

## PRODUCTION OF ALUMINUM-ALUMINUM NITRIDE NANO-COMPOSITES BY A GAS-LIQUID REACTION

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### **Abstract**

*An innovative method has been developed for synthesizing aluminum-aluminum nitride nano-composite materials wherein the reinforcing nano-sized aluminum nitride particles are formed in-situ in a molten aluminum alloy. This method, which circumvents most issues associated with the traditional ways of making nano-composites, involves causing a reaction between a nitrogen-bearing gas and a specially designed molten aluminum alloy. The method ensures excellent dispersion of the nanoparticles in the matrix alloy, which is reflected in enhanced room and elevated temperature mechanical properties.*

### **1. Introduction**

Aluminum alloys reinforced with nanoparticles exhibit attractive mechanical and physical properties including high strength, hardness, stiffness, and resistance to creep and thermal degradation. Unfortunately, making these materials is challenging, and numerous methods have been devised over the past decade to overcome the typical issues associated with their production. However, materials produced with these methods typically suffer from serious issues. For example, methods that are based on mechanical stirring nanoparticles in molten metal tend to produce materials in which the particles are clustered together [1]. Also, methods that are based on liquid infiltration of ceramic substrates made of nanoparticles [2], and methods that are based on powder metallurgy [3, 4] tend to produce materials that suffer from particle/matrix interface de-bonding. Similarly, methods that are based on ultrasonic-assisted cavitations are not easy to scale up to manufacturing practice and are uneconomical. In-situ synthesis of the nanoparticles in the molten metal is an answer to many of the challenges encountered with these ‘ex-situ’ manufacturing methods. In-situ synthesis of nano-composite materials is typically performed by introducing a reactive gas into a molten metal alloy to cause a chemical reaction that produces the nanoparticles [5]. The present article focuses on the synthesis of aluminum-aluminum nitride nano-composites by injecting a nitrogen-bearing gas into molten aluminum that has been pre-alloyed with lithium.

### **2. Apparatus and Procedures**

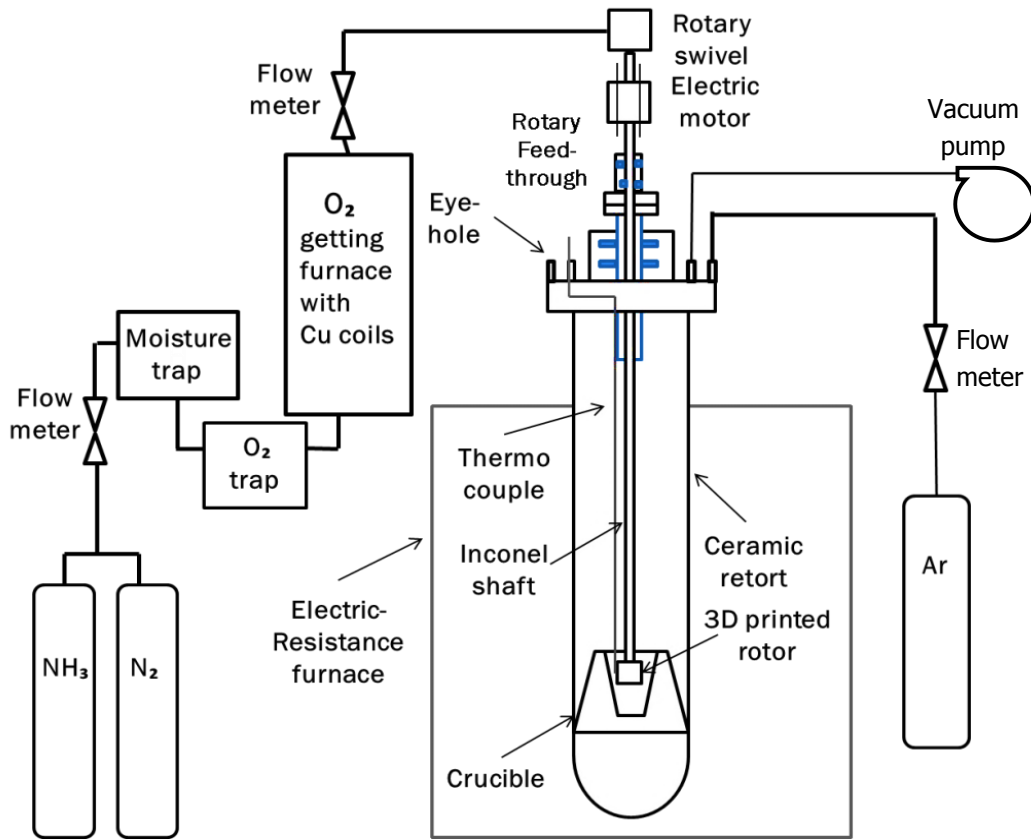
The apparatus shown schematically in Figure 1 was designed, built, and used to manufacture ingots of the composite material. High purity Al (99.9999%) and Al-5%wt. Li master alloy were used as starting materials. The positive role played by lithium in aluminum nitridation

