

Production of Al₂O₃-SiC composites from micrometer α -Al₂O₃ powder obtained via sol-gel

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Received 3 December 2022; accepted 28 December 2022

Alumina (Al₂O₃) is an advanced ceramic material developed for different applications as refractories, precision tools, pacemaker, etc. Solid state sintering of alumina or matrix ceramic composites (CMCs) compacts starts from powders. Once method to produce high quality aluminum oxide powders is the sol-gel technique. Alumina begins as pseudo-crystallized aluminum hydroxide gel which is produced under moderate reaction conditions through a colloidal suspension. In this work, Al₂O₃ powder was produced by precipitation of pseudoboehmite (PB) through sol-gel process. Subsequently, a mixture of Al₂O₃/SiC powders with 5 wt.% of SiC as reinforcement was produced. This mixture was used to manufacture green compacts by uniaxial pressing at 440 MPa. Afterward, some samples were applied a heat treatment (pre-sintered) at 1200°C for 6 h in air. Sintering was carried out in a vertical dilatometer Linseis L75 V up to 1500°C for 2h under argon atmosphere. Pseudoboehmite, alumina powders and Al₂O₃/SiC composites were characterized through X-ray diffraction technique and Scanning Electron Microscopy (SEM). Dilatometric shrinkage data into densification curves obtained were analyzed. Images obtained with SEM showed a uniform Al₂O₃ powder morphology of submicron size, otherwise Al₂O₃/SiC composite images showed the interaction of the reinforcement particles on the ceramic matrix. Experimental results demonstrated the pre-sintering reduce the decomposition of SiC particles on the compact surface. This behavior was attributed to formation of SiO₂ around the reinforcement particle due it act as protective barrier.

Keywords: Composites; alumina; sintering; sol-gel process; dilatometry.

DOI: <https://doi.org/10.31349/RevMexFis.69.031601>

1. Introduction

Commercial applications of aluminum oxide (Al₂O₃) or alumina have increased in biomedical area such as orthopedics implants, bionics prosthetics, oxygen sensors, dentistry tool, scaffolds [1]. The physical properties of alumina components depend on the particle size, porosity, and purity of the ceramic [2], which previously depend on the manufacture of raw material. The principal method used to produce alumina powders is the Bayer process which starts from bauxite ore [2-3]. Basically, bauxite is a hydrated alumina with impurities elements such as clay, silica, magnesium oxide and iron oxide, therefore the principal application of alumina for this route is to aluminum smelting industry [3-4]. Other route to obtain high purity alumina is the sol-gel technique [2,4-5]. Under moderate reaction conditions produced through a colloidal suspension, a pseudo-crystallized aluminum hydroxide gel is obtained [4,6]. Hence pseudoboehmite (AlOOH.xH₂O) is a synthetic aluminum hydroxide gel that acts he as a precursor to transition of alumina: AlOOH, γ , δ and α -Al₂O₃, depending on the heat-treatment conditions [2,7].

Nowadays, advanced alumina-based composite materials are developed with different manufacturing technologies [8,9]. Composite materials are fabricated using reinforcements particles which are added to ceramic powder in order to create heterogeneous materials called ceramic matrix com-

posites [8,9]. Principal application for ceramic matrix composites (CMCs) is for lightweight applications. Aluminum oxide matrix could be reinforced with different metal or ceramics materials. Those reinforcing materials are presented in addition to different forms such as particles, whiskers or fibers. The use of each form depends on the desired characteristics to be search like high strength or temperature stability. Silicon carbide (SiC) reinforcement is a frequently material used together aluminum oxide to increase the fracture toughness resistance at high temperature [8,6].

Mechanical, structural and electrical properties of composite materials are a function of the sintering method. One of the most common methods to produce advanced ceramic materials and CMCs, such as Al₂O₃ and SiC systems, is called conventional route or powder metallurgy route [8]. Conventional route of powder processing involves the mixing of matrix and reinforcement in a suitable aqueous or non-aqueous media, drying of the mixture, powder compaction, and densification at high-temperature [8-10]. That process must be carried out carefully. In some cases, the reinforcement can agglomerate during mixing of powders obtaining a non-homogeneous mixture or poor compaction. Consequently, these problems can produce defects within the green compact and cause important defects in the composite after sintering.

