

Pressureless Reaction Sintering of AlON Using Aluminum Orthophosphate as a Transient Liquid Phase

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Michael Bakas
Henry Chu

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PRESSURELESS REACTION SINTERING OF ALON USING ALUMINUM ORTHOPHOSPHATE AS A TRANSIENT LIQUID PHASE

Michael Bakas, Henry Chu
Idaho National Laboratory
Idaho Falls, ID USA

ABSTRACT

Use of aluminum oxynitride (ALON) in transparent armor systems has been difficult due to the expense and limitations of the processing methods currently necessary to achieve transparency. Development of a pressureless processing method based on direct reaction sintering of alumina and aluminum nitride powders would reduce costs and provide a more flexible and practical manufacturing method. It may be possible to develop such a processing method using liquid phase sintering; as long as the liquid phase does not remain in the final sample. AlPO_4 forms a liquid phase with Al_2O_3 and AlN at the temperatures required to sinter ALON, and slowly decomposes into P_2O_5 and alumina. Therefore, it was investigated as a possible transient liquid phase for reaction-sintered ALON. Small compacts of alumina and aluminum nitride with up to of 15.0 wt% AlPO_4 additive were pressed and sintered. It was found that AlPO_4 formed the requisite transient liquid phase, and it was possible to adjust the process to produce ALON samples with good transmission and densities of 3.66-3.67 g/cc. XRD confirmed the samples formed were ALON, with no trace of any remaining phosphate phases or excess alumina or aluminum nitride. Based on the results, it was concluded that AlPO_4 could be utilized as a transient liquid phase to improve the density and transmission of ALON produced by pressureless reaction sintering.

INTRODUCTION

Aluminum oxynitride (ALON) is a transparent polycrystalline material. Reviews of the history of the material and its development have been presented by Corbin (1989)¹ and McCauley et al (2009)². The most complete $\text{Al}_2\text{O}_3/\text{AlN}$ phase diagram³ was published by McCauley and Corbin and is provided in Figure 1 for reference. Interest in ALON is driven by its potential for use in armor and infrared detector applications. Currently the cost of ALON is high due to the hot pressing or HIPing necessary for pore-free microstructure and the expense of pre-synthesized ALON powder. The goal of this research was to develop a method for producing transparent ALON at reduced cost by eliminating the need for pressure assisted densification and utilizing cheaper starting powders.

An alternative to using ALON powder is reaction sintering of Al_2O_3 and AlN .^{1,2,4} Reaction sintering was used by McCauley and Corbin to produce translucent ALON in their initial work⁴ forming γ -ALON as a dense polycrystalline material. When fired in a pressureless process, ALON has intragranular porosity that is difficult to remove.^{5,6}

A liquid phase sintering process could possibly eliminate this porosity prior to it becoming intragranular. It is necessary for any liquid phase sintering of ALON to be transient as any remaining liquid phase would impair transmission. The sensitivity of transient liquid phase processes to processing conditions makes them difficult and time consuming to develop.⁷ Not only must the correct additive be identified, but numerous processing variables such as heating rate, maximum temperature, and hold times must be defined if porosity or swelling is to be avoided.^{7,8}

Previous research has discovered that certain additives can be beneficial to the sintering of ALON. Hartnett, Gentlemen, and Macquire have reported that additives such as yttrium and lanthanum improve the sintering and microstructure of ALON, and subsequent researchers have also reported on the beneficial nature of these additives.^{5,10} However, these additives can only be added in limited amounts; otherwise their solubility in ALON is exceeded and second phases form.^{5,10} An additive that

