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Sintering behaviour of nano-crystalline γ-Al_2O_3 powder without additives at 2–7 GPa

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Abstract

Al_2O_3 ceramics were fabricated without additives under high pressure (2–7 GPa) at different temperatures (600–1200 °C) using nanocrystalline alumina powder with metastable γ-Al_2O_3 phase as the starting material.

It was shown that high pressure increases the nucleation rate while reducing the growth rate of the transformed α phase so that its grain size decreases and nano-scale grains in the sintered structure can be achieved.

On the other hand the sintered samples at 7 GPa and high temperature (1000 °C) have shown micron-scale large grain sizes compared to those sintered at lower pressures, for the same temperature and sintering time. This could be attributed to the higher input energy in the system at high pressure and high temperature conditions, thereby reaching the final stage in sintering more quickly.

In this work, the best combination of grain size (∼200 nm) and density (98.0% TD) was obtained under the sintering condition of 1000 °C at 7 GPa with a holding time of 1 min.

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

Keywords: A. Sintering; B. Grain Size; Al_2O_3

1. Introduction

Nanopowders i.e., powders with particle size below 100 nm, have received growing interest, because of their potential benefits by reducing sintering temperatures and by improving the fracture strength, toughness and hardness of sintered monolithic compacts.

However, to take full advantage of improved properties consolidation of nanopowders into fully dense engineering parts is required. If this can be achieved without losing the nanosize structure, there is a potential to use the materials for structural, magnetic, electric or electronic applications.

It is difficult to obtain a fully dense ceramic with nanocrystalline grain size. Pressure-assisted densification offers a route to obtain nanometric grains in fully sintered compacts [1].

Modifications in the structure, by the application of high pressure, have been investigated by several groups [2–5]. 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. Grain growth is limited by the low sintering temperature and multiplicity of nucleation events in the γ-phase at high pressure creates a nanoscale α grain size [7].

Mishra et al. [6] have reported sintering of nanocrystalline γ-Al_2O_3 in the temperature range 650–1100 °C under 1 GPa pressure. The γ–α transformation temperature was reduced from 1200 °C at 1 atm to about 750 °C at 1 GPa. Fully dense alumina with a hardness value of 25.3 GPa and grain size of about 142 nm were obtained at 1000 °C and 1 GPa in 10 min.

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In this work the required conditions were examined to produce high-density nano-Al_2O_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.

2. Experimental procedure

Commercially available nano-size γ-Al_2O_3 starting powder (Aluminum Oxide Grade F, from Plasma & Ceramic Technologies Ltd. – Latvia) with an average diameter of 20 nm and specific surface area of 50 m^2/g was used in granulated form.

The powder was first preheated in the air at 700 °C for 3 h. After preheating, the pure Al_2O_3 powder without additives was uniaxially cold pressed (20 MPa) into cylinders (20 mm in diameter and 10 mm in height). The green density of compacts was approximately 53% of the theoretical density. All the green compacts were pellets of 4 g. Green compact was encapsulated in a cube die made of pyrophyllite.

The Al_2O_3 bodies were fabricated in cubic anvil high pressure (2–7 GPa) and varying temperature (600–1200 °C) for 1–15 min. High mechanical pressure was applied on all six faces of the die concurrently. The cubic type anvil can generate pressures more uniform in the pressure cell than that of the uniaxial pressure. The sample was pressurized first and after 3 s temperature was raised by passing current through the graphite heater for 900 s. After 15 min temperature was decreased to a lower temperature and hold for 2 min at this temperature (by this way, the effects of thermal stresses were minimised). Finally the heater was turned off and the load was removed at the same time.

The sintering time was also decreased from 15 min to 1 min in order to evaluate the effect of sintering time on microstructure and grain growth.

Bulk densities of the sintered samples were measured using Archimedes method with deionized water as the immersion medium. Grain sizes were estimated from high-resolution scanning electron micrographs taken from fracture surfaces. Phase analysis of the sintered samples was carried out by X-ray diffraction (XRD) and micro-hardness was determined on the polished surfaces using an applied load of 500 g.

3. Results and discussion

The optical micrographs of the opaque and translucent samples produced are shown in Fig. 1(a) and (b). Fig. 1(a) shows the translucent alumina sample (sintered at 7 GPa, 600 °C for 15 min) that was mechanically thinned to a 1 mm in thickness using lapping technique. Fig. 1(b) shows the sintered opaque alumina (at 7 GPa, 900 °C for 15 min) sample after laser cut for characterization.

