Development Of Nitrogen Concentration During Cryomilling Of Aluminum Composites

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DEVELOPMENT OF NITROGEN CONCENTRATION DURING CRYOMILLING OF ALUMINUM COMPOSITES

by

CLARA M. HOFMEISTER
B.S. University of Central Florida, 2010

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Materials Science and Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Summer Term
2013
ABSTRACT

The ideal properties of a structural material are light weight with extensive strength and ductility. A composite with high strength and tailorable ductility was developed consisting of nanocrystalline AA5083, boron carbide and coarser grained AA5083. The microstructure was determined through optical microscopy and transmission electron microscopy. A technique was developed to determine the nitrogen concentration of an AA5083 composite from secondary ion mass spectrometry utilizing a nitrogen ion-implanted standard. Aluminum nitride and amorphous nitrogen-rich dispersoids were found in the nanocrystalline aluminum grain boundaries. Nitrogen concentration increased as a function of cryomilling time up to 72 hours. A greater nitrogen concentration resulted in an enhanced thermal stability of the nanocrystalline aluminum phase and a resultant increase in hardness. The distribution of the nitrogen-rich dispersoids may be estimated considering their size and the concentration of nitrogen in the composite. Contributions to strength and ductility from the Orowan relation can be more accurately modeled with the quantified nitrogen concentration.
ACKNOWLEDGMENTS

First and foremost I would like to thank my family, especially my brother Chris Eagan, for their patience with my absence as I have focused on my research. Without your support and understanding this work would not have been possible.

I would like to thank my advisor and chairman Dr. Yongho Sohn for all that you have taught me and for guiding me through more lemon projects than I can count. I am especially grateful for your patience with me as I struggled to learn the basics of research. Thanks for an awesome five years of working together! I would like to also express gratitude to my committee members, Dr. Kevin Coffey and Dr. Challapalli Suryanarayana for your time and consideration of this thesis.

The use of the Materials Characterization Facility is gratefully acknowledged especially the excellent advice of Mr. Mikhail Klimov on secondary ion mass spectrometry. The ion-implanted standard was graciously provided by Dr. Fabian Naab from the University of Michigan. Powders were cryomilled at Pittsburgh Materials Technology (Jefferson Hills, PA).

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<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>#atoms_AIN</td>
<td>total number of Aluminum Nitride atoms in the composite</td>
</tr>
<tr>
<td>#atoms_N</td>
<td>total number of Nitrogen atoms in the composite</td>
</tr>
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<td>AlN</td>
<td>Aluminum Nitride</td>
</tr>
<tr>
<td>At.%N</td>
<td>Atomic Percent of Nitrogen</td>
</tr>
<tr>
<td>C</td>
<td>Number of measurements or data cycles</td>
</tr>
<tr>
<td>CG</td>
<td>Coarse Grain</td>
</tr>
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<td>CIP</td>
<td>Cold Isostatic Press</td>
</tr>
<tr>
<td>Cs</td>
<td>Cesium</td>
</tr>
<tr>
<td>d</td>
<td>Crater depth in cm</td>
</tr>
<tr>
<td>ṗ</td>
<td>Sputtering rate</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
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<td>FSP</td>
<td>Friction Stir Processing</td>
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<tr>
<td>HCDF</td>
<td>Hollow Cone Dark Field</td>
</tr>
<tr>
<td>HIP</td>
<td>Hot Isostatic Press</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>HSR</td>
<td>High Strain Rate</td>
</tr>
<tr>
<td>I'_b</td>
<td>Background ion intensity of impurity isotope in counts/s</td>
</tr>
<tr>
<td>I_b</td>
<td>Background ion intensity of impurity isotope in counts/cycle</td>
</tr>
<tr>
<td>I_i</td>
<td>Impurity isotope secondary ion intensity in counts/s</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$I_m$</td>
<td>Matrix isotope secondary ion intensity in counts/s</td>
</tr>
<tr>
<td>INLO</td>
<td>In-situ lift out</td>
</tr>
<tr>
<td>LN</td>
<td>Liquid Nitrogen</td>
</tr>
<tr>
<td>$M_i$</td>
<td>Atomic mass of element or compound $i$</td>
</tr>
<tr>
<td>MMC</td>
<td>Metal Matrix Composite</td>
</tr>
<tr>
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<td>Nitrogen</td>
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<td>$N_A$</td>
<td>Avogadro’s number</td>
</tr>
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<tr>
<td>$N_{B4C}$</td>
<td>Atomic density of B$_4$C</td>
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<tr>
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</tr>
<tr>
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<td>Atomic density of Nitrogen</td>
</tr>
<tr>
<td>$N_T$</td>
<td>Total number of atoms per unit volume</td>
</tr>
<tr>
<td>OM</td>
<td>Optical Microscopy</td>
</tr>
<tr>
<td>PCA</td>
<td>Process Control Agent</td>
</tr>
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<td>PM</td>
<td>Powder Metallurgy</td>
</tr>
<tr>
<td>RSF</td>
<td>Relative Sensitivity Factor</td>
</tr>
<tr>
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<td>Scanning Electron Microscopy</td>
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<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>$t$</td>
<td>Analysis time in seconds/cycle</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>$V$</td>
<td>Total volume of the system</td>
</tr>
<tr>
<td>$V_{AlN}$</td>
<td>Total volume of AlN in the composite</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>$V_{\text{cell},i}$</td>
<td>Volume of the unit cell</td>
</tr>
<tr>
<td>VHP</td>
<td>Vacuum Hot Press</td>
</tr>
<tr>
<td>$v_i$</td>
<td>Volume fraction of the element or compound $i$</td>
</tr>
<tr>
<td>$w_{B_4C}$</td>
<td>Total weight of $B_4C$ in the composite</td>
</tr>
<tr>
<td>$W_N$</td>
<td>Total weight of Nitrogen atoms in the composite</td>
</tr>
<tr>
<td>$W_T$</td>
<td>Total weight of the composite before cryomilling</td>
</tr>
<tr>
<td>$W'_T$</td>
<td>Total weight of the composite after cryomilling</td>
</tr>
<tr>
<td>wt.%N</td>
<td>Weight percent of Nitrogen</td>
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<tr>
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<td>Volume fraction of $\text{AlN}$ in the composite</td>
</tr>
<tr>
<td>$y$</td>
<td>Volume fraction of $B_4C$ in the composite</td>
</tr>
<tr>
<td>$\rho_i$</td>
<td>Density of element or compound $i$</td>
</tr>
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<td>$\Sigma I_i$</td>
<td>Sum of the impurity isotope secondary ion counts over the depth profile in counts-cycle/s</td>
</tr>
<tr>
<td>$\Sigma I'_i$</td>
<td>Sum of the impurity isotope secondary ion counts over the depth profile in counts-cm/s</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Ion implant fluence in atoms/cm$^2$</td>
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</tbody>
</table>
CHAPTER 1: INTRODUCTION

