

# Synthesis of die-castable nano-particle reinforced aluminum matrix composite materials by in-situ gas-liquid reactions

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## ABSTRACT

*Nano-particle reinforced aluminum matrix composites are attractive engineering materials for many automotive and aerospace applications because they exhibit numerous desirable mechanical and thermal properties, such as high specific strength, hardness, stiffness, and resistance to creep and thermal degradation. Unfortunately, making these materials is not easy and most of the methods that have been developed so far for their synthesis are either not robust, inefficient, or not cost effective. In this publication, we report on the synthesis of die-castable aluminum-aluminum nitride nano-composite materials by the reaction of a nitrogen-containing gas with molten aluminum-lithium alloy. Specifically, we report on the effect of (1) the lithium content of the alloy, (2) the composition of the reactive gas, and (3) the reaction time on (a) the amount, (b) the average size, and (c) the average cluster size of the aluminum nitride reinforcing particles; as well as (d) the hardness and (e) the thermal stability of the composite material.*

## RIASSUNTO

Materiali compositi a matrice di alluminio rinforzati con nano-particelle hanno grande valenza ingegneristica sia in ambito automobilistico che aerospaziale per le eccellenti proprietà meccaniche e termiche, come elevata resistenza specifica, durezza, rigidità e resistenza allo scorrimento viscoso e degradazione termica. Sfortunatamente, fabbricare tali materiali presenta numerose difficoltà e la maggior parte dei metodi che sono stati sviluppati finora sono non robusti e non convenienti. Nel presente lavoro, riportiamo la sintesi di materiali nanocompositi Al/AlN per pressofusione attraverso la reazione di un gas azotato con matrice di Al-Li. In particolare, si segnala l'effetto di (1) il contenuto della lega di litio, (2) la composizione del gas reattivo, (3) il tempo di reazione su (a) la quantità di AlN sintetizzati, (b) la dimensione media delle particelle (c) la dimensione degli agglomerati di AlN inoltre (d) la durezza e (e) la stabilità termica della materiale composito.

## KEYWORDS

*Aluminum, lithium, nano-composites, in-situ process, nitrogen-bearing gas, aluminum nitrides.*

## INTRODUCTION

Global efforts are continually being made in order to improve fuel economy in the automotive and aerospace industries. Fuel efficiency standards require manufacturers to increase fuel efficiency by 5% per year starting from 2012. Nano-particle reinforced metal matrix composites, particularly those based on an aluminum alloy matrix allow decreasing the weight of the vehicle while enhancing the strength and stiffness of components, which leads to significant improvements in the fuel efficiency of the vehicle. Traditionally, such materials are produced by powder metallurgy [1], mechanical alloying [2], spray deposition [3], and several casting methods that involve stirring particles of the reinforcing phase in the molten metal alloy [4] or infiltration methods [5]. Since these conventional fabrication techniques involve adding exogenous reinforcing particles to the metal alloy, they suffer from several drawbacks including contamination, interfacial reactions between the particles and the alloy matrix, and clustering of the particles due to their poor wettability by the matrix alloy [3,6]. A class of novel nano-composite material fabrication processes in which the particles are formed within the parent phase (in-situ) by means of a chemical reaction has been recently developed. Belonging to this class is the gas injection process, which is based on introducing a reactive gas into a molten metal to cause a chemical reaction that produces the reinforcing particles [6]. Uniform particle distribution, lack of contamination, and clean interfaces between the reinforcing particles and the matrix can be achieved by this process, and the process is easily scalable and inexpensive. The present study focuses on the synthesis of Al-AlN nano-composites, which