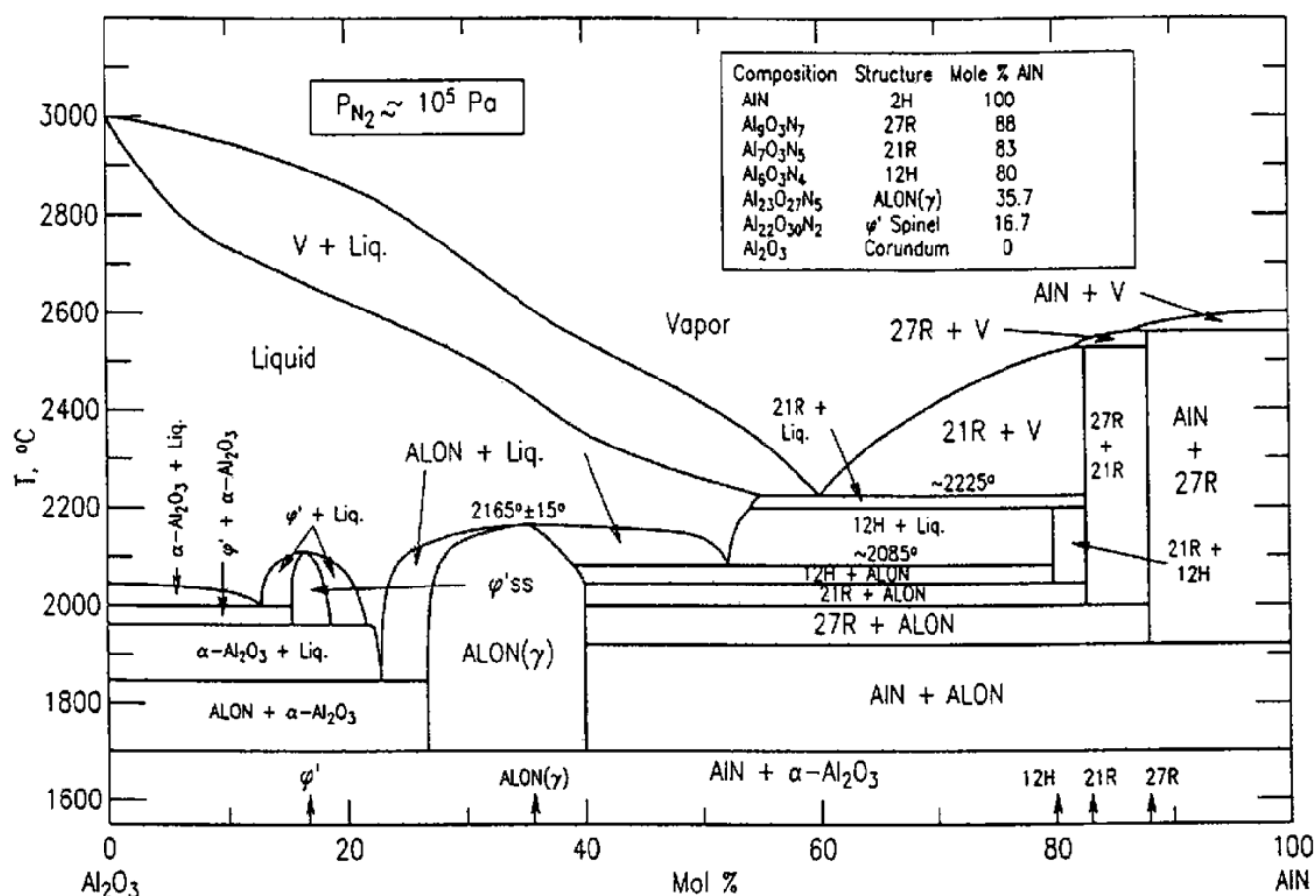


Figure 1. Phase Diagram of Al₂O₃/AlN system plotted by McCauley and Corbin. Printed with the kind permission of McCauley.³

can be added in amounts capable of eliminating nearly all porosity is needed if transparency is to be achieved. LiAl₅O₈ was investigated as such an additive by Cutler, Clay, Poslusny, Flinders, and Jacobs.¹¹ In this work, AlPO₄ was investigated as an additive that possibly meets this criteria.

AlPO₄ was chosen as a possible solution because the AlPO₄/Al₂O₃ phase diagram¹² indicates the formation of a liquid phase at ~1850°C. At temperatures greater than 1600°C, AlPO₄ decomposes into P₂O₅ gas and Al₂O₃.¹³ As the Al₂O₃ will react to form ALON, it should be possible to add as much AlPO₄ as desired without the formation of second phases.

EXPERIMENTAL PROCEDURE

The alumina powder used alternated between Ceralox SPA-0.5 and Alcoa calcined alumina. The aluminum nitride powder was high purity Tokuyama powder grade E, and the aluminum orthophosphate was produced by Acros Organics. The alumina and aluminum nitride were batched according to the desired AlN mol% relative to the alumina. Subsequent discussions that reference the AlN mol% of a sample or settling powder refer to this batched value, not the AlN mol% including other additives or the final AlN mol% of the sample. The AlPO₄ was added as a wt% to the batched alumina and aluminum nitride mixture, with the amount varying from 0.5 to 20.0 wt%. Batches of 20-35g of the desired mixture were dispersed in ethanol with PVP added as a dispersant and B60A as a binder. Mixing was performed with a high speed shear mixer for a minimum of ten minutes at 6000 rpm. The slip was subsequently poured into a drying tray and dried at 45°C for 24 hours. After drying, the powder cake was removed from the tray and ground with an alumina pestle and mortar. This mixture was then sieved through a 100 mesh and measured out into ~5g samples that were

