

Research on Technical Ceramics and their Industrial Application: Preparation Techniques and Properties of Transparent AlON Ceramics

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Abstract

Aluminium oxynitride (AlON) has a unique thermal and chemical stability that makes it the perfect candidate for a wide range of applications. This article provides a brief description and comparison of the most common AlON preparation methods along with their advantages and disadvantages. Although there has been extensive research on the material, especially more recently because of increased commercial interest, extensive systematic powder synthesis and processing studies have not been carried out to determine alternate, more cost efficient routes to fully dense transparent bodies. Further optimization of reaction sintering and transient liquid phase sintering could be important processing routes.

Keywords: AlON, transparent ceramics, Hot Isostatic Pressing (HIP), Spark Plasma Sintering (SPS).

1. Introduction

The discovery of aluminium oxynitride goes back to the 1970s, when researchers in Japan, the United States and France found that additions of nitrogen into aluminium oxide resulted in new spinel-like phases. This translucent aluminium oxynitride spinel ceramic was named AlON, a unique material exhibiting many important properties which make it useful in many applications and others yet to be determined. Currently commercially available AlON materials exhibit average grain sizes in the order of 150–200 μm ; however, development of new methods to control the grain size, especially at the nano-scale could create materials with improved properties. Because of its high hardness, there are still significant cost issues associated with final machining and polishing, especially for large bodies [1].

The individual properties of the AlON material lie in its unique crystal structure. Generally, it can be said that substitution of nitrogen for oxygen in Al_2O_3 or, conversely, substitution of oxygen into AlN stabilizes new phases with significantly different crystal structures and symmetry (space group): $\alpha\text{-Al}_2\text{O}_3$, AlON and AlN rhombohedral,

cubic, and hexagonal, respectively. AlON, having the cubic spinel structure, can be thought of as nitrogen stabilized cubic aluminium oxide. It has many properties comparable to $\alpha\text{-Al}_2\text{O}_3$, but because of its cubic crystal structure, fully dense, polycrystalline bodies can be completely transparent if processed properly [2]. Other properties, like dielectric loss tangent, can be extremely low because of the lack of thermal expansion-induced residual strain at grain boundaries. AlN is an intriguing material because its theoretical thermal conductivity at room temperature is extremely high for a dielectric material and comparable to, or higher than many metals [3].

2. Overview of preparation techniques

Over the years several different processing routes have been used to produce fully dense, transparent polycrystalline AlON ceramics [2–14]. Their main parameters are summarized in Table 1. McCauley [2] used reaction sintering of Al_2O_3 –AlN mixtures. The reaction sintering technique has also been used by others [15,16]. Generally, the pressureless sintering, hot pressing and hot isostatic pressing (HIP) techniques have used AlON

Table 1. Summary and characteristics of AlON techniques

Method		Advantages	Disadvantages	Ref.
Pressureless sintering	Sintering that is performed using only temperature.	<ul style="list-style-type: none"> – Production procedure is simple – Cost effective 	<ul style="list-style-type: none"> – Higher temperature is needed than in hot pressing techniques 	[4]
Hot pressing (HP)	Combination of uniaxial pressure and temperature.	<ul style="list-style-type: none"> – Production procedure is simple – Sintering density is high, – The quality of end products is good with high density 	<ul style="list-style-type: none"> – Expensive (high pressure, high temperature) – Only simple shapes can be created 	[5]
Hot isostatic pressing (HIP)	Simultaneous application of heat and hydrostatic pressure to compact and densify a powder.	<ul style="list-style-type: none"> – High density can be achieved – Densification can be completed in shorter times and at lower temperatures than conventional sintering – Products with complex geometry can be produced – The quality of end products is good 	<ul style="list-style-type: none"> – Expensive (high pressure and high temperature, expendable tools) – The processes are complex – Small production quantities 	[6, 7]
Spark plasma sintering (SPS)	The process applies pressure and (pulsed) current flow through the sample at the same time in vacuum	<ul style="list-style-type: none"> – Fast heating, – Effective for densification of a wide variety of materials – Densification occurs at lower temperature and is completed more rapidly than in other methods 	<ul style="list-style-type: none"> – Complicated setup and limited sample shape – Hard to operate, – Expensive pulsed DC generator is required 	[8–10]
Carbothermal synthesis (CT)	The technology uses graphite furnace at different temperatures (1700–1860 °C) and pressures (0.1–10 MPa) in N ₂ atmosphere	<ul style="list-style-type: none"> – Simple – Cost effective – Possible to obtain very fine powder with a low metal impurity 	<ul style="list-style-type: none"> – Higher temperatures and longer reaction times needed – Thermal decomposition process is too complex – Carbon impurities 	[13]
Direct nitriding	Thermochemical surface treatment process, Al–Al ₂ O ₃ starting mixtures	<ul style="list-style-type: none"> – Simple – Cost effective 	<ul style="list-style-type: none"> – Lower transparency – Lower quality of product 	[14]

powders to produce pore free, fully dense AlON ceramics. AlON powders can be synthesized by simple reaction of Al₂O₃ and AlN, carbothermal reduction of Al₂O₃. Significant variations in hardness, flexure strength and fracture toughness were observed. The friction, wear resistance and other mechanical properties of the Al₂O₃–AlON family of materials has also been systematically studied [17, 18]. High sintering temperature and long sintering time are two major problems in the above methods. Therefore, it is critical to lower the sintering temperature and reduce the sintering time without reducing material performance.

