

Engineering Materials

Lorella Ceschini · Arne Dahle
Manoj Gupta · Anders Eric Wollmar Jarfors
S. Jayalakshmi · Alessandro Morri
Fabio Rotundo · Stefania Toschi
R. Arvind Singh

Aluminum and Magnesium Metal Matrix Nanocomposites

 Springer

Engineering Materials

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Lorella Ceschini · Arne Dahle
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Fabio Rotundo · Stefania Toschi
R. Arvind Singh

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Lorella Ceschini
Department of Industrial Engineering (DIN)
Alma Mater Studiorum–University of Bologna
Bologna
Italy

Arne Dahle
School of Engineering
Jönköping University
Jönköping
Sweden

Manoj Gupta
Department of Mechanical Engineering
National University of Singapore
Singapore
Singapore

Anders Eric Wollmar Jarfors
School of Engineering
Jönköping University
Jönköping
Sweden

S. Jayalakshmi
Department of Mechanical Engineering
Bannari Amman Institute of Technology (BIT)
Sathyamangalam, Tamil Nadu
India

Alessandro Morri
Interdepartmental Center for Industrial
Research-Advanced Mechanics and Materials
(CIRI-MAM)
Alma Mater Studiorum–University of Bologna
Bologna
Italy

Fabio Rotundo
Interdepartmental Center for Industrial
Research-Advanced Mechanics and Materials
(CIRI-MAM)
Alma Mater Studiorum–University of Bologna
Bologna
Italy

Stefania Toschi
Department of Industrial Engineering (DIN)
Alma Mater Studiorum–University of Bologna
Bologna
Italy

R. Arvind Singh
Department of Aeronautical Engineering
Bannari Amman Institute of Technology (BIT)
Sathyamangalam, Tamil Nadu
India

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Preface

Lightweight materials are getting critically important for weight-saving engineering and biomedical sectors. The use of these materials is getting increasingly important for sustainable planet earth and human comfort. Aluminum and magnesium are two lightweight materials that are of paramount importance for engineers and material selectors. Efforts have been made in past few decades to evolve these two principal elements so that they can cater to a wider spectrum of applications. Composite technology utilizing micron length scale reinforcement was used actively in the past century to realize properties beyond the common alloying technique to enhance certain properties such as elastic modulus, strength, wear and damping response. With the advent of nanotechnology in the late 1990s, researchers worldwide started to use reinforcements at nano-length scale (<100 nm). The resultant nanocomposites exhibited superior combination of properties when compared to micro-composites with significantly reduced weight penalty. In view of significantly different response of elemental matrix in the presence of reinforcement at nano-length scale, it was realized by authors to put together current level of understanding of aluminum and magnesium based nanocomposites. It is hoped that this book will serve as a useful reference for students, teachers, engineers, and researchers to gain understanding of these fascinating materials.

Bologna, Italy

Jönköping, Sweden

Singapore, Singapore

Jönköping, Sweden

Tamil Nadu, India

Bologna, Italy

Bologna, Italy

Bologna, Italy

Tamil Nadu, India

Lorella Ceschini

Arne Dahle

Manoj Gupta

Anders Eric Wollmar Jarfors

S. Jayalakshmi

Alessandro Morri

Fabio Rotundo

Stefania Toschi

R. Arvind Singh

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Abbreviations

ADZ	Alumina Depleted Zones
ARB	Accumulative Roll Bonding
BM	Ball Milling
BPR	Ball-to-Powder Ratio
CARB	Cross Accumulative Roll Bonding
CMA	Complex Metallic Alloys
CNF	Carbon Nanofiber
CNT	Carbon Nanotube
CP	Cold Pressing
CRP	Continuous Rheo-conversion Process
CRSS	Critical Resolved Shear Stress
CTE	Coefficient of Thermal Expansion
CYS	Compressive Yield Strength
DMD	Disintegrated Melt Deposition
DRA	Discontinuously Reinforced Aluminium composite
EBSD	Electron Backscatter Diffraction
ECAP	Equal Channel Angular Pressing
EDS	Energy Dispersive X-ray Spectroscopy
EM	Elastic Modulus
EPMA	Electron Probe Microscopic Analysis
FESEM	Field Emission Scanning Electron Microscopy
FSP	Friction Stir Processing
GISS	Gas Induced Semi-Solid process
GNP	Graphene Nanoplatelet
HB	Brinell Hardness
HCF	High Cycle Fatigue
HE	Hot Extrusion
HIP	Hot Isostatic Pressing
H-NCM	Hong-Nano Casting Method
HPDC	High Pressure Die Casting

HRTEM	High Resolution Transmission Electron Microscopy
HV	Vickers Hardness
MA	Mechanical Alloying
MMCs	Metal Matrix Composites
MML	Mechanically Mixed Layer
MMNCs	Magnesium Matrix Nanocomposites
MPF	Master Powder Feeding
MW(C)NT	Multi-Walled Carbon Nanotube
NC-US	Non Contact Ultrasonic treatment
ND	Normal Direction
NDZ	Nano-alumina Dispersed Zones
NPs	NanoParticulates or Nanoparticles
NRC	New Rheo Casting process
PCA	Process Control Agent
PM	Powder Metallurgy
RDC	Rheo Die Casting process
RM	Reaction Milling
RSF	Rapid Slurry Forming
SADP	Selected Area Diffraction Pattern
SAED	Selected Area Electron Diffraction
SDAS	Secondary Dendrite Arm Spacing
SEM	Scanning Electron Microscopy
SL	Semisolid–Liquid
SLC	Sub-Liquidus Casting
SLM	Selective Laser Melting
SPS	Spark Plasma Sintering
SS	Semisolid–Semisolid
SSM	Semi-Solid Metal
SSR	Semi-Solid Rheo casting
TEM	Transmission Electron Microscopy
TSRM	Twin Screw Rheo Moulding
TYS	Tensile Yield Strength
UCS	Ultimate Compressive Strength
UFG	Ultra-Fine Grained
US	Ultrasonic treatment
UTS	Ultimate Tensile Strength
vol.%	Volume fraction
wt.%	Weight fraction
XRD	X-Ray Diffraction
YS	Yield Strength

Chapter 1

Metal Matrix Nanocomposites: An Overview

Abstract In this chapter, an overview on both Al and Mg based nanocomposites is given, emphasizing particularly on the importance of using reinforcements at nano length scale. The strengthening mechanisms at the basis of the reinforcing action exerted by nanoparticles (Orowan mechanism, enhanced dislocation density, grain refinement and load bearing effect) is described and their contribution discussed; modelling of the above mentioned mechanisms is also presented.

1.1 Metal Matrix Nanocomposites

The pressing need in reducing fuel consumption and emissions in ground and aerospace transportation has led in recent years to an increasing trend in employing light alloys for the production of structural components. Furthermore, high-performance and low-weight structural materials are increasingly required in a wide range of industrial applications, including thermal management and automatic precision devices. Some of these materials, such as aluminium and magnesium alloys, combine good mechanical properties, excellent castability and high thermal conductivity, being therefore very attractive for the production of complex shaped components. These alloys, however, present a noticeable decrease of mechanical properties at relatively low temperatures, less than about 200 °C [1, 2], which strongly limits their application for critical components, e.g. in the automotive and aerospace sectors. One of the most promising ways to enhance mechanical properties of light alloys, both at room and at high temperature, is the addition of a hard reinforcing phase, typically ceramic or carbon based, obtaining the so-called metal matrix composites (MMCs) [3–5], developed to combine the good ductility and toughness of the metal matrix and the high strength and stiffness of the reinforcement [3]. Among possible reinforcement shapes, i.e. fibers, whiskers or particles, the latter gained major interest as they enable obtaining a strong enhancement of mechanical properties while maintaining an isotropic behaviour, with relatively simple production routes [6–8] and possibility to apply secondary processes (machining [9], welding [10, 11], forming [3, 12]). Although traditional MMCs

may offer many advantages with respect to the unreinforced alloys, they present noticeable limitations, due to the micron length scale of the reinforcement, such as low ductility and toughness as compared to the unreinforced matrix [13], excessive wear damage of the counter-material in tribological application [14] and extremely high tool wear during machining [6, 15].

Aiming to solve these major issues and to obtain materials with enhanced tensile strength, hardness, and dimensional stability, coupled with good ductility and fracture toughness both at room and high temperatures, the length scale of reinforcing phase has been decreased to the nanometric levels (<100 nm) to produce metal matrix nano composites (MMNCs). One necessary condition to obtain sound nanocomposites with enhanced mechanical properties is to obtain a good dispersion of the reinforcement phase within the matrix, through a proper production route. MMNCs manufacturing processes are classified in *ex situ* routes, when the reinforcing phase is formerly produced then added to the matrix, or *in situ* routes, if the reinforcement is generated during the composite production, typically through controlled reactions [4, 5, 16, 17]. *Ex situ* processing techniques can be further classified between solid and liquid state routes. Liquid state processes are particularly attractive due to their relative simplicity and to the possibility to obtain near net shape components on an industrial scale, although they pose bigger challenges in terms of nanoparticles dispersion with respect to powder metallurgy based processes. In particular, due to the tendency to agglomerate and low wettability within the molten matrix, nano-sized particles present the tendency to generate clusters, with a detrimental effect on mechanical properties [4, 18–22].

This chapter aims at reviewing the most recent advances in *ex situ* production routes and properties of Al and Mg based MMNCs, focusing on liquid and semi-solid processes. A comprehensive list of references, mostly published in the last 10 years, is critically analysed. Mechanical properties of composites with different matrices and reinforcing phases are compared, in relation to the production method employed.

1.2 Strengthening Mechanisms

Yield strength (YS) of metallic materials is the stress required to move dislocations and to activate dislocation sources. It is therefore influenced by the additive and/or synergistic action of the obstacles that restrict their motion. Several approaches have been proposed for the modelling of constitutive relationships to predict the bulk mechanical properties of MMNCs as a function of the reinforcement, matrix, and processing routes. They take into account some or all of the following strengthening mechanisms.

Orowan strengthening. Orowan strengthening is due to the obstacle posed by closely spaced hard particles to the movement of dislocations. In conventional micro sized particulate-reinforced MMCs, Orowan strengthening is known to have limited significance since the reinforcement particles are coarse and the

interparticles spacing is large [23]. In particular, it has been demonstrated that in cast MMCs with particles of 5 μm or larger, Orowan strengthening has a secondary effect on material strengthening [24]. On the other hand, the Orowan mechanism is more favourable when highly dispersed fine particles are present [25, 26]. In particular, the presence of a dispersion of fine insoluble particles in a metal can considerably raise the creep resistance, even for only a small volume percent ($<1\%$) [23]. This is due to the Orowan bowing mechanism, wherein owing to the presence of the dispersed nano-sized particles in the matrix, dislocation loops form as dislocation lines bypass the particles.

Enhanced dislocation density. Since matrix and reinforcement are generally characterized by different CTE, thermal stresses arise around particles, e.g. during cooling from processing temperature. The stress level is often large enough to cause plastic deformation, especially at the matrix/reinforcement interface region [27], thus inducing an increase in the dislocation density [28], as also experimentally observed in refs. [29, 30].

Other possible sources of residual plastic strain and consequently of dislocation density increase are the matrix/reinforcement elastic modulus (EM) mismatch and work hardening during deformation processes (e.g. extrusion or forging) [31].

Load bearing effect. The shear transfer of load from the soft matrix to the hard ceramic particles is called the load bearing effect. This reinforcing mechanism is effective only if a strong cohesion between matrix and reinforcement can be achieved [32].

Grain refinement. When introduced in a molten matrix, nanoparticles can act as heterogeneous nucleation sites during solidification, thus giving rise to more refined and possibly equiaxed microstructure, as shown in Fig. 1.1 [33]. Moreover, in

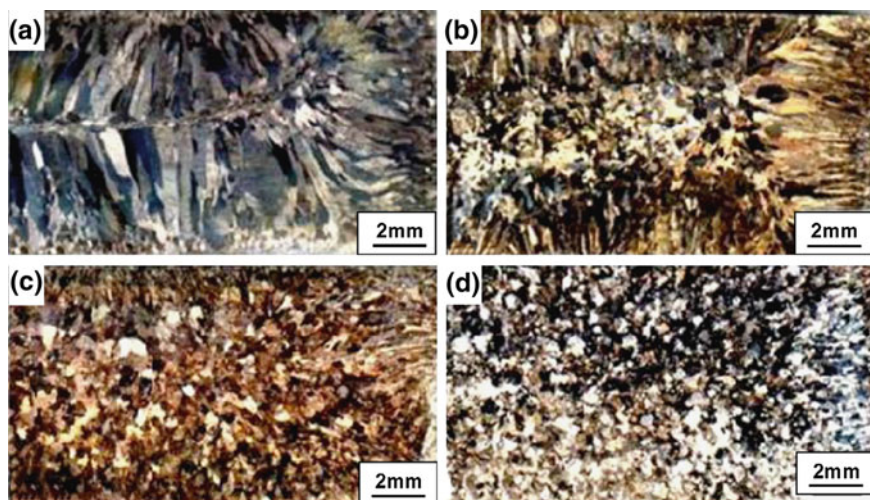


Fig. 1.1 Grain refinement effect in as cast Mg based nanocomposites: (a) Mg, (b) Mg–0.5 wt% Al_2O_3 , (c) Mg–1 wt% Al_2O_3 and (d) Mg–2 wt% Al_2O_3 [33]

wrought alloys, during high temperature plastic deformation the nano-particles hinder grain growth. Habibnejad-Korayem et al. [33] inferred that nanoparticles restrict the migration of thermally excited grain boundaries during the recrystallization process. Davies et al. [34] proposed that the nanoparticles pinning effect is the dominant contribution in the refinement of the matrix microstructure during dynamic recrystallization. However, it should be noted that when a dendritic structure is present in cast alloys, the strengthening effect is mainly dependent by SDAS (secondary dendrite arm spacing) rather than by grain size [35].

1.2.1 Modelling

Several approaches have been developed starting from the 1980s to model the yield strength of MMCs and more recently of MMNCs. Three main models have been hitherto proposed: arithmetic summation, quadratic summation, and compounding methods [36]. Summation methods are based on dislocation theory applied to single crystals, where quadratic and arithmetic summation are adopted to account for obstacles to dislocation motion respectively on the same structural scale and at significantly different scales [37]. On the other hand, the compounding method, based on the modified shear lag mechanism originally proposed by Nardone and Prewo for MMCs [38], treats all strengthening mechanisms as load-transferring mechanisms from the matrix to the reinforcement and it is represented mathematically by a series of improvement factors (f_i).

In order to take into account that multiple strengthening effects are simultaneously present, the rules of addition of strengthening contributions (arithmetic summation) was first developed [39]. However, the summing methods, in some cases, may over-predict the yield strengths of the composites [40]. An analytical compounding model to compute the YS of MMC, taking into account both additive and synergistic effects, was developed by Ramakrishnan [41] by integrating a modified shear lag model (accounting for the load bearing effect with a continuum mechanics approach) and an enhanced dislocation density model. The model can be expressed as follows:

$$\sigma_{yc} = \sigma_{ym}(1 + f_l)(1 + f_d) \quad (1.1)$$

where σ_{yc} is the YS of the MMCs, σ_{ym} is the yield strength of the unreinforced matrix, f_l is the improvement factor associated with the load-bearing effect of the reinforcement, f_d is the improvement factor related to the dislocation density in the matrix, caused by the thermal mismatch between the matrix and the reinforcement particles. Zhang et al. [23] integrated the Ramakrishnan model [41] as to take into account the Orowan strengthening, considered to be particularly important in the case of MMNCs, as follows:

$$\sigma_{yc} = \sigma_{ym}(1+f_l)(1+f_d)(1+f_{Orowan}) \quad (1.2)$$

where f_{Orowan} is the improvement factor related to Orowan strengthening. The predicted yield strength was found to be in good agreement with the experimental data, reported in the literature, although the grain refinement is not directly considered.

Several authors inferred that the contributions to the increase in the YS of the composites could be computed as the root of the sum of squares of the different mechanisms contribution [40, 42], as originally proposed by Clyne for MMCs [3], while a combination of the quadrature and additive methods was proposed in [33]. The improvement in yield strength with the quadrature method can be expressed as follows [36]:

$$\Delta\sigma = \sqrt{(\Delta\sigma_{load})^2 + (\Delta\sigma_{CTE})^2 + (\Delta\sigma_{EM})^2 + (\Delta\sigma_{Orowan})^2 + (\Delta\sigma_{Hall-Petch})^2} \quad (1.3)$$

Some of the strengthening factors can be omitted depending on the processing routes and assumptions. In the equation, the incremental contribution to YS by the load bearing effect can be expressed as [41]:

$$\Delta\sigma_{load} = 0.5 V_p \sigma_{ym} \quad (1.4)$$

where V_p represents the particle volume fraction and σ_{ym} the matrix yield strength. The incremental contribution of grain refinement to the strength levels can be estimated on the basis of the classical Hall-Petch equation [43, 44]:

$$\Delta\sigma_{Hall-Petch} = K d_m^{-1/2} \quad (1.5)$$

where K is the Hall-Petch coefficient and d_m is the matrix grain diameter. The effect of mismatch strain due to the difference between the CTE values of particles and that of the matrix is given by the Taylor equation as [40]:

$$\Delta\sigma_{CTE} = \sqrt{3}\beta G_m b \sqrt{\rho_{CTE}} \quad (1.6)$$

which, expressing the increase in geometrically necessary dislocations as detailed in [45], becomes:

$$\Delta\sigma_{CTE} = \sqrt{3}\beta G_m b \sqrt{\frac{12 V_p \Delta\alpha \Delta T}{b d_p}} \quad (1.7)$$

where the strengthening coefficient β is considered to be 1.25, $\Delta\alpha$ is the difference between CTE of matrix and particles, and ΔT is the difference between the processing and the tensile test temperatures, V_p and d_p are the volume fraction and diameter of the reinforcement particles.

The strength improvement by the modulus mismatch is approximated by [36]:

$$\Delta\sigma_{EM} = \sqrt{3}\alpha G_m b \sqrt{\rho_{EM}} \quad (1.8)$$

where α is the material-specific coefficient and

$$\rho_{EM} = \frac{6 V_p}{b d_p} \varepsilon \quad (1.9)$$

where ε is the bulk strain of the composite.

Starting from the Orowan equation, the increase in the material yield stress due to the Orowan mechanism can be expressed as [33]:

$$\Delta\sigma_{Orowan} = \frac{0.13 G_m b}{\lambda} \ln \frac{d_p}{2b} \quad (1.10)$$

where G_m is the shear modulus of the matrix, b is the Burgers vector, d_p is the average diameter of nanoparticles and λ is the inter-particle spacing, expressed as:

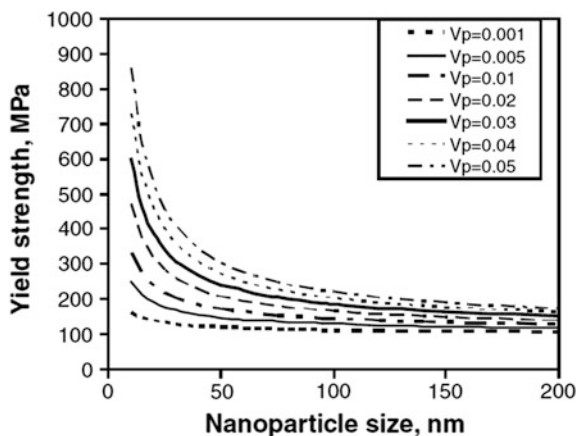
$$\lambda = d_p \left[\left(\frac{1}{2 V_p} \right)^{1/3} - 1 \right] \quad (1.11)$$

It is however clear that in case particles are aggregated in clusters, the Orowan dispersion strengthening is significantly reduced with respect to the computed values. Therefore in addition to the size, volume fraction (V_p) of nanoparticles, CTE difference and processing condition, the yield strength of MMNCs is also governed by particle distribution. It is worth noticing that no agglomeration factor has been hitherto taken into account in these models.

Although several studies have stated that the quadratic method exhibit the best match with experimental data [31, 40, 45], it should be noted that there is no general agreement as concerning which physical model best represents the real MMNC behaviour [36].

As regarding the contribution of each single mechanism to the improvement in the yield strength on MMNCs, the load bearing contribution was found to be low [40] or even negligible [33], also due to the fact that relatively low V_p (<5 %) are usually employed. The grain refinement effect was reported to be limited in some studies [40], and it is even neglected by others [23, 46], although Habibnejad-Korayem et al. [33] found a contribution of more than 15 % to the total YS increase in Mg/Al₂O₃ system. Conversely, the CTE mismatch between the matrix and the particles was deemed to be the most effective strengthening contribution, followed by Orowan strengthening [40]. In fact, Zhang et al. [46] inferred that the relative contribution of the Orowan strengthening effect increases as the size of nanoparticles decreases, up to critical particle size (5.44 times the Burger vector for Mg/Al₂O₃ and Ti/Y₂O₃ nanocomposites), below which the breakdown of Orowan strengthening effect occurs; in [23], it was more generally shown that

Fig. 1.2 Yield strength as a function of nanoparticle size for different volume fractions in nano- Al_2O_3 particulate-reinforced magnesium nanocomposites, predicted by model for 20 °C testing [23]



100 nm is a critical particle size, below which the Orowan mechanism is particularly effective and the yield strength increases remarkably with decreasing particle size [23], as also shown in Fig. 1.2.

The effect of grain refinement was recently reevaluated by Kim et al. [36] in a review on the prediction models and reinforcing mechanisms concerning the yield strength of particle reinforced MMNCs. It should be noted that the review was focused on Mg-MMNCs due to higher availability of data. Grain refinement was shown to be the predominant factor determining the overall yield strength of most Mg-MMNCs developed to date. Furthermore, it was inferred that yield strength is generally overestimated by all of the arithmetic, quadratic, and compounding methods when considering grain refinement, Orowan, CTE, and modulus mismatch strengthening mechanisms. In fact, the full activation of CTE mismatch strengthening mechanism in MMNCs is unclear as the absence of CTE effects on the strength improvement was reported e.g. for nanostructured [47] and traditional MMCs [48]; similar considerations were reported for modulus mismatch strengthening [36]. On the other hand, the three conventional summation methods using only grain refinement and Orowan mechanisms generally predict YS values lower than the experimental ones [36]. Therefore, by considering that CTE and modulus mismatch mechanisms are unlikely to be fully activated and the yield strength prediction based only on grain refinement and Orowan mechanism generally showed underestimation, it was concluded that the increase of dislocation density caused by work-hardening during post-processing of MMNCs applied by many studies is in part responsible for improvement to the yield strength of these materials [36].

It was computed that the theoretical strength of pure Mg-MMNCs could reach 380 MPa with a submicron matrix grain size and 7.5 vol.% particle addition, in case the Orowan strengthening fully activates, i.e. particles are perfectly distributed [36]. Such theoretical strength pose a challenge for MMNC production routes and technologies to be able to obtain a uniform particle distributions while preventing excessive generation of dislocations in effectively reducing matrix grain size.

1.3 Al-Based Nanocomposites

Aluminium alloys are widely used in the transportation industry due to their high strength-to-weight ratio, good castability and formability, high electric and thermal conductivity and good corrosion resistance. Further improvement in the mechanical properties can be achieved by precipitation heat treatment, where a coherent precipitation of very small intermetallic compounds efficiently hinders dislocation movement and therefore increases strength (peak-aged condition). Unfortunately, the coherency between the precipitate and matrix lattice disappears with excessive aging temperature (overaged condition), due to the growth of the reinforcing phases that lose the hardening effect. As a consequence, at temperatures in the range from 200 to 300 °C, the tensile strength of age-hardened Al alloys reduces very quickly. As an example, Al–Si–Mg–(Cu) alloys are largely used in the transport field to produce engine heads or pistons and they are generally put into operation in the peak-aged condition. However, local temperatures up to 290 °C can be reached under most severe operating conditions, leading to a relevant softening of the Al alloys.

The need for high specific strength, to be maintained even at high temperature, has led to the development of MMCs, where the synergistic combination of a tough metallic matrix with a hard reinforcement phase (often ceramic in nature) permits to significantly enhance stiffness, strength and wear resistance, even at high temperature. Al-based composites reinforced by carbides, borates, nitrides and oxides have been successfully fabricated by either powder metallurgy (PM) techniques or casting methods [49–51]. The development of MMCs was particularly in vogue in the 1980s and early 1990s among all major aluminium producers. MMCs have found applications in a wide spectrum of markets, such as automotive, electronic packaging, industrial products and recreational goods, with products including, in a non-conclusive list [52]: pick-up truck drive shafts, brake rotors and drums, diesel engine pistons, aeronautic engine fan exit guide vanes, aircraft ventral fins and fuel access covers, bicycle components, golf clubs and electronic packaging applications. In the automotive sector, the attention has been mainly devoted to discontinuously reinforced aluminium composites (DRA), which have been commercially used in this market for nearly 20 years. Properties of interest include increased specific stiffness, wear resistance, and improved high-cycle fatigue resistance and superplastic behaviour [11, 51, 53–57]. Although weight saving is very important in automotive applications, low-cost premiums are tolerated in this sector, thus requiring cost effective processes. On the other hand, while the raw material cost of MMCs is higher than that of the material typically replaced, the DRA component would weigh considerably less than steel, significantly improving the cost comparison [58].

Although Al-based metal matrix composites offer many advantages over monolithic alloys, they present significant limitations, such as low fracture toughness and ductility, poor machinability and weldability. Moreover, tribological problems must be taken into account when considering their use in engine design.

For example, their use in pistons can induce relevant wear damage of the cylinder lines [14]. Commercial particle reinforced Al based composites are generally reinforced by 10–20 vol.% of ceramic particles, with a size ranging from a few micrometers to several tens of micrometers. It is known that fracture of composites is controlled by fracture of the larger particles, as well as formation of cavities and voids at the particle/matrix interface, which in turn depends on the particle size [59]. Large particles (above 1.5 μm) act as micro-concentrators of stress and may give rise to cleavage, while medium size particles (0.2–1.5 μm) lead to the formation of cavities or pits through the loss of interphase cohesion [13]. A key role in fracture is also played by the presence of particle clusters that locally reduce MMC fracture toughness in a significant fashion. This has a strong effect on the fatigue behaviour of MMCs and also on their tribological performance, because, even though it is widely accepted that they perform better than the corresponding unreinforced Al alloys, they also lead to relevant wear damage of the counter-material, due to the abrasive action of the ceramic reinforcement [13]. As a consequence, the machining of particulate reinforced metal matrix composites is characterized by extremely high tool wear due to the abrasive action of the ceramic particles. Only a small group of extremely hard and expensive materials, such as polycrystalline diamond, are then suited to this task, since the cutting tool must be able to withstand intermittent cutting of hard (reinforcement) and soft (matrix) materials [60, 61]. The need of frequent tooling together with the high cost of tools considerably increases the cost of the machining process when compared with that of the monolithic alloys. On the other side, non-traditional processes like electrical discharge machining, abrasive waterjet cutting, and laser cutting are very costly and characterized by slow machining rates [62, 63]. Machining of MMCs still remains an issue to be addressed, so as to produce the required close dimensional tolerances and surface finish with cost effective processes.

