}_3$  powder



**Figure 11.** Relative density of sintered sample at 5 GPa as a function of sintering temperature.

### 3.3. Effect of pressure on the grain size of sintered samples

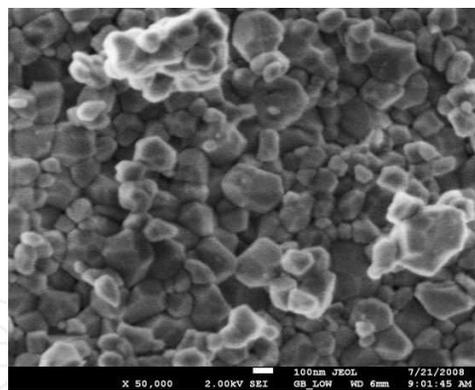
The microstructure of sintered samples obtained from  $\gamma$ - $\text{Al}_2\text{O}_3$  powders at 1000 °C and 5-7 GPa for 15 minute were examined. Representative SEM's of fracture surfaces are shown in figure 12.



**Figure 12.** SEM micrograph of fracture surface for samples sintered at 1000 °C and (a) 5 GPa, (b) 7GPa for 15 minutes.

As shown in Fig. 12 the overall grain size for the sample sintered at 1000 °C at 7GPa appeared coarser than the sample sintered at the lower pressures (5 GPa) ( for the same sintering temperature and time of 15 minutes).

Fig. 13 shows the SEM micrographs of the sample sintered at 1000 °C and 7 GPa for a shorter time (1 minute).



**Figure 13.** SEM micrograph of fracture surface for samples sintered at 1000 °C and 7GPa for 1 minute.

As shown in Fig. 13 the microstructure of the  $\text{Al}_2\text{O}_3$  ceramics sintered at high pressure (7GPa) and high temperature (1000 °C) for 1 minute is obviously different from the ceramic microstructure sintered at the same pressure and temperature for 15 minutes (see in Fig. 12 (b)).

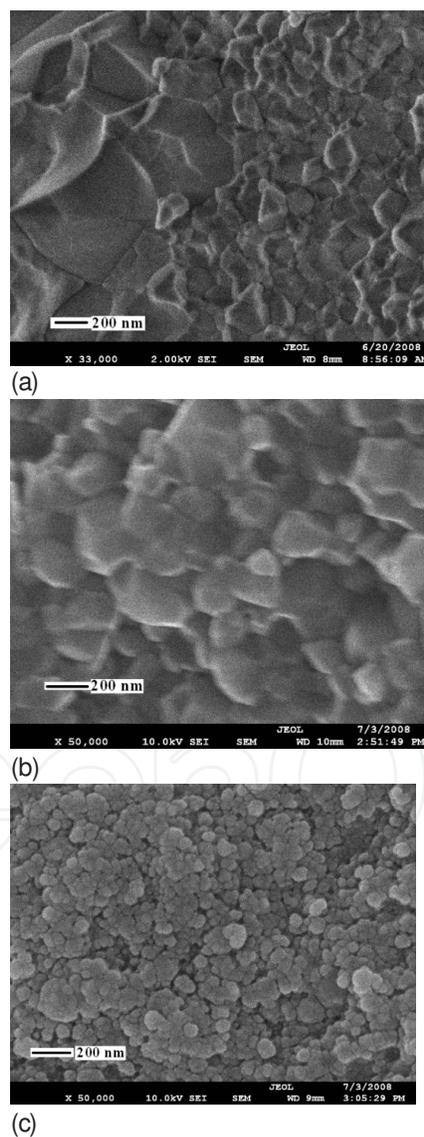
While Fig.13 contains much smaller fine grains, coarser grains are visible on the microstructure shown in Fig.12 ( b), showing the considerable effect of sintering time on the sintered grain size.

This could be attributed to the higher input energy in the system at high pressure and high temperature conditions, thus the final stage in sintering was reached quickly as was the grain

growth regime. Thus for high pressure high temperature conditions, either the sintering time or the temperature should be reduced to prevent grain growth.

