

Microstructure and Properties of Al₂O₃–SiC Nanomaterials

Oluwagbenga T. Johnson, *Member, IAENG*, Patrick Rokebrand, and Iakovos Sigalas

Abstract — The relationship between densification, microstructure and mechanical properties of Silicon carbide reinforced Alumina matrix were investigated. The composites were prepared from nano-powders in an attempt to produce composites with nanostructured grains and as a result improved hardness and fracture toughness values. The composite powders were sintered using a Spark Plasma Sintering (SPS) furnace which allows for high heating and cooling rates to be implemented. For the Al₂O₃-SiC composites it was evident that the densification of the materials containing 30% and 50% (by volume) of the reinforcing component was below 97%, whereas for the lower additions of the reinforcing components full densification was observed. The oxygen content of the starting powder was seen to strongly affect the densification behaviour of the Al₂O₃-SiC nano-composites and is also assumed to have resulted in deterioration of the mechanical properties in the Al₂O₃-SiC composites. The hardness values of the Al₂O₃-SiC nano-composite materials were up to 20.7GPa, while the fracture toughness was up to 4.7MPa.m^{0.5}.

Index Terms— Alumina, Silicon carbide, Densification, Microstructure, Mechanical properties.

I. INTRODUCTION

DURING the past 30–40 years there has been a major advance in the development of medical materials and this has been in the innovation of ceramic materials for skeletal repair and reconstruction. The successful performance of an orthopaedic implant is strongly related to its wear properties. During articulation, these implants produce wear debris that is extremely fine and if the particles are within the bioactive size range and high in volume then the surrounding bone degenerates through a process called osteolysis. This results in implant loosening and revision surgery. Therefore the particles generated during articulation must be fine, and of low volume fraction. Ceramic materials present excellent candidates for wear resistance implants, but in spite of this, these materials also have low toughness. The toughness of ceramic materials can be improved by the addition of fillers which reduce the porosity of the finished product, create residual stress fields around the particles and pin grain growth during production.

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O. T. Johnson is with the Department of Mining and Metallurgical Engineering, University of Namibia, Ongwediva campus, P. O. Box 3624. (Corresponding author: phone: +264-814-579-324; e-mail: Johnson.gbenga@gmail.com, ojohnson@unam.na).

Patrick Rokebrand and I. Sigalas are both with the School of Chemical and Metallurgical Engineering, University of the Witwatersrand, P/Bag 3, Wits, 2050, Johannesburg, South Africa. (e-mail: paddy_sa@hotmail.com, iakovos.sigalas@wits.ac.za).

If the fillers added to the ceramic are within a nanometer size range, considerable improvement in the toughness of the ceramic can be achieved through these mechanisms.

Corundum (α -Al₂O₃) is the phase of the alumina that is used for bioceramic materials. This material needs to be of high purity (> 99.9%) and free of impurities such as alkaline oxides and silicates. Alumina is a bioinert ceramic material and as a result it must have a high corrosion resistance in a physiological environment [2]. These high purity alumina bioceramics have been developed as an alternative to metal alloys that have previously been used for orthopaedic implants. The alumina bioceramic materials have a low friction coefficient, high hardness and have a high corrosion resistance which allows for the rate of wear on these materials in bioceramic application to be very low [3]. Alumina (Al₂O₃) is a very popular ceramic, used in various fields. However, it has three weak points: low bending strength, low fracture toughness and a low heat-resistance limit temperature for strength. These weaknesses restrict the application of Al₂O₃ for important components. To overcome some of these weaknesses, researchers began to introduce other ceramic phases into the Al₂O₃ phase [4].