The traditional fusion welding techniques (TIG, MIG, laser) of Al-based MMCs generally lead to microstructural defects, related to the presence of the ceramic reinforcement, which result in a decrease in their mechanical properties. In particular, the addition of high volume fractions of ceramic reinforcement causes higher viscosity in MMCs melts, particle segregation, evolution of the occluded gas and undesired matrix-reinforcement reactions [10], so that friction welding processes are often required to obtain sound joints [64–66]. These occurrences clearly outline the compelling need for an aluminium-based material whose strength is stable at higher temperatures, whose ductility and toughness is maintained and whose manufacturing and machining processes can be adapted to existing industrial infrastructures, thus overcoming the limitations of both monolithic aluminium alloys and conventional MMCs reinforced with relatively high volume fraction of micrometric particles.

Al-based nanocomposite have recently emerged as a class of materials suitable for this goal. The most popular and versatile reinforcements are ceramic nanoparticles, such as Al_2O_3 , SiC, TiC, AlN added to the Al alloys in relatively low volume fractions (usually lower than 5 wt%). Thanks to the presence of nano-sized particles homogeneously dispersed within the matrix, aluminium based nanocomposites can

present some relevant characteristics, as also widely discussed in Sect. 4.1, such as: superior specific stiffness comparing to the unreinforced matrix [67, 68]; significant improvement in strength (UTS, YS) with respect to the unreinforced Al matrix and enhancement of ductility comparing to the traditional MMCs [17]; noticeable improvement of creep resistance and thermal stability with respect to Al alloys [69, 70]; better wear resistance with respect to both Al alloys and MMCs [71]. Benefits of using nanoparticles, rather than micro-sized particles have been clearly highlighted by several studies. Sajjadi et al. [21] compared two A356 based composites reinforced through 20 μm and 50 nm Al_2O_3 particles. Compression tests on the produced samples revealed that the nanometric reinforcing phase caused a sensibly higher increase of strength, even with a lower reinforcement content (610 MPa with 3 wt% of nano-alumina, 453 MPa for 10 wt% of micro-alumina). Ma et al. [72] found that a 1 vol.% nano- $\text{Si}_3\text{N}_4/\text{Al}$ shows a UTS (180 MPa) similar to the one of a 15 vol.% micro-SiC-Al composite (176 MPa). A further study by Kang and Chan [13] compared nanocomposites with 1–7 vol.% of nano alumina, to a 10 vol.% micro-SiC reinforced composite, showing that YS and UTS of the 1 vol.% nanocomposite were comparable to the ones of the 10 vol.% micro-composite.

Despite their tremendous potential, aluminium based nanocomposites are still to be developed on a large industrial scale. Among possible production routes, liquid or semisolid based production routes are deemed to possess higher industrial scalability, although obtaining a homogenous particle distribution is still challenging. The state of the art on novel Al-nanocomposites, properties and manufacturing processes will be discussed in Chap. 2, with a particular focus on liquid-based production routes.

1.4 Mg-Based Nanocomposites

In the search for new light-weight materials for energy efficiency and emission reduction, magnesium (Mg), the lightest of the structural metals, is one of the most promising candidate, which is rapidly finding its niche in becoming the major high-volume structural metal. Considering the weight factor, pure Mg is $\sim 33\%$ lighter than aluminium (Al) and $\sim 75\%$ lighter than steel. Mg is also 100 % recyclable, energy efficient and sustainable (naturally abundant). It also exhibits good dimensional stability, machinability and damping capacity. In recent times, Mg-based materials are replacing conventional metals such as cast iron and steel in various applications, especially in automobile and aerospace applications. For example, replacing the cast iron engine block (~ 84.6 kg) in a V6 3.0 litre six-cylinder car by Mg (~ 30 kg) would result in a weight savings of $\sim 65\%$ [73]. Reports indicate that the overall weight savings in using Mg-materials as a replacement for Al-parts would lead to a fuel saving of the order of $\sim 20\text{--}30\%$, without any requirement of changes in design. The use of Mg-based materials by automotive industry is an excellent example of materials selection, whereby material properties, processability, cost, availability, environmental issues,

recyclability, fuel efficiency etc. are all taken into account. Mg-based materials prove to be robust for weight-critical structural applications.

Generally, Mg-alloy systems contain Al, Mn, Zn, Zr and rare-earth elements as alloying constituents and are designated by the alloy standards as AZ31 (Mg-3Al-1Zn), AM50 (Mg-5Al-0.1Mn), ZK60 (Mg-5.5Zn-0.7Zr) etc. [74]. However, certain drawbacks observed in these commercially available alloys include their low strength and poor ductility, which have limited their expansion as the major structural material for broader applications [75]. In order to overcome these limitations and also to enhance their performance, approaches such as: (i) incorporation of micron-scale ceramic reinforcements to form their metal matrix composites (Mg-MMCs) [76] and (ii) addition of metallic elements such as Ti, Mo, Nb etc., have been tried [77–79]. Considering the first approach, the low strength of Mg and its alloys are overcome by the addition of high strength/modulus micron-scale ceramic reinforcements (such as Al_2O_3 and SiC particles/fibers/whiskers). The introduction of such reinforcements into the Mg-matrix significantly improved the mechanical properties such as hardness, tensile strength, elastic modulus and yield strength, and also gave rise to excellent wear resistance, similarly to Al-metal matrix composites mentioned in the previous section. Although the Mg-MMCs show promising properties, the improvement in strength properties occurs at the expense of ductility, which has undermined their applicative potential for various real-time applications [76]. With the second approach, metallic elements such as Ti, Mo and Nb are added, in spite of the conventional alloying elements such as Al, Mn, Zn, Zr and rare-earth elements, which usually form brittle Mg-based intermetallic compounds such as $\text{Mg}_{17}\text{Al}_{12}$, MgZn_2 etc. thus reducing the ductility. Elements such as Ti, Mo and Nb are either insoluble or have negligible solubility in Mg, and do not give rise to any secondary/precipitate phase formation with Mg [80]. Reports show that these metallic elements can provide nominal improvement in ductility, while on the other hand they reduce the strength [77–79]. Given the above-mentioned facts, design and development of new Mg-materials becomes necessary.

In this context, it should be noted that similarly to Al-materials, Mg-materials are sought both in their cast and wrought forms (extrusions, rolling etc.). However, unlike Al-based materials, Mg-based materials (including Mg-alloys without any ceramic reinforcement) possess poor ductility. This is due to their inherent crystal structure, i.e. their low symmetry and the limited number of slip systems that exist in the hexagonal close packed (hcp) structure of Mg, when compared to the face centred cubic structure (fcc) of Al [81]. In Mg-systems, activation of dislocations slips and twinning modes is difficult at room temperature. The activation of these deformation modes are related to its critical resolved shear stress (CRSS) levels determined by Schmid factor, which in turn depends on the crystalline orientation (crystal texture) [82, 83]. The crystal texture may undergo evolution during casting, deformation, welding, and heat treatments. In Mg-castings, all possible orientations of the Mg-crystallites occur with equal frequency, whereby their orientation dependence disappears (random crystal orientation), and the material behaves isotropically [84]. In the case of wrought Mg-materials, strong orientation of

crystallographic planes is observed (i.e. texture evolution) that gives rise to anisotropic behaviour [85]. As an example, thermo-mechanical processing of Mg such as extrusion results in a strong texture development. Here, the basal planes are aligned strongly into the extrusion direction, which are highly unfavourable for the basal slip to occur. Due to this reason, the tensile ductility of extruded Mg-materials is limited if testing is carried out parallel to the extrusion direction [85, 86]. This calls for the use of higher temperatures during deformation processes that are cost-ineffective. The strong basal orientation also gives rise to tension-compression asymmetry [85, 86]. A favourable texture development can promote room temperature deformation characteristics.

Considering these facts, it should be understood that in addition to the major strengthening mechanisms detailed in Sect. 1.2, the deformation behaviour of Mg-materials is also significantly determined by its crystallographic orientation (texture). It is important to note that, given that the poor ductility is a major concern that hinders the complete utilization of both Mg-alloys and Mg-MMCs, the ductility of the currently existing Mg-materials remains to be improved by novel methods. This need has to be addressed without affecting the strength properties. With the advent of nanoscale materials, the use of nanoparticle reinforcements in Mg-matrices (Mg-nanocomposites, Mg-MMNCs) has proved promising in this regard [87]. Such advanced materials can be produced using traditional or unique processing techniques [88–91]. These new materials exhibit exceptional properties that are unobserved in conventional alloys/composites [92]. For example, the ductility of pure Mg was improved by ~ 70 – 100 % when incorporated with nanoparticles/CNT [93]. These new materials have greater ductility with retained/improved strength at room temperature, owing to the texture modification due to nanoparticle addition. Such change in crystallographic orientation due to nanoparticle addition results in the activation of non-basal slip systems/twinning, thereby contributing to the ductility improvement and/or strengthening effect [93]. To characterize the texture, pole figures using X-ray diffraction techniques are utilized. Alternatively, for micro-texture analyses electron back-scattered diffraction (EBSD) in association with scanning electron microscopy (SEM) and rapid analysis of electron diffraction patterns of grains by transmission electron microscopy (TEM) are employed. Given that nano-sized reinforcements can make distinct positive contribution towards enhancing the overall properties of Mg-materials, it is also important to note that such enhancement in properties can be attained at lower volume percents (<3 %), whereas for micron-scale particle reinforced MMCs higher volume fractions ($>>10$ %) are required.

Mg-MMNCs can be produced by both liquid and solid-state processing routes. While there is a wide misconception that incorporating nanoparticles via the liquid metallurgy route is difficult due to poor wetting and nanoparticle agglomeration [94], these may be true only when conventional liquid-state composite processes such as stir casting followed by gravity die-casting or squeeze casting are employed. Some of the novel processing methods such as the ultrasonic dispersion method and the disintegrated melt deposition method (DMD), have been quite successful in producing nanocomposites with good dispersion, matrix/particle

interfacial bonding and free of processing defects [91, 92]. Mg-MMNCs are seen to have enormous potential in diverse industrial and commercial sectors such as automotive, aviation, defense, biomedical, sporting equipments, consumer electronics, etc. To cater for such demands, the priority lies at first in improving the manufacturing technologies and followed with design/development of new Mg-nanocomposites. In the forthcoming sections, the state-of-the-art research trends that highlight the advancement in Mg-nanocomposite materials - their processing and novel Mg-nanocomposites development are presented. Research towards understanding the material characteristics under various loading/operating conditions using advanced characterization tools has also been presented.

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Chapter 2

Ex Situ Production Routes for Metal Matrix Nanocomposites

Abstract Among different production routes hitherto developed for the manufacturing of metal matrix nanocomposites, a distinction can be done depending upon the matrix state during the production process, which can be molten, solid or semi-solid. In this Chapter, an overview of ex situ production routes is given, highlighting their general potential and shortcomings. Relevant case studies on the most promising and widespread casting production routes will be discussed more in detail in Chap. 3.

2.1 Liquid State Processes

Compared to other methods, liquid state MMNCs processing routes are attractive due to the fact that they are relatively simple, cost effective and potentially scalable to industrial level for the production of near-net shape components [1–3]. Liquid routes include stir casting, ultrasonic assisted casting, infiltration techniques and disintegrated melt deposition.

Stir casting. Stir casting is one of the most widespread liquid-based technique employed for MMNCs production, due to its simplicity and cost effectiveness; moreover, it is suited to be applied to large volumes of metal [4–6]. The reinforcing phase is usually added to the matrix and distributed in the molten state by applying mechanical stirring through an impeller. MgO, Al₂O₃, ZrO₂ and SiC nanoparticles as well as CNTs have been added to aluminium and magnesium matrices by stir casting method [1, 2, 7–10]. A basic layout of the process is shown in Fig. 2.1.

The molten alloy together with the dispersed particles may be used for sand casting or permanent mold casting. Due to the low wettability of nanoparticles within the molten matrix, their tendency to agglomerate, and the differences in density between particles and matrix, it is usually difficult to obtain a homogeneous distribution of the nano-reinforcement. This results in clustering of nanoparticles [1, 2, 4, 11–13]. Moreover, due to the air entrapment induced by the rotating stirrer, a high porosity content can characterize the composite and, furthermore, undesired chemical reactions at the matrix/reinforcement interface may occur [2, 14].

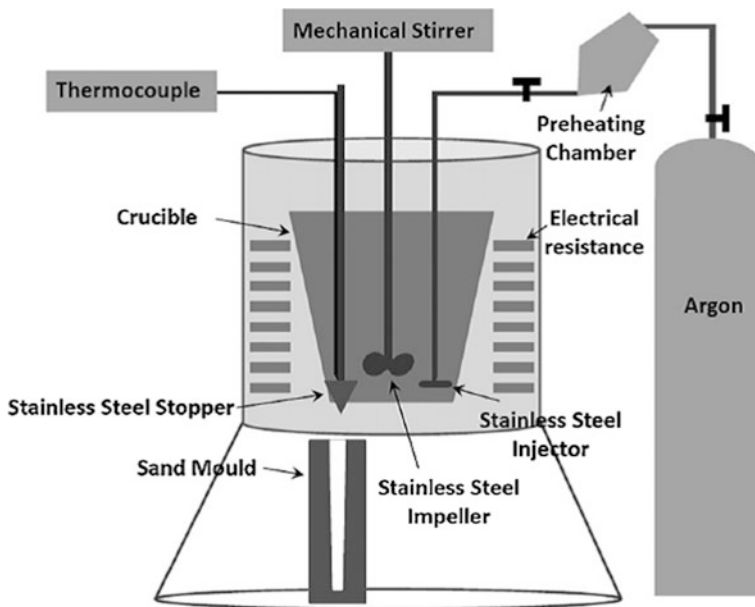


Fig. 2.1 Typical stir casting experimental set-up [2]

Particles may be added to the matrix directly into the molten stream while filling the mold or through an inert carrier gas; the dispersion may also be obtained through the so-called vortex method [4], consisting in vigorously stirring the melt, generating a vortex at the melt surface. The particles are introduced at the side of the vortex and subsequently transferred to the liquid matrix by the vortex, due to the pressure difference between the inner and the outer surface of the melt. As to eliminate the initial clustering and diminish wetting issues, nanoparticles may be pre-dispersed through ball milling on the surface of metal powders (Al or Mg based). The composite powders are then added to the molten metal and stirring is employed: during melting of the matrix powders, nanoparticles are released in the molten matrix. Nanocomposites reinforced with Al_2O_3 , SiC and CNTs have been produced in this way [1, 3, 13, 15–19].

Ultrasonic assisted casting. Ultrasonic assisted casting is reported to be effective in eliminating particle clusters which are generated due to agglomeration tendency and low wettability of nanoparticles [12, 20]. It consists of treating the melt with ultrasonic waves (usually in the frequency range 18–20 kHz) during or after adding the reinforcing phase; the treatment has been used for the production of Al and Mg based nanocomposites reinforced with SiC, Al_2O_3 , B_4C , CNTs and AlN [11, 12, 21–26]. A typical set up for ultrasonic treatment, in which a ultrasonic irradiating sonotrode is directly dipped into the melt, is shown in Fig. 2.2. Non-contact ultrasonic treatment was also applied for the production of Al/ Al_2O_3 nanocomposite by means of an ultrasonic chamber [22].

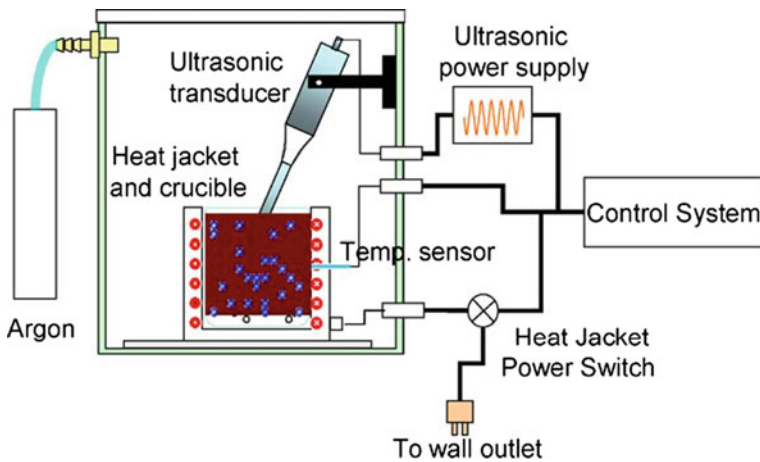


Fig. 2.2 Ultrasonic assisted casting set-up [23]

The sonotrode is usually made of titanium alloy (Ti6Al4V), stainless steel or niobium based alloy (e.g. C-103), due to their efficiency in transmitting ultrasounds and dimensional stability at elevated temperatures [27, 28]. Although costly, Nb sonotrodes possess higher chemical inertness when in contact with the molten metal matrix [26, 29], withstanding high processing temperatures with minimum ultrasonic cavitation induced erosion [30, 31]. To this end, Ti-based sonotrodes behave better than steel-sonotrodes and are widely used due to lower costs as compared to Nb ones.

Ultrasonic cavitation can produce transient (in the order of nanoseconds) micro “hot spots” with temperatures of about 5000 °C, pressures above 1000 atm, and heating and cooling rates above 10^{10} K/s [32]. Since nanoparticle clusters are loosely packed, the entrapped air inside the voids in the clusters, will serve as nuclei for cavitation [26]. The strong heating and cooling rates induced during the process, as well as the pressure gradient, are believed to be able to break nanoparticle clusters and to remove impurities from the particles surface. Despite its efficiency in dispersing nanoparticles and destroying clusters, ultrasonic technique seems quite difficult to be scaled up for industrial applications, as the volume of castings are limited to the power of the ultrasonic source. It has been reported, in fact, that high-intensity ultrasonic vibration requires at least an ultrasonic intensity of 100 W/cm^2 , while a fully developed cavitation occurs in the molten aluminium alloys when the threshold value of 80 W/cm^2 is achieved [33]. However, a possible solution for scaling up the process could be represented by melt flow processing, which involves forcing the melt to flow in a ultrasonic treatment chamber so that a small sonotrode can treat a large metal volume [34].

Infiltration process. Infiltration process involves the pressure-assisted injection of liquid metal into a porous preform (Fig. 2.3). This technique has been widely adopted for the production of composites with micro sized reinforcement, e.g. SiC

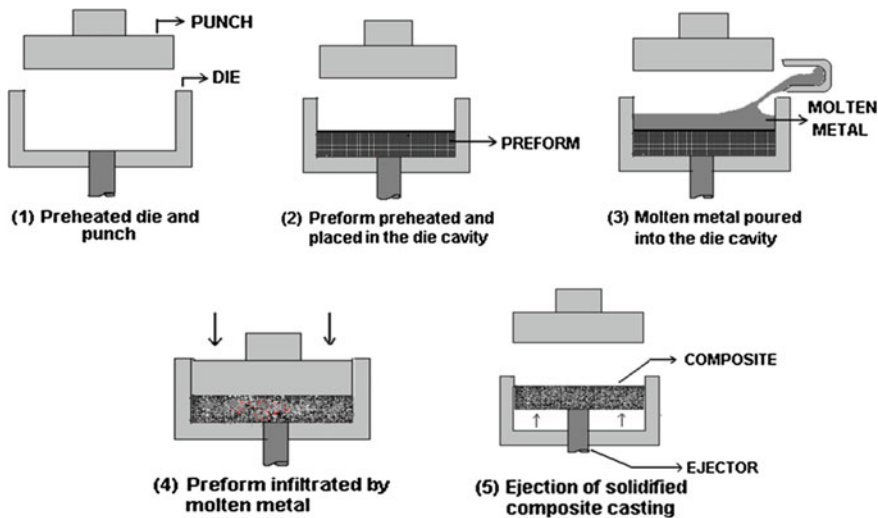


Fig. 2.3 Schematic of the infiltration method [134]

particles and foams, TiC, glass fiber, Al_2O_3 , AlN, and Al_4C_3 [35–40]. The preform is generally obtained by preparing a slurry consisting of a binder, a liquid carrier and the reinforcement phase, and then subjecting the slurry to filtration. Subsequently, the preform is dried and heat-treated to remain dimensionally stable during the pressure-assisted molten metal infiltration [41]. Infiltration process was adopted by Babu et al. [42] to produce Mg-based composites by infiltrating graphite nanofibers and alumina short fibers hybrid preforms. Recently, infiltration technique has been applied in a pressureless configuration, involving the spontaneous infiltration of the ceramic preform without the aid of externally applied pressure, nor vacuum [43]. The technique results to be more cost-effective than the traditional infiltration process, as it does not require expensive equipment, although long infiltration time are required. Al alloy based nanocomposites reinforced with SiC particles were produced by combining ball-milling and cold pressing to produce the preform, prior to pressureless infiltration [44, 45]. A similar technique was adopted by Zhou as to produce Al-based composites reinforced by CNTs, by melting and infiltrating LY12 alloy (Al–Cu–Mg) into the CNT–Al–Mg preforms, by using an infiltration time of 5 h [43]. With these techniques, processed metal volumes are limited by long infiltration times and preform costs.

Disintegrated melt deposition. Disintegrated melt deposition (DMD) technique was adopted to disperse nano-reinforcement in molten magnesium alloys. The process, developed for the synthesis of near-net shape discontinuously reinforced MMCs [46] is a combination of casting and spray processes. It involves incorporating the ceramic particles by stirring the molten alloy with an impeller as the particles are added. The resulting composite slurry is then disintegrated by jets of inert gas at a typical superheat temperature of 750 °C and subsequently deposited

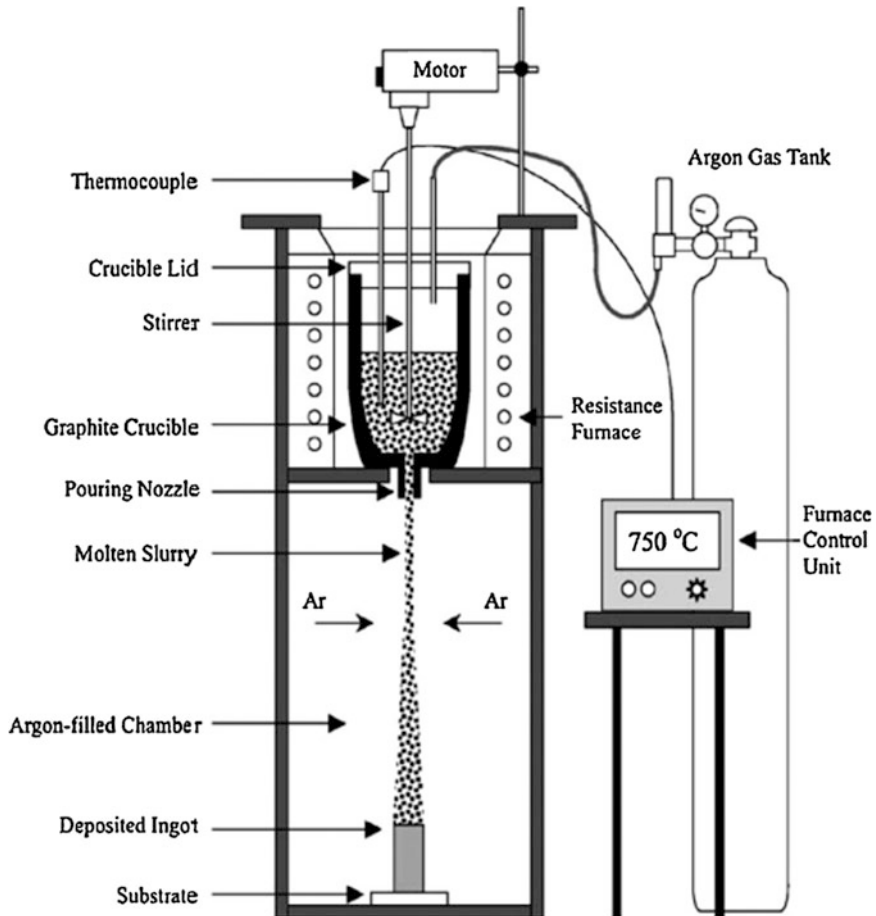


Fig. 2.4 Schematic of the DMD process [49]

on a metallic substrate. The ingot can be then extruded (Fig. 2.4). Although the method is suitable for making both Al- and Mg-nanocomposites, most of the studies are pertained to Mg-nanocomposites. This is possibly due to the reason that it can overcome the major drawbacks observed during conventional processing of Mg-materials, viz., (i) oxides in the final product due to the highly oxidisable nature of Mg and (ii) retention of reinforcement particles in the crucible, due to the density differences between the Mg-matrix and reinforcement. These together can give rise to impurities, insufficient volume fraction of reinforcement and non-uniform dispersion, which can seriously impair the properties. As DMD is a bottom-pouring technique it can ensure elimination of oxide entry into the deposited product and complete utilization of the reinforcement. Various nanoparticles such as Al_2O_3 , SiC , Y_2O_3 , B_4C , BN , ZrO_2 , ZnO etc. as well as multi-walled carbon nanotubes

(MWNT) have been added to Mg/Mg-alloys to produce Mg nanocomposites [47–51]. In most cases, the microstructural characterization of the extruded composites showed uniform distribution of the ceramic reinforcements, good interfacial integrity between the ceramic reinforcement and the metallic matrix and limited amounts of porosity. Due to these reasons, the mechanical properties of the Mg-nanocomposites have often shown significant improvement in terms of both strength and ductility [52].

High pressure die casting. Among the traditional liquid processes, aside from stir casting and semi-solid casting techniques, high pressure die casting (HPDC) has also been applied for the production of MMNCs. In general, the process enables obtaining more detailed components as compared to gravity and low pressure die casting methods. The molten metal is forced into the die cavity under pressure, and both filling speeds and solidification rates are particularly high. For this reason, HPDC is characterized by fast cycle times, which may range from seconds to several minutes, depending on size and wall thickness of the casting. On the other hand, the process inevitably induces gas entrapment due to the highly turbulent flow of metal in the cavity [53, 54]. Very few works have been reported on the application of HPDC for the production of MMC, especially in the case of nanocomposites. HPDC was applied by Li et al. [9] to manufacture CNT-reinforced Al-based composites. The method allowed obtaining an increase of both tensile stress and elongation to failure as compared to the unreinforced alloy.

2.2 Solid State Routes

Solid-state processes for the production of bulk nanocomposites are based on powder metallurgy. Matrix/reinforcement wetting issues related to nanoparticles are clearly and noticeably diminished with respect to liquid and semi-solid routes [55]. To some extent, similar to primary liquid and semi-solid processes, PM processes enable to produce near-net shape components. Competitive advantages of this processing route include the capability of incorporating a higher volume fraction of reinforcement, as well as the possibility to produce matrix/reinforcement systems not obtainable by traditional liquid casting routes. PM is also of great interest for manufacturing of large batches, typically for the automotive industry, although usually of small sized components [56]. Major drawbacks include the high cost of the powders and the high amount of porosity which could characterize the final product, requiring further working steps (secondary processes) such as extrusion, rolling, or forging [57].