This paper is focused on the synthesis of α - Al_2O_3 powders in order to manufacture composite compacts and the study of the effect of previous heat treatment (pre-sintering) applied to $\text{Al}_2\text{O}_3/\text{SiC}$ green compacts before sintering at high temperature.

2. Methodology

Pseudoboehmite powders was synthesized by sol-gel technique starting from preparation of a solution of commercial aluminum sulfate salt ($\text{Al}(\text{OH})_3 \cdot 18\text{H}_2\text{O}$) in distilled water at 0.5 M. The solution was stirred for 24 h. Subsequently, peristaltic pump was used to drop aluminum sulfate solution into an ammonium hydroxide solution at 60°C and $\text{pH} > 10$ [6]. The product obtained was filtered and washed with distilled water and then was dried at 100°C for 24 hours in air. Thereafter, the pseudoboehmite was sieved at 400 mesh and calcined at 1000°C and 1200°C for 5 hours in air. Pseudoboehmite powders were characterized by particle size, X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques.

Commercial SiC powder ($\leq 97.5\%$ purity) of ALDRICH Chemistry was used as reinforcement. Morphology of SiC particles was angular form, the analysis of particle size was $20.6 \mu\text{m}$ average size. For the fabrication of $\text{Al}_2\text{O}_3/\text{SiC}$ composite, a powder mixture of Al_2O_3 with 5wt.% of SiC was made by rotary evaporation technique using isopropyl alcohol as solvent. The solvent was eliminated at 80°C for 30 minutes during the mixture process. Then, two series of green compacts were produced at 440 MPa by uniaxial pressing; the first compacts were obtained with the mixture powders ($\text{Al}_2\text{O}_3 + \text{SiC}$) and the second compacts with Al_2O_3 powder without reinforcement. The green density in the compacts was about 47%. A set of green samples with 5 wt.% of SiC as reinforcement were a pre-sintered (heat treatment) at 1200°C for 6 h in air before sintering process. Sintering was carried out in a vertical dilatometer Linseis L75 V at $5^\circ\text{C}/\text{min}$ up to the temperature of 1500°C for 2 h under argon atmosphere. The composites produced were transversely cut and polished in order to analyze the interaction of the reinforcing particles

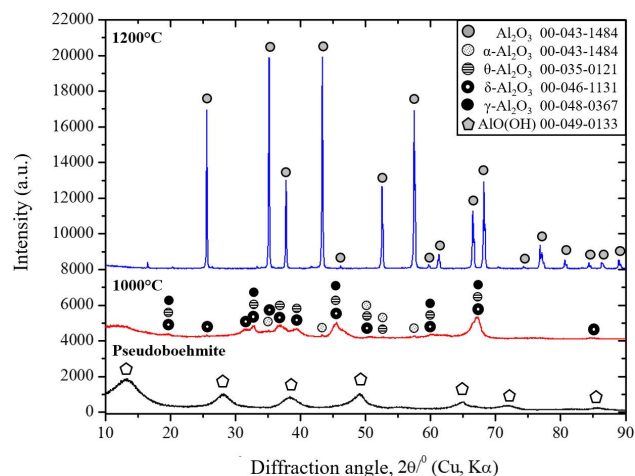


FIGURE 1. XRD patterns of pseudoboehmite powders before and after heat treatment at 1000°C and 1200°C .

in the ceramic matrix by SEM JEOL JSM 7600F. Through the sintering data obtained by the dilatometer, a densification graph was plotted and analyzed to understand the behavior of the material during the heating process.