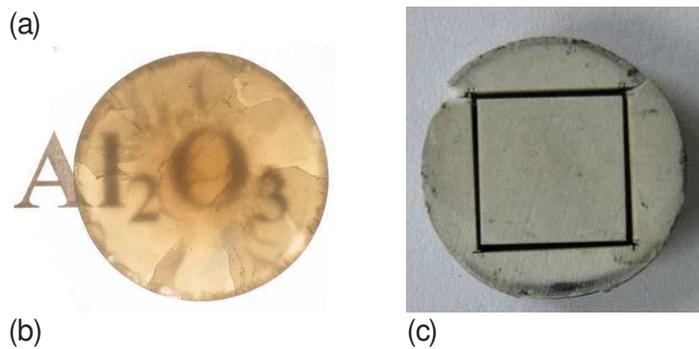
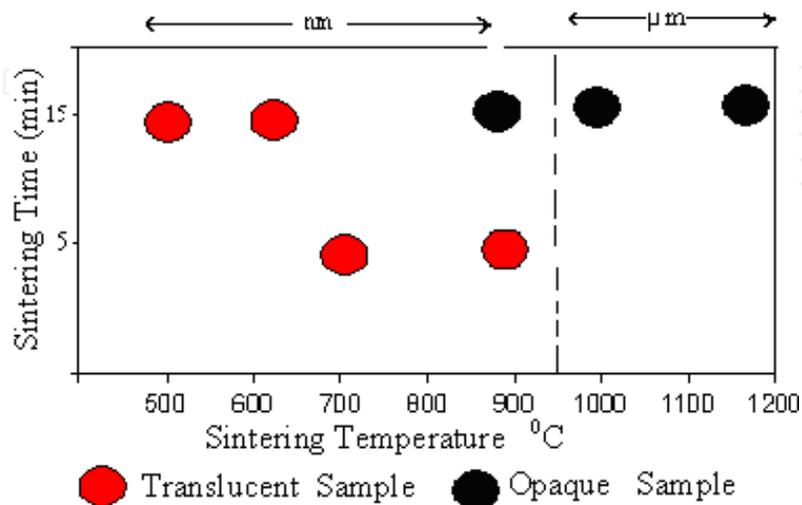
The effect of the sintering time on the microstructure can also be seen from the pictures shown in Fig.14. Sintering  $\gamma$ - $\text{Al}_2\text{O}_3$  at 900 °C at 7GPa for 15 min. resulted in obtaining the opaque sample while a translucent sample was obtained with a sintering time of 5 min. as shown in Figs.14 (a and b, respectively).

The opaque structure is considered as a result of abnormal grain growth of alumina, as shown in Fig.14 (a). But when the sintering temperature is lowered to 500 °C, a translucent alumina with the finest grain size and the gamma form is evident using a sintering time of 5 min. as shown in Fig.14 (c).



**Figure 14.** The fracture surfaces of  $\text{Al}_2\text{O}_3$  samples sintered at 900 °C at 7 GPa for sintering time 15 min. (a), 5 min. (b) and 5GPa (c) at 500 °C for sintering time of 5 min.

Fig.15 clearly indicates the relationships between the translucency of alumina, temperature and sintering time. For example, a translucent alumina can be achieved either using a high sintering temperature of 900 °C for 5 min. or low sintering temperature of 500 °C for 15 min., as shown in Fig.15(a)



**Figure 15.** a) The effect of sintering temperature on the optical appearance of sintered sample at 7GPa (b) the optical micrograph of the translucent alumina sample sintered at 7 GPa, at 900 °C for 5 min. that was mechanically thinned to a 1mm in thicknes using lapping technique. (c) opaque alumina sample (at 7 GPa, 900 °C for 15 min.) after laser cut for characterization.

### 3.4. Influnce of $\text{TiO}_2$ additives on alumina microstructure

As you can see Fig. 16 The secondary phase precipitates mostly at along the grain boundaries (white phase)..The existence of this secondary phase reduces the driving force for grain growth by pinning effect.

It can be shown that  $\text{TiO}_2$  additive leads to finer grain size after pressure assisted sintered at low and high temperature for same sintering pressure and time. ( Fig 17 -18)

From figure 17 – 18 it is obvious that average grain size of  $\text{TiO}_2$  doped sample is finer than that of undoped alumina sintered at the same temperature and pressure for same holding time.

