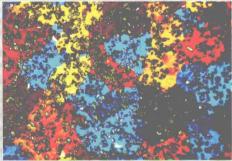
# Advances in Metal Matrix Composites

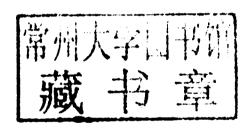




Edited by Lorella Ceschini Roberto Montanari

# Advances in Metal Matrix Composites

Special topic volume with invited peer reviewed papers only.



Edited by:

Lorella Ceschini and Roberto Montanari



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### **Preface**

Metal matrix composites (MMCs) have been the subject of scientific investigation and applied research for about three decades, but only in the past few years these materials became realistic candidates in engineering components, such as electronic heat sinks, automotive drive shafts, ground vehicle brake rotors, fighter aircraft fins and jet engine components.

Compared to conventional materials the advantage of MMCs is that their structure can be tailored to get various combinations of physical and mechanical properties and meet the highest requirements. For example, they offer superior specific modulus, strength, thermal stability and wear resistance. Therefore, these innovative materials open up new possibilities for modern material science and technological development.

This special issue presents 12 selected peer reviewed papers on different aspects of MMCs and aims to highlight recent findings in the field.

The papers are mainly focused on light metal matrix composites, based on Al, Mg, Ti alloys, reinforced by particles, nano-dispersoids and long fibres. The results come from both experimental investigations and computer simulations and the contributions deal with different key issues: production processes, microstructural characteristics, mechanical behaviour, welding by advanced techniques, workability and tribology.

We would like to express our gratitude to all the authors who contribute to the special issue; a special thank is due to Dr Riccardo Donnini for his help and dedication in collecting and organizing the selected papers.

Lorella Ceschini and Roberto Montanari

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# Manufacture of Aluminum Nanocomposites: A Critical Review

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**Keywords:** lightweight, nanocomposites, agglomeration, manufacturing routes, ex-situ processing, in-situ processing, gas-liquid reactions.

**Abstract.** In the last two decades, metal matrix nanocomposites have witnessed tremendous growth. Particulate-reinforced nanocomposites have been extensively employed in the automotive industry for their capability to withstand high temperature and pressure conditions. Several manufacturing approaches have been used to fabricate them. Non-homogeneous particle dispersion and poor interface bonding are the main drawbacks of conventional manufacturing techniques. A critical review of nanocomposite manufacturing processes is presented; the distinction between exsitu and in-situ processes is discussed in some detail. Moreover, in-situ gas/liquid processes are elaborated and their advantages are discussed. The thermodynamics and kinetics of the reaction between the precursor gas and the liquid metal have been analyzed and their role on particle formation studied. This critical review will provide the reader with an overview of nanocomposite manufacturing methods along with a clear understanding of advantages and disadvantages.

#### **Metal-matrix Composites in Context**

Metal-matrix composites are a hybrid material in which rigid ceramic reinforcements are embedded in a ductile metal alloy matrix. They tailor the best properties of two different materials, such as ductility and toughness of the metallic matrix and the high modulus and strength of ceramic reinforcements. Their first application can be traced back to the late 1960s, with the development of a steel-wire reinforced copper alloy [1]. The aerospace industry led the application and use of composite materials in spacecrafts components. High-performance and high-integrity materials are required for extreme environments and critical applications such as for space missions. It is interesting to note that during its lifetime, the International Space Station will undergo 175,000 thermal cycles from +125 C° to -125 C° as it moves in and out of the Earth's shadow. During the last 4 decades, aluminum matrix composites were specifically developed to meet both aerospace and defense needs. Continuous boron fiber reinforced aluminum was used in the Space Shuttle Orbiter as the frame and rib truss members in the mid-fuselage section; there are other applications such as landing gear drag link yielding 45% weight savings. A Gr/Al composite is the constituent of a high-gain antenna boom for the Hubble Space Telescope. This boom (3.6 m long) offers the stiffness required to maintain the position of the antenna during space maneuvers. In the 1980's and early 1990's, metal matrix composite development programs were in vogue and there was much activity at all major aluminum producers. Alcan, through its Duralcan subsidiary, established a 25 million pound per year production capability for particulate-reinforced aluminum composites. The Aluminum Association convened the Aluminum Metal Matrix Composites Working Group, a product of which was the ANSI H35.5 standard that established a nomenclature system for aluminum composites [2]. As expected, metal matrix composites found applications in a variety of other markets such as automotive, electronic packaging, industrial product and recreational products [3]; though not a conclusive list, the components given below illustrate applications that utilize Al based composites:

- Chevrolet Corvette and GM S/T pick-up truck drive shafts
- Plymouth Prowler brake rotors and GM EV-1 brake drums
- Toyota diesel engine pistons
- Pratt & Whitney 4000 series engine fan exit guide vanes
- Motorola's Iridium Satellites and GM EV-1 electronic packaging applications
- F-16 fighter aircraft ventral fins and fuel access covers
- · Bicycle components and golf clubs

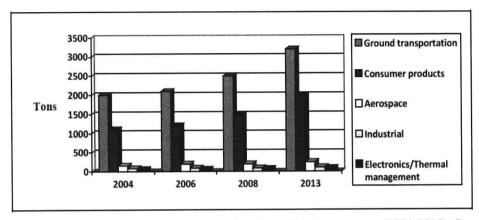


Fig.1. Global outlook of metal-matrix composites by application segment (2004-2013). Source: BCC Research.

An almost 70% increase in metal matrix composites is estimated to occur in the use of Al in vehicles from 2004 to 2013, see Fig.1. The choice of aluminum alloys as matrix is dictated by the compelling need to have vehicles with low fuel consumption and reduced emissions for a sustainable future. Because of their high strength-to-weight ratio, aluminum alloys are considered to be an alternative to conventional steels and to the more expensive superalloys. The amount of aluminum per automobile produced in USA has increased from 251 lb. of 1999 to 280 lb. forecast for 2014 [4,5]. In Europe it went from 220 lb. of 1999 to 462 lb. forecast for 2014 [6], see Fig.2. Aluminum-based composites have contributed to such growth by improving strength and hardness of the aluminum matrix, broadening the application field to more highly-rated regimes.

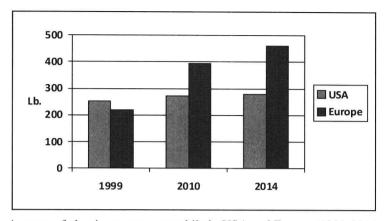


Fig.2. Amount of aluminum per automobile in USA and Europe (1999-2014) [4-6].

When compared to ferrous sand casting, high-production of metal matrix composite components through die casting, squeeze casting and semi-solid molding can compete effectively in terms of cost. In the commercial aircraft industry, weight savings has been estimated to be around \$450/kg; and in spacecraft, it can reach \$40,000/kg. For what concerns the automotive industry. Ford Motor Co. has placed the value of weight reduction at between \$0.35-3.50/kg depending on vehicle platform. In freight transport, the weight savings of a component translates to additional freight that can be hauled. For heavy-duty trucks, such savings has been valued from \$2-16/kg depending on the equipment's operational cycle [7]. Aluminum metal matrix composite also win out on iron components in terms of marketability and maintainability. Though metal matrix composites offer many advantages, they do have shortcomings such as low fracture toughness, low strength and hardness at high temperatures and poor machinability. The main concern of machining particulate metal matrix composites is the extremely high tool wear due to the abrasive action of the ceramic reinforcing particles. Tool selection is limited to a small group of extremely hard and expensive materials. The cutting tool must be able to withstand intermittent cutting of hard (reinforcement) and soft (matrix) materials. Polycrystalline diamond tools are often recommended for machining this particular class of materials and the high cost of such tools together with the need of frequent tooling changes increases the cost of the machining process [8]. Conventional machining methods have applied on composites with poor results. Non-traditional processes like waterjet, abrasive waterjet cutting, electrical discharge machining, ultrasonic machining and laser cutting provide precision finish but are characterized by very high costs and slow machining rates [9]. Therefore, machining still remains an issue to address since it will continue to be a necessary step to produce the required close dimensional tolerances and surface finish.

