PNNL-37070

Embedded Aluminum Nitride Sensors for Advanced Reactors

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U.S. DEPARTMENT OF ENERGY

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Abstract

This project aims to manipulate the of growth of aluminum nitride (AlN) inclusions in an iron-chromium-aluminum (FeCrAl) alloy, using the principle of powder metallurgy and heat treatment methods. to promote the formation of AlN phase within FeCrAl for embedded sensing. This effort seeks to fill in a gap with respect to robust sensor hardware for ubiquitous structural health monitoring of advanced nuclear reactors. A systematic evaluation of various solid-state methods will be performed to understand the influence of process conditions on AlN growth and to promote the growth of desirable AlN phase. Fabricated specimens will be analyzed to investigate the AlN structures that are formed using a suite of tools to characterize the concentration, morphology, and distribution of AlN within the FeCrAl substrate.

Summary

This study investigated the methods to grow aluminum nitride (AlN) crystals in-situ within a structural alloy matrix. AlN is a sensor material with piezo electric response that is active up to 1000C. FeCrAl has been selected as the alloy of interest, since it contains Al in solid solution. Oxide dispersion strengthened FeCrAl alloys are highly relevant for nuclear applications, especially for advanced reactors. Powder metallurgy techniques have been pursued for AlN crystal growth. It was noted that AlN phase can be generated within FeCrAl matrix, when heated under N_2 environment. However, fabrication of composite AlN + FeCrAl coupons were not successful. This is related to the requirement of very high temperature sintering needed for AlN phase. Use of solid-state reaction was partially successful in forming AlN in alloys that do not contain Al as an alloying element. This could be achieved by converting AlB_2 into AlN in a 316L stainless steel matrix. Thin film growth through laser sputtering appeared to give the best results.

Piezo electric behavior of in-situ grown AlN crystals were measured using piezo force microscopy (PFM), which is an adaptation of atomic force microscopy (AFM). Piezo response was linked to measurement of d33 property. In-situ grown AlN phase did not show high d33 values, since AlN crystal orientation was mostly random in nature. In comparison, better d33 values were noted in thin film AlN fabricated by laser sputtering.

Based on the current observation, AlN integration to a structural alloy would be better achieved by coming up with innovative ceramic to metal joining methods, for future research.

Acknowledgments

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1.0 Introduction

Aluminum nitride (AlN) is one of a few materials with potential to offer a piezoelectric function in harsh environments which provides potential in-situ sensor capabilities[1]. The key question this effort seeks to answer is: How can we develop methods to embed AlN phase in a structural alloy of interest for remote sensing. We have selected FeCrAl as the structural alloy for this study. Other key questions to address include characterizing the integrity of the bond between the AlN and surrounding FeCrAl substrate and the impact of the AlN formations on the mechanical integrity of the overall structure.

The ability to inspect the structural integrity of structures within nuclear power plants is crucial to maintaining their safe operation for extended periods. Ultrasonic testing plays a major role in maintaining the current fleet of operating light-water reactors through inspections conducted periodically during outages. For many advanced reactor concepts, these inspections will need to be performed at significantly elevated temperatures while the reactor is operating to accommodate online refueling or to prevent the coolant from freezing during outages.
The development of ultrasonic sensors capable of surviving in advanced reactor harsh environments is an active area of investigation[1-3]. Some key challenges include the basic tolerance of the sensor materials to the relevant environment, as well as the integrity of joints formed between various sensor subcomponents and between sensors and the structures to be surveilled[1-3]. AlN has excellent physical and chemical properties such as high hardness, corrosion resistance, mechanical strength, high electrical resistivity, and thermal stability[1-3].

2.0 Experimental Procedure

AlN is a non-oxide ceramic with a list of unique physical properties. For structural health monitoring through remote sensing, piezoelectric properties are of interest in a sensor material. AlN exhibits piezoelectricity, meaning it generates an electrical charge in response to mechanical stress. This makes it highly suitable for applications such as **pressure sensors, strain sensors, and accelerometers**. In these sensors, the deformation of the AlN material due to applied force or vibration results in an electrical signal that can be measured.

Compared to other piezoelectric materials such as PZT, AlN can offer piezoelectric properties at a temperature up to 1000C or higher. Most other piezoelectric material loses their sensing capability above 300-400C.High temperature piezoelectric properties observed in AlN makes it particularly interesting for use as sensor material in advanced nuclear reactors that are designed to operate at higher temperature (>600C) and in some cases, harsh chemical environments.

Currently, there are no known methods to bond AlN sensor to the underlying structural alloy substrate. Some tried methods include thin film deposition, adhesive bonding etc. In this research, we investigated methods to grow AlN phase in-situ in a structural alloy of interest.

FeCrAl has been selected as the structural alloy. FeCrAl alloy, when strengthened with oxide dispersion nano particles, can show attractive mechanical properties and corrosion resistance for use in harsh environments. In this research, we looked at methods to create AlN phase within FeCrAl matrix. Synthesis of AlN phase has been attempted using following methods listed below:

1. Use of heat treatment to form AlN crystals in-situ through precipitation in structural alloys.

2. Use of powder metallurgy (PM) to form AlN + structural alloy composite and explore feasibility of solid-state additive manufacturing (SSAM) to create AlN coupons.

