Influence of Sintering Routes on the Structure and Indentation Hardness of Nano α-Al_2O_3 Particles

Mohammad Sharear Kabir, Tamzid Ibn Minhaj, Ehsan Ahmed Ashrafi, Md. Maruf Hossain

Abstract*—In this study, the influence of single stage and double stage sintering routes on the microstructure and indentation hardness of nanoscale α-Al_2O_3 particles have been investigated. The nanoscale alumina particles were compacted by Uniaxial pressing technique. Sintered nanoscale α-Al_2O_3 particles have been shown to have excellent mechanical properties to be used in the manufacture of nanotubes and nanowires. Among the sintering routes, α-Al_2O_3 ceramic particles sintered by double stage sintering route showed comparatively higher resistance to indentation than single stage sintering route. The densification achieved by double stage sintering route is higher than single stage sintering route. Based on scanning electron microscope images, the microstructure of samples sintered by double stage sintering route contained less porosity than conventional/ single stage sintering route. The increase in hardness achieved by double stage sintering route can be attributed to higher densification and suppressed grain growth during final stage sintering.

Index Terms*— α-Al_2O_3, Uniaxial pressing, indentation hardness, double stage sintering route, single stage sintering route.

I. INTRODUCTION

Sintering is a process in which the compacted powders are heated to a certain temperature so that the particles can adhere to each other and it depends on the mass flow of material [1]. The microstructure evolution during sintering includes the changes in size and shape of grains and pores [1]. All these changes relate to the products' properties. During sintering, compacted materials are heated at gradually increasing temperatures until a certain point. There are several stages of sintering: pore consolidating, pore removal, components' shrinkage and grain growth [2]. Basically, the changes during sintering process can be catalogued into densification and coarsening [3]. With the evaporation and deposition of surface atoms, cohesive necks firstly grow at the particle contacts [4] and the pores will occur between these necks. Some of the pores can be exhausted while some of them will remain in the bulk forever [1].

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Alumina is one of the most widely used advanced ceramic materials due to its excellent chemical, thermomechanical and dielectrical properties. It makes this oxide an excellent material for catalysts, structural, wear resistant coating, microelectronic and technological applications, from bioceramics implants to electrical insulators inside the thermonuclear fusion reactors (5). Fabrication of nanoscale alumina powders is being developed due to the improved properties related to smaller particle size, and higher specific surface areas. It can be prepared through methods such as sol-gel [6]-[7], hydrothermal [8], co-precipitation, mechanical milling, vapor-phase reaction and combustion methods [9], [10]. Among different phases of alumina the α-phase i.e. Alpha alumina (α-Al_2O_3) has unique mechanical, electrical, and optical properties. Hence, it is utilized in many areas of modern industry [11]. α-Al_2O_3 is obtained from transition of γ-phase i.e. Gamma alumina (γ-Al_2O_3), which is the most common transition alumina phase as shown in equation (1). When γ-Al_2O_3 is heated, it undergoes a series of polymorphic transformations from a highly disordered cubic close packed lattice to the more ordered cubic close packed θ-Al_2O_3. When heated to approximately 1200^0C, θ-Al_2O_3 undergoes a reconstructive transformation by nucleation and growth, where the oxygen atoms rearrange into a hexagonal close packed structure to form thermodynamically stable trigonal α-Al_2O_3 [12], [13].

$$\gamma\text{-}Al_2O_3 \rightarrow \delta\text{-}Al_2O_3 \rightarrow \theta\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3 \quad (1)$$

Since reducing the grain size in the alumina ceramics improves not only their mechanical properties, such as hardness [14] – [16], strength [17] - [20], wear resistance [21], [22] and toughness [22], but also the transmittance of visible light [20], [24] – [26], substantial research has been done on reducing grain size to pursue these favorable properties. However, most of the efforts are undergone by using a simultaneous pressure application during sintering, such as hot pressing sintering [15], [27], hot isostatic pressing sintering [20], [24], [25] or spark plasma sintering [26], [28]. Double stage sintering route developed by Chen and Wang, is an effective approach to powder consolidation [29], [30]. In the first stage of sintering, the low temperature consolidated green sample is heated continuously to a temperature T_1, obtaining a density point of 70-75 % of theoretical density or more [29], [30]. Then, the sample is cooled rapidly to a temperature T_2 (dwell temperature), and held for a long time (from a few to over a dozen hours), which is enough to yield full densification. In such a case, the advantageous difference in kinetics between grain boundary diffusion and grain-boundary migration is generated, which