There is a compelling need for an aluminum-based material whose strength at high temperatures is retained and whose manufacturing process can be adapted to existing industrial infrastructures. Nanocomposite aluminum matrix materials have emerged as a viable alternative to overcome the limitations of aluminum (micro-) composites. Tensile strength, hardness and fracture toughness are enhanced as well as dimensional stability at high temperatures, see Fig.3 [12]. They currently represent a market segment of \$ 250 million, 80% of which is covered by automotive applications. Nanoparticles in castings are considered to be the most promising segment in casting material development [10]. However nanocomposites are challenging to produce as structural components due to difficulties in attaining a homogeneous distribution of the nano-phased particles. Clusters of secondary phases are detrimental for the final component performances and also affect post-processing techniques and the ability to machine the part. Representative metal nanocomposite systems and associated attributes are given in Table 1 [11].

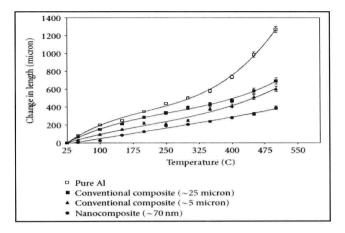


Fig.3. The variation of change in length versus temperature for aluminum and its composites at constant SiC content (7.5 Vol% SiC) [12].

Matrix/Nano-sized Reinforcement	Properties	
Al/SiC Mg/SiC Al/Al <sub>2</sub> O <sub>3</sub> Mg/Al <sub>2</sub> O <sub>3</sub>	Improved ultimate strength, hardness and elastic modulus	
Al/AlN	Higher compression resistance and low strain rate	
Ni/PSZ (partially- stabilized zirconia) and Ni/YSZ (yttria- fully stabilized zirconia)	Improved hardness and strength	
Cu/Al <sub>2</sub> O <sub>3</sub>	Improved microhardness	

Table 1. Metal Nanocomposite Systems of Interest and Associated Attributes [11].

Nano-particle reinforced composites. Nano-particles have progressively replaced other discontinuous reinforcement structures such as nano-fibers, nano-wires or nano-platelets. SiC, TiC, WC, TaC, TiB<sub>2</sub>, AlN, and  $Al_2O_3$  are some of the most common types of nano-particles that have been utilized. The characteristics of nano-particle reinforced composites can be summarized as follows:

- drastic change of fracture mode from inter-granular fracture in monolithic metal to transgranular fracture in nano-composites;
- moderate to significant improvement in strength;
- moderate improvement of fracture toughness;
- significant improvement of creep resistance, thermal shock resistance, and wear resistance;
- enhancement of dimensional stability at high temperatures.

Zebarjad et al. [13] compared the effect of 25  $\mu$ m, 5  $\mu$ m, and 70 nm SiC particles on dimensional stability in an aluminum alloy. The temperature sensitivity of aluminum decreases in the presence of both micro and nano-sized silicon carbide, though the effect of nano-sized silicon carbide on dimensional stability is much higher than that of micro-sized ones. Ren and Chan [13] added SiC nano-particles (50 nm) to 7075 aluminum alloy. They pointed out that this resulted in increased wear resistance and high temperature creep resistance compared to the same alloy reinforced with larger sized 13  $\mu$ m SiC particles. Furthermore, the volume percentage of nano-particles needed to achieve this result was considerably smaller than in the case of the 13 $\mu$ m SiC particles. Similarly, the tensile strength of an aluminum alloy reinforced with 1 % volume of Si<sub>3</sub>N<sub>4</sub> (10 nm) has been found to be comparable to that of the same alloy reinforced with 15 % volume of SiC particle in the micro-sized range (3.5  $\mu$ m); the yield strength of the nano-metric composite being significantly higher than that of the micro-metric one [14]. The existence of a threshold size ("critical size") below which the addition of particles improves properties has been reported – see Table 2) [11]. It must be noted that the mechanism responsible for property improvements remains a matter of debate among researchers.