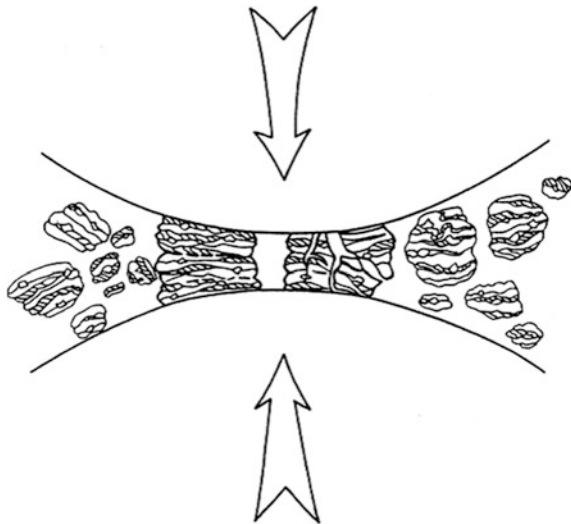
Powder metallurgy. Powder Metallurgy (PM) processes usually involve the following phases: blending of matrix alloy and reinforcing phase powders; compacting the blend, usually by cold pressing; degassing the compacted structure to remove volatile contaminants (lubricants, mixing and blending additives), water vapor and gases; green compacts can be then consolidated by different routes such as direct sintering, hot isostatic pressing (HIP), vacuum hot isostatic pressing,

hot extrusion or cold sintering [58]. Severe plastic deformation processes, such as equal channel angular pressing (ECAP), have been also applied to consolidate composite powders of e.g. Al7075 alloy and nano-TiO₂ [59].

Mechanical alloying. In the traditional PM process, the aim of the blending is simply to mix the powders without inducing material transfer between the mixed components. It is possible, however, to perform a high energy mixing through milling media, as to eliminate the voids between the matrix and the reinforcement powders, by incorporating hard ceramic particles into the matrix powder through a solid-state bonding [57]. For example, in mechanical alloying (MA), matrix and reinforcement are fused together by inducing cold welding, fracturing, and re-welding of the powder particles [55, 60, 61]. The strengthening of metallic alloys is achieved through grain size refinement and dispersion of nanometric particles. During the process, a small quantity of the base powders are loaded into a sealed container, together with the grinding media, then blended through agitation at high speed for a predetermined amount of time (Fig. 2.5). As the kinetic energy of the grinding balls depends on their mass and velocity, dense materials such as stainless steel or tungsten carbide are preferred. Main process parameters, influencing the quality of the composite, comprise ball-to-powder ratio (BPR), time and rotational speed of milling. After being milled, powders are compacted, degassed and consolidated.

A process control agent (PCA, usually referred to as lubricant or surfactant) is usually added while milling the powders, aiming to minimize the effect of cold welding and consequent formation of large powder clusters. Methanol, stearic acid, and paraffin compounds may be used for this purpose [62]. During the continuous severe plastic deformation, a refinement of the internal structure of the powders to the nanometer scale may occur, resulting in the production of nanostructured

Fig. 2.5 Mechanical alloying processing technique: milling action on the powders [61]

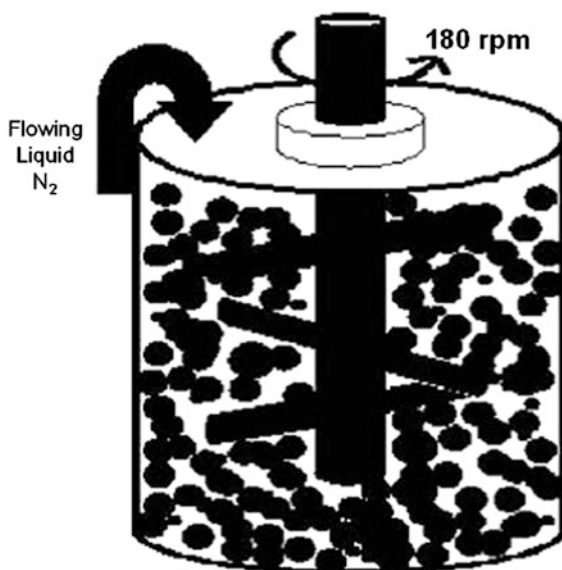


powders [60, 63]. The mechanisms of grain refining has been evaluated by Fecht [63]. The deformation is first localized in shear bands with high dislocation density. This initial phase is followed by annihilation and recombination of dislocations; as a result, nanometric sized grains may be formed during the milling process. As a third stage, the sub-grain boundary structure is transformed to randomly oriented high-angle grain boundaries. In the process, contamination of the powders must be carefully controlled. Possible sources of contamination are the milling tools, milling atmosphere, as well as the process control agent. During consolidation, impurities may influence microstructural evolution and grain growth, leading to a possible decrease of mechanical properties of the resulting composite [57, 61, 64, 65]. The milled powders obtained from mechanical alloying may also be employed as reinforcing particles for casting processes [1, 3, 13, 15, 16].

Mechanical alloying can also be accompanied by a solid state reaction, aimed to produce fine dispersion of oxides, nitrides and carbides in the light alloy matrix [56, 66–68]. In this case, the process is usually defined as *reaction milling* (RM). In order to allow the reaction to occur, the process control agent can be absent or a suitable milling atmosphere can be used to introduce reagents, i.e. oxygen, argon, nitrogen, or simply air [60]. Sometimes the PCA could be itself part of the reaction process [69].

In *cryomilling*, the milling phase is carried out at cryogenic temperatures (Fig. 2.6) or, in some cases, within a cryogenic medium, as liquid nitrogen [62]. A PCA (e.g. stearic acid) can be used to avoid severe sticking. During traditional milling process, the temperature increases due to the frictional heating. As a result, severe recovery and recrystallization of fine microstructures may occur [61]. On the contrary, when cryomilling is applied, recovery and recrystallization are suppressed

Fig. 2.6 Schematic of cryomilling process [62]



by the extremely low milling temperature, enhancing the beneficial effects of mechanical milling and leading to finer grain structures and more rapid grain refinement. As a result, nanocrystalline grain structures may be obtained [62]. Moreover, detrimental chemical reactions between matrix and reinforcement are also suppressed at such low temperatures [57, 60].

Microwave sintering. In microwave sintering, the principle of heating and sintering is fundamentally different. Microwave heating is a volumetric heating process involving conversion of electromagnetic energy into thermal energy, which is instantaneous, rapid and highly efficient [52]. It is unlike the conventional sintering processes wherein thermal energy is transferred from the outer surface of the materials to the inner surface. In microwave sintering, heat is generated from within the materials and radiates outward due to the penetrative power of the microwaves [52]. Metal in the form of powder will absorb microwaves at room temperature and will be heated very effectively and rapidly. The microwave energy is absorbed by the materials and is not dependent on the heat transfer from the outer surfaces. It is observed that in this method, higher temperatures exist at the core whereas the surfaces experiences lower temperatures [52].

Any method that gives rise to differential heating (core-to-surface or surface-to-core) in the sample causes variation in microstructure along the thickness of the sample, and would usually result in poor properties. To eliminate such a disadvantage, hybrid microwave heating has been developed, which is described below.

Bi-directional hybrid microwave sintering. In this process, microwave susceptors such as SiC particles/rods are used to assist in the reduction of thermal gradient during sintering [70]. Such a type of microwave heating set-up is shown in Fig. 2.7 [71], (which uses a simple household microwave oven) wherein the compacted metal/composite powder billets are placed in the inner crucible and SiC powder is placed between the inner and outer crucibles. SiC powder absorbs

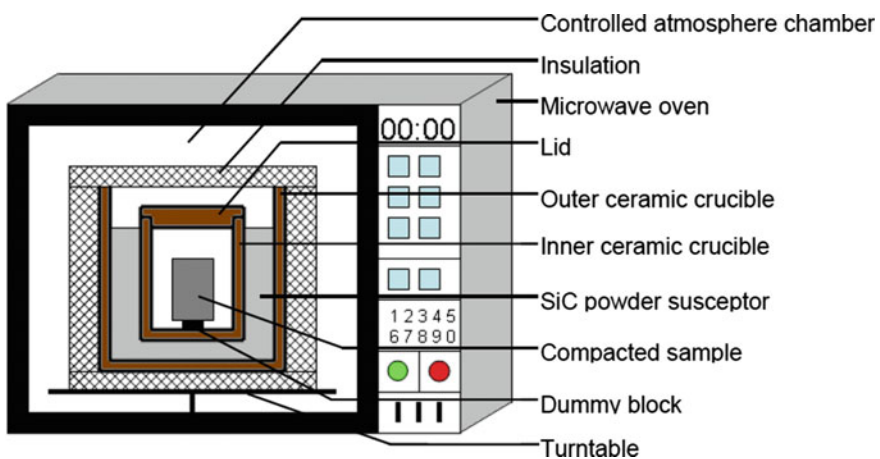


Fig. 2.7 Schematic of the bi-directional hybrid microwave-assisted sintering [71]

microwave readily and heats up quickly, providing radiant heat to externally heat the compacted billets (preforms). On the other hand, the compacted billets themselves absorb microwave and are heated from within. Thereby, uniform heat is experienced along the thickness of the specimen and the core-to-centre thermal variation is minimized [70].

The method has been used successfully for sintering light-metal (both Al and Mg) alloys and composites. Especially in the case of nanocomposites, as the bi-directional hybrid microwave sintering reduces the thermal variation, high sintering temperatures ($\sim 620\text{--}650\text{ }^{\circ}\text{C}$) can be utilized for a short period of time, which is almost close to the melting point of these metals [52, 70]. This ensures good bonding of the nanoparticles within the preforms and eliminates porosity at the particle/matrix interface, which is a major concern in conventionally sintered materials [70, 72]. The resulting microwave sintered nanocomposite product is dense with fine microstructural characteristics. The advantages of hybrid microwave energy for materials processing include: (i) time and energy savings, (ii) rapid heating rates, (iii) fine microstructures and hence improved mechanical properties and better product performance, (iv) does not require inert atmosphere, even for readily oxidisable materials such as Mg, and (v) lower environmental impact [52, 70].

Using the bi-directional hybrid microwave sintering technique nano-reinforcements such as Al_2O_3 , SiC, CNT, Y_2O_3 , BN etc., have been incorporated into pure Mg matrix. The sintered products are usually characterised for their microstructure and mechanical properties after hot-extrusion. In most studies, the density of the composites is much closer to the theoretical density indicating minimal porosity, a significant advantage that has given rise to better microstructural and mechanical characteristics, including enhanced ductility [70].

2.3 Semi-solid State Processes

Semi-solid casting processes involve the shaping of a partially solid mixture (slurry) with relatively small near-globular grains at solid fractions between 20 and 60 %. As a common advantage, semi-solid processes are in general characterized by low shrinkage and porosity, non-turbulent filling and lower processing temperature. They can be divided into two main groups of processes, namely thixo-processes and rheo-processes (compocasting).

Thixoprocessing. In thixo-processes a proper solid feedstock is reheated and partially melted. The base material is generated by allowing a liquid melt to partially solidify under controlled conditions (low superheat and rapid cooling, usually combined with significant convection in the liquid), as to induce the formation of crystals in the slurry. The feedstock may be produced in a variety of ways such as with mechanical stirring during solidification as in rheocasting [73–75], continuous casting combined with magneto-hydrodynamic stirring for grain refining [73, 76], and ultrasonic treatment [73, 77, 78] again for grain refinement. Other methods to

prepare a fine grained non-dendritic material is by spray casting [73, 79] and low-superheat casting [73, 80] processes. Many of the processes employ intense chemical inoculation to maximize the efficiency of the above mentioned processes, particularly magneto-hydrodynamic stirring and low-superheat casting [73, 81]. Usually, the semi-solid material is then injected into hardened steels dies as final stage process. Being the slurry obtainable in several ways, the process results to be tailorable and optimized for the production of MMNC [73, 82]. Although thixo-processes would offer a great possibility to premix nanoparticles into the feedstock through different production methods, to the authors' best knowledge, very few efforts strictly referring to thixocasting technology for MMNCs, aiming at the production of a globular microstructure, have been hitherto reported in the literature [31]. Nevertheless, it should be observed that several production routes involved the preparation of premixed ceramic/metallic or CNT/metallic feedstocks to be then diluted in the molten matrix [1, 3, 15, 16, 83, 84]. In the present review, such studies are reported in the stir casting or compocasting sections respectively in case the matrix is in its liquid or semisolid state.

Rheoprocessing. On the other hand, in rheo-processes, a special feedstock is not required, and the semi-solid slurry is generated starting from the liquid state by cooling the molten metal during the casting process itself. In common for all rheo-processes is that they are easier to implement in a foundry as they involve standard equipment for melting, transport, treatment, degassing and handling. The key difference between the various approaches is in the slurry making process, where great efforts are being made to create a robust on-demand slurry-making capability. Among rheo-processes techniques, it is worthwhile mentioning the ***New Rheo Casting process (NRC)***, which relies on a cooling slope to generate the initial slurry [85]. The molten metal is poured at low superheat (about 10 K) onto the side of a holing cup and a large amount of very small crystals are formed. The slurry is then held for a pre-set time in the cup, allowing the crystals to grow and spheroidise without additional shearing or stirring. Just before pouring, the temperature of the slurry is homogenised [86]. As a variation to the precedent, the ***Hong-Nano Casting method (H-NCM)***, [87], uses an electro-magnetic field in the pouring and cooling stages. This modification helps in homogenizing the temperature and increase the overall heat transfer, resulting in fast cooling and copious nucleation—approximately 1000 times higher than in the NRC process. Further, the ***Rheo Die Casting process (RDC)***, also known as Twin Screw Rheo Moulding (TSRM), involves the use of twin screws for mixing, providing a high amount of shearing. The molten metal is cooled at a controlled rate. The high level of shear is thought to break oxides into small, round particles which are well dispersed in the entire cast component [88, 89]. The slurry may be generated by letting the melt passing through a conversion reactor (a cooled copper or iron block with a twisting channel inside, causing the melt to cool and partially solidify under shear) in the so called ***Continuous Rheo-conversion Process (CRP)*** [89]. Other processes developed so far for semisolid metal processing are the ***Sub-Liquidus (SLC)*** [90, 91] and ***Semi Solid Rheo (SSR)*** casting processes [92], ***GISS*** process, ***Rapid Slurry Forming (RSF)*** [93, 94], ***Semi-Solid Metal (SSM)*** and ***ATS*** processes [95].

Although a multitude of different rheo-processes have been developed for semi-solid processing of metals, it appears that very little research has been conducted on adapting and using these methods for the production of MMNCs. In particular, as a result on literature survey, the most widespread technique employed is the so called compocasting route, which is a rheocasting process involving the injection of nanoparticles into semisolid state alloys.

Depending on the state of the matrix during casting operations, it is possible to distinguish between semisolid–semisolid (SS) and semisolid–liquid (SL) routes. In the first one, during casting operations, the matrix is partially liquid, while in the second one, the slurry containing nanoparticles is heated up to the fully liquid state before being poured into the mold [96]. Similarly to stir casting route, a vortex may be generated so as to introduce the particles within the semi-solid slurry. As concerning the metallic matrix to be processed through compocasting technique, it is a favourable feature to present a wide temperature interval for solidification (i.e. difference between solidus and liquidus temperatures). For example, as concerning aluminium alloys, one of the most used casting alloys is A356 alloy, which in fact solidifies in a temperature interval of 43 °C [96]. Compocasting is generally thought to be a processing route allowing to obtain quite uniform distribution of reinforcing particles, as well as to enhance particle wettability [97, 98]. It has been reported, in fact, that the primary solid particles which are formed in the semi-solid slurry are able to mechanically entrap the reinforcing phase and to prevent their gravity segregation, as well as to reduce their agglomeration tendency [99]. Moreover, the lower porosity which is usually observed in experimental studies, is attributed to the better wettability between the matrix and the reinforcement particles as well as the lower volume shrinkage of the matrix alloy [98]. Despite these advantages, some agglomerates, inevitably induced by the high surface-to-volume ratio, as well as to Van der Waals interactions are still reported [96].

Compocasting has been applied to produce MMNCs employing reinforcing phases such as SiC, CNTs and Al_2O_3 in aluminium matrices [100–102], while SiC has been used as to strengthen Mg alloys [103–110]. Some authors, such as Chen et al. [103], reported having successfully introduced nanoparticles within the matrix at the semi-solid state, while dispersing them through ultrasonication at the fully liquid state. In general, as a result of comparative studies, compocasting process is reported to induce less porosity in the composites and to obtain, at equal reinforcement fraction, higher mechanical properties than the traditional stir casting process [111–113].

2.4 Hybrid Methods and Other Routes

Nanocomposites can also be prepared through a combination of the above-mentioned processes. Often in these methods, powder-metallurgy techniques are utilized prior to producing the nanocomposite (e.g. by liquid-state or compocasting routes). Selective alloying element(s) of interest (micron/nano-sized

metal powders of suitable weight/volume fraction) are prepared in form of master powders by: (i) either mixing/blending with the reinforcement nanoparticles, or (ii) mechanical alloying using a ball-mill, which are then incorporated into the melt [114, 115]. In non-reactive powder mixtures, each of these intermediary steps is performed to ensure uniform distribution of the constituent elements in the liquid metal and further to avoid agglomeration of particles, which usually occurs when nanoparticles are added directly to the melt [114]. In reactive powder mixtures, the mechanical alloying process induces chemical reaction between the powders (such as intermetallic phase formation), which are controlled via processing parameters employed during mechanically alloying, and depends on the formation enthalpy [115].

It should be noted here that in the traditional method of adding the reinforcements/alloying elements to the melt (i.e. direct addition), the reaction of the constituent elements is controlled by their reaction with the molten metal, and hence usually forms intermetallic phases with matrix as the main constituent. This usually makes the matrix brittle [114, 115]. In contrast, the intermediary step of pre-processing of the constituent elements (alloying element/reinforcement) brings about a major advantage of the formation of matrix-free intermetallic phase and upon its addition to the melt, enhances the mechanical properties of the developed material by acting as a strengthening phase [114, 115]. Multiple-reinforcements (metal/ceramic reinforcements with micron/submicron/nano-sizes) can also be considered, as the intermediary process can be more effective. In the case of multiple reinforcements, wherein nano-sized particles are present along with micron-sized particles having irregular shape, size and sharp corners it has been observed that in the pre-processing step, the large-sized irregular particles (micron-sized) breakdown to small-sized (almost uniform) with rounded edges. By the reason that the shape/size of the large-sized irregular particles change during pre-processing step, the stress concentration reduces, thereby providing enhanced resistance to fracture [114, 115].

2.4.1 Other Processes

Friction Stir Processing (FSP). FSP is based on friction stir welding and was initially used to produce surface-reinforced composites [116]. In recent years, research efforts are being attempted to use the process as an alternative route to incorporate nanoparticles into the metal matrix to form bulk nanocomposites. During FSP, a rotating tool with a shoulder and a pin is plunged into the surface of the work piece (the desired base matrix) with grooves filled with the desired volume fraction of nanoparticles. As the tool rotates, it feeds forward to cover the region of interest [116]. A schematic showing the FSP is given in Fig. 2.8 [117]. Most studies have shown significant hardness improvement of the produced nanocomposites. However, the process is still in the developmental stage, as the uniform dispersion of nano-sized reinforcements remains a challenge and the thickness of the

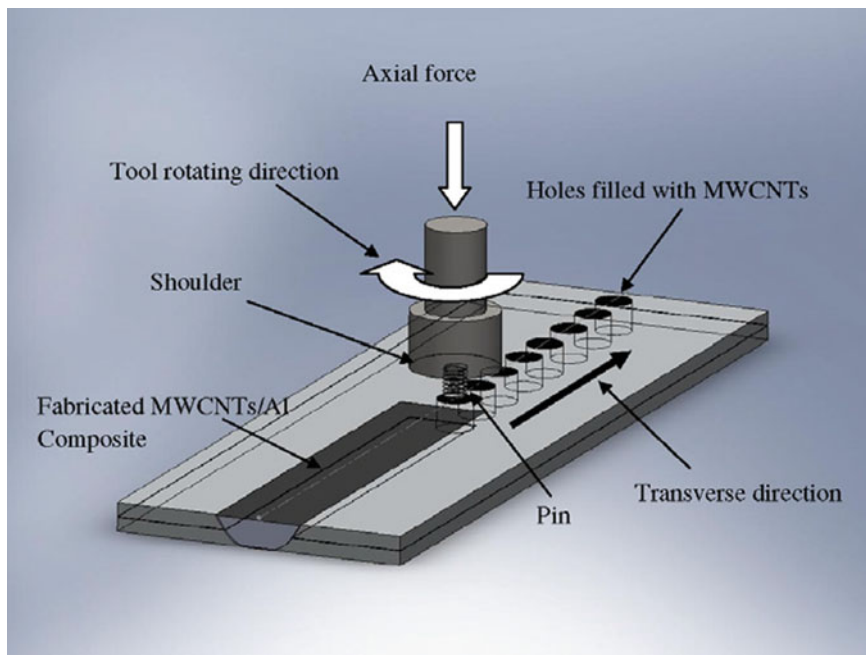


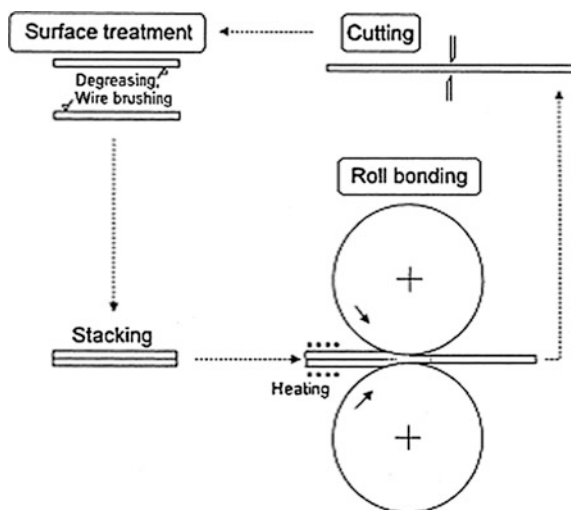
Fig. 2.8 Schematic of friction stir process (FSP) for Al/CNTs nanocomposites [117]

component is limited by the action of the stirring tool; either Al- [117–119] and Mg- [120, 121] based nanocomposite have been produced by FSP by incorporating ceramic or carbon based nano-reinforcement.

Accumulative roll bonding. Accumulative roll bonding (ARB) is a solid state method which enables to produce MMCs in the form of sheets, and was firstly developed in 2008 by Alizadeh et al., who produced nano-structured Al-SiC composites [122]. The method belongs to severe plastic deformation processes and, in addition to producing MMCs, allows to obtain nanostructured and ultrafine grained materials [123–125]. ARB process consists in roll bonding stacked sheets (about 50 % of thickness reduction), then cutting the roll-bonded material and rolling it again after stacking the pieces over each other [123] (Fig. 2.9).

Particles are usually distributed on the sheets before processing; by increasing the number of cycles, an enhancement in particles uniformity is usually reported, as well as a decrease in porosity content and an increase in the bonding strength between matrix and reinforcement [123]. As a result, mechanical properties of the ARB processed unreinforced metals and composites have been reported to increase (YS, compressive strength, wear resistance) [126–129]. Micrometric as well nano-sized reinforcing particles (e.g. Al_2O_3 , SiC, SiO_2 and B_4C particles) have been added to metallic matrices through ARB process [126, 130–132].

Fig. 2.9 Schematic of accumulative roll bonding (ARB) process [124]



Accumulative roll bonding (ARB) was also used to improve bonding of Multi-walled Carbon NanoTubes MWCNTs with the matrix and to reduce their agglomeration tendency by producing Al–MWCNT composite stripes to be then diluted in a molten Al-matrix of appropriate composition followed by squeeze casting [133].

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Chapter 3

Casting Routes for the Production of Al and Mg Based Nanocomposites

Abstract As previously described in Chap. 2, the different production techniques for metal matrix nanocomposites (MMNCs) may be classified depending on the matrix state: liquid, solid or semi-solid. In comparison to other methods, liquid and semi-solid state MMNCs processing techniques are particularly attractive since they are potentially scalable to industrial level for the high volume production of near-net shape components. Nevertheless, such methods pose critical issues related to the low wettability of nanosized particles, generally leading to clusterization and high casting defects content. In this chapter, the main liquid and semi-solid casting routes (stir casting, compocasting, ultrasonic assisted casting and disintegrated melt deposition, DMD) will be described; the results of recent and relevant case studies on Al and Mg based nanocomposites will be summarized and discussed, by highlighting the main drawbacks of such processes.

3.1 Stir Casting

3.1.1 Process Description

Stir casting is probably the simplest technique meant to produce MMNCs by a liquid state route. The process consists in melting the matrix, adding nanoparticles to the melt above the liquidus temperature of the molten alloy, and dispersing the reinforcing phase through mechanical stirring. At this scope, a stirrer is dipped into the melt and stirring is applied creating a vortex in the liquid matrix, so that the technique is often referred to as vortex method. To facilitate dispersion, particles are often added once the vortex is created. Even though single stage stirrers are the most common, multiple stage stirrers have been also used as to guarantee more uniform melt stirring [1, 2]. The molten composite is then cast, typically through gravity casting.

Processing MMCs through melt stirring presents some relevant advantages, namely low cost processing, relative simplicity, flexibility and possibility of large quantity production [3]. The method has been widely used for the production of

micro-metric reinforced composites [4]. However, nanoparticles are generally characterized by low wettability with respect to molten metals and agglomeration tendency [5, 6]. Furthermore, air entrapment due to stirring action is also likely to occur [3] and, due to the density differences between matrix and reinforcement, reinforcing particles tend to sink or float within the molten matrix [7–9], so that an even dispersion of the particles is usually difficult to achieve [10].

The processing of MMNCs through the simple stir casting technique is therefore recognized to be challenging; for this reason, ways to enhance the wettability of nanoparticles and to facilitate their incorporation have been developed and evaluated. Reinforcement feeding method has a strong influence on the final dispersion of nanoparticles [4]. Particles may be injected through an inert carrier gas at the bottom of the crucible, so that they are dispersed within the matrix as bubbles rise up through the melt [5, 11]. As to improve particles wettability, pre-heating of the ceramic reinforcement is often applied, as it helps in eliminating adsorbed gases from the particle surface as well as impurities [5, 11, 12]. Alloying elements meant to enhance wettability of nanoparticles, such as magnesium, may also be added to the matrix. Mg is a powerful surfactant, and hence it improves particles wetting by decreasing the surface tension of the matrix [7, 13]; moreover, it acts as oxygen scavenger by reacting with the gas present on the surface of particles, thinning the oxygen layer, thus improving wetting and reducing agglomeration tendency [7]. Nanoparticles may also be pre-milled together with metallic powders, as to produce a powder mixture free of gas layers and with improved wettability [2, 3, 8, 14–20].

