Synthesis of nanodiamond-reinforced aluminum metal composite powders and coatings using high-energy ball milling and cold spray
Synthesis of nanodiamond-reinforced aluminum metal composite powders and coatings using high-energy ball milling and cold spray

D.J. Woo a, B. Sneed b, F. Peerally a, F.C. Heer b, L.N. Brewer b, J.P. Hooper a, S. Osswald a,b,*

a Department of Physics, Naval Postgraduate School, 833 Dyer Road, Monterey, CA 93943, USA
b Department of Mechanical and Aerospace Engineering, Naval Postgraduate School, 700 Dyer Road, Monterey, CA 93943, USA

Abstract

Nanodiamond-reinforced aluminum metal matrix composites (ND–Al MMC) powders were synthesized by means of high energy ball milling. We present a systematic study of the effect of various milling conditions on the structure and properties of the resulting MMC powders. The described method can be used to control important powder characteristics, including particle size and shape, Al crystal size and residual strain, and structural integrity and dispersion of the nanoparticle inclusions, a crucial requirement for subsequent powder consolidation. Raman spectroscopy was utilized for the first time to directly verify the structural integrity and the dispersion of ND in the Al matrix. For low ball-to-powder ratios (BPR), average particle size and size range of the ND–Al composite powders were found to decrease during milling, while the hardness increases. A BPR of 10:1, a milling time of 10 h, and a ND content of 10 wt.% were most effective in obtaining small powder particle sizes, small Al crystal sizes, and improved mechanical properties reaching a hardness of 3.46 GPa, a 210% increase over the pristine, untreated Al powder (1.10 GPa). Finally, we demonstrate that the as-produced composite powders are well-suited for low-temperature consolidation processing by fabricating the first cold-sprayed ND–Al MMC coating.

1. Introduction

The need for lightweight, high strength materials has been recognized in numerous fields ranging from the automotive and aircraft industries, to shipbuilding, and a variety of military applications. As stiffness and hardness of a material increase, the mass required for a certain load-bearing application is reduced. This leads to several advantages, including a potential increase in the maximum payload and/or improvements in fuel efficiency. However, for many applications, the challenge lies in finding materials that possess the required mechanical strength, but that are also light weight and inexpensive. While few materials in their elemental form can meet these requirements, the development of nanostructure-reinforced metal matrix composites (MMCs) has opened new pathways for the design of new materials that exhibit a unique set of properties, such as high strength and low weight.

The performance of MMCs depends primarily on the ability (1) to adequately disperse the reinforcement agents in the metal matrix, (2) to maintain its structural integrity during composite synthesis and processing, and (3) to establish a...
suitable matrix-reinforcement agent interface [1–6]. The strength of a MMC can be further enhanced by reducing the crystal size of the metal matrix to the lower nanoscale [7].

The majority of the studies reported in the literature involving nanocarbon-based MMC’s focused their efforts on the reinforcement of ductile metals, such as aluminum (Al), magnesium (Mg), and copper (Cu). Owing to their exceptional mechanical properties and high aspect ratio, carbon nanotubes (CNT) have been the reinforcement agent of choice in most of these studies [1,8–10]. Carbon nanotube-reinforced aluminum MMCs (CNT-Al MMC) have successfully been produced using a variety of synthesis methods, including extrusion [3], sintering and extrusion [11,12], pressing and rolling [13], infiltration [14], and plasma spray [15]. In nearly all of these studies, CNT were mixed with Al powder, followed by ball milling, a crucial step required to properly disperse the nanostructures prior to powder compaction [3,16–18]. With CNT-contents ranging between 1.5 and 15 wt.%, the reported improvements in mechanical properties were primarily increases in yield strength, ultimate tensile strength and Young’s modulus [3,11–18]. For a detailed overview of existing literature on CNT-metal composites, the reader is referred to a recent review by Bakshi et al. [19]. While CNTs are a suitable reinforcement agent for a variety of applications, nanodiamond (ND) offers the possibility of achieving superior material hardness, well beyond that possible for CNT-Al MMCs. Increases in hardness generally scale with increases in yield strength, another critical mechanical property for most structural applications.

ND, another member of the carbon nanomaterial family that has recently sparked interest in the materials community [20], is considered the hardest naturally occurring material [21], making it an ideal candidate for the reinforcement of Al-based MMCs. The average size of the individual nanodiamond crystals is around 4–5 nm; however, due to the strong tendency of nanomaterials to agglomerate, the observed particle size typically ranges from 50 to 500 nm [22]. Current applications include biomedical imaging material [23], nanoscale magnetic sensors [24], biocompatible materials [25,26], cooling fluids [27], lubricants [28], electroplating baths [29] and composites [30–33].