Properties	Critical Reinforcement size (nm)
Catalytic activity	<5
Softening of hard magnetic materials	<20
Change of refractive index	<50
Producing electromagnetic phenomena such as super paramagnetism	<100
Strengthening and toughening	<100
Modifying hardness and plasticity	<100

Table 2.Critical Size for Properties Improvement in Nanocomposites [11].

Strengthening theory based on a continuum approach is not useful; since it ignores the influence of particles on micromechanics of deformation - i.e., location of particles, grain size, and dislocation density. Several discontinuous approaches have been formulated to include particle effects. The modified shear lag theory [16] of Nardone and Prewo, the Eshelby- based particle-compounded model and the EMA (effective medium approximation) model by Stroud are the most popular ones [16]. They take into account one or more of the following strengthening mechanisms:

Orowan mechanism: the stress that must be applied to force dislocations to by-pass an obstacle (such as a particle) is the principle of the Orowan strengthening mechanism. The stress arises due to the resistance of closely spaced hard particles as dislocations pass through. If the particles are coarse (in the micro-size range) and the inter-particle spacing is large, the Orowan effect is not significant [16]. When highly dispersed nano-sized particles are present, Orowan strengthening becomes more favorable. Creep resistance and thermal stability are consistently enhanced. TEM (transmission electron microscopy) observations

reveal strong dislocation bowing and tangling around the particles, confirming the operating mechanism [15, 16].

- Thermal mismatch: matrix and reinforcement have different coefficients of thermal expansion. During cooling of the component, plastic deformation is produced in the matrix at the various interfaces. These deformations increase the density of dislocation [16].
- Load-bearing: the strong bond due to the cohesion between particles and the matrix contributes to load-bearing capacity [16].

When all these factors are taken into account, the increase in mechanical properties with the decrease in size can be estimated.

#### Critical Issues in Processing of Nanocomposites

The main challenge for nanocomposites is how to make them – the processing routes to manufacture them. Dispersing the second phase particles in the matrix and achieving a strong interfacial bond are the two main processing challenges. Most fabrication processes fall short of fulfilling these tasks. Clusters of particles and weak matrix-reinforcement interfaces compromise the ability of the composite material to function under extreme conditions, such as high temperature and pressure typical of automotive applications (especially Diesel engines).

Uneven dispersion and agglomeration. Agglomeration is a common phenomenon that occurs when a solid particle comes into contact with a non-wetting medium [17, 18]. The clustered particles significantly reduce the failure strain of the composite; degradation is attributed to preferential nucleation of cracks in clustered regions. Final fracture is produced by the crack propagating to other clusters. Clustering occurs due to combined effects of agglomeration, sedimentation (particle settling rate) and particles pushing by the advancing solidus-liquidus interface. Particle clustering occurs since the system tends to minimize its free energy. A solid inclusion is never perfectly smooth: its surface is covered with cavities filled with gas, which contribute to increasing the system's Gibbs energy. This is can be seen by analyzing the equation describing the Gibbs energy of a gas-liquid-solid system [17]:

$$\Delta G = (\mu_g(T, P) - \mu_l(T, P)) + \gamma_{lg} \Delta S_{lg} + \gamma_{sg} \Delta S_{sg} + \gamma_{sl} \Delta S_{sl}$$
(1)

where T is the temperature, P the pressure in the liquid,  $\mu_g$  and  $\mu_l$  the chemical potentials of gas and the liquid,  $\Delta S$  is the change in interfacial areas and  $\gamma$  surface energies. When the particle size is brought down to the nano-scale range, surface energy is enhanced by three orders of magnitude (Table 3), introducing strong instability in the system and hindering particle wetting by the molten metal.