The starting powder was found to consist of γ-Al_2O_3 phase as determined by X-ray diffraction (XRD) as shown in Fig. 2. The powder was also shown to consist of spherical granulated particles with an average diameter of about 20 μm as shown in Fig. 3. It can be seen from Fig. 3 that the size of the granulates

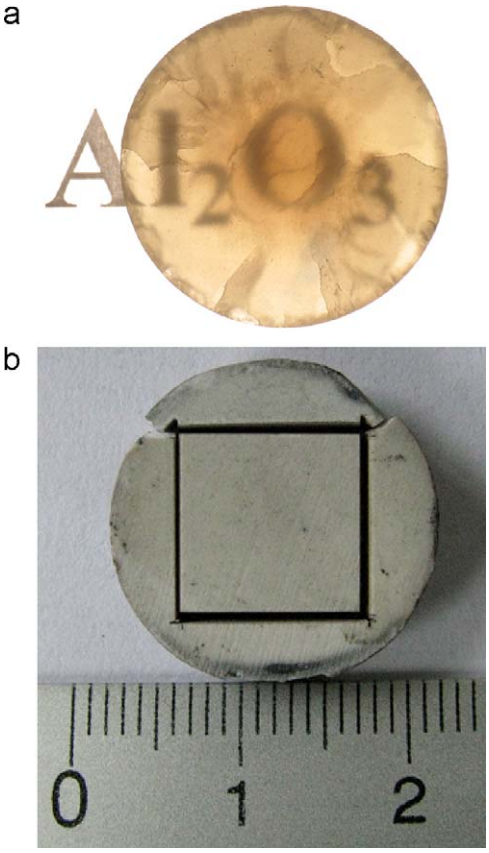

Fig. 1. The optical micrographs of the opaque and translucent sintered samples. (a) Translucent alumina sample (sintered at 7 GPa, 600 °C for 15 min) that was mechanically thinned to a 1 mm in thickness using lapping technique. (b) Opaque alumina sample (at 7 GPa, 900 °C for 15 min) after laser cut for characterization.

of this powder is very wide which is considered to be beneficial to obtain better compaction resulting in higher densities.

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

Some typical XRD traces for the samples sintered at 600 °C at different pressures are shown in Fig. 4. As shown Fig. 4(b) and (c), at 5 and 7 GPa respectively, traces show only α-Al_2O_3 phase while at 2 GPa (Fig. 4 (a)), the traces indicate the presence of γ-Al_2O_3 phase.

An alumina hydrate, AlO(OH), phase (denoted D in Fig. 4) was found in the samples sintered at 5 GPa and 600 °C. This phase is caused by trapped water or surface OH groups which forms the hydrate phase during low temperature sintering. In the presence of hydrates, grain growth control of the transformed α-phase even at a pressure as high as 5 GPa and temperature as low as 600 °C, is difficult.

Figs. 5–7 show the effects of pressure on the microstructure of alumina for sintering temperatures of 600, 1000 and 1200 °C, respectively for a constant sintering time of 15 min. On the other hand, Fig. 8 shows the SEM micrograph of the sample sintered at 7 GPa, 1000 °C for 1 min.

The experimental conditions and some properties obtained for the sintered samples are given in Table 2. The sintering temperature was varied from 600 °C to 1200 °C to determine the effect of temperature on densification and grain growth.

