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Preparation of AlON ceramics via reactive spark plasma sintering

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Abstract

Al_2O_3 and AlN powder mixtures were used to synthesise AlON ceramics using the reactive spark plasma sintering (SPS) method at temperatures between 1400 and 1650 °C for 15–45 min at 40 MPa under N_2 gas flow. AlON phase formation was initiated in the samples sintered above 1430 °C, according to the X-ray analysis. The complete transformation of the initial phases (Al_2O_3 and AlN) into AlON was observed in the samples that were spark plasma sintered at 1650 °C for 30 min at 40 MPa. A high spark plasma sintering temperature together with a low heating rate produced a greater amount of AlON formation at a constant process time. The densification, microstructure and mechanical properties of the produced ceramics were analysed. The highest hardness value was recorded to be 16.7 GPa, and the fracture toughness of the sample with the highest AlON ratio was measured to be 3.95 MPa $m^{1/2}$.

Keywords: Spark plasma sintering; Aluminium oxynitride; Powder solid state reaction; Microstructure-final; X-ray methods

1. Introduction

Aluminium oxynitride is a relatively new ceramic that is mostly utilised in applications such as abrasives and armour materials because of its desirable mechanical and optical properties.[1,2] Over the years, various methods have been used to obtain AlON ceramics, including hot pressing, pressureless sintering and hot isostatic pressing. These methods were not only applied to AlON powders but also to mixtures of Al_2O_3 and AlN in different ratios.[3–6] Because the process is low-cost and it is easy to obtain high-purity AlON fine powders in the final product, the reaction sintering of Al_2O_3 and AlN is the preferred synthesis method.[2]

The sintering process for AlON ceramics has typically been carried out at temperatures above 1650 °C and with very high soaking times. For instance, Zientara et al.[5,7] hot pressed their powders at 1950 °C for 2 h. Boey et al.[8] sintered green tapes at 1550, 1600 and 1640 °C with soaking times ranging from 5 to 10 h to produce composites containing Al_2O_3, AlN and AlON. Kumar et al.[9] processed AlON by gel casting and slip casting of aqueous colloidal AlN/Al_2O_3 powder mixtures, then sintered the mixtures at 1925 °C for 2 h, obtaining at least 99% theoretical density. Zhang et al.[10] proposed a new one-step pressureless sintering using α-Al_2O_3 and aluminium powder as raw materials. The starting material was first nitridised into high activity AlN, and then $Al_{23}O_{27}N_5$ was synthesised in situ from AlN and α-Al_2O_3. The optimal one-step pressureless sintering process was determined to occur at 1750 °C for 2 h, which caused the flexural strength to increase to 321 MPa. Subsequently, Clay et al.[11] produced aluminium oxynitride ceramics by hot isostatic pressing at 2000 °C for 1–15 h duration. Cai et al.[12] sintered the powders at 1650 °C for 2 h under an Ar atmosphere in a muffle furnace and at 1750 °C for 1 h under an Ar atmosphere in an induction furnace. Lower sintering temperatures and shorter durations, such as 1650 °C for 1 h, could only be achieved by the microwave sintering reaction of Al_2O_3 and AlN into AlON performed by Cheng et al.[2]

From the phase diagram produced by Corbin[13], the 13 aluminium oxynitride phases can be classified into two groups based on their crystallographic structures: wurtzite and spinel. It is known that the stability range for the spinel phase occurs near the $9Al_2O_3{\cdot}5AlN$ composition (64.3 mol% Al_2O_3, 35.7 mol%

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AlN).[2,11,13–15] Studies have been done to investigate the effects of different Al_2O_3 and AlN ratios on the composition as well.[14,16]

In recent years, a new sintering process, spark plasma sintering (SPS), has attracted attention because it allows the rapid compaction of highly dense ceramics and alloys at relatively low temperatures and with shorter holding times compared to conventional techniques. In addition to these stated advantages, SPS also provides high heating rates that increase the possibility of obtaining fine-grained products; these advantages make SPS uniquely suitable for manufacturing ceramics that have advanced mechanical, thermal and optical properties.