3. State of the art in development of AlON

The most commonly used and promising techniques in industry are the HP, HIP and SPS. Shan et al. [9] used spark plasma sintering (SPS) in their research work with Al₂O₃ and AlN powder mixtures to produce AlON ceramics. The SPS was performed at temperatures between 1400 and 1650 °C for 15–45 min. at 40 MPa under N₂ gas flow. They found that AlON phase formation was initiated in the samples sintered above 1430 °C. The complete transformation of the initial phases (Al₂O₃ and AlN) into AlON was observed in the

samples that were spark plasma sintered at 1650 °C for 30 min at 40MPa. A high spark plasma sintering temperature together with a low heating rate yielded a greater amount of ALON formation at a constant process time.

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 produced 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 [9]. The ALON ceramics can also be prepared by SPS at low temperature (<1650 °C) and short sintering time (5–15 min.), however, the hardness and the relative density became a little higher and a little grain growth was found with increasing soaking time. Although relative density increased and pores gradually disappeared, the grain size of ALON also grew with the holding time. Larger grains led to a decrease in the flexural strength and elasticity modulus. Fully dense ALON ceramics cannot be fabricated by SPS without sintering additives whether under nitrogen or vacuum. Moreover, ALON ceramics possessed better properties fabricated under vacuum than under N_2 atmosphere [10, 11]. By using different additives, the residual porosity of transparent ALON can be reduced to a minimum. Although sintering additives can reduce the sintering temperature and increase the density of ALON ceramics, it is important to avoid generating a second phase that would reduce the transparency of ALON ceramics [12].

Chen et al. [7] prepared highly transparent ALON composite ceramics by hot isostatic pressing (HIP) of the sintered bodies composed of fine grains (~20 μm). They also found that sintering additives play a huge role in the porosity and pore positions of the sintered ALON bodies, which can determine the final pore elimination during HIP sintering. They claimed that compared to single Y_2O_3 or La_2O_3 additive, the co-doping of $\text{Y}_2\text{O}_3/\text{La}_2\text{O}_3$ additive is more effective in preparing a sintered ALON body with small intergranular pores and lower porosity. The developed transparent ALON ceramic had an in-line transmittance as high as 85.0 % at 1100 nm with low concentration of additives. The transmittance was sensitive to the microstructure of presintered ALON bodies.

Except for the strong driving force enabled by HIP method, the small amount of $\text{Y}_2\text{O}_3/\text{La}_2\text{O}_3$ additives was effective in fabricating pre-sintered ALON bodies with small intergranular pores and lower porosity. Such ALON bodies were then easy to densify during HIP sintering and were significant to give high transparency. The necessary additives for the HIP-ed ALON ceramics (4.2 mm thick) to achieve full density were 0.08 % Y_2O_3 and 0.02 % La_2O_3 , much lower than previously reported data in pressureless sintered samples (0.12 % Y_2O_3 and 0.09 % La_2O_3).

The densities and transparency characteristics of ALON prepared by different techniques are compared in Figure 1. It can be seen that the relative densities of ALON prepared by different methods are all close to 100 %, which demonstrates their effectiveness in obtaining pure and dense ceramics. According to the thorough literature survey, the transparency of ALON ceramics produced by different methods shows significant differences. The lowest transparency was measured in the case of the CT method (65 %), while in the other methods the transparency values of all samples were above 75 %. The highest transparency was measured in the case of SPS technology (79.2±2.4 %).

Nowadays, there are several companies that produce ALON ceramics for different use.

The pathway of incident and reflected light is illustrated schematically in Figure 2.

