IN-SITU MANUFACTURING OF ALUMINUM-ALUMINUM NITRIDE CASTABLE NANOCOMPOSITE MATERIALS

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Abstract
In this contribution we present a novel manufacturing process in which aluminum nitride nanoparticles are synthesized in-situ within a specially formulated aluminum alloy by means of a controlled gas-liquid reaction to produce an aluminum matrix composite material wherein nano-sized aluminum nitride particles are homogeneously dispersed. Also in this contribution we address the effect of the manufacturing process parameters and the chemical composition of the matrix alloy and reactive gas on the efficiency of the aluminum nitridation reaction.

1 Introduction

Aluminum matrix-ceramic nanoparticle composite materials have mechanical and physical properties that make them attractive for many applications in the aerospace, automotive and microprocessor industries. However, producing these materials on a large scale remains difficult despite the numerous attempts that have been made to overcome the typical issues associated with their manufacture. These methods include mechanical and ultra sonic agitation, powder metallurgy, powder infiltration, and spray deposition [1, 2]. Unfortunately, most of these methods are expensive, and each one of them has its own limitations. Manufacturing methods that are based on adding ex-situ particles to molten metal and employing mechanical stirring to disperse them [3], methods that are based on liquid infiltration of ceramic substrates [4], and methods that are based on powder metallurgy [5, 6] have serious limitations when dealing with nanometer size particles (e.g., particle clustering and particle/matrix interface de-bonding). Also more recent fabrication methods, such as spray deposition [1], ultrasonic-assisted cavitations [7], and plasma synthesis [8] all suffer from the lack of scalability and high cost. In-situ fabrication of the reinforcing particles inside the metal matrix overcomes many of these issues because the nano-sized particles are formed directly within the melt by means of a controlled chemical reaction between the molten alloy and an appropriate gas. In-situ particle synthesis ensures good distribution of the reinforcing particles in the matrix alloy, a small particle size, and a clean thermodynamically stable particle/matrix interface [9]. In this contribution, we report on our efforts to assess the feasibility of the in-situ process for synthesizing aluminum-aluminum nitride nanocomposites and the effect of the process parameters on the characteristics of the resulting material.

2 Apparatus, Materials, and Procedures

The apparatus shown schematically in Figure 1 was designed, built, and used to manufacture ingots of the composite material. Two hundred grams of the metal 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 purified nitrogen-bearing 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. 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.
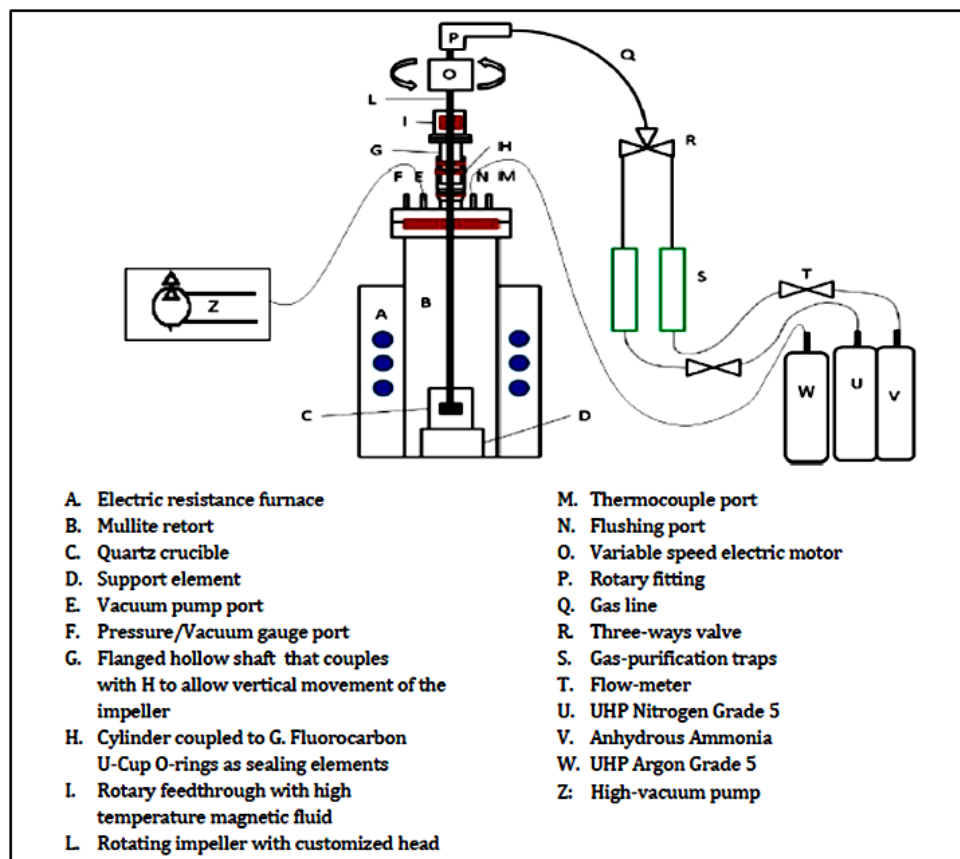