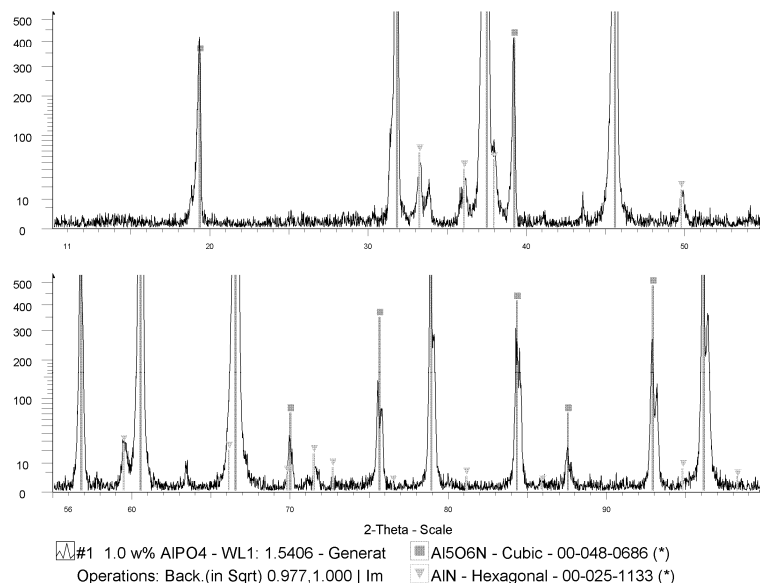


Figure 2. XRD of sample batched to 35.0 mol% AlN with 1.0 wt% AlPO₄ added, fired at 1950°C for 18 hours.

AlON,¹⁴ samples were packed in a settling powder mixture of alumina, aluminum nitride, and occasionally other additives, such as boron nitride or yttria, for protection. The settling powder mixtures were mixed dry for 1 hour in a Turbula mixer in a Nalgene bottle. Prior to firing, a small bed of settling powder was laid out on the bottom of the crucible. The sample was placed on this powder bed and covered with additional settling powder.

After firing, sample densities were measured using Archimedes's method with water. A Bruker-AXS D8Advance X-ray diffraction system was used to identify the primary phases present. For microscopy, samples were polished to a 1 micron finish and etched with hot phosphoric acid for ten minutes. Optical microscopy was performed using a Keyence DHX digital microscope, and scanning electron microscopy was performed with a Phillips XL 300 ESEM with an attached EDAX EDS system for compositional analysis. When trace compositional analysis was needed, samples were analyzed with a JEOL 8900 electron microprobe.

RESULTS

First Series of Experiments

The goal of the first series of experiments was to determine if the AlPO₄ could be used for reaction sintering of AlON without any phosphate phases remaining in the final sample. Samples fired with small amounts (0.5 wt% to 1.0 wt%) of AlPO₄ do not have phosphate phases measurable with XRD. Figure 2 is an XRD of a sample batched to 35.0 mol% AlN with 1.0 wt% AlPO₄ that was fired for 18 hours at 1950°C. It indicates that the primary phase present is γ -AlON, with some AlN peaks from incomplete reaction. The appearance of the samples is white with limited translucency.

Having demonstrated that AlPO₄ could be added without adverse effect on the reaction sintering of AlON, the amount of AlPO₄ was increased in subsequent experiments. Sample appearance becomes more translucent with increasing AlPO₄ content. These early samples were fired in a settling powder mixture of Al₂O₃ and AlN batched to 35.0 mol% AlN. A problem occurs with the settling powder as AlPO₄ content increases. While the settling powder is easily brushed off samples with little or no AlPO₄, additions of 10.0 wt% of AlPO₄ cause the settling powder to bond to the surface of the

pressed with a ram pressure of 10,000 lbs/in². Samples were subsequently CIPed at a pressure of 60 ksi. After CIPing, samples were fired in air at 600°C for 15 hours to remove any binder and organics. Samples were stored in a desiccation chamber that was first put under vacuum and subsequently flooded with nitrogen to minimize any reaction of AlN with moisture.