Particle size [cm]	Total surface area [cm <sup>2</sup> ]	Surface energy [J/g]
0.1	28	5.6×10 <sup>-4</sup>
0.01	280	5.6×10 <sup>-3</sup>
0.001	2.8 ×10 <sup>3</sup>	$5.6 \times 10^{-2}$
$10^{-4}$	2.8×10 <sup>4</sup>	0.56
$10^{-7}$	2.8×10 <sup>7</sup>	560

Table 3. Variation of Surface Energy with Particle Size (1 g of sodium chloride) [20].

The natural tendency towards equilibrium is the "spring" that allows the system to assume a physical configuration for which the Gibbs energy is lowered to a minimum value. With this perspective, agglomeration acts like a "stability configuration": several nano-particles cluster in one micro-agglomerate (Fig.4), providing a less extended total interfacial area. The dynamics of the relative motion of two nano-sized particles has been extensively studied [18, 20]. Due to the complexity of the problem, the analysis is usually limited to two main mechanisms: Brownian diffusion/motion (or perikinetic aggregation), and inter-particle forces (electrostatic and Van der Waals). External forces are not considered and particle inertia is neglected.

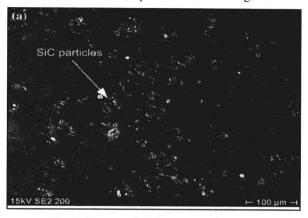


Fig. 4. Clusters of SiC nano-particles [19].

**Brownian motion.** It has been demonstrated [18] that a suspended particle is randomly bombarded from all sides by thermally-excited molecules coming from the liquid. Brownian diffusion ensures continuous collision between particles [19]. It can be defined as the incessant random motion exhibited by microscopic particles immersed in a fluid. Einstein noticed that if one solid inclusion is small enough to behave like a gas molecule, it is continuously collided by liquid molecules and displaced as a consequence. The magnitude of the displacement follows a Gaussian statistic distribution according to the relation:

$$d = \sqrt{\frac{2kTt}{6\eta\pi r}}\tag{2}$$

where  $\eta$  is the viscosity of the medium, t the time, r the particle radius, T the temperature and k the Boltzmann's constant. The displacement increases with decreasing particle radius, thus enhancing the probability of a collision to occur. It has been confirmed [18] that for particles smaller than 3.5  $\mu$ m, Brownian motion totally dominates the agglomeration dynamics. The aggregation rate for 20 nm particles has been evaluated to be four orders of magnitude higher when compared to particles in the range of 1  $\mu$ m [20]. This behavior can be explained by the fact that as the particle size increases the potential energy of repulsion increases, thus making aggregation less likely.

Inter-particle forces: Van der Waals attraction and electrostatic repulsion. According to Van der Waals, the non-ideality of gases can be attributed to the existence of molecular or atomic interactions [21]. Such dynamic interactions are established between the instantaneous dipoles formed in an atom's orbiting electrons. Thus, the resulting force is weak and becomes significant only at a short particle distance. Hamaker [21] found such interactions to exist between particles and modified Van der Waals' formulation through the so called "additivity concept" (single atoms or molecules make up the particle). When the cavities located on a solid inclusion are filled with

gas, negative Van der Waals forces come into play, causing particle agglomeration. Attraction is favorable because it reduces the value of the Gibbs free energy by  $\theta$ :

$$\theta = \frac{-Ar}{12H^2} \tag{3}$$

where A is the Hamaker constant, which depends on the polarization properties of the molecules on the particle surface, r is the reduced particle radius and H the inter-particle distance [18]. When the dimension of the particle is smaller than 1  $\mu m$ , Van der Waals forces dominate. Coulomb force of repulsion competes with Van der Waals attraction. It can be noted from Fig.5 that the electrostatic repulsion is overcome by the Van der Waals attraction force for a inter-particle distance down to 1 nm. For smaller values, the Born repulsion of adjacent electron clouds dominates.