Niihara *et al.* [5-9] were the first to demonstrate that the incorporation of submicron SiC particles can significantly improve the mechanical behaviour of Al₂O₃. Specifically, the addition of as little as 5 vol.% 0.3 μ m SiC not only increased the unindented strength from 380 to 1000 MPa, but also improved the toughness from 3.25 to 4.7 MPa^{1/2}. Thermal annealing at 1300°C for 2 h further enhanced the nanocomposite strength to over 1500 MPa. Subsequently, Zhao *et al.* [10] studied the room-temperature mechanical behaviour of this system. These workers confirmed that the nanocomposite exhibited superior mechanical properties compared with Al₂O₃, but only when both materials had been hot pressed and subjected to industrial machining and subsequent annealing. Annealing for 2 h at 1300°C increased the unindented strength of the nanocomposite from 760 to 1000 MPa. In contrast, the apparent toughness of the nanocomposite (derived from indented strength values) slightly *decreased* after annealing, although it was still higher than the toughness of the machined/annealed Al₂O₃. Although other researchers have made efforts to repeat those results, the strength and toughness reported by Niihara are still difficult to reach so far. The dispersion of SiC homogeneously into Al₂O₃ matrix is found to be very important to fabricate the nano-composites [11].

This study is therefore focussed on enhancing the mechanical properties, especially fracture toughness of Al_2O_3 -based materials by incorporating SiC of different volume content as the secondary phase.

II. PROCEDURE

In this study, Al_2O_3 powder with an average particle size of 100nm (Krahn Chemie GmbH), was mixed with different volume content of SiC (3, 10, 30 & 50 vol %) with an average size of 100nm using lubrizol 2155 (Carst and Walker) as dispersing agent and hexane as a solvent in a planetary mill (Fritsch Pulversette 6). The mill was operated at a speed of 300 rpm for 4 h using 2mm zirconia balls in order to disperse the materials. The mass ratio of grinding balls to the amount of powder being milled was kept at 5:1. After mixing, the powder was dried in a rotary evaporator. The powders were sieved using 20mm diameter Retsch® sieves with 400 μm , 250 μm and 150 μm mesh sizes respectively. The sieving of the powders was carried out in a glove bag under an inert atmosphere made up of argon gas. This was done in order to limit the exposure of the materials to air in order to prevent oxidation.

The sieved powders were then carefully measured into vials with enough powder to produce samples that are 20mm in diameter and 4mm thick. Before the samples can be sintered, it is required that the dispersant present be removed from the samples. This was done by placing the powders that had been sieved in ceramic boats and inserting them into a tube furnace which was heated up to 500°C. A heating rate of 5°C/min was used for both the heating and the cooling of the powders and they were held at the burn-off temperature for one hour. The burn-off of the dispersant was done in an inert atmosphere consisting of 5% Hydrogen – Argon gas.

All the powders were sintered using an FCT HP-D5 Spark Plasma Sintering furnace. The heating rate used in the sintering of the Al_2O_3 -SiC materials was 250°C/min and slowed down to 100°C/min for the final 100°C before reaching the sintering temperature (1400°C- 1700°C) in order to prevent overshooting the sintering temperature. The dwell time used when sintering the materials was 5 minutes.

After sintering the materials were ground on the surface to remove any decomposed layer. The density of the samples was determined using Archimedes principle. Cross-sections of the materials were polished using diamond slurry and were characterized in terms of phase composition using X-ray diffraction, with Cu $K\alpha$ radiation. Diffractograms were collected over a 2θ range of 10-80°, with a step size of 0.02°. All the microstructure observations were done using scanning electron microscopy (Philips, XL30 SERIES) with attached EDX system. The Vickers hardness (H_v) and fracture toughness (K_{IC}) were measured using indentation techniques under 5kg load. The average of five measurements was used to determine the properties of the samples. The K_{IC} was determined via the direct crack measurement method using Anstis's equation [12], with the calibration constant $\xi=0.016$.

III. RESULTS

After binder burn-out, the admixed powders were densified using the SPS machine at temperatures between 1400°C and 1700°C using a heating rate of 250°C /min applying a load of 50 MPa with holding time of 5 min under vacuum in a partially hBN coated graphite tool. The sintered Al_2O_3 -SiC samples were characterized by measuring the density, hardness and the fracture toughness of the materials. For Al_2O_3 - based materials with up to 10 vol.% SiC, more than 98% theoretical density was achieved while the densification began to decrease with increase in the SiC content.