Samples were fired in BN crucibles machined from Saint Gobain AX06 BN. The furnace used was an Astro Industries 1000A series furnace with carbon elements. The atmosphere was dry nitrogen at a pressure of 2 psig. Temperature was controlled with an optical pyrometer.* As carbon has been established to be detrimental to

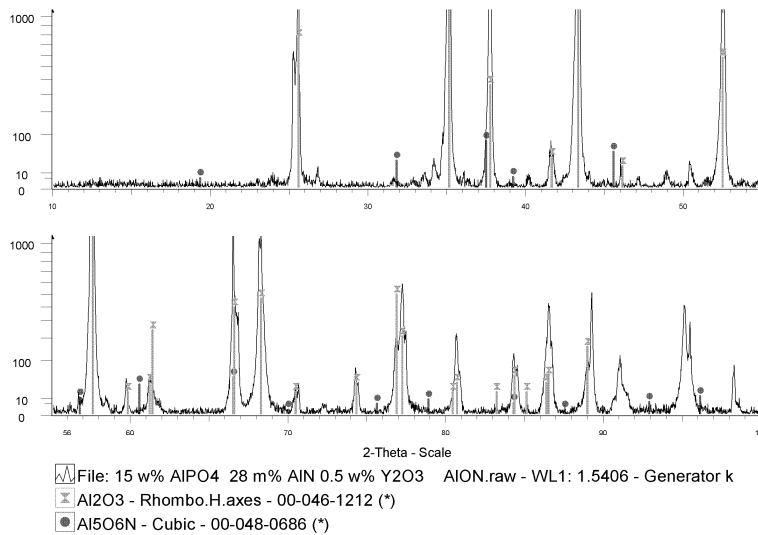


Figure 3. XRD of 28.0 mol% AlN sample with 15.0 wt% AlPO_4 fired at 1950°C for 18 hours in a 28.0 mol% AlN settling powder with 0.5 wt% Y_2O_3 .

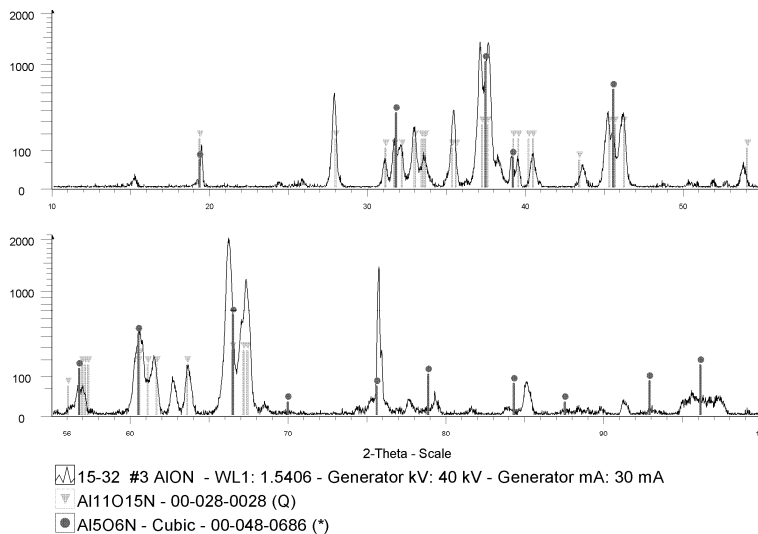


Figure 4. XRD of 32.0 mol% AlN sample with 15.0 wt% AlPO_4 fired at 1950°C for 18 hours in 28.0 mol% AlN settling powder with 0.5 wt% Y_2O_3 .

samples in such a manner that mechanical grinding is necessary to remove it. In an attempt to prevent this bonding, 10.0 wt% of BN was added to the settling powder.

BN powder did not prevent the settling powder from bonding to the sample. A subsequent XRD found non-AlON phases in the sample. Even accounting for the Al_2O_3 added by the decomposition of the phosphate, the composition of these samples should have been within the single phase AlON region of the phase diagram in Figure 1. A subsequent sample fired without any settling powder had an extremely low density. Based on these results, it was suspected that the bonding of the settling powder to the sample was indicative of a more significant interaction than first suspected.

Second Series of Experiments

The goal of the second series of experiments was to further investigate the interaction between AlPO_4 containing samples and the settling powder and determine if this interaction could be of a beneficial nature. The results of this series indicate that during the course of the interaction, material is introduced from the settling powder into the sample. This additional material can shift the AlN mol% of the sample from its nominal batched value and introduce additives in the settling powder into the

sample. The greater the degree of interaction, the greater the magnitude this compositional shift is. The phases observed in the final sample depend on the initial compositions of sample and settling powder and the severity of the interaction. Results indicate that settling powder composition, temperature, and sample composition all influence the degree of interaction. Different phases observed in various samples included the desired γ -AlON, a phase tentatively identified as ϕ' phase AlON,** and

corundum. Figures 3 and 4 show some example XRD patterns of samples created in this series. Temperatures of greater than 1900°C are necessary for any significant densification to occur. Increasing the temperature seemed to increase the degree of interaction, causing the compositional shift to be of greater magnitude and sample density to increase. Increases in the AlPO_4 content up to 15.0 wt% assist the interaction, while amounts greater than 15.0 wt% appear to be detrimental to densification. Y_2O_3 additions in the settling powder, even in small amounts (0.3-0.5 wt%), greatly increase the degree of interaction. SEM performed on samples fired in settling powders with Y_2O_3 additions found yttrium rich phases on the grain boundaries.