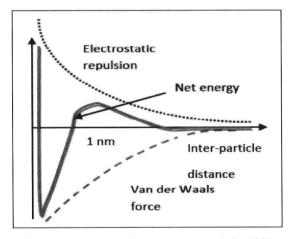


Fig. 5. Forces acting between two particles [20].

**Interface debonding.** Interface bonding between particles and the matrix is critical as it affects load transfer from the matrix to the particle and for delaying the onset of particle—matrix decohesion. Voids nucleation and growth have also been observed to be correlated with the loss of coherency at particle/matrix interface. All these aspects have a profound effect on the strength and stiffness of the composite. Interface debonding caused by large thermal mismatch between metal and ceramic has been noticed to be the main mechanism responsible for fracture of the material [22]. Matsunaga et al. [23] measured the effect on strength and fracture toughness of surface oxidation of SiC particles, according to the reaction:

$$2SiC + 3O_2 \rightarrow 2SiO_2 + 2CO(gas) \tag{4}$$

They detected enhanced strength only for thick oxide layers (1.4 µm), while fracture toughness consistently decreased after the oxidation process for all temperatures and exposure times. Therefore, crack initiation on particle surface is more likely to occur, affecting life duration of the component. It's difficult to determine whether cracking of the oxide layer is responsible for the frailure mechanism of the composite materials. Exposure of clusters of bare particles on the fractured surface (Fig.6) could be an indication of such phenomenon. EDS analysis confirms the presence of silicon dioxides on particles surface (Fig.7). Other studies [24,25,26] found that the wettability of the reinforcement by liquid aluminum is improved when an oxide coating is applied. However, the very thin film character of silicon dioxide makes it brittle, fragile and easy to breakdown during particle incorporation and vigorous stirring. In addition to this, when a high percentage

of coating material is used in the oxidation process the interfacial bonding between particle and matrix is degraded and a typical bondless morphology underlines the non-wetting characteristic between both surfaces. Therefore, wettability is enhanced only for specific coating thickness and for layers that are continuous, which is a feature connected to the nature of the heat treatment. Oxidation in air has shown not to improve the contact angle between particle and matrix [27], whereas it is improved in oxygen supported atmosphere. Large thermal mismatches between particle and matrix can also cause interface debonding and fracture upon cooling to room temperature [28].

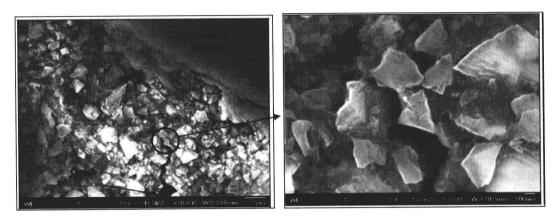


Fig.6. SiC nano-particles on an A356 aluminum alloy fractured surface.

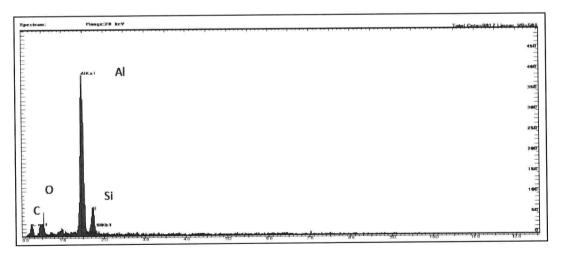


Fig.7. EDS spectrum of a SiC nano-particle on the fractured surface.

