Temperature-dependent Thermal Properties of Spark Plasma Sintered Alumina

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Abstract:
In this work, we report temperature-dependent thermal properties of alumina powder and bulk alumina consolidated by spark plasma sintering method. The properties were measured between room temperature and 250 °C using a thermal constants analyzer. Alumina powder had very low thermal properties due to the presence of large pores and absence of bonding between its particles. Fully dense alumina with a relative density of 99.6 % was obtained at a sintering temperature of 1400 °C and a holding time of 10 min. Thermal properties were found to mainly dependent on density. Thermal conductivity, thermal diffusivity, and specific heat of the fully dense alumina were 34.44 W/mK, 7.62 mm²/s, and 1.22 J/gK, respectively, at room temperature. Thermal conductivity and thermal diffusivity decreased while specific heat increased with the increase in temperature from room temperature to 250 °C.

Keywords: Alumina; spark plasma sintering; thermal conductivity; thermal diffusivity; specific heat

1. Introduction

Recently, applications of sub-micron powders had increased significantly because of their exceptional properties, controlled functionality, and increased reactivity [1]. This led to the development of new sintering techniques, such as spark plasma sintering, to consolidate these powdered materials [2]. Alumina, an abundant and low cost material, is widely used for production of cutting tools, biomedical materials, electrical insulators, and wear resistant parts and coatings [3-7]. Hot-pressing (HP), uniaxial pressing followed by furnace sintering, hot isostatic pressing (HIP), and spark plasma sintering (SPS) were used to consolidate alumina. The SPS [8], also named field assisted sintering (FAST), is a binder less and a direct process to sinter powdered materials at relatively low sintering temperatures and in short sintering times. It involves the application of uniaxial force and high intensity current at low voltage. The process allows the retention of the initial fine structure of the material, which leads to superior properties. In addition, SPS is a cost-effective process due the fact that it is binder less, direct and does not require initial compaction, and performed at low temperatures for short times compared to other powder metallurgy processes [8]. Different mechanisms have been proposed by researchers to explain densification in SPS such as vaporization condensation, plastic deformation, surface diffusion, grain boundary diffusion, and volume diffusion [9-12]. The three factors believed to be responsible for fast densification in SPS are
applied pressure, rapid heating rates, and pulsed DC current [13].

Fully dense alumina has been successfully sintered using SPS [12-17]. Gurt and co-
workers [14] reported two densification regimes during spark plasma sintering of alumina: densification without grain growth occurring at low temperature and grain growth without further densification. The effect of sintering parameters on densification, microstructure, and mechanical properties of spark plasma sintered alumina was investigated by Shen et al. [12]. The authors reported that small amount of MgO was effective in restricting grain growth during sintering. Wang and co-workers [15] found that the use of fine initial particle size of alumina powder resulted in larger densification compared with coarse starting powders. Production of nano-alumina was possible starting from micron-sized powder and optimized SPS parameters [16]. The authors concluded that the grain-refining effect was probably due to rearrangement of dislocations through thermo-mechanical fatigue. Higher densification was achieved using spark plasma sintering, at short sintering time and high heating rate, compared with hot pressing sintering [13]. Alumina sintered through SPS was found to have more homogeneous structure, higher density, and better mechanical properties than the conventionally sintered alumina [17]. The SPS alumina had double flexural strength than the conventionally sintered sample. Analysis of literature showed that extensive research was published on mechanical properties of spark plasma sintered alumina [7, 12, 16-21]. However, very limited work is available on thermal properties of alumina either conventionally sintered or spark plasma sintered [3, 22-25].