However  $\text{TiO}_2$  addition did not has significant effect on the density of sintered samples

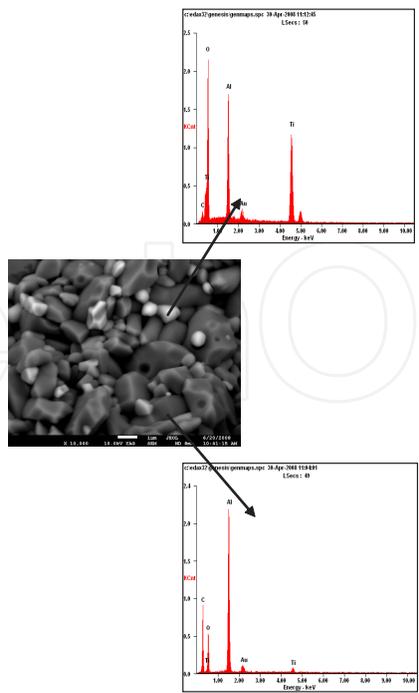


Figure 16. Typical microstructures and EDS spectrum of TiO<sub>2</sub> doped Al<sub>2</sub>O<sub>3</sub> sintered sample.

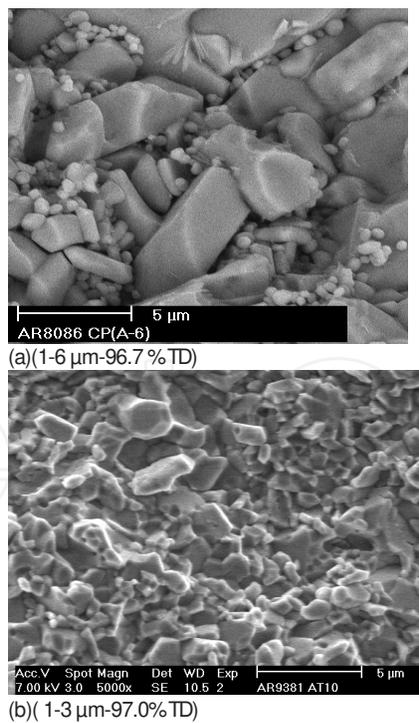
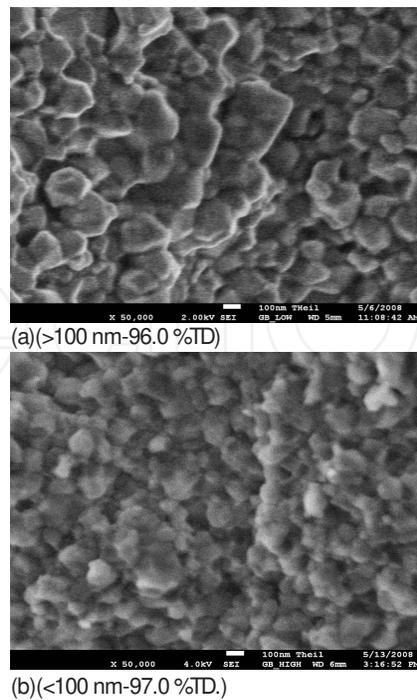


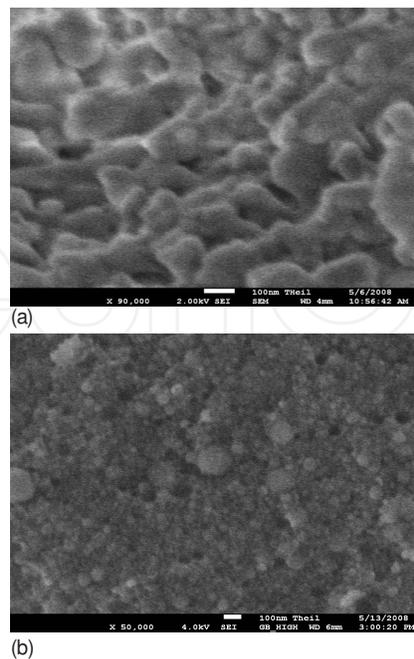
Figure 17. SEM micrographs of Al<sub>2</sub>O<sub>3</sub> (a) and Al<sub>2</sub>O<sub>3</sub> + 10 wt% TiO<sub>2</sub> (b) sintered at 5GPa and 1200 °C for 15 min.