Particle distribution depends on several processing parameters, such as stirring temperature, speed and time as well as shape and position of the stirrer within the melt [4, 9]. After mixing, before solidification, redistribution of particles occurs, thus influencing the final microstructure of the composite and its mechanical properties [9]. Relevant studies on the stir casting method and further development of the technique, applied to both Al and Mg liquid matrices, are presented and discussed in the forthcoming sections.

3.1.2 Al-Based Nanocomposites

Aluminium based nanocomposites were produced by pure stir casting technique, using as reinforcing phases MgO, Al₂O₃, ZrO₂ and SiC. Kawabe et al. [21] made an early attempt to disperse SiC nanoparticles in Al matrix by a vortex method, although in semi-solid state. More recently, Ansary Yar et al. [22] produced an A356-based composite reinforced with 1.5, 2.5 and 5 vol.% of MgO nanoparticles (50 nm). The powders were wrapped in aluminium foils and added to the molten metal during stirring, performed at various melt temperatures, that is 800, 850 and 950 °C, while stirring was performed at constant rate (420 rpm) for 14 min. MgO particle agglomeration was observed in the sample containing the highest volume fraction of nanoparticles (5 %). Increasing the reinforcement content or increasing the process temperature was reported to reduce the density of the composite and to

increase particle agglomeration. The sample produced at 850 °C, containing 1.5 vol.% of nanoparticles, presented a fairly homogenous microstructure as well as the best mechanical properties.

Abdizadeh et al. [23] compared A356/MgO_p nanocomposites produced by stir casting technique and powder metallurgy routes. MgO particles, 70 nm in size, were used as reinforcing phase. X-ray diffraction results proved the presence of Al and MgO phases without detrimental chemical reactions at the various casting temperatures (800, 850, and 950 °C). Density of the composite was reported to be higher than the one of the matrix, due to the difference in density between MgO and A356 alloy. Similar to the previous study, increasing MgO content, from 0 to 1.5 vol.%, resulted in enhancing the compressive strength; on the other hand, for higher contents, up to 5 vol.%, the strength decreased due to increased porosity and nanoparticles agglomeration. Cast samples showed MgO agglomeration, while powder metallurgy samples contained higher quantity of porosity, as shown in Fig. 3.1. Owing to a lower crack formation tendency and better matrix continuity of cast composites, the PM process was reported to induce lower hardness and compressive strength as compared to the casting technique.

As previously mentioned, Mg is expected to improve wetting by increasing the surface energy of the solid particles, decreasing surface tension of the liquid, and/or decreasing the solid/liquid interfacial energy at the particle/alloy interface [24]. Depending on Mg concentration, one or more reactions between the molten metal and the reinforcements can contribute to reactive wetting [25]. In particular, Mg is thought to scavenge oxygen from the surface of alumina particles, thus eliminating the surface gas layers and promoting wetting, according to the reaction: $2\text{Mg (l)} + \text{O}_2 = 2\text{MgO}$ [26]. As to enhance wettability of nanoparticles, stir mixing combined to reactive wetting was studied by Schultz et al. [26]. Al–Cu–Mg composites reinforced with Al₂O₃ nanoparticle were fabricated through gravity

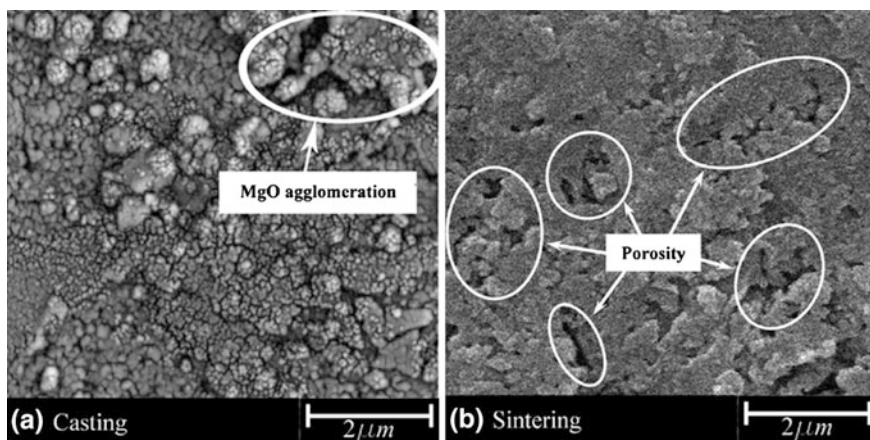
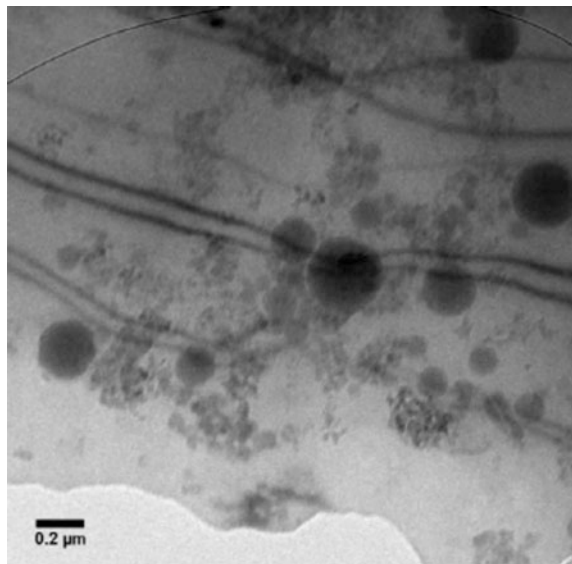


Fig. 3.1 SEM images of (a) cast and (b) sintered 2.5 vol.% MgO–Al nanocomposites (fabricated respectively at 950 and 625 °C) [23]

casting and squeeze casting by adding Mg as wetting agent. Alumina nanoparticles (47 nm) were mixed with Mg chips and packed into aluminium foil packets, pre-heated then dipped into the melt at 900 °C while a vortex was created through a turbine style graphite impeller (45° pitched blade) rotating at 350 rpm. Several combinations of Al_2O_3 (0, 2.5, 5 wt%) and Mg (5, 7 wt%) and mixing times (10, 15, 20 min) were studied using aluminium alloy A206 as the matrix. It was found that reactive wetting of Al_2O_3 nanoparticles in Al–Cu–Mg alloys, combined with mechanical stirring, can induce a relevant hardness increase in gravity cast MMCNs, provided a reaction between the reinforcement and the matrix was either on-going or recently completed at the time of solidification. Clustering was found to increase with increasing mixing time and Al_2O_3 concentration, due to higher particle collision frequency (Fig. 3.2).

Sajjadi et al. [5, 11] applied stir casting to reinforce the A356 matrix with micro (20 μm) and nano (50 nm) Al_2O_3 particles. The particles were initially pre-heated at 1100 °C for 20 min in an inert atmosphere, and later injected in the melt through argon gas. The molten composite was stirred at different stirring speeds (200, 300 and 450 rpm) before and after the incorporation of the particles, as to avoid settling of the particles. Samples without gas injection and without pre-heating of the particles were also produced for comparison. The proposed method had the ability to successfully produce samples up to 5 wt% of micron sized and 3 wt% of nano sized Al_2O_3 reinforcement. The best distribution of particles was obtained at 300 rpm, being the lower stirring speed not efficient in dispersing Al_2O_3 particles, while higher speed caused wastage of microparticles and also more porosity. SEM analysis revealed the tendency of nanoparticles to separate at the interdendritic regions. Due to the higher surface area and surface energy, nanoparticles generated

Fig. 3.2 TEM image of Al–Cu–Mg with 5 wt% Mg mixed with 2.5 wt% Al_2O_3 composite for 20 min [26]



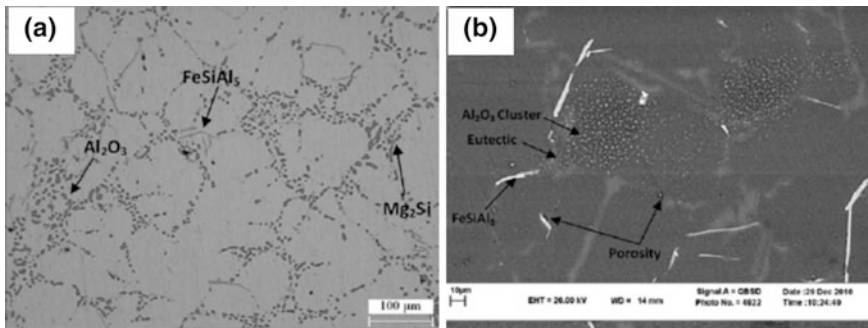


Fig. 3.3 (a) Optical image of A356—1 wt% micro composite and (b) SEM image of A356-1 wt% nano composite [5]

more agglomeration than micro reinforcement particles (Fig. 3.3). The amount of porosity was increased by increasing particle wt% and decreasing particle size. 10 wt% micro-composite was comparable to 3 wt% nanocomposite in terms of hardness, but the compression strength of the latter was by far superior.

Mazahery et al. [27] produced SiC reinforced A356 nanocomposites, by comparing stir casting to compocasting processing route. Particles with average size of 50 nm were used as reinforcement; nanoparticles were added to the molten matrix and stirring of molten Al was employed under nitrogen protecting atmosphere. Composites with reinforcement volume fractions up to 4.5 % were produced. Porosity was confirmed to increase with increasing the fraction of nanoparticles. Compared with the unreinforced alloy, hardness, UTS and YS increased, although ductility decreased, with the maximum strengthening effect in correspondence to 3.5 vol.% of reinforcement. Grain size of the matrix has been reported to decrease with increasing reinforcement vol.% (from 48 μm of the unreinforced matrix to 15 μm in the 4.5 vol.% reinforced composite) as a result of heterogeneous nucleation induced by the dispersion of nanoparticles. Compocast composites were reported to contain lower porosity, finer grains and consequently better mechanical properties than stir cast composites. This has been related to the restricted movement of particles within the melt during solidification of compocast samples, as a result of the increased viscosity, which in turn can induce a more uniform particle distribution.

Master powder feeding. As a result of aggregation tendency and low wettability related to surface gas layers, once the stirring action stops, nanoparticles tend to return to the surface of the melt or to generate clusters. Furthermore, a sort of gas bridge may be present if a critical quantity of nanoparticles is added to the melt, resulting in the complete rejection of the particles by the liquid metal. Pre-milling of metallic powders and reinforcing particles has been proposed as a possible solution to eliminate gases from nanoparticle surface and to improve wettability. During the ball milling process, as a result of the action of milling media, cold welding and repeated fracturing processes, most of the hard ceramic particles are pressed into the

soft metal powders (usually Mg or Al based). The obtained powders mixture, usually referred as master powders, are then added to the molten matrix, enabling a gradual release of ceramic powders within the matrix [2, 7, 28].

A356/ Al_2O_3 nanocomposites were produced through ball milling of master powders and subsequent casting process by Mazahery et al. [3], wherein nano-alumina powders with average size of 50 nm were ball milled with 16 μm aluminium powders using WC/Co balls. The dried powder mixtures were cold pressed (200 MPa), crushed and then passed through 60 mesh screen. The powder mixture was inserted into aluminium foils which were added into molten metal. A graphite stirrer generated a vortex at every 20 s and stirring was applied for 15 min at 600 rpm. The specimens were produced with different vol.% of reinforcement (0.75, 1.5, 2.5, 3.5 and 5 vol.%). Composites containing pure Al_2O_3 particles were produced as well for comparison. Tensile tests showed that for equal content of nano-alumina, tensile properties of the composite obtained with $\text{Al}_2\text{O}_3/\text{Al}$ master-powders were higher than those of the composite reinforced with pure alumina. SEM micrographs indicated that nano- Al_2O_3 particles were well dispersed throughout the composite samples, with few agglomerated particles (Fig. 3.4). The grain size of the composites (12–16 μm depending on alumina content) was smaller than that of unreinforced aluminium matrix (48 μm). YS and UTS strength of the pre-milled composite presented an initial increasing trend with increasing volume fraction of nano reinforcement, reaching the highest value for 1.5 vol.% of nanoparticles. A further increase in ceramic content caused an increase of agglomeration and micro-porosity, decrease in both UTS and YS, and an increase in debonding at the matrix-ceramic particle interface due to thermal mismatch. The same technique was employed in Ref. [19] to produce a 50 nm SiC-A356 composite. Magnesium was added in 1 wt% as a wetting agent. TEM microscopy on

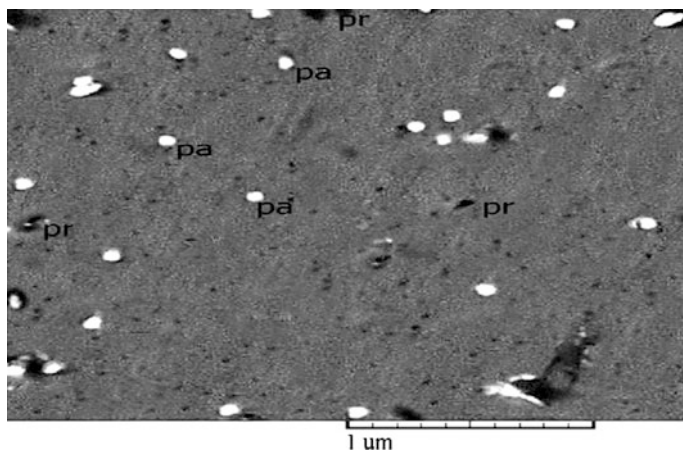


Fig. 3.4 SEM image of $\text{Al}_2\text{O}_3/\text{A356}$ nanocomposite, showing dispersed particle (pa) and porosities (pr) [3]

nanoparticles reinforced composites revealed a uniform distribution of SiC nanoparticles.

As a common result to the previously mentioned studies of Mazahery et al. [3] grain size was reported to decrease with increasing the SiC content, due to the heterogeneous nucleation induced by the uniformly distributed nanoparticles. The composite presented enhanced mechanical properties with respect to the unreinforced matrix, with the maximum strength properties corresponding to 3.5 wt% of SiC. Further addition of nanoparticles led to a slight decrease in HB, UTS and YS, due to increased quantity of entrapped porosity and agglomeration. Nanoparticles addition was reported to deteriorate the ductility of the matrix, decreasing elongation to failure.

Wrought aluminium alloys have been also employed as matrix. AA2024 alloy was used by Su et al. [2] to produce a nano- Al_2O_3 reinforced composite. Al_2O_3 powders (average diameter 13 nm) were mixed by ball milling with pure aluminium powders in 1:9 weight proportion, under argon atmosphere. The mixture was sintered at 400 °C for 2.5 h to remove stearic acid used as PCA during milling. SEM images revealed that a sufficient dispersion of the ceramic phase in the Al powders was obtained only after 10 h of milling. After adding the powders in the molten matrix, under argon atmosphere, the liquid was stirred for 10 min. In the nanocomposite containing 0.6 wt % of alumina some little clusters were found, while single nanoparticles were uniformly distributed inside the matrix. Mechanical properties of the nanocomposite were compared to the ones of a traditional stir cast 0.6 wt% nanocomposite. The YS, UTS and hardness were improved respectively by 59, 58 and 16 %.

A study on stir casting process parameters was done by Hamedan et al. [18], who produced 1 wt% SiC-A356 nanocomposites as to evaluate the effect of stirring speed (450–950 rpm), stirring temperature (650–800 °C) and master powders type (Al–20 wt% SiC and Al–40 wt% SiC). SiC particles of 25–50 nm were ball milled with aluminium powders as to produce master powders containing 20 and 40 wt% of SiC. The milled powders were inserted into the melt through a steel tube, while mechanical stirring was activated. The best mechanical properties as well as the best nanoparticle distribution, were obtained with 700 rpm of stirring speed and 750 °C as processing temperature. A higher temperature (i.e. 800 °C) induced a more turbulent flow which caused increased porosity content. Increasing the rotational speed of the stirrer allows applying higher forces to melt and powders, resulting in better nanoparticles dispersion. On the other hand, it may cause an increased air entrapment inside the melt due to the turbulent flow. Therefore, as also observed by Sajjadi [5], the optimum value of rotational speed balanced the two opposite effects, giving the optimal results in terms of compressive strength. Master powders with the lowest weight fraction of nanoparticles (Al-20 wt% SiC) induced higher mechanical properties and nanoparticle distribution. In this case, with 700 rpm and 750 °C as process parameters, an increase of 24 % in UTS and 52 % in YS in comparison to those of the cast alloy processed at the same stirring temperature were observed.

As reported in the previous studies, master powders are generally produced by milling together ceramic reinforcement and powders of the same base metal which composes the matrix. Akbari et al. [20, 29] demonstrated that different metallic powders may be used to produce master powders even more effective than

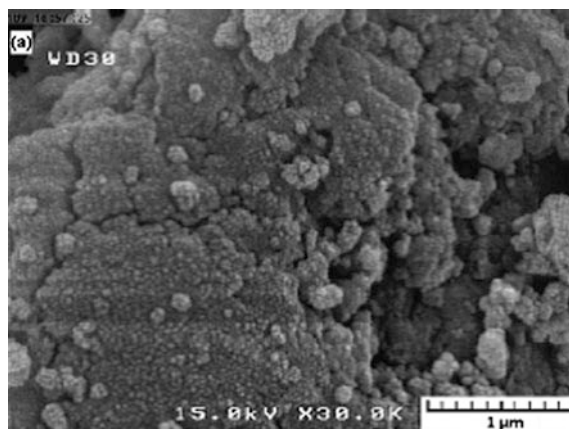


Fig. 3.5 FESEM image of the surface of the produced masterpowders, revealing the distribution of alumina nanoparticles on metallic powders [29]

aluminium based ones in reinforcing the matrix. Al_2O_3 particles (20 nm) were separately milled with micrometric aluminium and copper powders (Fig. 3.5) and incorporated into A356 alloy, via stir casting method, to produce A356/1.5 vol.% nano- Al_2O_3 composite (Fig. 3.6).

Milling time was evaluated by milling both Al and Cu powders with Al_2O_3 from 1 to 24 h [29]. Even if the porosity content in samples stirred for equal time was almost the same, the Al_2O_3 -Cu composites presented higher hardness values than the Al_2O_3 -Al ones. Moreover, increasing milling and stirring time resulted to induce an increased amount of porosity. Tensile testing results revealed that Al_2O_3 /Cu reinforcing powders are more effective in strengthening the matrix compared to pure Al_2O_3 and Al_2O_3 /Al powders. This effect was primarily related to a higher tendency of Al_2O_3 /Cu particles to be captured by the solid front than Al_2O_3 /Al powders. Moreover, strengthening effect of dissolved copper phase should also be

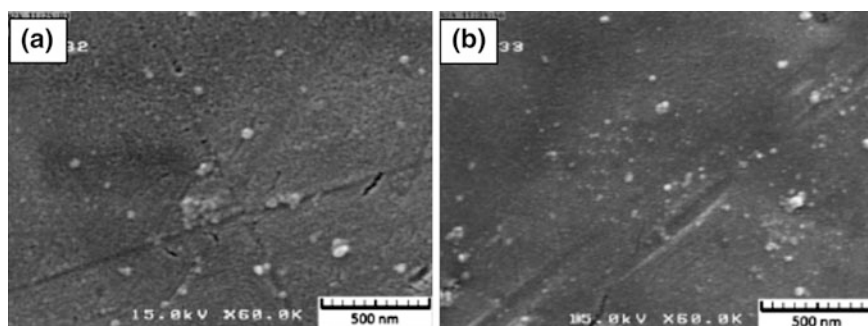
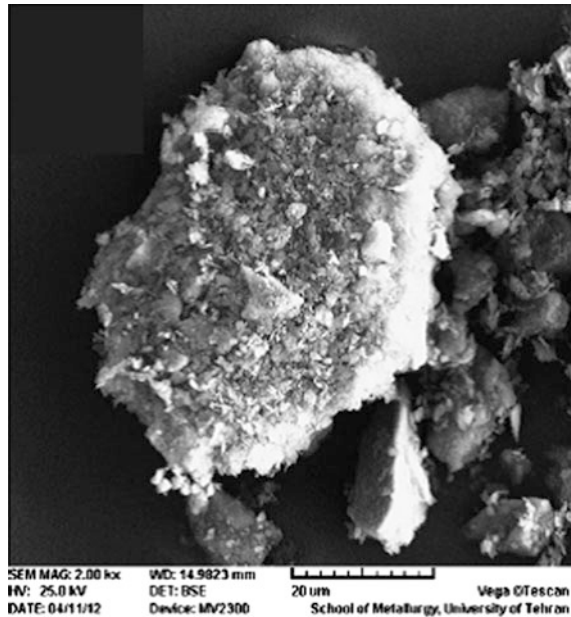


Fig. 3.6 SEM images of composites produced by the addition of (a) Al_2O_3 -Al and (b) Al_2O_3 -Cu masterpowders to A356 matrix [29]

Fig. 3.7 SEM image of Al–50 % alumina powders after 3 h of milling and then extra milled for 3 h with Mg powders [8]



taken into account. It was also reported that longer milling time led to higher oxidation of metallic powders, which may reduce the efficiency of the strengthening effect of the milled powders.

Magnesium was also introduced as a wetting agent in the composite via master powders in the A206/5 vol.% Al_2O_3 composite fabricated by Tahamtan [8]. 100 nm Al_2O_3 particles were incorporated through simple stir mixing, after a pre-milling phase with Al and Mg micro sized powders, with and without cold pressing (Fig. 3.7). For comparison, composites reinforced with rough alumina particles as well as with micrometric reinforcing particles were also produced. Powders were dispersed at 745 °C through the vortex generated by a graphite impeller (rotating at 1200 rpm for Al_2O_3 and 400 rpm for master powders). Depending on the kind of reinforcement (alumina/milled powders), particles were dispersed for 15–30 min. SEM microstructural analysis revealed that adding pure alumina through simple stir casting induced high porosity and agglomeration, especially in the case of nanometric particles. On the contrary, the use of pre-milled master powders strongly diminished the porosity content, reaching the minimum value in the case of the cold-pressed powders and enabled to obtain a more uniform particle distribution (Fig. 3.8). Mechanical properties of the composite reinforced with pre-milled powders were higher than the ones of the pure- Al_2O_3 reinforced matrix, especially in the case of cold pressed powders, which induced the maximum UTS and YS values.

Carbon based nano-reinforcement. Carbon nanofibers (CNF) reinforced aluminium nanocomposites were fabricated by Oh et al. [15]. CNFs were coated with

mechanical properties with respect to the unreinforced alloy, including YS (+33 %), UTS (+55 %), elastic modulus (+17 %), and hardness (+23 %), while elongation to failure was reported to decrease.

Multi walled carbon nanotubes (MWCNTs) were used by So et al. [17] to produce an A356 Al based nanocomposite. Due to the low wettability between aluminium and nanotubes, SiC coating on the nanotubes was employed. From literature [30, 31], the contact angle between aluminium and SiC is lower than that of aluminium and carbon substrate. SiC is supposed to improve the interfacial strength between matrix and reinforcement by the generation of covalent bonds. As the formation of the detrimental Al_4C_3 phase is supposed to occur when CNTs come in contact with the Al–Si matrix, it is preferable that the SiC layer is generated prior to the mixing of aluminium matrix and CNTs. Multi-walled CNTs were ball milled with Si powders for 10 h at 230 rpm (Figs. 3.10 and 3.11).

Composites were then produced by three steps: ball milling of SiC-CNTs and pure Al powders, stir casting of pre-milled powders in molten A356 alloy (500 rpm in vacuum) and die casting. Tensile tests revealed that with 1 wt% of coated CNTs, UTS, YS and elastic modulus increased by 15, 25 and 79 % respectively, when compared to the A356 alloy. On the contrary, elongation to failure decreased from 2.8 to 1.7 %. Hardness was measured after T6 heat treatment, showing that nanosized reinforcement acted as obstacles for solute dissolution, as higher temperatures are required to complete the solution treatment.

Li et al. [32] utilized high pressure die casting process (Fig. 3.12) to produce Al-based composites reinforced with CNTs. MWNTs were wrapped in Al foils and put at the entrance of the die. The molten matrix (AlSi10 Mg alloy) was pushed into the die at 250 m/s, as to obtain a turbulent flow to disperse MWNTs. Tensile tests showed that 0.05 wt% of MWNTs induced a sensible increase of both tensile stress and elongation to failure as compared to the unreinforced alloy, of 8 and 27 %, respectively. No carbide formation was observed through XRD measurements due to the low content of MWNTs and also probably due to the brief contact time between MWNTs and Al melt before solidification.