3. Use of reaction sintering to form AlN crystals in a structural alloy.

4. Use of thin film deposition to grow AlN film.

3.0 Results

This study primarily used the concept of powder metallurgy to investigate growth of AlN phase. Therefore, formation of AlN phase through solid state reactions was the major focus of this research. As outlined in the experimental section, methods to grow AlN phase was attempted by developing heat treatment procedures, sintering conditions etc. Following subsections report our findings for different methodologies tried.

3.1 Use of heat treatment to grow AlN phase in-situ

The main synthesis methods for AlN are carbothermal reduction, chemical vapor deposition (CVD), and direct nitridation. Direct nitridation is a key method for the commercial production of AlN powders from metallic Al powder. This cost-effective technique uses a straightforward nitridation system. Full nitridation is typically achieved at temperatures up to 1500 °C with flowing nitrogen-based gases. However, this process often leads to agglomeration of AlN powders due to the low melting point of aluminum, which is lower than the temperature needed for nitridation.

We explored the direct nitridation method to grow AlN phase in-situ in a metallic alloy. FeCrAl alloy, a ferritic stainless steel, has been used for this study. The FeCrAl alloy used in this study contains 20 wt.% Cr, 5 wt.% Al, and rest Fe. Since there is a good amount of Al in solid solution, we explored the possibility of converting Al into AlN by heat treatment. Following heat treatment schemes were employed, as noted in Table 1.

Table 1. Details of heat treatment scheme tried on FeCrAl discs

Heat treatment #	Temp	Time	Environment	Status	AlN
1	1000C	2 h	air	No wt gain	Negligible amount
2	1100C	12 h	air	1.15% wt gain	Negligible amount
3	1100C	48 h	air	1.13% wt gain	Negligible amount
4	1000C	139 h	N_2	3.02% wt gain	Large, blocky
5	1100C	48 h	N_2	1.7% wt gain	Large, blocky
6	1100C	120 h	N_2		

As summarized in Table 1, FeCrAl discs show higher weight gain when heat treated under flowing N_2, compared to air. There is an effect of heat treatment time as well, with longer time leading to higher weight gain. This behavior indicates solid state reaction happening in FeCrAl matrix, when heated under N_2. SEM imaging was carried out to check for the formation of AlN crystals within FeCrAl matrix after high temperature heat treatment.

Fig. 1 shows a comparison between air vs. N_2 heat treatment when FeCrAl coupons are heated to 1100C for 48 h. FeCrAl matrix remains unchanged, and presence of large equiaxed grains are observed when heat treatment is carried out in air (Fig. 1a). however, the same FeCrAl matrix shows formation of large, blocky phase when heat treated under N_2. EDS elemental mapping was carried out on N_2 heat treated FeCrAl sample. EDS elemental map data is shown in Fig.2, which conclusively proves those blocky phases to be AlN. Therefore, it appears that heat treatment of FeCrAl alloy under flowing N_2 is an effective method to create AlN phase in-situ.

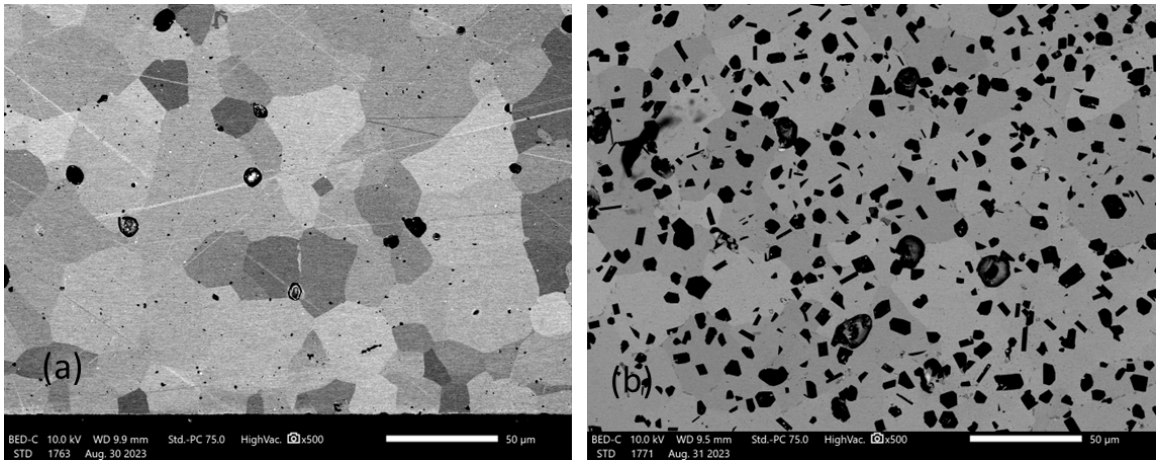


Figure 1. SEM image of the FeCrAl coupon after heat treatment:
at, (a) 1100C, 48 h, air; and (b) 1100C, 48 h, N_2, numerous AlN phase has formed.