has received considerable attention in recent years [7-10]. Aluminum nitride has low density ( $3.026 \text{ g/cm}^3$ ), low coefficient of thermal expansion ( $4.5 \times 10^{-6} \text{ K}^{-1}$  in the temperature range 293-673 K), and good thermal conductivity ( $110\text{-}170 \text{ W.m}^{-1}\text{.K}^{-1}$ ), which makes it an attractive material for electronic substrates and optoelectronic parts. Moreover, AlN is much more wettable by aluminum than other compounds, such as  $\text{Al}_2\text{O}_3$ , is chemically stable and does not decompose or in aluminum. However, and despite their many attractive characteristics, Al-AlN nanocomposites have not been widely used because of the high cost of AlN nano-powders. Zheng and Reddy [7-10], Hou et al. [11], Huashun et al. [12] and others [13,14,15] have demonstrated the feasibility of synthesizing Al-AlN nanocomposites by the gas injection process. The mechanism of AlN formation has also been discussed, as well as the detrimental effect of oxygen on the nitridation of aluminum [8]. In this paper, we report on the synthesis of die-castable aluminum-aluminum nitride nano-composite materials by the reaction of a nitrogen-containing gas with molten aluminum-lithium alloy. Specifically, we report on the effect of (1) the lithium content of the alloy, (2) the composition of the reactive gas, and (3) the reaction time on (a) the amount, (b) the average size, and (c) the average cluster size of the aluminum nitride reinforcing particles; as well as (d) the hardness and (e) the thermal stability of the composite material.

## MATERIALS AND PROCEDURES

Fig. 1 shows a schematic representation of the apparatus used in the gas injection process. It consists of a mullite retort placed inside a resistance

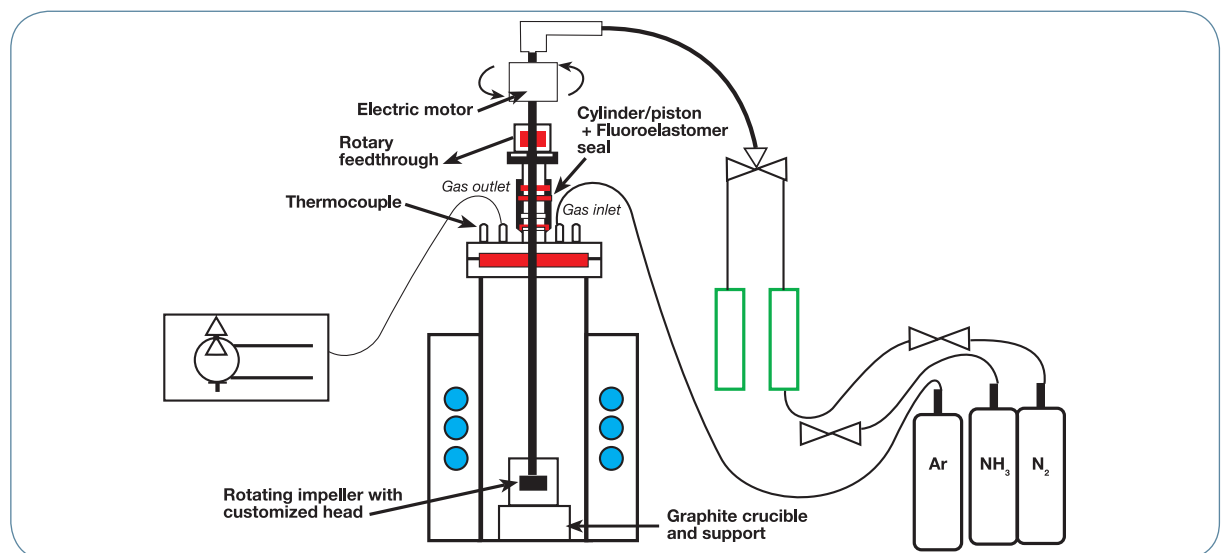


Fig. 1: Apparatus used to synthesize Al-AlN composite materials.

furnace. A graphite crucible was used to melt the alloy. The gas bubbling impeller has a customized head with 24 holes each 3 mm in diameter. The rotor head was printed from a ceramic powder (80% Al<sub>2</sub>O<sub>3</sub>- 20% SiO<sub>2</sub>) and coupled to an Inconel 601 tube by means of a large-pitched thread that is sealed with a high temperature cement. Al-5 wt% Li master alloy was used as the starting material and high purity Al (99.9999%) was added when dilution of the master alloy was required. The total weight of the charge was about 250g. Nitrogen gas (GRADE 4) and anhydrous ammonia were used as reactive gases. Drierite traps, moisture traps, and oxygen traps were used to purify the nitrogen-bearing gases so that the impurities are at the parts-per-billion (ppb) level. The reaction temperature was kept constant at 1000°C, and the reaction time was varied between 2 and 4 hours. The gas flow rate [0.4 and 0.6 liter per min (lpm)] was maintained by a flow meter. After the desired reaction time, the melt was left to cool down to room temperature in the furnace under an inert atmosphere.

