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Review

Metal Matrix Composites Reinforced by Nano-Particles—A Review

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Abstract: Metal matrix composites reinforced by nano-particles are very promising materials, suitable for a large number of applications. These composites consist of a metal matrix filled with nano-particles featuring physical and mechanical properties very different from those of the matrix. The nano-particles can improve the base material in terms of wear resistance, damping properties and mechanical strength. Different kinds of metals, predominantly Al, Mg and Cu, have been employed for the production of composites reinforced by nano-ceramic particles such as carbides, nitrides, oxides as well as carbon nanotubes. The main issue of concern for the synthesis of these materials consists in the low wettability of the reinforcement phase by the molten metal, which does not allow the synthesis by conventional casting methods. Several alternative routes have been presented in literature for the production of nano-composites. This work is aimed at reviewing the most important manufacturing techniques used for the synthesis of bulk metal matrix nanocomposites. Moreover, the strengthening mechanisms responsible for the improvement of mechanical properties of nano-reinforced metal matrix composites have been reviewed and the main potential applications of this new class of materials are envisaged.

Keywords: MMNC; metal matrix nano-composite; nano-reinforcements; CNT

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1. Introduction

Metal matrix composites (MMCs) reinforced with nano-particles, also called Metal Matrix nano-Composites (MMnCs), are being investigated worldwide in recent years, owing to their promising properties suitable for a large number of functional and structural applications. The reduced size of the reinforcement phase down to the nano-scale is such that interaction of particles with dislocations becomes of significant importance and, when added to other strengthening effects typically found in conventional MMCs, results in a remarkable improvement of mechanical properties [1–4].

The main issue to be faced in the production of MMnCs is the low wettability of ceramic nano-particles with the molten metal matrix, which do not allow the production of MMnCs by conventional casting processes. Small powder aggregates are in fact prone to form clusters, losing their capability to be homogeneously dispersed throughout the matrix for an optimal exploitation of the strengthening potential. For this reason, several alternative methods have been proposed in order to overcome this problem.

The production methods can be categorized into two major groups: *ex situ* and *in situ*. The first synthesis route consists of adding nano-reinforcements to the liquid or powdered metal, while *in situ* processes refer to those methods leading to the generation of ceramic nano-compounds by reaction during processing, for example by using reactive gases. Several methods have been developed for *ex situ* synthesis of MMnCs. In particular, different powder metallurgy techniques were successfully employed. Moreover, ultrasound-assisted casting plays a particularly promising role for its high potential productivity. Alternative methods are listed and discussed in a following section.

The methods used for the characterization of MMNCs are the same of those used for conventional MMCs and alloys. Of course, the downsizing of the reinforcement implies the use of higher resolution techniques for characterization of morphology and local chemistry of the constituents.

In the literature, different kinds of matrix metals have been coupled with several types of nanometric phases. Ceramic compounds (SiC, Al_2O_3, *etc.*), intermetallic materials and carbon allotropes were used to reinforce Al, Mg, Cu and other metals and alloys. Particular importance is assigned to carbon nanotubes (CNT), which are characterized by very high strength, stiffness and electrical conductivity. These properties confer higher mechanical strength while improving electrical and thermal properties of the base material [5,6]. Moreover, MMnCs revealed to be able to improve other interesting engineering properties, such as damping capacity [7,8], wear resistance [9] and creep behavior [10].

This paper is aimed at reviewing the theoretical and experimental background related to bulk MMnCs and the major results achieved in this field. Structural properties and mechanical performance induced by nano-particle and nano-tube addition to base metals will be presented and the state of art of the synthesis methods will be described.

2. Strengthening Mechanisms

The high mechanical resistance of MMnCs is the result of several strengthening mechanism contributions, namely: load transfer effect, Hall-Petch strengthening, Orowan strengthening,

coefficient of thermal expansion (CTE) and elastic modulus (EM) mismatch [1–4]. In the following sections, each strengthening methods will be discussed separately.

2.1. Load Transfer Effect

The load transfer from the soft and compliant matrix to the stiff and hard particles under an applied external load, contributes to the strengthening of the base material. A modified Shear Lag model proposed by Nardone and Prewo [11] is commonly used to predict the contribution in strengthening due to load transfer in particulate-reinforced composites [1–3]:

$$\Delta\sigma_{\mathrm{LT}} = v_{\mathrm{p}}\sigma_{\mathrm{m}}\left[\frac{(l+t)\mathrm{A}}{4\mathrm{l}}\right] \tag{1}$$

where v_{p} is the volume fraction of the particles, σ_{m} is the yield strength of the unreinforced matrix, l and t are the size of the particulate parallel and perpendicular to the loading direction, respectively. For the case of equiaxed particles Equation (1) reduces to [3]:

$$\Delta\sigma_{\mathrm{LT}} = \frac{1}{2}v_{\mathrm{p}}\sigma_{\mathrm{m}} \tag{2}$$

2.2. Hall-Petch Strengthening

The grain size has a strong influence on metal strength since the grain boundaries can hinder the dislocation movement. This is due to the different orientation of adjacent grains and to the high lattice disorder characteristic of these regions, which prevent the dislocations from moving in a continuous slip plane [12]. The Hall-Petch equation relates the strength with the average grain size (d) [12]:

$$\Delta\sigma_{\mathrm{H-P}} = \frac{k_y}{\sqrt{d}} \tag{3}$$

where k_y is the strengthening coefficient (characteristic constant of each material).