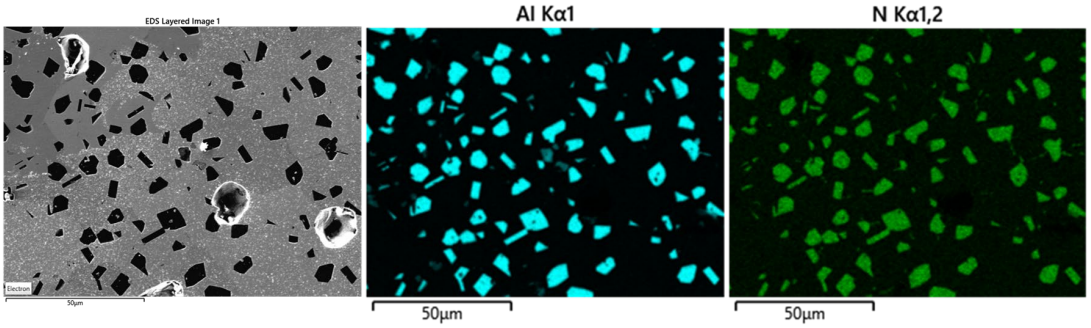


Figure 2. EDS elemental mapping confirms blocky phase as AlN, when FeCrAl disc is heat treated under N_2 environment.

3.2 Use of powder metallurgy to fabricate AlN + FeCrAl composite

Commercially available AlN powder was mixed with FeCrAl powder, and later sintered at high temperature to create a composite sample. The idea behind this approach was to explore the possibility of making composites containing AlN, where AlN quantity can be tailored to the need of a user. Afterwards these composites could be inserted as sensor material into a substrate structural alloy, at the places of interest.

An example of AlN + FeCrAl composite coupon, after sintering at 1350C for 6 h, is shown in Fig. 3. The composite coupon, shown in this optical micrograph, has AlN mixed with FeCrAl in a 1:1 ratio by weight. Since density of AlN is 3.26 g/cc, and density of FeCrAl is 7.15 g/cc, the volume fraction of AlN phase in the shown composite is ~ 70%. Bright phases, shown by the arrow represents FeCrAl particle. Lack of sintering is evident in this sample. This is because of the high temperature required for sintering AlN phase. Overall, fabrication of composite coupons by traditional powder metallurgy route was not successful.

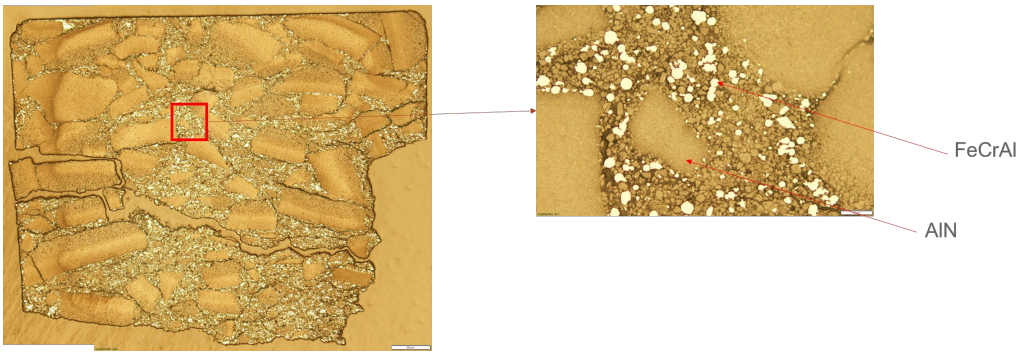


Figure 3. Optical micrograph of FeCrAl powder mixed with AlN powder, sintered at 1350C.

For benchmarking purpose, commercially available AlN powder was pressed into cylindrical shaped pellets and sintered at 1850C for 4 h. For AlN sintering, small amounts of sintering aids such as $CaCO_3$, Y_2O_3 were added with AlN powder to achieve better densification. Temperature profile of the sintering run for pure AlN powder is shown in Fig. 4. Since, smaller particle size leads to better densification, as-received AlN powder was milled at PNNL, and later sintered. Powder size distribution of AlN powder in as-received (AR) and after milling, is reported in Fig. 5. Milling resulted in significant particle size reduction, with D90 value becoming ~50% less than AR particle size.

