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COMPACTION RESPONSE AND SINTERING BEHAVIOR OF ALUMINA NANO PARTICLE: EFFECT OF AGGLOMERATION AND PARTICLE COORDINATION

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Alumina nanoparticles with ~35nm average grain size were used to determine the applied pressure required for breaking of the agglomerates during milling. Effect of the deagglomeration process on the sintering behavior of the alumina nanopowders was investigated. The powders were formed by different shaping methods such as cold isostatic pressing (CIP) and slip-casting (SC). Based on the

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experimental results, the fracture point of the agglomerates decreased with prolonged milling time at 150 to 75 MPa pressure. Maximum value of the final density was obtained by 60min milling and 5h sintering at 1600^{o}C with ~2.2 µm average grain size.

Keywords: Nano alumina; compaction; sintering; agglomeration.

1. Introduction

It is well known that sintering behavior of ultra fine powders is related to the raw materials characteristics and processing approaches. In the case of nanometric ceramic powders, agglomeration tendency increases and the compaction of nanopowders becomes difficult with lowering of the grain size. Among the advanced ceramic materials, alumina is a well-known substance having high hardness, desirable wear resistance, acceptable corrosion behavior, enough thermodynamic stability and in some cases, good transparency. Alumina can, therefore, be used to make sliding and cutting tools, refractory compounds, implants, optic objects, etc. But brittle nature limits its applications.

Lots of investigations are based on Hall-Petch relationship to increase hardness and strength.[1-3] High energy and high interface density stored in fine and ultra fine structures are also important subjects for investigation.[4-6] Due to high surface area of nanopowders, tendency to form agglomerates is a matter of concern.[7, 8] The higher surface area of the nanopowder, the higher the driving force for decreasing of the interfacial energy by joining the particles together. Literature survey shows that by using dry pressing, green bodies include micrometric inter-agglomerate pores and inter-crystalline pores which degrade densification.[7]

It is important to eliminate the agglomerates. At high temperatures, grain growth occurs. Krell et al. [9] reported that the important factors to gain sub- micrometer structures are not only selecting the fine raw materials but also processing to avoid any strong agglomerated powders. They have concluded that free aggregated powders used as raw material provide less sintering temperature associated with less grain growth.

Colloidal processing methods can produce pieces with green densities as good as or superior to those produced by dry pressing method for micron-sized powders. In contrast, in nano-sized powder, lower green densities are often achieved. [7]

In dry pressing sintering, another important factor is how the granules and agglomerated powders flow and fill the forming die and also how granules deform during compaction [10]. In fact higher fill density provides a higher green density and consequently, higher sintered density. [11] Moreover, inter particle and particle-die interactions influence on powder compaction.

Ferkel and Helming [8] claimed that by modifying the nanopowder as raw material, sintering activity and green densities of compact samples are improved. In fact, deagglomeration of ceramic nano particles, reduces necks shape between adjacent particles and leads to obtain better sintering behavior.

In the case of nano ceramic as raw materials, by decreasing the particle size, the van-der-waals interaction and bonding between particles result in strong agglomerates.

Therefore, filling the forming die with powder encounter the problems and green density of compact sample tends to decrease. Ultimately, sinter ability affected by aforementioned phenomena. It is notable that the granules should be weak enough to deform and break at low pressure and also strong enough to lead rearrangement sufficiently.

In general, there are three stages during compaction process: (a) the intersection of low-pressure in which the particles are rearranged; (b) and (3) extensive deformation of the agglomerates which occurs by increasing the applied pressure.[10]

The present work attempts to understand the applied pressure required for achieving the break-point of the agglomerates. Compaction response and its influence on sintering behavior of alumina nanopowders have also been investigated.

2. Experimental procedure

Two types of alumina powders with mean particle size of 35 nm (Alfa Aesar, Ward Hill, MA, USA) and 150 nm (Taimicron TM-DAR; Taimei Chemicals Co., Ltd., Tokyo, Japan) were employed as raw materials. To modify and deagglomerate, 35 nm alumina powders were milled via high energy mill (Spex sample prep, 8000D mixer/mill) for different times. In this procedure, ethanol (Merck Co., Darmstadt, Germany) was used as a process-control agent (PCA). The weight ratio of ball-to-powder was 10:1.