has been thoroughly investigated by Scholz and Greil [6] and by Borgonovo and Makhlouf [7-11]. Lithium combines with oxygen to form  $\text{Li}_2\text{O}$  at low oxygen levels and  $\text{LiAlO}_2$  at higher oxygen levels according to reactions (1) and (2).



Therefore, lithium is an oxygen getter that mitigates aluminum oxidation and by doing so it permits the aluminum nitridation reaction to proceed. Aluminum nitridation is also helped by the presence of lithium in the system because of its ability 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 (i.e., Li and  $\text{Li}_2\text{O}$ ) from the reaction chamber, thus maintaining non-equilibrium conditions that generate very high flow of the volatilizing lithium. The high partial pressure of the lithium-containing vaporized species in the furnace environment causes nitridation of aluminum on the surface of the melt first. Channels in the aluminum-lithium melt formed by the rising nitrogen bubbles and the stirring action of the impeller allow nitridation to proceed into the bulk of the melt.

Two hundred grams of the Al-5%wt. Li master alloy were ultrasonically cleaned in acetone and placed in a graphite crucible that has been previously coated with a boron nitride emulsion. The mullite chamber of the resistance furnace was first evacuated down to 60 mTorr and refilled with UHP argon at 20 mTorr. This was repeated three times in order to remove as much oxygen as possible from the furnace atmosphere. The chamber was then filled with argon gas at atmospheric pressure and then heating was started. The heating rate was kept constant at 4°C/min in order to avoid excessive thermal stress on the mullite body of the retort. A K-type thermocouple (enclosed in a ceramic tube to prevent its degradation) was placed in the crucible to monitor the temperature. Once the process temperature was reached, the impeller was immersed in the melt and the reactive gas (nitrogen, ammonia or a combination of both) was injected into the melt. The impeller is connected to an electric mixer (Mixer Direct, 1/15 hp, 115 V) that provides rotation at a constant rpm. Gas purification devices were used to remove oxygen and moisture from the reaction gas down to the parts-per-billion level. Drierite (10-20 mesh) and activated alumina desiccants were used to remove moisture and a high-efficiency oxygen trap (VICI) containing a manganese-based getter material and an oxygen trap (RESTEK) were used to minimize the oxygen content. An oxygen-getting furnace set to 500°C and filled with Cu coil was placed in line for further gas purification. Plug valves at the beginning and at the end of the gas line isolate the traps in order to avoid contamination from the atmospheric air when they are not being used. Once gas injection was completed, the rotor was extracted from the melt and argon gas was pumped in the chamber to cool the composite material down. The composite was left in the chamber to solidify under the argon atmosphere.



**Figure 1.** Schematic representation of the apparatus.

The process parameters shown in Table 1 were used to produce ingots that contained 4 vol. % aluminum nitride nanoparticles with 58 nm average particle size. These ingots were added to commercial grade A356 alloy in order to produce dilute castable A356-AlN nano-composite materials. To this end, four pounds of molten commercial grade A356 aluminum alloy were melted in an induction furnace and then transferred to an electric resistance furnace that was maintained at  $730^\circ\text{C}$ . A constant flow of Argon gas was maintained in the electric furnace in order to minimize oxidation of the melt.