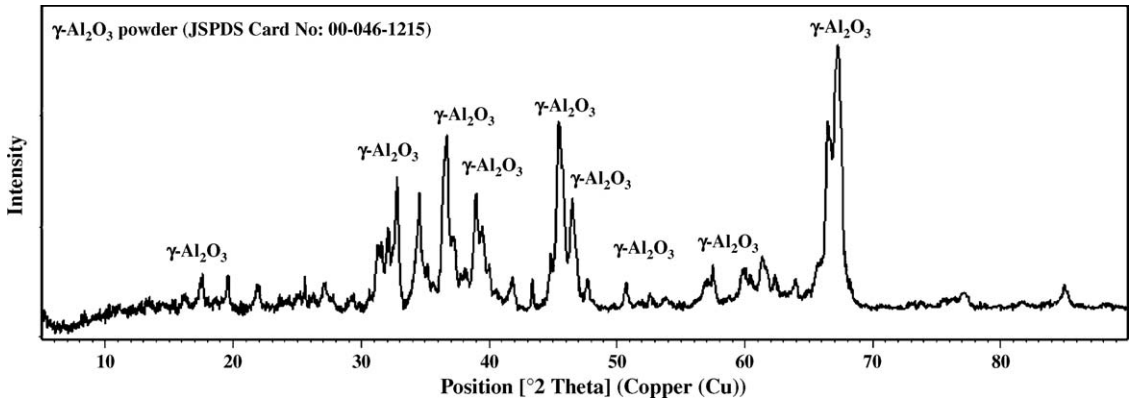

Fig. 2. XRD spectrum of the starting γ-Al_2O_3 powder (JSPDS Card No: 00-046-1215).

When low sintering temperature was used (600 °C) the benefits of higher pressures in achieving higher % theoretical density (TD) are clearly observed as shown in Table 2. For example, the sample sintered at 2 GPa and 600 °C (for 15 min) achieved a TD of just over 88.9%, whereas a TD of >96% was obtained at the same temperature when a higher pressure of 5–7 GPa was applied for the same holding time (as shown in Table 2). In the case of a low sintering pressure of 2 GPa, a high theoretical density could not be achieved even when the temperature was increased to 1200 °C (only 96% TD was achieved for the same holding time—as shown in Table 2).

Anomalous behaviour was observed for the 5 GPa and the 7 GPa samples, and a dip in the TD results in the 1000–1200 °C regime was observed. For example the sample sintered at 1200 °C and 7 GPa (for 15 min) showed a TD (%) of 96.2. However, if the sintering time is reduced to 1 min at 1000 °C (7 GPa), a high TD (%) of 98.0 can be achieved due to control of the grain growth.

Based on the results obtained, the best combination of grain size and density was obtained at 1000 °C and 7 GPa for 1 min as shown in Table 2.

It should be noted that the samples obtained at low temperature (600 °C) and low pressure (2 GPa) showed cracks in the surface, as well as in the bulk as shown in Table 2. This is caused by the low overall densities of these samples.

As can be seen in Figs. 5 and 6, the morphology of the sintered samples at high temperatures was different from those sintered at lower temperatures.

Samples sintered at a low sintering temperature (600 °C) showed fine (about 200 nm) equiaxed grains under all applied pressures as shown in Fig. 5. Abnormal grain growth was however observed at the higher sintering temperature (1000 °C) under all applied pressures as shown in Fig. 6.

The observed microstructures for sintering at 1000 °C, which consists of a mixture of coarse and fine grains was indicative of energy been consumed in the growth of some grains as illustrated in Fig. 6(a), while sintering had not taken place amongst the finer grains. Increasing the sintering temperature (1200 °C) for the 2 GPa samples resulted in more energy input into the system and therefore accompanied by

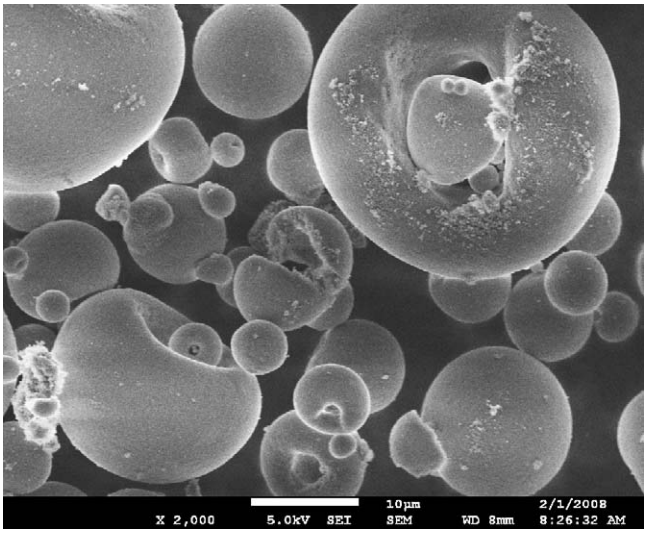

Fig. 3. SEM micrograph of the starting granulated γ-Al_2O_3 powder.

Table 1
The chemical composition of the starting γ-Al_2O_3 powder.