Aluminum powder metallurgy (PM) parts are becoming increasingly prevalent in business machines, vehicles, aerospace components, power tools, appliances and to a lesser extent structural parts [1]. Traditionally PM produced small parts which were not load-bearing. The strength in PM parts can be improved by mechanical attrition of the powders which refines the grain size. Mechanical attrition also breaks up and uniformly distributes the native oxide on the surface of the powder thus creating an oxide dispersion strengthened material [2].

A structural material is required to be strong to bear loads, light in weight for vehicular applications and ductile to be formed into large sheets or plates. This combination of properties is not known in any one metal or alloy but can be approximated through combining of materials into composites. High strength metal matrix composites (MMC) have been manufactured through severe plastic deformation processes which produce nanocrystalline grains and a uniform distribution of ceramic reinforcements.

A low density composite has been designed with aluminum and boron carbide (B₄C) phases to create a material with a density of about 1/3 that of steel. In general, ductility decreases with grain size [3-5]; therefore, it becomes necessary to add other components such as coarse grain (CG) aluminum (~50μm). The increase in ductility is directly proportional to the fraction of CG added. This combination of nanocrystalline and micron-sized phases creates a multi-scale hierarchal composite.
The goal of this thesis is to support modeling efforts in designing hierarchal composites with optimal mechanical properties by providing relevant experimental data regarding the processing, properties, and microstructure relationships. The concentration and form of nitrogen containing phases will be addressed in relation to the cryomilling time.
CHAPTER 2: LITERATURE REVIEW

2.1 Cryomilling

Ball milling has been used extensively in industry and research to create high strength alloys and composites, especially in the field of oxide dispersion strengthened alloys. For composites, milling is often used to provide a uniform distribution of reinforcements [6, 7]. An attritor-type ball mill (see Figure 1) consists of several parts: a tank, center rotating shaft, and steel balls. The tank houses the center shaft, balls and the powder to be milled. The center shaft rotates transferring momentum to the steel balls.

![Attritor ball mill](image)

Figure 1: Attritor ball mill

Cryomilling is a low temperature variation of attritor ball milling that uses the same equipment only modified to allow for continuous flow of liquid cryogen. It is important to note that the term cryomilling has been used loosely in the literature as either ball milling at cryogenic temperatures or in a cryogenic medium.

If aluminum or any other highly reactive metals are milled at cryogenic temperatures in air, significant oxidation can occur due to localized temperature spikes.
from ball collisions [8] which assist in the formation of alumina (Al$_2$O$_3$). Too much alumina results in a lower ductility for the PM part. For the case of milling in a cryogen, nitrogen is heavier than air so it displaces the oxygen and allows for milling in an inert environment. This helps prevent oxidation of the newly fractured metal surfaces and therefore a retention of ductility. For this reason, aluminum is typically milled within a liquid nitrogen environment and in the remainder of this document cryomilling will be considered as milling in a cryogen where the cryogenic medium is liquid nitrogen (LN). Some of the benefits of cryomilling include: the suppression of recrystallization in metals [9], the breakup of prior particle boundaries while uniformly distributing them throughout the bulk [1, 6], and it has been shown to significantly increase hardness in 5083 Al [10].

2.2 Stearic Acid as a Source of Contamination

Cold welding and fracturing of the powder is facilitated by collision of the balls with each other and the jar walls. A process control agent (PCA) controls agglomeration by inhibiting cold welding through the lowering of the surface tension of the powders [11-13]. Too little PCA results in a lower yield of powder recovered from attritor due to powders welding to the balls and wall of the attritor which is irrecoverable [11, 13, 14]. The more PCA used, the more contamination (carbon, oxygen and hydrogen) is present in the final powder [11]. Therefore the amount of PCA added should be optimized so as to maximize yield while minimizing contamination of the powder.

It has been found that ball milling with organic surfactants adds carbides to the mix [1, 10]. The amount of C and O contamination is related to amount of PCA used in milling
Benjamin et. al. reported that the amount of retained carbon is approximately equal to the amount of Carbon added through the addition of the PCA [6].