The powder was firstly shaped in a cylindrical die with 10 mm diameter under various uniaxial pressures. Cold isostatic pressing (180 MPa) had also been performed on the pellets which were pre-shaped with uniaxial pressing at 50 MPa. It was clear that an ideal ejection of the pressed compact was accompanied with fewer cracks like defects and laminations. Lubricant was, therefore, used to decrease the effect of die wall friction. Slip-casting was carried out into a porous Plaster Molds. Dolpaix (CE64, Zschimmer & schwarz, Lahnstein, Germany; 0.8 wt% related to alumina) and polyethylene glycol (1%wt, Merck, Darmstadt, Germany) were used as additive dispersant and binder, respectively. Slurries of nanopowders were dispersed by ultrasonic treatment in distilled water. The prepared green samples were produced by slip-casting, cold isostatic pressing and uniaxial press sintering at 1600^{o}C for 2 h and 5 h.

The densities of the sintered samples were determined by Archimedes principle. A transmission electron microscope (TEM, Philips CM200 TEM) and scanning electron microscope (SEM, Philips XL30 of the Netherland) were used to observe morphology, agglomeration condition and mean particle size of the sintered bodies.

3. Result and discussion

Figure 1 shows TEM pictures of alumina nanopowders with average 35nm particle size. The powders of spherical particles have narrow distribution. It is clear that a high-agglomeration amount leads to coexistence of strong particle groups, contrasting the free-agglomerate sub-micron alumina powders reported by Mazaheri et. al [5]. It was, hence,

expectable that green bodies of submicron alumina samples were more than the nano-sized ones.

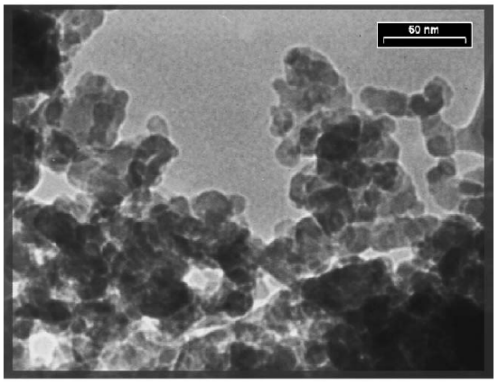

Fig. 1. TEM picture of Al_2O_3 nanopowders (35nm).

Figure 2 represents the fractional density of the nano and the submicron (150 nm) Al_2O_3 samples versus the applied pressure. It is obvious that fractional density of the green compact increases with the applied pressure. The green density of the as-received Al_2O_3 compact had its lowest value (~44%TD) even when applying 700MPa pressure. Another important issue in these curves was that by modifying and milling process, the Al_2O_3 nanoceramic (35 nm) at 3, 20 and 60min, with the highest pressure, the fractional density increased up to 47, 49 and 50%TD, respectively. In comparison with the unmodified alumina powders, better compaction process resulted in ~7% higher density in green bodies. Additionally, sub micrometer powder revealed better green density (at least 10%) than nanometric ones because it had free agglomerated particles.

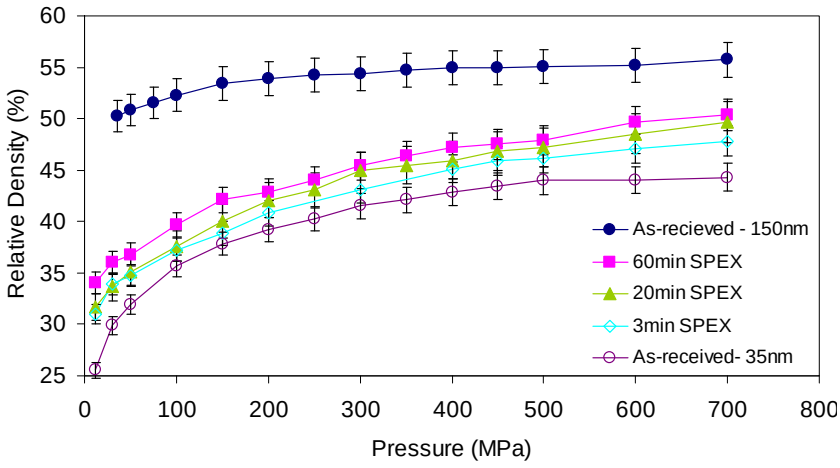

Fig. 2. Effect of the applied pressure on relative green density of Al_2O_3 compacts.