Alloy composition	Gas composition	Processing time (h)	Rotational speed (rpm)
Al-2.5 wt.% Li	$\text{N}_2$	2	450

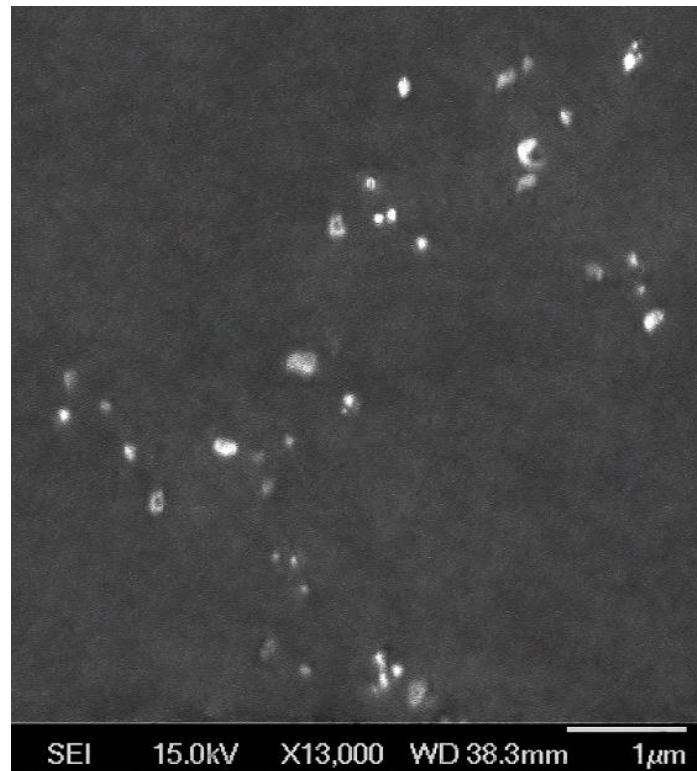
**Table 1.** Process parameters used to produce the ingots.

The nano-composite ingots were added to this molten A356 alloy together with silicon metal (in order to compensate for dilution of the A356 alloy with aluminum from the nano-composite ingot). A356-AlN nano-composite materials with three different levels of AlN particles, namely 0.5 vol. pct., 1.0 vol. pct., and 2.0 vol. pct., were thus produced. In each case, the melt was ultrasonically degassed for 25 minutes and then the melt temperature was raised to  $780^\circ\text{C}$ . After equilibrating at  $780^\circ\text{C}$ , the melt was poured in an ASTM-E8 mold that has been preheated to  $400^\circ\text{C}$  in order to make specimens for tensile property measurements. Molten A356 alloy without the nano-particles was also ultrasonically degassed for the same length of time and poured into the same pre-heated mold in order to make tensile test specimens for comparison.

The room temperature tensile properties of the nano-composite materials were measured with a Universal Testing machine according to ASTM standard B557. The tensile tests were performed at 300°C according to ASTM standard E21. The data from both room temperature and elevated temperature tensile property measurements was analyzed to obtain ultimate tensile strength (*UTS*), yield strength (*YS*), elongation (*e*), and modulus of elasticity (*E*). The impact toughness of the nano-composite materials was measured with an Instron impact machine utilizing the Charpy simple-beam impact test (ASTM standard E23) and un-notched specimens that are 10 mm × 10 mm × 55 mm. The specimens were polished with 600 grit silicon carbide paper before performing the measurements and at least eight specimens were used in each case.