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suppresses the final stage grain growth [29], [30]. In other words, grain boundary diffusion of the specimen is maintained but the grain boundary migration could be frozen under pressureless sintering conditions. The resultant material shows an optimized combination of the fine-grained, even nanograined microstructure and high density, leading to improvement in properties dependent on fine grain size. This method has been also applied in various materials, such as ZnO [31], ZrO_2 [32], [33], Al_2O_3 [34] and SiC [35]. In this present study, the influence of single stage and double stage sintering routes on the microstructure and indentation hardness of nanoscale alpha alumina particles has been investigated. This primary focus of this investigation is to point out major differences in sintering routes and advantages of double stage sintering route over conventional sintering/single stage sintering.

II. Experimental

A. Preparation of Polyvinyl alcohol (PVA) binder and addition to nano alumina powder

PVA (solid in normal room temperature) was used to provide plastic strength to the alumina powder. Since the use of thick binders hinders homogeneous mixing, dilute binder was prepared by adding 6 milligrams of PVA to 100 ml of distilled water. The 100 ml distilled water was heated on a hot plate while stirring was continued with a magnetic stirrer. The weighed amount of PVA i.e. 6mg was added to the distilled water to dissolve PVA powder creating a homogeneous PVA solution. This solution was cooled and stored in an airtight bottle. This PVA solution was added to nano scale alumina powder of particle size 60 nm at a rate of 8 ml for 20 gm of powder i.e. 0.4 ml for 1 gm nano scale alumina powder.

B. Uniaxial pressing of powder mix

For investigating hardness of nano α-Al_2O_3 particles, the powder mixture was consolidated into a compacted shape by Uniaxial pressing by SIEMENS HERZOG pressing unit prior to sintering. Around 1.2 grams of the powder mixture was poured into a cylindrical die cavity of 10 mm diameter and a pressure of 40 KN to form a green body (cylindrical shaped tablet of 10 mm diameter). Two batches of samples were made by Uniaxial pressing technique and were dried in an oven for more than 24 hours.

C. Density measurement

The bulk density of the green and sintered samples was measured by Archimedes' method following the ASTM C372-73 standard [36].

D. Single stage sintering of α-Al2O3 powder

The single stage sintering for specimen is shown in Fig. 1. The specimen was heated at a rate of 3°C/min up to 550°C and kept constant at this temperature for one hour. The specimen was then heated at a rate of 10-20°C/hr up to 1500°C and kept constant at this temperature for 3 hours. The specimen was cooled after holding at 1500°C for three hours.

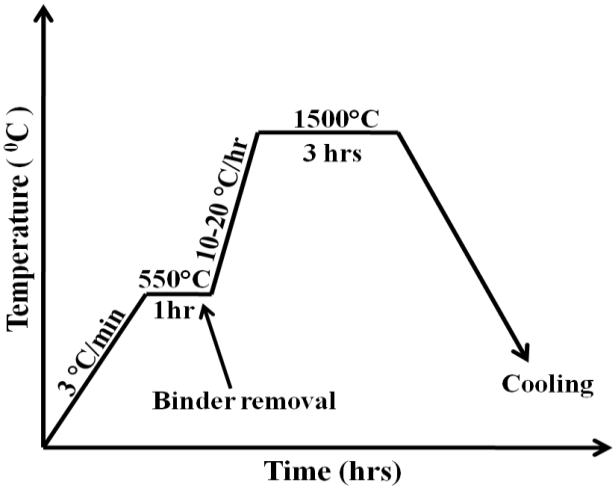

Fig. 1 Temperature Profile for Single Stage Sintering Route

E. Double stage sintering of α-Al2O3 powder

The double stage sintering process for specimen is shown in Fig. 2. The specimen was heated at a rate of 3°C/min up to 550°C and kept constant at this temperature for one hour. The specimen was then heated at a rate of 10-20°C/hr to a temperature of 1700°C and then cooled down immediately to temperature range between 1450°C - 1550°C. The specimen was held at this temperature range for three hours and then cooled down at a rate of 3°C/min.