Table 1 summarizes the design of experiments. After

each run, samples from the resulting composite material were removed and etched with diluted 10 vol% NaOH. The microstructure of each sample was examined by a scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer. The samples were also examined by X-ray diffraction (XRD). A Matlab-based computer program [16] was optimized and used to quantitatively characterize the microstructure, including calculating the volume fraction of the AlN particles, the mean free space length, the average AlN particle size, and the average AlN cluster size. The free space length is a scale-dependent measure of particle distribution and can be related to the other microstructural variables. It decreases with increasing volume percentage of particles, decreasing particle size and cluster size. The hardness of the composite materials was measured with the Rockwell B scale utilizing a total load of 100Kgf. On average 15-20 hardness measurements were made on each sample. Thermal stability of the AlN particles was assessed by holding the samples at 450°C for 24 hours in an electrical box furnace and then measuring the increase in size of the AlN particles.

*Table 1. Design of Experiments.*

Experiment #	Alloy composition	Gas composition	Processing time
1	Al-5 wt% Li	N <sub>2</sub>	2
2	Al-5 wt% Li	N <sub>2</sub>	4
3	Al-5 wt% Li	N <sub>2</sub> / NH <sub>3</sub> =1/1	2
4	Al-5 wt% Li	N <sub>2</sub> / NH <sub>3</sub> =1/1	4
5	Al-5 wt% Li	NH <sub>3</sub>	2
6	Al-5 wt% Li	NH <sub>3</sub>	4
7	Al-2.5 wt% Li	N <sub>2</sub>	2
8	Al-2.5 wt% Li	N <sub>2</sub>	4
9	Al-2.5 wt% Li	N <sub>2</sub> / NH <sub>3</sub> =1/1	2
10	Al-2.5 wt% Li	N <sub>2</sub> / NH <sub>3</sub> =1/1	4
11	Al-2.5 wt% Li	NH <sub>3</sub>	2
12	Al-2.5 wt% Li	NH <sub>3</sub>	4

## RESULTS AND DISCUSSION

Microstructure characterization – Table 2 shows the quantitative results of the microstructure characterization. No AlN was detected in the samples when N<sub>2</sub> gas is injected in Al-5 wt% Li alloy for 2 hours. When the processing time was increased to 4 hours, XRD analysis (Fig. 2) shows the presence of AlN. Both the quantitative analysis and the micrograph (Fig. 3) reveal a uniform distribution of fairly small AlN particles (~600nm) in the alloy matrix. When ammonia was mixed with nitrogen, the volume of AlN particles that formed increased after 2 and 4 hours processing time compared to the case when only N<sub>2</sub> gas was used and the average particle size was around 400 nm. However, some clustering of the AlN particles occurred when the gas mixture was injected for 2 hours, but the average cluster size was relatively small – around 1300 nm as seen in Fig. 4. For 4 hours processing time, the average particle size remains more or less the same, but the average cluster size slightly increases to 1500 nm as seen in Fig. 5. Further increase in the volume of AlN particles occurred when ammonia only is used as the reactive gas. In this case, 48 vol% of AlN particles formed after processing for 4 hours. The microstructure appears to be very homogeneous for both processing times (Figs. 6 and 7). Clustering seems to be significantly diminished, the average cluster size is reduced to around 1µm, and the average particle size is also reduced to 300nm.