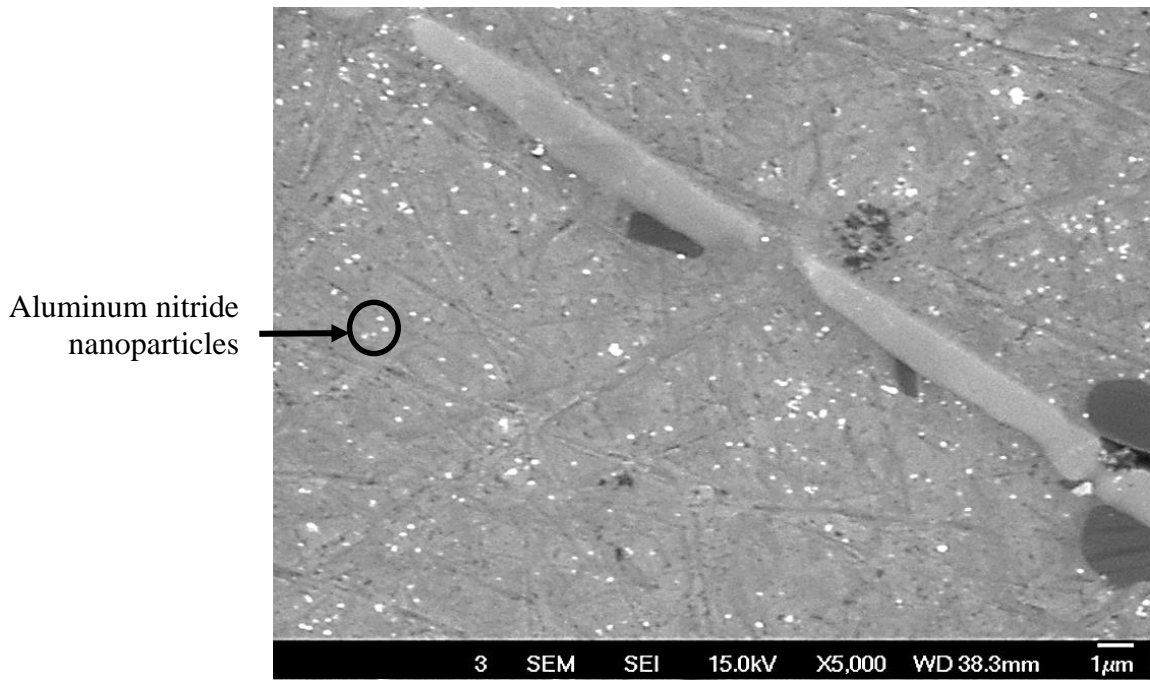
### 3. Results and discussion

Figure 2 shows the microstructure of the nano-composite material. The average particle size is 60 nm and clusters that are larger than this average particle size are not detected. The aluminum nitride particles constitute 4 vol. pct. of the material. This relatively small volume fraction of reinforcing particles may be attributed to the short (2 hours) gas injection time. The smaller particle size, on the other hand, is a direct consequence of bubble break-up during stirring.



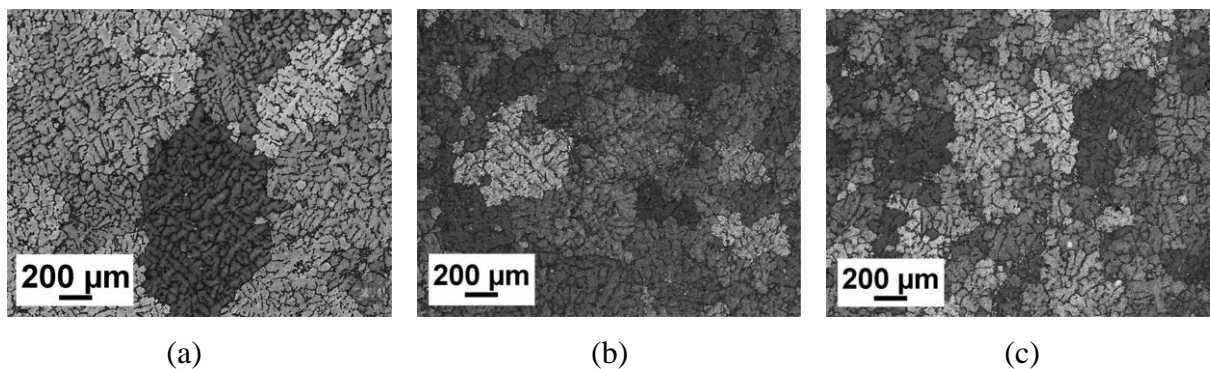
**Figure 2.** SEM photomicrograph showing the distribution of the aluminum nitride particles in the aluminum-lithium alloy.

Figure 3 shows the microstructure of the A356-AlN nano-composite material. Clearly, distribution of the aluminum nitride particles in the matrix alloy was not affected by the re-melting, dilution, and casting processes. The aluminum nitride particles are well distributed in the matrix alloy even around the silicon particles where they typically tend to cluster. This material contains 2 vol. pct. aluminum nitride particles.



**Figure 3.** Microstructure of A356 alloy containing 2 vol. pct. aluminum nitride nanoparticles.

Figure 4 shows the grain size of the base alloy (A356) and the A356-AlN nano-composite material and Table 2 shows the measured average grain size values. Table 2 shows that the aluminum nitride nanoparticles have an obvious grain refining effect.



