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Densification and Mechanical Properties of Alumina Ceramics via Two-Step Sintering with Different Holding Times

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ABSTRACT
The densification and mechanical properties of alumina ceramics were investigated via two-step sintering (TSS) with different holding time. The alumina ceramics were sintered at 1450 °C for 1 min during the first stage, followed by sintering at 1350 °C with different holding times (2-24h). Conventional sintering (CS) was also performed on the alumina ceramics at 1450 °C for 2 h for comparison purpose. It was found that dense alumina with a relative density above 98% could be attained when TSS with a holding time of more than 12 h. The samples exhibited Vickers hardness between 5-8 GPa and fracture toughness of about 6 MPa.m$^{1/2}$. In contrast, conventional sintered alumina yielded low relative density (85%), large grain size (2 μm), low Vickers hardness (4.23 GPa) and fracture toughness (4.73 MPa.m$^{1/2}$). This study revealed that TSS is a viable approach in aiding densification, suppressing grain growth, and improving the mechanical properties of alumina ceramics.
Keywords: Two-step sintering, Alumina, Grain size, Mechanical properties.

1 INTRODUCTION
Alumina (Al_2O_3) is one of the widely used engineering ceramics in biomedical and aerospace industries owing to its excellent biocompatibility, strength, hardness, and stability in physiological environment [1-2]. However, the sintering of alumina using the conventional method at lower temperatures frequently resulted in lower density, fracture toughness and flexural strength. As such, various sintering techniques and approaches have been employed to enhance its mechanical properties, such as addition of dopants [3], microwave sintering [4], spark plasma sintering [5] and two-step sintering [6]. Since high sintering temperatures (>1450 °C) were generally required to produce high-density alumina ceramics using pressureless sintering [7], two-step sintering has been experimented to lower the densification temperatures and suppressing abnormal grain growth in order to retain a fine microstructure [8].

Two-step sintering (TSS) is a sintering method that consists of two stages sintering. At the first stage, the green sample is heated to a high temperature of T_1 and holding at this temperature for a very short period. This is followed by the second stage, where the temperature is lowered to T_2 and holding at this temperature for a longer holding time to allow densification to proceed without grain coarsening. Based on the literatures, the intermediate relative density of about 70% should be attained at the first stage before proceeding to the second stage of sintering [9]. Numerous studies have been examined the effect of various sintering parameters such as T_1, T_2 and holding time to achieve better densification. It was revealed that the densification rate of alumina was enhanced when T_1 was selected between 1400-1450 °C, with a relative density of 72-88%. When T_1 was higher than 1450 °C, the densification rate has been found to decrease rapidly [10]. In another study, it was found that $T_1 \leq 1450$ °C could avoid rapid alumina grain growth. The researchers reported that sintering at 1450 °C for an hour and further cooled down to 1350 °C for 34 h yielded alumina ceramics with relative density above 96% with no grain growth observed [11]. As for the second sintering temperature T_2, it was proposed to be lower than 1400 °C to suppress grain growth. By employing T_1 at

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1450 °C, the authors revealed that a flatter grain size-density slope was evidenced when T_2 was set at 1350 °C (4, 8 and 12 h holding time), as compared to 1400 °C (4 and 8 h holding time). Besides, fully dense alumina has been reported within 12 h of holding time at T_2 of 1350 °C [10].

Based on the research works, it was proposed that the two-step sintering temperatures T_1 and T_2 be set at 1450 °C and 1350 °C, respectively. However, documented works on detailed mechanical properties are rarely available. Thus, this work aimed to evaluate densification and mechanical properties of alumina via conventional and two-step sintering. With the recommended sintering temperatures, different holding time was employed in the second stage of sintering. The results obtained were then compared with the conventional sintered alumina.