Thermal properties of conventionally sintered α-alumina were evaluated by Munro [3]. The author added small amount of MgO to Al₂O₃ to control its grain size; and at least 98 % of the theoretical density and a nominal grain size of 5 μm were obtained. Charvat and Kingery [22] measured thermal conductivity, between 0 and 1000 °C, of Al₂O₃ single crystals and polycrystalline alumina of controlled microstructure. They found that conductivity of pure single-phase dense polycrystalline alumina agreed with that of the corresponding single crystal alumina at temperatures below the onset of radiant-heat transfer. The authors reported that thermal conductivity of polycrystalline alumina was sensitive to impurities and pore geometry. The effect of grain boundaries on heat transfer through polycrystalline alumina between 20 °C and 500 °C was investigated by Smith and co-workers [23]. The authors found that thermal grain boundary resistance in porous alumina materials was larger than in dense alumina materials. They reported values of 1.3x10⁻⁸ m².K.W⁻¹ for fully dense alumina and 2.2x10⁻⁸ m².K.W⁻¹ for alumina sample having porosity volume fraction of 0.3. The increase in thermal grain boundary resistance in the porous material was attributed to the decrease in effective thermal conduction cross-section. This increased thermal boundary resistance in the porous material decreased the thermal conductivity.

Zhan and Mukherjee [24] consolidated nanostructured alumina using SPS at 1150 °C for 3 min. They obtained fully dense alumina with room temperature thermal conductivity of 27.5 W/mK. The authors reported a decrease in thermal diffusivity from 0.088 to 0.03 cm²/sec with the increase in temperature from 25 to 500 °C. Thermal conductivity, between 300 to 800 K, of Al₂O₃ (200 nm) spark plasma sintered at 1400 for 3 min (50 MPa) was reported by Ahmad and co-workers [25]. They observed a decrease in thermal conductivity from around 34 to 13 W/mK with the increase in temperature from 300 to 800 K.

In the above few studies [24, 25], not all thermal properties of spark plasma sintered alumina were fully characterized and investigated. Moreover, influence of process parameters on the properties was not explored. Thermal properties are known to depend on microstructural features and the measured values are not generally applicable unless the effects of microstructure on these properties are understood [22]. In this work, we report temperature-dependent thermal properties of alumina powder and bulk alumina consolidated by spark plasma sintering. The influence of sintering temperature and time on densification and thermal properties will be investigated.
2. Materials and Experimental Procedures

Alpha sub-micron alumina powder having average particle size of 150 nm (99.85 % purity, procured from ChemPUR Germany) was used in this investigation. The powder was directly charged into graphite die of 30 mm in diameter. The samples were sintered in vacuum using fully automated Spark Plasma Sintering equipment (FCT system, Germany), model HP D 5. Heating rate and sintering pressure were kept constant at 100 °C/min and 50 MPa, respectively. Samples were sintered at 1300, 1400, and 1500 °C for 1, 5, and 10 min. Sintering temperature was measured using a thermocouple inserted in a drilled hole in the die. Density of the sintered samples was measured using Metler Toledo balance density determination KIT model AG285 and quantified according to Archimedes principle. Density of samples showing high porosity (density < 92 %) was measured using dimensional method. A high resolution x-ray Diffractometer (Bruker D8, USA, with a wavelength $\lambda = 0.15405$ nm) was used to record x-ray diffraction (XRD) patterns to characterize the samples and calculate the crystallite size (sub-grain size) [26]. The as-received alumina powder was characterized using a Philips transmission electron microscope (TEM), model CM200 200 kV. A Tescan Lyra-3 Field Emission Scanning Electron Microscope (FE-SEM) was used to analyze the microstructure of sintered samples. Thermal properties of sub-micron alumina powder and spark plasma sintered alumina were measured based on the theory of the Transient Plane Source technique, according to ISO standard (ISO/DIS 22007-2.2) [27], using a Hotdisk Thermal Constants Analyser model TPS 2500S. In contrast to the laser flash method where thermal conductivity is calculated from measurements of thermal diffusivity, specific heat, and bulk density [24, 25], the equipment used in this work allows simultaneous determination of thermal properties from a single and quick measurement. Disc shaped specimens with diameter of 30 mm and thickness of 6 to 8 mm were used for thermal measurements taken in the direction of the applied pressure. Each measurement was repeated five times and the average value was reported.