3. Results and discussion

X-ray diffraction pattern of the pseudoboehmite before and after heat treatment at 1000°C and 1200°C are shown in Fig. 1. Because pseudoboehmite without heating is an aluminum hydroxide $\text{AlO}(\text{OH})$ phase, water alters interplanar distances in a crystalline structure showing widening peaks [10-11]. The transitional metastable phases of Al_2O_3 , α , θ , δ and γ were identified after heat treatment at 1000°C . When heating was at 1200°C , the α - Al_2O_3 phase is exclusively present, corresponding to the most stable phase of aluminum oxide [5-7,10-11]. Therefore, 1200°C is the appropriate temperature to produce α - Al_2O_3 . Results of particle size distribution after calcination reveals principally a bimodal behavior that is shown in the graph in Fig. 2a). Sieving at 400 mesh controls the size of particles smaller than $38.5 \mu\text{m}$. Conse-

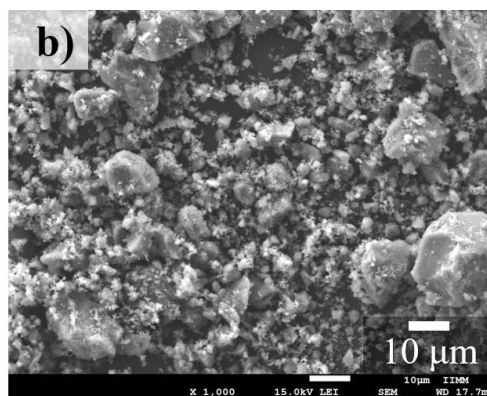
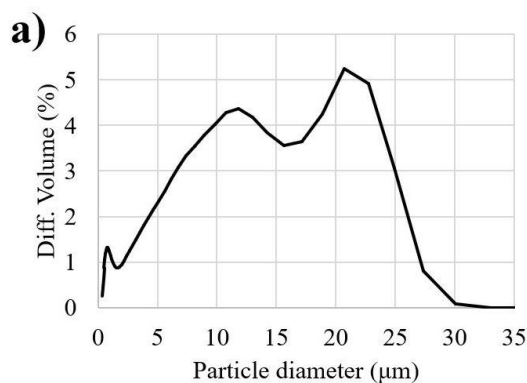


FIGURE 2. α - Al_2O_3 Powders analysis by particle size, a) particle size graph and b) SE-SEM image of powder morphology.

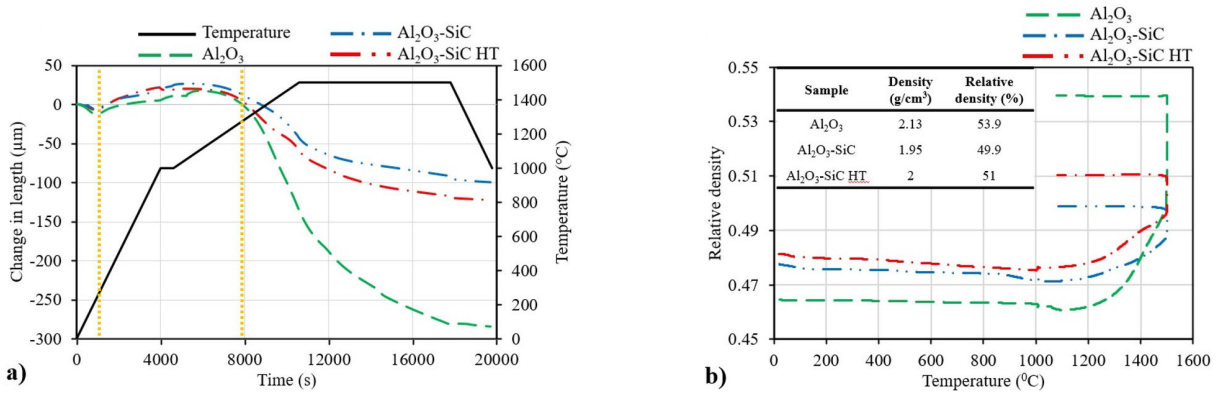


FIGURE 3. a) Shrinkage and b) densification obtained during the sintering process in the dilatometer (1500°C/2h) for the three different compacts (Al_2O_3 , Al_2O_3 -SiC-5% and Al_2O_3 -SiC-5% HT).

quently, graph show a particle size distribution from 30 μm to 0.3 μm , with a mode of 21.69 μm and size average of 6.21 μm respectively. That result is verified in the SEM image at Fig. 2(b). Particle morphology was spherical, with an observed size of less than 10 μm and longer than 20 μm . Larger particles are agglomerates of finer particles which are composed of an extended interconnected porous structure, this phenomenon is called vermicular structure. The sintering of vermicular structures should be carried out at high temperature and pressure to achieve highly densified bodies [11].