Samples containing primary phases of γ -AlON and ϕ' phase AlON appeared to have good translucency compared to other samples produced in the second series. Microscopy confirmed the presence of a second phase on the grain boundaries, and EDS indicated the composition of these phases was similar to that published for ϕ' phase AlON. These samples can be produced reliably using a settling powder mixture of 20.0 mol% AlN, and 0.5 wt% Y_2O_3 . These samples of γ -AlON and ϕ' phase AlON have a translucent appearance, but when polished appear to have small areas of transparency. Subsequent anneals of these samples do not eliminate the ϕ' phase AlON.

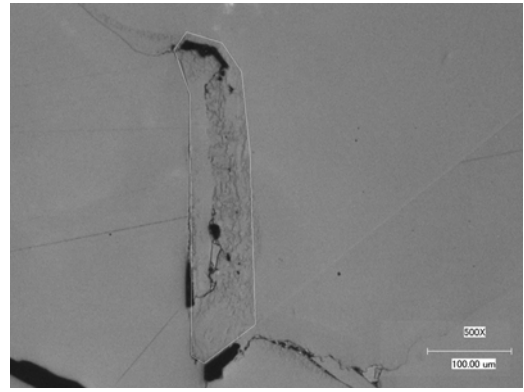


Figure 5. 500X Optical Micrograph of 44.0 mol% AlN sample. ϕ' phase AlON is faintly outlined.

Third Series of Experiments

This series of experiments focused on improving the appearance of the samples by eliminating the ϕ' phase AlON. It was hypothesized that the interaction with the settling powder was driving the AlN content of the sample out of the γ -AlON region and into a region of γ -AlON and liquid (see Figure 1), with the liquid phase forming ϕ' phase AlON upon cooling. An increase of the AlN mol% could compensate for this shift and produce samples of pure γ -AlON. A series of samples containing 15.0 wt% AlPO_4 and increasing amounts of AlN were fired with all other factors kept constant. The settling powder composition was a 20.0 mol% AlN mixture, with a 0.5 wt% Y_2O_3 addition. Hold time was 18 hours at 1950°C, with 10°C/min heating and cooling rates.

As AlN mol% in the sample increases, the XRD peaks identified with ϕ' phase AlON are less prominent relative to those of γ -AlON. At 44.0 mol%, the XRD patterns appear to be pure γ -AlON, but microscopy finds ϕ' phase AlON present. Figure 5 shows an optical micrograph of the ϕ' phase AlON and Figure 6 shows the appearance of this sample. While somewhat transparent, the ϕ' phase AlON is clearly visible in the sample and impairing transmission. Increasing AlN mol% to 46.0 mol% eliminates the ϕ' phase AlON, but sample density decreases and appearance becomes poor. Subsequent experiments indicate that samples of a nominal

44.25 mol% AlN or greater have poor density under the firing conditions in this series. As can be seen from Table I, the drop in density is quite abrupt for samples of greater than 44.0 mol% AlN.

Table I Densities of Selected Series 3 Samples

Sample AlN mol%	Density	AlON Phases Present
40.0%	3.632 g/cc	ϕ' and γ
41.0%	3.619 g/cc	ϕ' and γ
44.0%	3.637 g/cc	ϕ' and γ
44.25%	3.545 g/cc	γ
46.0%	3.563 g/cc	γ

Fourth Series of Experiments

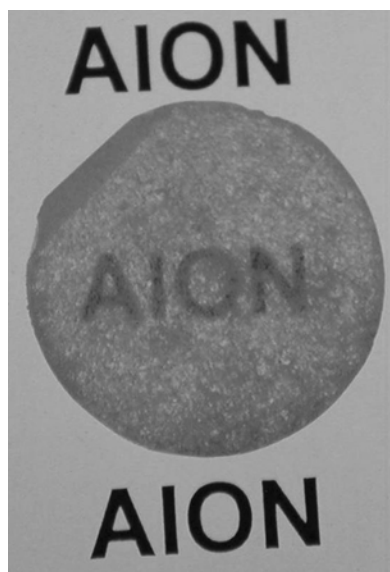


Figure 6. 44.0 mol% AlN sample with ϕ' phase AlON on grain boundaries.

The fourth series of experiments focused on finding methods to improve the density of samples containing greater than 44.0 mol% AlN. Increases in hold times, peak temperature, and Y_2O_3 content were all explored as possible solutions.

