Opportunities for aluminum-based nanocomposites

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Abstract. High performance aluminum alloys are conventionally made by heat treating alloys containing a variety of alloying elements in solid solution. Key performance attributes are controlled at the microstructural level by tailoring sizes and morphology of nano-sized second phases. This enabled the successful development of aluminum alloys having properties optimized in strength, damage tolerance and corrosion resistance. However, this process is naturally limited by the solubility of alloying elements in the aluminum matrix. In real world products, significant effort is deployed to achieve a homogeneous distribution of the alloying elements both at the macro and micro scales. Despite these efforts, heat treatable alloys can exhibit chemical gradients at grain boundaries, resulting in sub-optimized properties. Additionally, due to the very nature of the strengthening mechanisms, the properties of heat-treatable alloys are decreasing when exposed to elevated temperatures. To step outside the boundaries given by the solubility of alloying elements in the aluminum matrix, the extrinsic addition of nano-sized particles to the aluminum matrix is being evaluated.

1. Introduction
Improving the properties of aluminum alloys has a long history. A combination of the established metallurgical mechanisms, cold work, solid solution strengthening and precipitation strengthening, has enabled highly engineered materials to be developed for demanding customer requirements. These requirements typically focus on strength and damage tolerance, while at the same time being of low cost enabling wide spread applications. Many text books cover the underlying mechanisms and how they can be utilized to tailor a materials performance to an application.

For a material to be successful commercially, it needs to fulfill a spectrum of property requirements as well as meet a target cost point. Results of new materials or processes are frequently being reported as achievements in tensile strength; however, a successful material for most technical applications must meet not only strength but other properties such as damage tolerance [1] and/or formability. To date, aluminum alloys used for aerospace structures have driven most of the major advancements in material properties. With improvements to manufacturing process and cost structure, these alloys are now finding additional uses in other applications such as transportation. It is not the objective of this paper to review the state of advanced aluminum alloys.

Over the years, attempts have been made to step outside of the spectrum enabled by precipitation strengthening and other basic metallurgical methods by using a composite approach. This means adding an extrinsic material in small or large volume fractions to the aluminum matrix to not only improve strength but to also modify the modulus. This material class is commonly referred to as Metal Matrix Composites (MMCs) [2]. When MMCs were developed, most second phase materials that were combined with the aluminum matrix where particles with sizes of tens of microns in diameter. With
today’s availability of low cost inorganic particles with dimensions of less than one hundred nanometers in diameter, the development of new aluminum composites with enhanced properties can be envisioned. There is a need for composite materials which can be manufactured at low cost, are mass producible and achieve property combinations outside of the product portfolio of current aluminum alloys.

2. Motivation
A new class of materials are composites made of aluminum with added nanoparticles (Aluminum Nano Composites, AlNCs). Here non-metallic, thermodynamically stable oxide, carbide or nitride particles of submicron sizes are used to alter the properties of aluminum alloys. Related to this class are AlNCs based on carbon based nanoparticles, e.g. buckeyballs, carbon nanotubes (CNTs) or graphene platelets. The anticipated advantages over conventional aluminum alloys are:

1. The volume fraction of second phase particles is not controlled by the solubility of elements in the aluminum matrix. Thus, materials with very high room temperature strength could be developed.
2. Such particles do not change their geometric dimensions when exposed to temperatures below the melting point of aluminum. Therefore, a material strengthened by nanoparticles would keep a significant portion of its mechanical properties at operating temperatures. Current aluminum alloys lose their properties either due to recovery of the cold deformed structure or due to coarsening and dissolution of strengthening phases.
3. In precipitation strengthened alloys, solute from the matrix is used to form the strengthening phases in the matrix. However, at defects such as grain boundaries or in some systems around constituent phases, a depletion of solute occurs due to the formation of (near-)equilibrium phases, also known as Precipitation Free Zones (PFZs). The solute gradient and the (near-)equilibrium phases increase the susceptibility to corrosion as well as affecting crack nucleation and crack growth under monotonic or cyclic loading, with or without environmental influence. In a system where the strengthening phases are extrinsically added to the aluminum matrix (AlNC), it is expected that corrosion resistance and damage tolerance are improved.
4. The dissolution of precipitates in a heat affected zone from a welding operation will be eliminated, promising weldable, high strength aluminum materials.
5. Improving strength without solute additions to the aluminum matrix would allow for materials of both high strength and high electrical conductivity. Extrinsically added strengthening phases would not inherently reduce the conductivity of the aluminum matrix, making high strength, high conductive electrical connectors possible. The electrical conductivity would be reduced by the volume fraction of aluminum replaced with the second phases.
6. By eliminating the need to homogenize solute elements in the aluminum matrix with high temperature heat treatments or re-solutionizing solute after hot working operations, a lower cost production flow path is anticipated for aluminum nano-composites.

