

# Light Metals 2014

**LIGHT-METAL  
MATRIX (NANO)-COMPOSITES**

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## **Microstructure-Property Relationships I**

*SESSION CHAIR*

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## EFFECT OF PROCESS CONTROL AGENT ON THE MICROSTRUCTURE AND MECHANICAL BEHAVIOR OF AN ALUMINUM AND B<sub>4</sub>C METAL MATRIX COMPOSITE

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Keywords: Process Control Agent, Aluminum, Composite, Boron Carbide, Trimodal, Cryomilling

### Abstract

AA5083 and B<sub>4</sub>C powders were cryomilled in liquid nitrogen utilizing oleic, caprylic and stearic acids individually in order to determine the effect of each process control agent on the resultant microstructure and mechanical properties. The microstructure of the powders was examined and consolidated samples were mechanically tested in compression. Chemical analysis was performed to determine impurity concentrations of nitrogen, hydrogen and oxygen. Microstructural analysis of the powders revealed three types of agglomerates: composite powders of AA5083 with uniformly distributed B<sub>4</sub>C particulate, un-milled spherical AA5083 powder and deformed AA5083 powder. These three types of agglomerates were found in similar size and proportion regardless of the process control agent used. Nitrogen concentration correlates directly to the oxygen concentration in the sample. There was a slight increase in compressive strength with the increase in oxygen and nitrogen concentrations.

### Introduction

Aluminum composites reinforced with B<sub>4</sub>C have increasingly become a material interest in research because of its excellent strength-to-weight considerations [1]. The strengthening mechanisms of this composite include nanocrystalline aluminum 5083 grains, dispersoids, and a high dislocation density [2]. In order to incorporate these strengthening mechanisms into the composite, cryomilling is performed on the precursor powders. Cryomilling in liquid nitrogen (LN<sub>2</sub>) can produce a finer grain size compared to conventional ball milling and introduce grain stabilizing/strengthening nitride-dispersoids from the LN<sub>2</sub> environment [2, 3]. A process control agent (PCA) is typically used to control the agglomeration of the powders. This PCA may also introduce carbides into the powders providing additional strengthening [4]. In this study, the effect of the PCA choice on the microstructure and resultant mechanical properties of the consolidated composites, where cryomilling was carried out with different PCAs (namely caprylic, oleic, and stearic acids), was determined. Some physical and chemical properties of these acids are listed in Table I. The carbon and hydrogen concentrations for the three acids are similar, however caprylic acid has almost double the amount of oxygen.

After cryomilling, degassing is a required processing step to remove any residual moisture or process control agent absorbed by the powder [4]. Therefore, in addition to varying the PCA, the degassing temperatures were also varied to determine the optimal degassing parameters that would result in a composite of minimum impurity and maximum mechanical properties. The goal of the

project is to optimize the cryomilling and degassing process in order to manufacture high strength-low density aluminum composites for structural applications. In this paper, we present preliminary results that demonstrate the process-dependent chemistry and properties.

Table I: Physical and chemical properties of Stearic, Oleic and Caprylic acid [5].

	C (wt.%)	H (wt.%)	O (wt.%)	b.p. (°C)	Decomposition Temp (°C)	Physical State at Room Temp
Stearic Acid	76	12.75	11.25	383	90-100	Waxy solid
Oleic Acid	76.54	12.13	11.33	286	80-100	Oil
Caprylic Acid	66.63	11.18	22.19	239.7	n/a	Oil

### Experimental

A Szegvari Union Process 1-S attritor was modified to allow for continuous flow of LN<sub>2</sub>. Powders were cryomilled in LN<sub>2</sub> for 8 h with a ball to powder weight-ratio of 32:1. AA5083 (-325 mesh from Valimet Inc) and B<sub>4</sub>C (2 to 5 μm Micro Abrasives Corporation) powders were blended in a V-blender for up to 24 h before cryomilling. To determine the effect of the PCA on the microstructure and mechanical properties, 0.25 wt.% of oleic, caprylic or stearic acid was added to the powder to be cryomilled. Stearic acid was V-blended with the powder prior to cryomilling to ensure a uniform distribution of PCA. Oleic and caprylic acids are liquid at room temperature and could not be added directly to the blender; therefore, these acids were mixed with LN<sub>2</sub> and added directly into the attritor.