Figure 17 shows that Abnormal Grain Growth did not occur at 1200 °C in using 10 wt% TiO<sub>2</sub> additive



**Figure 18.** SEM micrographs of  $\text{Al}_2\text{O}_3$  ( a ) and  $\text{Al}_2\text{O}_3 + 10 \text{ wt } \% \text{ TiO}_2$  ( b ) sintered at 5GPa and 700 °C for 15 min.

Although Translucent Alumina is obtained with the alumina sample at 6GPa and 600 °C for 15 min ( Fig 19 ( a ) ). it is not possible to obtained translucent alumina with the alumina containing 10 wt%  $\text{TiO}_2$  sample at same sintering conditions (Fig 19 ( b ) )



**Figure 19.** Fracture surfaces of  $\text{Al}_2\text{O}_3$  ( a ) and  $\text{Al}_2\text{O}_3 10 \text{ wt } \% \text{ TiO}_2$  ( b ) samples sintered at 600 °C and 6 GPa for 15 min

### 3.5. Effect of pressure and sintering time on the hardness of sintered samples

Sintering time has a strong effect on the grain size and hence the hardness. For example, a sample sintered at 1000 °C (at 7 GPa) for 15 min. shows a hardness value of 8.30 GPa while a sample sintered at the same temperature for 1 min. provides a hardness value of 11.46 GPa.

The increment in hardness depending on the decrease in sintering time can be correlated with the grain size as shown by the SEM micrographs in Figs.12 b and 13. As shown in Fig. 12b, the sample sintered at 1000 °C for 15 min. (the applied pressure is at 7 GPa )contains much bigger alumina grains (the main grain size is about 5 microns) compared with sample in Fig.13 that was sintered at the same temperature and pressure for 1 min (the main grain size is about 200 nm).

Using applied pressures of 7 GPa and 5 GPa and lower sintering temperature of 600 °C, translucent  $\alpha$ -alumina could be obtained with the hardness value of 13.89 and 13.35 GPa, respectively.

The highest hardness value of 20.31 GPa is achieved for the TiO<sub>2</sub> doped sample sintered at 700 °C for 15 min (the applied pressure is at 5 GPa) due to presence of very fine alumina grains with the main grain size of < 100 nm, as shown in Fig.18 b.

## 4. Conclusions

In the present work, the sintering behavior of a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder subjected to different pressure, temperature and time conditions is examined.

Applying pressure drops  $\gamma$ -  $\alpha$  Al<sub>2</sub>O<sub>3</sub> transformation temperature and increase nucleation rate making it possible to obtain nano grain size sintered sample.

It was also found that, when using nano-size starting powder, the sintering time should be optimised in order to control the final sintered grain size under the same sintering temperature and applied pressure.

Chemical impurity in initial powder is very important to reduce grain growth during sintering.

To produce lower than 100 nm sintered sample it is very important to eliminate the hydrates & impurities before sintering.

TiO<sub>2</sub> additive in initial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> leads to finer grain size after pressure assisted sintered

Using applied pressures of 5-7 GPa and lower sintering temperature of 500- 600 °C, translucent  $\alpha$ -alumina could be obtained

Translucency can be controlled by increasing the applied pressure from 5 GPa to 7 GPa for a sample sintered at 700 °C for 15 min. or decreasing the sintering temperature and time. As the sintering pressure is decreased, the sintering temperature also needs to be decreased in order to obtain translucent samples.

The hardness of the sintered 10 wt % TiO<sub>2</sub> doped Al<sub>2</sub>O<sub>3</sub> nanocomposites were higher than undoped Al<sub>2</sub>O<sub>3</sub> at same sintering conditions.

The highest hardness value of 20.31 GPa is achieved for the TiO<sub>2</sub> doped sample sintered at 700 °C for 15 min. (the applied pressure is at 5 GPa)

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## Author details

Nilgun Kuskonmaz

Yildiz Technical University, Metallurgy and Materials Engineering, Davutpasa Campus, Esenler, Istanbul, Turkey

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