XRD analysis was performed on each of the compositions of the sintered Al_2O_3 -SiC samples. Figure 1 shows the results obtained for the Al_2O_3 -30%SiC and the Al_2O_3 -50%SiC composites. From these results, it is evident that there is a silicon oxide containing phase present in each of the composites investigated. This was determined to be mullite, an aluminium silicate phase with the chemical formula Al_2SiO_5 . The effect of increasing the SiC on the various composites is observed in Figure 1. As the amount of SiC is increased, the intensity of the α - Al_2O_3 begins to decrease as is expected. It is also clear from the XRD analysis that with increasing the SiC composition, the amount of mullite (Al_2SiO_5) that is present clearly increases.

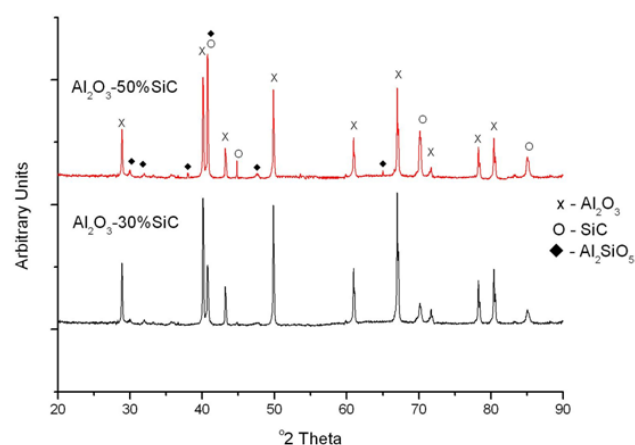


Fig. 1: XRD analysis comparing the Al_2O_3 -30%SiC and the Al_2O_3 -50%SiC composites that were sintered at 1700°C and 50MPa.

SEM images of Al_2O_3 -SiC materials doped with 3 and 50 vol% SiC are shown in Figure 15 and 16 respectively. It can be seen that the grains of the material doped with 3 vol% SiC are well faceted together as compared with the 50 vol% doped material, hence better densification. From the densification results, this composite was found to have been fully densified. However, it is clear that there is some porosity within the sample and the composite has in fact not been fully densified. It is evident from the SEM analysis of Al_2O_3 -50vol% SiC composites it is clear that the composites appear have been fully densified however, from the density measurements it was seen that this composite has a relative density of 93.5%. It is suspected that the discrepancies in these result is due to oxygen contamination in the SiC material and the presence of a SiO_2 containing phase. XRD analysis confirms that there is in fact an alumina silicate phase present within the composites. EDS analysis also

showed the presence of residual carbon within the materials as seen in Figure 2. Each of these will result in a reduction of the theoretical density and therefore increase the relative density and reduce the porosity.

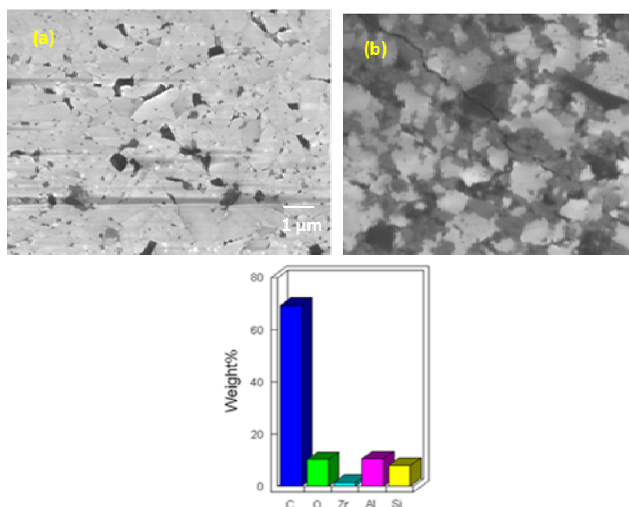
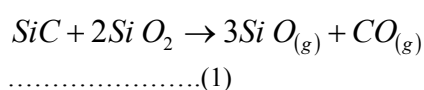


Fig. 2: SEM images of (a) Al₂O₃- 3vol% SiC at 1400°C (b) Al₂O₃- 50vol% SiC materials at 1700°C, 50 MPa for 5 min.