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

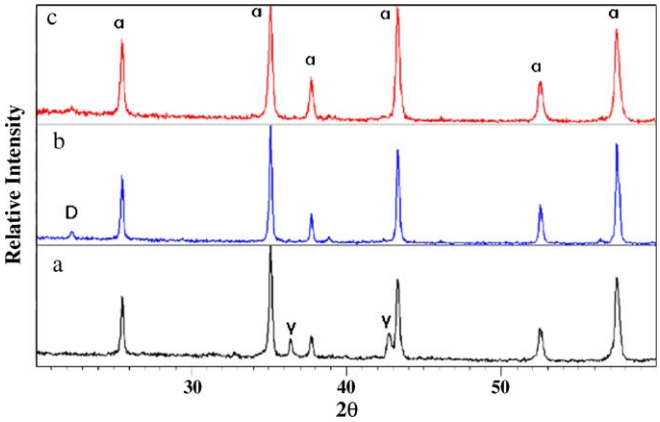

Fig. 4. XRD patterns of Al_2O_3 sintered at 600 °C (a) 2 GPa, (b) 5 GPa, (c) 7 GPa. (D: AlO(OH), α: α-Al_2O_3, γ: γ-Al_2O_3).

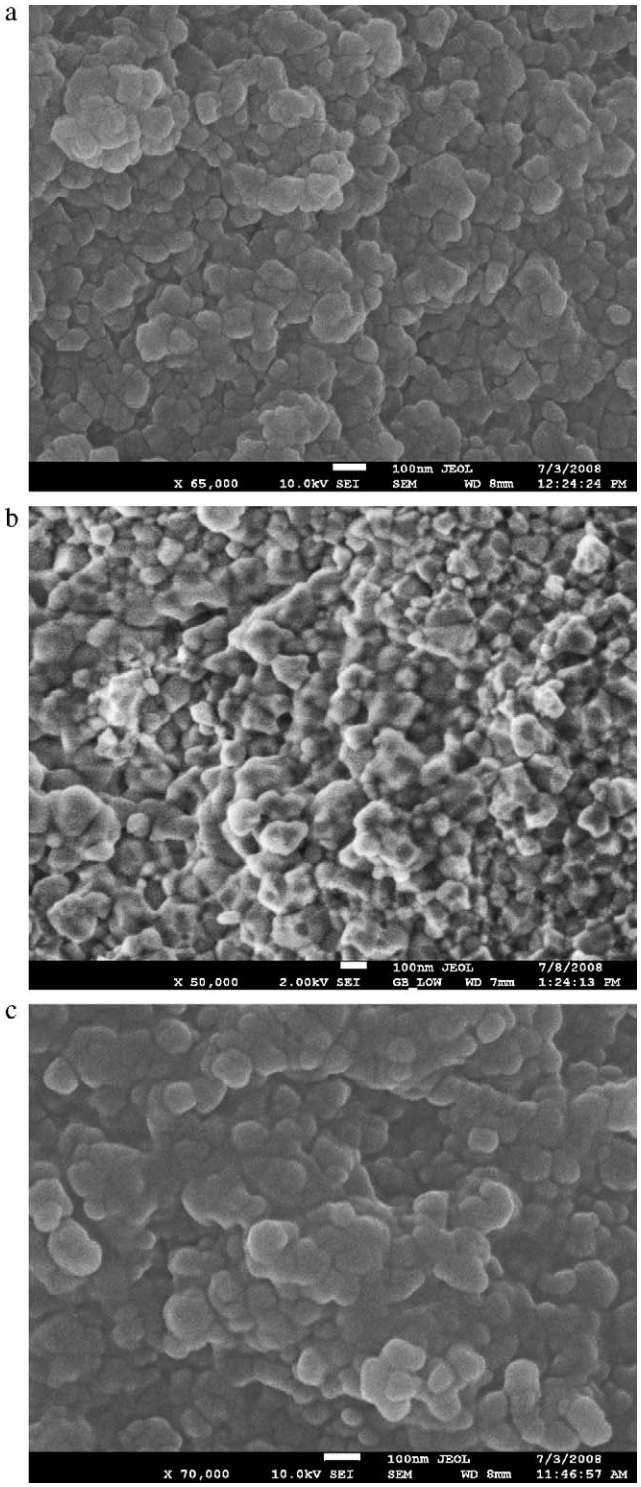

Fig. 5. The fracture surfaces of Al_2O_3 samples sintered at 600 °C and (a) 2 GPa, (b) 5 GPa, (c) 7 GPa for 15 min.