3. Target strength properties
Two mechanisms can affect the strength of a material when nanoparticles are added to the matrix. As such particles are incoherent and cannot be cut by dislocations, Orowan strengthening will occur if the particles are nearly homogeneously distributed in the metal matrix. If the nanoparticles accumulate at dendrite or grain boundaries strengthening from a refined grain size according per the Hall-Petch relation will occur.

An approach for estimating yield strength for homogeneously dispersed second phases has been described in [3]. However, it is expected that the distribution in a commercial product is not homogeneous; therefore, a modification for random distribution of obstacles [4] was considered, resulting in an about 15% reduction in predicted yield strength.
Assuming an aluminum product of commercial purity, also referred to as AA1100, and \( \gamma\)-\(\text{Al}_2\text{O}_3 \) as the nanoparticle phase, the resulting yield strength for a fully annealed material was estimated as a function of volume fraction and particle size (figure 1). Yield strength predictions for a strain hardening alloy, AA5083, with the same class of nano particles is also shown. For very large particles and at low volume fractions such as constituent phases, the effect on the yield strength is negligible. However, for particles in the less-than 50 nm range, a significant effect on the yield strength can be expected, even at volume fractions in the 0.5 vol\% range. If one assumes a strain-hardening material such as AA5083 for matrix, the simulations of the strain hardened material suggest that with 2 to 5 vol\% of a second phase in the less than 50 nm range, a yield strength comparable to or even higher than current advanced aluminum alloys could be achieved.

The simulation indicates very large enhancements are possible for room temperature yield strength. With such potential for improvement, one needs to evaluate what potential fabrication paths could enable aluminum nanocomposites.
4. Processing options for making AlNC

Many processing routes can be considered to embed nanoparticles into an aluminum matrix, with several having been reported on [5-7]. For varies practical reasons, the use of CNTs and engineered nanoparticles (NPs) is separated. For one, CNTs with their high aspect ratio will have a different strength response than the nearly spherical particles, which are the bases of the strength simulations above. Additionally, CNTs will provide a different challenge than engineered nanoparticles in establishing a production method. This is due to the implications from the graphite character of its surface on interface bonding, to be discussed later.

![Aluminum Nano Composites Diagram](image)

**Figure 2.** Processing Path for obtaining Aluminum Nanocomposites (AlNCs)

#### 4.1. Powder Metallurgy

The most common method for making aluminum based nanocomposites is based on well-established powder metallurgical processes used for making MMCs. Many different approaches have been reported for mixing and milling, even sometimes under cryogenic temperatures [8], of an aluminum powder with nanoparticle or CNTs. Due to the high reactivity of aluminum powder, the metal particle size is usually in the tens of micrometers in diameter range. Adding nanoparticles in the sub-50 nm range provides a significant processing challenge to obtain a homogeneous powder distribution due to the fact that the second phase particles are several orders of magnitude smaller than the matrix powder itself. Nanoparticles will accumulate during mixing of both powders in voids between aluminum particles, causing an inhomogeneous distribution of the second phase in the matrix.

#### 4.2. Ingot Metallurgy

While the emphasis of this discussion is on the addition of extrinsic nanoparticles, it is necessary to mention also an intrinsic process path, which makes use of the in-situ formation of small particles in the melt [9]. Utilizing the fact that the solubility of an alloying element is higher in a melt than in a solid, it has been demonstrated that a salt-based liquid reaction of a salt containing carbon particles with alloying elements in the molten metal can achieve large volume fractions of a second phase in the melt, resulting in a dispersion strengthened product. However, as the size of these second phase particles is controlled by the high reaction kinetics, it is difficult to consistently control the size of the particles formed in the melt to below one micrometer.