2 METHODS AND MATERIALS

Commercially available pure alumina (Kyoritsu Co. Ltd., Japan; 99.8% Al_2O_3 content, 150 nm mean particle size), was used in this study. The alumina powder was uniaxially pressed and cold isostatic pressed at 200 MPa (Riken Seiki, Japan) to form solid samples. The alumina samples were first sintered at 1450 °C (T_1), with a heating rate of 10 °C/min and hold for 1 min. The temperature was then lowered to 1350 °C (T_2) and hold at this temperature at different holding times of 2, 4, 6, 8, 10, 12 and 24 h. Conventional sintering (CS) was also carried out for the alumina sample at 1450 °C / 2 h hold for comparison purpose. Detailed sintering stages of CS and TSS are listed in Table 1.

The sintered samples were then ground using SiC papers with grit sizes ranging from 120 to 1200, before polished with diamond paste of 6 μm and 1 μm to achieve reflective surfaces (Imtech Grinder-Polisher). Phase analysis was conducted using X-ray diffraction (XRD; Rigaku Geiger-Flex diffractometer, Japan), operated with a 2θ scanning range from 20° to 50°. The XRD patterns were identified using Standard Joint Committee for Powder Diffraction Standard (JCPDS) files no. PDF#42-1468. According to Archimedes' principle, the bulk density was measured using water immersion method (Densi-Meter, AG204 Mettler Toledo, Switzerland). The relative density of the sintered alumina was calculated by taking the theoretical density as 3.98 g/cm^3. Vickers hardness and fracture toughness were determined using Vickers indentation technique. Vickers hardness was performed using a pyramidal diamond indenter (Wolpert Wilson Instruments, USA), with an applied load of 10 kgf, according to ASTM E384-99 and ISO 14705. Fracture toughness was evaluated using the formula proposed by Shetty et al. [12]. Microstructure analysis was analysed via the scanning electron microscope (SEM) (Philips XL30 SEM, The Netherlands). The average alumina grain size was then measured using the line-intercept method.

Table 1: Sintering stages of conventional (CS) and two-step (TSS) sintering

Sintering Method	Sintering Stage (temperature/holding time)
CS	1450 °C/2 h
TSS1	1450 °C/1 min → 1350 °C/2 h
TSS2	1450 °C/1 min → 1350 °C/4 h
TSS3	1450 °C/1 min → 1350 °C/6 h
TSS4	1450 °C/1 min → 1350 °C/8 h
TSS5	1450 °C/1 min → 1350 °C/10 h
TSS6	1450 °C/1 min → 1350 °C/12 h
TSS7	1450 °C/1 min → 1350 °C/24 h

3 RESULTS AND DISCUSSION

3.1 Phase Analysis, Densification and Microstructure Evolution

The XRD phase analysis revealed the presences of alumina phases for conventional and two-step sintered alumina samples, as shown in Figure 1. Alumina traces were detected at the angles of 25.5°, 35.2°, 37.8° and 43.4°, respectively. All the conventional and two-step sintered samples exhibited highly crystalline structures, regardless of the sintering holding time up to 24 h.

The relative density and grain size of sintered alumina with different sintering holding time are presented in Figure 2. For two-step sintered samples, it was observed that the relative density linearly increased with sintering holding time up to 8 h, followed by a significant increment from 92.8% (8 h) to 95.8% (10 h), with no abnormal grain growth observed. With the further increased of holding time, the relative density increased gradually and achieved highly dense samples with a relative density of about 98% (12 and 24 h). This was also accompanied by minor grain growth from 1.35 μm (12 h) to 1.65 μm (24 h). On the other hand, conventional sintered alumina showed a low relative density of 85.6% and a large average grain size of 1.93 μm, as compared with all the two-step sintered samples. Figure 3 shows the correlation between grains size and relative density of the sintered samples. The results showed that there were two grain size-densification trajectory which represents the densification rate as depicted by the slope of the linear line in Figure 3 could be observed for the alumina ceramic. Comparison between the two trajectory slopes, indicated that rapid grain growth was observed when relative density reached 95.8% and above, where the grain size grew rapidly from 1.15 μm to 1.65 μm. Li & Ye [11] also reported similar findings, where fast

grain growth was noticeable when relative density of alumina exceeded 90%. Also, they found that two-step sintered alumina ceramics (1450 °C/1 h → 1350 °C/34 h and 1380 °C/1 h → 1330 °C/50 h) resulted in better densification and smaller grain size.