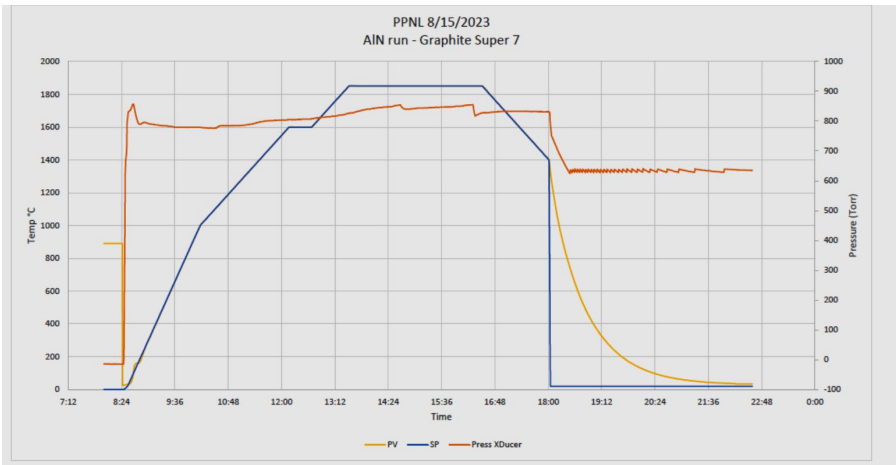


Figure 4. Temperature and pressure profile for pure AlN sintering at 1850C, 4 h

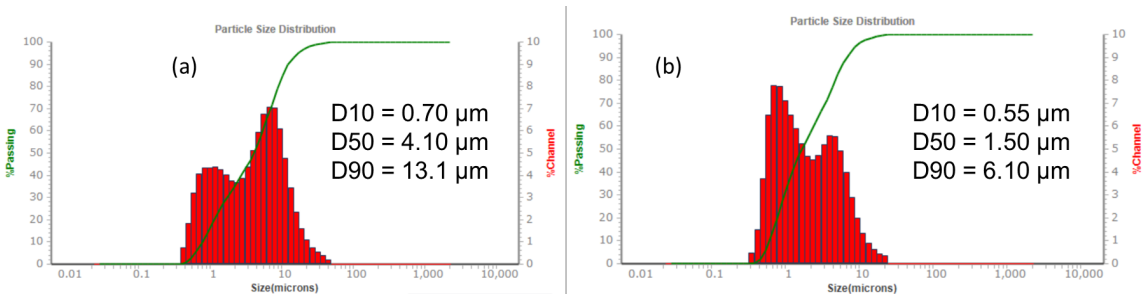


Figure 5. Powder size distribution of AlN powder, (a) as received, (b) after milling

Solid state additive manufacturing (SSAM) of AlN was also tried, using fused filament fabrication (FFF) method. AlN powder was mixed with appropriate polymeric binders to create a filament, which was later used to print small test coupons (25 x 7 x 3 mm). Fig. 6 shows images of pressed pellets, and FFF-fabricated coupons after sintering. Pellets, which were 6 mm tall in height, mostly retained their shapes. However, FFF-printed coupons show some degree of warping, which is due to binder burnout and related effect on final shape.

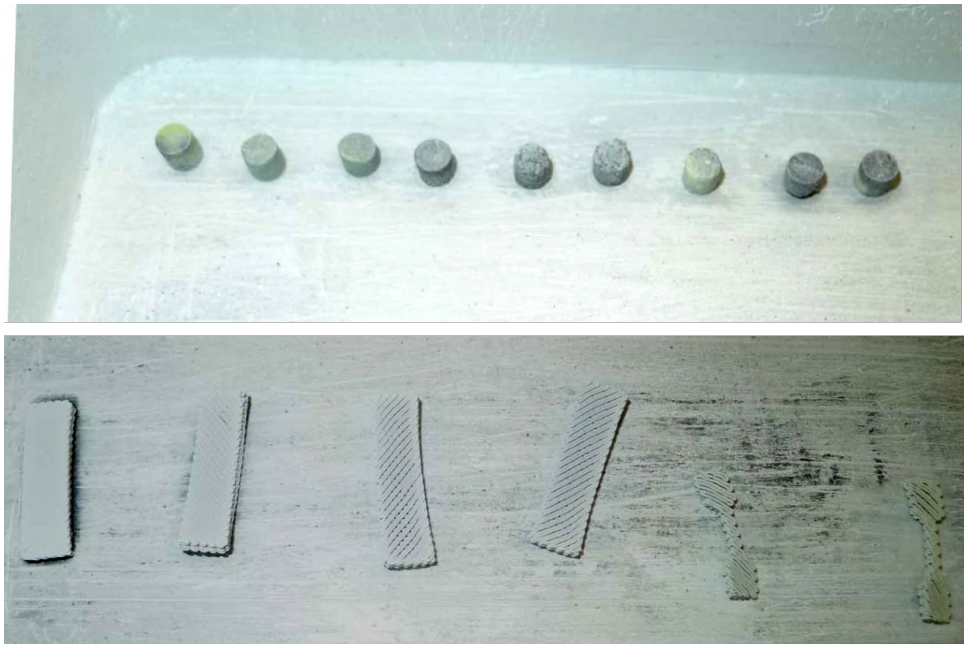


Figure 6. Pure AlN pellets and FFF-printed coupons after sintering

Microstructure and chemical composition of sintered AlN samples were examined by SEM and EDS method. Fig. 7 shows cross-section image of FFF-fabricated AlN coupon after sintering, at various magnifications. AlN powder in AR condition was used for printing these coupons. Low-magnification image of the printed coupon in thickness direction shows that it is possible to create dense layers by FFF method, with minimal defects (Fig. 7a). Large voids between vertical layers are a common printing-induced defect experienced in FFF-based SSAM method. However, at a higher magnification, presence of large porosities could be noticed, which indicate incomplete sintering, and therefore, lack of densification (Fig. 7b and 7c). Further process optimization, such as use of a finer grade of AlN powder for filament fabrication, FFF printing process optimization, and sintering time and temperature modification is required to obtain fully dense AlN coupon after FFF-based fabrication.