#### **Manufacturing Routes**

Classification of processing routes. Metal matrix composite manufacturing processing can be divided into two general categories: ex-situ and in-situ. Ex-situ is when the reinforcement is externally added to the matrix. In-situ synthesis involves the production of reinforcements within the matrix during the processing stage [33, 34]. The same classification applies for nanocomposite manufacturing as well. Ex-situ manufacturing techniques can be further classified into two main processing schemes [33,36]: solid-state and liquid-state. In some instances when the processing is in the semi-solid range (such as in droplet consolidation or similar techniques) then the classification could be further expanded to solid-state, liquid-state and semi-solid state. For the purposes of this review we will limit ourselves to the first two processing routes. Among solid-state techniques, powder metallurgy and mechanical attrition are the most popular ones. The nano-scale can be easily reached, although the cost of the powder is significantly high. Interfacial and surface wetting issues are considerably diminished. This is because both phases remain in the solid state, where diffusivity is much lower [29, 30]. The final products are generally affected by a high amount of porosity, which strongly decreases the fatigue resistance and requires further metalworking. When the process involves attrition at high temperatures chemical modification of the initial constituents is likely to occur [31, 32]. Liquid-state routes can be sorted into four major categories: infiltration, agitation, spraying and ultrasonic cavitation based solidification. Semi-solid casting of nanocomposite materials is still an open field; a novel method of melting, compacting and solidifying semi-solid billets has been tested in [35]. Liquid metal is generally less expensive and easier to handle than powders, and the shape flexibility constitutes a significant advantage. Liquidstate processes are generally fast and easy to scale-up. Despite this, they are affected by the lack of wettability of the reinforcement and by interfacial reactivity. Moreover, they are often limited to low melting point metals [29, 30]. In-situ metal matrix composites are not affected by the shortcomings typical of ex-situ composites, although control of process variables still remains an issue. In-situ fabrication methods can be divided into two major categories according to the physics of the process itself: "reactive" routes, where the reinforcement is synthesized within the metal matrix through a gas-liquid, liquid-liquid, or solid-liquid reaction, or "morphological" routes, where a favorable composite architecture evolves as a consequence of processing.

Other methods, which cannot be used for mass production of near net shape parts can be traced in the literature [31,36]. The most important are laser deposition, spray deposition, sol gel synthesis, nano-sintering and electroplating. They are costly, time and energy consuming processes. Therefore, their application is unlikely to be extended to the industrial scale. Such techniques are generally used for coating and thin films deposition. In this review, only mass production methods see table, which could be adapted to existing industrial infrastructure and can meet the need to large production volumes will be taken into account.

Process	System (matrix/reinforcement)	Reinforce ment size	Main features
Ex-situ: solid-state (Section 3.2.1)			
- Powder metallurgy	Al/ $Al_2O_3$ , $Al/ Si_3N_2$	15-100 nm	+ Near net shape; +Industrially scalable; - Non homogeneous particle size distribution; -Costly.
<ul> <li>Mechanical attrition and alloying</li> </ul>	$AI$ -Fe/ $AI_5$ Fe $_2$ , $AI$ / $AI_4$ C $_3$ , $AI$ /SiC	9-27 nm	
Ex-situ: liquid state (Section 3.2.2)			
- Stir casting	Al/SiC	40 nm	+Industrially compatible +Industrially scalable; +Inexpensive; -Particle clustering and debonding.
<ul> <li>Ultrasonic cavitation based solidification</li> </ul>	Al-Si/SiC, Al/ $\mathrm{Al}_2\mathrm{O}_3$	< 100 nm, 10 nm	+Good particle dispersion; +Inexpensive; -Industrially non-scalable.
- Infiltration	Al-Cu-Mg/ $\mathrm{Al}_2\mathrm{O}_3$	50 nm	+Good mechanical properties; -Expensive equipment (preform); - Un-easy to scale up.
In situ: reactive routes (Sections 3.3.1,3.3.2,3.3.3)			
- Combustion synthesis	Al/TiB <sub>2</sub>	30-100 nm	
- Exothermic dispersion	Al/TiB <sub>2</sub>	< 0.7 μm	+Good particle dispersion and particle/matrix bonding; +Inexpensive; +Industrially scalable; -Difficult process control.
- Substitutional chemical reaction	$\begin{aligned} &\text{Al/ } A l_3 Z r + A l_2 O_3 \\ &\text{Cu-Ti/ } T i B_2 \end{aligned}$	80 nm 50 nm	
- MixAlloy by Sutek	Cu/TiB <sub>2</sub>	50 nm	
- Gas-liquid process	Al alloys/AlN, SiC, TiC	100-500 nm	
In-situ: morphological (Section 3.3.4)			
- Rapid solidification	Al-Fe/ $Al_{100-x}Fe_x$ , Al/TiC	20-150 nm, 40-80 nm	

Table 4. Manufacturing Methods for Metal Matrix Nanocomposites (Mass Production).