IV. DISCUSSION

Figure 3 shows the dependence of the percentage theoretical density on the SiC content of the sintered Al₂O₃-SiC materials at 1400°C, 1500°C, 1600°C and 1700°C respectively. It was observed that for each sintering temperature investigated, the density of the sintered materials decreased sharply with increase in the SiC content of the composites. This can be attributed to the fact that increasing SiC particles and its agglomerates can strongly retard densification mechanisms by hindering the grain boundary movement. However, it must be noted that if it was porosity that was causing the poor densification, then with increasing temperature the amount of porosity would decrease. This was not the case for the Al₂O₃-30%SiC and the Al₂O₃-50%SiC composites. This suggests that the lower densities are also a result of the carbon content or the formation of glassy phases with lower densities. Therefore the densities are a lower limit of the real densities achieved.

The decrease in the densification results is suspected to be mainly due to the percolation limit being exceeded. However, when looking at the porosity within the composites it is suspected that decomposition of the SiO₂ phase present has also occurred according to the following reaction:



The reaction could be responsible for the decrease of density for the 1600°C and 1700°C sintering temperatures.

Table 1: Mechanical properties of hot pressed B₆O materials

Sintered materials	Dens. (g/cm ³)	Rel. Dens. (%)	Hardness (GPa)	Fracture toughness (MPa.m ^{0.5})
1400 Al ₂ O ₃ .3SiC	3.97	99.8	18.4±0.7	4.7±0.1
1500 Al ₂ O ₃ .3SiC	3.96	99.6	16.8±0.4	4.0±0.1
1600 Al ₂ O ₃ .3SiC	3.96	99.6	20.0±0.6	3.8±0.0
1700 Al ₂ O ₃ .3SiC	3.95	99.3	10.8±1.9	3.8±0.1
1400 Al ₂ O ₃ .10SiC	3.87	98.7	19.1±0.4	3.4±0.2
1500 Al ₂ O ₃ .10SiC	3.87	98.7	17.7±1.2	4.4±0.1
1600 Al ₂ O ₃ .10SiC	3.87	98.7	20.7±0.2	3.3±0.0
1700 Al ₂ O ₃ .10SiC	3.86	98.4	16.2±1.2	4.2±0.4
1400 Al ₂ O ₃ .30SiC	3.65	97.0	17.4±2.0	4.7±0.1
1500 Al ₂ O ₃ .30SiC	3.64	96.7	14.6±0.8	4.5±0.2
1600 Al ₂ O ₃ .30SiC	3.64	96.7	14.5±1.2	4.4±0.3
1700 Al ₂ O ₃ .30SiC	3.62	96.2	13.6±2.0	4.3±0.3
1400 Al ₂ O ₃ .50SiC	3.42	94.9	11.0±0.5	3.9±0.5
1500 Al ₂ O ₃ .50SiC	3.41	94.6	11.1±0.4	4.3±0.1
1600 Al ₂ O ₃ .50SiC	3.38	93.8	14.5±0.1	4.3±0.0
1700 Al ₂ O ₃ .50SiC	3.35	92.9	12.7±0.4	4.6±0.1

Hardness and fracture toughness measurements were performed on the Al₂O₃-SiC materials by means of a Vickers indentation method. The loading force on the microhardness tester was set at 5kg-force. An average was taken from 5 measurements. Table 1 summarizes the mechanical properties of the sintered materials. Hardness values between 11.0 and 20.0GPa and fracture toughness in the range of 3.27 and 4.72 MPa.m^{0.5} were measured depending on the volume content of the secondary phase present in the sintered materials. From the results it is evident that the hardness values obtained for the Al₂O₃-30% SiC and Al₂O₃-50% SiC composites are low. This is attributed to the fact that these samples contain a high amount of glassy phase and residual carbon.