3. Results and Discussion

![TEM image of alumina powder](image)

**Fig. 1.** TEM image of alumina powder.

A TEM image of alumina sub-micron powder is presented in Fig. 1. The powder exhibits a particle size distribution with an average particle size of 150 nm.
Fig. 2 shows XRD spectrum of the alumina powder. Characteristic peaks of $\alpha$-Al$_2$O$_3$ phase such as (012), (104), (113), and (116) can be clearly seen. The average crystallite size (sub-grain size) of the $\alpha$-Al$_2$O$_3$ phase calculated using Scherrer equation was 27.5 nm. Thermal properties of alumina powder, measured between room temperature and 300 °C are presented in Fig. 3.

Fig. 2. XRD spectrum of alumina powder.

Fig. 3. (a) Thermal conductivity, (b) thermal diffusivity and specific heat of alumina powder.

The thermal conductivity, thermal diffusivity, and heat capacity values, of alumina powder at room temperature (25 °C) were 0.15 W/mK, 0.15 mm$^2$s$^{-1}$, and 0.26 J/gK, respectively. These low values are due to the presence of large amount of pores in the powder and the absence of bonding between its particles. In ceramics, thermal conduction is generally due to lattice vibrations called phonons. These phonons interact with the pores and internal defects of the material and are scattered in different directions, resulting in reduced thermal properties. In the case of a powder, the large porosity leads to further reduction of thermal properties. Overall, the increase in temperature from 25 °C to 300 °C decreased thermal conductivity and diffusivity and increased specific heat. The thermal conductivity decreased from 0.15 to 0.131 W/mK i.e. a decrease of 12.66 %. The same trend was observed with the thermal diffusivity, which decreased from 0.15 to 0.097 mm$^2$s$^{-1}$ i.e. a decrease of 35.33 %. However, the specific heat increased from 0.26 to 0.343 J/gK i.e. an increase of 31.92 %.

Fig. 4 shows the relative density of alumina samples sintered at 1000, 1300, and 1400 °C for 1, 5, and 10 min. The sample sintered at 1000 °C for 1 min had a relative density of 60.5 %, which increased to 62.5 and 66.5 % with the increase in sintering time to 5 and 10 min, respectively. When the temperature was increased to 1300 °C, a relative density of 98.5 % was achieved at a sintering time of 1 min. The increase in sintering time to 5 and 10 min led only to a marginal increase in the relative density. Further increase in temperature to
1400 °C resulted in very small increase in the relative density. Almost fully dense alumina with a relative density of 99.6 % was obtained at a sintering temperature of 1400 °C and sintering time of 10 min. Overall, the relative density of sintered samples increased with the increase in sintering temperature and sintering time to reach high value at 1400 °C and 10 min.

This is due to the enhanced diffusion rate [28]. Therefore, the higher the sintering temperature and time, the higher the diffusion rate and the lower the remaining porosity. This can be explained through the dependence of density on sintering temperature [29] as follows:

\[ \rho = s \left( \frac{T}{T_m} \right) + b \]  

where, \( \rho \) is the relative density, \( s \) is the temperature sensitivity, \( T \) is the sintering temperature, and \( T_m \) is the melting temperature.