Figure 2: Dispersoids in cryomilled Aluminum MMCs [16]. a) Aluminum Carbide, Al$_4$C$_3$; b) Theta-Alumina, $\theta$-Al$_2$O$_3$; Kappa-Alumina, $\kappa$-Al$_2$O$_3$

Oxide dispersoids are formed due to the breakup of the native oxide layer on the Aluminum powders and the presence of the PCA. An example of the types of carbides and oxides found in Al MMCs are given in the HRTEM images in Figure 2. These dispersoids are typically less than 10nm in diameter and are typically located at the nanocrystalline Al grain boundaries [16]. The images in Figure 2 are from a cryomilled Al MMC but similar dispersoids are expected in conventionally mechanically milled composites processed under similar conditions.

Stearic acid is the most commonly used PCA for milling of aluminum powders [13, 15-19] and is typically used from 1-3wt.% [18]. The chemical structure of stearic acid is C$_{18}$H$_{36}$O$_2$, has a melting point of 67-70°C and a boiling point of 183-184°C under vacuum [13, 20].
2.3 Degassing

Moisture is easily adsorbed by Al powder during handling and storage. This moisture is redistributed into the bulk during cryomilling but may be removed by degassing [1, 15]. If degassing is not performed, the moisture in the powder reacts with the aluminum to form Alumina and hydrogen gas. This gas can pose a potential safety hazard if the powder is confined or lead to residual porosity [21]. Degassing is also performed to remove any residual PCA from the powder. The most common method of degassing is the static vacuum degas where powder is placed into a canister to which a vacuum is slowly applied. Once the canister and powder are under high vacuum, a heat treatment is applied to help remove moisture and residual PCA from the powder [15]. Degassing is typically conducted at about 400°C and held for 4-8 hours [16, 19, 22].

2.4 Processing Effect on Microstructure

Powders are consolidated into a billet and then a secondary processing step is applied. Secondary processing is critical to disrupt prior particle boundaries [23]. Powders can be vacuum hot pressed (VHP), cold isostatic pressed (CIP), or hot isostatic pressed (HIP) then extruded, forged or rolled. HIP followed by extrusion is the most common consolidation process [15]. Yao et. al. has shown that typical consolidation processes result in only a marginal increase in n-Al grain size [24]. Grain growth is highly sensitive to the amount of strain applied at high temperature; therefore, there is typically a significant increase in grain size after secondary processing [16].
2.5 Strengthening Mechanisms

In order to develop the optimal balance of properties, a tri-modal or three-part composite has been developed. The composite consists of nanocrystalline AA5083 (nano-Al), B₄C particulate reinforcement and coarser grained AA5083 (CG-Al). It is known that the interface between the reinforcement and matrix is critical for load transfer and overall strength. Studies have shown that cryomilling provides good bonding between the nanocrystalline Aluminum and B₄C reinforcement [16].

The high strength of these composites is generally attributed to the small grain size through the Hall-Petch relation [1, 15]. The grain size of as-cryomilled powders is typically less than 30nm and can be as small as 20 ± 2 nm [16]. These grains typically exhibit a high thermal stability due to impurity drag [15, 19, 25-29]. These impurities also contribute to strengthening through Orowan Strengthening [19] and are mostly located at the nano-Al grain boundaries [16].

Dispersoids previously observed were Al₄C₃, θ Al₂O₃, and χ Al₂O₃ [2, 16]. Oxide dispersoids are formed by the breakup of the native oxide on the aluminum powder [2]. Other dispersoids that have been observed were platelets formed in cryomilled oxide dispersion strengthened Al which consisted of nitrogen in the tetrahedral positions of Al or a layer of oxygen in octahedral positions in Al [30]. Also observed are amorphous dispersoids which can crystallize during high temperature processing [16].

These dispersoids are dislocation sources during milling and suppress dislocation annihilation during consolidation processes [1]. They are also a source of strength for the composite through the process of dislocation entanglement. Dislocation densities in nano-
Al and CG Al phases have been measured to be $1.9 \cdot 10^{16} \text{m}^{-2}$ and $1.2 \cdot 10^{15} \text{m}^{-2}$ respectively after consolidation [16].
CHAPTER 3: EXPERIMENTAL

3.1 Materials

Gas atomized AA5083 (<45µm) from Valimet Inc (Stockton, CA) and Boron Carbide (B₄C) particles (1-7µm) from ESK Ceramics (Saline, MI) were used as starting materials for the composites. The chemical composition of AA5083 is displayed in Table 1.

Table 1: Composition of AA5083 [31].

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
<th>Others</th>
<th>Al (max)</th>
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</thead>
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<tr>
<td>AA5083</td>
<td>≤0.40</td>
<td>≤0.40</td>
<td>≤0.10</td>
<td>0.4-1.0</td>
<td>4.0-4.9</td>
<td>0.05-0.25</td>
<td>≤0.25</td>
<td>≤0.15</td>
<td>≤0.15</td>
<td>Balance</td>
</tr>
</tbody>
</table>

3.2 Composites

The AA5083 and B₄C powders were blended with a weight ratio of 4:1 respectively. A modified 1S Szegvari attritor was used for cryomilling. A charge of 1 kg of blended powders was cryomilled in a LN slurry with the attritor operating at 185rpm. 1/4” stainless steel milling balls were used with a ball to powder weight ratio of 32:1. To mitigate agglomeration of the powders, 0.2 wt.% stearic acid was added to the attritor as a process control agent. Samples were cryomilled for 8, 12, 16 or 24 hours which yielded composite agglomerates of nanocrystalline AA5083 and B₄C. After cryomilling, the powder and liquid nitrogen slurry was transferred to a glove box to allow for the liquid Nitrogen to boil off. Samples were then sieved with a -325 mesh to remove any excessively large agglomerates. To make the 3-part or tri-modal composite, additional gas-atomized AA5083 powder was added to the mix and V-blended (see [32]) for up to 24 hours to ensure a
homogenous distribution of the three components. The AA5083 MMCs consisted of 30 wt.% CG-Al, 14 wt.% B₄C and 56 wt.% n-Al. A type 304 Stainless Steel container was used to hold the powders during vacuum degassing. The powders were degassed at 395°C for 6 hours under vacuum. The powders were consolidated by CIP at 310MPa and then High Strain Rate (HSR) extruded with a reduction ratio of 6:1 at 524°C. Composite samples were polished down to 1µm for secondary ion mass spectrometry (SIMS) chemical analysis.