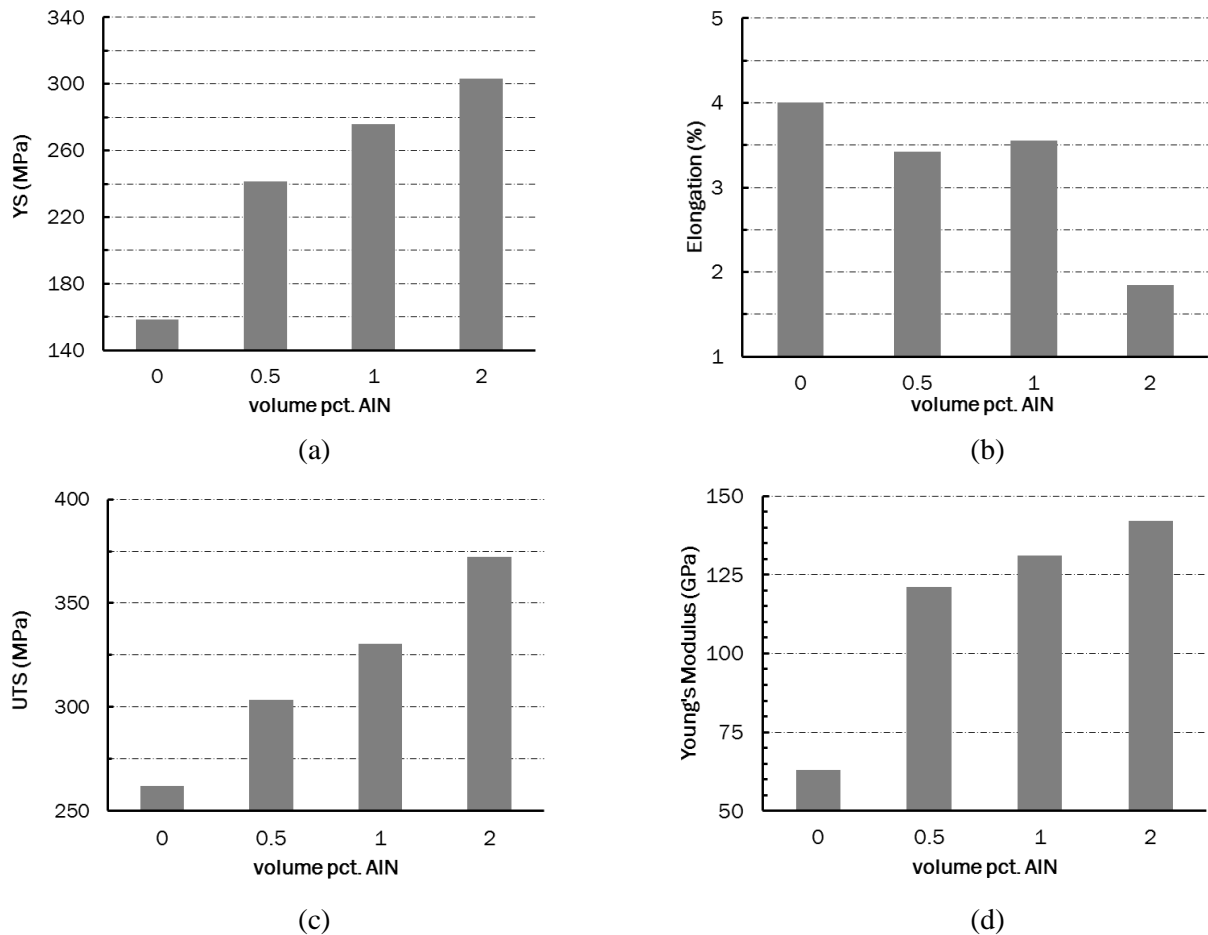
**Figure 4.** Grain size of A356 and A356-AlN nano-composite materials. (a) A356 alloy, (b) A356-1.0 vol. pct. aluminum nitride, (c) A356-2.0 vol. pct. aluminum nitride.

	A356	A356 + 1.0 vol. pct. AlN	A356 + 2.0 vol. pct. AlN
<b>Grain size (µm)</b>	708	441	222

