The Application of CNT-Aluminum Nanocomposite in Mechanical Alloyning: A Short Review

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Abstract
The ball milling of powders is a non-equilibrium technique (similar to rapid solidification processes) that can be used for production and structural modification of materials. Carbon nanotubes (CNTs) are relatively new materials with excellent combination of properties. They are one of the advanced reinforcement materials for engineering composites. Besides the polymer and ceramic matrices, interests are growing recently on the metallic matrices such as aluminum alloys for potential structural applications. Mechanical alloying (MA) is one of the best processing methods for synthesizing Al/CNTs nanocomposites, which results in the uniform dispersion of the reinforcement, inhibits the formation of undesired phases, and produces a nanostructured microstructure. It is of great importance to understand the mechanical alloying of Al/CNTs powder mixture for preparing nanocomposites. As a result, the current short review deals with the basics of the MA process, preparation of nanocomposites by MA, and summarizing the current knowledge on Al/CNTs nanocomposites processed by MA.

Keywords
Nanocomposites, Carbon Nanotubes, Mechanical Alloying

1. Introduction
High energy ball milling is one of the most common techniques for processing of novel materials. The ball milling of powders is a non-equilibrium technique (similar to rapid solidification processes) that can be used for production and structural modification of materials. Ball milling has two types: (I) the milling of elemental or compound powders (mechanical milling, MM) and (II) the milling of dissimilar powders (mechanical alloying, MA) in which material transfer occurs. These methods are first used to develop oxide dispersion strengthened superalloys and are now being considered as methods for producing materials with unique microstructures and/or structures [1]. On the one hand, material production by MA can take place at room temperature which can have advantages over high temperature synthesis, in particular for synthesis of materials with high melting points. On the other hand, microstructural modification (e.g. producing nanostructured materials) during MA/MM can significantly enhance the overall properties of materials, especially for composite materials that are brittle in nature. MA/MM produces nanostructured materials by structural decomposition of coarse-grained structures as the result of heavy plastic deformation. This is similar to severe plastic deformation techniques from this standpoint. Ball milling is a widely used method to synthesize nanocrystalline materials because of its simplicity, the relatively inexpensive equipment and the applicability to essentially all classes of materials [2-6].
MA/MM has several drawbacks. Fresh atomic surfaces constantly created during mechanical milling, so contamination by oxygen and nitrogen is a real problem. Other impurities originate from pot, balls and process control agent material. Another problem with MA/MM is the low powder yield obtained in some systems due to powder cold welding to the container wall and milling balls. Finally, the need to consolidate the powder product while maintaining the nanostructured feature of the material is another major problem. However, despite the problems associated with ball milling, it is an appropriate method for producing nanocrystalline intermetallics [6,7].

In MA, mixtures of elemental or pre-alloyed powders are subjected to grinding under a protective atmosphere in an equipment capable of high-energy compressive impact forces. The repeated cold welding and fracturing of particles (Figure 1), the creation of high density of lattice defects induced by severe plastic deformation, and development of an alternate layered microstructure (Figure 2) are among the main events that happen during ball/powder/ball collisions [8, 10, 11].

![Figure 1: Ball/powder/ball collision of powder mixture during mechanical alloying](image1)

![Figure 2: Formation of an alternate layered microstructure during mechanical alloying of two different ductile powders](image2)

In the metallurgical processes of MA/MM, powder particles are subjected to severe mechanical deformation at high strain rates from collisions with steel or tungsten carbide balls and are
repeatedly deformed, cold welded and fractured. The large amount of energy transmitted to powders results in a dislocation cell structure within shear bands, which transforms to random nanostructured grains with increasing milling time as shown schematically in Figure 3.

Figure 3. Development of nanocrystalline structure during ball milling: (a) original grain, (b) severely deformed grain, (c) formation of low-angle grain boundaries, and (d) formation of high-angle grain boundaries [18]

The rate of reduction in crystallite size at the first stage of mechanical milling is high but drops rapidly by an increase in milling time, and finally, the crystallite size reaches to a discrete value at a critical milling time. At this stage, the rate of reduction in crystallite size dramatically decreases and the effect of milling time on the crystallite refinement will be almost negligible. In other words, milling process finally reaches a macroscopic steady state condition. This critical milling time may be considered as effective milling time. This value is important from the practical standpoint. Accordingly, the crystallite size at this time is named as the effective crystallite size. These aspects are schematically shown in Figure 4 [17, 19, 20].