3.3 Extended hour 100% nano-Al Samples

AA5083 powder was cryomilled utilizing a modified 1S Szegvari attritor with 1 kg of blended powders in a LN slurry operating at 188rpm. 3/16” Stainless Steel milling balls were used with a ball to powder weight of 32:1. To mitigate agglomeration of the powders, 0.126 wt.% graphite was added to the attritor as a process control agent. Samples were cryomilled for 24, 48, 60, 67 and 72 hours. After cryomilling, the powder and liquid nitrogen slurry was transferred to a glove box to allow for the liquid Nitrogen to boil off. Samples were then sieved (-325 mesh) to remove any excessively large agglomerates. The 24, 48, 60 and 67hr powders were sent to Spectrographic Technologies (Pittsburgh, PA) for chemical quantification through gas fusion analysis. The 60hr and 72hr powders were cold pressed in air to form compacts and polished down to 1µm for SIMS analysis.

3.4 Characterization

An Olympus LEXT OLS 3000 CSM optical microscope (OM) was used to verify the integrity of the composite. In other words, it was used to locate any cracks, porosity, or
inhomogeneities. A FEI TEM-200 focused ion beam was used to prepare samples for transmission electron microscopy (TEM) utilizing in-situ lift out with a microprobe.

The FEI/Tecnai F30 300keV TEM/STEM was used to examine the nanocrystalline microstructure. Grain size quantification through X-ray diffraction is not feasible due to the distribution of grain sizes and presence of coarse grains in the composite. Therefore, in order to determine grain size, TEM was employed. Hollow cone dark field provides increased grain contrast over conventional bright field or dark field TEM, therefore this technique was chosen for quantification [33]. X-ray energy dispersive spectroscopy utilizing scanning TEM mode, was unable to detect nitrogen due to the low concentration in the samples. Electron energy loss spectroscopy was able to distinguish a nitrogen peak only in select (uncommon) areas. These areas were chosen for high resolution (HR) TEM.

Rockwell hardness was conducted on the composite samples employing a MacroMet 5100 series hardness tester operating on the B scale. The large indenter size allowed for an average hardness of the micro-constituents of the composite.

The PHI Adept 1010 Dynamic SIMS System was used to determine the relative sensitivity factor of nitrogen for SIMS and the nitrogen concentrations in the extended hour 100% nano-Al cryomilled samples. The PHI Adept utilized Cs ions in positive secondary mode at 90nA and analyzed the following ion pairs: $^{133}\text{Cs}^{27}\text{Al}$, $^{133}\text{Cs}^{24}\text{Mg}$, $^{133}\text{Cs}^{55}\text{Mn}$, $^{133}\text{Cs}^{14}\text{N}$, $^{133}\text{Cs}^{12}\text{C}$, $^{133}\text{Cs}^{16}\text{O}$ and $^{133}\text{Cs}^{11}\text{B}$. The $^{133}\text{Cs}^{27}\text{Al}$ signal was used for quantification.

The CAMECA IMS3F SIMS Ion Microscope was used in High Mass Resolution mode to analyze the composite samples utilizing Oxygen positive ions. The signals analyzed were
$^{27}$Al, $^{14}$N, $^{13}$C, $^{10}$B+$^{11}$B, $^1$H, $^{25}$Mg/2 and $^{55}$Mn. The Al2 signal was used for quantification in order to analyze all of the signals in the same filter (Electron Multiplier).

3.5 Ion-implantation to Determine Nitrogen Concentration from SIMS

SIMS quantifies the concentrations of elements via counting of mass to charge ratios. These counts are highly dependent on operating parameters such as current and ionizing gas [34]. Therefore an ion-implanted standard is required in order to quantify these counts into weight or atomic percent. A 400kV ion implanter (National Electrostatic Corporation) operating at 232kV was used to produce the AA5083 ion implanted sample. Mass separation was used to insure that the ion implanted species was $^{14}$N and the sample surface was scanned at a 7° tilt. The fluence that was implanted was 2.12E16 atoms/cm$^2$.

The PHI Adept 1010 Dynamic SIMS utilized the previously mentioned parameters to determine the distribution of ions in the sample.

3.5.1 Terminology

A relative sensitivity factor (RSF) is a conversion factor used to convert secondary ion intensity (counts/sec) from SIMS to atomic density (atoms/cm$^3$). It is defined by the equation [35]:

$$N_i = \frac{I_i}{I_m} \times RSF$$

where, $N_i$ is the impurity atom density (atoms/cm$^3$), $I_i$ is the impurity isotope secondary ion intensity (counts/s), and $I_m$ is the matrix isotope secondary ion intensity (counts/s).
An RSF can be determined from an ion-implanted calibration sample (assuming constant impurity background) utilizing the following equation [35]:

\[ RSF = \frac{\phi C I_m t}{d \sum I_i - d I_b C} \]  

(2)

where, \( \phi \) is the ion implant fluence (atoms/cm\(^2\)), \( C \) is the number of measurements or data cycles, \( d \) is the crater depth in cm (measured externally with a profilometer), \( \Sigma I_i \) is the sum of the impurity isotope secondary ion counts over the depth profile, \( I_b \) is the background ion intensity of the impurity isotope (counts/cycle) and \( t \) is the analysis time (seconds/cycle).