The interference between the incident light and the polycrystalline ceramics can be understood by further examination of the mechanism

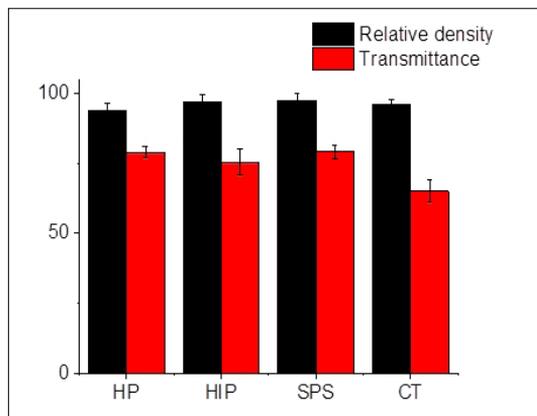


Figure 1. Relative densities and transmittance percentages (in visible wavelength range) of ALON samples prepared by different techniques. The relative density was calculated using a theoretical density of 3,71 g/cm³

of refraction and reflection of light. In general, distortion often occurs close to the surface of a ceramic and at grain boundaries. Local distortion and strained layers resulting from surface processing give rise to localized changes of refractive index, causing light to be scattered and affecting the optical transmittance (Figure 3).

In Figure 4 és 5 we demonstrate the applied characteristic temperature ranges of investigated preparation techniques as well as the hardness values of the yielded transparent ceramics. It can be seen that the hardest AlON ceramic can be achieved by SPS method at the lowest preparation temperature. AlON can serve as a model material for polycrystalline ceramics and, because of its transparency, real time diagnostic observations can be easily carried out in many mechanical tests. Other possible applications of AlON materials include transparent armour, EM domes and windows, military aircraft and missile domes, IR windows, hyper-hemispherical domes, laser windows, military aircraft lenses, semiconductor processing applications, and scanner windows (point of sale (POS) windows).

Figure 6 shows the flexural strength of different AlON samples. It is visible that the highest strength belongs to the AlON ceramic prepared by SPS method, while the differences in the values of flexural strength in the cases of ceramics prepared by HP and HIP methods are insignificant. The sample prepared by CT method has the lowest strength.

The other important mechanical property for possible industrial application is fracture toughness. The changes of this parameter in samples prepared with different methods are presented in Figure 7.

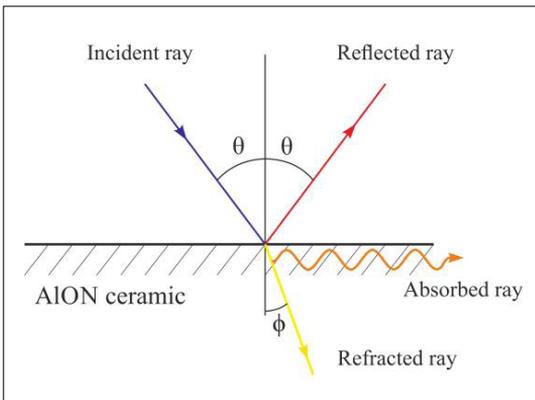


Figure 2. Schematic illustration of the reflection and re-fraction mechanism of light

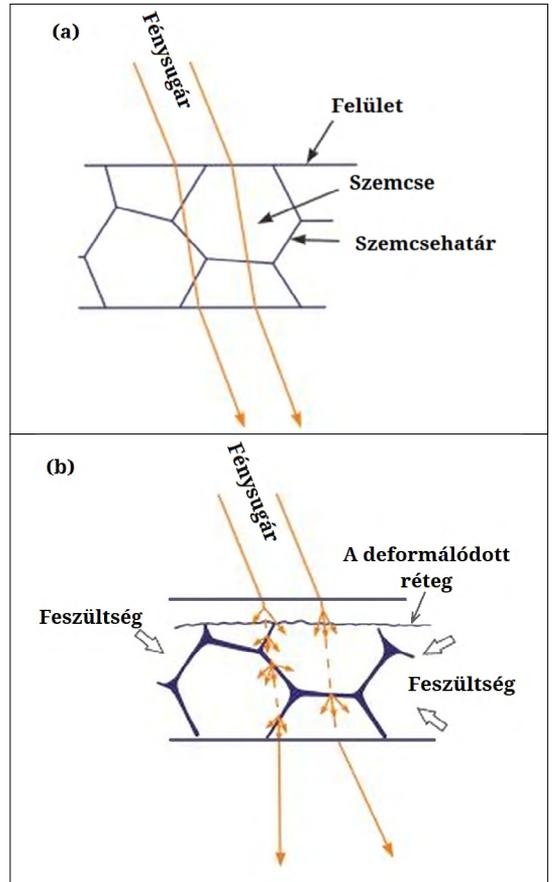


Figure 3. Interaction scheme between the light and the isotropic polycrystalline ceramics. (a) Ideal homogenous polycrystal with theoretical density. Light is not scattered about grain boundaries. (b) Polycrystal with internal strain and external stress. Light is scattered in the inhomogenous region