Figure 4. Concepts of effective milling time and crystallite size [21, 22]

2. Aluminum-based Nanocomposites
Metal-matrix composites (MMCs) have been developed to combine the good ductility and toughness of the metallic matrix and the high strength and elastic modulus of the reinforcement.
Very small particles must be used as the reinforcement material in the metallic matrix to enhance mechanical properties. Moreover, the distribution of the particles in the matrix is of vital importance. Therefore, based on the nature of the ball milling process, it is very useful to develop fine and high performance MMCs. Nanocomposites are defined as multi-phase solid materials wherein one of the phases has dimensions of less than 100 nm in at least one direction. It is also possible that the sizes of both the matrix and the reinforcement have nanometer dimensions. The possible distribution of the reinforcement and matrix phases is shown in Figure 5 [23-26]. The effects of a single collision on each type of constituent powder particle are shown in Figure 6: (I) Flattening and work hardening of ductile metal powder particles, (II) Fracturing and refinement of brittle intermetallic powder particles, and (III) More severe comminuting of oxide dispersoid particles. With continued milling, the ductile powder particles get work hardened, the lamellae get convoluted, and refined, and the brittle particles get uniformly dispersed, if they are insoluble, in the ductile matrix or get alloyed, if the brittle phase is soluble. Thus, a composite is formed.

Figure 5. Possible distribution of the matrix and reinforcement phases in a nanocomposite: (a) distribution of reinforcement phases along the grain boundaries of the matrix, (b) distribution of reinforcement phases inside the matrix grains, (c) distribution of reinforcement phases inside the grains and along the grain boundaries, and (d) both the matrix and reinforcement grains are uniformly distributed.

Figure 6. Deformation characteristics of representative constituents of starting powders in mechanical alloying

The addition of hard particles to soft Al alloys can increase the strength and wear resistance at both ambient and elevated temperatures. However, a homogeneous and uniform distribution of the reinforcement is essential to exploit its load-bearing capacity more effectively. Otherwise,
agglomeration or inhomogeneous distribution of reinforcement can lead to lower ductility, strength, and toughness of the composites. Enhanced mechanical properties can be obtained when the reinforcement particles are very small in size, typically less than about 1 µm, where high-energy ball milling is a viable method in this respect. A number of different reinforcements have been added to Al and its alloys to achieve the desired improvement in the properties. The CNT as the reinforcement is the main interest of the present review.

3. Aluminum-CNT Nanocomposites

The shape and size of CNTs as well as the size of starting Al powders affect the MA behavior and also the resulting mechanical properties of the nanocomposite. The effects of the structure and morphology of CNTs on the MA behavior powder mixtures is of great importance. In this respect, ball-milling of Al powder with single-walled (SW), double-walled (DW), and multi-walled (MW) CNTs will be summarized in this section.

A SWCNT, i.e., a nanotube made of only one graphite sheet rolled-up in a cylindrical form, has a Young’s modulus as high as 1800 GPa and a tensile strength as high as 150 GPa, values which are one to two orders of magnitude superior to the best-known steels. In contrast, MWCNTs display lower but still exceptional mechanical properties, and they are easier to synthesize [15]. SEM images of the Al powder, SW, DW, and MW CNTs are shown in Figure 7.

The morphological change of the MA product with increasing ball-milling time is shown in Figure 8 based on the results of Choi et al. [15]. For pure Al, the shapes and sizes of the particles do not change considerably up to 36 h, but significant agglomeration of the particles happens at higher ball-milling times. When CNTs were added, the powers deformed to flake-like shape initially (12 h), but continued grinding reduced the portion of flake-like particles whereas the particles having granular shape increased in population especially in case of the MWCNT.

Figure 7. SEM images of the starting materials (a) Al powder, (b) MWCNTs, (c) DWCNTs, and (d) SWCNTs
As mechanical properties, SWCNT are single surface carbon nanotubes and for exploiting especially the electronic properties which vary with their chirality, you have to use only SWCNT. MWCNT are multi-surface materials and would lose special electronic properties. They will show an average effect of all chiral tubes. Therefore, use of these in mechanical and thermodynamically properties will be fine. MWCNT are cheaper to produce, much cheaper compared to SWCNT. Therefore, they can be profitably used to make polymer or other composites enhancing their mechanical, thermal and electrical properties. This characters also were showed at the composites of MWCNT and SWCNT.

It can be seen that the presence of CNTs can alter the grinding behavior of Al powder and that the MA process is also affected by the type of CNTs incorporated. Especially, MWCNTs function as a kind of grinding aid while they were dispersed within the Al matrix power through the MA process. CNTs having tangled curly thread shapes functioned as a kind of grinding aid during the MA by forming a network of weak interfaces between the CNT and the Al matrix due to the shape and size effects when embedded within the Al powder matrix. These networked weak interfaces then acted as crack initiators on impact by the Al particles in the ball mill thereby maintaining a state of equilibrium between cold-welding and fracturing of the particles. Similar roles of SWCNTs and DWCNTs may be expected, but in these cases, since the CNTs have much smaller diameters and therefore higher specific surface areas, it is likely that they cover substantial portions of the surfaces of Al powders [3]. These CNTs covering the surfaces of Al powders would hinder the cold welding of particles on collision. In addition, smaller diameter and small number of carbon shells imply that they have substantially lower flexural stiffness and buckling loads as compared to the MWCNTs. Therefore, these CNTs on the surfaces of Al powders can easily deform during inter-particle collisions to absorb part of the impact loads thereby further preventing the direct contact between...
Al powders. This way, SWCNTs and DWCNTs hinder the MA process itself, which would not be desirable for their homogeneous dispersion within Al powder matrix as observed elsewhere for small-diameter MWCNTs.