Existing studies on using ND as a reinforcing agent for MMCs include incorporation into aluminum [10,34], copper [35,10], and aluminum–magnesium [36], aluminum–copper [10] and copper–tungsten alloys [10]. As expected, hardness is the most thoroughly investigated characteristic of ND-reinforced MMCs. Using planetary ball milling, Livramento et al. dispersed 10 and 20 wt.% ND in a nanocrystalline copper matrix, yielding a 20% and 40% increase in Vickers hardness, respectively, as compared to pure nanocrystalline Cu [35]. In their study, the saturation point of ND in the Cu-based MMC was ~30 wt.%. Bobrovnitchii et al. demonstrated the potential of ND as reinforcement agent in Al. Using a combination of powder mixing and high pressure sintering, they increased the hardness of Al by incorporating up to 50 wt.% ND into Al matrix and reported a nearly linear increase in MMC hardness with ND content [10]. In their study, incorporation of 10 wt.% ND lead to composite hardness of ~2.34 GPa after mixing and sintering at 2.0 GPa and 700 °C for 3 min, a ~138% increase over pure Al (0.98 GPa). While the authors reported the formation of aluminum carbide phases, as expected under these conditions, no information on the structural integrity and dispersion of the ND was given. Hardness measurements on powder particles were not conducted.

Kaftelen and Öveçoğlu [34] synthesized Al–ND MMCs containing up to 10 wt.% ND by employing a combination of high-energy ball milling and sintering. Precursor powders were milled for up to 2 h using 6-mm steel balls and a ball-to-powder ratio (BPR) of 7:1. A maximum ND–Al MMC powder particle hardness of ~1.4 GPa (10 wt.% ND) was reported. After sintering, the hardness increased to ~3.3 GPa, indicating some discrepancies between the hardness measurements of the precursor powders and the consolidated MMC. Similar to the study by Bobrovnitchii et al., they reported a linear relationship between ND content and hardness in the sintered composites. The sintering also led to substantial carbide formation, suggesting strong chemical interaction between ND and Al matrix. Again, no data on ND dispersion in powder particles or its structural integrity after milling and sintering was reported.

Since most MMC synthesis techniques utilize some form of powder consolidation, the structural and compositional characteristics of the precursor powder are of great importance and strongly affect the properties of the consolidated MMC. For example, without any treatment of the precursor powders, the best obtainable dispersion of the reinforcement agents consolidation methods such as pressing, sintering, rolling, extrusion, and thermal spray [37–39], would be limited to the size of the powder particles. In the case of thermal spray methods, particle size and shape, hardness, and residual strain in precursor powders control important processing parameters such as particle velocity, deposition efficiency, and coating density [40]. The ability to fully control both structural characteristics and mechanical properties of the composite powders is therefore crucial for further processing and consolidation, particularly when employing thermal spray techniques. Control over these powder characteristics can be achieved by ball milling, also known as mechanical alloying (MA), a versatile powder processing method commonly utilized to mix different powdered elements into a homogeneous composite [37,41].

While previous studies have demonstrated the great potential of ND as reinforcement agent for lightweight metals, these studies focused primarily on the consolidated (typically sintered) composites rather than the precursor powders and therefore lack a comprehensive analysis of the relationship between synthesis conditions and resulting powder characteristics.

In this paper, we utilize MA to synthesize ND-reinforced Al MMC (ND–Al MMC) precursor powders, intended to be used for cold spray deposition, a low-temperature thermal spray method. The primary focus is on investigating the effects of milling parameters such as milling time, ball-to-powder mass ratio (BPR) and ND concentration, on both the structural characteristics and the mechanical properties of the MMC powder.

2. Experimental

2.1. Materials

The Al powder (H-10) was purchased from Valimet Inc. (Stockton, CA). Particle size and purity were given by the manufacturer as ~325 mesh and 99.7%, respectively. ND powder was
obtained from the International Technology Center (Research Triangle Park, NC, USA). Average ND crystal and agglomerate size were reported as 4–5 nm and 200 nm, respectively. The process control agent (PCA) used in this study was stearic acid (Sigma–Aldrich) with a purity of >95%. All chemicals were used as-received, without further purification.