SEM micrographs of the conventional (CS) and two-step (TSS) sintered alumina samples are shown in Figure 4, which were generally comprised of equiaxed alumina grains. Figure 4(b-c) shows the two-step sintered alumina at different holding time of 6 h, 10 h and 24 h, where the grain size gradually grew with the increase of holding time. It was observed that all the TSS samples (with holding time up to 24 h) exhibited smaller grain size (≤ 1.65 µm), as compared to the CS samples (1.93 µm). This suggested that TSS has the potential to suppress alumina grain growth when compared to CS method Although there was a substantial reduction in grain size for TSS3 (0.98 µm) as compared to the CS samples, there were some porosities observed among the grains as shown in Figure 4(b). When the sintering holding time was increased from 6 to 10 h, the grain size grew to 1.15 µm and was accompanied by a reduction in porosities (Figure 4(c)). This observation shows that the densification was still incomplete at the holding time of 10 h. However, as the holding time was increased to 24 h, a densified and homogeneous microstructure was attained as depicted in Figure 4(d). TSS7 successfully demonstrated the effectiveness of two-step sintering in suppressing grain growth coupled with improved densification as compared to CS technique. Loh et al. [6] have also reported smaller grain size with limited grain growth for two-step sintered alumina ceramics as compared to conventional sintered sample.

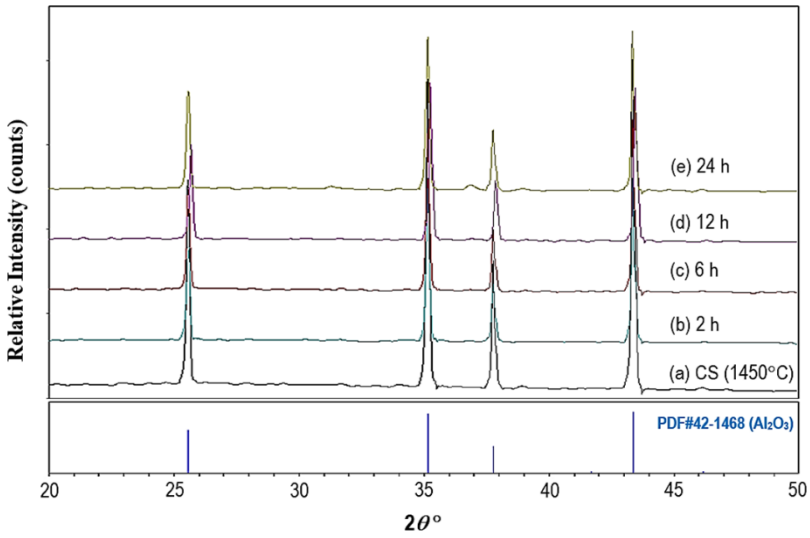

Figure 1: X-ray diffraction patterns of conventional (CS) and two-step sintered alumina samples at different holding time