A. Electric resistance furnace
B. Mullite retort
C. Quartz crucible
D. Support element
E. Vacuum pump port
F. Pressure/Vacuum gauge port
G. Flanged hollow shaft that couples with H to allow vertical movement of the impeller
H. Cylinder coupled to G. Fluorocarbon U-Cup O-rings as sealing elements
I. Rotary feedthrough with high temperature magnetic fluid
L. Rotating impeller with customized head

M. Thermocouple port
N. Flushing port
O. Variable speed electric motor
P. Rotary fitting
Q. Gas line
R. Three-ways valve
S. Gas-purification traps
T. Flow-meter
U. UHP Nitrogen Grade 5
V. Anhydrous Ammonia
W. UHP Argon Grade 5
Z. High-vacuum pump

Figure 1. Schematic representation of the apparatus.

3 Design of Experiments

The design of experiments is summarized in Table 1.

| Constants	Independent variables	Dependent (measured) variables
– Heating rate = 4°C/min	– Alloy composition	– Volume percent aluminum nitride
– Temperature = 1050°C	– Processing time	– Distribution of aluminum nitride in the matrix (Mean free path)
– Rotation speed = 250 rpm	– Gas composition	– Average size of aluminum nitride particles
– Gas flow rate ≈1 l/min		– Average size of aluminum nitride clusters
		– Hardness of composite material

Experiment #	Alloy composition	Gas composition	Processing time
1	Al-5 wt% Li	N_2	2
2	Al-5 wt% Li	N_2	4
3	Al-5 wt% Li	$N_2/ NH_3=1/1$	2
4	Al-5 wt% Li	$N_2/ NH_3=1/1$	4
5	Al-5 wt% Li	NH_3	2
6	Al-5 wt% Li	NH_3	4
7	Al-2.5 wt% Li	N_2	2
8	Al-2.5 wt% Li	N_2	4
9	Al-2.5 wt% Li	$N_2/ NH_3=1/1$	2
10	Al-2.5 wt% Li	$N_2/ NH_3=1/1$	4
11	Al-2.5 wt% Li	NH_3	2
12	Al-2.5 wt% Li	NH_3	4

Table 1. Design of experiments.

Samples were taken from the top and the medium-lower sections of the ingots in order to determine the amount of aluminum nitride that formed in these locations. The samples were first ground with silicon carbide paper and then with a diamond suspension. The final polishing was performed with a silica suspension and then the samples were ultrasonically cleaned for 45 minutes in order to remove all contamination that may have been caused by the sample preparation process. The samples were etched with a 10% NaOH solution for 5 seconds in order to improve visualization of the aluminum nitride particles. X-ray diffraction (XRD) was used to confirm the presence of aluminum nitride and a scanning electron microscope (SEM) was used to create photomicrographs of the material. A Matlab-based program [2] was used to analyze the bitmap micrographs and to determine the volume fraction of the aluminum nitride phase, the mean length of the free space between the aluminum nitride particles, the average size of the aluminum nitride particles, and the average size of the aluminum nitride clusters. In order to ensure statistical validity of the measurements, a minimum of ten micrographs for each sample were used. Hardness measurements were made by means of a 1.6 mm steel ball and 100 kg total load (Rockwell B). An average of fifteen measurements was made on each sample.