### 2.2. Composite synthesis

#### 2.2.1. MMC powder

MMC powders were produced using a SPEX 8000 M high-energy ball mill (1735 RPM) with a SPEX 65 ml-hardened steel vial and 5 mm-hardened steel grinding balls. Sample vials were sealed in an argon-filled glove box to remove oxygen and moisture from the vial prior to a ball milling. For all experiments, 3.0 wt.% stearic acid was added to the powder mixture as a PCA to prevent agglomeration. The ND content in the Al matrix was varied between 0.5 and 10 wt.%. Milling conditions included ball-to-powder mass ratios of 10:1, 20:1 and 30:1, and milling times of 1, 4 and 10 h, leading to a total of 27 different MMC powders.

#### 2.2.2. MMC coating

MMC powders were consolidated using a Series C cabinet cold spray system from CenterLine (Windsor) Limited, Supersonic Spray Technologies (SST), Canada. The system was operated using a vibrational feed hopper and a computer controlled 2-axis robotic spray gun. Powders were deposited on an externally heated (~160 °C) 1018 steel substrate. Prior to the deposition, the substrate surface was cleaned and roughened using aluminum oxide grit (SST-G0002) from CenterLine. Nitrogen was selected as spray gas with temperature and pressure set to 450 °C and 250 psi, respectively.

### 2.3. Material characterization

The morphology of the ball-milled MMC powders was characterized using a Zeiss Neon 40 field emission gun scanning electron microscope—focused ion beam (FIB–SEM) instrument (Jena, Germany) operated at a voltage of 20 kV.

A laser diffraction particle size analyzer (Partica LA-950, Horiba, Kyoto, Japan) was used for quantitative particle size analysis. Around 300 mg of each sample was mixed with isopropanol (dispersant liquid), and transferred to an analytic glass cell. Raman spectra were recorded with an inVia Raman Microspectrometer from Renishaw (UK) using 325-nm HeCd laser, a 2400 l/mm grating, and 10× objective (spatial resolution ~0.8 μm). For Raman imaging of the cross-section of composites, polished samples for nanoindentation were dispersed in an epoxy resin. EpoFix resin and hardener from Struers (Cleveland, OH) were mixed together in a mass ratio of 5:1 and transferred to a silicone rubber mold containing the composite powders. After curing at ambient temperature for 24 h, the embedded powder sample was mechanically polished using 400, 800, 1200, and 4000 grit paper with 0.1 and 0.05 μm-aluminum oxide suspensions. The hardness of the composites was characterized by a G200 nanoindenter from Agilent Technologies (Santa Clara, CA, USA). Indentation data was collected using the continuous stiffness monitoring (CSM) method. A Poisson’s ratio of 0.33, a measuring depth of 100–200 nm from the depth limit of 500 nm, an allowable thermal drift rate of 0.05 nm/s, a strain rate of 0.05 1/s, a harmonic displacement target of 2 nm, a frequency of 45 Hz, and a surface approach velocity of 10 nm/s and an approach distance of 1000 nm were set for the test condition. The Berkovich tip shape consisting of diamond was calibrated using a fused silica reference standard. Dependent upon the sample’s surface, a 60× or 100× objective lens was used to locate nanoindentation points on the center of individual powder particle cross sections; 10–15 different points were measured on each sample. Because the powder particles were suspended in epoxy, the effective machine compliance for each particle varied and was corrected using the approach of Buchheit and Vogler [44]. In this approach, the effective machine compliance is measured for each powder particle and then used to adjust the indentation measurement such that the stiffness-square divided by the load is constant for all depths.

### 3. Results and discussion

#### 3.1. Particle morphology

In the scope of this study, a full-factorial series of 27 different Al–ND composites was produced by varying ND content and critical milling parameters, including milling time and ball-to-powder ratio, all at three levels. Fig. 1 shows the SEM images of three MMC samples that contain 5 wt.% ND, in

\[
\beta_{\text{sample}} \cos \theta = \frac{\varepsilon}{\lambda} \sin \theta + \frac{k}{L}
\]
comparison to the as-received Al powder. All of these powders were milled using a ball-to-powder ratio of 10:1, but different milling times ranging from 1 (b) to 4 (c) to 10 h (d). It can be seen that both particle size and shape change notably upon milling, as expected. The average particle size decreases with milling time, but remains larger for all milled samples as compared to the as-received powder. The size distribution of the powder particles also narrows significantly as the milling time increases. During the initial phase of the milling process, powder particles are cold-welded together and flattened by the milling media, leading to a substantial increase in particle size. With increasing milling time, particles are work hardened, start to fracture, and become more rounded, leading to a decrease in particle size and a more homogeneous powder with respect to shape and size distribution. Both particle size and shape are crucial process parameters for many powder-based consolidation methods. For example, in cold spray deposition, particle shape and size are directly linked to the impact energies upon deposition [45], which in turn determine deposition efficiency and bond strength.