After cryomilling, the powders were collected and placed in a glove box to allow for the LN<sub>2</sub> to boil-off. To improve ductility of the composite, additional un-milled AA5083 powders were added to the cryomilled powders and V-blended for 24 h. The final composite consisted of 60 wt.% nanostructured AA5083, 10 wt.% B<sub>4</sub>C, and 30 wt.% coarse grain AA5083. The powders were degassed between 275-410°C in a custom-made static vacuum degasser with a maximum vacuum of ~10<sup>-6</sup> torr. Once high vacuum was achieved, the furnace was ramped to the desired temperature over 6 hours, soaked for 8 hours, and then the heater was shut off, and allowed to cool to room temperature. The degassing temperatures were chosen to ensure removal of the PCA from the powder. The boiling (b.p.) and decomposition temperatures for each surfactant is given in Table II. Powder was consolidated

through cold isostatic pressing at 310 MPa followed by preheating in an oven at 525°C for 30 min and high strain rate extrusion, which was carried out on a Dynapak press at 13.4 m/s with a reduction ratio of approximately 6:1. Table II summarizes the process variation of specimens examined in this study with sample designations.

Table II: Variation in PCA and degassing temperature for the specimens examined in this study with sample designation.

Sample ID	S-D410	O-D310	C-D275	O-D410	C-D410
PCA	0.25 wt.% Stearic Acid	0.25 wt.% Oleic Acid	0.25 wt.% Caprylic Acid	0.25 wt.% Oleic Acid	0.25 wt.% Caprylic Acid
Degassing Temp (in °C)	410	310	275	410	410

The agglomerate size and distribution of the powders was observed with an Olympus LEXT OLS 3000 confocal optical microscope (OM). Scanning electron microscopy (SEM) was conducted on the as-cryomilled powders using a Zeiss ULTRA-55 field emission scanning electron microscope operating at 15 kV and 8 mm working distance to examine the microstructure of the as-cryomilled powders. Mechanical testing was conducted on the samples according to ASTM standard E9 for compression testing. The composition analysis for the hydrogen, nitrogen and oxygen impurities in the consolidated samples were determined by inert gas fusion technique (Spectrographic Technologies; Pittsburgh, PA).

#### Microstructure of the Cryomilled Powders

Optical micrographs of the powders cryomilled for 8 h (prior to degassing) utilizing oleic, caprylic or stearic acid are presented in Figure 1. They show similar microstructure regardless of the PCA used. Three types of agglomerates were identified in the powders: composite agglomerate (i.e., AA5083 and B<sub>4</sub>C) with rounded shape (arrow 1 in Figure 1c); circular, un-deformed AA5083 agglomerate without B<sub>4</sub>C (arrow 2 in Figure 1c); and “pancake-shaped”, deformed aluminum agglomerates without B<sub>4</sub>C (arrow 3 in Figure 1d).

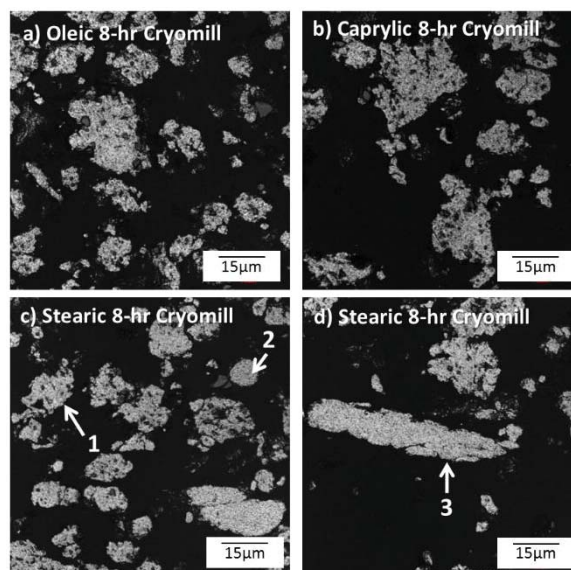


Figure 1: Optical micrographs of aluminum composite agglomerates after cryomilling. Powders were cryomilled for 8 h with (a) oleic acid, (b) caprylic acid, and (c, d) stearic acid.