The particles play a fundamental role in final grain size found in metal matrices of composites since they can interact with grain boundaries acting as pinning points, retarding or stopping their growth. The increase of v_{p} (volume fraction) and the decrease of d_{p} (particle diameter) lead to a finer structure, as theoretically modeled by the Zener equation [3]:

$$d_{\mathrm{m}} = \frac{4\alpha d_{\mathrm{p}}}{3v_{\mathrm{p}}} \tag{4}$$

where α is a proportional constant.

2.3. Orowan Strengthening

The so-called Orowan mechanism consists in the interaction of nano-particles with dislocations. The non-shearable ceramic reinforcement particles pin the crossing dislocations and promote dislocations bowing around the particles (Orowan loops) under external load [12]. The Orowan effect can be expressed by the following expression:

$$\Delta\sigma_{OR} = \frac{0.13bG}{d_{\mathrm{p}}\left(\sqrt[3]{\frac{1}{2}v_{\mathrm{p}}} - 1\right)} \ln\left(\frac{d_{\mathrm{p}}}{2b}\right) \tag{5}$$

where b is the Burger's vector and G is the matrix shear modulus.

2.4. CTE and EM Mismatch

The mismatch in coefficient of thermal expansion (CTE) and in elastic modulus (EM) between the reinforcements and the metal matrix is accommodated during material cooling and straining by the formation of geometrically necessary dislocations (GNDs).

GND density due to CTE and EM mismatch can be estimated by the following expressions [3]:

$$\rho^{CTE} = \frac{A\Delta\alpha\Delta T v_{\mathrm{p}}}{bd_{\mathrm{p}}(1 - v_{\mathrm{p}})} \tag{6}$$

$$\rho^{EM} = \frac{6v_{\mathrm{p}}}{\pi {d_{\mathrm{p}}}^3}\varepsilon \tag{7}$$

where A is a geometric constant, $\Delta\alpha$ is the difference in CTE and ΔT is the difference between test and processing or heat treatment temperatures. Then, the combined strengthening due to CTE and EM mismatch can be calculated by means of the Taylor equation [13]:

$$\Delta\sigma_{\mathrm{CTE+EM}} = \sqrt{3}\beta Gb\left(\sqrt{\rho^{\mathrm{CTE}}} + \sqrt{\rho^{\mathrm{EM}}}\right) \tag{8}$$

where β is a constant.

2.5. Sum of Contributions

The final strength of the composite, σ_{c}, can be evaluated by summing the above contributions related to the single strengthening effects, $\Delta\sigma_{\mathrm{i}}$, with the original yield strength of the unreinforced matrix, σ_{m}, therefore:

$$\sigma_{\mathrm{c}} = \sigma_{\mathrm{m}} + \sum_{\mathrm{i}} \Delta\sigma_{\mathrm{i}} \tag{9}$$

Several studies proposed alternative methods to calculate σ_{c}, taking into account the superposition of the effects [2,14]. A simple approach [3,14] suggests calculating the final strength of the composite by summing the root of the squares of all the single strengthening contributions, as:

$$\sigma_{\mathrm{c}} = \sigma_{\mathrm{m}} + \sqrt{\sum_{\mathrm{i}} {\Delta\sigma_{\mathrm{i}}}^2} \tag{10}$$

Another common method that takes into account Orowan strengthening mechanism, CTE mismatch effect, and load-bearing effect was proposed by Z. Zhang and D.L. Chen [1,2]:

$$\sigma_{\mathrm{c}} = (1 + 0.5v_{\mathrm{p}})(\sigma_{\mathrm{m}} + A + B + \frac{AB}{\sigma_{\mathrm{m}}}) \tag{11}$$

where A is the term relative to CTE mismatch and B is the coefficient related to Orowan effect:

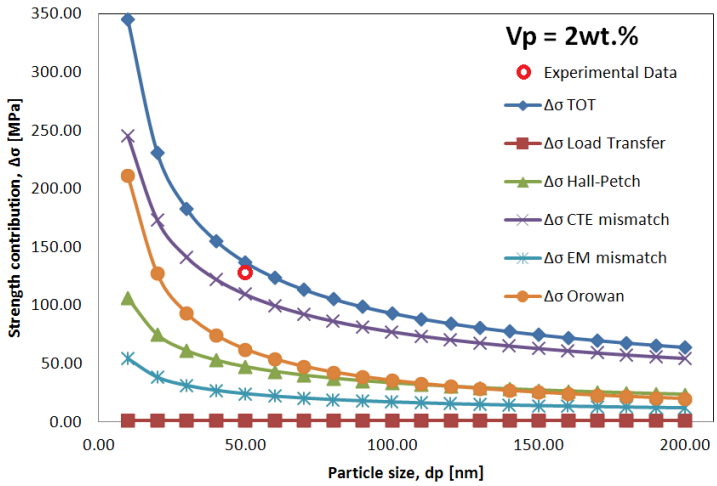
$$A = 1.25G_{\mathrm{m}}b\sqrt{\frac{12\Delta\alpha\Delta\mathrm{T}v_{\mathrm{p}}}{\mathrm{b}d_{\mathrm{p}}(1-v_{\mathrm{p}})}} \tag{12}$$

$$B = \frac{0.13G_{\mathrm{m}}\mathrm{b}}{d_{\mathrm{p}}\left[\left(\frac{1}{2v_{\mathrm{p}}}\right)^{\frac{1}{3}}-1\right]}\ln\frac{d_{\mathrm{p}}}{2\mathrm{b}} \tag{13}$$

Few papers are available in literature about this topic. This lack does not allow a comprehensive evaluation and comparison of the proposed methods. For this reason, the approaches are simply reported and not compared and deeply discussed.

Figure 1, modified from ref. [15] depicts the effect of each strengthening contribution and the total strengthening increment calculated according to Equation (10) for a 2 wt.% Al_2O_3 reinforced Al matrix processed at 400 °C. The most important contributions are achieved mainly due to CTE mismatch and Orowan effect, especially when the particle diameter is lower than 50 nm. Since in MMnCs, very small amounts of ceramic particles are used to reinforce the matrix without impairing toughness and other properties (e.g., electrical and thermal conductivity), very small contribution from load transfer is expected. The same graph shows that for the system Al/2wt.%Al_2O_3 the proposed model is consistent with experimental data.

Figure 1. Effect of strengthening contributions and total resulting strengthening increment calculated by Equation (10) for a 2 wt.% Al_2O_3 reinforced Al matrix composite.



3. Matrix Alloys and Available Reinforcements

Several metallic materials have been considered as matrix constituent for the preparation of MMnCs. In particular, the most interesting metals for industrial applications are Al [8,11,16–39], Mg [40–48], Ti [4,49,50], Cu [5,51–53] and their alloys. Pure and alloyed aluminum is the most investigated material with the largest number of published research studies describing Al-based composites as possible candidates for structural application. Different species of nano-sized oxides (Al_2O_3, Y_2O_3) [19,26,27,32–34,52,54], nitrides (Si_3N_4, AlN) [45], carbides (TiC, SiC) [11,24,29,35,36,39,41–44], hydrates (TiH_2) [47] and borides (TiB_2) [28,51] have been employed

as reinforcement agents. Especially, carborundum and alumina are the most common ceramic reinforcements for MMNCs. Moreover, different allotropes of carbon (carbon black [18], fullerenes [48] and carbon nanotubes [5,6,8,30,31,46,53]) have been investigated as fillers for several research works published in literature. The most used particles are CNTs: they confer very high mechanical properties to the metal matrix and, meanwhile, they lead to increased electrical conductivity, which makes MMnCs very attractive materials for electrical applications. Single wall carbon nanotubes (SWCNT) and multi wall carbon nanotubes (MWCNT) are both used for MMnCs production. In this regard, for example copper-0.1 wt.% MWCNT composites revealed a 47% increase in hardness and bronze-0.1 wt.% SWCNT showed a 20% improved electrical conductivity [5]. Finally, intermetallic compounds (NiAl, Al_3Ti) have also been successfully used as reinforcement phase in MMnCs [25,55]. Al–Al_3Ti nanocomposite revealed good mechanical behavior at high temperature [55], while TiAl–NiAl MMnCs showed low fracture toughness and high hardness [25].

4. Preparation Methods and Properties

For the large-scale production of metal matrix nanocomposites, the main problem to face is the low wettability of ceramic nano-particles, which does not allow the preparation of MMnCs by conventional casting processes since the result would be an inhomogeneous distribution of particles within the matrix. The high surface energy leads to the formation of clusters of nanoparticles, which are not effective in hindering the movement of dislocations and can hardy generate a physical-chemical bond to the matrix, thus reducing significantly the strengthening capability of nanoparticles [6,23]. Several unconventional production methods have been studied by researchers in order to overcome the wettability issue, either by formation of the reinforcement by *in situ* reaction or by *ex situ* addition of the ceramic reinforcement by specific techniques. Hereafter, the most studied and successful methods are described by classifying them into liquid, semisolid and solid processes.