In order to obtain more quantitative information on changes in particle size and size distribution of the MMC powders upon milling, we analyzed all samples using dynamic light scattering. Fig. 2 illustrates the particle size distributions of the composites powders shown in Fig. 1. The particle size distribution curves (Fig. 2a) were used to determine the average (mean) particle size and the size range of powder particles in each sample. The size range, marked as the distance between \( D_{10} \) and \( D_{90} \), is referring to the 10% and 90% diameter of the size distribution, respectively (Fig. 2a). The average particle sizes and size ranges of the powders shown in Fig. 1 are 10.6, 63.4, 52.3 and 51.1 \( \mu m \) and 8.3, 117.0, 99.1, and 86.5 \( \mu m \) with the order of as-received Al, 1, 4 and 10 h of milling, respectively. These values were determined by averaging the results of three consecutive measurements. The error bar in Fig. 2b reflects the obtained standard deviation. The size ranges of the composites narrow with increasing milling time (Fig. 2b), suggesting that longer milling times yield more uniform powders and lower overall particle sizes. Thus the size analysis using laser diffraction is in good agreement with SEM observations.

Fig. 3 shows the effects of ND content and BPR on the particle size distribution. Both particle size and size range of the composites were found to increase with increasing BPR, suggesting that smaller BPRs are more effective in reducing the particle size of the composite powders for the given vial size. Although higher BPRs generate more collisions between milling media and powder, the larger number of balls increases the number of ball-to-ball collisions and reduce the total volume available for ball acceleration, both of which reduce the impact energy of the milling media. The larger number of collisions also results in enhanced sample heating, which promotes particle agglomeration [46]. In addition, a higher BPR means that less powder material can be processed per batch by the MA approach. It was observed that with increasing ND content, both the particle size and size range decrease regardless BPR. Similar results were previously reported for other carbon nanostructure-reinforced Al-MMCs [34,47]. As the ND alters the mechanical properties of the MMC (particularly hardness and fracture toughness) it affects the milling behavior of the powders. The hardness of the MMC particles increases with increasing ND content. The harder particles are more brittle and tend to fracture easier, leading to smaller particles size for a given milling time. This effect will be discussed in more detail later. The mean particle sizes of the MMC powders containing 5 and 10 wt.% ND range from ~26 to 60 \( \mu m \). This is a suitable size range for thermal spray applications, allowing the as-produced MMC to be used as feedstock powders, for example, for cold spray processing.

Fig. 1 – SEM micrographs of the (a) as-received Al in comparison to ND–Al MMC powders (5 wt.% ND) ball-milled for, (b) 1 h, (c) 4 h and (d) 10 h using a BPR of 10:1.
3.2. Structural integrity and dispersion of ND

In this study, ND–Al MMC powders were synthesized by high-energy ball-milling, employing stearic acid (3 wt.%) as a process control agent (PCA). Different BPRs and milling times were used to investigate the dispersion of ND in the Al matrix and its structural integrity during milling.

Raman spectroscopy was utilized to verify the presence of ND in the composite particles and to evaluate the dispersion of the reinforcement agent upon milling. Raman spectroscopy is a powerful tool for the analysis of carbon nanostructures and carbon nanostructure-containing composites as it can provide information on both the structural integrity and the dispersion of the nanostructures [48,49]. Fig. 4 shows the Raman spectra of two MMC powders containing 5 and 10 wt.% ND, in comparison to Al and as-received ND. Both MMC and Al powders were milled for 1 h using a BPR of 10:1. The as-received ND powder exhibits two distinct Raman features: a downshifted and asymmetrically broadened diamond peak around 1325 cm\(^{-1}\), and a broad band between 1500 and 1800 cm\(^{-1}\) often referred to as the “G band” [50,51]. This band consists of at least three different Raman peaks resulting from the contributions of sp\(^2\) carbon (1590 cm\(^{-1}\)), O–H (~1640 cm\(^{-1}\)), and C=O (1740 cm\(^{-1}\)) species [52]. The milled Al sample does not show any significant Raman signal, suggesting that contributions of the stearic acid to the Raman signal of the MMCs can be neglected.