It is worth mentioning here that full densification of alumina was achieved at a relatively low sintering pressure of 50 MPa, a relatively low temperature of 1400 °C, and short sintering time of 10 min. This can be attributed to the following facts. First, sub-micron particles are characterized by high surface area which enhances diffusion rate. Second, sub-micron powders have high tendency to sintering due to the curvature effect [30]. The “neck region between two particles in contact has a concave surface, which results in reduced pressure. Atoms usually migrate from convex surfaces with positive curvature (high positive energy) to concave surfaces with negative curvature (high negative energy), leading to the coalescence of particles and the elimination of the neck region” [30]. Third, the externally applied pressure contributes to the rearrangement of particles and breakdown of agglomerates, particularly in sub-micron powders. This leads to the increase in driving force for sintering [31]. Third, in SPS process, spark plasma, spark impact pressure, Joule heating, and an electrical field diffusion effect could be generated by the DC pulse discharge. The formation of plasma enhances sintering, however, the role of current is still not clear. It is believed that a local high temperature state momentarily occurs in the gap between particles of the powder because of the spark discharge. This induces vaporization and melting of the surfaces of the powder particles, which significantly increases diffusion rate and leads to higher densification [8].

Similar trend of increase in relative density of alumina with the increase in sintering
temperature was reported by Gurt and co-workers [11]. However, the authors used very high heating rate and applied pressure and reported high densification at a relatively low temperature of 1100 °C. They concluded that holding time could be used as a key to control the porosity in sintered samples. In addition, similar densification behavior of alumina was reported by other researchers [9, 10, 12, 15-18].

![Figure 5](image)

Fig. 5. FE-SEM images of fractured surfaces of alumina samples sintered for 10 min at (a) 1000 °C, (b) 1300 °C, (c) 1400 °C.

FE-SEM images of fractured surfaces, at the same magnification, of alumina samples sintered for 10 min at 1000 °C, 1300 °C, and 1400 °C are shown in Fig. 5. As can be clearly seen in Fig. 5(a), although neck regions were formed between the particles, when alumina powder was sintered at 1300 °C, large pores remained and particles were not fully bounded. However, a dense alumina, almost free from pores, was obtained with the increase in sintering temperature to either 1300 °C or 1400 °C as can be seen in Figs. 5(b) and 5(c), respectively. The microstructure results are in agreement with density results. It is known that if polycrystalline materials are heated to and left at high temperature, grain growth takes place to reduce the excess energy associated with grain boundaries [32]. Fig. 5 shows that the increase in sintering temperature resulted in grain growth; and the higher the temperature, the more this grain growth was because of the enhanced diffusion. Isothermal grain growth dependence on temperature and time is generally described using the following simple equation:

$$G^n - G_n^n = Kt$$

(2)
Where $G_0$ and $G$ are the grain sizes at initial time $t_0$ and isothermal holding time $t$, respectively. $K$ is the material’s constant that depends on the temperature:

$$K = k_0 \exp\left(-\frac{Q}{RT}\right)$$

(3)

where $Q$ is the activation energy for grain growth. $R$ is the gas constant and $T$ is temperature. Although sintering led to grain growth, crystallite size (sub-grain size) of alumina, as measured using XRD remained below 120 nm as presented and discussed below.

XRD spectra of sintered samples were used to calculate the crystallite size (sub-grain size) of alumina using the Scherrer equation [26]:

$$t = \frac{0.94\lambda}{B\cos\theta}$$

(4)

where $t$ is the crystallite size, $\lambda$ is the wavelength of x-ray beam and $B$ is the full width at half-maximum of the diffraction peak on the $2\theta$ scale. The average crystallite size was determined using the (012), (104) (113) and (116) reflections; and presented in Fig. 6. It is known that, “in XRD analysis, when the size of a crystal is used, it usually refers to the size of crystallites concerning a factor, which makes a diffraction peak broad” [33].