Adding particles directly to molten metal is an established technology [5, 6, 10]. Various technical approaches enable fabrication of an aluminum matrix containing extrinsically added second phase particles. The issue of segregation due to gravity as encountered in MMC fabrication is not anticipated in the case of nano-sized particles. However, other known challenges, both metallurgical and economical, are likely to occur. It is thus necessary to develop effective strategies to investigate effects and roles of NP’s during both liquid-solid stage and post-solidification processing.
Consideration for the aluminum matrix is as follows: in an age-hardening aluminum system, it is very likely that the precipitation kinetics will be affected by the presence of nanoparticles. Nanoparticles will both act as a sink for vacancies as well as nucleation sites for strengthening phases, likely altering the precipitation kinetics and morphology. Thus, using a strain-hardening aluminum matrix promises better results.

One needs to anticipate many hurdles when considering a molten-metal route:

Most engineered particles are known to have a high wetting angle with regards to molten aluminum. However, wetting at the nanoscale is not fully understood. Engineered nanoparticles have a different surface layer in chemistry and crystallography than at the particle core. These surface layers could be oxides or carbon-contaminations, depending on the process used to fabricate nanoparticles. Additionally, processes for determining and controlling the largest particles in the distribution, those exceeding a few micrometers and thus could be crack nucleation sites, need to be developed.

After having overcome the issues of wetting, the next hurdle will be obtaining a homogeneous dispersion of nano-particles in the aluminum matrix. The properties of the final product will depend on those material volumes that shows either agglomerations or absence of nanoparticles. The dispersion is correlated to the wetting. Feed processes need to break-up any agglomerates of the feedstock and need to avoid agglomeration in the melt. While the latter are mechanical hurdles, the dispersion of nanoparticles in the solidified aluminum can also be affected by the solidification process: it is very much possible that the solidification front pushes the nanoparticles ahead of itself, resulting in an agglomeration at interdendritic spaces in the final material.

One needs also to consider the effects on processing such materials on existing equipment. As the target properties are primarily significant increases in strength, at room and elevated temperatures, processing equipment such as rolling mills and extrusion presses would experience higher loads. Consequently, continuous casting processes such as roll casting or similar, would be the preferred manufacturing methods.

Finally, one needs to ensure that all processing steps are compliant with environmental and health regulations. When full wetting can be achieved, the final product does not differ from a precipitation strengthened aluminum material and thus no engineered nanoparticle will be released during forming and/or machining operations. However, handling engineered nanoparticles from receiving, quality control to process additions requires new methods to ensure that such particles are not released into the environment.

5. Processing
Melt stirring is a common process. The use of ultrasonic agitation in assisting wetting and dispersion during melt stirring has been widely reported [e.g. 10]. However, in view of the need to adapt any process at the commercial scale, emphasis was taken on melt stirring without ultrasonic agitation. The material classes from which the nano particles were selected, were based on reported wetting characteristics (e.g. [11], that is boron carbide (B4C) and silicon carbide (SiC)). However, wetting at the nano scale could potentially behave differently than presently reported for micron-sized ceramic particles. Commonly available alumina and carbon nanotubes were evaluated, specifically the following particle classes of the respective, nominal particle diameter were used in this evaluation: B4C (50 nm), γ-Al2O3 (10 nm), SiC (60 nm) and nitrogen-doped SWCNTs (200 nm length).

The aluminum matrix was smelter grade aluminum of 99.5% purity, sometimes alloyed with magnesium. Magnesium extends the freezing range compared to unalloyed aluminum. The solidification front in an alloy with a longer freezing range provides more time for a reaction between the particle and the melt. Magnesium also is known to affect wetting of ceramic materials, but this alloying element was selected as it enhances work hardening. Additionally, halide salts, known for the capability to remove surface oxides and to increase wetting [12], were evaluated as wetting aids for the nanoparticles.

Varies methods were developed for safely adding nano-particles to the molten metal. Nano particles need to be delivered under the surface of the melt. Thus, nanoparticles and, when used, halide salts were encapsulated in aluminum containers which then were submerged in the melt. Upon melting of the
In the container, the nanoparticles were released into the stirring melt. Stirring needed to be slow enough not to create a vertex as the latter would pull in oxides from the surface, even when working under a protecting inert atmosphere.

The melt was cast into rectangular copper molds, allowing for solidification rates corresponding to those typically found for Direct Chill (DC) ingot casting, that is in the 30 K/s range. All ingots were extruded and heat treated before samples for metallurgical and mechanical evaluation were cut.