**Table 2.** Effect of aluminum nitride nanoparticles on the measured average grain size of A356 alloy.

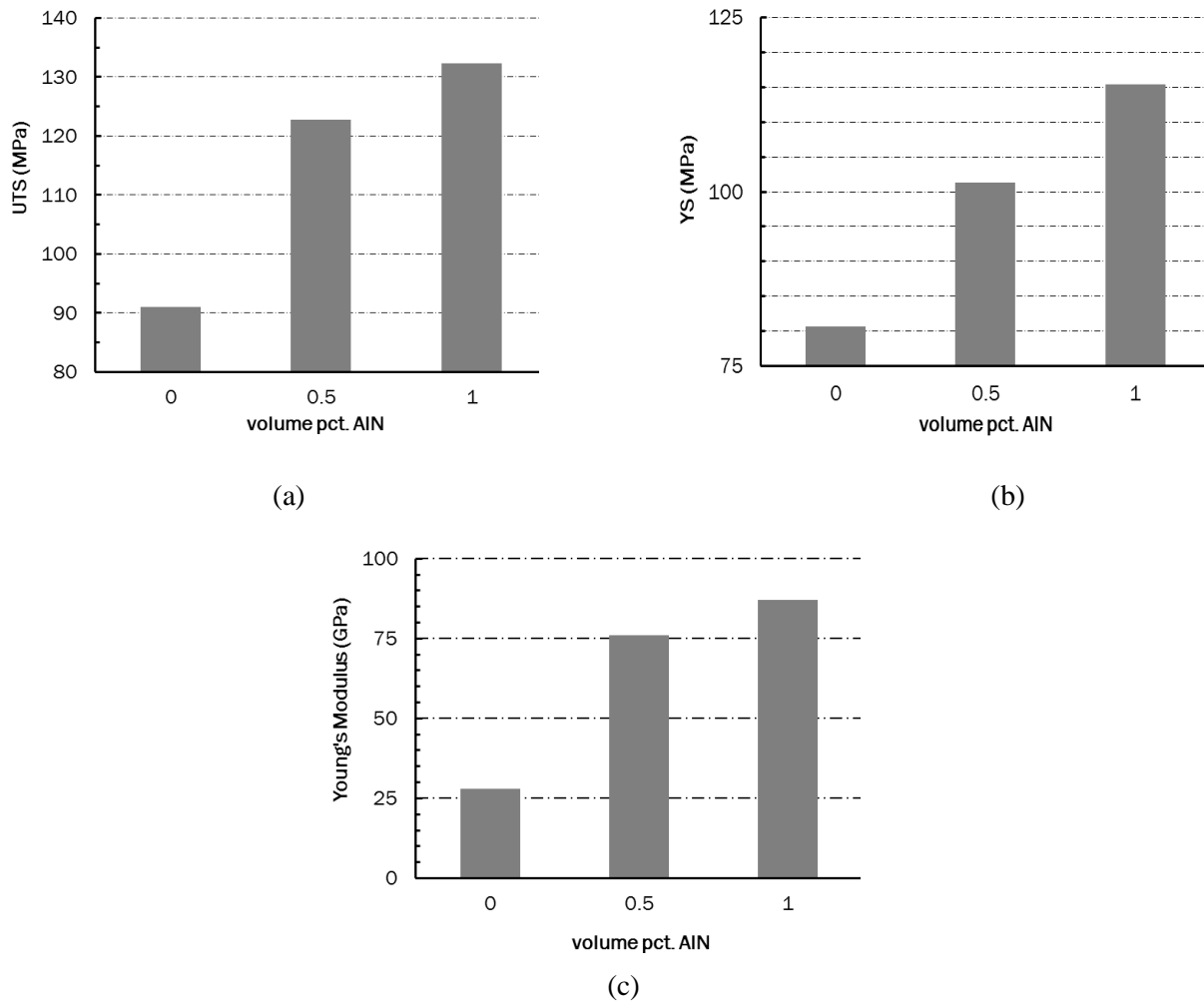
Figure 5 shows the room temperature tensile properties of the nano-composite materials as function of vol. pct. Aluminum nitride. Figure 4(a) shows that at 2 vol. pct. aluminum nitride, the room temperature ultimate tensile strength (*UTS*) of the nano-composite material is 46% higher than that of the matrix alloy. Similarly, Figure 5(b) shows that at 2 vol. pct. aluminum nitride, the room temperature yield strength (*YS*) of the nano-composite material is 90% higher than that of the matrix alloy. Figure 5(b) also shows that an improvement in *YS* of about 50%

may be achieved by the presence of as little as 0.5 vol. pct. aluminum nitride. Figure 5(c) shows that elongation decreases by only 10 % with up to 1 vol. pct. aluminum nitride; and at 2 vol. pct. aluminum nitride, it decreases by 50%. Figure 5(d) shows that the room temperature modulus of elasticity ( $E$ ) of the nano-composite material with 0.5 vol. pct. aluminum nitride is 100% higher than that of the matrix alloy, and  $E$  of the composite material with 2 vol. pct. aluminum nitride is 120% higher than that of the matrix alloy. The observed increase in strength is most likely due to dislocation bowing around the aluminum nitride particles [16] since the particles are too large (60-80 nm) to be sheared by the dislocations.