However, to date there have been no reports of attempts to produce AlON ceramics by a spark plasma sintering process, which could enable the use of lower temperatures and shorter processing times.

In this study, the rapid densification of reaction-sintered AlON with a composition of 64.3 mol% Al_2O_3 and 35.7 mol% AlN by spark plasma sintering at relatively low temperatures ($\leq$1650 °C) was attempted. The phases present in the sintered sample were analysed by X-ray diffractometry. Additionally, the effects of variation of the sintering parameters, such as temperature, heating rate and holding time on the AlON formation, hardness and microstructures of ceramics were analysed.

2. Materials and methods

Al_2O_3 (Inframat Advanced Materials Farmington, CT, 99.99% purity) with an average particle size of 100 nm and AlN (Grade E, Tokuyama Soda Ltd.) with an average particle size of 1 μm were used as starting materials.

The powders were weighed in quantities corresponding to a composition of 64.3 mol% Al_2O_3 and 35.7 mol% AlN. They were mixed by ball milling for 24 h with alumina balls in an ethanol medium. The dried and granulated powder mixtures were loaded to a graphite die with a 50 mm inner diameter. A graphite sheet was inserted into the small gap between the punches and mould, and the graphite mould was covered with carbon heat insulators.

Samples were sintered using a spark plasma sintering apparatus (SPS-7.40MK-VII, SPS Syntex Inc.) at a mechanical pressure of 40 MPa under a nitrogen atmosphere. A pressure of 40 MPa was applied at room temperature in order to ensure the proper electric contact between the powder and the graphite die, and the pressure was kept steady during heating. The heating process used a 12:2 DC pulse sequence, implying that the current was ON for 12 pulses (3.3 ms each) and OFF for two equivalent time intervals.

Experiments were conducted in three groups to investigate AlON formation by varying spark plasma temperature, time and heating rate. In the first group of experiments, the powder mixtures were spark plasma sintered at 1400, 1430, 1500 and 1520 °C for 15 min at a heating rate of 100 °C/min. The second group of experiments was carried out at 1500 °C for 15, 30 and 45 min at a heating rate of 50 °C/min. In the third group of experiments, the samples were spark plasma sintered at 1500, 1550, 1580 and 1650 °C for 30 min at a heating rate of 50 °C/min. The temperature of the SPS process was measured with an optical pyrometer that was focused on the surface of the die. The current was controlled manually. The linear shrinkage of the specimens during the SPS process was continuously monitored by displacement of the punch rods. The effect of the thermal expansion of the graphite punch rods with increasing specimen temperature was negligible. The sintered specimens were in the form of discs that were 50 mm in diameter and 2 mm thick, which were sand blasted in order to remove the graphite sheet.

The surfaces of the specimens were polished carefully for further mechanical, chemical and microstructural characterisations. The bulk densities of the specimens were determined by the Archimedes' method, using distilled water as a wetting agent. The crystalline phases of the sintered specimens were identified by X-ray diffractometry (XRD, PANalytical X-Pert Pro) in a 2θ range of 10–90° with Cu Kα radiation. The hardness and fracture toughness (K_{IC}) were obtained from indentation measurements using a Vickers diamond indenter (Struers, Duramin A300) at a load of 9.8 N. The fracture toughness values were evaluated from the half-length of a crack formed around the indentations using the following equation.

$$K_{IC} = 0.016\left(\frac{E}{H}\right)^{1/2}\left(\frac{P}{c^{3/2}}\right) \quad (1)$$

where K_{IC} is the fracture toughness, E is the elastic modulus, H is the hardness, P is the load and 2c is the full crack length produced by Vickers H_v indentation. The average of the 20 measurements for each sample was used for evaluation of the sample hardness and toughness. The microstructures of the specimens were observed by scanning electron microscopy (SEM, Model JSM 7000F, JEOL).