After characterization of α - Al_2O_3 micrometer powders, they were used as a matrix to mix with reinforcement silicon carbide powder to produce green compacts. Therefore, three different samples were analyzed: 1) monolithic samples called Al_2O_3 , 2) composites with 5 wt.% of SiC called Al_2O_3 -SiC and 3) same compacts but heat treated (HT) at 1200°C for 6 h in air before sintering called Al_2O_3 -SiC HT. Figure 3a) shows the shrinkage as a function of time during the sintering cycle for the different samples. In this graphic it is observed a low expansion of samples at the initial heating, as the temperature rises from approximately at 1260°C, the contraction of compacts begins, whereas sintering is activated, and it continues until the heating process ends (1500°C/2h). Al_2O_3 sample exhibit the greater shrinkage, as well as the greatest densification of the material, which occurs during the holding time at 1500°C, but the con-

traction continues during all process. The Al_2O_3 ceramic is a material that can be easily sintered. It's not necessary the use of pressure and heating simultaneously (non-conventional route) to obtain a consolidate compact, and it can even be sintered without an inert atmosphere [1]. Al_2O_3 -SiC and Al_2O_3 -SiC HT composites presents a constant contraction at 1500°C. However, in both cases the axial contraction is slower compared with the monolithic sample (Al_2O_3). Al_2O_3 -SiC HT sample reaches a shrinkage of around 2 more than Al_2O_3 -SiC. The relative density was calculated with data obtained as a function of the temperature shown in Fig. 3b).

Initially Al_2O_3 compact had 46.5% of green density. Subsequently, the heating increase the relative density since 53.9% to 1500°C. Composite materials had a green density of approximately 47.5% before sintering. When sintering is achieved, Al_2O_3 -SiC sample reaches 49.9% of relative density, and Al_2O_3 -SiC HT reaches 51% of relative density. However, in both cases a high density is not reached, which can be attributed to the conditions of the starting powders, low density obtained in the green compact through uniaxial pressure, and temperature used in the conventional sintering route.

Figure 4 shows SEM images of microstructure of the three different samples. The area of analysis is a cross-section near the outer surface of samples that were in contact with argon atmosphere. The surface of Al_2O_3 compact in

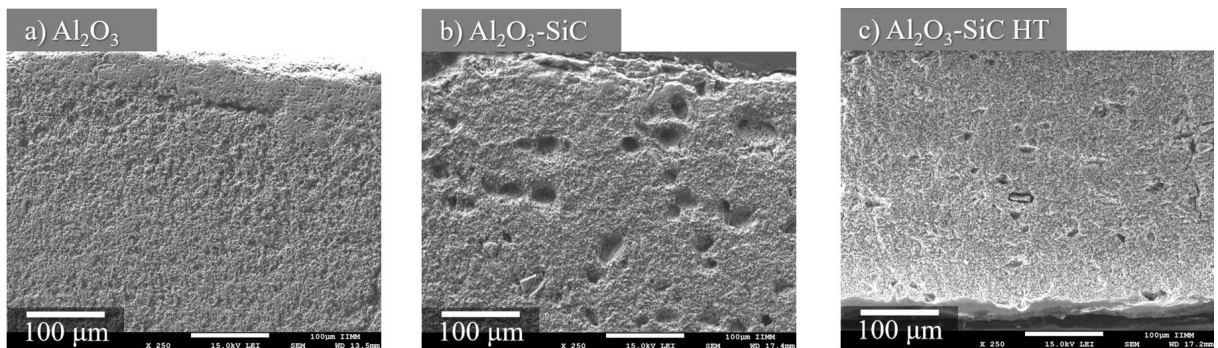


FIGURE 4. SE-SEM images of morphology of sintered compacts at 1500°C/2h, a) Al_2O_3 , b) Al_2O_3 -SiC and c) Al_2O_3 -SiC HT.