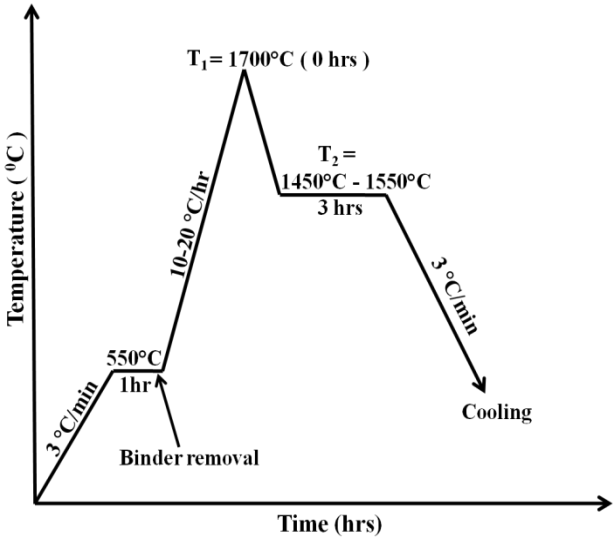

Fig. 2 Temperature Profile for Double Stage Sintering Route

F. Hardness testing and microstructural analysis

The hardness values of the sintered ceramic tablet produced by dry pressing method were tested by Vickers hardness test, where a square-based shard pyramidal diamond indenter was used. A load of 1000 gm was applied for duration of 30 seconds. The indentation diagonal lengths were measured by observing under scanning electron microscope (SEM). The mean was calculated, and this value was then employed to calculate a hardness number by the following formula:

$$HV\ (P) = 1854.4(P/d^2) \quad (2)$$

Where HV (P) is the hardness number at applied load P, and where d is the mean length of the diagonals of the indentation.

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III. Results and Discussions

A. Binder removal and Differences in temperature profile in sintering routes

From Fig. 1 and Fig. 2 it is clearly evident that the two sintering routes are quite different. A common trait in the temperature profile of both sintering processes was binder removal by slowly heating the sample at a rate of 3°C/min to 550°C. Binder removal was carried out by holding the ceramic tablets at 550°C for 1 hour. Proper binder removal was accomplished by slow heating and holding the sample to a temperature at which the binder can completely volatilize. Furthermore, slow heating of the sample during binder removal ensures uniform heating and reducing the chances of crack formation. Moreover, precautions were taken by drying the samples to reduce the chances of moisture absorption. The presence of moisture together with binder presents a high risk of damage to the samples when heated to 550°C. The removal of excess amount of gaseous products from the sample may spoil the shape of the sample. In the single stage sintering route (Fig. 1), the sample is heated to a maximum temperature of 1500^0C. This yields only 92% densification as calculated by Archimedes method. The sample sintered by double stage sintering route yields 98% densification when measured by Archimedes method. Double stage sintering is a promising approach to obtain fully dense nanoscale ceramics grains because this sintering route suppresses grain growth in the final stage of sintering unlike single stage sintering route [37]. When sample is cooled down to dwell temperature (lower temperature than T_1) in the double stage sintering route, full densification is achieved and an advantageous difference in grain boundary diffusion kinetics and grain boundary migration kinetics is generated. This difference in kinetics suppresses grain growth [37]. Grain boundaries in alumina are anisotropic in nature; as a result their characteristics differ greatly from boundary to boundary [38]. To arrest grain growth in the second step, it is imperative to lower the temperature so that all four-grain junctions are immobile. Most likely, this may also cause inactiveness of some grain boundaries in diffusion, which hinders densification. Therefore, it is more difficult to identify a kinetic window in materials that have highly heterogeneous grain boundary properties. In Fig. we can see that temperature in the double stage sintering route was initially raised to 1700^0C, this temperature is sufficient to yield 70-75% of the theoretical density during initial sintering stages. The improvement due to double stage sintering route is on the standard deviation of properties and reliability against failure. Many ceramic properties like elastic, thermal expansion, dielectric, magnetic etc. are strongly correlated to grain size distribution, which normally broadens rapidly during final-stage sintering. Since double stage sintering route has no grain growth in the second step, it entirely avoids such a broadening phase. Hence, uniform properties are obtained.