3. Results and discussion

The specimen densification during the SPS process was evaluated based on the displacement of punch rods caused by shrinkage of the samples. Fig. 1 shows the displacement and shrinkage rate of the Al_2O_3/AlN powder mixtures that were spark plasma sintered at a temperature up to 1430 °C for 15 min at a heating rate of 100 °C/min (Fig. 1a) and 1650 °C for 30 min at a heating rate of 50 °C/min (Fig. 1b). The specimen heated to 1430 °C began to shrink at 1185 °C, and shrinking was completed at 1430 °C. The specimen that was spark plasma sintered at 1650 °C started to shrink at 1136 °C, and shrinking was completed at 1650 °C. In Fig. 1a, in the temperature range from 600 to 1430 °C, a single, narrow shrinkage peak can be observed at 1297 °C, indicating fast consolidation.

However, in Fig. 1b, in the temperature interval between 600 and 1650 °C, two shrinkage peaks can be detected at 1245 °C and 1650 °C. Sintering began at 1136 °C, when the material was still composed of two phases (Al_2O_3 and AlN). A sudden expansion of the specimen occurred at 1397 °C, which corresponds to the beginning of the reaction between Al_2O_3 and AlN. The slightly volume increase is due to the difference between the unit cell volumes of starting material and AlON. The shrinkage

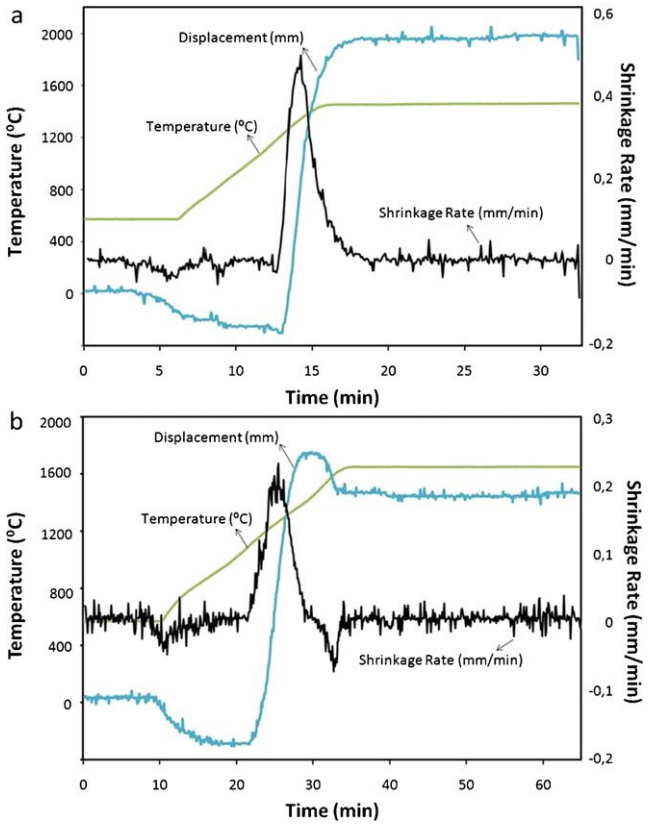

Fig. 1. Displacement and shrinkage curves for the sintering compaction with increasing temperature in SPS under pressure of 40 MPa: (a) heating to 1430 °C for 15 min at a heating rate of 100 °C/min and (b) heating to 1650 °C for 30 min at a heating rate of 50 °C/min.

rate began to increase when the temperature reached 1542 °C. The formation of a liquid phase caused further densification between 1542 and 1650 °C. These results were also compared with the study by Ashuach[17], in which AlON was formed by reactive sintering of an Al_2O_3/AlN powder mixture by heating the mixture up to 2000 °C at a rate of 5 °C/min for 15 h. Sintering started at 1100 °C, close to the usual sintering start temperature in this study. Specimen expansion took place at a temperature of 1760 °C, higher than that of the AlON forming spark plasma sintered specimens.