6. Results and Discussion

6.1. AlNCs based on Engineered Nanoparticles

Overall it was found that all the nanoparticles in evaluation were embedded in the solidified aluminum, especially when a halide salt were used as a wetting aid [13]. As expected the success rate was higher in the Mg-containing alloys. Figure 3 shows γ-alumina particles with a nominal particle diameter of 10 nm embedded in an Al-1.0 wt% Mg sample.

Figures 3a and 3b are the same area containing a grain boundary, taken under two different imaging conditions in the TEM, in Fig 3a both grains are in non-diffracting condition, while in Fig 3b, the grain on the right side is in strongly diffracting condition, indicated by the trace of the grain boundary. It is clear from these two images, that the nanoparticles are not pushed ahead of the moving solidification front and thus do not agglomerate at the interphase. Also, stirring is sufficient to have in this field of view a sufficiently good dispersion of the nanoparticles in the aluminum matrix. However, a similar sample with γ-alumina of nominal 60 nm in diameter observed with a larger field of view by SEM (figure 4), shows a similar dispersion in the aluminum matrix as observed in the TEM. Near a constituent phase particle (an iron-bearing phase), a higher density of nanoparticles can be detected. This indicates that during solidification not all nanoparticles are embedded in the matrix but that some accumulate in the remaining liquid at the end of the freezing range, resulting in an inhomogeneous distribution of the nanoparticles.

![Image](image-url)

**Figure 3.** TEM micrograph of Al-1%Mg +1Vol% γ-alumina (10 nm) same area, two different orientations of TEM foil normal to electron beam to show position of grain boundary.
Figure 4. SEM micrograph of Al-1%Mg +1Vol% γ-alumina (60 nm) alumina in matrix and surrounding constituent particle.

Figure 5. TEM micrograph of Al-1%Mg +1Vol% SiC (60 nm)

Similar results as with the γ-alumina were obtained for SiC particle addition having a nominal particle diameter of 60 nm (Fig 5). Also in this case the nanoparticles are not preferentially located at a grain boundary. A few particles can be observed at the triple junction and a grain boundary.

Figure 6. Aluminum matrix containing a carbon nanotube embedded by molten metal processing

Figure 7. True strain – true stress curves for an AlNC with 0.1 wt% embedded CNTs
6.2. AlNCs based on CNTs
The graphite character of the surfaces of CNTs does not allow a CNT to physically bond with aluminum. On the other hand, if the whole surface would react with aluminum, aluminum carbide would form, detrimentally affecting corrosion and other properties. Thus, defect containing (nitrogen-doped) CNTs were selected for molten metal additions, with the particular CNTs having a bamboo structure. The concept was that aluminum can bond to the CNT at the defect site. Also here, salts were used as a fluxing material to enable embedding of CNTs to an aluminum matrix of smelter grade pure (99.5%). Assuming that no CNTs were lost during processing, the sample contains 0.1 wt% CNTs.

TEM analysis (figure 6) verified that CNTs were embedded in the aluminum matrix. As the sample had been plastically deformed, dislocations interacting with the CNT can be observed. Specifically note the dislocation loops in the center of the image around the CNT. It is important to note that at the given resolution, aluminum carbides at the interface between the aluminum matrix and the CNT were not detected.

Tensile testing (figure 7) shows an improvement of about 30% when compared to a control. The control has been processed the same way as the AlNC, incl. applying salt additions, however without the addition of CNTs.

7. Summary
With all the success in embedding nanoparticles in the solidified aluminum matrix without agglomeration, where are the issues? While large material volumes showed a distribution of nanoparticles similar to the TEM images shown above, some material volumes were found to not contain any nanoparticles. When nanoparticles were observed in the matrix, they were reasonably well dispersed. However, all the target properties discussed above require a near-homogeneous dispersion throughout the whole material volume. The objective of this approach was to achieve high strength aluminum materials similar to precipitation hardening materials, without the high solute content. Any material volume not achieving high strength due to the absence of strengthening nanoparticles will determine the macroscopic plastic behavior negatively. In the current work, the material behaved like a two-phase material, with the soft phase defining the plastic behavior. While initial results are promising, developing AlNCs with commercially relevant properties via a pure molten metal processing path remains a challenge.

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