Small increases of Y_2O_3 in the settling powder improve the density of the samples. Additions of roughly 0.7 wt% to 0.9 wt% Y_2O_3 seem to consistently produce samples with high density. Some examples of the densities achieved under different conditions can be viewed in Table II. Additions of Y_2O_3 greater than 0.9 wt% cause the settling powder to fuse to the sample in such a manner that the distinction between the settling powder and sample is lost. Instead of a layer distinct from the sample that can be removed with minimal grinding, the settling powder in the “fused” samples forms a hard and dense layer requiring extensive grinding.

Longer hold times improve density to a limited extent. Samples eventually achieve a maximum density that additional time does not improve. This peak density is achieved faster with increased Y_2O_3 content. Prolonged holds of 30 hours or greater often cause sample/powder fusion similar to that caused by high Y_2O_3 additions.

Higher temperature improves densification slightly, but significant problems emerge at these temperatures. Very high temperatures ($>1980^\circ C$) often cause the entire sample to melt. While high, these temperatures should not completely melt AlON. It is unknown if this behavior is caused by the phosphate, poor temperature control in the furnace, or an unexpected shift in composition. Temperatures of $1965^\circ C$ - $1975^\circ C$ improve density, but also speed the sample/powder fusion.

The results of the fourth series indicate that while adjustments can be made to improve the densities of >44.0 mol% samples, too great an increase in any particular direction can cause fusion of sample and settling powder. Y_2O_3 additions in a range of 0.7 wt% to 0.9 wt% combined with hold times of 18-30 hours at 1930 to 1950 $^\circ C$, (less time is needed with greater Y_2O_3 content or temperature) can consistently avoid sample/powder fusion while producing dense samples of γ -AlON. However, the appearance of these samples is not significantly improved over the 44.0 mol% AlN sample shown in Figure 6. The increase in Y_2O_3 necessary to achieve higher density also increases the yttrium rich phases on the grain boundaries. While smaller in size than the ϕ' phase AlON regions in previous samples, these phases are still sufficient to cloud the samples and often give them a yellow tint. Elimination of these phases is necessary to attain a transparent sample.

Fifth Series of Experiments

Table II- Densities of Selected Samples Fired in Series 4. Firing Temp 1950 $^\circ C$

Sample AlN mol%	Time Fired	Y_2O_3 in Powder	Density
44.5 mol%	18 hours	0.7 wt%	3.644 g/cc
45.0 mol%	18 hours	0.7 wt%	3.560 g/cc
45.0 mol%	18 hours	0.9 wt%	3.671 g/cc
44.25 mol%	18 hours	0.7 wt%	3.663 g/cc
44.25 mol%	18 hours	0.9 wt%	3.668 g/cc
44.25 mol%	30 hours	0.7 wt%	3.663 g/cc
44.25 mol%	30 hours	0.9 wt%	3.661 g/cc

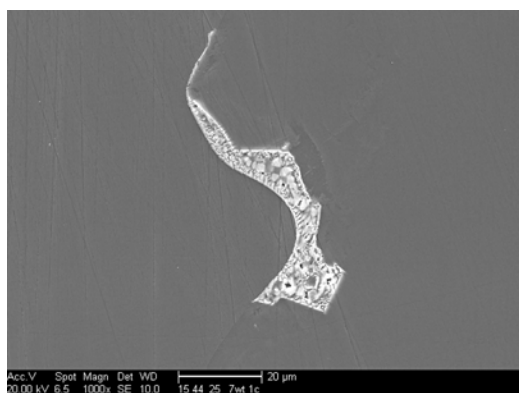


Figure 7. 1000X SEM micrograph of yttrium containing phase.

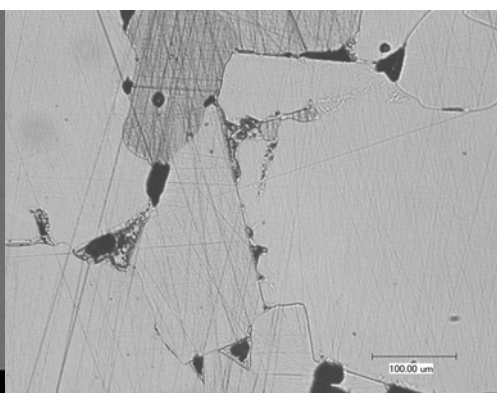


Figure 8. 500X Optical micrograph of yttrium containing phases.

Yttrium rich phases had been observed throughout the development of the process, and after the completion of the fourth series of experiments they appear to be the primary defects that prevent transparency. The polishing process frequently pulled out or damaged these

phases. Figures 7 and 8 contain micrographs showing examples of these yttrium rich phases. Elimination of these phases is the focus of the fifth series of experiments. This series of experiments is the current stage of development.