XRD patterns as a function of spark plasma sintering temperature are given in Fig. 2 for the samples containing 64.3 mol% Al_2O_3 and 35.7 mol% AlN densified by reactive spark plasma sintering at a heating rate of 100 °C/min for 15 min. It can be seen that spark plasma sintering at 1400 °C did not result in the synthesis of single spinel-phase AlON. A part of the AlON phase began to develop in the sample that was spark plasma sintered at 1430 °C, but a considerable amount of the unreacted Al_2O_3 and AlN phases still existed. The amount of AlON that was formed dramatically increased between 1430 and 1500 °C. Further increase in the spark plasma sintering temperature did not cause any additional increase in AlON formation. With increased spark plasma sintering temperature, AlON appeared as a reaction product, while the intensities of peaks belonging to the starting materials simultaneously decreased. No other intermediate phase formation could be observed. These results are

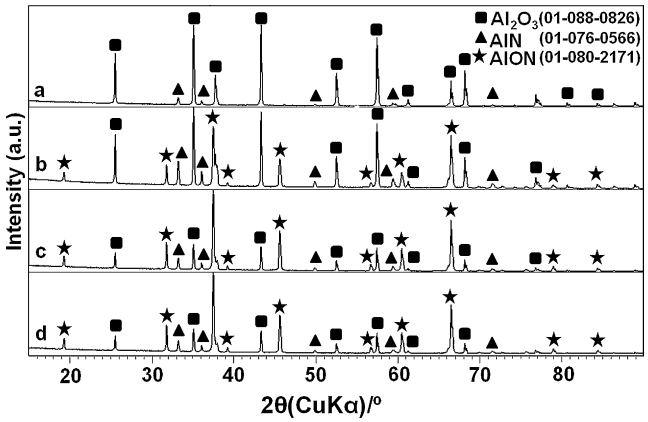

Fig. 2. XRD patterns of samples spark plasma sintered at (a) 1400 °C; (b) 1430 °C; (c) 1500 °C and (d) 1520 °C for 15 min.

similar to those reported by Boey et al.,[8] proving that the higher temperature facilitated ionic diffusion.

The XRD spectra of the samples sintered at 1500, 1550, 1580 and 1650 °C at a heating rate of 50 °C/min for 30 min are compared in Fig. 3. Unreacted AlN existed up to 1580 °C and disappeared at 1650 °C. Supporting the results of an XRD Rietveld analysis, shown in Table 1, the reaction yield remained low up to 1430 °C. The AlON content increased and reached a maximum value of 66.3% at 1520 °C in the samples that were spark plasma sintered with a 100 °C/min heating rate for 15 min. Al_2O_3 disappeared completely within 30 min during spark plasma sintering at 1500 °C. Further increase in the holding time did not cause any change in AlON content. The amount of AlON was 97.2% in the ceramic that was spark plasma sintered at 1580 °C, as shown in Table 1. Total AlON conversion was observed in the sample that was spark plasma sintered at 1650 °C.

According to investigation by Bandyopadhyay et al.[18] temperature and time affected the reaction sintering of the Al_2O_3/AlN mixture for reactions started above 1560 °C, and AlON appeared as a single phase after a 2.5 h treatment at 1800 °C.

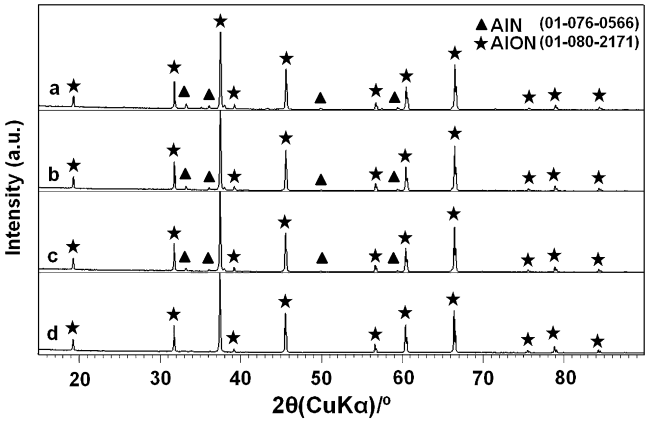

Fig. 3. XRD patterns of samples spark plasma sintered at (a) 1500 °C; (b) 1550 °C; (c) 1580 °C and (d) 1650 °C for 30 min.