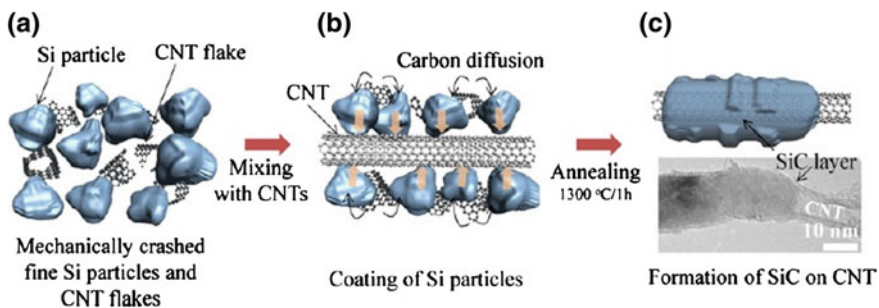


Fig. 3.10 Schematic of CNT coating procedure: (a) mechanically crushed Si particles and CNT flakes, (b) coating of Si particles on CNT and (c) TEM image of SiC layer on a CNT [17]

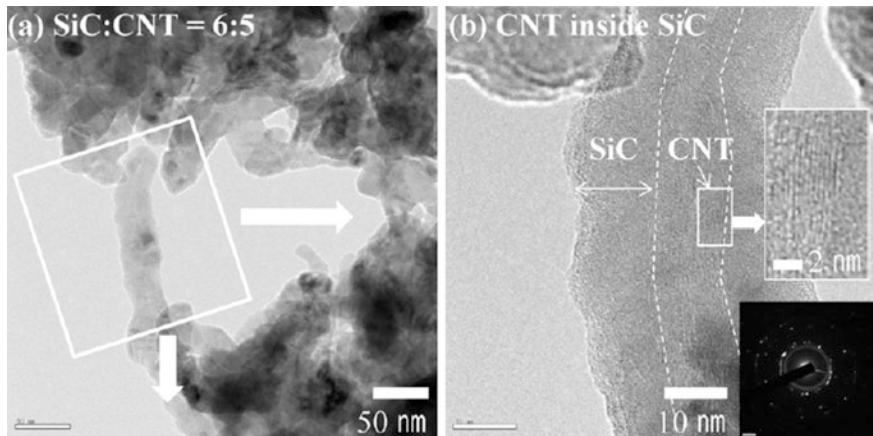


Fig. 3.11 (a) TEM images of SiC layer on CNTs and (b) SiC-CNT structure [17]

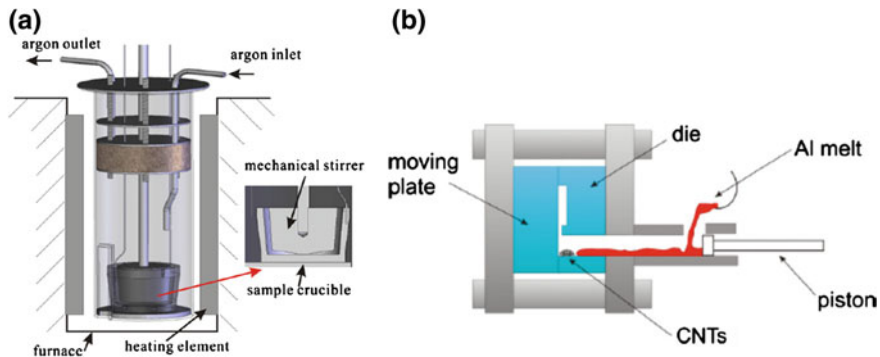


Fig. 3.12 Schematic of (a) melt stirring equipment and (b) high pressure die casting process for CNT-Al composites fabrication [32, 34]

3.1.3 Mg-Based Nanocomposites

Al_2O_3 reinforced Mg-based nanocomposites were fabricated by Habibnejad-Korayem et al. [33] through stir casting process. Weight fractions of 0.5, 1 and 2 % of 100 nm alumina nano-particles were added to pure Mg and AZ31 magnesium alloy using a Mg–8 wt% Al_2O_3 nano-composite master alloy. The molten composite was stirred for 2 min using a stainless steel rod. A uniform distribution of the Al_2O_3 nano-particles induced a refined grain structure of the cast materials (Fig. 3.13) and decreased the coefficient of thermal expansion (CTE), improving the dimensional stability of both pure magnesium and AZ31 alloy. Some cast samples were hot rolled and annealed, as to investigate the pinning effect of nanoparticles on the recrystallization and consequent mechanical behavior.

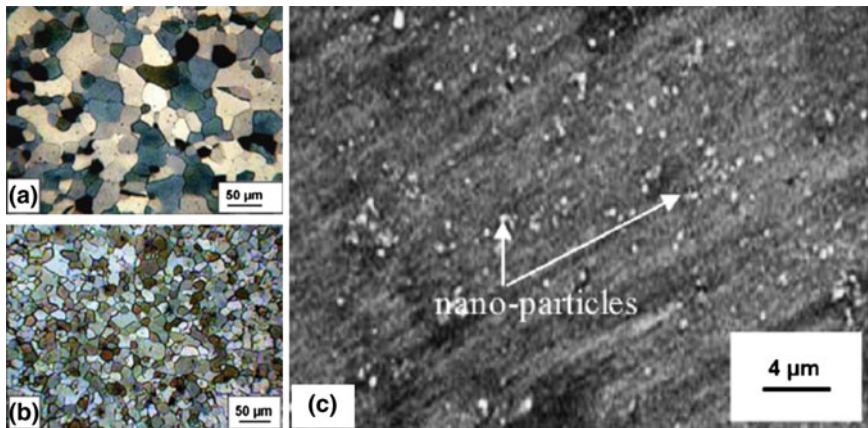


Fig. 3.13 Optical images of (a) pure Mg and (b) 2 wt% Al_2O_3 composite showing the grain refining effect of nanoparticles after hot rolling and full recrystallization; (c) SEM image of 2 wt% Al_2O_3 -Mg as cast composite [33]

Mechanical characterization of the composites revealed that the presence of nanoparticles significantly increased yield stress and tensile strength. The highest mechanical properties of both Mg and AZ31-based composites were obtained with 2 wt% of nano- Al_2O_3 . However, compared to the monolithic matrix, alumina particles induced a noticeable reduction in the ductility of the composites.

Carbon based nano-reinforcement. Magnesium matrix nanocomposites based on AZ91 alloy with carbon based reinforcement (multiwall carbon nanotubes, MWCNTs) were produced by Li et al. [34] by a two-step process. In the first production stage, a copolymer was used to pre-disperse MWCNTs on Mg alloy chips surface, by ultrasonic vibration in an ethanol based solution. After drying, the Mg chips covered by the MWNTs were melted (650 °C) and stirred at 370 rpm for 30 min. A quite successful dispersion of MWCNTs on the surfaces of the Mg alloy chips was achieved. Mechanical properties (compressive testing) have been significantly improved by the addition of a small amount of MWCNTs (0.1 wt%) with respect to the unreinforced AZ91 matrix. Compared to the AZ91 Mg alloy, the compression at failure of the MWCNT/Mg composite was improved by 36 %, yield strength by 10 % while the ultimate compressive strength was improved by 20 %.

The same processing was applied by Li et al. [32] to produce MWCNT-AZ91D composites reinforced with different CNTs fractions, that is 0.1, 0.5 and 1 wt%. Compression at failure and ultimate compressive strength were increased, comparing to the AZ91 matrix; by adding 0.1 wt% of MWCNTs, their enhancement was reported to be respectively of 40 and 20 %. On the contrary, no noticeable enhancement of compressive yield strength was reported. Further, compression properties did not change significantly by increasing the amount of MWCNTs, due to the fact that in 0.5 and 1 wt% composites MWCNTs were not uniformly pre-dispersed, inducing agglomeration (Fig. 3.14) and tendency of CNTs to be segregated at the top or at the bottom of the melt.

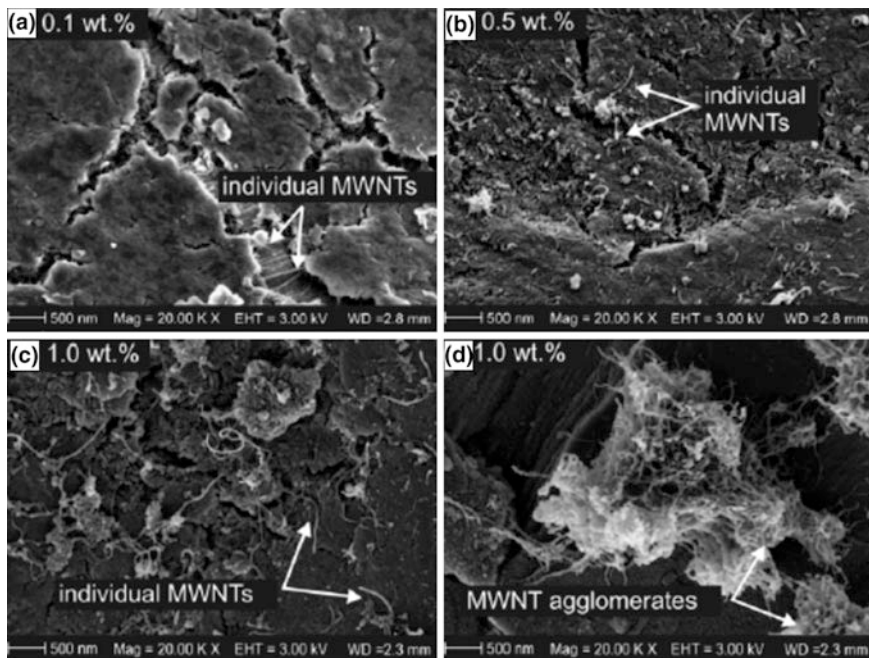


Fig. 3.14 SEM images of MWNTs dispersed on the surface of AZ91 chips in weight fraction of (a, b, c) 0.1, 0.5 and 1 % and (d) agglomerates of MWCNTs found on 1 wt% Mg chips [32]

3.2 Compocasting

3.2.1 Process Description

Semi-solid state processes are of great interest in MMNCs production as they are thought to help nanoparticles incorporation and distribution in the metal matrix [35]. As already mentioned in Sect. 2.3, among these processes, compo-casting technique is probably the most widespread one. Compocasting is reported to induce a relatively uniform distribution of the reinforcing phase, as well as to obtain good wettability between particles and matrix [36, 37], one of the most critical issues for liquid state processes such as the traditional stir casting route [4, 5, 18, 20, 38, 39]. Since in the semisolid state the metal temperature is lower than in the liquid state, feeding nanoparticles into the semi-solid alloy avoids the severe oxidation and burning of nanoparticles, despite their high surface area [35]. Moreover, the viscosity of the semisolid metal, higher than in the liquid state, depends on the volume fraction of solidified metal, which in turn depends on the melt temperature. Therefore, through temperature control, a suitable viscosity can be tuned as to prevent nanoparticles from floating or precipitation settling [35]. Despite wettability issues appear to be improved through semi-solid processes, porosity and particle

clustering may still be present and negatively affect mechanical properties of the semi-solid processed composites. Therefore, secondary processes such as forging, hot extrusion and roll bonding may be applied on cast MMNCs as to eliminate voids and to disaggregate clusters [36, 40–43], as well as ultrasonic processing is often applied to achieve a more uniform particle dispersion [35, 40, 44–47].

3.2.2 Al-Based Nanocomposites

The first reported attempt to produce an Al-based composite reinforced with submicron-size particles through a semi-solid state processing route was realized by Kawabe et al. in 1999 [21]. SiC particles with a diameter of 0.3 μm were incorporated into AA6061 matrix by semi-solid state vortex method, consisting of deagglomeration of the powders, Ca addition and semi-solid state stirring. The authors affirmed the produced composites were characterized by absence of agglomerated particles, and related the clustering tendency of particles to the yield of SiO_2 layer on the SiC particles, as well as to the void ratio of the reinforcing powders.

More recently, Abbasipour et al. [37] produced an A356-based CNT reinforced composite through compocasting technique, by adopting a CNT pre-treatment so as to solve wettability issues related to nanosized particles, i.e. reinforcement agglomeration as well as gravity segregation. In particular, MWCNTs were deposited onto aluminium micrometric particles by Ni–P electroless plating technique (Fig. 3.15). Aluminium coated nanotubes were then injected into the matrix at 700 $^{\circ}\text{C}$ through an injection tube aided by an argon gas flow, and stirred by a coated steel impeller (Fig. 3.16). Mg was added to the melt in 1 wt% fraction to increase the wettability of nanoparticles. The slurry, containing 2 vol.% of CNTs, was then cast in semisolid conditions (at 0.15 and 0.3 solid fractions, obtained by continuously cooling to 610 and 601 $^{\circ}\text{C}$), as well as at the liquid state (700 $^{\circ}\text{C}$) for comparison. Beyond Mg action, wettability of Al–CNT system was increased by the Ni–P coating on individual CNT, inducing a good bonding with the matrix. Grain

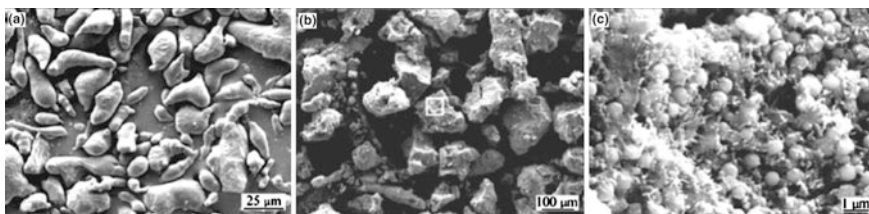
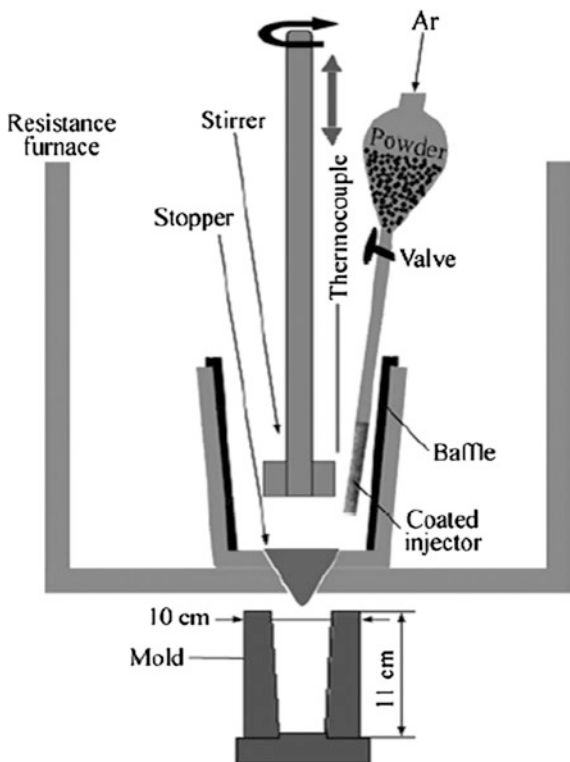


Fig. 3.15 SEM images of aluminum particles: (a) before coating, (b) after coating and (c) higher magnification of area marked by rectangle in (b) [37]

Fig. 3.16 Compocasting experimental set-up [37]



refinement induced by CNTs in liquid cast samples was reported, as well as a reduction of average equivalent diameter of α particles in semi-solid composites, as compared to their respective matrices. Hardness of the semisolid processed samples was found to be higher than that of their unreinforced matrix, as well as higher than that of liquid processed composites due to both the reinforcing action of CNTs and the induced grain refining effect. With respect to the unreinforced matrix, the A356-based MWCNT reinforced composite realized by compocasting presented an increase in mechanical properties (YS, UTS, E) and retaining good ductility, both at room and high temperature [48].

El-Mahallawi et al. [49] reinforced the A356 matrix with 50 nm γ - Al_2O_3 particles by a compocasting technique. Alumina particles were wrapped up in aluminium foil packs and pre-heated at 200 °C, before being dipped into the semi-solid slurry at 590–605 °C and stirred for 1 min. Composites with 1, 2, and 3 % wt% of Al_2O_3 were produced. A decrease in the dendrite arm length was reported, as well as a decrease of inter-lamellar spacing of eutectic silicon phases (Fig. 3.17).

Nanoparticles addition up to 3 wt% induced an increase in tensile properties and in elongation to failure both in the as cast and in the T6 state with respect to the

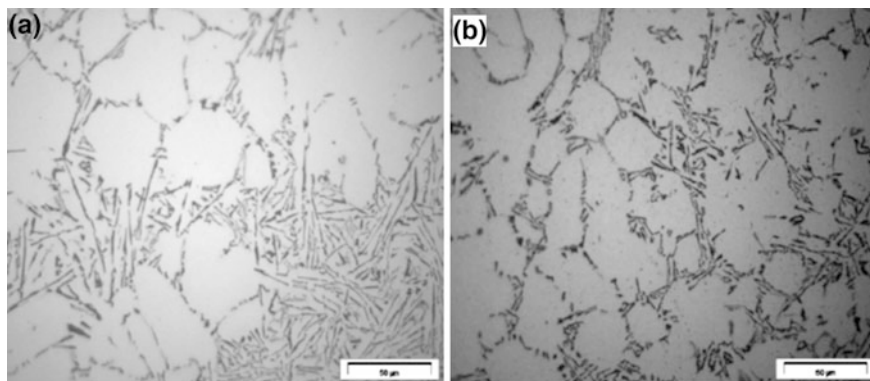


Fig. 3.17 Optical images of (a) A356 unreinforced matrix and (b) A356-1 wt% composite showing the refining effect of nanoparticles [49]

unreinforced alloys, with a maximum at 2 wt%. However, the unreinforced matrix showed the highest hardness after T6 heat treatment. Since no Mg was detected in the eutectic phase of nano-reinforced A356 alloy, it was inferred that the presence of nanoparticles may have prevented the formation of Mg_2Si precipitates.

The thixoforming technology has also been considered for the production of Al-MMNCs by preparing feedstock material with the help of ultrasonic processing [47, 50]. Kandemir et al. [47] made an attempt to produce a thixoforming feedstock material based on the A356 alloy reinforced by β -SiC nanoparticles (20–30 nm). A356-SiC feedstock was prepared by adding 0.2 wt% SiC to the matrix through ultrasonic method by two different feeding methods (i) double capsule method that involves wrapping up of nanoparticles into two AA1200 foils so as to induce a gradual release into the melt, and (ii) crucible placement approach, that consists of placing the particles on the bottom of the melting crucible. Together with ultrasonic processing, mechanical mixing was performed aiming to disperse nanoparticles and to force clusters to pass under the ultrasonic probe. Feeding of nanoparticles has been considered to be challenging as Al foil capsules did not fully melt, probably due to the oxide layer on the Al-foil, whereas the particles fed by crucible placement approach remained on the bottom of the crucible. Ultrasonic processing seemed however to be promising in producing thixoforming feedstock material as the samples treated at 650, 665 and 700 °C presented globular microstructures.

Sajjadi et al. [51] made a comparative study on compocasting process parameters as to evaluate the effects of stirring speed as well as particle dimension (micro vs. nano) for the semi-solid production of Al-based composites. Al_2O_3 micro (3, 5 and 7.5 wt%) and nano (1, 2, 3 and 4 wt%) particles were injected by argon gas into A356 matrix at semi-solid state, after being pre-heated at 300 °C. Mechanical stirring was performed at different speeds (200, 300 and 450 rpm). The produced composites presented non-dendritic structure, and alumina nanoparticles tended to move to inter-dendritic regions, being surrounded by silicon eutectic (Fig. 3.18).

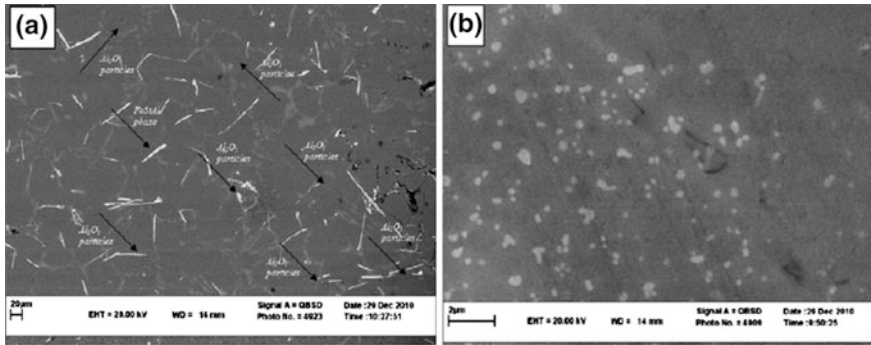


Fig. 3.18 SEM images of A356 composite containing 2 wt% of nano- Al_2O_3 at (a) low and (b) high magnification [51]

The particles were uniformly dispersed within the matrix up to 3 wt% for nano and 5 wt% micro particles, while further alumina additions caused agglomeration. As a result, by increasing particles weight fraction and decreasing particle size led to a hardness increase. Also, increasing stirring speed and time up to 300 rpm and 30 min led to hardness homogeneity optimization.

As reported in Sect. 3.1, several authors compared the production of Al-based nanocomposites through stir casting technique and compocasting. Generally, compocast composites were reported to contain lower porosity, finer grains and better mechanical properties than those processed in the fully liquid state [8, 27, 52].

Compocasting process has also been coupled with secondary processes. Ardakani et al. [36] applied roll bonding to compocast SiC-A356 MMNC. The particles (<100 nm), were added to the matrix at the semi-solid state at 607 °C (0.2 solid fraction) through argon gas. As cast specimen were machined into rectangular samples, annealed at 540 °C for 2 h, so as to improve their rolling capacity and were then subjected to cold rolling (reduction of 62 %). Then CARB process (Cross Accumulative Roll Bonding) was then applied (Fig. 3.19). Initially, the surface was prepared by degreasing in acetone and scratch brushing. Two strips of composite were stacked over each other and subjected to roll bonding. Eight cycles at room temperature were performed by rotating the samples to 90 °C after each rolling cycle. While the as cast specimen showed high level of porosity, MMNCs processed through CARB process was reported to decrease the porosity significantly after three cycles of process, owing to the applied shear and compressive forces which induced the aluminium matrix flowing and filling the voids. By increasing the number of passes, a more uniform distribution of nanoparticles is achieved, thereby enabling to eliminate SiC clusters in the 8 cycles (Fig. 3.20). A significant increase in mechanical properties (UTS, YS and elongation to failure) as compared to the unreinforced matrix was obtained, owing to the ultra-fine grained (UFG) microstructure induced by the CARB process.

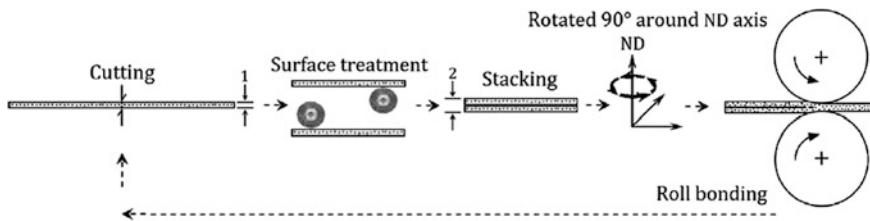


Fig. 3.19 Schematic of CARB process [36]

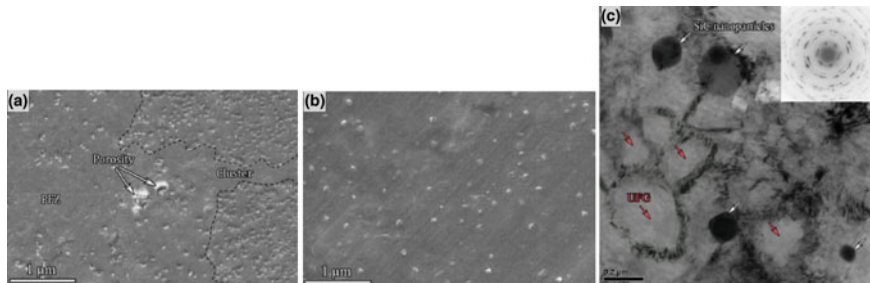


Fig. 3.20 SEM images of (a) as cast samples and eight cycles CARB processed samples by (b) SEM and (c) TEM microscopy [36]

3.2.3 Mg-Based Nanocomposites

Similar to that of Al-based nanocomposites, the use of semisolid technology can be part of production processes of Mg-based MMNCs, in which different techniques are combined. In particular, nanoparticles are often fed and stirred when the alloy is in its semisolid state so as to take advantage of their better wettability with the semisolid alloy. To this end, Nie et al. [44–46], incorporated 1 vol.% of SiC nanoparticles to AZ91 Mg alloy kept in its semisolid state; the slurry was then mechanically stirred before increasing the temperature so as to bring the alloy in liquid state after which ultrasonic vibration was employed. It was reported that while semisolid stirring was effective in incorporating nanoparticles and facilitating macroscopic dispersion, ultrasonic stirring in liquid state was necessary to break nanoparticle clusters. However, by increasing the semisolid stirring time from 5 to 25 min, the viscosity of molten magnesium melt was found to increase thus decreasing the effect of the subsequent ultrasonic vibration, resulting in a higher degree of particle agglomerates, as shown in Fig. 3.21.

In a similar two step processing, combining semisolid-state mechanical mixing and liquid-state ultrasonic vibration, a AZ31 alloy was successfully reinforced with a bimodal size SiC particulates (1 vol.% of nano SiCp and 14 vol.% of micron SiCp), before hot extrusion [40]. Furthermore, Chen et al. [35] was able to incorporate a very high volume fraction of nanoparticles by combining this two

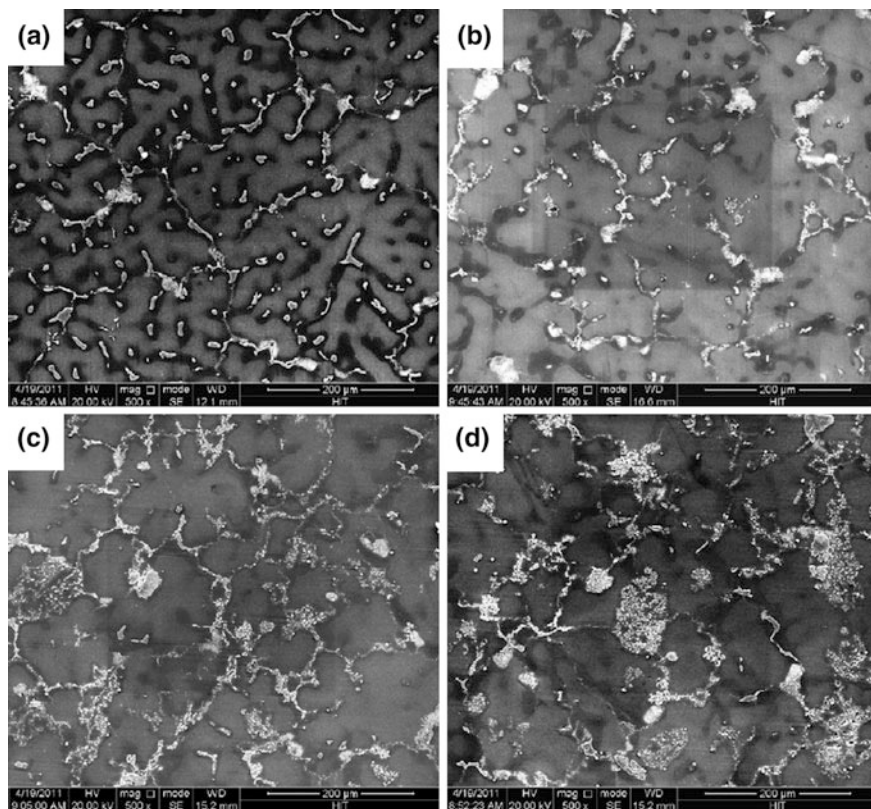


Fig. 3.21 SEM micrographs of (a) AZ91 alloy; SiCp/AZ91 nanocomposites realized by semisolid stirring and ultrasonic processing stirring for (b) 5 min, (c) 10 min and (d) 25 min [44]

techniques. In particular, 6 vol.% of SiC nanoparticles were fed into Mg–18 wt% Zn alloy. It was reported that semisolid-state mechanical stirring at the optimal conditions (1400 rpm, 575 °C, 25.4 mm diameter rotating blade) enabled driving and trapping nanoparticles into the semisolid metal due to its high viscosity, while vigorous stirring refined the size of nanoparticle clusters [35], before applying ultrasonic processing (discussed in Sect. 3.3) was to disperse the nanoparticles in the liquid state.

Deng et al. used semisolid stirring to introduce 200 nm SiC particles to AZ91 alloy prior to hot forging and hot extrusion [41–43]. The AZ91 alloy was first allowed to reach a molten state (720 °C) then cooled to the semisolid state (590 °C). SiC particles were then added (0.5, 1, 1.5, 2, 3 and 5 vol.% [43]) and the melt was stirred for 30 min, before reheating to 720 °C for casting. The melt was poured into a preheated steel mould (450 °C) and solidified under a 100 MPa pressure. As-cast ingots were forged at 420 °C with 50 % reduction and subsequently extruded at 370 °C with the ratio of 1:16 at a constant ram speed of 15 mm/s. After

secondary processing, it was reported that the composite was characterized by a relatively uniform reinforcement distribution, significant grain refinement and presence of minimal porosity. With respect to the unreinforced matrix, the composite showed improved thermal stability, micro-hardness and elastic modulus. The 0.2 % yield strength increased with the increasing content of submicron-SiC particulate (up to 2 vol.%), but decreased with further increase due to excessive particle clustering. The presence of agglomerated submicron-SiC particulates caused particle cracking and low UTS.