The sputtering rate, \( \dot{d} \), is the rate at which material is removed from the sample surface and defined by the following equation:

\[ \dot{d} = \frac{d}{Ct} \]  

(3)

After substituting into equation (2):

\[ RSF = \frac{\phi I_m t \dot{d}}{\sum I_i - I_b C} \]  

(4)

The sputtering rate can be applied to convert the x-axis from cycles to depth in nanometers which would change equation (4) to:

\[ RSF = \frac{\phi I_m}{\sum I'_i - I'_b d} \]  

(5)

where, \( \Sigma I'_i \) is sum of the impurity isotope secondary ion counts over the depth profile (counts·cm/s) and \( I'_b \) is background ion intensity of the impurity isotope (counts/s).
Figure 3: Schematic of an Ideal depth profile of an ion-implanted standard demonstrating how to use the RSF equation [equation (5)] for SIMS quantification.

In Figure 3, the shaded area under the curve represents the counts that are collected from the implanted ions only. Once the RSF is known, equation (1) can be applied to determine the nitrogen concentration in terms of atomic density (number of atoms per unit of volume) for samples with a similar matrix.

3.5.2 Atomic Density to Atomic and Weight Percent

3.5.2.1 Assumptions & Atomic Percent Definition

Assume that all of the atoms of nitrogen are in the crystal structure of aluminum nitride (AlN) or in an amorphous structure of similar density (mathematically it will be treated as AlN). Atomic percent is given by,
\[ \text{at.\%N} = \frac{N_N}{N_T} \times 100\% \]  

(6)

where, \( N_N \) is the number of nitrogen atoms per unit volume (measured) and \( N_T \) is the total number of atoms per unit volume. \( N_T \) is given by:

\[ N_T = \left( N_{Al} (1 - x - y)V + N_{AlN} \cdot x \cdot V + N_{B4C} \cdot y \cdot V \right)/V \]

where, \( N_{Al} \) is the atomic density of aluminum, \( N_{B4C} \) is the atomic density of B\(_4\)C, \( x \) is the volume fraction of AlN in the composite, \( y \) is the volume fraction of B\(_4\)C in the composite, and \( V \) is the total volume of the system. Simplifying,

\[ N_T = N_{Al} (1 - x - y) + N_{AlN} \cdot x + N_{B4C} \cdot y \]

(7)

Therefore:

\[ \text{at.\%N} = \frac{N_N}{N_{Al} (1 - x - y) + N_{AlN} \cdot x + N_{B4C} \cdot y} \times 100\% \]  

(8)

### 3.5.2.2 Atomic Density Calculation

Atomic density, \( N_i \), of element or compound i can be determined by:

\[ N_i = \frac{\rho_i N_A}{M_i} \]  

(9)

where, \( \rho_i \) is the density of element or compound i, \( N_A \) is Avogadro's number, and \( M_i \) is the atomic mass of element or compound i. Or, the atomic density may be expressed in terms of the number of atoms in its unit cell, \( n_i \) and the volume of the unit cell, \( V_{cell,i} \):

\[ N_i = \frac{n_i}{V_{cell,i}} \]  

(10)
3.5.2.3 Determination of B₄C volume fraction, y

B₄C and nitrogen do not interact during or after the cryomilling process therefore the volume fraction of B₄C is the same before and after cryomilling (Assume that the increase in volume due to the formation of AlN is negligible). In order to determine y, it is necessary to convert from weight fraction (before cryomilling) to volume fraction. The weight of B₄C in the composite is given by:

\[ W_{B4C} = V \cdot \rho_{B4C} \cdot y \]  \hspace{1cm} (11)

The total weight is given by:

\[ W_T = \sum V_i \cdot \rho_i \cdot v_i \]  \hspace{1cm} (12)

where \( v_i \) is the volume fraction of the element or compound i. Assume grain size does not significantly affect density. The nano-Al and CG aluminum are grouped into one volume fraction:

\[ v_{Al} = 1 - y \]  \hspace{1cm} (13)

The weight fraction is given by:

\[ w_{B4C} = \frac{W_{B4C}}{W_T} \]  \hspace{1cm} (14)

Substituting (11), (12) & (13) into (14),

\[ w_{B4C} = \frac{V \cdot \rho_{B4C} \cdot y}{V \cdot \rho_{B4C} \cdot y + V \cdot \rho_{Al} (1 - y)} \]

Solving for y,

\[ y = \frac{w_{B4C} \cdot \rho_{Al}}{\rho_{B4C} - w_{B4C} \rho_{B4C} + w_{B4C} \rho_{Al}} \]  \hspace{1cm} (15)
3.5.2.4 Determination of AlN volume fraction, $x$

The total number of atoms of nitrogen is equal to half the number of atoms of AlN (from stoichiometry).