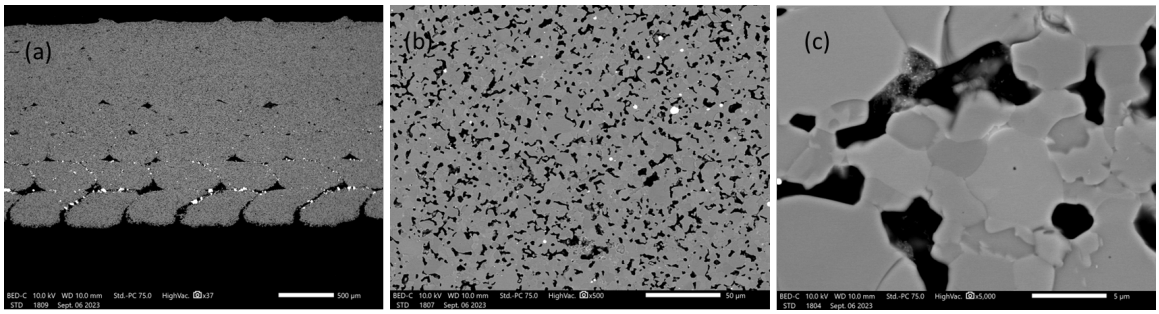


Figure 7. Micrographs of FFF-printed and sintered coupons;
(a) low-magnification overview, (b) intermediate magnification shows porosity, (c) high magnification captures grain structure.

For comparison, microstructure of pressed and sintered pellets made using (i) milled AlN powder, and (ii) milled AlN powder + sintering aid are shown in Fig. 8 and Fig. 9. Milling of AlN powder results in better densification after sintering (Fig. 8a). Higher magnification image of milled AlN powder sintered sample shows irregular morphology (Fig. 8b), which is most likely induced by milling event. Milled AlN powder with addition of sintering aids also shows good densification behavior (Fig. 9a). Presence of sintering aids are mostly noted along the AlN grain boundaries, and there is a distinct change in the shape of AlN grains when sintering aids are used (Fig. 9b).

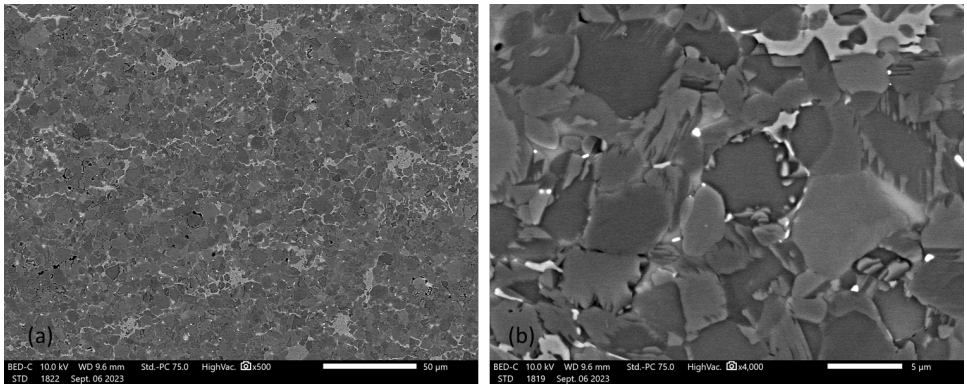


Figure 8. Microstructure of pure AlN after milling;
(a) low-magnification, (b) high magnification showing irregular grain morphology

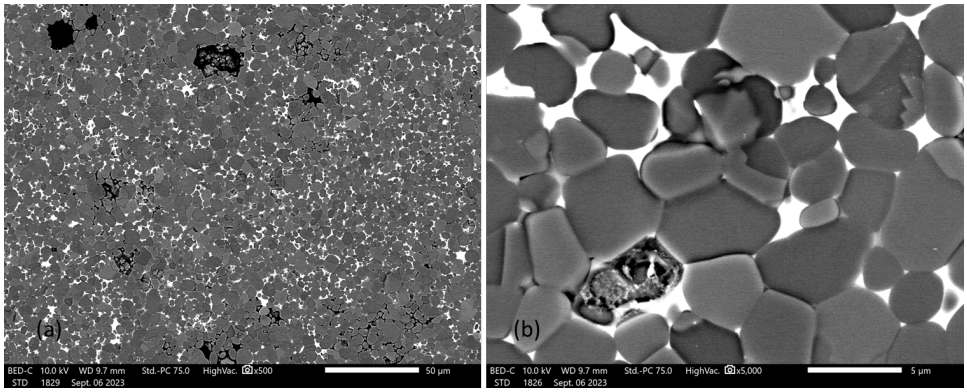


Figure 9. Microstructure of pure AlN after milling and with sintering additives;
(a) low-magnification, (b) high magnification showing rounded grain morphology

EDS elemental mapping of sintered pellet made by AlN powder with sintering aids is captured in Fig. 10. Good densification is apparent, in comparison to sintering behavior of AR AlN powder, shown in Fig. 7b and 7c. Y_2O_3 and $CaCO_3$ has been used as sintering aids, confirmed by EDS elemental mapping. Sintering aids are uniformly present in the AlN matrix.