To find out how the compaction response is, logarithmic scale is plotted (Figure 3). From these curves it can be concluded that by increasing the apply pressure, except the as-received samples, the break point was appeared. At the break-point, curve slope is changed which means the second step of compaction is started. In other words, the strong agglomeration and neck shapes between adjacent particles was broken, therefore, further increase of apply pressure lead to higher green densities and easily sliding of granules into voids could take place. There are three break-points at 150, 100 and 75Mpa for 3, 20 and 60 min milled samples, respectively. Although, shifting down the position of break-point is as result of increasing the milling time but no extremely changes was observed after 20min milling time. From Figure 3, it is notable that no break point was observed for as-received nanopowder compacts. It can be attributed to very strong aggregate in nanometer powders.

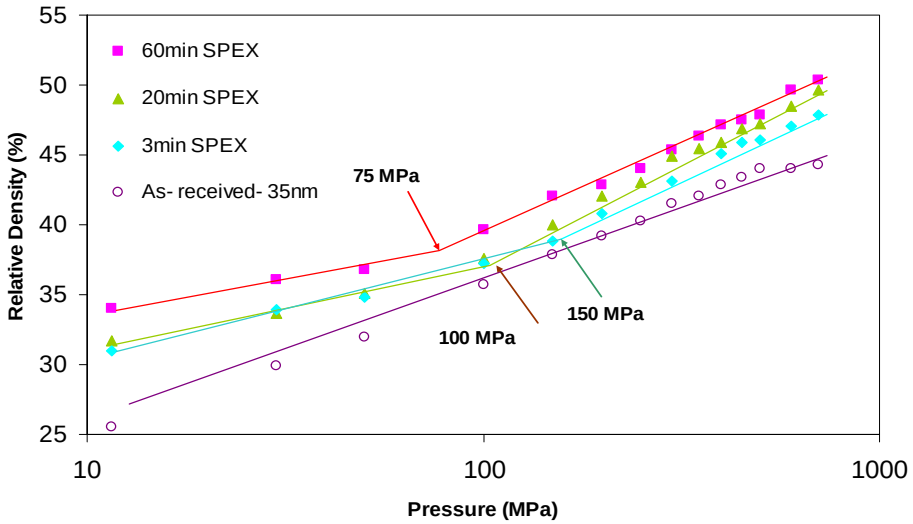

Fig. 3. Compaction response of 35 nm alumina powders (logarithmic scale).

The fractional density of alumina nano ceramic form starting nanopowders which sintered at 1600^{o}C for 2 and 5 h as function of apply pressure on the green compacts pellets is shown on Figure 4. From this figure, fractional density of as received powder compact not be upper than 70%, however, the highest density was obtained by milling at 60min (89.5%) after 2h sintering. Moreover, 20 and 60min milled powders exhibit the same densification trend. On the other hand, fractional densities of 20, 60 min milled powder compact are almost constant after 600Mpa applied pressure. The fractional density of 3min milled samples increases rapidly with increasing compaction pressure below 600Mpa, whereas its densification after 600Mpa become slowly. Obviously, higher dwelling time (5h) results in higher fractional density. Considerably, with increasing the sintering time from 2 to 5 h, fractional density of as received compact powder increase ~12% at 700Mpa. Another fact is with increasing the milling time up to

60min, fractional densities of compact samples increase. Li and Ye [12] reported that the relative density of alumina compacts from stating nanopowders of a mean particle size of 48nm which pressed at 1420Mpa and sintered at 1500°C for 5h was over 95%. The maximum value of present alumina nanopowder sintered density (96.2% TD) is obtained at 500Mpa after 6omin milled sample. Densification trend of 5h sintered pellets after 3, 20 and 60 min milling time are closely the same. In fact, after 500Mpa applied pressure, fractional density trend to constant value and even decrease slightly. It can be attributed to grain growth and release of residual stress which forced the grain during the compaction process.