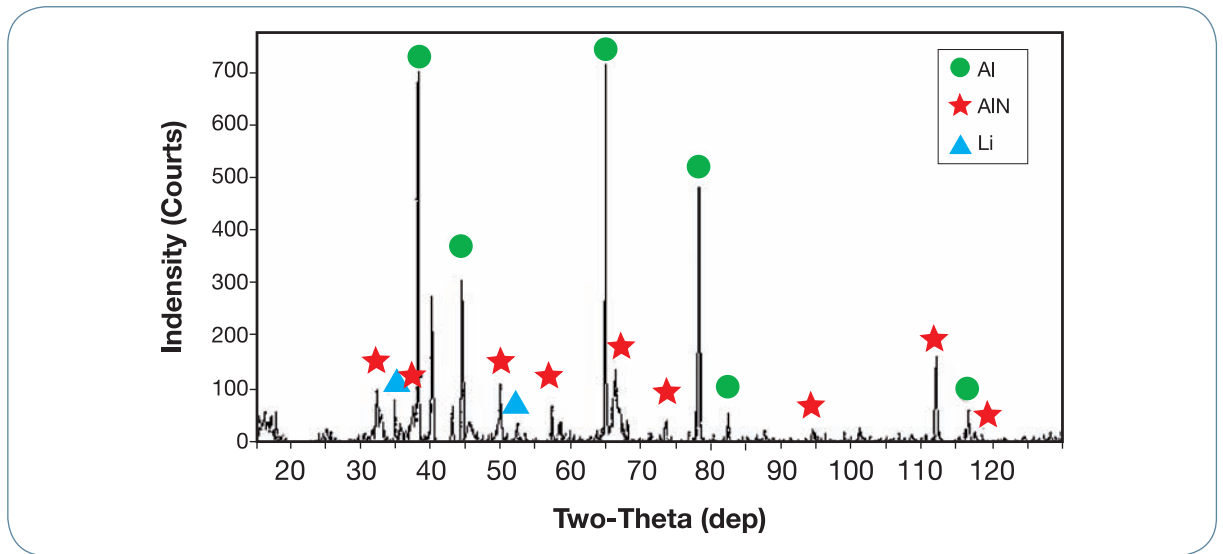


Fig. 2: XRD pattern of the Al-AIN composite produced by Experiment #2.

Table 2: Microstructure parameters of the composite materials processed according to Table 1.

Experiment #	Volume fraction (%)	Mean free space length (nm)	Average particle size (nm)	Average cluster size (nm)
1	-	-	-	-
2	6.2%	1890 nm	643 nm	1540 nm
3	9.5%	1723 nm	489 nm	1327 nm
4	26%	1262 nm	453 nm	1552 nm
5	21%	1649 nm	274 nm	966 nm
6	48%	861 nm	312 nm	1114 nm
7	-	-	-	-
8	-	-	-	-
9	-	-	-	-
10	7.4%	2670 nm	655 nm	924 nm
11	12.8%	2416 nm	409 nm	1012 nm
12	31%	1635 nm	293 nm	785 nm

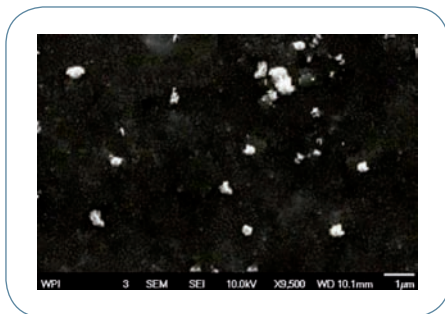


Fig. 3: SEM image of the Al-AIN composite produced by Experiment #2.

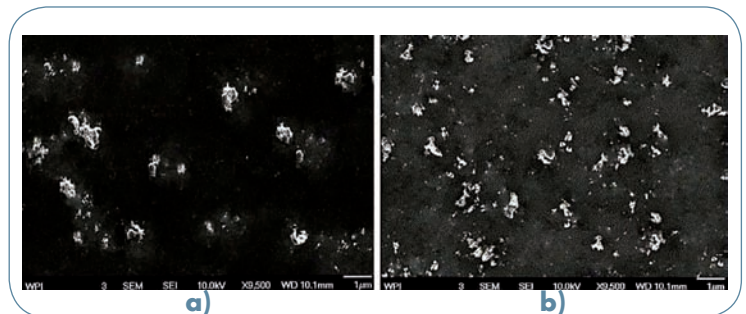
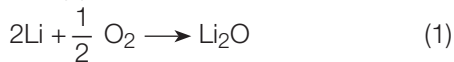


Fig. 4: SEM image of the Al-AIN composite produced by (a) Experiment #3, and (b) Experiment #4.

In the experiments performed with the 2.5 wt% Li alloy, no AlN particles were detected when nitrogen only was used as reactive gas for 2 or 4 hours. Also, no AlN particles were found when the mixture of nitrogen and ammonia gases was injected in the alloy for 2 hours; however, when the processing time was 4 hours, around 7 vol% AlN was formed as seen in Fig. 6. This amount is about four times less than the amount that formed when the Al-5 wt% Li alloy was used. Also, the large mean free space length of this composite material (2670 nm) reveals that clustering is more severe than in previous experiments, despite the fact that the average cluster size is less than 1 μm and the average particle size is around 650 nm. When ammonia is used with the 2.5 wt% Li alloy, the average AlN particle size is decreased to around 400 nm for 2 hours processing time, and 300 nm for the 4 hours processing time. The volume fraction of AlN is 31% for the 4 hours processing time, which is almost 30% less than when the 5 wt% Li alloy is used. Localized clustering can still be observed (See Figs. 7 and 8), but the average cluster size is around 700 nm.