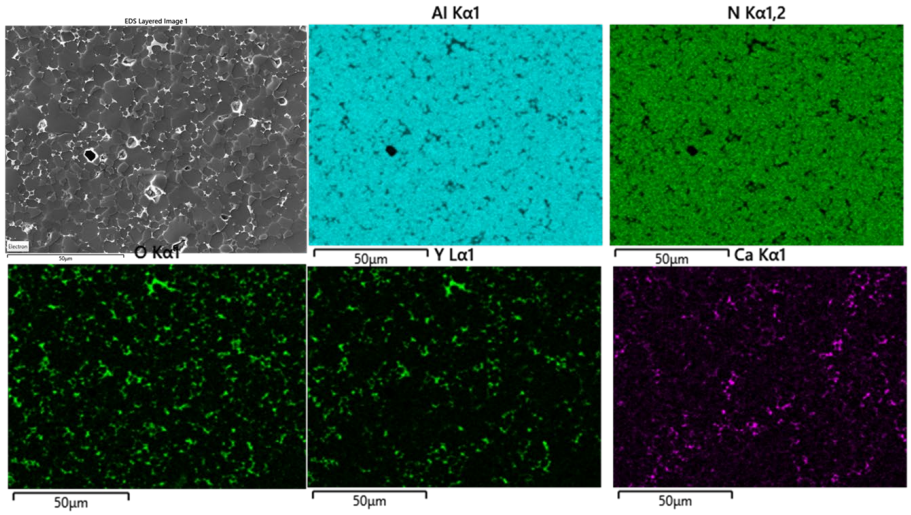


Figure 10. EDS elemental map of AlN with sintering additives confirms presence of Y_2O_3 and $CaCO_3$

3.3 Use of reaction sintering to form AlN in-situ

During initial phase of this study, we used FeCrAl as our candidate structural alloy for in-situ formation of AlN phase. Since FeCrAl contains Al in solid solution, it was first choice as a structural alloy. However, austenitic stainless steels such as 304L SS, 316 L SS are common structural alloys used in the nuclear energy sector. Therefore, we explored the possibility of forming AlN phase in a stainless-steel matrix using solid state method.

We specifically studied the reaction sintering route, where we aimed to convert a non-nitride compound to AlN by solid state reaction. Following chemical reaction has been explored (Fig. 11). 316L SS powder (70% by vol.) was mixed with AlB2 powder (30% by vol.), and was heat treated in N_2 environment at 1100C for 120 h. The composite sample did show formation of AlN. However, the solid-state reaction route needs significant process optimization to generate reasonable amount of AlN for effective piezo response.

$$22AlB_2 + 9.33N_2 \rightarrow 18.66AlN + 2Al_{1.67}B_{22}\ (1000\ °C),$$

$$Al_{1.67}B_{22} + N_2 \rightarrow BN + AlN\ (>1400\ °C).$$

Figure 11. Solid state chemical reaction explored for converting AlB_2 to AlN in-situ

3.4 Use of thin film deposition method to grow AlN film

Aluminum nitride (AlN) thin films were synthesized by pulsed laser deposition (PLD). A KrF excimer laser (248 nm wavelength) operated at 10 Hz was directed on an AlN ceramic target (K.J. Lesker, Inc.) at a repetition rate of 10 Hz in a background gas of 10 mTorr N_2. The ablated target material was captured on fused silica, or 301 stainless steel (SS) substrates held at 800°C.

Grazing incidence X-ray diffraction (GIXRD, Rigaku SmartLab) was utilized to evaluate the crystallinity of the resulting AlN thin films. As tabulated in Table 2 and shown in Fig. 12(a, c), the AlN films deposited on fused silica at a substrate temperature of 800°C were amorphous under higher N_2 background pressure (10 mTorr and 20 mTorr) and weakly crystalline under lower N_2 background pressure of 1 mTorr. From these results, 800°C and 1 mTorr N_2 were chosen as optimum deposition parameters for AlN thin films.

The amorphous AlN films were treated similarly to the SS alloys studied elsewhere in the project that developed AlN inclusions after heat treatment in an N_2 atmosphere. The amorphous AlN films were annealed in an N_2 atmosphere at 1100°C for 120 hrs. This thermal treatment did not result in crystalline AlN, although the conditions were sufficient to crystallize the fused silica into cristobalite and quartz (Fig. 12(b)). Magnetite (Fe_3O_4) was also observed but was attributed to contaminant powders acquired during the anneal.

Table 2. PLD deposition conditions for AlN films deposited on fused silica substrates. Film crystallinity was assessed by GIXRD.

Substrate temperature	N_2 flow rate / pressure	Film crystallinity
800°C	10 sccm / 10 mTorr	Amorphous
800°C	10 sccm / 25 mTorr	Amorphous
800°C	10 sccm / 1 mTorr	Weakly crystalline

To mimic the AlN inclusions in SS studied elsewhere in the project, AlN thin films were deposited on polished 301 SS substrates under optimized conditions of 800°C substrate temperature and 1 mTorr N_2 pressure. These AlN thin films were confirmed to be partially crystalline by GIXRD, as shown in Fig. 12(d).