B. Microstructure and Hardness evaluation

The microstructure of sample sintered by single stage sintering route is given in Fig. 3 and the indentation of the sample is given in Fig. 4.

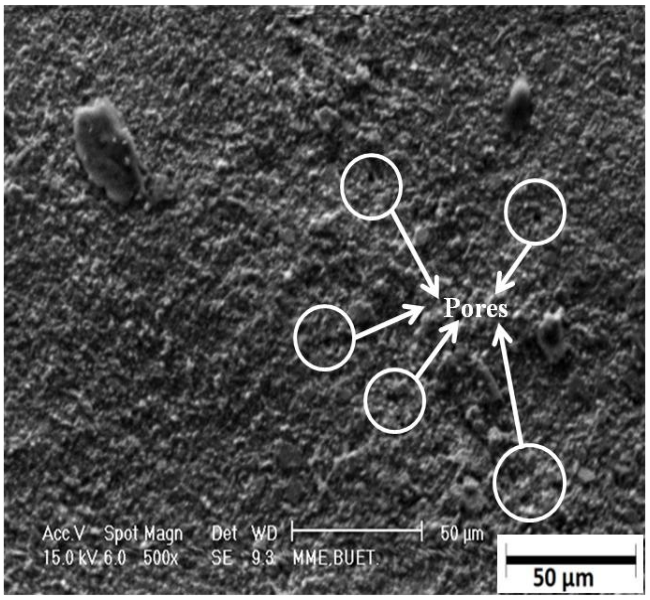

Fig. 3 Microstructure [Magnification: 500X] of Sample Sintered by Single Stage Sintering Route

From Fig. 3 we can see that the sample sintered by single stage sintering route contained fair amount of pores. High porosity can be confirmed from densification results obtained by Archimedes method, which yields 92% densification in single stage sintering route.

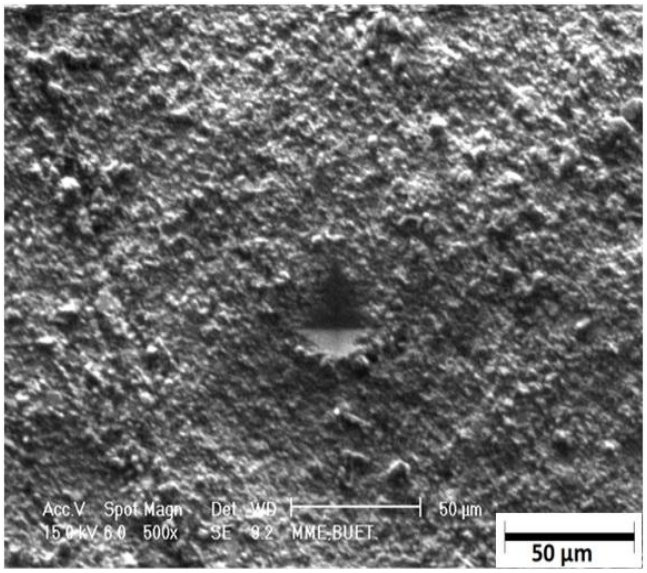

Fig. 4 Indented Region of the Sample Sintered by Single Stage Sintering Route [Magnification: 500X]

The diagonal lengths of the indentation were measured and an average was taken. The Vickers hardness value calculated is as follows:

Microhardness ; $HV(P)=1854.4(P/d^2) =1.322$

Where P = 1 kg and d = 37.45 µm

The microstructure of sample sintered by double stage sintering route is given in Fig. 3 and the indentation of the sample is given in Fig. 4.