Figure 3 shows the dependencies of the hardness and fracture toughness of sintered Al₂O₃-SiC materials on the SiC content of the starting mixture and sintering temperature. As general tendency it can be seen that the hardness decreases with increase in SiC content of the materials at all temperatures investigated. Additionally, it is interesting to note that the trend followed for the fracture toughness of materials sintered at 1400°C and 1600°C are similar to each other, while those of 1500°C and 1700°C are similar to each other. A possible reason for this is that with increasing the SiC content, the SiO₂ content also increased.

This could result in the formation of glassy phases which would improve densification but, on the other hand, it would form a very brittle and not hard glassy phase. The glassy phase would also result in the SiC not being strongly bonded in the matrix.

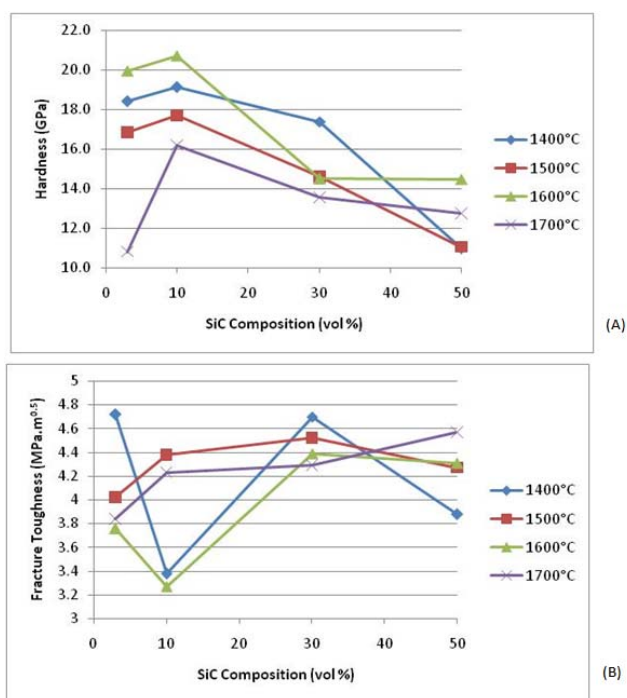


Fig 3: (a) Hv₅& (b) K_{IC} of Al₂O₃-SiC materials as a function of volume content of SiC.

When comparing these results with those from literature [13-14]; it is evident that the Al₂O₃-3%SiC and Al₂O₃-10%SiC composites sintered at 1400°C, 1500°C and 1600°C have hardness values comparable to those in literature. The drop in the hardness is for the remaining composites is suspected to be a result of the formation of glassy phases due to SiO₂ contamination. The residual carbon in the samples is also detrimental to the hardness. The fracture toughness of all the materials are comparable to those seen for alumina based composites from literature.

V. CONCLUSION

Al₂O₃ reinforced with different volume content of SiC were sintered using Spark Plasma Sintering furnace between 1400°C to 1700°C at 250°C/min applying a load of 50 MPa with holding time of 5 min. The properties obtained from the sintered materials showed that there is a decrease in the relative density of the Al₂O₃-SiC nano-composite materials when the reinforcing component (SiC) concentration is increased. The oxygen content of the starting powder was seen to strongly affect the densification behaviour of the Al₂O₃-SiC nano-composites and is also assumed to have resulted in deterioration of the mechanical properties in the Al₂O₃-SiC composites. It is worth suggesting that lower heating rates may improve the densification of the nanomaterials, this would be an option for the sintering of the Al₂O₃-30%SiC composites.

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