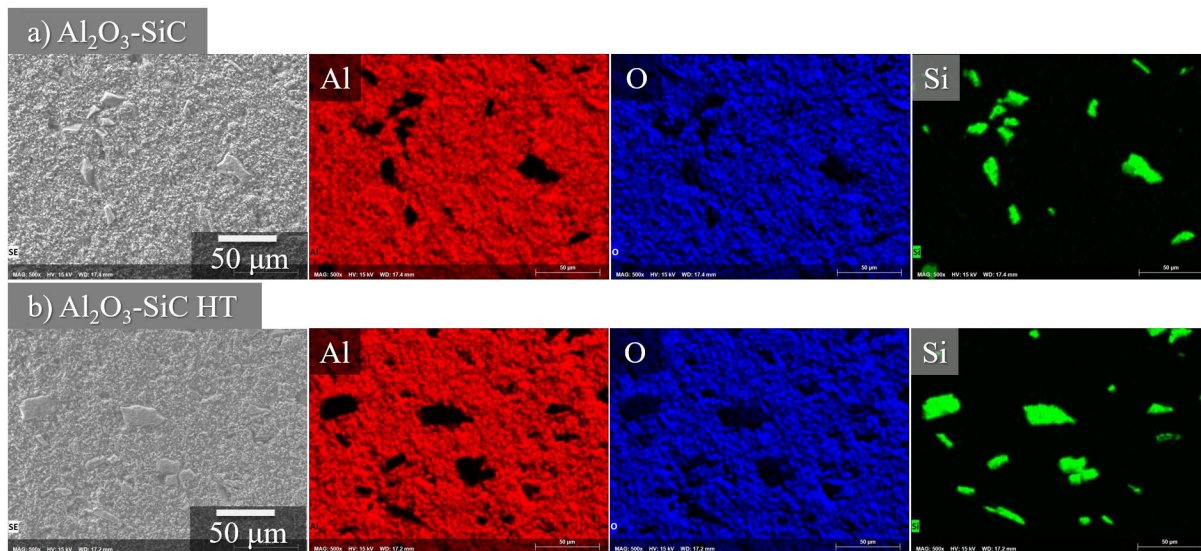


FIGURE 5. Elemental mapping obtained by SEM of the sintered samples, a) $\text{Al}_2\text{O}_3\text{-SiC}$ composite and b) $\text{Al}_2\text{O}_3\text{-SiC HT}$ composite.

Fig. 4a) presents a vermicular microstructure similar to described by E. Yalamac *et al.* [12], he observed low intrinsic nucleation accordingly singly crystal grains of $\alpha\text{-Al}_2\text{O}_3$ at micrometer scale. Those grains were surrounded by continuous pores, which generated a compact of low density. The compact obtained had many pores due the development of low grain boundary. It was as low as reported by Y. Hirata *et al.* [13]. Despite ceramic particles are in contact during the formation of neck, the micro-pores are still open, this indicates an early stage of the sintering process due the development of low grain boundary [14]. Sintered composites in Fig. 4b) and 4c) exhibits a decomposition of SiC reinforcement on the analysis area. The sample $\text{Al}_2\text{O}_3\text{-SiC}$, which was sintered at 1500°C without pre-sintered, show macro pores. Silicon carbide oxidation can occur in the temperature range of $1200\text{-}1400^\circ\text{C}$ as reported by J. Costello and R. Tressler [15]. This means SiC powder is still susceptible to oxidation under the atmosphere of 99.98% pure inert gas. Otherwise, the cross-section of $\text{Al}_2\text{O}_3\text{-SiC HT}$ in Fig. 4c) show a smaller amount of pores. Because a slightly film of SiO_2 was created on the surface of SiC particles during the sintering step, it acted as barrier in the sintering process. The oxidation of SiC in $\text{Al}_2\text{O}_3\text{-SiC}$ was associated with the low contraction of the composites observed in the dilatometry graph. Unlike to $\text{Al}_2\text{O}_3\text{-SiC HT}$, the first undergoes the decomposition of the reinforcement and the densification of the material simultaneously.

To analyze the behavior of the reinforcement particles (SiC) away from the influence of inert atmosphere, an elemental mapping by SEM was carried out inside of samples. Figure 5 show a cross-section of samples, the area of analysis of each one was just on the middle of the piece.

Figure 5a) show these have vermicular microstructure and non-volumetric damage is observed. The reinforcement particles surrounded by the Al_2O_3 matrix in both compos-

ites is clearly and degradation isn't observed. Therefore, SiC particles did not undergo oxidation when reinforcement particles were directly exposed to gas flow and temperature conditions. As a result, particles retaining its original form and shape. The $\text{Al}_2\text{O}_3\text{-SiC HT}$ characteristic reported in Fig. 5b) is similar to 5a).