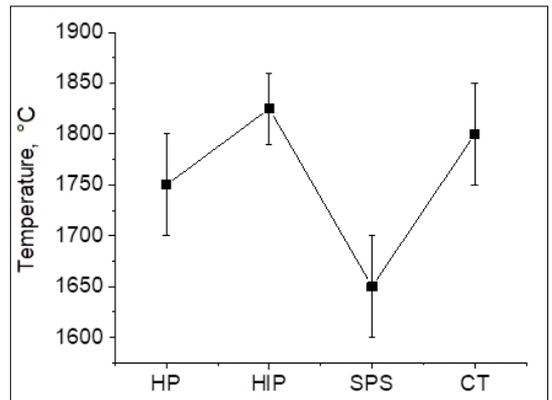


Figure 4. The applied temperature ranges in different techniques

In this case, similarly, the sample prepared by SPS has the highest fracture toughness, while the lowest toughness value belongs to samples prepared by CT method.

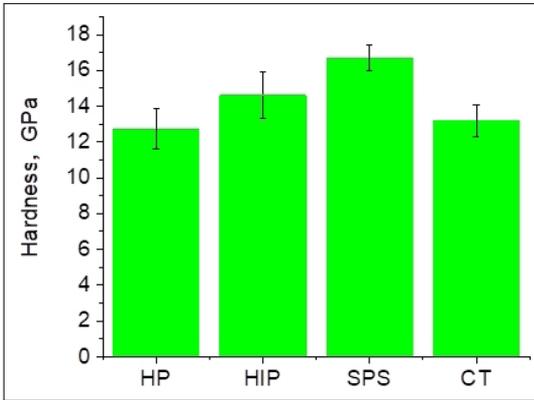


Figure 5. The hardness values of AION samples prepared by different techniques

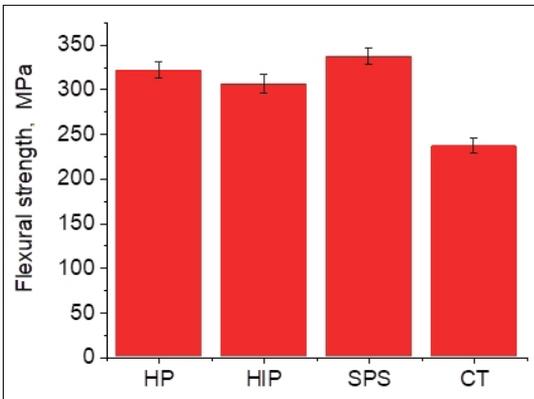


Figure 6. Flexural strength values of AION samples prepared by different techniques

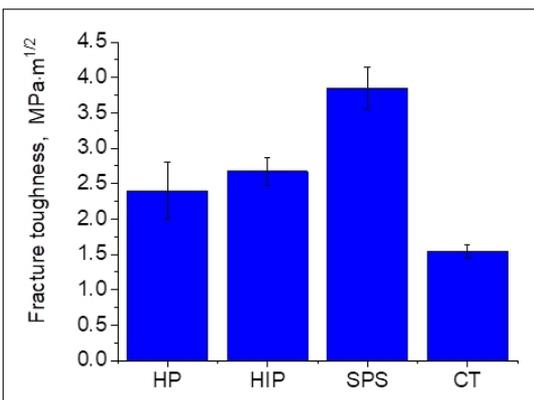


Figure 7. Fracture toughness of AION samples prepared by different techniques

Zhao et al. [5] studied the effect of different additives, such as SiC and ZrN nano-particles on the mechanical properties of AlON ceramic. Their work revealed that the nano-sized additives positioned at grain boundaries of micro-sized AlON particles and the presence of SiC and ZrN nano-particles resulted in the reduction of both porosity and grain size, and a change of fracture mode from intergranular cracking in AlON to intragranular cracking in composites. With presence of small amount (5-8 %) of additive particles, the relative density, microhardness, flexural strength and fracture toughness increased owing to the hindered crack propagation processes. Li et al. [11] prepared transparent AlON ceramic by SPS method. Their results showed that fully dense AlON ceramics cannot be fabricated by SPS without sintering additives whether under nitrogen or vacuum. There was even a contradiction between transparency and mechanical properties of AlON ceramics with increased holding time, heating rate and sintering temperature. Although sintering additives can reduce spark plasma sintering temperature and increase the density of AlON ceramics, generation of a second phase that would reduce the transparency of AlON ceramics should be avoided.

4. Conclusions

According to the thoroughly studied literature data and the state of the art on AlON preparation we can conclude that the currently available and used techniques are still all expensive, as well as being energy and time consuming. High temperatures above 1600–1900 °C are needed for a long time to achieve appropriate phase and densification. We intend to develop an eco-friendly preparation method of AlON in which we develop a novel way to reduce the temperature and/or time thus requiring lower energy (technique, temperature and so on). Moreover, we are planning to recycle and utilize the industrial by-products or aluminium waste (such as aluminium cans) as Al source.

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