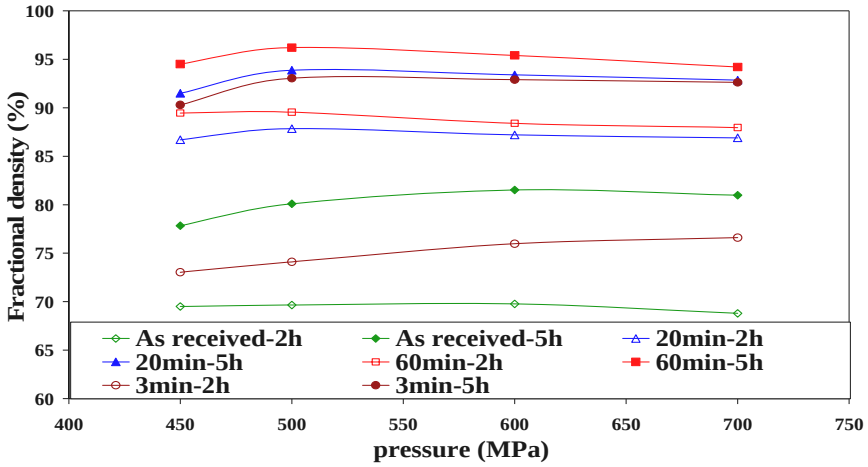

Fig. 4. Fractional density of nanoalumina compacts after 2 h (open symbols) and 5 h (solid symbols) sintering.

The SEM micrograph of the as-sintered alumina from starting nanoparticle (35 nm) is shown in Figure 5. It indicates that 3 min milled powders and sintered for 2h, result in 0.75µm grain diameter. Further increasing the milling time led to finer sintered grain. For instance, less than 0.6 µm was obtained only by 60min milling process.

Regarding to longer sintering regime (5h), it is needless to say that grain growth will be more. For instance, the average grain size of 60min milled powder that sintered for 5 h was close to 2.2 µm. Interestingly, with increasing the milling time from 20 to 60 min, no extremely differences in grain size of Al_2O_3 sintered pellets observed.

Wet shaping method was another approach to compare the effect of deagglomeration of alumina nanopowder. However the fractional densities of slipped cast samples and cold isostatic compacts without preparation (milling) are closely the same (~ 77.5% TD after 5h at 1600°C) which are shown at Table 1, but the microstructures are different. Figure 6 (a, b) shows that the finer grains obtained by pressing powders isostatically. In contrast, slip casting method result in 1.7 µm average grain size even after 60 min milling time of starting powders. In fact, densification rate of wet shaped samples was greater than another one. It can be noticed that more homogenous samples are contributed to the CIP samples.