$$# \text{atoms } N = 1/2(# \text{atoms } \text{AlN}) \quad (16)$$

The total number of AlN atoms can be expressed in terms of its atomic density and the volume of AlN, $V_{\text{AlN}}$, in the composite,

$$# \text{atoms } \text{AlN} = N_{\text{AlN}}(V_{\text{AlN}}) \quad (17)$$

The volume fraction of AlN is defined as:

$$x = V_{\text{AlN}} / V$$

Solving for $V_{\text{AlN}},$

$$V_{\text{AlN}} = x \cdot V \quad (18)$$

Substituting (18) into (17),

$$# \text{atoms } \text{AlN} = N_{\text{AlN}} \cdot x \cdot V \quad (19)$$

Substituting (19) into (16),

$$# \text{atoms } N = 1/2 \cdot N_{\text{AlN}} \cdot x \cdot V \quad (20)$$

Dividing (20) by the total volume,

$$N_{N} = 1/2 \cdot N_{\text{AlN}} \cdot x$$

Solving for $x,$

$$x = \frac{2 \cdot N_{N}}{N_{\text{AlN}}} \quad (21)$$
Once the volume fractions $x$ and $y$ have been determined, the atomic percent may easily be calculated by equation (8).

3.5.2.5 Weight Percent Calculation

To determine the mass fraction of nitrogen it is necessary to calculate the total weight of nitrogen atoms, $W_N$, in the volume, $V$.

$$W_N = \frac{\text{# atoms } N \cdot M_N}{N_A} \quad (22)$$

The total weight of the composite after cryomilling is given by:

$$W'_T = V \left( \rho_{\text{AN}} \cdot x + \rho_{\text{B4C}} \cdot y + \rho_{\text{Al}} (1 - x - y) \right) \quad (23)$$

The weight percent of N may be found by substituting (20) into (22) and dividing by (23):

$$\text{wt.\%} N = \frac{N_{AN} \cdot x \cdot M_N}{2N_A \left( \rho_{\text{AN}} \cdot x + \rho_{\text{B4C}} \cdot y + \rho_{\text{Al}} (1 - x - y) \right)} \cdot 100\% \quad (24)$$
CHAPTER 4: RESULTS AND ANALYSIS

4.1 Microstructure of Tri-modal MMCs

Figure 4a and b show representative OM images of tri-modal MMCs in transverse and longitudinal directions respectively. The dark particles are B₄C, the medium-gray agglomerates are nanocrystalline Al and the white regions are coarse grain Al agglomerates.

![Figure 4: Microstructure of Tri-modal MMCS. a) & b) is an OM image of composite where a) is the transverse and b) is the longitudinal direction. The dark particles are B₄C, the light grey regions are CG Al and the medium grey regions are nanocrystalline Al. Image c) is a BF TEM image which illustrates the excellent bonding between the three components of the composite. Image d) is an example of a HCDF image of the nano-Al grains. The interface between the B₄C and nanocrystalline Al matrix is shown in the BF TEM image in Figure 4c. There is no obvious porosity in the consolidated composite. An example of a typical HCDF TEM image of the nanocrystalline Al grains is given in Figure 4d. The grains](image-url)
show in Figure 4d are about 100nm in diameter; however, grains in cryomilled Al composites can be as small as 20nm and vary depending on the processing conditions [16]. Nitrogen was not detected by EDS on the TEM. EELS is more sensitive than EDS for light elements and detected nitrogen in select areas of the sample.

Figure 5: Typical EELS plot illustrating the Nitrogen and Oxygen peaks that are detected when the beam is focused on a nitrogen-containing dispersoid. This graph was measured while focused on an amorphous dispersoid containing both Nitrogen and Oxygen [16, 19]. An example of an EELS Spectrum of an amorphous dispersoid with an identified nitrogen peak is given in Figure 5. When nitrogen was detected by EELS, HRTEM was conducted in that area to find nitrogen-rich dispersoids.
Nitrogen-rich dispersoids in tri-modal MMCs [16]. a) Aluminum Nitride, AlN; b) amorphous, nitrogen-containing region within a nanocrystalline grain; c) amorphous interface between B₄C reinforcement and the nanocrystalline phase which also contained Nitrogen

Nitrogen was found in two types of dispersoids: amorphous regions and crystalline AlN (see Figure 6). [2, 16]. Amorphous dispersoids typically contain a mixture of O, C, N and Al [19]. Dispersoids were primarily found in the nano-Al grain boundaries but can also be found in in the B₄C-nanoAl interface [16]. TEM was able to confirm the presence of nitrogen containing dispersoids but was unable to determine the distribution due to the narrow field of view.

4.2 SIMS Depth Profiling to determine the RSF for Nitrogen in AA5083

In order to convert nitrogen concentration from counts to useful units such as atomic or weight percent, a standard was employed to determine how sensitive the instrument was to nitrogen under the given instrument parameters. The depth profile of the AA5083 nitrogen standard with a fluence of 2.12E16 atoms/cm² is given in Figure 7.
Figure 7: SIMS depth profile of the Nitrogen Ion-implanted Standard. The integration limits, for Nitrogen quantification, were chosen so as to avoid the surface contamination.

The $^{133}\text{Cs} + ^{27}\text{Al}$ signal is the matrix signal and $^{133}\text{Cs} + ^{14}\text{N}$ is the impurity signal of interest. The integration limits were chosen so as to avoid surface effects. The integration was calculated manually through trapezoidal Riemann sums. The matrix intensity was determined using an average intensity of the $^{133}\text{Cs} + ^{27}\text{Al}$ signal. The impurity background signal, $I_b$, is noted in Figure 7. After the ion-implanted peak, the average of the $^{133}\text{Cs} + ^{14}\text{N}$ signal was calculated as the background impurity intensity. The depth, $d$, was measured based on the limits of integration in Figure 7.