The powders are not homogeneous after 8 h of cryomilling. Inhomogeneous microstructure has been observed in other studies with similar milling conditions [6, 7]. Cracks in the powder, as seen in Figure 2, may be due to insufficient energy in the mill or too much PCA (limiting the cold welding of the agglomerates).

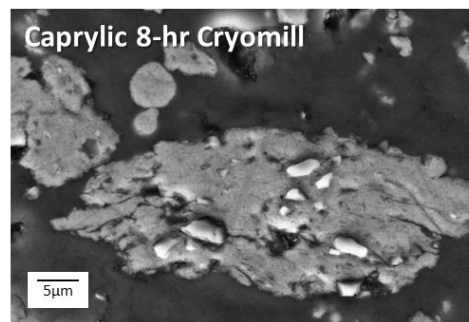


Figure 2: Secondary electron micrograph of the aluminum composite agglomerate after cryomilling with caprylic acid as the PCA.

It is expected that B<sub>4</sub>C can assist in the cold fracturing of the powder during cryomilling, and therefore reduce the final grain size [8]. Therefore the grain size in the powder likely varies between the powder agglomerates with and without B<sub>4</sub>C. It is important to note that although it is unlikely that the powders have a uniform grain size, it is expected that the three powders analyzed in this study have the same variation in grain size because they have similar types and distribution of agglomerates. Therefore the overall contribution to strength by grain size is expected to be similar for all three powders. Currently we are examining the microstructure of the powders via TEM for more quantitative details.

#### Hydrogen, Oxygen and Nitrogen Impurities

In Figure 3, hydrogen concentration has been plotted as a function of degassing temperature. Hydrogen concentration decreases with an increase in degassing temperature. Hydrogen may be released

from the powder in one of three ways: (1) through the removal of moisture from the powder, (2) from the reaction of absorbed moisture with the aluminum matrix, which produces alumina and hydrogen gas and/or (3) from the decomposition of the PCA.

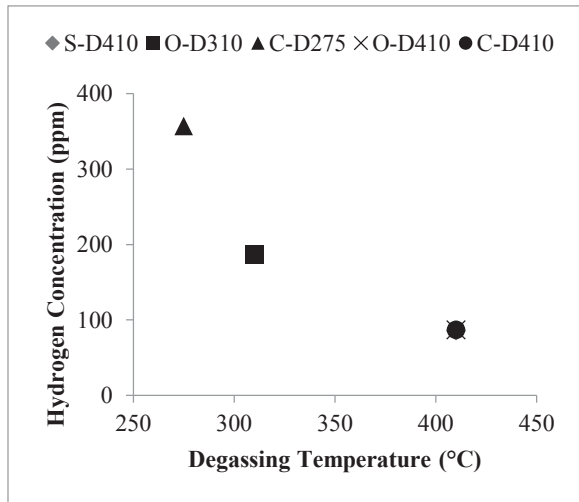


Figure 3: Hydrogen Concentration vs. Degassing Temperature.

At the highest degassing temperature, the removal of hydrogen is equally efficient regardless of the PCA chosen. Assuming that all of the powders had a similar absorbed moisture concentration before degassing and moisture is the primary degassing product, there would be a correlation between residual hydrogen and oxygen concentration in the sample. As presented in Figure 4, no such correlation exists. On the other hand, assuming that the majority of the moisture reacts with the aluminum matrix to produce hydrogen gas, it would be expected that at the highest temperature, 410°C, where the most hydrogen is removed from the sample, there would also be the highest amount of oxygen retained in the sample. Upon examining Figure 4, this correlation is not observed either. Therefore it may be suggested that both the degassing of moisture and the reaction of moisture with the aluminum matrix occurs. Further research is required to determine the dominant mechanism.