The Raman spectra of the milled MMCs show several distinct changes as compared to the as-received ND, indicating structural changes in the sample upon milling. For both samples, the diamond Raman peaks are absent, while the G band is noticeably narrowed and downshifted towards lower wavenumbers. In addition, two new Raman bands appear around 850 and 1370 cm\(^{-1}\). The latter one is referred to as D band, a defect-activated, double-resonant Raman feature corresponding to the breathing vibration of the hexagonal rings of graphitic carbon [53]. The Raman peak around 850 cm\(^{-1}\) is assigned to aluminum carbide (Al\(_4\)C\(_3\)) [54]. The observed changes can be explained as follows, in agreement with previous studies [55]. During milling, surface atoms are con-
verted from sp$^3$ to sp$^2$ carbon, leading to the surface graphitization of the ND crystals. As the hexagonal ring structure of the sp$^2$-phase develops, the D band appears in the Raman spectra. At the same time, the sp$^2$-contribution to the G band increases, resulting in the observed shape changes that appear as a downshift. The graphitic surface of the ND reacts partially with the surrounding aluminum to form aluminum carbide. The formation of a thin layer of aluminum carbide at the ND–Al interface may be beneficial to the overall performance of the MMC as it improves the bonding strength between the reinforcement agent and the metal matrix. Thus, the Raman spectra recorded from the milled samples do not provide direct evidence for the existence of the diamond core.

However, previous studies investigating the graphitization of ND showed that the observed changes in the Raman spectra can be ascribed to surface graphitization and the related shielding effects rather than a complete sp$^3$-to-sp$^2$ conversion\[55\]. It is well known that the Raman scattering cross section of sp$^2$ carbon is much larger than that of sp$^3$ species\[55\]. Thus, the diamond core is effectively shielded from Raman measurements, leading to the disappearance of the diamond Raman peak in the ND–Al MMC powders, suggesting that the observed changes are only surface effects and the ND core maintains its diamond structure.

Since Al metal is not Raman active\[59\], the Raman features of ND can also be used to evaluate the dispersion of the reinforcement agent in the metal matrix. We therefore recorded a Raman map from the cross-section of single MMC particle and plotted the absolute integrated intensity (area under curve) between 1100 and 1800 wave numbers, relative to the Al background (baseline). Because the cross sectional surface was finely polished, the entire mapping area was in the focal plane of the objective and intensity changes can be assigned solely to the content of ND in the Al matrix.

Fig. 5a–d show the cross-sectional optical photograph and the corresponding integrated intensity Raman maps of a MMC powder particle (10 wt.% ND) after milling (BPR of 10:1) for 1 and 10 h, respectively. It can be seen that the recorded ND Raman intensity distributions match the optical images recorded through the microscope, suggesting that the ND

![Fig. 4 – UV Raman spectra (325 nm excitation) of ND–Al MMCs containing 5 and 10 wt.% ND, in comparison to as-received ND and Al milled with 10:1 BPR for 1 h. Spectra were normalized with respect to the maximum intensity in the plotted spectral window, but were recorded using different measurement times.](image)

![Fig. 5 – Raman image of cross-sectioned ND–Al MMC powder particles containing 10 wt.% ND, milled with 10:1 BPR for 1 (a and b) and 10 h (c and d). (left: optical microscope image, right: distribution of integrated intensity of ND Raman signal in the range 1100–1800 cm$^{-1}$).](image)
Agglomerates have been dispersed homogenously within the Al particles, even after short milling times. However, it should be noted that since the spatial resolution of the Raman spectrometer is limited to about 0.8 μm, statements about ND dispersion below this limit cannot be made. These results demonstrate that high-energy ball milling is an effective means for size reduction and dispersion of ND agglomerates in an Al matrix, in analogy to CNT-Al composites [2,3].

In order to identify changes in the crystal size of the Al matrix and the extend of residual strain after milling, we recorded the XRD patterns of all MMC powders. Fig. 6a shows the diffraction pattern of two MMC samples containing 5 and 10 wt.% ND and pure Al powder after milling (BPR of 30:1) for 4 h. The XRD pattern of as-received ND and as-received Al are shown for comparison. While both MMC samples exhibit the diffraction peaks of Al, the characteristic (111) peak of ND is not observed. Unlike Raman spectroscopy, which is highly surface sensitive in solid samples, the X-ray diffraction signal requires constructive interference from many atomic layers and is thus proportional to the volume of the crystals. The intensity of diffraction signals coming from surface layers and nanocrystals is relatively low and typically overshadowed by the much stronger XRD signal from the metal matrix. Therefore, while both ND and Al4C3 were detected by Raman spectroscopy, they are not observed in the XRD pattern of the MMCs (Fig. 6b).