4 Results and Discussion

Figure 3 shows SEM photomicrographs of the materials processed according to the conditions outlined in Table 1. Results from analyzing these photographs are summarized in Table 2.

(a)

(b)

(b)

(d)

(e)

(f)

(g)

(h)
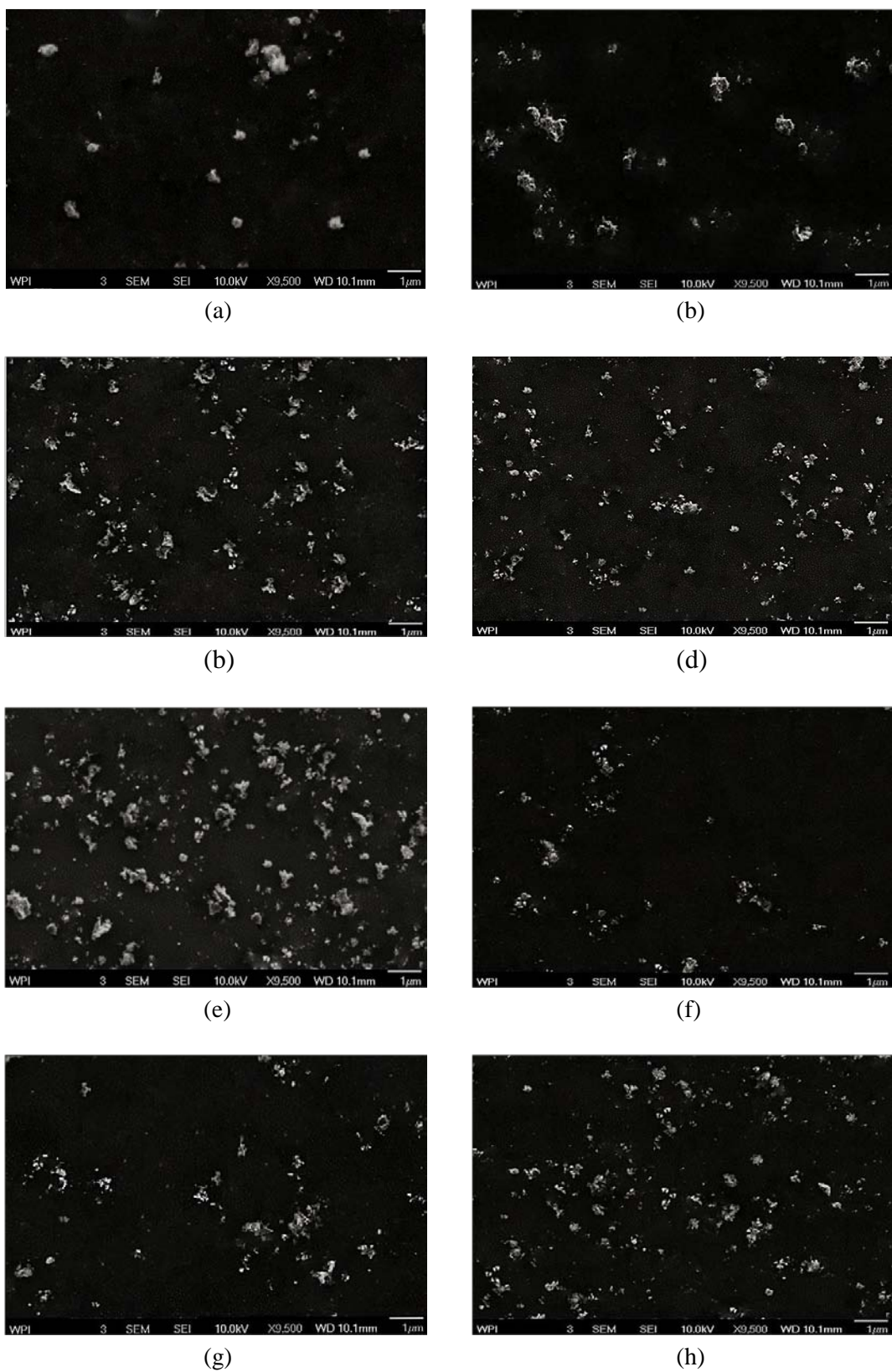
Figure 3. SEM photomicrographs of samples from materials processed according to the conditions outlined in Table 1. (a)-(h) are for samples from experiments 2, 3, 4, 5, 6, 10, 11, and 12; respectively.