Table 1
Al_2O_3, AlN and AlON contents obtained from XRD Rietveld analysis.

Sintering temperature (°C)	Holding time (min)	Heating rate (°C/min)	Al_2O_3 Relative percentage (%)	AlN Relative percentage (%)	AlON Relative percentage (%)
1400	15	100	95.2	4.8	–
1430	15	100	55.7	12.1	32.2
1500	15	100	26.5	8.4	65.1
1520	15	100	25.0	8.7	66.3
1500	15	50	9.9	7.3	82.8
1500	30	50	–	4.7	95.3
1500	45	50	–	4.9	95.1
1550	30	50	–	3.4	96.6
1580	30	50	–	2.8	97.2
1650	30	50	–	–	100

The density values of the spark plasma sintered AlON ceramics at 1400, 1430, 1500 and 1520 °C and 40 MPa pressure for 15 min at a heating rate of 100 °C/min and 1550, 1580, and 1650 °C for 30 min at a heating rate of 50 °C/min under a nitrogen atmosphere are given in Table 2. Because of the presence of an unreacted Al_2O_3 phase at 1400 and 1430 °C, these densities are found to be higher than the theoretical density of AlON (3.71 g/cm^3), and they are much closer to the density of Al_2O_3. The density values had a tendency to approach to the theoretical density of AlON with increasing spark plasma sintering temperature, holding time and reduced heating rate. However, 98.7% of the theoretical density was achieved by spark plasma sintering at 1650 °C for 30 min, where some residual pores in the sample prevented transparency.[19]

The hardness values of ceramics containing more than % AlON are listed in Table 3, ranging between 16.7 and 18.0 GPa.

Table 2
Measured density values of AlON ceramics.

Sintering temperature (°C)	Holding time (min)	Heating rate (°C/min)	Measured density (g/cm^3)
1400	15	100	3.91
1430	15	100	3.72
1500	15	100	3.68
1520	15	100	3.67
1500	15	50	3.67
1500	30	50	3.66
1500	45	50	3.65
1550	30	50	3.66
1580	30	50	3.67
1650	30	50	3.66