The role of Li in aluminum nitridation has been investigated by Scholz and Greil [17]. They indicate that Li may act as an “oxygen-getter” to locally lower the oxygen content in aluminum and allow the nitridation reaction, which competes with aluminum oxidation, to take place. According to phase equilibrium calculations in the Al-Li-O-N system, Li combines with oxygen to form Li<sub>2</sub>O at low oxygen levels and LiAlO<sub>2</sub> at higher oxygen levels according to reactions (1) and (2).



Aluminum nitridation may also occur because of the ability of Li to remove the gaseous reaction products from the reaction site so that equilibrium conditions are never achieved. The continuous flow of the nitrogen-bearing gas in the furnace chamber removes the evaporating species (Li and Li<sub>2</sub>O) from the reaction chamber, thus maintaining non-equilibrium conditions that generate very high mass flow of volatilizing Li. Therefore, the high partial pressure of the Li-based vaporized species in the furnace’s environment causes nitridation of aluminum on the surface of the melt first. Channels in the aluminum-lithium melt derived from the rising nitrogen bubbles and the stirring action of the impeller are probably responsible for nitridation of the bulk of the metal.

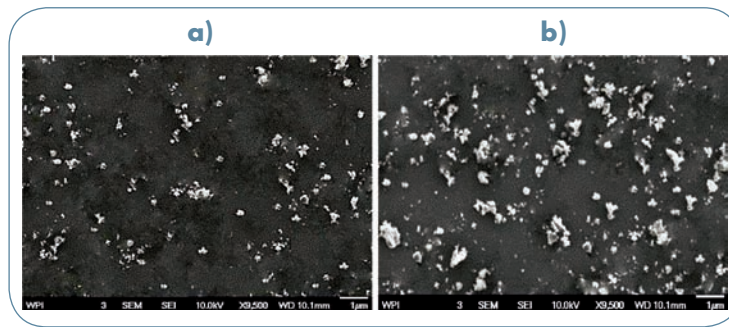


Fig. 5: SEM image of the Al-AIN composite produced by (a) Experiment #5, and (b) Experiment #6.

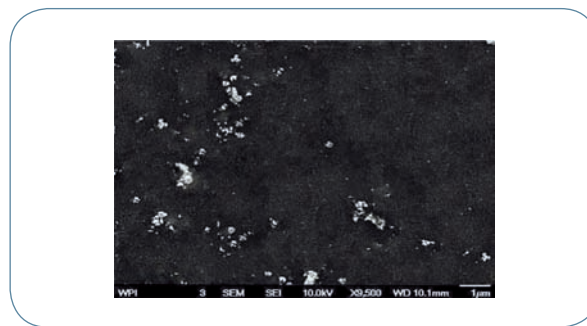


Fig. 6: SEM image of the Al-AIN composite produced by Experiment #10.

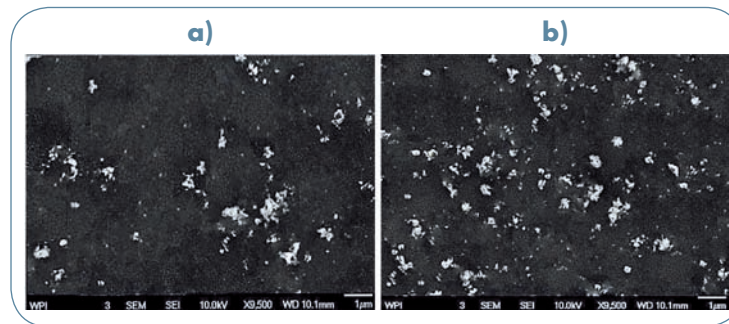


Fig. 7: SEM image of Al-AIN composite produced by (a) Experiment #11, and (b) Experiment #12.