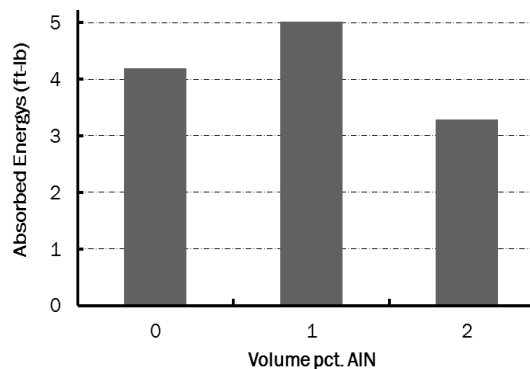
**Figure 5.** Room temperature tensile properties of nano-composite materials diluted with commercial grade A356 alloy as functions of vol. pct. aluminum nitride. (a) UTS, (b) YS, (c) elongation, and (d) modulus of elasticity.

Figure 6 shows the elevated temperature (300°C) tensile properties of nano-composite materials as function of vol. pct. aluminum nitride. Figure 6(a) shows that at 1 vol. pct. aluminum nitride, the elevated temperature ultimate tensile strength ( $UTS$ ) of the nano-composite material is 40% higher than that of the matrix alloy. Similarly, Figure 5(b) shows that at 0.5 vol. pct. aluminum nitride, the elevated temperature yield strength ( $YS$ ) of the nano-composite material is 90% higher than that of the matrix alloy. Figure 6(b) also shows that an improvement in  $YS$  by 25% may be achieved by the presence of as little as 0.5 vol. pct. aluminum nitride and 50% by the presence of 1 vol. pct. aluminum nitride. The most significant result is the substantial increase in elevated temperature modulus of elasticity ( $E$ ), which increases over that of the matrix alloy by 200% at 0.5 vol. pct. aluminum nitride and by 240% at 1 vol. pct. aluminum nitride as shown in Figure 6(c).



**Figure 6.** Elevated temperature (300°C) tensile properties of nano-composite materials diluted with commercial grade A356 alloy as functions of vol. pct. aluminum nitride. (a) UTS, (b) YS, and (c) modulus of elasticity.

Figure 7 shows the impact toughness of the nano-composite materials as function of vol. pct. aluminum nitride. The impact toughness of the base alloy increases with the addition of 1 vol. pct. aluminum nitride by about 19%, but decreases when the amount of aluminum nitride is 2 vol. pct. This may be attributed to the significant decrease in ductility of the material at the higher aluminum nitride content.



**Figure 7.** Impact toughness of nano-composite materials diluted with commercial grade A356 alloy as functions of vol. pct. aluminum nitride.

#### 4. Conclusion

With optimum processing conditions, aluminum nitride particles that are 60-80 nm in diameter were synthesized in an aluminum-lithium alloy. When ingots of this nano-composite material are added to commercial A356 casting alloy, the aluminum nitride particles remain well-distributed in the matrix alloy and they effectively refine the alloy's grain structure. Moreover, they significantly improve the alloy's hardness, as well as its room temperature and elevated temperature tensile properties. With 0.5 vol. pct. aluminum nitride, the room temperature ultimate strength, yield strength, and modulus of elasticity of commercial grade A356 alloy are increased by 16%, 52%, and 92%, respectively without significant loss of ductility. Similarly, with 0.5 vol. pct. aluminum nitride particles, the ultimate strength, yield strength, and modulus of elasticity of commercial grade A356 alloy at 300°C are increased by 35%, 25%, and 171%, respectively.

It is worth mentioning that the method used to make the tensile specimens from the nano-composite materials, namely diluting (Al-Li)-AlN nano-composite ingots with commercial grade A356 aluminum alloy and then gravity casting the resulting melt in cast iron molds, allowed making tensile specimens with a maximum loading of 2 vol. pct. aluminum nitride. It was not possible to evaluate materials with higher particle loading as the high content of the nanoparticles raised the melt's viscosity to the point where it was not possible to gravity-pour the melt. It is submitted that tensile specimens with considerably higher aluminum nitride particle loading can be obtained by the high pressure die casting process or by any one of its variants, e.g., squeeze casting or semisolid metal casting.

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