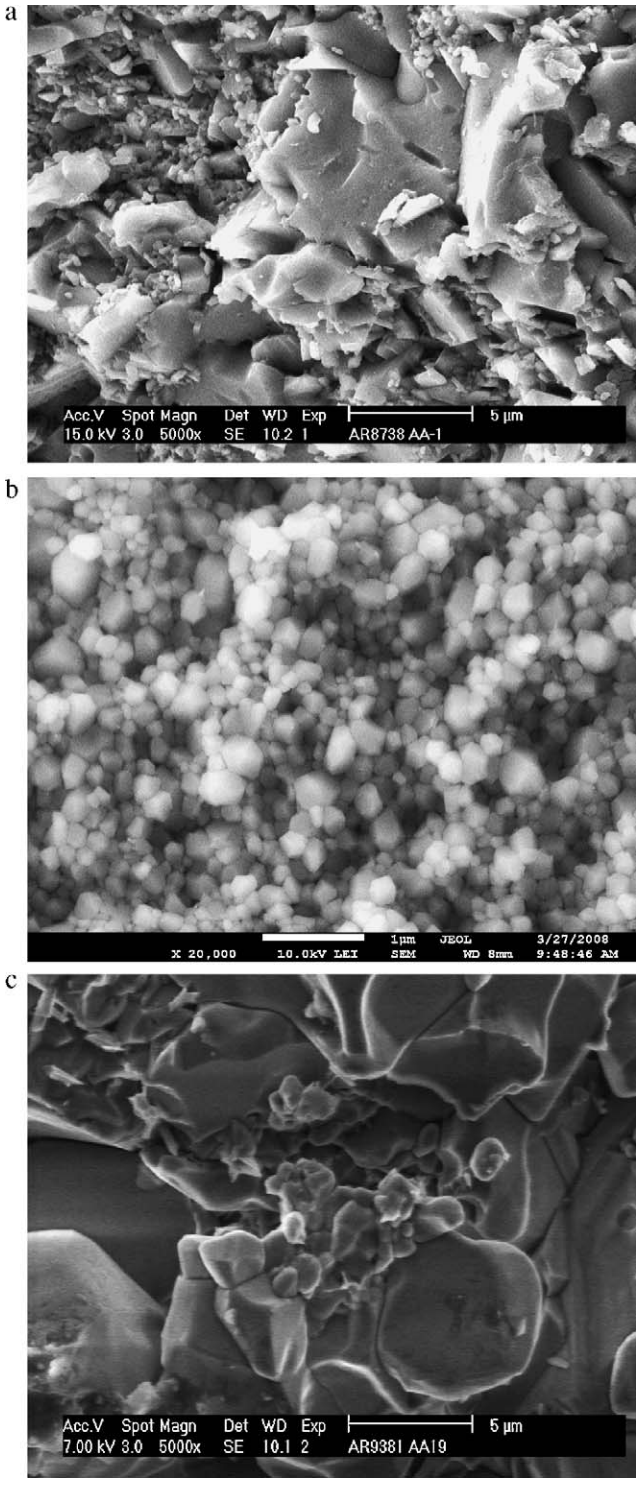

Fig. 6. The fracture surfaces of Al_2O_3 samples sintered at 1000 °C and (a) 2 GPa, (b) 5 GPa, (c) 7 GPa for 15 min.

grain growth of the fine grains were observed as shown in Fig. 7(a).

It has been shown, in Table 2, that using an applied pressure of 2 GPa, transformation to the α-phase occurred at low temperatures as low as 600 °C. Low transformation temperature results in equiaxed grain (see Fig. 5(a)) morphology and the newly precipitated grains will initially have a fine grain size in the nano-meter range. The grain morphology, however, changes with increasing sintering temperature accompanied by grain growth (see Figs. 6–7(a)). Based on the results obtained in the present work the ideal processing temperature is just above the transformation temperature. (For 2 GPa applied pressure, the sintering temperature could be around 600 °C.)