3.3 Ultrasonic Assisted Casting

3.3.1 *Process Description*

In liquid-state processing of MMNCs a uniform distribution of nanoparticles in metal matrix is rarely achieved even at low reinforcement volume fractions. This is due to the reason that nanoparticles have the tendency to float or settle due to the poor wettability with the molten metal and form clusters due both to the attractive van der Waals force and the lack of a repulsive force. Furthermore, they are normally pushed to the grain boundary by solidification fronts [53].

It is known that high-intensity ultrasonic waves are able to generate relevant non-linear effects in liquids, namely transient cavitation and acoustic streaming [54, 55]. Acoustic streaming is a macroscopic flow effect showing return circulation due to acoustic pressure gradient within the bulk of the liquid and hence found to be effective in stirring [56]. In acoustic cavitation, cyclic high-intensity ultrasonic waves induce the formation, growth (during the negative pressure cycle), pulsating, and collapsing (during the positive pressure cycle) of tiny bubbles in the liquid phase. At every cavitation cycle, bubbles implasively collapse in less than 10^{-6} s, producing micro “hot spots” that can reach temperatures of about 5000 °C, pressures of about 1000 atm, and heating and cooling rates above 10^{10} K/S during microseconds transient [57].

Transient cavitation and acoustic streaming can be exploited in metal casting processing to achieve microstructures refining, degassing of liquid metals, and particle dispersive effects. The application of ultrasonic cavitation based dispersion of nanoparticles in metal melts was introduced in 2004 by Li and co-workers for magnesium [58] and for aluminium alloys [6, 59]. As concerning the dispersion of nanoparticles, it is believed that air or vapour entrapped inside cluster voids could serve as nuclei for cavitation. Transient cavitation could be strong enough to break up fine particle clusters, dispersing them more uniformly in the molten matrix with the help of acoustic streaming, as shown in Fig. 3.22 [58]. Moreover, the pressure achieved during cavitation could produce impacts that can remove or desorb the gases or other impurities on the surface of the ceramic particles. The wettability

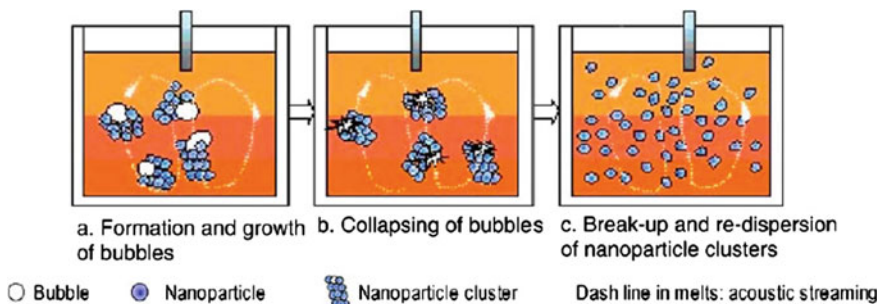


Fig. 3.22 Schematic of the cavitation and streaming effects for nanoparticle dispersion and wettability enhancement in metal melts [58]

between the molten metal and particles is then enhanced significantly due to both local increase in temperature in the micro hot-spots of the molten metal and cleaning of the particle surface [56]. Relevant studies, developments and findings concerning the application of the techniques to Al- and Mg-based MMNCs are discussed in the following.

3.3.2 Al-Based Nanocomposites

Li and co-workers [6] demonstrated the feasibility of producing bulk Al-based nano-composites with 0.5, 1.0 and 2.0 wt% of nano-sized SiC particles by ultrasonic-assisted casting method. Spherical β -SiC nanoparticles (with average diameter ≤ 30 nm) were successfully dispersed in A356 (Al-Si-Mg) matrix by means of a titanium waveguide (sonotrode) coupled with a 20 kHz, 600 W ultrasonic converter dipped into the melt for ultrasonic processing at 610 °C. SiC particles were added into the melt during the process from the top of the crucible and the Al-melt pool was protected by argon gas. Although SiC possesses a specific density slightly higher than molten Al, particles tended to float on the melt surface, due to the high surface tension of the melt and the poor wettability between the particles and the melt. It was found that the acoustic streaming, induced by applying high intensity ultrasonic waves, was effective in trapping the nanoparticles into the melt, while acoustic cavitation was deemed to be able to break nanoparticle clusters and disperse single particles in the melt, although small clusters could still be observed (Fig. 3.23). The yield strength of A356 alloy was found to increase more than 50 % with 2.0 wt% of SiC nanoparticles.

In a later work, Yang et al. [60] introduced the use of Niobium-based sonotrode, that can withstand high processing temperature with minimum ultrasonic cavitation-induced erosion, and investigated the different feeding techniques for adding SiC nanoparticles into the A356 melt. Although demanding long ultrasonic processing time, adding nanoparticles into the melt was successful by manual handling

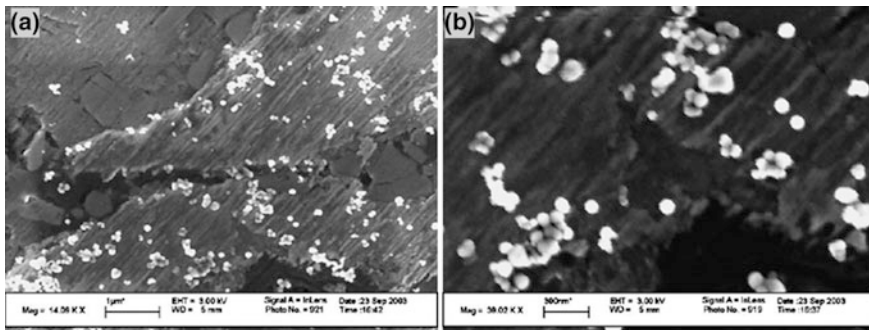


Fig. 3.23 Nano-SiC particle distribution in A356 matrix after ultrasonic assisted casting at different magnification (a, b) [6]

and mechanical delivery. The use of nano-SiC/micro-A356 master powders was unsuccessful due to strong oxidation of the Al phase and difficulties in melting the master powder compacts, while the use of a spray gun to feed nano-particles resulted in the formation of large clusters with low specific density which could not penetrate the melt surface.

Mula et al. [61] developed a non-contact ultrasonic casting method for dispersing ceramic nanoparticles in Al matrix, in which a mold is tightly fitted to an ultrasonic vibrating chamber and partially immersed in water so that the ultrasonic waves can effectively be transmitted to the mold. Commercially pure Al was melted and then poured in the mold together with 2 wt% Al_2O_3 nanoparticles (average size 10 nm). The mold was subjected to a 35 kHz vibration for 300 s, while a heater close to the liquid metal delayed solidification. The resulting nanocomposite comprised fairly continuous nano-alumina dispersed zones (NDZs) near grain boundaries, encapsulating alumina depleted zones (ADZs) (Figs. 3.24 and 3.25). Although the authors claimed to expect cavitation to occur, the effective ultrasonic energy density delivered to the molten metal was not discussed. A marginal increase in the elastic modulus was found, while a significant increase in the hardness (92 %), and tensile strength (48 %) with reduction in the ductility was measured in the nanocomposite with respect to those of the ultrasonically cast Al without reinforcement. In a later work, Mula et al. [62] applied cold and hot rolling to commercially pure Al reinforced with 2, 3.57 and 4.69 wt% of nanoparticles by the ultrasonic non-contact method, finding that the workability was reduced by increasing the weight percentage of reinforcement.

Choi et al. [63] applied ultrasonic cavitation based dispersion technique to fabricate nanocomposites based on Al-7Si-0.3 Mg alloyed with 0.5 wt% Cu, reinforced with 1 wt% of $\gamma\text{-Al}_2\text{O}_3$ nanoparticles. A niobium probe working at 20 kHz and a maximum 600 W power was used, while a double-capsulate feeding method was used to feed nanoparticles into the melt. Nanoparticles were wrapped with 0.0127 mm thin Al foil (alloy 1000), which was then rolled into a rod shape (first capsule); the Al foil rod was wrapped again with another thin Al foil with

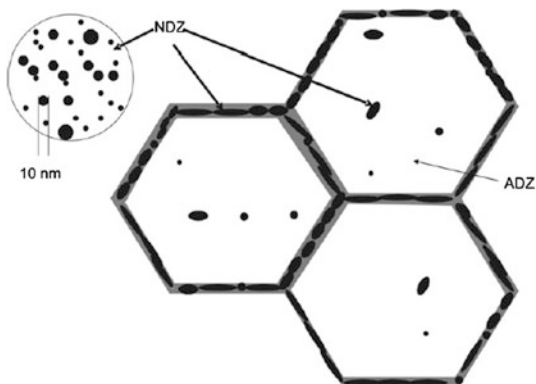


Fig. 3.24 Schematic representation of Al–Al₂O₃ nanocomposite microstructure obtained by ultrasonic assisted casting including nano-alumina dispersed zones (NDZs) and depleted zones (ADZs) [61]

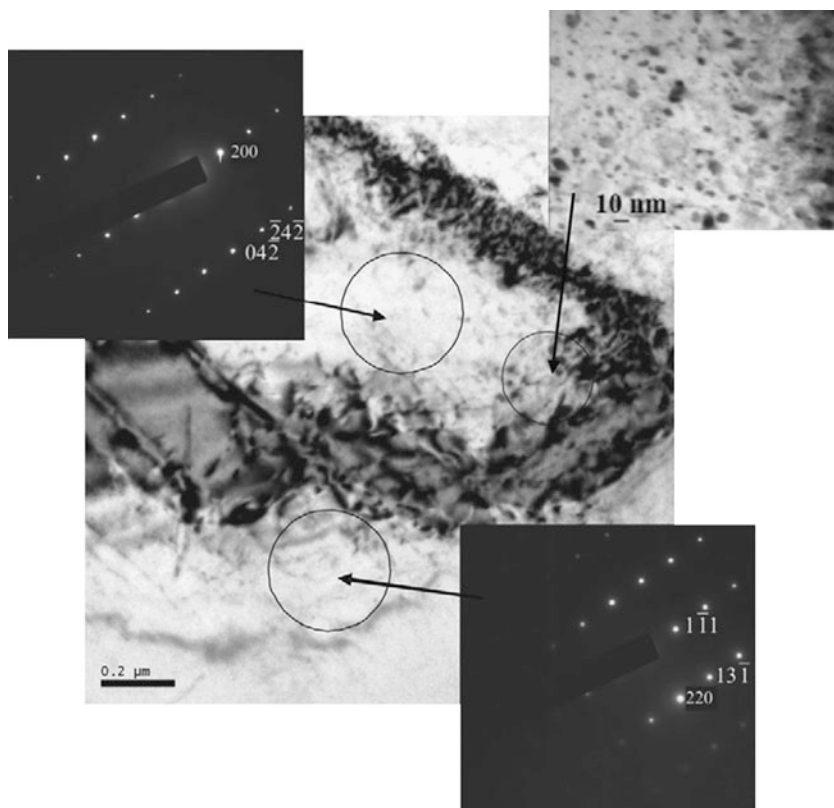


Fig. 3.25 Electron diffraction pattern of selected areas showing different grain orientation on two sides of a NDZ and particle distribution in the NDZ [61]

thickness of 0.0254 mm (second capsule). The gradual melting of the thicker wall of the capsule should allow nanoparticles to be gradually discharged into the melt. The tip of the niobium ultrasonic probe was inserted about 12.7 mm in depth into the melt kept at 700 °C and ultrasonic vibration with a frequency of 20 kHz and a peak-to-peak amplitude of 60 μm was applied while feeding pre-heated nanoparticle capsules. The melt was ultrasonically processed for 15 min for each Al foil capsule, for a total processing time of 45 min. Although some Al_2O_3 micro-cluster were still found in the matrix, it was shown that the combined addition of 0.5 % Cu with 1 % Al_2O_3 nanoparticles significantly increased the yield strength, tensile strength, and ductility of the as-cast Al–7Si–0.3Mg alloy also due to refinement of primary α -Al and modification of eutectic Si and θ - CuAl_2 phases.

The ultrasonic assisted dispersion method was also applied to disperse 1–3 wt% fly ash particulate in the AA 2024 matrix [64]. Fly ash, available in large quantities as solid waste by product from combustion of coal in thermal power plants and generally composed of crystalline compounds such as quartz, mullite and hematite, glassy compounds and other oxides, was reduced to an average crystallite size of 23 nm by high energy ball milling (30 h) and mixed with pure Al-microparticle to enhance wettability. After powder mix addition to the melt through mechanical stirring, the ultrasonic Ti probe was inserted in the melt at 770 °C and operated at 20 kHz, 1 kW for 15 min. The process was successful in producing nanocomposites with increased hardness and compression strength.

The effect of different ultrasonic treatment temperatures was investigated by Su et al. [1] in the production of 1 wt% nano- Al_2O_3 /2024 composites [1]. Pure Al powder (particle size of 80–100 μm) and Al_2O_3 nano-powder (average diameter 65 nm) were mixed via ball milling in stearic acid and sintered. 2024 aluminium alloy was melted and maintained at 750 °C, prior to introduction of Al/ Al_2O_3 composite powder, which was stirred for 10 min by a multistage stirrer. After degassing the melt, ultrasonic vibration at 20 kHz was applied for 60 s with a ultrasonic power of 300 W, at 650, 670, 680 and 700 °C melt temperature. The primary α -Al phase resulted to be globular and refined; in particular, treating at 670 °C resulted in the finest microstructure, with an average grain size of 25 μm . The UTS and YS of the 1 wt% nano- Al_2O_3 /2024 composite were enhanced by 37 and 81 %, respectively. The refinement action could be related to the interaction of the ultrasonic vibration with primary α -Al and nanoparticles. It is known that introducing ultrasonic vibration into the solidifying melt, the ultrasonic acoustic flows facilitates the extraction of latent heat decreasing the temperature gradient in the solidification front, thus leading to instability at the liquid/solid interface [65]. In addition, ultrasonic vibration has a destructive effect on dendrites by causing fracture of their arms. Acoustic flows are able to carry away fragmented dendrite arms from their mother grains so that they can act as nuclei for new grains, giving rise to refined and uniform microstructures. Furthermore, since transient cavitation can break up the clustered particles, a portion of them act as nuclei during solidification [58]. In the model proposed by Su et al. [1] to describe the microstructural evolution of nano- Al_2O_3 /2024 composite melt during the solidification under the ultrasonic field, some Al_2O_3 particulates are captured by the growing grains so that

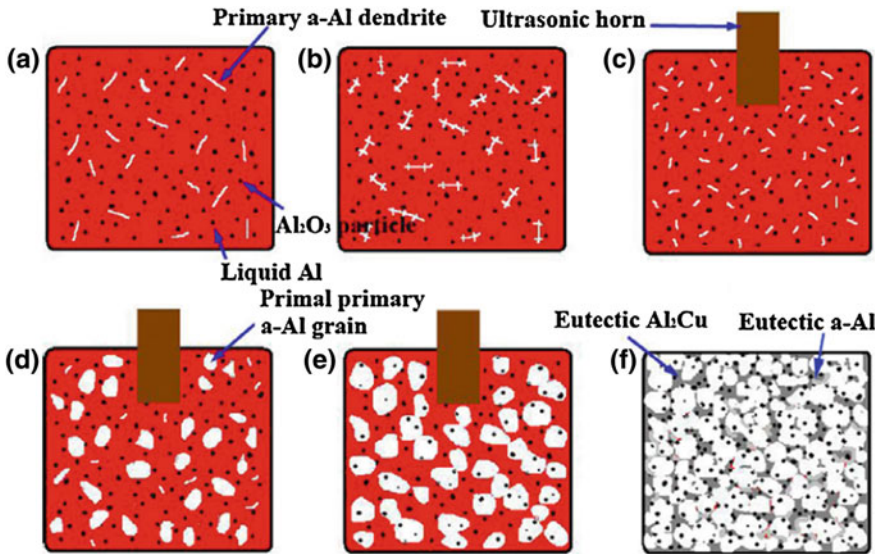


Fig. 3.26 Microstructure evolution scheme of nano- Al_2O_3 /2024 composite melt during the solidification under the ultrasound field: (a) formation of primary α -Al dendrites; (b) formation of dendrite arms; (c) breakage of the dendrites under the ultrasound field; (d) and (e) the growth of α -Al grains and (f) completion of the solidification [1]

when the temperature of the composite slurry decreases to the solidus temperature, the eutectic phase forms in the inter-grains regions and those Al_2O_3 particulates pushed by the growing grains will be surrounded by the eutectic (Fig. 3.26).

With the decrease of the melt temperature, the viscosity increases so that cavitation and acoustic streaming are prevented to occur, also considering that the presence of nanoparticles would increase the viscosity of the melt, too. In the absence of ultrasonic vibration, the Al_2O_3 nanoparticles are pushed to grain boundary or final solidification regions as a consequence of poor wettability (Fig. 3.27a–c), while under ultrasonic vibration during solidification some Al_2O_3 nanoparticles are distributed inside the grains and single nanoparticles are located along the grain boundaries, though some degree of clustering still exists (Fig. 3.27d–f).

3.3.3 Mg-Based Nanocomposites

Lan et al. [58] investigated the use of ultrasonic vibration to disperse 2 and 5 wt% of 30 nm SiC particles into molten AZ91D (Mg–Al–Zn) alloy. An ultrasonic power of 80 W from the transducer was used to treat the melt held at 620 °C. Although some small clusters (less than 300 nm) were still found, SiC nanoparticles were

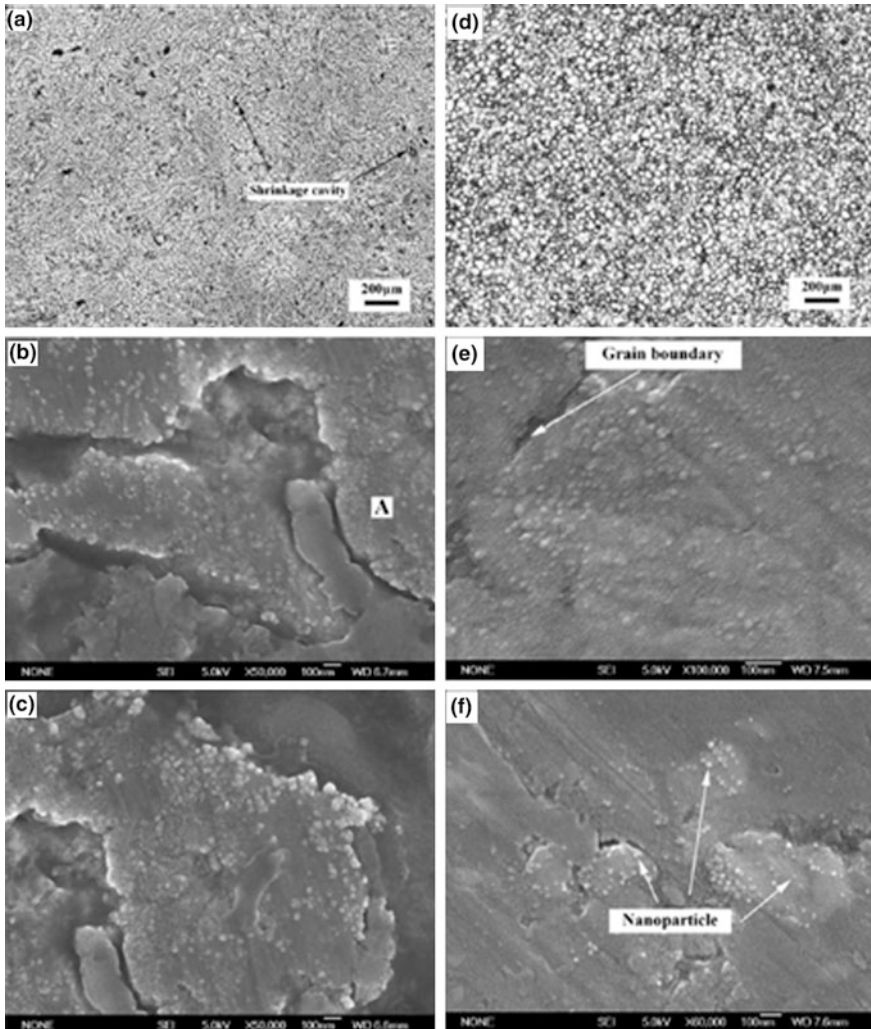


Fig. 3.27 Microstructures of nano-Al₂O₃/2024 composite in the normal casting condition: (a) Optical microstructure; (b) grain boundary; (c) high magnification of region A in (b); Microstructures of nano-Al₂O₃/2024 composite under the ultrasound field: (d) Optical microstructure; (e) grain inside and (f) grain boundary [1]

fairly distributed in the matrix. A comparison of particle distribution between stir casting and ultrasonic assisted casting is shown in Fig. 3.28. The presence of Mg₂Si compounds in the composite was related to the interfacial reactions during ultrasonic processing between Mg and the SiO₂ layer on the SiC nanoparticles surface, which normally is partially oxidized. Microhardness increased by 75 % compared to that of AZ91D matrix in the case of the AZ91D/5 wt% SiC composite.

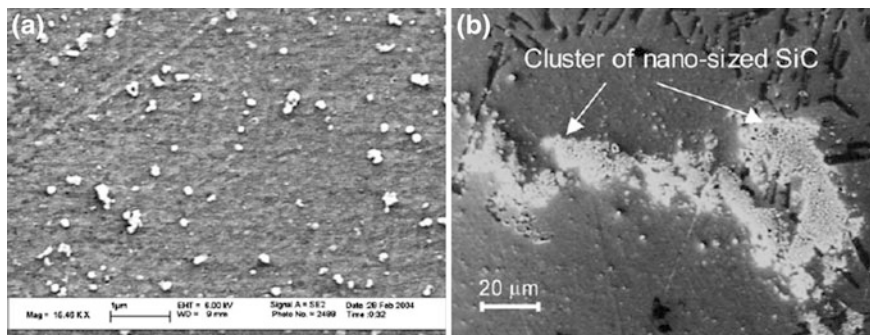


Fig. 3.28 Comparison of particle distribution in the AZ91 after (a) ultrasonic method and (b) stir casting [58]

Cao et al. [66] applied ultrasonic cavitation for the production of Mg–2Al–1Si and Mg–4Al–1Si based composites reinforced with 2 wt% of SiC particles (50 nm). A niobium ultrasonic probe was inserted about 25–31 mm into the melt at 700 °C, generating a 17.5 kHz ultrasonic wave with a maximum 4.0 kW power, while SiC particles were fed into the Mg alloy melt through a steel tube. The microstructural characterization showed that the grain size of both Mg–2Al–1Si and Mg–4Al–1Si was refined by the addition of SiC nanoparticles and ultrasonic treatment. Some micro-clusters were located along the grain boundaries, while single SiC nanoparticles were mostly embedded inside the grains. A good interface bonding between SiC nanoparticles and Mg–(2, 4) Al–1Si metal matrix was observed through TEM, excluding the formation of an intermediate phase. UTS and YS of the Mg–2Al–1Si/2 % SiC and Mg–4Al–1Si/2 % SiC nanocomposites were improved significantly, retaining a ductility comparable to that of the magnesium alloy matrix. Cao et al. also successfully fabricated Mg–4Zn/1.5 wt% SiC, Mg–6Zn/1.5 wt% SiC and Mg/0.5–4 wt% SiC nanocomposites [66–68].

Cicco et al. [69] demonstrated that by ultrasonically dispersing SiC nanoparticles in magnesium-zinc alloys (Mg–4Zn/1.5 wt% SiC, Mg–6Zn/1.5 wt% SiC, Mg–8Zn/3 % SiC) both ductility and strength of the matrix were significantly enhanced. The ductility enhancement was attributed to the influence of ceramic nanoparticles on intermetallic phases, in particular, suppressing the formation of microscale Mg_7Zn_3 and Mg_2Zn_3 in favor of a nanoscale MgZn_2 phase. The latter was identified among SiC nanoparticle clusters in hypoeutectic compositions, as verified by thermal analysis, TEM and XRD (Fig. 3.29). From this work it can be conceptualized that rather than the direct strengthening effects of nanoparticles, the properties of metallic materials can be significantly improved, by utilizing nanoparticle induced phase manipulation.

In the ultrasonically cast AZ91/SiC nanocomposite, a difference in the distribution and morphology of intermetallic phases with respect to the unreinforced alloy was observed by Nie et al. [70, 71]. SiC nanoparticles of volume fraction 0.5, 1 and 2 % (average size 60 nm) were introduced in the molten matrix under

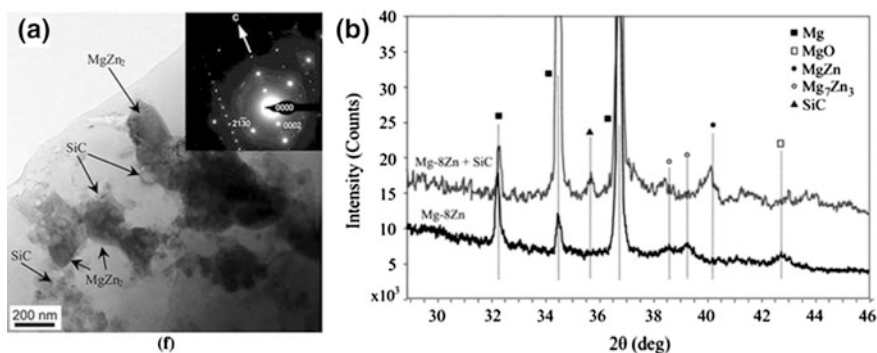


Fig. 3.29 (a) TEM images showing MgZn₂ phase in Mg-6Zn/1.5 wt% SiC with SAED pattern of the MgZn₂ area shown in the inset; (b) XRD results from Mg-8Zn and Mg-8Zn/3 wt% SiC samples quenched from 550 °C [69]

CO₂/SF₆ atmosphere, which was then treated with ultrasonic vibration at 700 °C, at 480 W and 20 kHz for 20 min, while a 100 MPa pressure was applied during solidification. The composite was characterized by grain size reduction, as well as different distribution and morphology of Mg₁₇Al₁₂ phase, which changed from coarse plates in the AZ91 alloy to lamellar precipitates in the composites. When compared with the matrix, increasing the nano SiC content induced a decrease in grain size, and refinement in the Mg₁₇Al₁₂ phase. SEM and TEM observations revealed that most of the particles were homogeneously distributed within the matrix in composites containing 0.5 and vol.% of SiC (Fig. 3.30a–b). As a result, YS, UTS and elongation to fracture were enhanced. On the contrary, samples containing 2 vol.% of SiC presented an increased quantity of agglomerates along the grain boundaries (Fig. 3.30c), leading to a decrease of both UTS and ductility.