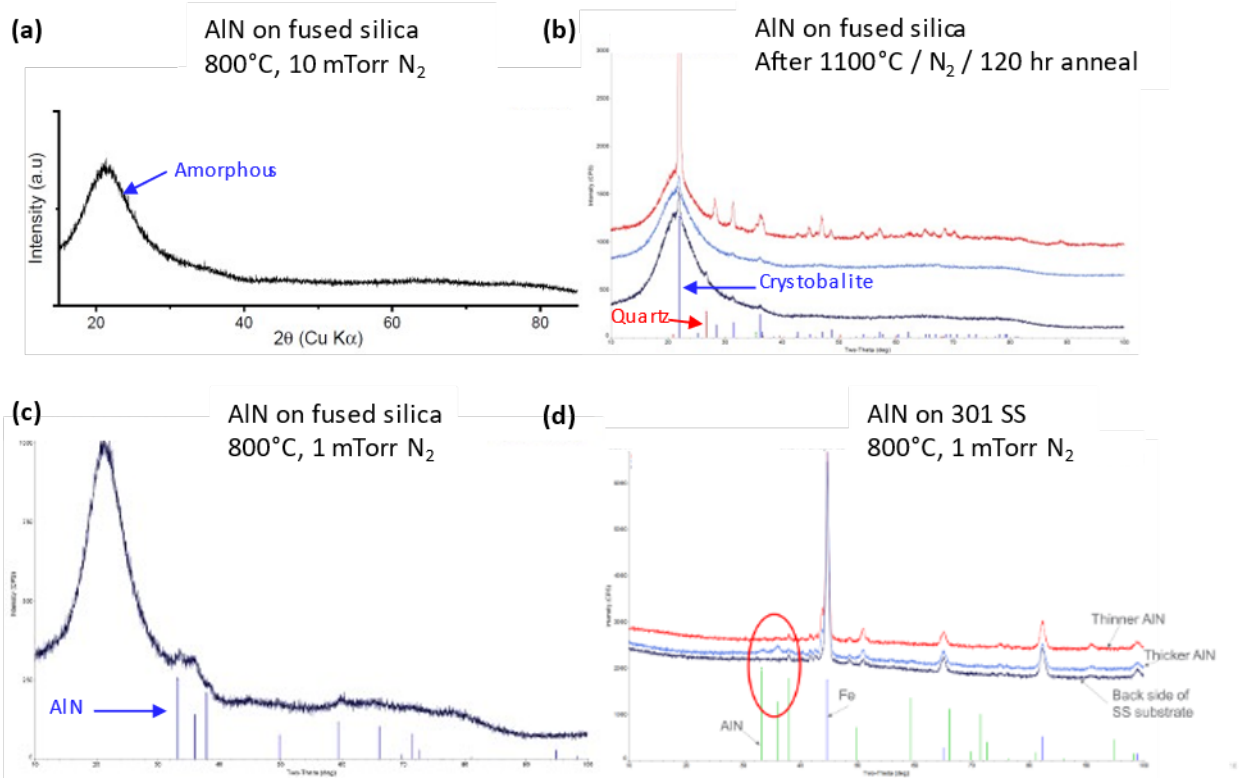


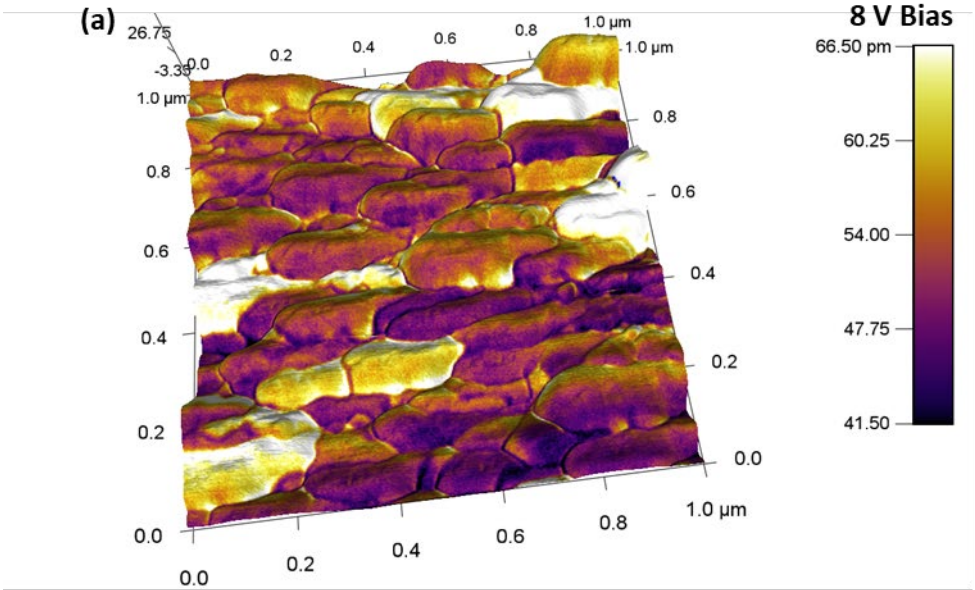
Figure 12. GIXRD patterns of AlN thin films deposited by PLD.
(a) Amorphous AlN deposited on fused silica at 800°C, 10 mTorr N_2. (b) Amorphous AlN thin films after annealing in N_2 atmosphere at 1100°C for 120 hrs. (c) Weakly crystalline AlN deposited on fused silica at 800°C, 1 mTorr N2. (d) Weakly crystalline AlN deposited on 301 SS at 800°C, 1 mTorr N_2.