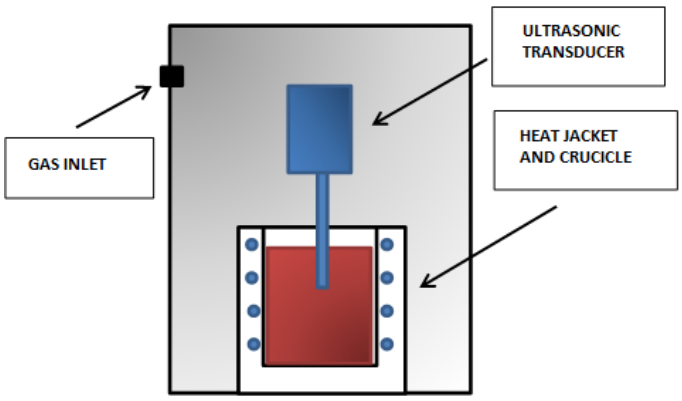
4.1. Liquid Processes

For composites prepared by the conventional liquid metallurgy route, severe aggregation of nanoparticles frequently occurs even when mechanical stirring is applied before casting. This is due to poor wettability and high viscosity generated in the molten metal owing to high surface-to-volume ratio of the nano-sized ceramic particles. The density of nanoparticles do not play an important role in the production process of nanocomposites. Such small particles are supposed to float on the top of the molten bath even if their density is relatively higher than that of the liquid matrix. This issue was indeed of paramount importance in micron-sized particle reinforced composites but it is felt that in nano-reinforced materials, other effects such as those induced by extensive surface tension play a much more important role [56].

High-intensity ultrasonic waves revealed to be useful in this context since they produce acoustic transient cavitation effects, which lead to collapsing of micro-bubbles. The transient cavitation would thus produce an implosive impact, strong enough to break the nanoparticle clusters and to uniformly disperse them in the liquid metal. According to this technique, a good dispersion of 2% vol. of SiC nano-particles (d < 30 nm) in aluminum alloy 356 was achieved by Li and co-workers [24] by means

of the experimental setup schematized in Figure 2 equipped by ultrasonic source. An improvement of 20% in hardness over the unreinforced alloy was achieved.

Figure 2. Scheme of experimental setup used by X. Li *et al.* [24].



Lan *et al.* produced nano-sized SiC/AZ91D Mg alloy composites through the same method. A fairly good dispersion of the particles was achieved although some small clusters still existed into the matrix. Owing to general improvement of the dispersion, the 5 wt.% SiC reinforced composite led to a microhardness increase of 75% [57].

As already mentioned, the nanoparticles also play a fundament role in grain refinement, working as pinning points hampering the grain growth and leading to improved mechanical properties according to Equation (4). In this regard, it has been reported that an addition of 1 wt.% nano-SiC into pure Mg strongly acts in this direction. Under comparative processing conditions, the Mg/SiC composite featured an average grain size of 72 μm whereas the unreinforced pure Mg of 181 μm [41]. Moreover, De Cicco and co-workers [38,39] proved by a droplet emulsion technique (DET) that nanoparticles can catalyze nucleation, thereby reducing undercooling. For A356 alloy based nano-composites produced by ultrasonic assisted casting, γ-Al_2O_3 revealed a better nucleation catalyzer than α-Al_2O_3 probably due to its lower lattice mismatch with the metal matrix. Other tests were also conducted in the same research [39] with TiC and SiC of different sizes.

Tensile tests performed on AZ91D alloy and on the same material reinforced by 1 wt.% of nano-AlN produced by ultrasound-assisted casting, revealed an increase of yield strength in MMnCs at room temperature of 44% and of 21% at 200 °C when compared to the unreinforced AZ91D alloy. For the same materials, a decrease of fracture strain at room temperature was achieved while an enhanced ductility was measured at 200 °C [45]. Improved ductility was detected by Wang *et al.* [42] even at room temperature. The yield strength (YS), ultimate tensile strength (UTS) and fracture elongation of an AZ91 alloy were 104 MPa, 174 MPa and 3.6%, respectively whereas the corresponding values for the AZ91 alloy reinforced by 0.5 wt.% of 50 nm SiC were: 124 MPa, 216 MPa and 6.6%, respectively.

In a research work by Cao and co-authors [58], the addition of 1.5 wt.% SiC to Mg–4Zn alloy obtained by an ultrasonic cavitation-based solidification process led to an increase of RT ductility of more than twice as well as to improved YS and UTS. A reduction of grain size was also observed by the same authors in reinforced sample (150 μm *vs.* 60 μm), which increased the castability of the alloy. This behavior was supposed to be related to an improved casting quality, since the resulting finer grain

size of the composite can improve melt feeding characteristic minimizing porosity, shrinkage and enhancing hot-tearing resistance.