The average crystallite size (sub-grain size) of the alumina powder was 27.5 nm before sintering, and increased to around 70 nm for samples sintered at 1000 °C. A further increase in sintering temperature to 1400 °C increased the crystallite size to around 120 nm, as seen in Fig. 6. This clearly shows that the increase in sintering temperature resulted in large increase in crystallite size. However, at the same sintering temperature, the change in crystallite size with time was marginal at 1000 and 1400 °C. This is in agreement with the fact that grain boundary migration and grain boundary diffusion believed to be responsible for grain growth during sintering are largely dependent on sintering temperature and less sensitive to sintering. However, too large holding time may also result in excessive grain growth [9]. Similar trend was observed by Gurt and co-workers [11] were the increase in holding time from 0 to 5 min did not affect grain growth, although the relative density increased from 90.8 to 96.8 %. The authors, proposed the use of holding time to control porosity within samples instead of grain growth. Other researchers reported that alumina
microstructure could be refined using SPS, however, this refinement depends on the starting particle size and is a strong function of sintering temperature, which leads to grain growth. They concluded that both sintering temperature and sintering time need to be optimized to obtain fine-structured ceramics [16]. The small crystallite sizes obtained when samples were sintered at 1000 and 1400 °C for 10 min compared with the relatively large crystallite sizes obtained at the same temperatures but for sintering time of 5 min may be due to refinement effect that may take place during sintering using SPS [16].

Alumina sintered at 1000 °C for 1 min had a low thermal conductivity of 5.29 W/mK. The increase in sintering time to 5 and 10 min led to a marginal increase in thermal conductivity to 6 and 7.24 W/mK, respectively. However, the increase in sintering temperature to 1300 °C resulted in large increase in thermal conductivity to 30.6, 31.37, and 31.72 W/mK at sintering times of 1, 5, and 10 min respectively. Further increase in sintering temperature to 1400 °C only led to marginal increase in thermal conductivity to 32.23, 33.84, and 34.44 W/mK at sintering times of 1, 5, and 10 min, respectively. The same behavior was observed with the thermal diffusivity where alumina sintered at 1000 °C for 1 min had a low thermal diffusivity of 2.6 mm²s⁻¹. The increase in sintering time to 5 and 10 min led to a marginal increase in thermal diffusivity to 2.95 and 3.15 mm²s⁻¹, respectively. However, the increase in sintering temperature to 1300 °C resulted in the increase in thermal diffusivity to 7.18, 7.32, and 7.52 mm²s⁻¹ at sintering times of 1, 5, and 10 min respectively. Further increase in sintering temperature to 1400 °C only led to marginal increase in thermal diffusivity to 7.56, 7.59, and 7.62 mm²s⁻¹ at sintering times of 1, 5, and 10 min, respectively. On the other hand, specific heat followed the same trend as thermal conductivity and diffusivity. Alumina sintered at 1000 °C for 1 min had a low specific heat of 0.84 J/gK. The increase in sintering time to 5 and 10 min led to a marginal increase in specific heat to 0.83 and 0.87 J/gK, respectively. However, the increase in sintering temperature to 1300 °C resulted in the increase in specific heat to 1.13, 1.14, and 1.15 J/gK at sintering times of 1, 5, and 10 min respectively. Further increase in sintering temperature to 1400 °C only led to marginal increase in specific heat to 1.15, 1.20, and 1.22 J/gK at sintering times of 1, 5, and 10 min, respectively.

Thermal conduction in ceramics is mostly due to lattice vibrations called phonons. Phonons’ scattering is quite sensitive to internal defects and porosity. The increase in thermal conductivity, thermal diffusivity, and heat capacity with the increase in sintering temperature and sintering time is due to the increase in relative density and the decrease in porosity as explained above. This trend is in agreement with what published in literature [34]. In addition, the increase in crystallite size and the decrease in sub-grain boundaries contribute to the increase in these thermal properties. The change in thermal properties was more sensitive to sintering temperature compared with sintering time, the same behavior was observed with density and crystallite size.