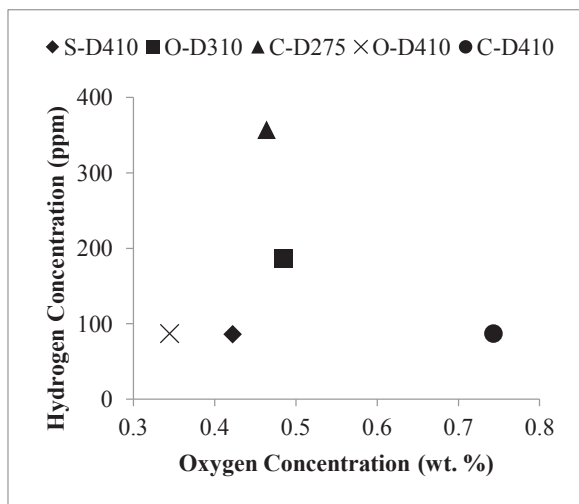


Figure 4: Hydrogen concentration vs. Oxygen concentration.

Figure 5 shows that there is a clear correlation between the concentrations of oxygen and nitrogen. Similar results have been

reported previously for aluminum composites reinforced with AlN [9]. This data suggests that the mechanism behind nitrogen storage is directly related to the oxygen retained in the sample.

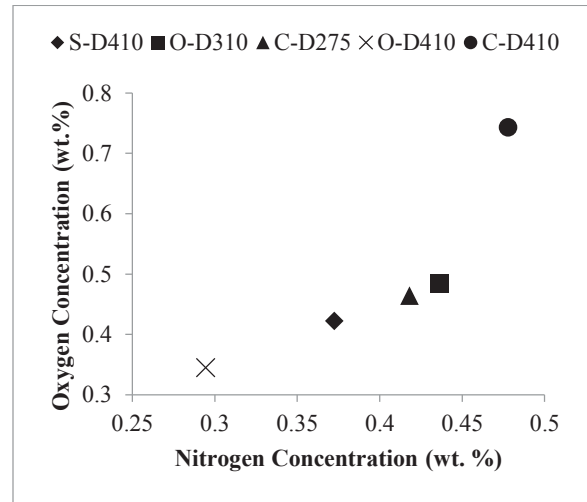


Figure 5: Nitrogen concentration vs. Oxygen concentrations

If only the samples degassed at 410°C were considered, it is clear that the choice of PCA affects the resultant oxygen and therefore the nitrogen content. Recall that the concentration of oxygen is similar in oleic and stearic acids but much less than that of caprylic acid. Therefore it is logical that there would be higher oxygen impurity in the powder treated with caprylic acid. However, if the C-D275 and C-D410 are considered, both cryomilled with caprylic acid but degassed at 275° and 410°C, respectively, it is obvious that the choice of degassing temperature is also critical in controlling the final oxygen and nitrogen concentrations.

### Compressive Strength

In Figure 6, compressive strength has been plotted against hydrogen concentrations of the samples. It can be seen that strength decreases with an increase in hydrogen concentration. For the most part, the mechanical properties are similar regardless of PCA chosen.

As shown previously in Figure 6, the composite produced from C-D275 powder contains a very high hydrogen content as compared to the other composites tested. In Figures 7 and 8, this composite shows a low strength but it would be unreasonable to conclude that this is a result of the nitrogen or oxygen concentrations in the sample. Therefore when discussing the trend in strength with nitrogen and oxygen, this data point is ignored. As a result, it may be observed that the increases in oxygen and nitrogen concentration (as presented in Figure 7 and 8, respectively) results in a *slight* increase in compressive strength.