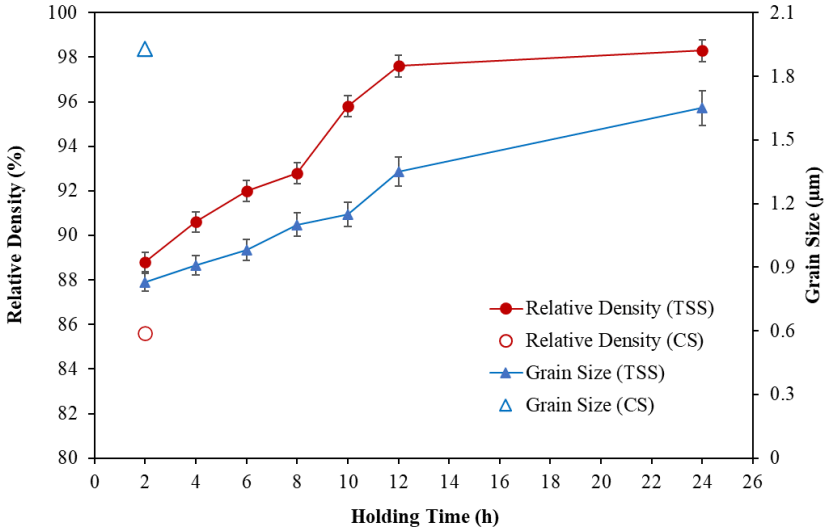

Figure 2: The relative density and grain size of conventional and two-step sintered alumina with different sintering holding time on the. *Key*: CS – conventional sintering, TSS – two-step sintering

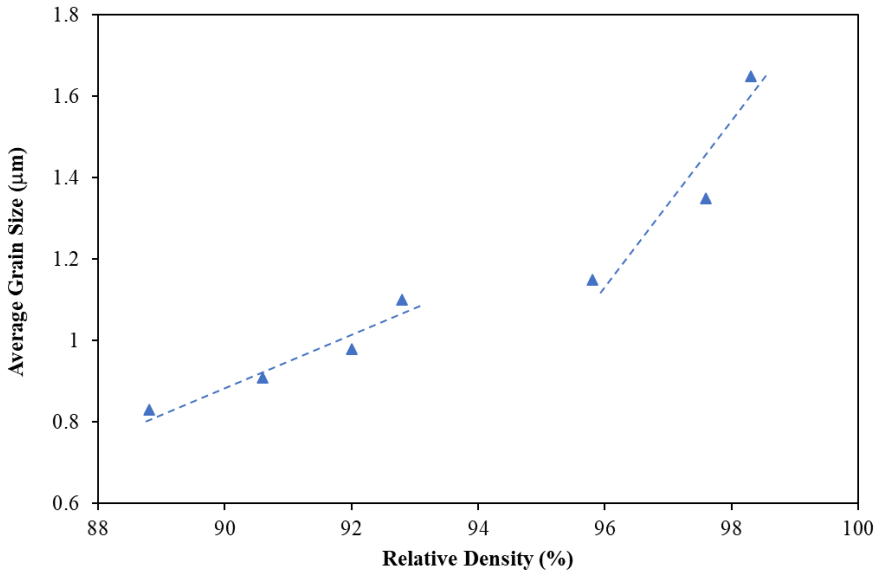

Figure 3: The grain size as a function of relative density for two-step sintered alumina