Compositional analysis using EDS finds yttrium, aluminum, oxygen, and nitrogen present in these phases, although the atomic percentages of the elements, especially yttrium, varies between and even within phases. A range of from 1.5 to 9.2 at% yttrium has been observed thus far. Small amounts of calcium ranging from 0.02 to 0.75 at% are sometimes observed in these phases. This calcium content is likely from trace impurities in the starting powders. The yttrium content in the AlON grains measured with the electron microprobe ranged from 0-250 ppm with up to 450 ppm detected in material very close to an yttrium rich phase. These measurements are below the solubility of Y in γ -AlON, defined as ~ 1700 ppm at 1870°C by Miller and Kaplan.¹⁰

Some samples produced in the fourth series were annealed at various temperatures in an attempt to eliminate these phases. Sample densities dropped after annealing and sample appearance was unimproved. Examples of typical results achieved with these anneals are presented in Table III. Low temperature anneals (1650°C - 1775°C) diffuse yttrium out of the phases, but SEM reveals that non-AlON phases containing Al, N, and O remain. Subsequent high temperature anneals of these low temperature annealed samples reduce density and do not improve appearance.

In an attempt to more uniformly disperse the phases, the cooling rate was slowed to $1^{\circ}\text{C}/\text{min}$ down to 1725°C for one sample. Sample composition was 44.25 mol% AlN, and was fired for 30 hours at 1950°C in a settling powder mixture of 20 mol% AlN, 0.7wt% Y_2O_3 . Below 1725°C , a $10^{\circ}\text{C}/\text{min}$ rate was resumed to room temperature. Yttrium rich phases are still present in this sample, but are reduced in number and size. The density of this sample improved from 3.663 g/cc (see Table II) when cooled at $10^{\circ}\text{C}/\text{min}$ to a value of 3.676g/cc. XRD of this sample (see Figure 9) finds only γ -AlON peaks. Figure 10 shows the microstructure of this sample. Grain sizes are quite large, ranging from 50 to >150 microns in size. A slower cooling rate of $0.5^{\circ}\text{C}/\text{min}$ resulted in fusion of the sample to the settling powder. Additional adjustments and changes to the firing cycle are planned so slower cooling rates can be employed.

Table III- Densities of Selected Series 4 Samples Subjected to 60 hour Anneal at 1870°C

Pre Anneal Density	Post Anneal Density
3.661 g/cc	3.617 g/cc
3.659 g/cc	3.623 g/cc
3.670 g/cc	3.617 g/cc

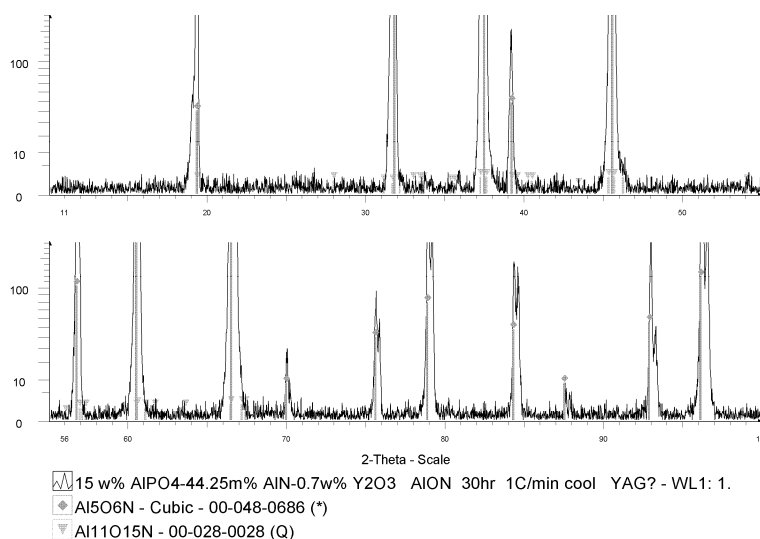


Figure 9. XRD of 44.25 mol% AlN sample fired for 30 hours at 1950°C in a settling powder with 0.7 wt% Y₂O₃ cooled at 1°C/min to 1725°C.

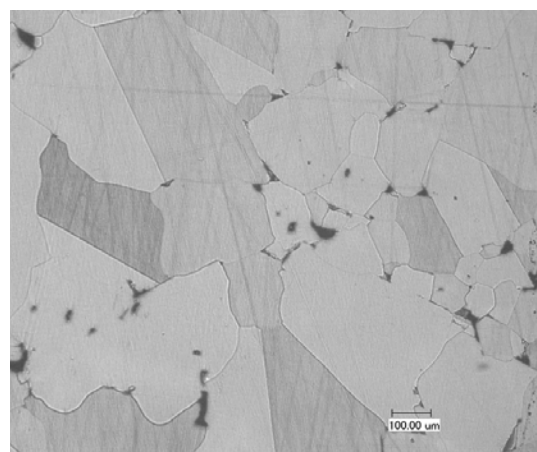


Figure 10. 200X optical micrograph of 44.25 mol% AlN sample fired for 30 hours at 1950°C in a settling powder with 0.7 wt% Y₂O₃ and cooled at 1°C/min to 1725°C.