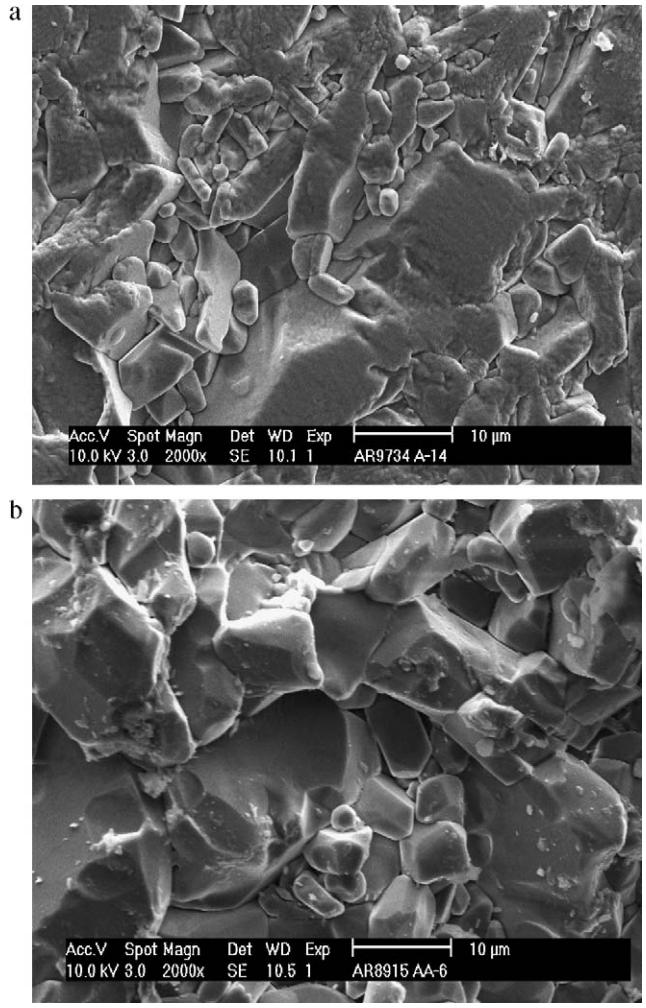

Fig. 7. SEM micrographs of the fracture surfaces for samples sintered at 1200 °C for 15 min. (a) 2 GPa, (b) 7 GPa.

As shown in Fig. 7 the overall grain size for the sample sintered at 1200 °C at 7 GPa appeared coarser than the sample sintered at the lower pressures (2 GPa) (for the same sintering temperature and time of 15 min). This finding is in a good agreement with Lioa et al. [7] who suggested that the higher green density of samples sintered at high pressures (8 GPa) promoted grain growth during sintering, because of the much reduced porosity (i.e., more intimate contacts among particles).

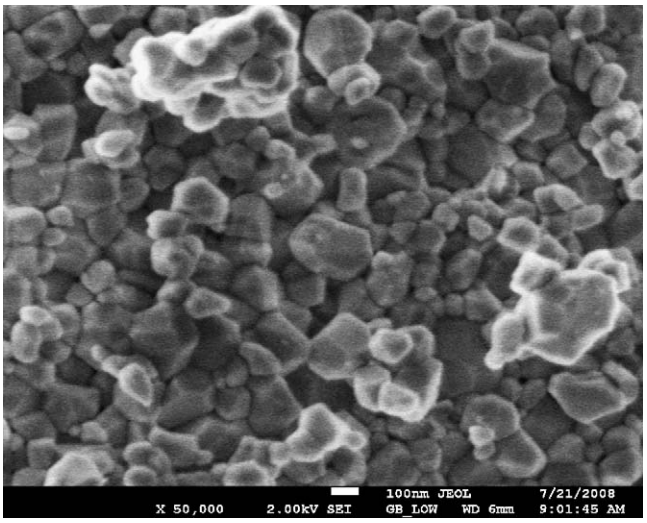

Fig. 8. SEM micrograph of fracture surface for samples sintered at 1000 °C and 7 GPa for 1 min.

Fig. 8 shows the SEM micrographs of the sample sintered at 1000 °C and 7 GPa for a shorter time (1 min). As shown in Fig. 8 the microstructure of the Al_2O_3 ceramics sintered at high pressure (7 GPa) and high temperature (1000 °C) for 1 min is obviously different from the ceramic microstructure sintered at the same pressure and temperature for 15 min (see in Fig. 6(c)). While Fig. 8 contains much smaller fine grains, coarser grains are visible on the microstructure shown in Fig. 6(c), 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.