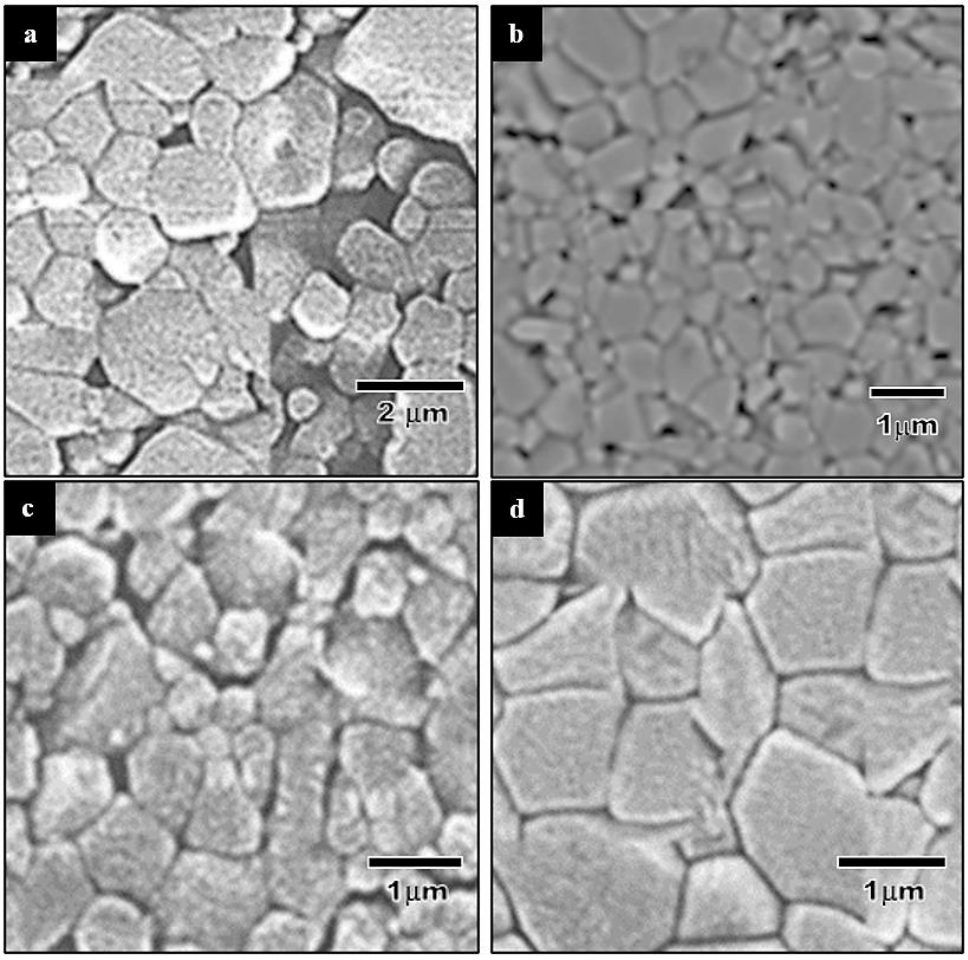

Figure 4: SEM micrograph of sintered alumina: (a) CS, (b) TSS3, (c) TSS5, (d) TSS7

3.2 Vickers Hardness and Fracture Toughness

Figure 5 shows the Vickers hardness and fracture toughness of sintered alumina with different holding time. The two-step sintered samples demonstrated a gradual increased in hardness with the holding time, from 5.12 GPa (2 h) to 6.3 GPa (10 h). This was followed by a steep increase in hardness with the further increment of holding time and reached hardness of about 8.13 GPa for holding time of 24 h. There was a substantial improvement in hardness for all the two-step sintered samples as compared to the conventional sintered sample (4.23 GPa). The Vickers hardness of the alumina was found to be strongly dependent on the relative density as shown in Figure 6.

The fracture toughness of the two-step sintered alumina ceramics was found to vary in the range of 5.5-5.9 MPa.m$^{1/2}$ when held at different duration. In general, fracture toughness of the alumina did not change very much for holding times of 8 h and above, indicating that the holding time did not have significantly affected the toughness of the ceramic. Nevertheless, the fracture toughness obtained for the TSS was higher than that of the CS sample (4.73 MPa.m$^{1/2}$). Loh et al. [6] found that two-step sintering (1550 °C/0 min → 1450 °C/8 h) did not enhance the densification, Vickers hardness and fracture toughness of alumina ceramics, despite obtaining a lower grain size as compared to conventional sintered sample. This discrepancy could be associated with the different starting material used as well as the different TSS regime employed.