3.5 Use of Piezoresponse force microscopy (PFM) for piezo property measurement

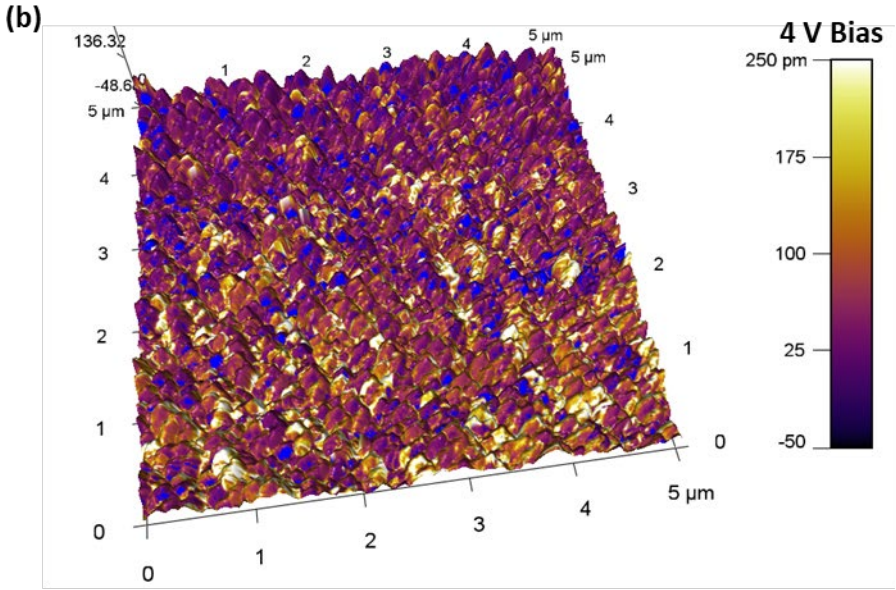
Piezoresponse force microscopy (PFM) in conjunction with atomic force microscopy (AFM, Asylum MFP-3D) was utilized to evaluate the piezoelectric properties of the AlN thin films. Piezo response is measured as d33, where larger values of d_{33} indicate a stronger response. The piezo response of the AlN thin films is summarized in Fig. 13. Weakly crystalline AlN thin films deposited on both fused silica and 301 SS exhibited a measurable piezo response. The response of the AlN film on 301 SS, d_{33} = 14.2 pm/V, was two times the response of the AlN film on fused silica (d_{33} = 6.7 pm/V). However, it should be noted that the film thicknesses were not established, and it might be expected that thicker films would exhibit a stronger piezo response than thinner films.

A comprehensive summary of PFM measurement analysis carried on select samples that contained AlN phase is reported in Table 3. It appears that the best piezo response is noted for pure AlN material, in as-sintered condition. PFM measurement method has been benchmarked by using a standard BiTiO3 reference. Piezo response of pure AlN, although in poly crystalline

form, appears to be quite high (73 pm/V). AlN phase, grown in-situ within FeCrAl alloy by heat treatment does show piezo response as well, although the magnitude of the response remains low (9.9 pm/V).



Average piezo response: d_{33} = 6.7 pm/V



Average piezo response: d_{33} = 14.2 pm/V

Figure 13. PFM response of AlN thin films.
(a) Overlay of topography (from AFM) and piezoresponse (from PFM) for weakly crystalline AlN thin film deposited on fused silica. (b) Overlay of topography and piezoresponse for weakly crystalline AlN thin film deposited on 301 SS.

Table 3.Summary of PFM measurement carried on select samples.

Sample composition	PFM	
	Bias, V	d33 pm/V
FeCrAl, NO AlN	10	0.88
BiTiO, Reference	0.5	89
33% by vol AlN +67%316L+2 wt.% Y_2O_3	1	8
33% by vol AlN + 67% FeCrAl + 2 wt.% Y_2O_3	2	4
50% by vol AlN 50% by vol FeCrAl	5	6
Sintered FeCrAl disc Heat treated at 1100C for 120h under N_2	4	9.9
100% AlN pellet sintered	4	73
AlN thin film deposited on fused silica	8	6.7
AlN thin film deposited on stainless steel	4	14.2

4.0 Conclusion

Piezo electric sensors for use at harsh environment is needed for structural health monitoring of advanced nuclear reactor fleet. AlN is a good piezo electric material for use at harsh environment for a variety of excellent thermophysical properties. Integration of AlN to a structural alloy is challenging because it involves joining a non-oxide ceramic to metal. This study looked at growing AlN phase in-situ within candidate structural alloys. Heat treatment of FeCrAl under N_2 environment leads to AlN formation. PFM measurement shows presence of piezo response in areas within FeCrAl that contains AlN. This method needs further investigation to come up with larger quantity of AlN phase and control the crystal orientation of in-situ grown AlN phase.

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