#### **Ex-situ** methods

#### Solid state

**Powder metallurgy.** Prior work in synthesizing nanocomposites involves the use of powder metallurgy techniques, which are usually not cost-effective. Blending of matrix and reinforcement

powders followed by hot or cold pressing and sintering is a standard fabrication sequence; a schematic of a typical powder metallurgy (P/M) processing scheme is shown in Fig.8. In P/M processing, agglomeration can be minimized only if the size of the matrix powder is in the size range of the reinforcement phase. In addition, further working of the product via P/M may cause the reinforcement phase to break up and deform the surrounding matrix, leading to stress concentration and cracking [34]. The advantages of the process are flexibility and the ability to produce near-net shaped components. The size range of metal powders available on the market is quite wide which it is an advantage. P/M has been used [14] to add 50 nm alumina particles to aluminum powder. The process consists in wet mixing (aluminum powder mixed with varying volume fraction of Al<sub>2</sub>O<sub>3</sub> powder in a pure ethanol slurry), followed by drying at 150°C and cold isostatic pressing to compact the powder. The compacted powder is then vacuum sintered at 620°C (approximately 60°C) below the melting temperature of aluminum). Massive clustering has been observed, and its occurrence increases with decreasing particle size. Ma et al. [37] fabricated via P/M processing nanometric silicon-nitride reinforced aluminum composites. They reported the presence of several agglomerates in the aluminum matrix. Peng et al. [38] created a novel and simplified process for producing aluminum matrix nanocomposites reinforced with oxide particles. The novelty lays in the use of Al<sub>2</sub>O<sub>3</sub> surface layers existing on matrix aluminum particles as the ceramic reinforcement. A good distribution has been achieved, although the process does not allow satisfactory control of the process. Moreover, the effectiveness and the scalability of the method remain to be proven.

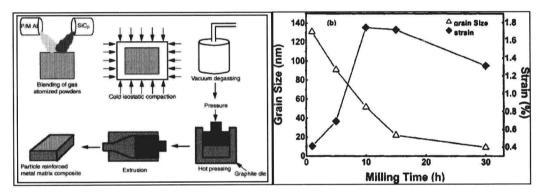


Fig.8. Processing routes for particulate reinforced composites [34].

Fig. 9. Grain size and strain vs. milling for WC particles [39].

Mechanical attrition and alloying. Mechanical alloying was invented in 1980 to manufacture particle strengthened metal alloys. In the last ten years, the method of high-energy milling gained much attention as a non-equilibrium process able to produce nano-scale microstructures. A variety of ball mills have been developed for different purposes including tumbler mills, attrition mills, shaker mills, vibratory mills, and planetary mills [32]. In the high-energy ball milling process, alloying occurs as a result of repeated breaking up and welding of matrix and reinforcement particles. Both powders are subjected to severe plastic deformation due to collision with the milling tool. Deformation occurs at high strain rates; thus, after extended milling (Fig.9), the average powder grain size can be reduced to few nanometers [32,39]. It should be noted that aluminum nanocomposites with the trade-name DISPAL, reinforced with Al<sub>4</sub>C<sub>3</sub> particles, are manufactured via mechanical alloying [14]. Flexibility and scalability are key advantages of the process; contamination by the milling tool and the atmosphere are the main disadvantages of the process. Milling of refractory metals (tungsten) in a high-frequency shaker for extended times can result in iron contamination of more than 10 at% [38]. To prevent contamination, the process should be carried out in an inert atmosphere and the mills ought to be coated. Another major issue is the