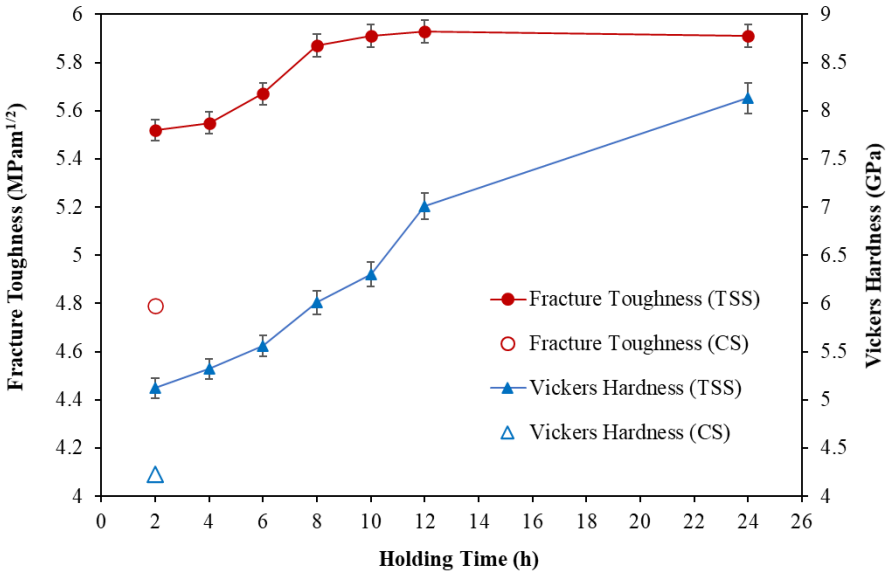

Figure 5: The Vickers hardness and fracture toughness of conventional and two-step sintered alumina with different sintering holding time. *Key*: CS – conventional sintering, TSS – two-step sintering

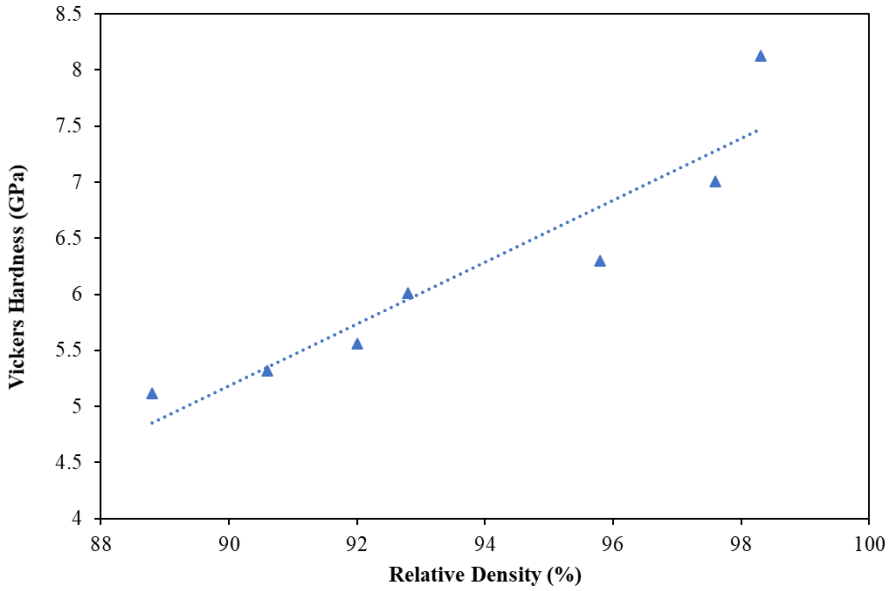

Figure 6: The relationship between Vickers hardness and relative density of sintered alumina

4 CONCLUSIONS

Based on the current study, the effect of second stage sintering holding time (2 to 24 h) on the densification and mechanical properties of two-step and conventional sintered alumina ceramics were investigated. It was found that two-step sintered alumina (1450 °C/1 min → 1350 °C/24 h) yielded a highly dense sample (>98%), small grain size (1.65 μm), high Vickers hardness of 8.13 GPa and fracture toughness of 5.91 $MPam^{1/2}$. It was also found that the fracture toughness of two-step sintered alumina ceramics was not significantly affected by the sintering holding time duration. A linear relationship between Vickers hardness and densification of alumina was also identified. This work revealed that two-step sintering method was beneficial in suppressing alumina grain growth and resulted in improved densification and mechanical properties when compared to conventional sintering method.

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