A closer inspection of the (111) Al peak of the as-received and the milled Al powders (Fig. 6c) reveals a commonly observed increase in peak width upon milling, which indicates a reduction in crystal size and/or presence of residual lattice strain. The same changes were observed for the milled ND-Al MMCs.

3.3. Residual strain and crystallite size

The observed changes in the position and width of the Al XRD peaks can be used to determine changes in crystal size and residual strain in the metal matrix upon milling. Peak broadening in XRD is caused by three primary factors: (1) reduction in crystallite size, (2) presence of micro-strain, and (3) instrumental broadening [56]. There exist numerous methods that utilize the observed broadening to quantify both crystal size and residual strain, the most common being the Williamson–Hall [42] and the Warren–Averbach [57] methods. In this study we employed the Williamson–Hall method to determine changes in crystal size and lattice strain upon milling. The results of the XRD peak analysis for the ND-Al MMC with 10wt% ND are depicted in Fig. 7. For comparison, the crystal size (and lattice strain) of the as-received powder was above the measurable size range of the Williamson–Hall analysis, suggesting crystal sizes of >150 nm.

A continuous reduction in crystal size with increasing milling time was observed for a BPR of 10:1 BPR. This BPR provides suitable kinetic energy to break up crystallites and to deform the lattice due to the high impact velocity of the milling media. In contrast, in the case of the highest BPR (30:1), the crystal size increases with increasing milling time. However, after only 1 h of milling, the crystal size is already slightly lower than that measured after 10 h of milling using a BPR of 10:1. Higher BPRs reduce the vial volume available for acceleration and increase the number of ball-to-ball collisions, both of which lower the effective speed of the grinding balls and reduce the impact energy [46]. Higher BPRs also lead to increased friction between grinding balls [58], which can cause sample heating and heat-induced crystal growth. High BPRs and long milling times thus undermine the crystal reduction in the Al matrix. One can therefore picture the milling process as follows: The reduction of the crystal size to a certain value requires a certain number of grinding ball-powder collisions. As higher BPRs lead to an increased number of collisions per time interval, crystal size reductions can be achieved in shorter milling periods as compared to low BPRs. Due to increased heating, longer milling times result in crystal subsequent crystal growth. Thus, higher BPR accelerates the crystal size reduction, but is also subject to increased sample heating that can cause crystal growth for longer milling times. The increased temperature during milling with high BPR may also lead to enhanced agglomeration and car-

![Fig. 6 – X-ray diffraction pattern of ND–Al MMCs containing 5 and 10 wt.% ND in comparison to as-received ND, and as-received and milled Al. MMCs and Al were milled for 4 h using a BPR of 30:1.](https://example.com/fig6.png)
bide formation. For example, while high BPRs and short milling times lead to small crystal sizes, the mean particle size and size range of the corresponding samples are much larger than that of samples produced using low BPRs and long milling times (see Fig. 3).

The residual strain was not strongly affected by the variations in milling conditions, but does appear to be more sensitive to the impact velocity rather than the number of collisions in ball-milling, in spite of more sample heating, as short milling times (1 h) at a BPR of 30:1 cause less residual strain than a BPR of 10:1.

3.4. Hardness

The hardness of the MMCs was evaluated by nanoindentation on the polished cross-section of individual Al-ND MMC powder particles. The highest hardness value (3.46 GPa) was measured for the ND–Al MMC containing 10 wt.% ND, after milling for 10 h using a BPR of 10:1, a more than 210% increase over the pristine, unmilled Al (1.10 GPa) and an almost 100% increase over pure Al milled under the same conditions. Fig. 8a shows the increases in hardness as a function of ND content for different BPRs (10 h milling time). The smallest BPR (10:1) was found to yield the highest hardness after 10 h milling for powders containing 10 wt.% ND. Although high BPRs (30:1) and short milling times (1 h) were found to yield similar crystal size reductions, the resulting MMC hardness (not shown) was only 1.68 GPa, suggesting that low BPRs are more effective in dispersing ND in Al while maintaining small crystal sizes in the metal matrix [58]. In order to separate the effects of the ND inclusions and ball milling on the hardness, we measured the hardness of the pristine Al before and after milling. In the case of the lowest BPR (10:1), milling for 10 h leads to a hardness increase of ~67%. The inclusion of 10 wt.% ND results in an additional ~150% increase in hardness, clearly demonstrating the effect of ND reinforcement of Al and providing further evidence for the survival and dispersion of the ND agglomerates in the Al matrix.