DISCUSSION

The exact mechanics that govern this interaction are currently unknown. It is possible that the large amount of liquid phase formed by the AlPO₄ additions causes the sample to incorporate some of the surrounding powder. However, the interaction seems to proceed long after the liquid from the AlPO₄ additions should have decomposed. Infiltration of an Al₂O₃/Y₂O₃ based liquid phase into a SiC compact has been reported by Taguchi, Ribeiro, and Balestra.¹⁵ It is possible that similar mechanisms are applicable in this process. The decomposition of the phosphate should cause significant porosity in the sample. A liquid phase formed in the settling powder would be in the position to infiltrate the sample via the porosity formed by the decomposition of the AlPO₄. Figure 1 indicates a liquid form at 20.0 mol% AlN at the temperatures used in this process. Ternary phase diagrams of the AlN-Al₂O₃-Y₂O₃ system were plotted by Medraj, Hammond, Thompson, and Drew.¹⁴ These diagrams indicate eutectics at 1776°C and 1783°C¹⁶ and the presence of a liquid phase for the settling powder compositions at the temperatures used in this process. Based on these different phase diagrams, the settling powder mixtures will form liquid phases at the temperatures used in this process. Higher temperatures and/or greater yttria content increases the amount of liquid phase. This suggests a possible explanation as to why increases in either of these factors can cause an increase in the speed of the interaction. However, infiltration is simply one possible explanation for the observed behavior. It is possible that other mechanisms govern or influence the interaction, and further work is necessary to better define the nature of this interaction.

The yttrium-rich phases appear to be the remains of an unstable liquid phase. In their modeling of transient liquid phase sintering kinetics, Turriff and Corbin¹⁷ indicate the removal of a transient liquid phase can become slower at higher temperatures, and in extreme cases, the liquid may become a persistent liquid phase. This offers an explanation as to why the yttrium rich phases occur when the yttrium content is below the solubility limit for γ -AION. While elimination of these phases may be possible at lower temperatures, the cooling rate of 10°C/min used in the majority of experiments does not allow the liquid phase sufficient time to dissolve. The drop in density observed for annealed samples may be caused by the removal of these phases by either dissolution or a reformed liquid penetrating the grain boundaries. The solution to the problem of the yttrium rich phases may be to prevent their formation by slower cooling rates combined with holds at lower temperatures to allow time for the complete dissolution of the liquid phase. The promising results achieved with a slower

cooling rate of 1°C/min seem to indicate that slower cooling rates improve the process. The problem of sample/powder fusion encountered at slower cooling rates may be prevented by further adjustments to the process, and should not yet be considered an insurmountable obstacle.

The optical properties or mechanical of the AION produced by this process have yet to be measured. Transmission measurements will be performed once the yttrium rich phases are eliminated.

CONCLUSIONS

Reaction sintering of AION can be accomplished using additions of AlPO_4 . Sufficient addition of AlPO_4 causes interaction with settling powders surrounding the sample. The exact nature of this interaction is unknown, but is possibly caused by infiltration of the sample by a liquid phase formed in the settling powder. Under the correct conditions, this interaction can be used to produce dense reaction sintered AION. Transparency of this AION is currently impaired by second phases caused by yttria additions in the settling powder. Further development of the process is needed to eliminate these phases and to better understand the underlying mechanisms governing the process.

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FOOTNOTES

* Unfortunately, it was discovered later in this work that there were inaccuracies in the temperatures measured by the pyrometer, and some uncertainty as to the uniformity of the hot zone due to an aging heating element. The degree of inaccuracy was measured by comparing pyrometer measurements with temperatures measured by a type C thermocouple, and the values reported have been compensated from the initial pyrometer reading based on this comparison. However, there is still some uncertainty as to the actual temperatures due to the non-uniform hot zone. Based on results obtained after a new element was installed, all temperatures reported in this paper should be treated as possibly exceeding the actual temperature by a margin of up to 20°C.

** The diffraction pattern available for identification of ϕ' phase AION was considered of questionable quality. Based on the composition of these phases measured with EDS, and for simplicity, these observed phases will be referred to as ϕ' phase AION in discussion, but some uncertainty exists that it is genuine ϕ' phase AION.

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