Table 2: Values used to calculate the RSF for an AA5083 N-implanted standard

<table>
<thead>
<tr>
<th>$\varphi$ (atoms/cm$^2$)</th>
<th>$I_m$ (counts)</th>
<th>$\Sigma I'_i$ (counts-cm)</th>
<th>$I'_b$ (counts)</th>
<th>$d$ (cm)</th>
<th>RSF (atoms/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.12E16</td>
<td>3.21E+06</td>
<td>1.00E-02</td>
<td>1.80E+01</td>
<td>1.19E-04</td>
<td>8.68E+24</td>
</tr>
</tbody>
</table>
Table 2 is a summary of the values determined from this depth profile as well as the RSF calculated from these values. Equation (1) was applied to determine the nitrogen concentration in terms of atomic density.

Although RSFs can vary significantly with the matrix [34], it is not possible to get an accurate RSF from an ion-implanted tri-modal composite sample due to: a) aluminum and B₄C do not sputter at the same rate leading to inaccurate depth quantification and b) the composite has a relatively high nitrogen background which hides the ion-implanted intensity. Therefore, the AA5083 ion-implanted standard was used for all samples including the tri-modal composites.

4.3 SIMS Depth Profiling to determine Nitrogen Concentration

Figure 8 is a representative depth profile of a 24hr cryomilled tri-modal MMC. The depth was calculated based on the total time of acquisition and the sputtering rate determined from the AA5083 N-implanted standard. Several matrix signals are plotted (\(^{133}\text{Cs} + ^{27}\text{Al}, ^{133}\text{Cs} + ^{24}\text{Mg}\) and \(^{133}\text{Cs} + ^{55}\text{Mn}\)) as well as the reinforcement chemistry (\(^{133}\text{Cs} + ^{11}\text{B}\) and \(^{133}\text{Cs} + ^{12}\text{C}\)) and common impurity elements (\(^{133}\text{Cs} + ^{14}\text{N}\) and \(^{133}\text{Cs} + ^{16}\text{O}\)). The 100% cryomilled nano-Al samples have a similar depth profile to that shown in Figure 8 only the boron and carbon signals are much lower.

Because SIMS is sensitive to each element differently, it is important to note that the relative concentration of each element cannot be directly compared from this graph. However, we can note that all of the signals level off suggesting that the composite has a uniform composition beyond the surface (~250nm).
Figure 8: Typical depth profile of a tri-modal composite

The depth profile in Figure 8 was quantified by normalizing the N signal to the Al matrix signal and multiplying by the RSF (see Figure 9). This gives the Nitrogen atomic density as a function of depth. The atomic Density of Nitrogen for the tri-modal 24hr cryomilled composite was determined to be $1.72 \cdot 10^{21}$ atoms/cm$^3$. 
Utilizing equations (8), (15), and (21); the Nitrogen Concentration was calculated as 3.00 at. % or 1.51 wt.% utilizing equation (24). This value is comparable to the 3.3 wt.% (as measured by Spectrographic Technologies) for a 100% nano-Al 24hr cryomilled sample.

4.4 Nitrogen as a Function of Cryomilling Time

The technique applied in the previous section for the 24hr cryomilled tri-modal MMC was applied to the composites cryomilled for 8, 12, and 16 hours as well as the extended hour 100% nano-Al samples cryomilled for 60 and 72 hours. This result along with the analysis by Spectrographic Technologies is plotted in Figure 10. According to Figure 10, nitrogen increases as a function of cryomilling time up to 72 hours.
The wt.%N for a 100% cryomilled sample was estimated utilizing the 14:30 composite samples for the shorter cryomilling times (8, 12, 16, 24hr) according to the following equation:

$$\frac{wt.%N}{56wt.%Al} = \frac{Estimated\ wt.%N}{100wt.%Al}$$  \hspace{1cm} (25)

Employing equation (25), it is easier to compare the composites to the 100% nano-Al samples (see Figure 11).
Figure 11: Nitrogen Concentration as a function of cryomilling time for 100% cryomilled nanocrystalline Aluminum from 8 to 72 hours.

It is known that B₄C helps nitrogen retention [36], therefore the nitrogen concentration calculated from the 14:30 composite samples is likely overestimated. Despite this, the nitrogen concentration calculated through the SIMS method corresponds well to that calculated through the gas fusion technique. In Figure 11 a roughly continuous curve can be found from 8 to 72 hours cryomilling time.

The values plotted in Figure 10 and Figure 11 are summarized in Table 3.
Table 3: Summary of Nitrogen Concentration