Table 2
Summary of experimental conditions and some properties of the sintered samples.

Sintering conditions Pressure(GPa)/Temp.(°C)/time(min)	Physical appearance	Phases present	Relative density (%TD)	Micro-hardness (GPa)
2/600/15	Cracked – Opaque	α–γ	88.9	–
2/900/15	Good – Opaque	α	96.7	11.17
2/1000/15	Good – Opaque	α	97.5	–
2/1200/15	Good – Opaque	α	96.0	8.32
5/600/15	Cracked – Translucent	α–D	97.2	13.35
5/900/15	Good – Opaque	α	98.0	11.97
5/1000/15	Good – Opaque	α	97.2	8.55
5/1200/15	Good – Opaque	α	97.2	–
7-600-15	Good – Translucent	α	96.7	13.89
7-900-15	Good – Opaque	α	97.2	–
7-1000-15	Good – Opaque	α	96.7	8.30
7-1000-1	Good – Opaque	α	98.0	11.46
7/1200/15	Good – Opaque	α	96.2	–

Good: No cracks, α: α-Al_2O_3, γ: γ-Al_2O_3, D: AlO(OH).

As shown in Table 2, with the exception of the sample sintered at 2 GPa and 600 °C for 15 min all the sintered samples showed the presence of the α phase, with no evidence of any remaining γ phase.

Table 2 also shows that the highest hardness value of 13.89 GPa is achieved for the translucent sample sintered at 600 °C for 15 min (the applied pressure is at 7 GPa) due to presence of very fine alumina grains with the main grain size of 100 nm, as shown in Fig. 5(c).

As shown in Table 2, sintering time has a strong effect on the grain size and 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, as shown in Table 2. 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. 6(c) and 8. As shown in Fig. 6(c), the sample sintered at 1000 °C for 15 min contains much bigger alumina grains (the main grain size is about 5 μm) compared with sample in Fig. 8 that was sintered at the same temperature and pressure for 1 min (the main grain size is about 200 nm).

4. Conclusions

In the present work, the sintering behaviour of a γ-Al_2O_3 powder subjected to different pressure, temperature and time conditions is examined.

The samples obtained at low pressure (as low as 2 GPa) and low temperature (600 °C) showed cracks because of the low densities attained.

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. From the results presented here, it was shown that fine grain structure is achievable using a sintering temperature of 1000 °C under on applied pressure of 7 GPa for 1 min holding time resulting in a hardness value of 11.46 GPa. It was demonstrated that if the sintering time is increased from 1 min to 15 min, abnormal grain growth takes place during sintering.

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

Acknowledgments

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References

[1] Y.-F. Hsu, S.-F. Wang, Y.-R. Wang, S.-C. Chen, Effect of niobium doping on the densification and grain growth in alumina, Ceramics International 34 (5) (2008) 1183–1187.
[2] Y. Ishitobi, M. Shμmada, M. Koizumi, Reactive pressure sintering of alumina, Ceramic Bulletin 59 (12) (1980) 1208–1211.
[3] M.R. Gallas, A.R. Rosa, T.H. Costa, J.A.H. da Jornada, High pressure compaction of nanosize ceramic powders, Journal of Materials Research 12 (3) (1997) 764–768.
[4] E.J. Gonzalez, B. Hockey, G.J. Piermarini, High pressure compaction and sintering of nano size γ-Al_2O_3 powder, Materials and Manufacturing Processes 11 (6) (1996) 951–967.
[5] R.S. Mishra, V. Jayaram, B. Majumdar, C.E. Lesher, A.K. Mukherjee, Preparation of a ZrO_2–Al_2O_3 nanocomposite by high-pressure sintering of spray-pyrolyzed powders, Journal of Materials Research 14 (3) (1999) 834–840.
[6] R.S. Mishra, C.E. Lesher, A.K. Mukherjee, High-pressure sintering of nanocrystalline γ-Al_2O_3, Journal of American Ceramic Society 79 (11) (1996) 2989–2992.
[7] S.C. Lioa, Y.J. Chen, B.H. Kear, W.E. Mayo, High pressure/low temperature sintering of nanocrystalline alumina, Nanostructured Materials 10 (6) (1998) 1063–1079.