Experiment #	Volume AlN (%)	Avg. particle size (nm)	Avg. cluster size (nm)	Distribution index
1	No aluminum nitride particles were detected			
2	6.2	643	1540	0.58
3	9.5	489	1327	0.37
4	26.0	453	1552	0.51
5	21.0	274	966	0.82
6	48.0	312	1114	0.74
7 - 9	No aluminum nitride particles were detected			
10	7.4	655	924	0.31
11	12.8	409	1012	0.73
12	31.0	293	785	0.65

Table 2. Summary of the findings.

Experiments #1 and 2 – Almost no aluminum nitride was detected in the ingots after injecting pure nitrogen gas into molten Al-5 wt% Li alloy for 2 hours. When nitrogen gas was injected for 4 hours (Experiment #2), XRD analysis of the resulting ingot (Figure 3) shows the presence of aluminum nitride in the top and the middle-bottom sections of the ingot.
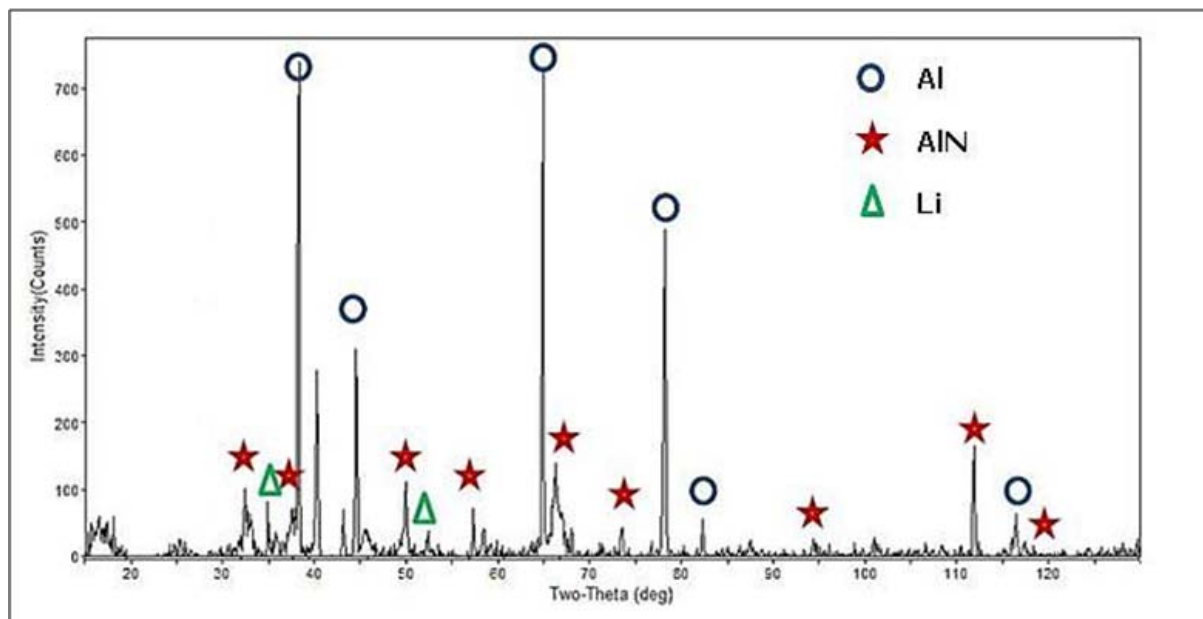

Figure 3. XRD pattern from a sample of the ingot produced in Experiment #2.

Experiment #3 – A relatively high volume fraction of aluminum nitride is synthesized with these process parameters although the processing time is relatively short. This confirms the higher reactivity of ammonia (compared to nitrogen), which speeds up the aluminum nitridation reaction even when it is mixed with nitrogen gas. The average particle size in this case is small, but the mean length of free space between particles is slightly higher than expected and some particle clustering occurs.

5

Experiment #4 – The volume fraction of aluminum nitride is considerably increased while the average cluster size is only slightly increased when these process parameters are used. This indicates that the aluminum nitride particles tend to aggregate when a long processing time is used.