In situ MMnCs have been successfully prepared by liquid metallurgy processes. 50 nm-TiB_2-reinforced copper-matrix composites were produced by adding B_2O_3, C and Ti in a Cu–Ti melt [59]. The composites exhibited significantly improved mechanical properties. In particular, the YS of Cu and Cu/TiB_2 was 298.7 MPa and 509.6 MPa, respectively. Al/TiB_2 nanocomposites were also synthesized by an *in situ* method, by adding a mixture of potassium hexafluorotitanate (K_2TiF_6) and potassium tetrafluoroborate (KBF_4) salts in an Al melt under argon atmosphere [60].

Disintegrated Melt Deposition (DMD) is a further liquid metallurgy process successfully employed for nano-composite production. Alumina nanoparticles have been well dispersed in Al–Mg alloys by heating the metal in argon atmosphere and adding the ceramic particles by means of a vibratory feeder. The melt was stirred and poured, then disintegrated with argon gas jets and deposited onto a metallic substrate. Finally, the MMnCs were extruded to reduce porosity down to very low levels and to achieve a good dispersion of the particles [61,62].

Selective laser melting (LSM) was also used to produce Ti-based composites reinforced by nanoparticles [63]. Powders were milled by high-energy ball milling and then melted by laser beam under protective atmosphere. Through this method, a unique microstructure very different from the initial microstructure of the reinforcement was achieved. A proper decrease in volumetric energy density led to the development of TIC whisker and of uniformly dispersed nano-lamellar TiC starting from dendritic TiC. The same research confirmed that well dispersed nano-particles induce improved mechanical and wear properties to the Ti matrix.

Melt stirring, high-pressure die casting [46] and arc-discharge plasma method [64] were also used to produce AZ91/CNT composites and *in situ* Al/AlN MMnCs, respectively.

Finally, it was highlighted that the main problem to be faced in production of CNT-MMnCs by the liquid metallurgy method is the interaction of the nanotubes with the liquid metal. In fact, the process may cause damage to CNTs or formation of chemical reaction products at the CNT/metal interface [6,65,66]. Therefore, this synthesis route is mainly indicated for composite matrices having low-melting temperatures and reduced reactivity with the reinforcement phase. The problem of low wettability of CNTs can be partially overcome by coating CNT with metal layers (for example Ni) [6,67]. The field of surface modification appears as quite promising and it is open to innovation for attenuating the drawbacks on wettability and tendency to clustering of nanoparticles.

4.2. Semi-Solid Processes

Only few works are available in literature about this topic even if this method has been widely applied for micrometer-size particle-reinforced MMCs, and it would be extremely interesting for large-scale production.

A356/Al_2O_3 MMnCs were produced by using a combination of rheocasting and squeeze casting techniques [68]. Rheocasting is a semi-solid phase process, which has several advantages: it is performed at lower temperatures than those conventionally employed in foundry practice, resulting in reduced thermochemical degradation of the reinforcement surface. Moreover, the material shows thixotropic behavior typical of stir cast alloys and production can be performed by conventional

foundry methods. During rheocasting, the pre-heated nanoparticles are added in the semi-solid slurry while it is vigorously agitated in order to achieve a homogenous particle distribution. Then the slurry is squeezed using a hydraulic press. Mg alloy AZ91 ingots reinforced by nano-SiC particles were produced by semisolid stirring-assisted ultrasonic vibration [44]. After homogenization treatment and extrusion, the SiC reinforcement featured a fairly good dispersion although bands of accumulated nanoparticles were present and their amount could be reduced by increasing the extrusion temperature.

An innovative method named semi-solid casting (SSC) was proposed by De Cicco *et al.* [69]. Zinc alloy AC43A reinforced by 30 nm β-SiC was used for samples preparation by SSC. The SSC experiments were carried out by pouring ultrasonicated molten MMNC material (450 °C) from a graphite crucible into a steel injection device, which was preheated to 400 °C. Liquid MMnC was cooled down to 386 °C achieving less than 30% of solid fraction. Then, the injection sleeve was inverted and placed on top of a steel mold. The plunger was activated and the semi-solid material was injecting into the mold. The produced samples showed strength properties comparable to those by ultrasound-assisted casting but with improved ductility.