The effect of temperature on thermal properties of alumina sintered at different temperatures for different times is presented in Fig. 7. A significant increase in thermal properties is observed with the increase in sintering temperature from 1000 to 1300 °C even at short sintering time. Further increase in sintering temperature to 1400 °C only led to marginal change in thermal properties. The same trend was observed in the change of room temperature thermal properties with sintering temperature and time. Overall, thermal conductivity and diffusivity values continued to decrease with an increase in temperature. However, specific heat increased with the increase in temperature. Samples sintered for 10 min at 1000, 1300, and 1400 °C had thermal conductivity values of 7.24, 31.72, and 34.44 W/mK, respectively, at a temperature of 25 °C. These values decreased to 5.18, 18, and 18.3 W/mK, respectively, with the increase in temperature to 250 °C. The same samples had thermal diffusivity values of 31.5, 7.52, and 7.62 mm²s⁻¹, respectively, at a temperature of 25 °C. These values decreased to 1.64, 2.93, and 2.98 mm²s⁻¹, respectively, with the increase in temperature to 250 °C. However, for the
same samples, heat capacity values of 0.87, 1.15, and 1.22 J/gK, respectively, at a temperature of 25 °C, increased to 1.20, 1.54, and 1.55 J/gK, respectively, with the increase in temperature to 250 °C. The change in the obtained results is in agreement with published works [24, 25]. Zhan and Mukherjee [24] consolidated alumina using SPS at 1150 °C for 3 min. They obtained fully dense alumina with room temperature thermal conductivity of 27.5 W/mK. The authors reported a decrease in thermal diffusivity from 0.088 to 0.03 cm²/s with the increase in temperature from 25 to 500 °C. Thermal conductivity, between 300 to 800 K, of Al₂O₃ (200 nm) spark plasma sintered at 1400 for 3 min (50 MPa) was reported by Ahmad and co-workers [25]. They observed a decrease in thermal conductivity from around 34 to 13 W/mK with the increase in temperature from 300 to 800 K.

![Fig. 7.](image)

Fig. 7. (a) Thermal conductivity, (b) thermal diffusivity, and (c) specific heat of sintered alumina.

This work focused on the influence of spark plasma sintering parameters and temperature on thermal properties of sub-micron alumina. The experimental results indicate that thermal properties mainly depend on the densification of samples. Room temperature thermal properties increased with the increase in sintering temperature and time because of the increased densification and reduced porosity. On the other hand, thermal conductivity and thermal diffusivity decreased while specific heat increased with the increase in temperature.
4. Conclusion

In this work, temperature-dependent thermal properties of sub-micron alumina powder and bulk alumina consolidated by spark plasma sintering were reported. The influence of sintering temperature and time on densification, crystallite size (sub-grain size), and thermal properties was investigated. Alumina powder had very low thermal properties due to the presence of large pores and absence of bonding between its particles. Fully dense alumina with relative density of 99.6% was obtained at a sintering temperature of 1400 °C and a holding time of 10 minutes. Thermal properties were found to mainly depend on density. Thermal conductivity, thermal diffusivity, and specific heat of the fully dense alumina were 34.44 W/mK, 7.62 mm²s⁻¹, and 1.22 J/gK, respectively, at room temperature. Thermal conductivity and thermal diffusivity decreased to reach 18.3 W/mK and 2.98 mm²s⁻¹, respectively, at 250 °C. While specific heat increased with the increase in temperature and reached a value of 1.55 J/gK at 250 °C.

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5. References


Садржај: У овом раду, разматрана су термичка својства у зависности од температуре за прах алумине и узорке добијене синтеровањем у плазми. Својства су мерена у температурском интервалу од собне до 250 ºC анализатором са константном температуром. Прх алумине има ниске вредности термичких својстава услед присуства велике порозности и одсуства повезаности честица. Алумин са релативном густином од 99.6 % добијен је синтеровањем на 1400 ºC током 10 мин. Утврђено је да термичка својства зависе главном од густине узорка. Термална проводљивост, термална дифузија и специфична топлота синтероване алумине износе 34.44 W/mK, 7.62 mm²/s, и 1.22 J/gK, истим редом, на собној температури. Термална проводљивост и дифузија опадају док специфична топлота расте са порастом температуре од собне до 250 ºC.

Кључне речи: алумина, синтеровање у плазми, термална проводљивост, термална дифузија, специфична топлота.

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