Experiment #5 – When pure ammonia is used as reactive gas; both the average particle size and the average cluster size are relatively small and the particle dispersion is satisfactory

Experiment #6 – When pure ammonia is injected in the melt for 4 hours, a large amount of aluminum nitride is formed. Despite this, the particles are fairly uniformly dispersed in the matrix and the particle clusters are relatively small. The slightly increased particle size shows the tendency of the particles to grow when held at the processing temperature for a relatively long time. Figure 4 shows the particle size distribution produced in this experiment.
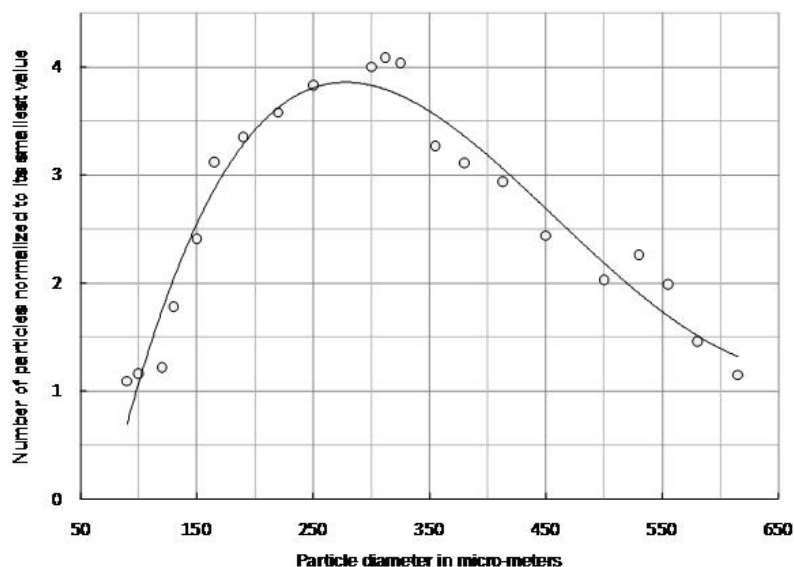
**Figure 4.** Particle size distribution produced in Experiment #6.

Experiments #7, 8, and 9 – The aluminum nitride phase was not detected in these experiments. The absence of aluminum nitride from samples prepared according to the conditions of Experiment #7 and 8 is most likely due to the evaporation of lithium from the melt, which causes the lithium content of the melt to drop to such levels where its catalytic effect on the aluminum nitridation reaction is significantly diminished. This is in addition to the lower reactivity of nitrogen (compared to ammonia). In the case of Experiment #9, the absence of aluminum nitride from the microstructure may be attributed to, in addition to the short processing time (only 2 hours) in addition to the low lithium content.

Experiment #10 – In this case the initial lithium content of the alloy is low (2.5 wt%), but the injection time is increased to 4 hours and the reactive gas contains ammonia, for this reason aluminum nitride particles did form; however the particles are different from those formed in Experiment #4 in that they are smaller in size and tend to agglomerate more.

Experiment #11 – In this case pure ammonia is used as the reactive gas so the amount of aluminum nitride particles that formed is relatively high. However, there is a relatively higher tendency for the aluminum nitride particles to agglomerate. Nevertheless, the particles are small and the cluster size is acceptable.

Experiment #12 – The conditions used in this experiment result in a composite material in which the average particle size is the lowest among all 12 experiments, an average particle cluster size that is very small, and a distribution of particles in the matrix that is fairly uniform.