4.3. Solid Processes

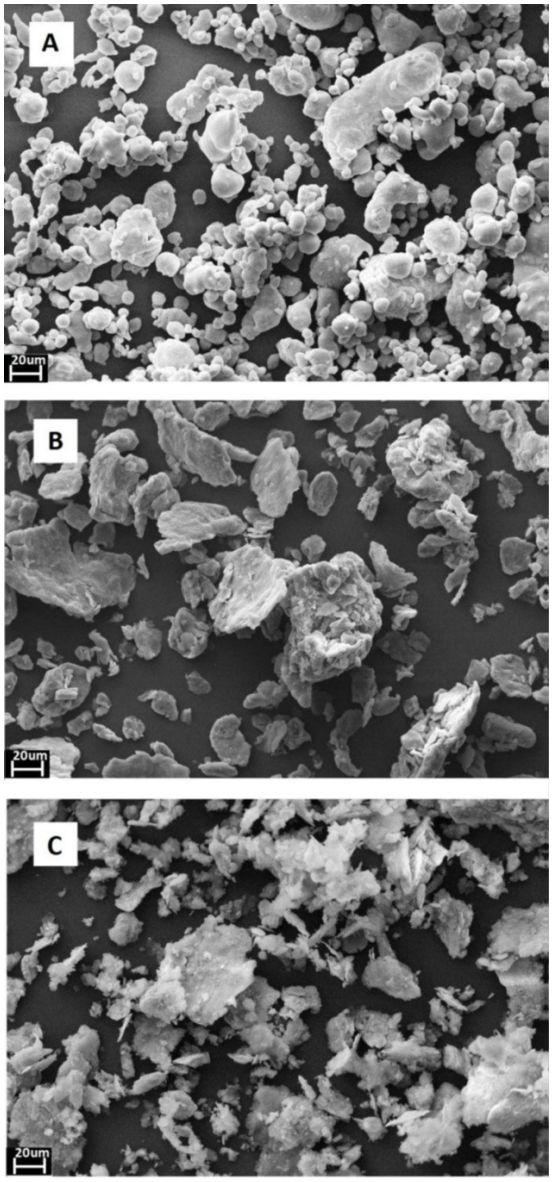
Several solid methods were studied and developed for preparing MMnCs. In particular, different powder metallurgy techniques were successfully employed in this respect. Some papers focus on mechanical alloying which is a powder metallurgy technique consisting in repeated cold welding, fracturing and re-welding of powder particles in a high-energy ball mill. The typical morphological evolution of Al powders during high-energy ball milling is depicted in Figure 3. This technique is of fundamental importance since it allows achieving a better dispersion of nano-powder into the composite by breaking up the ceramic clusters. It can also be exploited for the formation of alloys by diffusion mechanisms starting from pure metals, and to produce performs by *in situ* reaction of nano-reinforcements. Therefore, mechanical alloying, which cannot be separated from the opportunity of breaking up of the nano-ceramic clusters, is a value-added option offered by this particular processing route [9,33,35,39,47,51,70–78].

It has been proved that the presence of nanoparticles can accelerate the milling process (stimulating plastic deformation, cold welding, and particle fragmentation) and grain refinement mechanism [73,75]. Process control agent (PCA) has a strong influence on morphological evolution of powders during ball milling [34]. The addition of 1.5% stearic acid as PCA prevents cold welding of Al particles during ball milling and leads to an increase of hardness of the hot-compacted samples. Speed and time of milling, mass of balls and powder, and ball diameter also contributes to final hardness development. In particular, a pronounced decrease in energy transfer from the balls to the powder was found by raising the amount of balls [35].

High-energy ball milling proved to be a suitable technique for production of *in situ* MMnCs. Al–TiN composite was prepared by milling elemental Al and Ti powders with ring-type organic compound pyrazine in benzene solution [71]. Mg 5 wt.% Al alloy *in situ* reinforced with TiH_2 was also prepared by mechanical alloying of elemental powder of Mg, Al and Ti, using polyethylene-glycol to provide hydrogen for the formation of TiH_2 and to prevent excessive cold welding during ball milling. After attritioning, the powders were cold isostatically pressed (CIP), extruded and thermal treated. The

mechano-chemically milled specimens showed very fine microstructure and good dispersion of fine reinforcements, a slight increase in YS and ductility was observed [47,76]. Iron-wustite (Fe–FeO) nanocomposites were also produced by mechano-chemical processing starting from Fe and Fe_2O_3 powder with different mole ratios. These materials showed a ferromagnetic-like behavior, which was interpreted according to spinel-like defect, clusters [72]. In another research work by Lu *et al.* [74], Mg-5Al-10.3Ti-4.7B (wt.%) powder mixture was ground using high-energy ball milling and subsequently extruded. They observed the formation of non-equilibrium Ti_3B_4 phase in extruded samples. Lu and co-authors also investigated the *in situ* formation of TiB_2 via chemical reaction among Al, TiO_2 and B_2O_3. The powders were cold compacted into green compacts and sintered at different temperatures. By this method, 53% of increment in YS and UTS was achieved [28]. *In situ* TiB_2 reinforced Cu alloy composite was indeed achieved via argon atomization at 1400 °C followed by hot isostatic pressing (HIP) at 200 °C under 200 MPa pressure [51].