The increases in hardness in the present work were comparable to those observed in earlier studies on ND–Al MMCs. Bobrovnitchii et al. [10] reported a hardness of 2.34 GPa after sintering an Al powder containing 10 wt.% ND. Kaftelen and Övezoğlu [34] synthesized ND–Al MMC composite powders containing up to 10 wt.% ND using a combination of ball mill-

Fig. 7 – Crystal size (a) and residual strain (b) of ND–Al MMC containing 10 wt.% ND.

Fig. 8 – (a) Hardness of ND–Al MMC with different ND content milled for 10 h using BPR of 10:1, 20:1, and 30:1 (cross bar: as-received Al powder). (b) Linear relationship between hardness of ND–Al MMC, produced using a BPR of 10:1, and ND content for different milling times.
ing and sintering. The hardness of the powder particle was reported to reach 1.4 GPa at 10 wt.% ND after milling for 1.5 h using a BPR of 7:1, which is much lower than the values achieved in this study. Subsequent sintering yielded a hardness of ~3.3 GPa. Previous studies revealed a nearly linear relationship between MMC hardness and ND content [10], which is in good agreement with our experiments (Fig. 8b).

By combining the measured hardness data with the crystal size data (Fig. 9), we suggest that both the dispersion strengthening and the crystal refinement of the metal matrix control the hardness of the ND–Al MMC composite powders. In metals, hardness is closely related to yield strength and can be increased by several factors, including a reduction in crystal/crystallite size, an increase in the volume fraction of a non-shearable second phase (dispersion strengthening), an increase in dislocation density, and the addition of a solid solution strengthening agent. To first order, the strengthening mechanism for the ND–Al MMC is dominated by dispersion strengthening and crystal refinement. Solid solution strengthening is irrelevant for MMC materials studies in this paper. However, it is difficult to separate the contributions of dislocation density and crystal size for nanoscale metallic structures. The influence of crystal size on hardness is quite strong for all of the ball milled MMC samples, with or without addition of ND. The hardness of the as-received Al powders is much lower than that of the milled, pure Al. This difference in hardness is likely due to the combined effects of crystal refinement and increased dislocation density that take place during ball milling. While the hardness increases significantly as ND is added, the crystallite size stays in the range 30–60 nm (Fig. 9). This observation strongly suggests that ND is well dispersed, well below the ~1 μm spatial resolution limit of Raman spectroscopy and is causing the increase in hardness through a dispersion strengthening mechanism. This also indicates that, unlike in polymer-based composites, ball milling of MMC effectively breaks up larger ND agglomerates, present in the as-received ND powders. While the crystal size of the metal matrix remains the same with increasing milling time, ND agglomerate size is reduced, resulting in a finer dispersion of the reinforcement agent.

Therefore, while a linear relationship between MMC hardness and ND content can be justified within the experimental error of this study (Fig. 8b), we would like to point out that the milling behavior of Al-ND composites is more complex and that the resulting hardness does not necessarily scale linearly with ND content. The hardness of the composite powder varies for different ND contents and similar milling times will result in different metal matrix grain sizes and residual strain, both of which directly affect the hardness of the composite, in addition to the dispersion strengthening of ND, as discussed above.

We can conclude that for milled ND–Al MMC powders, both dispersion strengthening and crystal refinement play an important role in the strengthening of the material, with dispersion strengthening becoming more dominant as the amount of ND increases. Finally, it should be noted that the formation of third phases, such as aluminum carbide, at the metal matrix-reinforcement agent interface can significantly alter the mechanical properties of the composite. Further research will be conducted to investigate the formation of carbide phases and to study their effect on the mechanical properties of the composite, for example, by controlling the level of graphitization of the ND surface prior to milling.

![Fig. 9 – Relationship between measured hardness and metal matrix crystal size for as-produced ND–Al MMC powders, in comparison to milled and as-received pure Al.](image)

![Fig. 10 – SEM image of cold sprayed (a) ND–Al MMC (10 wt.% ND) and (b) pure Al. In both cases, precursor powders were milled for 0.5 h using a BPR of 10:1. The inset in (b) shows the as-received ND particles.](image)
3.5. Young’s modulus

We also measured the Young’s modulus ($E$) of the ND–Al composites using nanoindentation. However, it should be noted that while $E$ shows a relative increase with increasing diamond content, the absolute values for $E$ of the MMC powders are not reliable, given the experimental conditions of the measurement (powder dispersed in epoxy matrix). Therefore, only relative increases are given. In this study, it was found that the addition of 5 and 10 wt.% ND resulted in a ~7 and ~45% increase in Young’s modulus, respectively, relative to the value of the pure Al powder milled under the same conditions (3 h, BPR of 10:1).