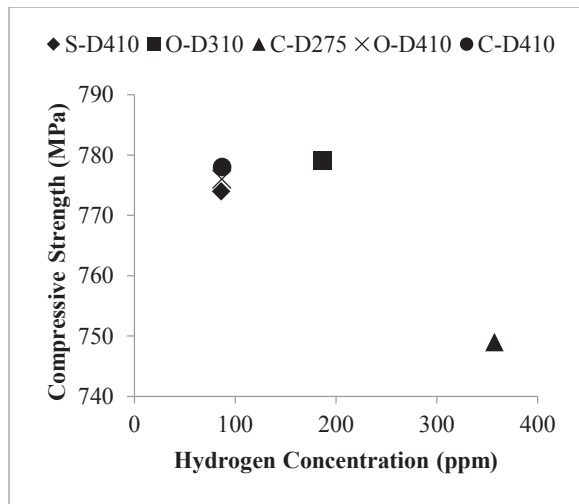


Figure 6: Hydrogen Impurity Concentration vs. Strength

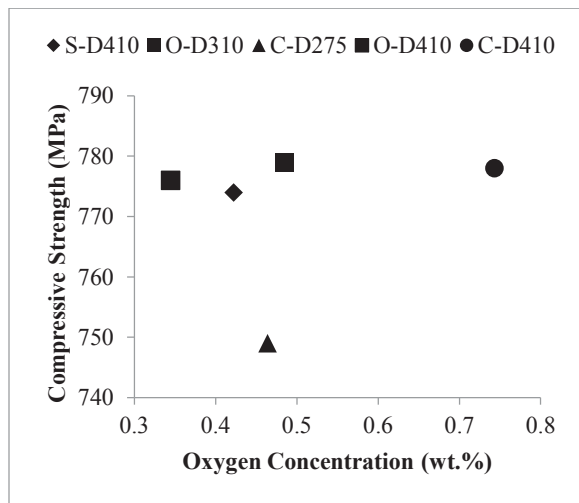


Figure 7: Oxygen Impurity Concentration vs. Compressive Strength.

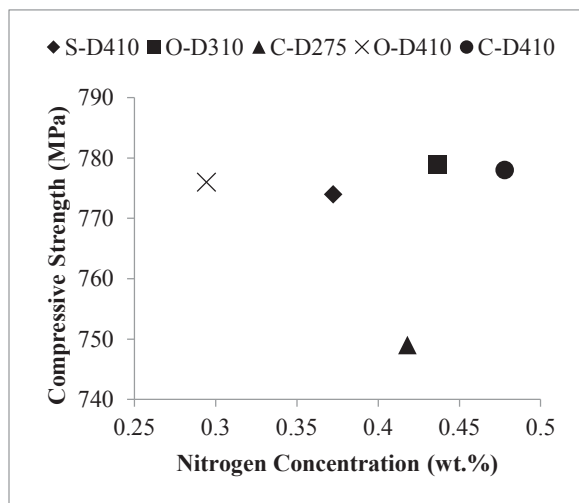


Figure 8: Nitrogen Impurity Concentration vs. Compressive Strength.

## Conclusion

Chemistry, microstructure and compressive strength of B<sub>4</sub>C reinforced AA5083 composites were examined with respect to impurity content arising from cryomilling in liquid nitrogen. Microstructure of the as-cryomilled powders was similar regardless of the PCA used. Hydrogen content decreased with increasing temperature of degas anneal. A clear correlation between oxygen and nitrogen content was also observed. A slight increase in the compressive strength was observed with increases in oxygen and nitrogen concentrations. However, excessive hydrogen content had a strong deleterious influence on the composite compressive strength. Tensile tests are being carried out to determine the influence of hydrogen, oxygen and nitrogen on the tensile properties. A correlation between compressive and tensile properties is also being investigated in light of the impurity content.

## Acknowledgments / Disclaimer

Research was sponsored by the U.S. Army Research Laboratory and was accomplished with funds under Cooperative Agreement W911NF-11-2-0020 to University of Central Florida. The use of specific trade names does not imply endorsement of products or companies by the U.S. Army Research Laboratory but are used to fully describe the experimental procedures. The views, opinions, and conclusions made in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the U.S. Army Research Laboratory or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein.

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