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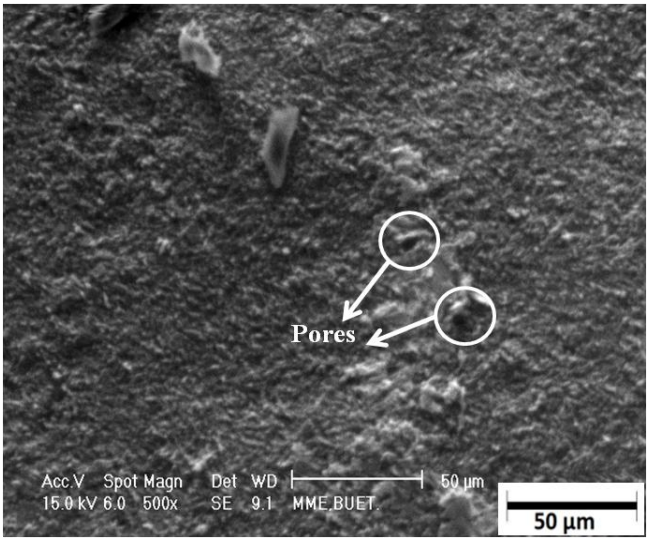

Fig. 5 Microstructure [Magnification: 500X] of Sample Sintered by Double Stage Sintering Route

From Fig. 5 it can be seen that the sample sintered by double stage sintering route contains less porosity than sample sintered by single stage sintering route. This is due to higher densification i.e. 98% achieved due to double stage sintering.

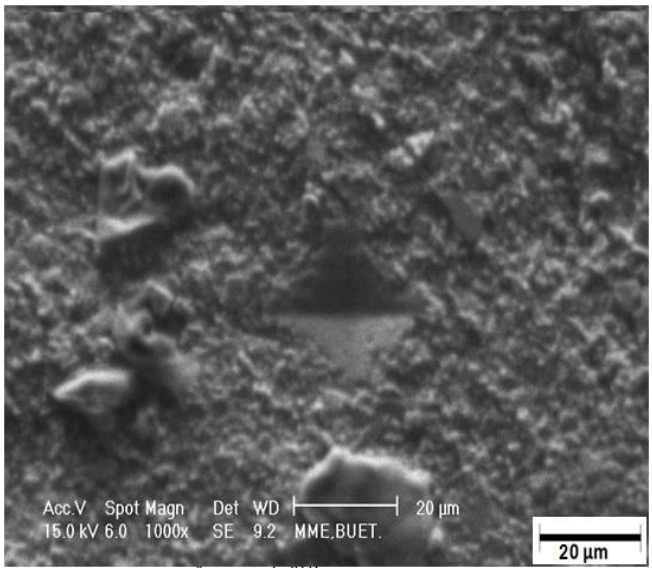

Fig. 6 Indented Region of the Sample Sintered by Double Stage Sintering Route [Magnification: 1000X]

The indentation spot on the sample sintered by double stage sintering route was smaller than the other sample. As a result magnification had to be doubled to view the spot. The diagonal lengths of the indentation were measured and an average was taken. The Vickers hardness value calculated is as follows:

Microhardness ; $HV(P)=1854.4(P/d^2) = 2.582$

Where P = 1 kg and d = 26.80 µm

From hardness calculations it is clearly evident that the indentation hardness of the sample sintered by double stage sintering method is higher than the sample sintered by single stage sintering route. The hardness of the sample sintered by double stage sintering route is almost twice that of the other sample. This implies that the grain size of the sample sintered by double stage sintering route is smaller than the other sample and higher densification yields higher hardness.

IV. Conclusions

The effect of different sintering routes on the microstructure and indentation hardness of nanoscale α-Al2O3 particles has been explored. The temperature opted for binder removal has been found to be accurate, as no sign of cracks were noticed on the ceramic tablet. On the basis of scanning electron microscope images, it can be said that, double stage sintering method produces higher densification and less porosity compared to single stage sintering method. This increase in densification leads to increased hardness in sample sintered by double sintering route. Although, increase in hardness may be a direct implication of smaller grain size, further experimental study needs to be carried out to establish whether grain size refinement is achieved in double stage sintering process for nanoscale α-Al2O3 particles.

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