It was observed that SiC particles remain without any damage or problem within the matrix, also Al_2O_3 matrix presents the vermicular structure that indicates low density. The SiC starting powders have an average size of $20\ \mu\text{m}$ with irregular morphology. In the central part of the compact, these characteristics are maintained. On the other hand, in the upper and lower part of compact, a reduction in size is clearly exhibited (as seen in Fig. 4). The rounding and size decrease of reinforcement particles probably occurred during the sintering of green compact, where silicon carbide being an oxide-free material, is susceptible to oxidation at high temperatures [16]. Analysis of XRD in Fig. 6 show three phases formed in the composite sintered at 1500°C in pres-

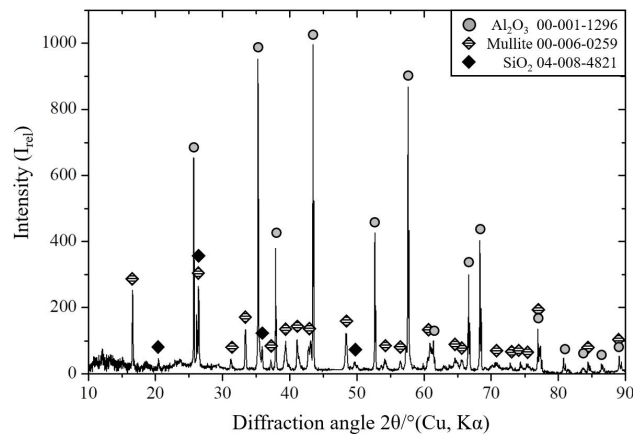


FIGURE 6. XRD patterns of composite $\text{Al}_2\text{O}_3\text{-SiC}$ sintering at 1500°C .

ence of protective argon atmosphere. The reinforcement of SiC reacted with Al_2O_3 matrix to form SiO_2 and aluminum silicate (mullite). As the time is longer, more aluminum silicate is formed. Continuous oxidation of SiC diminishes the particle size until all SiO_2 behaves mullite. If SiC particle size is too big, the final result is a pore with SiC-particle shape surrounded of mullite. Likewise, it has been studied that silicon commonly forms a thin layer of silicon dioxide (passive oxidation) on its surface to suppress further oxidation [13,17]. That is, at very low diffusion rates, a protective layer of SiO_2 is formed. The formation of superficial SiO_2 protects SiC particles from total decomposition of particle and they prevent the appearance of macro-pores in the Al_2O_3 matrix.

4. Conclusions

The results showed a uniform Al_2O_3 powder morphology of submicron size by synthesizing sol-gel technique. Crushing and sifting are necessary prior the heating of PB. To obtain α - Al_2O_3 phase, calcination at temperatures above $1000^\circ C$ is necessary. At lower heating, the transition phases γ , δ or θ of Al_2O_3 are obtained, which can affect subsequent processes.

Through the sintering curves obtained by the dilatometer, the densification of the material during heating was an-

alyzed. The results reveal that the relative density obtained in sintered composite only reaches 51%, because SiC is susceptible to decomposition under the atmosphere of inert gas. Monolithic Al_2O_3 densification increases at higher temperature and longer holding time. By means conventional route, it is possible produce porous compacts with 53.9% relative density. Elemental mapping showed a homogeneous distribution of the reinforcing particles in the ceramic matrix. Microstructural analysis reveals that the two different sintered composites present a decomposition of SiC reinforcement particles on their surface, leaving pores in the material. However, when pre-sintered is performed at $1200^\circ C$ and then sintering, the reinforcement particles do not decompose. Instead, they present a decrease in size and rounding of particles attributed to the formation of SiO_2 on the surface of the SiC. Thus, experimental results demonstrate that pre-sintered treatment reduce the decomposition of SiC particles on the surface.

Acknowledgments

The authors would like to thank Universidad Michoacana de San Nicolás de Hidalgo (UMSNH) and Consejo Nacional de Ciencia y Tecnología (CONACYT) for financial support for this study.

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