In the ball milling method, a large amount of energy is involved, since the dispersion is achieved by collisions of dense and rigid balls with the CNTs. Due to this high-energy milling, CNTs suffer damage, which causes a degradation of their properties. However, this method performed with lower energy and shorter times can be used with the aim of reducing the length of the nanotubes. Simões et al. have reported that the mixture obtained by ball milling shows flake-shaped particles of non-homogenous shape and size (Figure 9). However, the observation of the CNTs is difficult; the clusters are small and some CNTs seem to be embedded in the Al powders.

![Figure 9. SEM image of the mixture of Al and CNTs produced by ball milling [27]](image)

As is well known, good bonding between the matrix and the reinforcement is necessary to achieve satisfactory mechanical properties of composites. The excellent mechanical properties of the composite were reported to be due to the formation of an amorphous layer between the Al matrix and the MWCNTs, which could have led to a better wetting behavior of CNTs by the Al matrix.

Figure 10 shows the changes in porosity of the nanocomposite samples after consolidation and sintering. For pure Al samples, porosity increases rapidly by the milling time. However, porosity of the sintered composite samples shows a plateau during increasing with the milling time. Moreover, the nanocomposite samples show relatively lower porosities. In fact, during sintering, porosity can be reduced if particles have size distributions such that sufficient number of smaller particles can fill the gaps between the larger particles effectively. In this respect, increasing porosity of pure Al samples with longer ball milling times is attributed to the agglomeration of powders compared with the nanocomposite samples [15, 20, 22]. The relatively poorer dispersion of SWCNTs and DWCNTs into the Al powders compared with MWCNTs and to the relatively larger sizes of the ground products results in the lower porosity in the samples containing MWCNTs.
The hardness of the sintered nanocomposites is shown in Figure 11. It can be seen that the hardness of all samples increases with milling time. However, the level of hardness of the mechanically alloyed Al/MWCNTs is much higher. Therefore, SWCNTs and DWCNTs have no meaningful contribution to the improvements in mechanical properties of the nanocomposites. It is presumed that this is the result of poor dispersion of these CNTs within the Al powder matrix.

The MWCNTs, however, takes the form of three-dimensionally tangled curly thread. If such a shape can be maintained at least partially after MA process while the CNTs are uniformly dispersed, the CNTs will impede the deformation of Al matrix by anchoring it under external loads. Such a mechanism seems to be related to the recent observation in epoxy-based composites reinforced with coiled CNTs which proposes that the coiled shape of CNTs hinder the deformation of epoxy matrix.

Ayatollahi et al. investigated the effects of multi-walled carbon nanotubes content on the properties of epoxy-based nanocomposites using the nanoindentation and nanoscratch techniques. In this study, the nanoindentation and nanoscratch tests were conducted on MWCNT reinforced epoxy nanocomposites with three different percent contents of MWCNTs in order to determine their near surface mechanical properties such as elastic modulus, hardness, friction, and self-healing properties. Results showed that in higher nanofiller contents, the plasticity index values, the amount of pile-ups and the scratch depths decreased while the elastic recovery increased. The frictional properties of nanocomposites showed that the ploughing term of friction solely depends on the elastic-plastic behavior. An equation was also proposed to correlate the ploughing friction with the plasticity index [27].
Figure 11. SEM images of the mechanically alloyed materials: (a) Al powder, (b) Al/MWCNTs, (c) Al/DWCNTs, and (d) Al/SWCNTs

Figure 12. The hardness of the sintered nanocomposite samples versus milling time

4. Summary
Carbon nanotubes (CNTs) are relatively new materials with excellent combination of properties. They are one of the advanced reinforcement materials for engineering composites. Besides the polymer and ceramic matrices, interests are growing recently on the metallic matrices such as aluminum alloys for potential structural applications. Mechanical alloying (MA) is one of the best processing methods for synthetizing Al/CNTs nanocomposites, which results in the uniform dispersion of the reinforcement, inhibits the formation of undesired phases, and produces a nanostructured microstructure. It is of great importance to understand the mechanical alloying of Al/CNTs powder mixture for preparing nanocomposites. As a result, the current short review deals
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5. References