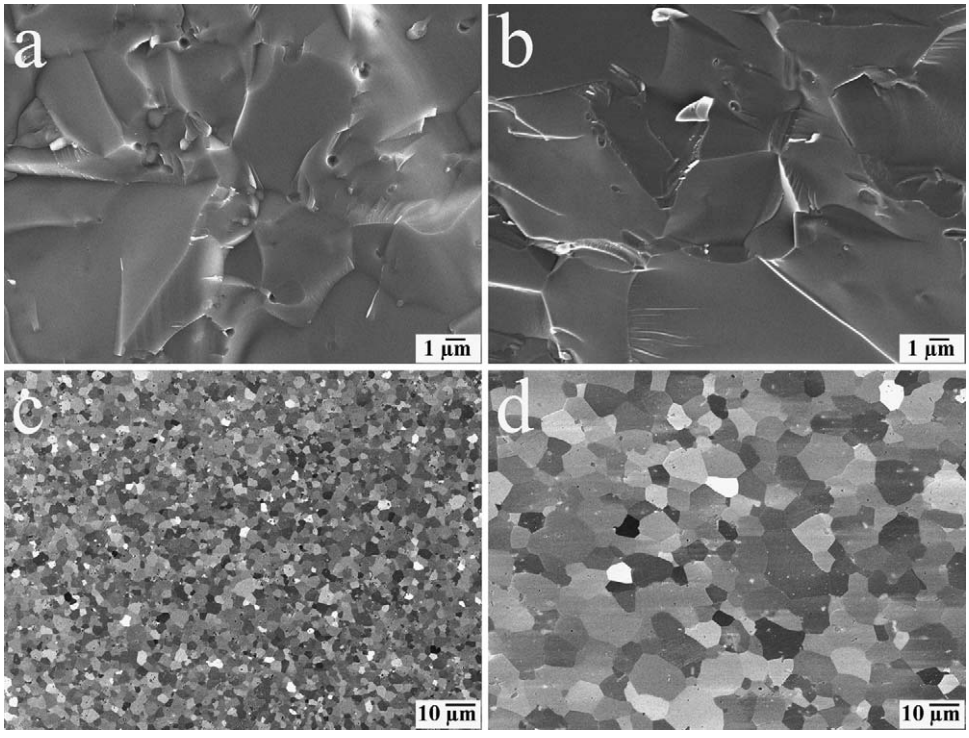

Fig. 4. SEM images of fracture surfaces of AlON ceramics spark plasma sintered at (a) 1550 °C for 30 min; (b) 1650 °C for 30 min. SEM images of polished surfaces of AlON ceramics spark plasma sintered at (c) 1550 °C for 30 min and (d) 1650 °C for 30 min.

Table 3
Hardness values of AlON ceramics.

Sintering temperature (°C)	Holding time (min)	Hardness (GPa)
1500	15	18.0 ± 0.4
1500	30	16.9 ± 0.2
1550	30	17.4 ± 0.4
1580	30	17.1 ± 0.6
1650	30	16.7 ± 0.7

The specimen that had the highest alumina phase content, sintered at 1500 °C for 15 min, resulted in the highest hardness value. The sample with the highest AlON ratio, spark plasma sintered at 1650 °C for 30 min, had a hardness of 16.7 ± 0.7 GPa and a fracture toughness of 3.95 ± 0.3 MPa $m^{1/2}$. This fracture toughness result is comparable with the sample that was hot pressed at 1800 °C at 25 MPa in N_2 gas flow for 3 h, reported by Xidong et al.[20]

The SEM images of the fracture surfaces of the samples that were spark plasma sintered at 1550 °C for 30 min (Fig. 4a) and 1650 °C for 30 min (Fig. 4b), along with the SEM images of the polished surfaces of the samples that were spark plasma sintered at 1550 °C for 30 min (Fig. 4c) and 1650 °C for 30 min (Fig. 4d) are presented in Fig. 4. The fracture mode appears to be transgranular fracture. Because of the increased spark plasma sintering temperature, larger grain sizes and dense microstructures were observed in the sample that was spark plasma sintered at 1650 °C for 30 min, while some occasional pores were found in the samples that were spark plasma sintered at 1550 °C for 30 min. According to EDS analysis, it was found that the colour differences in the microstructures are caused by the different orientations of grains, not to composition differences.

4. Conclusions

AlON ceramics were produced by reactive spark plasma sintering of an Al_2O_3/AlN powder mixture. AlON formation by spark plasma sintering in the temperature range of 1400–1520 °C with a holding time of 15 min and a heating rate of 100 °C/min under nitrogen was investigated. Further experiments were carried out in the temperature range of 1500–1650 °C for different holding times with a 50 °C/min heating rate. According to the XRD results, no AlON formation occurred in the samples that were spark plasma sintered at 1400 °C. Reducing the heating rate from 100 to 50 °C/min and increasing the holding time from 15 to 30 min increased the degree of AlON formation. Moreover, increasing the spark plasma sintering temperature from 1430 to 1650 °C significantly increased the degree of AlON phase formation. Although most of the studies on AlON formation by reaction sintering of Al_2O_3 and AlN powders have indicated that sintering temperatures above 1650 °C and a sintering duration longer than 2 h require volume diffusion to obtain pure, dense AlON ceramics, spark plasma sintering yielded pure AlON ceramics above 98.5% of the theoretical density by sintering at 1650 °C for 30 min with a 50 °C/min heating rate. The hardness of this ceramic was recorded to be 16.7 GPa, and the fracture toughness was measured to be 3.95 MPa $m^{1/2}$.

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