Figure 3. SEM micrographs (secondary electrons) of pure aluminum powder (**A**) as received, (**B**) after 2 h of ball milling and (**C**) after 5 h of ball milling [78].



Moreover, Cu-Al_2O_3 nanocomposites have been prepared by two chemical routes: through decomposition of $Al(NO_3)_3$ to Al_2O_3 by calcination of a paste of CuO–$Al(NO_3)_3$ followed by H_2 reduction and sintering, or through hydrolysis of $Al(NO_3)_3$ solution followed by calcination, reduction and sintering. The latter method led to the formation of finer Al_2O_3 (30 nm *vs.* 50 nm) and promoted enhanced properties in terms of relative density, microhardness and abrasive wear resistance [9]. Submicron-sized titanium carbide was successfully sintered from the reaction of Ti salt (K_2TiF_6) and activated carbon, by controlling the degree of reaction through temperature and amount of C. In this respect, it was observed that at low temperatures, formation of Al_3Ti was predominant while at high temperatures (above 1000 °C), the intermetallic compound was not stable and TiC was preferentially formed [36].

Several techniques have been used to perform the compaction of composite powders. The most common routes are HIP [51], hot pressing [52] and cold pressing [9,26,28,54,77,78] or CIP [47,76] followed by a sintering treatment. Conventional hot extrusion [7,10,30,79] or equal channel angular extrusion (ECAE), also known as equal channel angular pressing ECAP) [15,18,19,21,32,34,37,53,80,81] revealed to be suitable methods to achieve full dense composites.

Hot extrusion was used to sinter Al-2%CNT composite powders blended by high-energy ball milling observing a tensile strength enhancement of 21%. Extrusion was also found to promote alignment of CNTs along the extrusion direction that may lead to anisotropic properties of the material [30]. In the same work, CNTs have been found to act as nucleation sites for void formation during tensile tests. Both CNTs pullout and MW-CNT inner tubes slippage were observed in fractured surfaces suggesting poor interfacial bond between CNTs and Al matrix.

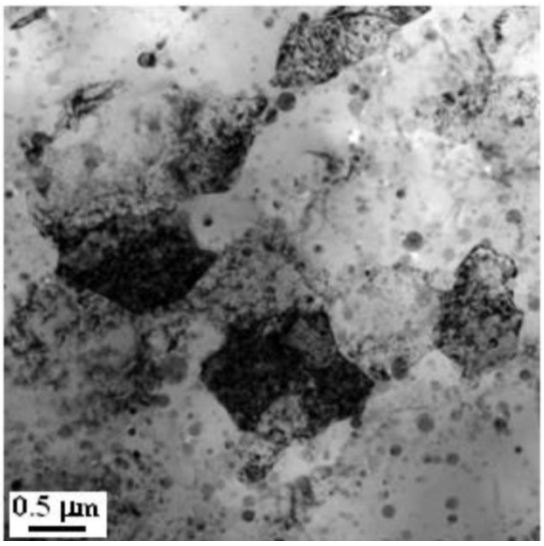
Ferkel *et al.* extruded at 350 °C pure Mg powders and two composite powders consisting of Mg and 3 wt.% nano-SiC. One batch had been ball milled and the second one had been conventionally mixed [10]. The study was focused on high temperature (HT) mechanical behavior of the produced nanocomposites. The milled composite showed the largest gain in strength but also the lowest ductility at all testing temperatures (RT, 100 °C, 200 °C and 300 °C). Moreover, significant difference in the creep response was been observed at 200 °C in favor of the ball milled composite.

Al-based samples sintered by ECAP and sintered by cold pressing followed by heat treatment and extrusion were compared in [32]. The best results were achieved by the former method since the hardness values after three ECAP passes was 67% higher than the extruded samples. Higher compressive strength and increased wear resistance were also achieved in the ECAP processed samples.

It was demonstrated that the mechanism of powder consolidation in severe plastic deformation (SPD) processes associated to ECAP is different from that of sintering-based routes. In ECAP, the deformation of the particles, rather than the atomic diffusion, would cause the bonding between particles. By this way, fully dense compaction can be achieved at lower temperatures and in shorter times compared to conventional sintering processes. The best results in terms of bonding between the particle and absence of porosity were obtained when the particles were shear-deformed during the process instead of forced to slide one over the other. This effect is promoted by larger, softer and irregular shaped particles, high friction between particles with clean metallic surfaces (no oxide), higher pressure and temperature [19,80].