Erman et al. [72] prepared pure Mg reinforced with 2 wt% SiC nanoparticle (n-SiC) by ultrasonic cavitation-based dispersion method. Microstructural analyses of the as-cast specimens showed a 60 % reduction in grain size in the average grain size of the composite (~70 μm when compared to 180 μm for pure Mg). TEM studies [72] showed good local dispersion of SiC nanoparticles, with few small largely spaced agglomerates and clean interface between SiC nanoparticles and the Mg matrix (Fig. 3.31).

Nie et al. [44] developed a process for producing nano-SiC reinforced AZ91 composite by combining semisolid stirring and ultrasonic treatment of the melt, as shown in Fig. 3.32. The initially molten matrix was brought to 590 °C (semi-solid state) prior to adding 1 vol.% of particles (60 nm) which were pre-heated at 550 °C. The semisolid slurry was mechanically stirred from 5 to 25 min before ultrasonic treatment in fully liquid state (700 °C) for 20 min. The composite was subsequently cast at 720 °C and solidified under a pressure of 100 MPa. A decrease in grain size with respect to the AZ91 matrix was reported in the composite stirred for 5 min. Some particle agglomerates were observed along the matrix grain boundaries, which increased in quantity with increasing stirring time, while increasing the

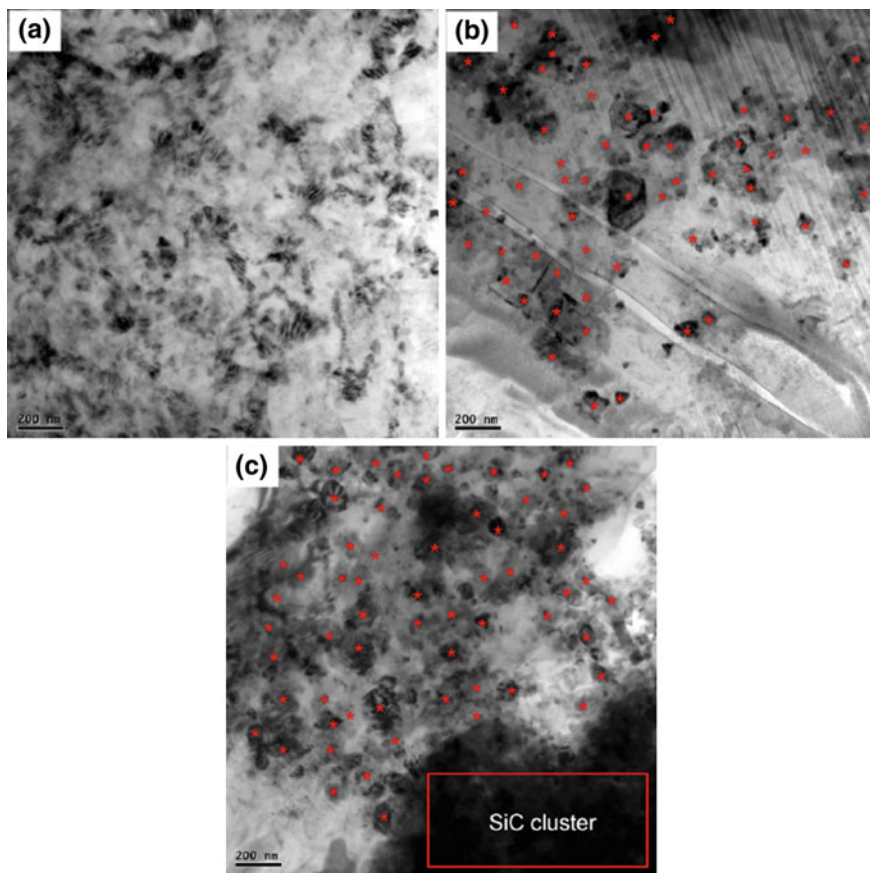


Fig. 3.30 TEM micrographs of (a) 0.5 vol.% SiC_p/AZ91 nanocomposite, (b) 1 vol.% SiC_p/AZ91 nanocomposite and (c) 2 vol.% SiC_p/AZ91 nanocomposite [71]

stirring time had negligible effect on the grain size of matrix alloy. Comparing to the AZ91 matrix, YS was maximum in the sample stirred for 10 min, while UTS increased about 45 % in the case of the composite stirred for 5 min. Elongation to fracture was noticeably enhanced with 5 min of stirring (from about 2 to 7 %) while it decreased for higher stirring times.

Semisolid-state mechanical mixing and liquid-state ultrasonic processing was also successfully used by Chen et al. [35] to produce an unprecedented high volume fraction reinforced nanocomposite. The Mg–18Zn matrix was reinforced by 6 vol.% of SiC nanoparticles, added to the semi-solid matrix through mechanical stirring performed at 1400 rpm and 575 °C. Ultrasonic processing (20 kHz, peak to peak vibration amplitude of 60 μm) was then applied to the composite at the liquid state. Separated nanoparticles were distributed uniformly in both the magnesium matrix and the intermetallic phase (Fig. 3.33), although submicron clusters composed of a

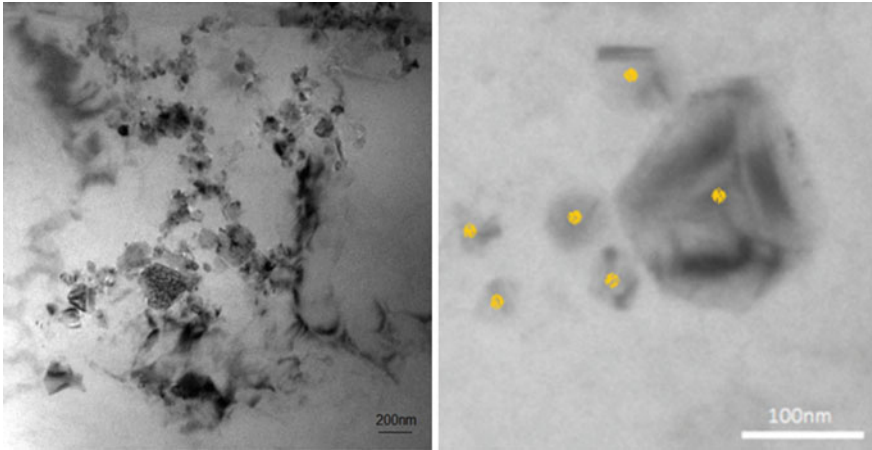
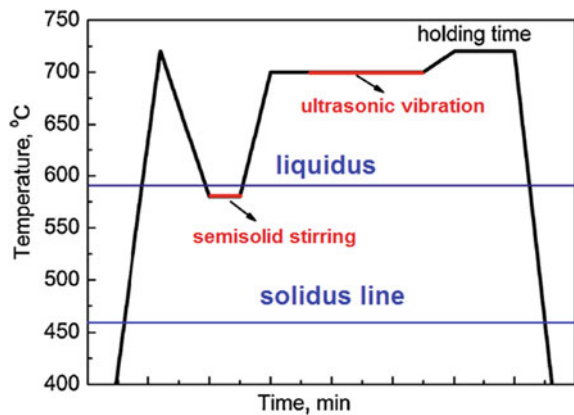


Fig. 3.31 TEM images showing (a) good dispersion of n-SiC with few agglomerates and (b) clean interface between SiC nanoparticles and the Mg matrix [72]

Fig. 3.32 Schematic illustration of the temperature–time sequences for semisolid stirring assisted ultrasonic vibration; regenerated from [44]



few nanoparticles also existed. Image analysis allowed to evaluate nanoparticle distribution in the samples (Fig. 3.34), showing that the distances between the edges of the nanoparticles are mostly greater than 25 nm, suggesting that the majority of them were dispersed in the metal matrix. The authors reported a great enhancement (+140 %) of microhardness comparing to the unreinforced matrix, as well as a strong increase with respect to most of the works reported in the literature.

Similarly, Zhou et al. [73] combined semisolid stirring assisted ultrasonic cavitation method to produce Mg-hybrid composites. AZ91 was used as the alloy matrix with different hybrid ratios of CNTs and n-SiC nanoparticles as hybrid reinforcements. The combined processing method provided relatively uniform dispersion of the reinforcements and refinement in grain size [73].

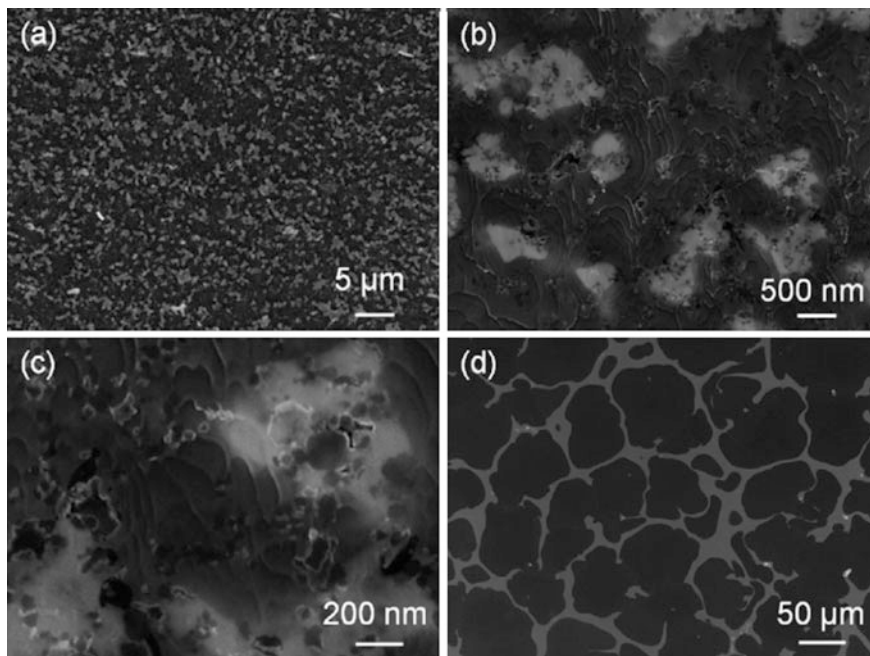


Fig. 3.33 (a–c) SEM images of Mg18Zn–6 vol.% SiC at different magnifications; (d) SEM image of Mg18Zn. The dark phase is the Mg matrix, the bright phase is the intermetallic phase and the tiny spots are SiC nanoparticles [35]

Choi et al. [74] implemented ultrasonic cavitation based casting process using a cage enclosure so as to isolate the cavitation zone. Pure Mg and Mg–1 % SiC nanocomposite billets were fabricated for cold and hot extrusion at 350 °C. A ultrasonic probe made of niobium C-103 alloy was dipped 13 mm into the melt to generate a 17.5 kHz and 3.5 kW power output vibration for melt processing at 700 °C for 15 min. A thin walled niobium cage (254 μm wall thickness) in a shape of truncated cone was used to confine the nanoparticles inside the melt pool in a selective region for ultrasonic processing, while the molten metal was still allowed to flow in and out of the cage through 55 holes (Fig. 3.35). After extrusion, the nanoparticles arranged mainly in microbands along the extrusion direction (Fig. 3.36).

The effect of hot extrusion and of extrusion temperature was studied by Nie et al. [45, 46] on AZ91/SiC nanocomposites produced through semisolid stirring and subsequent ultrasonic treatment. Hot extrusion at 350 °C with an extrusion ratio of 12:1 induced dynamic recrystallization and refining of the microstructure [45]. UTS, YS and elongation to fracture were enhanced by hot extrusion due to the good distribution of particles achieved. Nevertheless, some clusters were observed in SiC nanoparticles bands induced by the process. It was also shown that increasing the

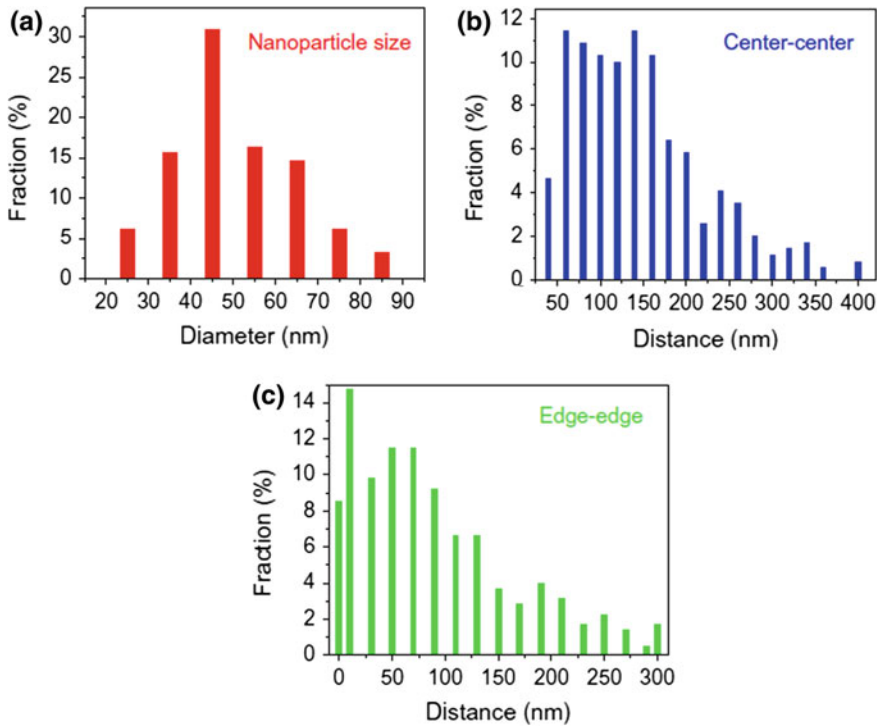


Fig. 3.34 Size and distribution of SiC nanoparticles estimated by a statistical method. (a) Diameter of SiC nanoparticles (last column: >80 nm). (b) Distance between centers of adjacent nanoparticles (last column: >400 nm). (c) Distance between edges of adjacent nanoparticles (last column: >30 nm) [35]

extrusion temperature from 250 to 350 °C leads to a decrease in the amount of SiC nanoparticle bands, as well as an increase in YS and UTS [46].

While the Mg/SiC composite system has been widely studied, Cao et al. [38] fabricated a AZ91D based composite reinforced with 1 wt% AlN particles characterized by an average size of 25 nm. A 17.5 kHz, 3.5 kW ultrasonic vibration (corresponding to a peak-to-peak displacement of the ultrasonic probe of about 40 μ m [67]) was used to treat the melt at 700 °C. Most nanoparticles were successfully separated by 15 min ultrasonic treatment, although it was stated that some areas contained more AlN nanoparticles than other areas. The microstructure of both AZ91D and AZ91D/1 %AlN was mainly composed of α -Mg, massive β -phase and lamellar β phase, but the latter was found to be much finer for the composite, despite the small percentage of AlN nanoparticles (Fig. 3.37). The finer lamellar phase may also contribute to strengthening of AZ91D alloy, while retaining the ductility.

Micro and nanoparticles have also been used synergistically to strengthen magnesium matrix. Shen [40] produced a SiC/AZ31B bimodal composite through

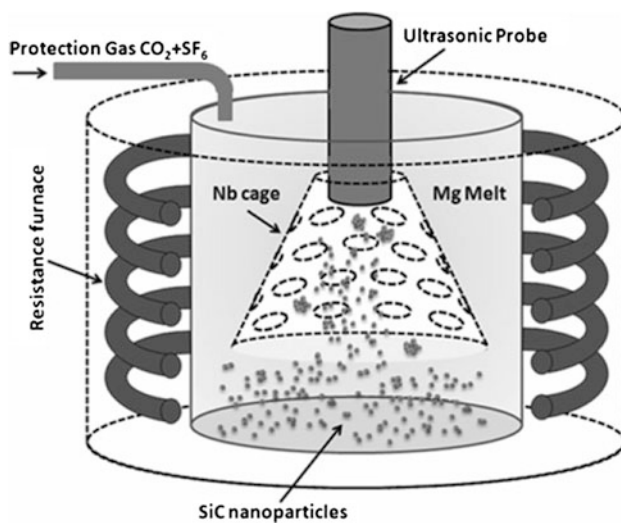


Fig. 3.35 Schematic setup of ultrasonic cavitation confinement gage for nanoparticle dispersion [74]

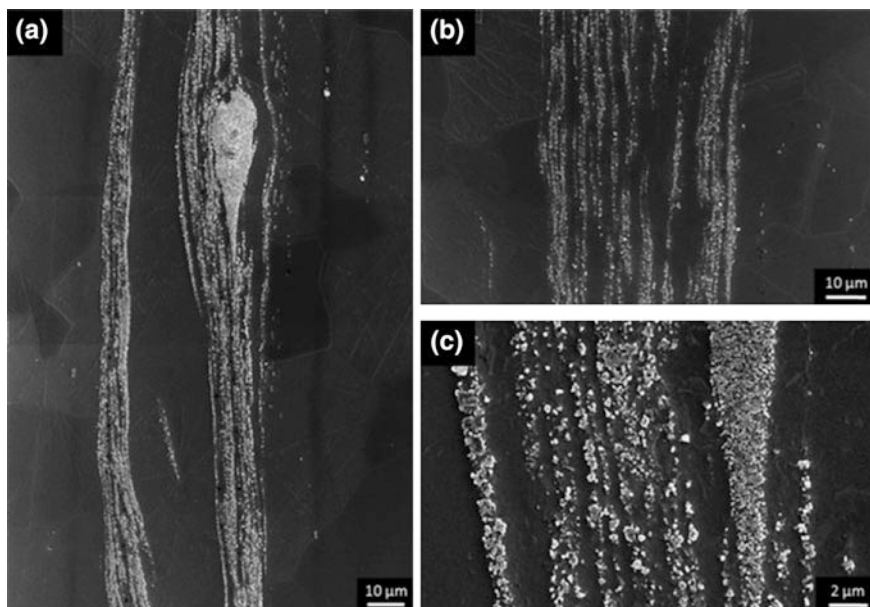


Fig. 3.36 SEM micrographs of the ultrasonically cast Mg-1 wt% SiC after extrusion at 25 °C, showing the micro-banded structure and particle free zones at different magnifications [74]

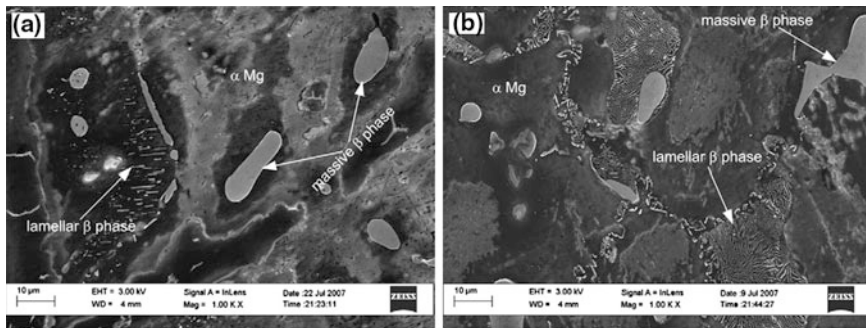


Fig. 3.37 Low magnification SEM images of (a) AZ91D and (b) AZ91D/1 %AlN [38]

semisolid stirring assisted with ultrasonic vibration method and subsequent hot extrusion. Manually mixed micro and nano SiC particles (respectively 1 vol.% of 60 nm SiC_p and 14 vol.% of 10 μm SiC_p) were added into Mg matrix at semi-solid state (620 °C). Stirring was performed for 10 min. under protective atmosphere (CO₂-SF₂). Ultrasonic treatment of the composite at 450 W was performed at liquid state for 20 min by re-heating the matrix at 720 °C. Lastly, the composite was solidified under 100 MPa of pressure in a preheated steel mould. Cast billets were homogenized at 400 °C for 12 h and extruded at 350 °C with 12:1 extrusion ratio. For comparison, AZ31B matrix, 15 vol.% micro composite and 1 vol.% nano composite were produced in the same manner. As a result of tensile tests, the bimodal composite exhibited enhanced UTS and YS comparing to the unreinforced AZ31B matrix and single size SiC_p reinforced composites. On the contrary, elongation to fracture decreased, that was lower than the unreinforced matrix and as that of the composite reinforced with particles of single size. Grain size of the bimodal composite was smaller compared to the micro or nano composite, as well as the unreinforced matrix.

Carbon based nanoreinforcements. In addition to ceramic nanoparticles, carbon based nanoreinforcements have been also dispersed in Mg matrix by ultrasonic method. Graphene NanoPlatelets (GNP, graphite thin sheets with a thickness of less than 100 nm) are attractive due to their extraordinary mechanical, electrical, and thermal properties [75, 76]. The large surface area and thin sheet geometry make it extremely difficult to disperse graphene nanoplatelets (GNP) into metal melts. Chen et al. [77] incorporated GNP in molten magnesium by a process combining liquid state ultrasonic processing and solid state stirring. GNP were first added by a feed-screw based system to molten Mg at 700 °C under ultrasonic treatment by a niobium probe generating peak-to-peak vibration amplitude of 60 μm. After feeding, sonication was applied for 15 min, and the melt was cast to 6 mm thick plates. Although well incorporated in the matrix, micrometer-sized clusters were still observed (Fig. 3.38a). Friction stir processing (FSP) was then applied through a pin of 5 mm diameter rotating at 1800 rpm and 25 mm/min. SEM observations revealed that, after FSP, graphene nanoplatelets were more uniformly distributed

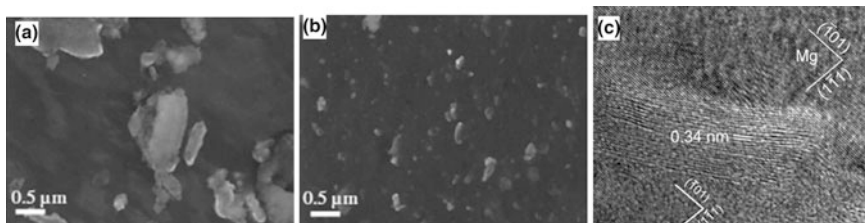


Fig. 3.38 SEM images of the (a) as-cast ultrasonic processed plate and (b) ultrasonic processed + solid state stirred sample; (c) HRTEM image showing same orientation of Mg matrix around the graphene nanoplatelet indicating that the graphene nanoplatelet was embedded inside the Mg grain (good interfacial bonding) [77]

within the matrix (Fig. 3.38b) and the microhardness of the composite was enhanced by $\sim 78\%$ with respect to pure Mg subjected to the same process. Further, from TEM studies (Fig. 3.38c), neither cavities nor reaction products were observed indicating good bonding between the graphene nano-platelet and the Mg matrix. In addition, the orientation being same between the Mg matrix around the graphene nanoplatelets indicated that the graphene nanoplatelet was embedded inside Mg grain [77].

Carbon nanotubes were also used as reinforcement for AZ91D matrix by Liu et al. [78], employing stir casting technique and ultrasonic treatment. 1.5 % CNTs (20–40 nm diameter and length in the range of 1–5 μm) were added to the matrix through the vortex, induced by a stirring speed of 300/500 rpm, applied for 2 min. As to further disperse the nanotubes in the matrix, ultrasonic treatment of the melt was performed for 15 min at 20 kHz through a titanium waveguide. CNTs resulted to be well dispersed within the matrix, inducing an increase in UTS, YS and ductility of 22, 21 and 42 % respectively, compared to the unreinforced matrix.

3.4 Disintegrated Melt Deposition (DMD)

3.4.1 Process Description

The DMD technique (shown in Sect. 2.1) is a liquid-state processing method, which has the combined advantages of both gravity die casting and spray forming processes. Unlike spray process, the DMD employs primarily lower impinging gas jet velocity with the end product being only bulk alloy/composite material, and provides high solidification rates [79]. It employs a bottom-pouring technique, which effectively eliminates impurities/oxides (i.e. no requirement for any complex flux additions). The method includes both melting and pouring together in a single step, thereby making the process less intensive in terms of time and labour/cost. It is one of the most cost-effective processes tested successfully to synthesize nanocomposites [79]. The inherent merits of the DMD method are listed below:

- Combined advantages of casting and spray forming processes
- Eliminates the need for separate melting and pouring units
- Removes oxides and slag/dross and least metal wastage
- Flexibility of addition/incorporation of alloying/nanoparticle elements
- Eliminates the retention/settling of the nano-reinforcements in the crucible
- High process yield and gives rise to fine-grained materials with minimal porosity
- Capability to be up-scaled from laboratory-to-industrial level.

The prime advantage of DMD process is that it produces materials with fine grain size with minimal/negligible porosity. To highlight this further, a comparison of microstructure of pure Mg produced by gravity die-cast and DMD process are shown in Fig. 3.39a, b. In gravity die-cast Mg [80], very large grains are observed ($\gg 200\ \mu\text{m}$), wherein the DMD method produces Mg with grain size $< 100\ \mu\text{m}$. Generally, when secondary processing methods such as extrusion are employed, it is well-known that the grain size reduces much further. Given the fact that if defects such as impurities/shrinkage etc. exist in the cast product, it is difficult to eliminate them during the secondary processes (although the secondary process is known to reduce the grain size). As could be seen from the Fig. 3.39c, it is evident that not only does the grain size is refined ($\sim 20\text{--}40\ \mu\text{m}$) but also that the microstructure upon extrusion is almost free of porosity/defects. The properties and advantages of Mg-based materials obtained using the DMD method (given in Table 3.1) are superior to those obtained using conventional gravity die-cast process. In particular, the DMD method has been used successfully to produce Mg-MMNCs [79] due to the advantages mentioned above. Discussions pertaining to the detailed process of DMD technique and the investigations related to the Mg-MMNCs developed by this method are henceforth presented.