3.6. Cold spray deposition

In order to demonstrate the suitability of the produced ND–Al MMC powders as feed-stock for low-temperature consolidation methods, we cold spray deposited two ND–Al MMC powders (10 wt.% ND) that were milled (BPR of 10:1) for 0.5 and 3 h, respectively. A milling time of 0.5 h was selected because the cold spray deposition efficiency was significantly higher as compared to longer milling times (~1 h). Since both Raman imaging and hardness measurements revealed good ND dispersion after 1 h of ball milling, we decided to further reduce the milling time. Fig. 10 shows the SEM image of a cold sprayed ND–Al MMC (0.5 h milling time) deposit in comparison to cold sprayed pure Al. The composite film shows ND agglomerates in the size range 30–200 nm, well-dispersed in the Al matrix. The average size of ND agglomerate in the cold-sprayed composite measures 75–100 nm, which is similar to the value of the as-received ND powder (inset in Fig. 10b). The estimated average inter-particle distance is around 100–200 nm. While this data was obtained from the composite film, the ND dispersion is believed to be similar in the as-produced MMC powder as cold spray only consolidates the powder particles (average size ~28 µm). Moreover, since good ND dispersion was achieved for relatively short milling times (~0.5 h), samples milled for longer periods are expected to exhibit at least similar dispersion levels.

The highest hardness, ($3.26 \pm 0.25$) GPa, was found for ND–Al MMC (10 wt.% ND) after milling the precursor powder for 3 h, as expected. For comparison, the hardness of cold sprayed pure Al was found as ($1.47 \pm 0.34$) and ($2.41 \pm 0.16$) GPa for as-received and ball-milled powders (Fig. 10b), respectively. The corresponding values for the Young’s modulus were measured as ($92.3 \pm 7.1$), ($72.9 \pm 4.2$), and ($74.2 \pm 6.7$) GPa for the ND–Al MMC, the as-received Al, and the ball-milled Al powders, respectively.

While a detailed analysis of the relationship between MMC powder characteristics and cold spray performance is outside the scope of this study, the results clearly demonstrate that ball milling is a powerful method for the synthesis of MMC powders and their application as feed-stock for cold spray consolidation.

4. Conclusions

We have successfully synthesized a series of nanodiamond-reinforced aluminum metal matrix composite (ND–Al MMC) powders using high energy ball milling, and have presented a systematic study of the effects of the various milling parameters and the ND content on the structural characteristics and mechanical properties of the as-produced MMC powders. The results presented in this study demonstrate that high energy ball milling is a feasible means for the synthesis of ND–Al MMC powders as it provides excellent control over (1) particle size distribution, (2) crystal size and residual strain of the metal matrix, and (3) structural integrity and dispersion of the ND reinforcement agent.

It was found that while higher BPRs accelerate the crystallite size reduction for short milling times, during milling, they lead to crystallite growth for longer milling, likely due to increased sample heating. Moreover, higher BPRs are less effective in ND dispersion and particle size reduction of ND–Al composites, rendering low BPRs and longer milling times more suitable for MMC synthesis. Using a BPR of 10:1 and a ND content of 10 wt.%, the hardness of the Al MMC increased by ~210%, reaching 3.46 GPa after 10 h of milling, the highest ever reported value for ND–Al MMC with similar ND content. The increased hardness is caused primarily by the ND reinforcement, accounting for approximately three-quarters of the total observed enhancement. Raman spectroscopy revealed a homogeneous dispersion of ND in the individual MMC powder particles, at a maximum resolution of 0.8 µm, and the formation of a thin Al$_4$C$_3$ film at the ND surface, which may serve as an interfacial bonding layer between the reinforcement agent and the metal matrix.

Finally, we employed cold spray deposition to consolidate the as-produced MMC powders and demonstrated their feasibility as feed-stock material for thermal spray applications. The produced MMC coatings showed homogenous dispersion of ND agglomerates, yielding hardness values exceeding 3 GPa.

Acknowledgments

The authors would like to thank Dr. Sarath Menon (NPS) for his assistance with SEM analysis and Mr. Douglas Seivwright (NPS) for his help with cold spray deposition. This work was supported by the Office of Naval Research.

REFERENCES