ECAP powder pressing was successfully used to consolidate 1% CNTs in copper matrix at room temperature, avoiding CNT surface reaction with metal matrix [53]. Al nanocomposites reinforced by carbon black (CB) or by Al_2O_3 were also produced by using back-pressure ECAP (BP-ECAP) at 400 °C [18,19,21]. In particular, good dispersion of Al_2O_3 and CB nanoparticles was achieved by mechanical milling followed by 8 BP-ECAP passes (Figure 4). Compression tests on these materials showed that the YS of unreinforced sample reached 58 MPa, while that of the composite with addiction of 5% CB reached 260 MPa. Moreover, after 8 BP-ECAP passes, full dense pure Al showed a Vickers hardness of 37.1 HV, while the Al-5%Al_2O_3 MMnC showed an hardness of 96.5 HV and the Al-5%CB system an hardness of 81 HV [18,21].

Figure 4. TEM microstructure of the Al-10 wt%Al_2O_3 nanocomposite showing the homogeneous dispersion of Al_2O_3 nanoparticles (<50 nm in sizes) in the Al matrix [21].



Al composites reinforced by 5%, 10% and 15% nano-Al_2O_3 were also produced by powder metallurgy route. The powders were mixed in ethanol by ultrasonic treatment, wet attritioned by high-energy ball milling and finally compacted by ECAP at 200 °C. The best results in terms of microhardness and compressive yield stress were achieved by adding 10% nano-alumina after 4 ECAP passes [37].

Milling associated to ECAP process of chips revealed to be a promising route for the use of metal scraps [4,15,80]. Ceramic nanoparticles (AlN) were successfully added to Mg-5%Al alloy chips even though no significant improvement in strength could be achieved [15].

5. Applications

So far, to the authors' best knowledge, metal matrix composites reinforced by nanoparticles or nanotubes are not yet being employed in relevant commercial applications due to their very recent development. However, MMnCs show higher mechanical properties than micro-particles reinforced composites, without any evidence of a strong drop in thermal and electrical conductivity [5,6]. For this reason, they are considered as possible candidates for substituting conventional MMCs or related monolithic alloys in structural and electrical RT and HT applications. For example, CNT composites

could replace, thanks to their higher strength and stiffness, carbon fibers composite in many applications, especially in high-temperature environments. Another good opportunity for the substitution of traditional MMCs with nano-sized counterparts is related to the loss in fracture toughness and ductility occurring in micro-reinforced MMCs. Toughness can be substantially preserved in nano-reinforced composites owing to the reduced particle volume fraction required to achieve strengthening.

The enhanced wear resistance [9,63] and the good thermal conductivity combined to the high specific strength make MMnCs attractive materials for aircraft brakes. Moreover, the specific strength and elastic modulus could be exploited in sport industry, for instance for rackets or bicycle frames and other components. A further field of potential application is in electronic devices, for example for heat sinks and solders (thanks to their thermal properties) or as antennas (thanks to their electrical properties and stiffness). Aerospace and automotive industries may exploit all the above properties for different kind of applications such as structural radiators, gears, aircraft fins, cylinder liners, disk brakes and calipers.

The improved damping capacity of MMnCs could also be exploited to reduce vibrations and noise of structures. In Mg–Al_2O_3 samples extruded at 350 °C after powder milling, a significant damping ability was highlighted and attributed to interface character of MMnCs [7]. Indeed, CNT/2024 Al composites showed improved damping properties at high temperature as high as 400 °C [8].

6. Conclusions

A number of processing routes are available for the synthesis of nanoreinforced MMCs based either on solid sintering or on liquid processing. Consolidation of powder, generally preceded by high-energy ball milling, is carried out both by conventional technique (HIP, forging or CIP followed by heat treatment) or alternative methods, firstly by ECAP or hot extrusion. Indeed, among the liquid processes, promising results were achieved by ultrasonic assisted casting.

Metal matrix nanocomposites are very interesting materials with high potential for use in a large number of industrial applications. Some recent research works highlighted the real possibility to produce composites characterized by exciting mechanical properties, which can be further enhanced by optimizing the particle dispersion. In particular, remarkable results in terms of hardness, mechanical strength, wear resistance, creep behavior and damping properties were achieved. By the adoption of this class of metal matrix composites, expensive heat treatment currently carried out on conventional monolithic alloys could be avoided and the range of available alloys for structural and functional applications could be broadened.

Notwithstanding their properties, there are still some aspects to be improved in production of MMnCs. Fabrication of MMnCs is much more complicated than that of micro-MMCs. When the particles scale down from the micro- to the nano-level, many additional difficulties have to be solved and new issues have to be faced. The reaction between ceramic nanoparticles or carbon nanotubes with the matrix is still unclear. The inappropriate bonding interface may lead to the failure of the composites. Clustering of particles is another issue of paramount importance, to be solved especially in large parts.

Conflicts of Interest

The authors declare no conflict of interest.

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