<table>
<thead>
<tr>
<th>Volume Fraction of AlN, x (%)</th>
<th>Nitrogen Concentration (wt.%)</th>
<th>Cryomillling Time (hr)</th>
<th>B₄C Weight Fraction (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 hours MMC</td>
<td>0.53</td>
<td>0.45</td>
<td>8</td>
</tr>
<tr>
<td>12 hours MMC</td>
<td>0.77</td>
<td>0.65</td>
<td>12</td>
</tr>
<tr>
<td>16 hours MMC</td>
<td>1.05</td>
<td>0.89</td>
<td>16</td>
</tr>
<tr>
<td>24 hours MMC</td>
<td>1.88</td>
<td>1.59</td>
<td>24</td>
</tr>
<tr>
<td>60 hours</td>
<td>7.67</td>
<td>6.33</td>
<td>60</td>
</tr>
<tr>
<td>72 hours</td>
<td>16.26</td>
<td>13.17</td>
<td>72</td>
</tr>
<tr>
<td>2nd run 48 hours</td>
<td></td>
<td>3.50</td>
<td>48</td>
</tr>
<tr>
<td>3rd run 24 hours</td>
<td></td>
<td>3.27</td>
<td>24</td>
</tr>
<tr>
<td>3rd run 48 hours</td>
<td></td>
<td>4.31</td>
<td>48</td>
</tr>
<tr>
<td>3rd run 60 hours</td>
<td></td>
<td>6.48</td>
<td>60</td>
</tr>
<tr>
<td>4th run 24 hours</td>
<td></td>
<td>3.53</td>
<td>24</td>
</tr>
<tr>
<td>4th run 48 hours</td>
<td></td>
<td>6.45</td>
<td>48</td>
</tr>
<tr>
<td>4th run 67 hours</td>
<td></td>
<td>9.46</td>
<td>67</td>
</tr>
<tr>
<td>Calculated 8 hours</td>
<td>0.80</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>Calculated 12 hours</td>
<td>1.16</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>Calculated 16 hours</td>
<td>1.59</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>Calculated 24 hours</td>
<td>2.84</td>
<td></td>
<td>24</td>
</tr>
</tbody>
</table>
CHAPTER 5: DISCUSSION

5.1 How Nitrogen is Stored in the Composite

Nitrogen is trapped between agglomerate interfaces and mechanically alloyed with Al during cryomilling [19]. This entrapment is assisted by the excess of defects (including vacancies, dislocations and grain boundaries) produced by milling. The increased surface area provided by the abundance of grain boundaries allows for supersaturation of elements [1] which may destabilize the Al crystal leading to amorphous phases [19]. Davis et. al. have developed a model of the localized spikes in temperature due to ball collisions [8]. These localized spikes in temperature may provide the thermal energy required for the formation of phases such as AlN. Further research is necessary to verify the mechanism of nitrogen mechanical alloying in cryomilled metals.

5.2 Hardness vs. Nitrogen Concentration

Hardness increases with nitrogen concentration (see Figure 12). It is generally considered that grain size is the major strength contributor as compared to the other mechanisms [15, 16, 19, 37]. Therefore, the increase in hardness is likely due to the difference in grain size of the nanocrystalline Al phase.
Figure 12: Rockwell Hardness as a function of Nitrogen Concentration for the 8, 12, 16 and 24 hours cryomilled Al MMCs

5.3 Nanocrystalline Grain Size vs. Nitrogen Concentration

The grain size was only quantified for the composite samples. Grain size decreases as a function of Nitrogen concentration as seen in Figure 13. It has been shown that after about 4 hours of milling, the nanocrystalline Al reaches its minimum grain size [15]; therefore, the difference in grain size, represented in Figure 13, can be related to the ability of the nitrogen-rich dispersoids in the sample to pin the grain boundaries.
Figure 13: Grain Size as a function of Nitrogen Concentration for the 8, 12, 16 and 24 hours cryomilled Al MMCs

In other words, the more nitrogen, the more dispersoids, the more pinning of the grain boundaries thus inhibiting grain growth [19].

Table 4: Grain Size and Rockwell Hardness values for the Composite samples

<table>
<thead>
<tr>
<th></th>
<th>Grain Size (nm)</th>
<th>Rockwell Hardness B Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Std Dev</td>
</tr>
<tr>
<td>8 hours MMC</td>
<td>104.1</td>
<td>5.205</td>
</tr>
<tr>
<td>12 hours MMC</td>
<td>84.2</td>
<td>4.21</td>
</tr>
<tr>
<td>16 hours MMC</td>
<td>70.4</td>
<td>3.52</td>
</tr>
<tr>
<td>24 hours MMC</td>
<td>54.64</td>
<td>1.33</td>
</tr>
</tbody>
</table>

The grain size determined via HCDF and the Rockwell Hardness of the 14:30 composite samples are reported in Table 4.
CHAPTER 6: SUMMARY AND CONCLUSIONS

Nitrogen has been found in small, less than 10nm diameter, dispersoids. In order to estimate the nitrogen concentration and distribution, a method to determine the concentration of nitrogen in aluminum MMCs from SIMS was developed. Nitrogen was found to increase as a function of cryomilling time up to 72 hours and has been proven to aid in the retention of the nanostructured grain size. For samples processed for extended cryomilling times, future work includes determining the size and shape of the dispersoids and comparing to the findings of the 8, 12, 16 and 24 hours cryomilled samples.

In order to estimate the strength contributions of each dispersoid, it is necessary to know their size and distribution in the composite. It has been previously published that the Carbon introduced into the sample through the surfactant remains in the sample in the form of $\text{Al}_4\text{C}_3$ [2]. Therefore, the density of $\text{Al}_4\text{C}_3$ in composites is a function of the type and amount of PCA used. Nitrogen distribution can be estimated based on the AlN and amorphous dispersoid size alongside the nitrogen concentrations determined in this study. Oxygen dispersoids are formed as a result of the breakup of the native oxide formed on the aluminum powders during gas atomization or powder handling. In order to determine the distribution of these dispersoids detailed analysis of the as-received powders is necessary. The role of the surfactant in the development of oxygen-rich dispersoids is not yet clearly understood and requires further study.

This study determined the form and concentration of nitrogen in aluminum MMCs as a result of the cryomilling time. Based on these results, modelers may better develop
strength and ductility models to determine appropriate processing conditions in order to
develop a MMC with balanced strength and ductility. Future work includes the
development of a model which would estimate the strength and ductility of a composite
considering the contributions of each dispersoid along with the other strengthening
mechanisms.
LIST OF REFERENCES