### Hardness and thermal stability

Fig. 8 shows the measured hardness values of the composite materials shown in Table 2. The hardness measurements made on the samples produced with the 5 wt% Li alloy have an error range of 14%, while hardness measurements made on the samples produced with the 2.5 wt% Li alloy have an error range of 20%. This is most likely due to “macro” agglomeration, i.e. particles, and also clusters, located on interconnected paths so as to create a relatively large mean length of free space. Accordingly, it is possible that during measuring the hardness, the indenter has a higher tendency to hit areas of the metal matrix



where there are almost no particles. Notice how the hardness values dramatically increase for the materials produced in Experiments #6 and #12. This is because of the high volume fraction of AlN particles in these materials.

### Thermal stability

The thermal stability of the Al-AlN composite

materials was assessed by measuring the increase in size of the AlN particles after the samples were maintained at 450°C for 24 hours. In all samples, the average particle size did not change ( $\pm 5\%$  accuracy) except for the sample produced in Experiment #2 in which the average AlN particles size increased by about 14%. This sample will be further analyzed in order to find the reason for this behavior.

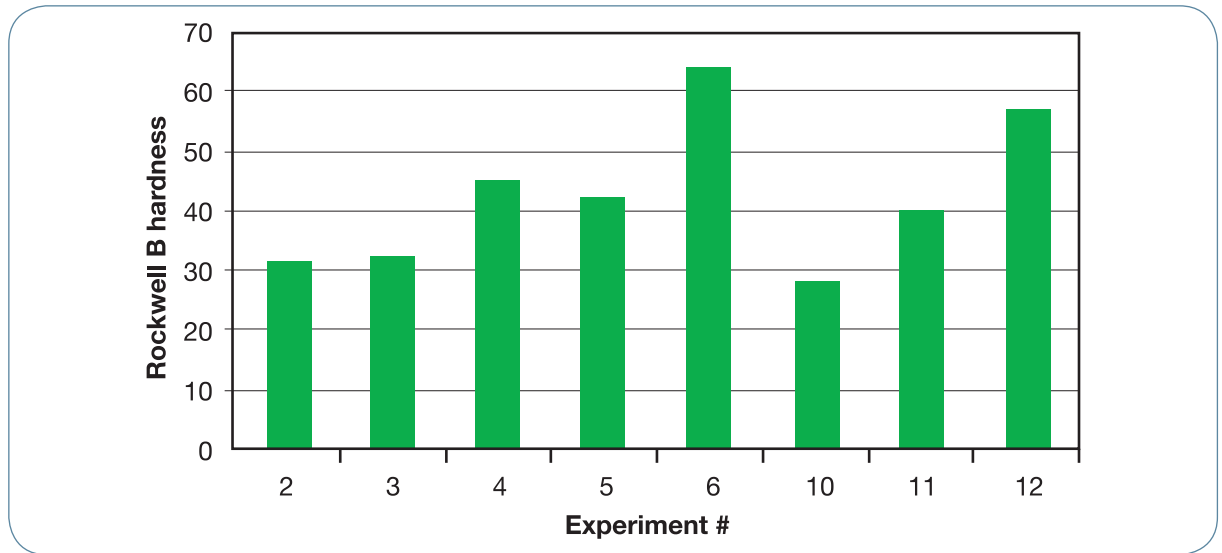


Fig. 8: Measured hardness of the Al-AlN composite materials shown in Table 2.

## SUMMARY AND CONCLUSIONS

- ▶ Al-AlN composite material was synthesized by the reaction of a nitrogen-containing gas with molten aluminum-lithium alloy.
- ▶ The effect of different lithium levels in the molten aluminum alloy, gas composition, and processing time on the structure of the composite material was investigated.
- ▶ The average size of the AlN particles was found to be in the sub-micron range and the average size of the AlN clusters was found to be around 1  $\mu\text{m}$ .
- ▶ Lithium in the melt acts as a catalyst for the aluminum nitridation reaction and results in composites with a higher volume fraction of AlN.
- ▶ Ammonia as the reactive gas results in composites with a higher volume fraction of AlN particles. Also, as expected, longer processing times (4 hours compared to 2 hours) result in composites with a higher volume fraction of AlN.

- ▶ Particle clustering appears to be more severe for the 2.5wt% Li alloy than in the 5 wt% Li alloy although the average cluster size is smaller.
- ▶ Hardness measurements show a significant increase when ammonia is used as the reactive gas and for longer processing times.
- ▶ The Al-AlN composites produced with this in-situ method have excellent thermal stability.

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