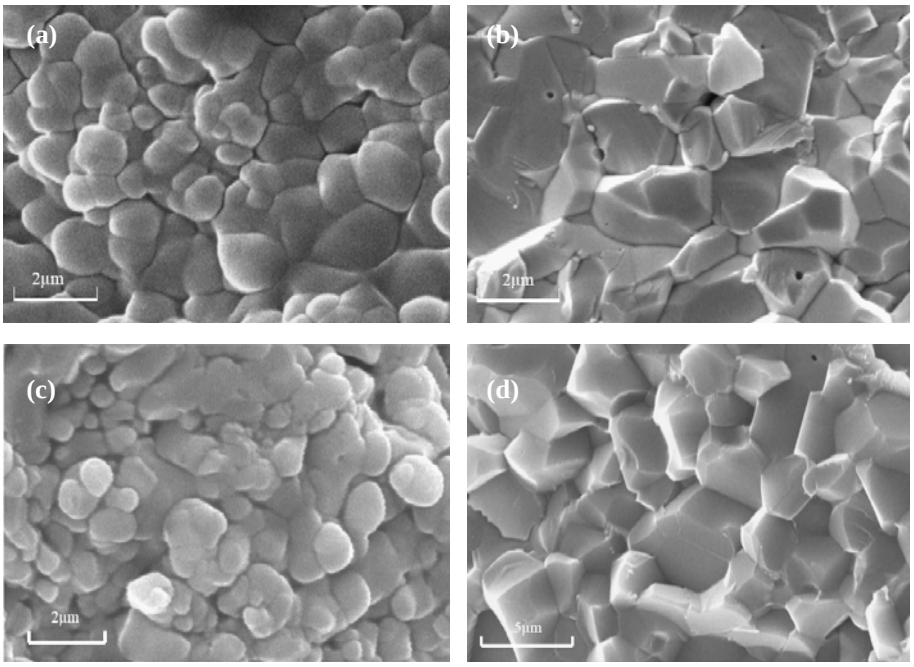

Fig. 5. SEM micrographs of fracture surfaces of alumina compacted at 700Mpa and sintered at 1600°C. Powders were: (a) milled for 3 min and sintered for 2 h, (b) milled for 3 min and sintered for 5 h, (c) milled for 60 min and sintered for 2 h and (d) milled for 60 min and sintered for 60 min.

Table 1. Green and final densities of alumina modified powders with different shaping methods

Forming	Sample	Green Density	Final Density (2h)	Final Density (5h)
CIP	As received	37.4	71.6	77.5
	Milled	41.8	75.5	84.2
Slip caste	As received	31.6	63.7	68.3
	Milled	35.3	70.4	77.3

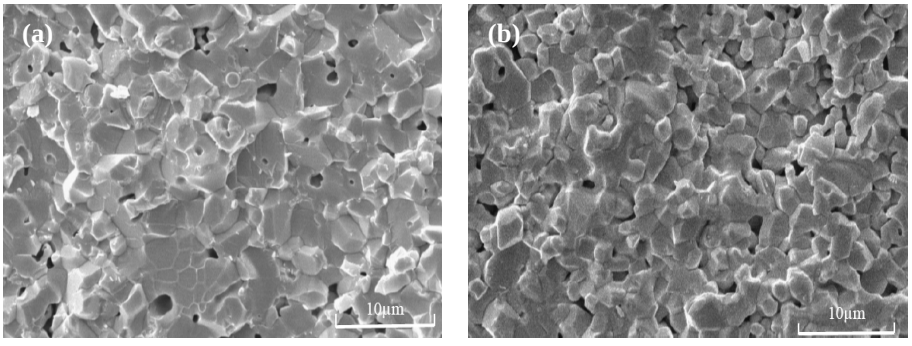

Fig. 6. SEM picture of: (a) CIP result and (b) wet-shaped alumina nanoparticle after 5h sintering at 1600°C.

4. Conclusion

Compaction response of alumina powders with a mean particle size of about 35 nm with hard agglomerates was investigated. It was shown that by deagglomerating nanopowders with high energy ball milling, green and sintered densities were increased. Longer milling time shifted the break point downward. Slip casting and cold isostatic press were employed to determine the effect of shaping method on densification of the modified nanopowders. It was concluded that dry pressing/sintering is preferred to the wet shaping approach. Higher fractional densities and grain growth were obtained at longer sintering time (5 h).

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Abstract

Alumina nanoparticles with ~35nm average grain size were used to determine the applied pressure required for breaking of the agglomerates during milling. Effect of the deagglomeration process on the sintering behavior of the alumina nanopowders was investigated. The powders were formed by different shaping methods such as cold isostatic pressing (CIP) and slip-casting (SC). Based on the experimental results, the fracture point of the agglomerates decreased with prolonged milling time at 150 to 75 MPa pressure. Maximum value of the final density was obtained by 60min milling and 5h sintering at 1600 °C with ~2.2 μm average grain size.

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