Figure 5 shows the measured hardness of the composite materials produced according to Table 1. Measurements performed on the materials from Experiments #2, #3, #4, #5, and #6 have an error range of 14% while measurements performed on the materials from Experiments #10, #11, and #12 have an error range of around 20%. This is most likely due to "macro" agglomeration, i.e. particles, and also clusters, locate 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 composite material where there are almost no particles. Notice the high hardness values for the materials produced by Experiments #6 and #12. This is because of the high volume fraction of aluminum nitride particles in these materials.
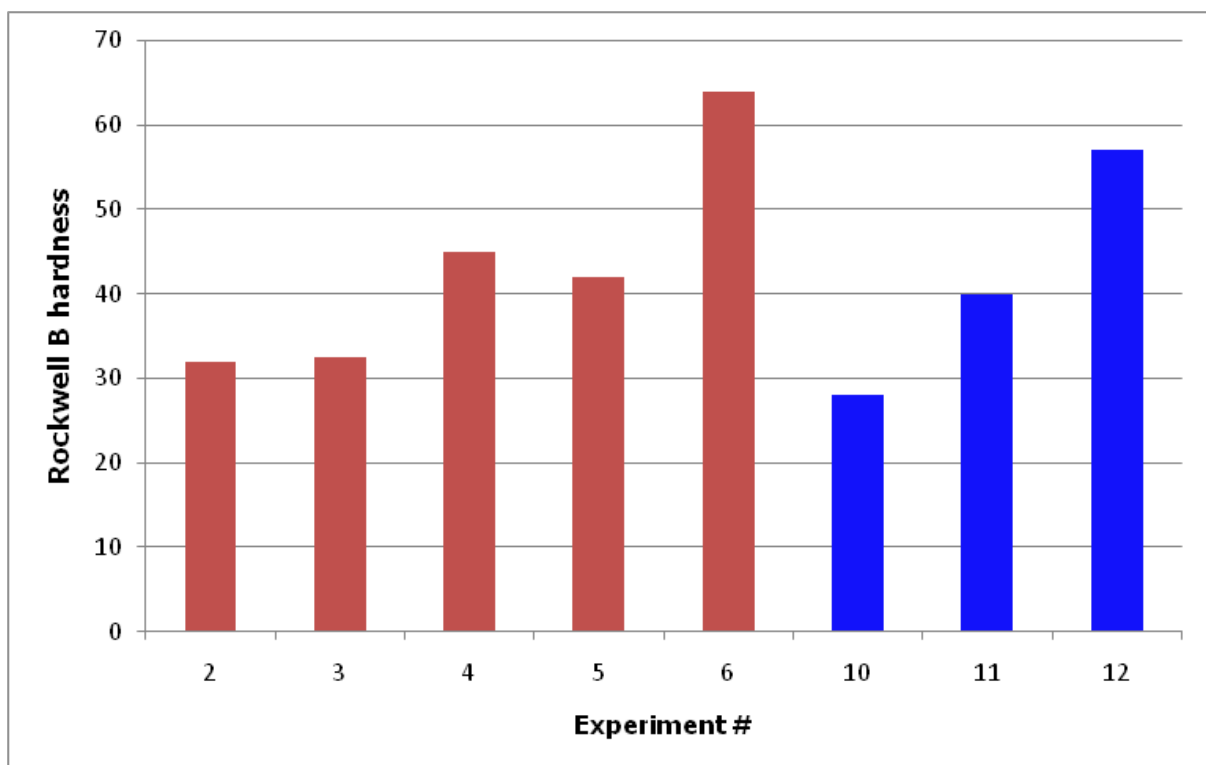
Figure 5. Measured hardness of the composite materials made according to the conditions outlined in Table 1.

Summary and Conclusions
The feasibility of producing aluminum alloy matrix-aluminum nitride nanoparticle composite materials by means of an in-situ chemical reaction between molten aluminum alloys and a nitrogen-bearing gas was demonstrated.

A robust apparatus was built, optimized, and used for the demonstration and for establishing the operation window for the process. The apparatus is inexpensive and may be easily scaled up for industrial production of the composite materials.

The microstructure of the resulting composite materials was quantitatively characterized, and the volume fraction of aluminum nitride particles and their average size, the average size of aluminum nitride clusters, and the mean length of free space, which describes particle distribution, were all determined as function of processing parameters.

The investigations indicate that aluminum alloys with a relatively high lithium content result in a higher volume fraction of aluminum nitride particles. However, melts with relatively lower lithium content produce finer particles – although the particle distribution in these alloys is less homogeneous than in alloys with higher lithium content.

The investigations also indicate that ammonia is more efficient than nitrogen in nitriding aluminum-lithium alloys. More than 40 volume percent aluminum nitride particles can be produced in an aluminum-5 wt% lithium alloy when the melt is injected with anhydrous ammonia for 4 hours at 1000°C.

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