Standardized DMD Process. The DMD process is an innovative processing technology (shown in Sect. 2.1), and the details on the method utilized to produce Mg-based materials with enhanced performance capability are given here. For the synthesis of Mg-based materials, the Mg materials and the desired amount of reinforcements are first weighed and placed in a graphite crucible. The crucible was designed with an arrangement for bottom-pouring. The materials are normally

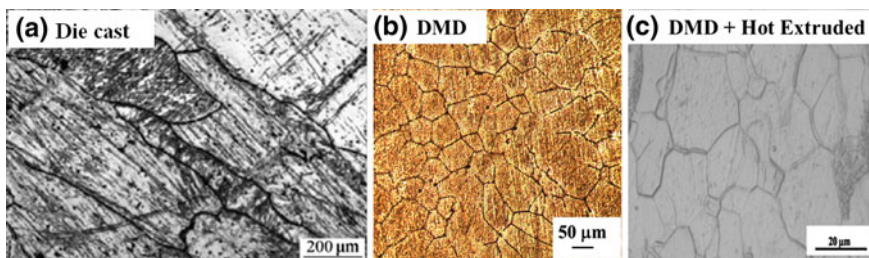


Fig. 3.39 Comparison of microstructures of pure Mg produced by (a) gravity die-cast [80] and (b) DMD process. (c) Microstructure of DMD Mg after hot extrusion [109]

Table 3.1 Properties and advantages of Mg-based materials produced using the Disintegrated Melt Deposition (DMD) method

Features	Result	Properties	Quality
Porosity	Extremely limited	Improved ductility	✓
Shrinkage defects	Extremely limited	Defect free	✓
Inclusions (Dross)	No evidence in the bulk material	Medium to high strength	✓
Impurity/segregation	No evidence in the bulk material	Medium to high strength	✓
Process yield	>90 %	Cost effective	✓
Microstructure (Cast)	Grain size <100 μm	Medium strength	Good
Microstructure (Extruded)	Recrystallized fine grains (sub-microns to $\sim 20 \mu\text{m}$)	High strength, high ductility	Excellent

superheated to 750 °C (1023 K) in a resistance furnace under an inert argon environment. Upon reaching the superheat temperature, the molten composite melt (includes Mg-base matrix, alloying elements and nanoparticles) is mechanically stirred using a twin-blade mild steel impeller (with pitch 45°) to facilitate the incorporation and uniform distribution of reinforcement materials in the metallic matrix. The impeller is coated with a water-based zircon wash (Zirtex 25: 86 % ZrO_2 , 8.8 % Y_2O_3 , 3.6 % SiO_2 , 1.2 % K_2O and Na_2O and 0.3 % trace inorganic) to prevent any possible iron contamination of the melt. The melt is then released through a 10 mm diameter orifice at the base of the crucible. The composite melt is subsequently disintegrated by two jets of argon gas oriented normal to the melt stream. The argon gas flow rate is maintained at 25 l/min. The disintegrated composite melt is subsequently deposited onto a metallic substrate situated at the base. The Mg-ingot so produced is hot extruded at 350 °C (with prior soaking for 1 h at 400 °C) at an extrusion ratio ranging from 12:1 to 25:1, to obtain rods of 10 to 7 mm diameter, which is used for further materials characterization.

3.4.2 Pure Mg-Based Nanocomposites

Mg-MMNCs were first attempted using nano-alumina ($n\text{-Al}_2\text{O}_3$) as reinforcement, the main advantage of using $n\text{-Al}_2\text{O}_3$ being its limited reactivity with molten Mg. Hassan and Gupta [81] synthesized pure Mg-based composite with 1.1 vol.% of $n\text{-Al}_2\text{O}_3$ particulates (size $\sim 50 \text{ nm}$) reinforcement using DMD followed by hot extrusion. Microstructural characterization of the materials revealed grain refinement of magnesium matrix due to uniform distribution of reinforcement. The uniform distribution of reinforcement particulates was attributed to [81]: (a) limited agglomeration of reinforcement during melting of matrix due to uniform arrangement of raw materials in crucible for melting, (b) minimal gravity-associated

segregation due to judicious selection of stirring parameters, (c) good wetting of reinforcement by the matrix melt and (d) disintegration of the composite slurry by argon jets, and subsequent deposition in metallic mold. Almost zero standard deviation in density measurement was obtained (density estimation conducted using Archimedes' principle). This reflected the negligible porosity and absence of shrinkage cavity in the ingot, giving rise to defect free extrusions. Further, the interfacial integrity between the matrix and reinforcement was found to be good due to the limited reaction between the Mg-matrix and $n\text{-Al}_2\text{O}_3$, which was assessed in terms of interfacial debonding and nano-voids at the particulate-matrix interface. The significant grain refinement obtained in the nanocomposite (average grain size $\sim 14\text{ }\mu\text{m}$, a 70 % reduction when compared to pure Mg) was attributed to the presence of uniformly distributed fine nanoparticles that acted as nuclei for grain nucleation, but also restricted grain growth during solidification. The matrix grain refinement was also influenced by the hot extrusion process ($T > 0.5T_m$), as it facilitated dynamic recrystallization and inhibited growth of the recrystallized grains. A comparative work on pure Mg incorporated with Al_2O_3 at varying length scales (nano, submicron and micron) showed that nano and submicron-sized particles reinforcements ensured better microstructural properties with respect to micron-sized ones [82].

Carbon nanotubes (CNT) is another reinforcement which has been widely used in Mg-matrices. Goh et al. [83, 84] fabricated Mg nanocomposites containing 0.3, 1.3, 1.6 and 2 wt% carbon nanotubes (CNTs), that were hot extruded and characterized for their material behaviour. A detailed study was conducted on the texture (crystallographic orientation) and dislocation structures present in pure Mg and Mg-1.3 wt% CNT nanocomposite. Based on X-ray diffraction pole figures analyses, they observed that in the nanocomposite, the basal, prismatic and pyramidal planes were not exactly aligned at 90° , 0° and 45° respectively along the normal direction (ND); rather they were tilted randomly within about 20° from their respective positions [84]. Further, a thorough TEM investigation on dislocation structures in pure Mg and Mg-1.3CNT nanocomposite showed that only basal dislocations were present in pure Mg (no prismatic or pyramidal), whereas in Mg-1.3CNT nanocomposite, basal and prismatic slip planes were observed (Fig. 3.40) [84]. These additional slip systems observed in the CNT reinforced nanocomposites indicated the effect of nano-reinforcement addition in activating the non-basal slip systems [85]. Such an occurrence would eventually influence the mechanical behaviour (deformation characteristics) of the nanocomposites, such as improving the ductility.

Other nanoparticles such as nano- Y_2O_3 and $-\text{ZrO}_2$ have also been incorporated in pure Mg-matrix [85–87]. Thermally stable oxide ceramics particulates such as Y_2O_3 and ZrO_2 are expected to be capable of forming chemical bond at the metal–reinforcement interface. In pure Mg– $n\text{-Y}_2\text{O}_3$ composites (with 0.22, 0.66 and 1.11 vol.% respectively), microstructural studies showed uniform reinforcement distribution with good reinforcement–matrix interfacial integrity (Fig. 3.41), and significant grain refinement with the average grain size of $\sim 6\text{ }\mu\text{m}$ at 0.66 vol.%. Furthering the study, Goh et al. [87] used TEM investigations and showed excellent

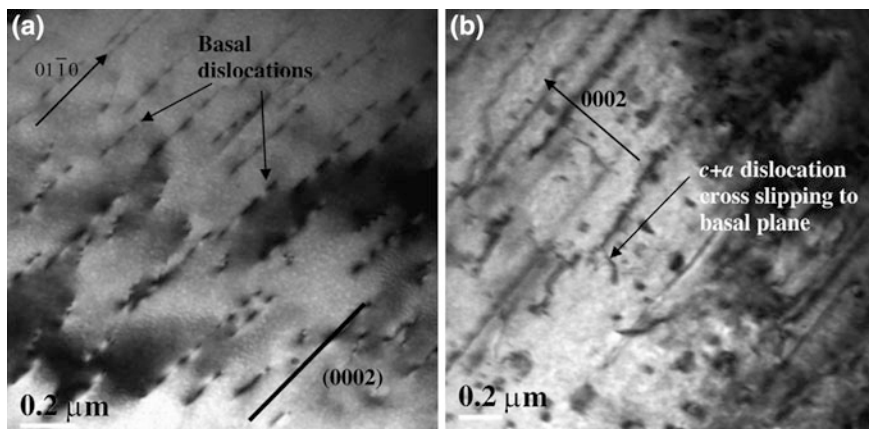


Fig. 3.40 Dislocation structures in Mg-1.3CNT nanocomposite on: (a) $(2\bar{1}\bar{1}0)$ foil plane when $g = 0\ 1\ \bar{1}\ 0$ and (b) $(2\bar{1}\bar{1}0)$ foil plane when $g = 0\ 0\ 0\ 2$. Basal plane trace common to (a) and (b) is indicated by black line [84]

interfacial adhesion between the particle and the matrix, with no debonding or cracks (Fig. 3.41b). However, with further increase in vol.%, clustering of nanoparticles occurred [85, 87]. In addition, the majority of the dislocations in Mg- Y_2O_3 nanocomposite were observed to be basal dislocations, unlike the multiple (non-basal) systems observed in the Mg-CNT system (mentioned above). Hassan and Gupta [86] synthesised pure Mg-n-ZrO₂ (of size 29–68 nm) composites with 0.22, 0.66 and 1.11 vol.% respectively, and observed that the refinement in grain size was significant ($<6\ \mu\text{m}$) and at the highest volume fraction of 1.11 % it reduced to as low as $2\ \mu\text{m}$ [86].

3.4.3 Mg-Alloys Based Nanocomposites

Nanocomposites based on Mg-Al alloy systems. AZ31 class of Mg-alloy is a commercial Mg-alloy, widely used in automobile, aerospace and transportation industries. Nguyen and Gupta [88] reported the synthesis of AZ31B alloy based nanocomposite by incorporating n-Al₂O₃ with three volume fractions (0.66, 1.11 and 1.50 %). While the effect of nanoparticle on grain size was not very prominent (3–4.5 μm in the nanocomposite), considering the inherent fine grain size of the AZ31B alloy ($\sim 5.5\ \mu\text{m}$), near equiaxed grains (representative figures of unreinforced alloy and 1.11 % nanocomposite is given in Fig. 3.42a, b), with decreasing size and roundness of second phase was obtained with increasing n-Al₂O₃ content [88]. Further, uniform distribution of nano-particulates along with good interfacial bonding was also reported (Fig. 3.42c [88]). A similar work by Paramsothy et al. [89] reported the effect of n-Al₂O₃ on AZ31 alloy, which showed that the nanoparticles were uniformly distributed, and were located both at the grain

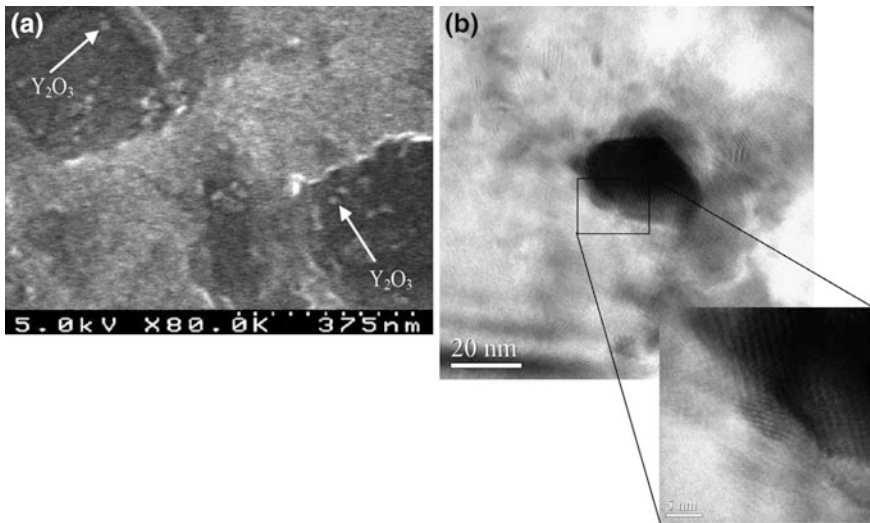


Fig. 3.41 Mg- Y_2O_3 nanocomposite: (a) FESEM image showing uniform distribution of $n\text{-Y}_2\text{O}_3$ and (b) TEM image showing good Mg/ $n\text{-Y}_2\text{O}_3$ interface bonding [85, 87]

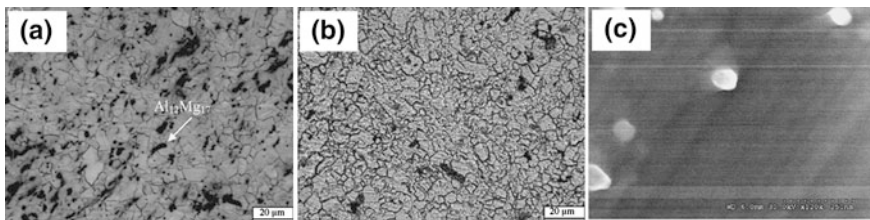


Fig. 3.42 Optical microscopic images that show fine and equi-axed grains in (a) AZ31B alloy and (b) AZ31B- $n\text{-Al}_2\text{O}_3$ composite. (c) FESEM image at high magnification showing good matrix/ $n\text{-Al}_2\text{O}_3$ interface bonding [88]

boundary and within the grain [89]. Further, based on x-ray diffraction peaks, possible texture orientation was identified [89]. In AZ31 alloy, the dominant textures along the transverse and longitudinal directions were prismatic (1 0–1 0) and pyramidal (1 0–1 1) [and basal (0 0 0 2)], whereas in the nanocomposite, they were prismatic (1 0–1 0) and pyramidal (1 0–1 1) [89]. Another study reported the properties of AZ31 alloy reinforced with CNT [90]. Microstructural features such as refinement in grain size and second phase morphology were similar to that observed in AZ31- $n\text{-Al}_2\text{O}_3$ composites [90] wherein the distribution of CNT was observed within the grain and along the grain boundary. However, based on the relative intensity of the x-ray diffraction peaks showed that in AZ31 alloy, the dominant texture in the transverse and longitudinal directions were prismatic (1 0–1 0) and pyramidal (1 0–1 1) [and basal (0 0 0 2)], whereas in the CNT reinforced

nanocomposite, the dominant texture was pyramidal (1 0–1 1) [90]. Such change from the dominant textures [89, 90] indicate a change in preferred crystal orientation that has occurred due to the addition of nanoparticles, which would influence the mechanical characteristics.

In order to further the work on AZ31B–n–Al₂O₃ nanocomposite, so as to modify the microstructural characteristics and enhance the mechanical behaviour, additions of other metallic elements to AZ31B alloy was attempted. Nguyen and Gupta [91, 92] reported the addition of Ca to AZ31B alloy with 1.5 vol.% n–Al₂O₃. Microstructural investigations, as shown in Fig. 3.43a [92], indicate that the Mg-based eutectic phase Mg₁₇Al₁₂ decreased with increasing Ca content and a new phase (MgAl)₂Ca was formed. Further, the grain size reduced ($\sim 1\ \mu\text{m}$), given that the AZ31B alloy and that of AZ31B–nAl₂O₃ nanocomposite showed low grain sizes (5–6 and 3–4.5 μm respectively). Another work by the same authors [93] showed that the addition of micron-sized Cu particles too influenced the microstructural characteristics. In this work, two weight percentages of Cu (10 and 18 %) were used. The Cu-content was selected based on a previous work on Mg–Cu, wherein the specified Cu contents gave rise to high strength but poor ductility [94]. Metallographic investigations showed significant modifications in the microstructure such that the grain sizes were in the submicron range ($<1\ \mu\text{m}$) in the AZ31B–Cu–n–Al₂O₃ composites [93], which were due the presence of additional Cu-based second phases Mg₂Cu, AlCuMg and Cu. These phases were believed to serve both as nucleation sites for grain nucleation to occur and as obstacles for grain growth, during the DMD and hot extrusion process [93]. Further, image analyses on the second phases showed that the average size of second phases ($\sim 1\ \mu\text{m}$) were much smaller than the original size of Cu particulates (8–11 μm), that suggested interaction between Cu and AZ31B alloy. However, individual Cu-particles were also detected indicating incomplete reactions. Representative micrographs of AZ31B–Cu–n–Al₂O₃ can be seen in Fig. 3.43b and c [93]. The incorporation of low contents of micron-sized Cu (2, 4 vol.% %) and n–Al₂O₃ in AZ31 alloy was investigated in Ref. [95]. In this work, only Mg₁₇Al₁₂, Mg₂Cu and Cu phases were observed and the MgAlCu phase was absent probably due to low Cu content [95]. However, the presence of Cu peaks in the x-ray diffractogram indicated the low solubility of Cu in Mg (Mg–Cu phase diagram [96]). Interestingly, the grain sizes were in the submicron range and were significantly low ($\sim 0.3\ \mu\text{m}$) [95]. Similar to

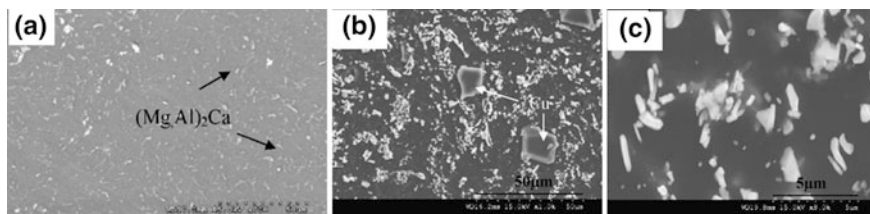


Fig. 3.43 SEM images of: (a) Eutectic second phases in AZ31B–nAl₂O₃–Ca [92]; (b, c) distribution and interface characteristics in AZ31B–nAl₂O₃–Cu system [93]

Cu-addition, the AZ31B alloy was also incorporated with micron-sized Ni particles (3.11 and 2.93 wt%) in combination with n-Al₂O₃ particle reinforcement [97]. Phase analyses on AZ31B–Ni–n-Al₂O₃ showed Mg₁₇Al₁₂ and Mg₂Ni intermetallic phases, while additional Ni-peaks were identified in 3.1 Ni. Other microstructural features were similar to that observed in AZ31B–Cu–n-Al₂O₃ [97].

Other works on Mg–Al alloys based nanocomposites included the incorporation of n-Al₂O₃ particles with or without Ca addition in newly developed AZ41 and AZ51 alloys [98, 99], and in hybrid AZ31/AZ91 alloy [100]. The main aim of these studies were to control the microstructure and hence the mechanical properties by manipulating the volume fraction and type of secondary phases. It was observed that in all these nanocomposites, the eutectic/intermetallic phases were present along the grain boundaries. The grain sizes in these composites were <2 μm [98].

Other nanoparticles such as n-Si₃N₄ and n-TiC were used as reinforcement (1.5 vol.%) in AZ31/AZ91 hybrid alloy [101, 102]. In these nanocomposites, the grain size remained almost unchanged, when compared to the unreinforced counterpart. Further, it is interesting to note that in all the hybrid alloy reinforced nanocomposites [100–103], the texture analyses based on relative intensity of x-ray diffraction peaks showed that both in the unreinforced hybrid alloys and in the nanocomposites, the dominant texture in the transverse as well as the longitudinal directions was (1 0–1 1) pyramidal texture. These together indicate that the nanoparticles: (i) neither do they contribute to particle stimulated grain nucleation and eventual grain refinement, (ii) nor do they influence a change in bulk texture modification. Hence in these cases, it can be claimed that if any improvement in mechanical properties occur, such enhancement would be solely due to the presence of nanoparticles alone, rather than change in texture due to nanoparticles (considering that no new intermetallic phase form, other than the Mg₁₇Al₁₂ intermetallic).

Nanocomposites based on other Mg-alloy systems. Mg–Zn–Zr alloys (ZK series) are non-Al containing Mg-alloys. ZK60 alloy based nanocomposites have been developed with reinforcements such as n-Al₂O₃, CNT, n-TiC and n-Si₃N₄. In these works the nano-reinforcement volume fraction was usually ~1.5 %. Jayaramavar et al. [104] synthesized ZK60–n-Al₂O₃ nanocomposite, with 1 and 1.5 vol.%. After extrusion, these alloys were given a low temperature heat treatment. It was reported that the nanoparticle addition did not contribute to grain refinement (14–15 μm in both the unreinforced alloy and the nanocomposites), and did not change the bulk texture. The distribution of nanoparticles was fairly uniform, several aggregates were also found [104]. When n-TiC particles were added, micrographs revealed that grain size remained statistically unchanged [105]. The n-TiC particles were found to be present both at the grain boundary and within the grain and there was no modification in the bulk texture of the nanocomposite [105]. In the ZK60A-CNT nanocomposite [106], a 50 % reduction in grain size was observed. The CNT addition also reduced the presence of intermetallic phase, but without changing the bulk texture. Similar results were obtained when AZ60A alloy was reinforced with n-Si₃N₄ particles [106]. In a recent work, n-AlN (1.5 vol.%) was introduced as reinforcement in AZ91/ZK60 hybrid alloy [103]. In this nanocomposite, TEM and selected area diffraction pattern (SADP) studies revealed

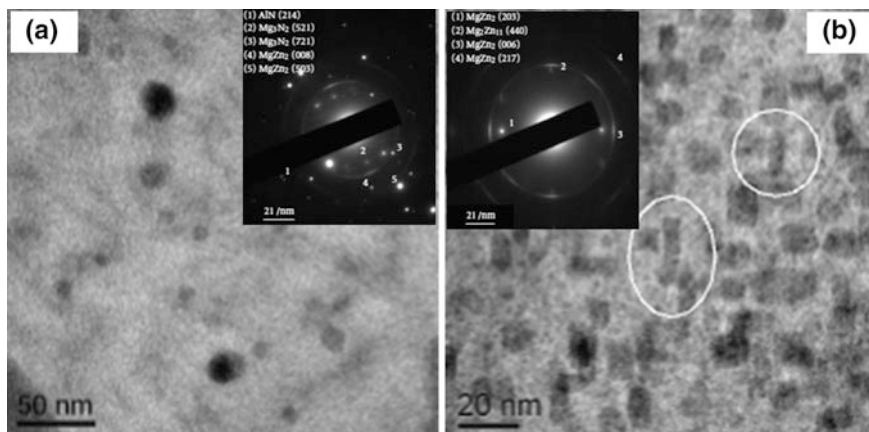


Fig. 3.44 TEM images and selected area diffraction pattern (SADP) of AZ91/ZK60A/AlN nanocomposite: (a) individual nitride nanoparticles and fine intermetallic particles and (b) presence of Mg-Zn rod-shaped nanoparticles [103]

[103] partial reaction of AlN with the Mg alloy matrix to form Mg₃N₂ (Fig. 3.44a) and occurrence of Mg-Zn nanorods (Fig. 3.44b), that were not observed in the unreinforced hybrid alloy. This nanorod phase was attributed to the well-dispersed AlN nanoparticles which may have aided the Mg-Zn precipitation [103].

Recently, hybrid composites, i.e. Mg-matrix incorporated with hybrid reinforcements, are being developed. Hybrid reinforcements usually mean a combination of reinforcements, which may be metal/ceramic, ceramic/ceramic, micron/nano-sized particles. In this context, metallic element such as Ti, is often considered as a metallic reinforcement, and not an alloy, as Ti has negligible solubility in Mg. The Mg-Ti system has been studied by various authors and processed both at liquid state and solid state [107, 108]. In one of the initial studies on hybrid reinforcements, pure Mg was reinforced with 5.6 wt% Ti particles (micron-size) and 2.5 wt% n-Al₂O₃ particles [109]. The hybrid reinforcement addition into the Mg matrix was carried out in two ways: (i) by direct addition of the reinforcements into the Mg-matrix, Mg-(5.6Ti + 2.5n-Al₂O₃) and (ii) by pre-synthesizing the composite reinforcement by ball milling and its subsequent addition into the Mg-matrix, Mg-(5.6Ti + 2.5n-Al₂O₃) BM. (This method of pre-processing the reinforcements was described as hybrid process in Sect. 2.4.) The following microstructural characteristics were reported and are represented by Fig. 3.45 [109]: (i) when compared to pure Mg, the grain size reduced 2–3 times depending on the mode of addition, (ii) pre-processed hybrid reinforcements were uniformly distributed in the matrix (with n-Al₂O₃ being embedded on micron Ti), unlike directly added reinforcements (dominant clusters), (iii) uneven sized sharp-edged Ti-particles transformed to large number of uniformly sized Ti-particles with blunted corners and rounded edges and (iv) absence of reaction products between Ti and n-Al₂O₃, as well as between Mg-Ti and n-Al₂O₃ [109].

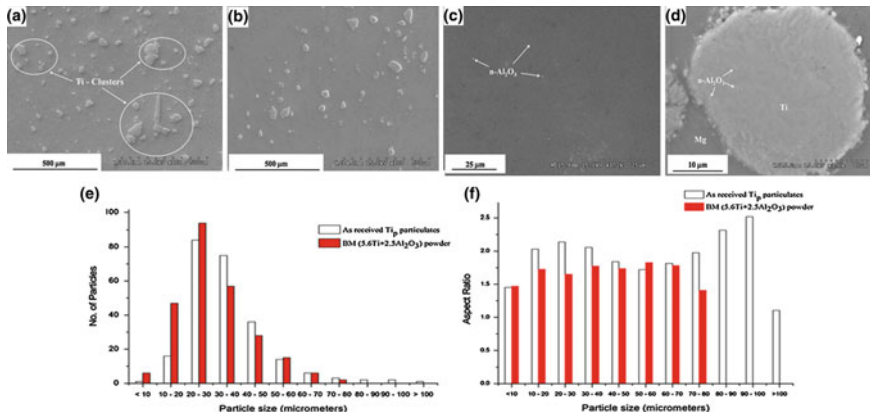


Fig. 3.45 SEM micrographs showing the microstructural characteristics in: (a) distribution of uneven sized Ti particulate clusters in Mg-(5.6Ti + 2.5Al₂O₃) composite, (b) distribution of Ti particulates in Mg-(5.6Ti + 2.5Al₂O₃)BM composite, (c) presence of n-Al₂O₃ in Mg-(5.6Ti + 2.5Al₂O₃) composite, (d) n-Al₂O₃ embedded in Ti particulates in Mg-(5.6Ti + 2.5Al₂O₃)BM composite, (e) no. of particles versus particle size and f particles aspect ratio versus particle size [109]

Such modification in the morphology, number and distribution of the hybrid reinforcements in the Mg-matrix is believed to subsequently influence the mechanical characteristics in terms of mechanical/thermal/residual stress distribution, load bearing/load transfer capacity, and related strengthening and fracture mechanisms.

In a more recent investigation, pure Mg was incorporated with hybrid Ti+n-SiC particles [110]. In this study, similar to the work mentioned above, hybrid reinforcements involving Ti and n-SiC (with varying vol.%) were prepared by reinforcement pre-processing. An in-depth investigation was conducted on the microstructural evolution using advanced characterization techniques. Electron probe microscopic analysis (EPMA) (Fig. 3.46) showed that the n-SiC particles were found to be intact and distributed on the Ti-particle (brought forth by reinforcement pre-processing), and thereby prevented the brittle Mg₂Si phase formation [110]. This was understood by the absence of high intensities of Si and C distribution in the matrix. Detailed EBSD and inverse pole figure (IPF) analyses (Figs. 3.47 and 3.48) were also conducted to identify the grain/grain boundary characteristics and texture evolution [110]. Based on these studies, it was shown that in both Mg-Ti and Mg-Ti-n-SiC nanocomposite, the bulk crystallographic orientation was similar (no texture change), i.e. in both cases the basal planes were parallel to the extrusion direction [110]. Interestingly, the addition of n-SiC increased the volume fraction of recrystallized grains, which indicated that nanoparticle addition supported particle stimulated grain nucleation [110]. These studies further highlight the fact that in Mg-nanocomposites, the ensuing strengthening mechanism upon loading would depend on various factors such as

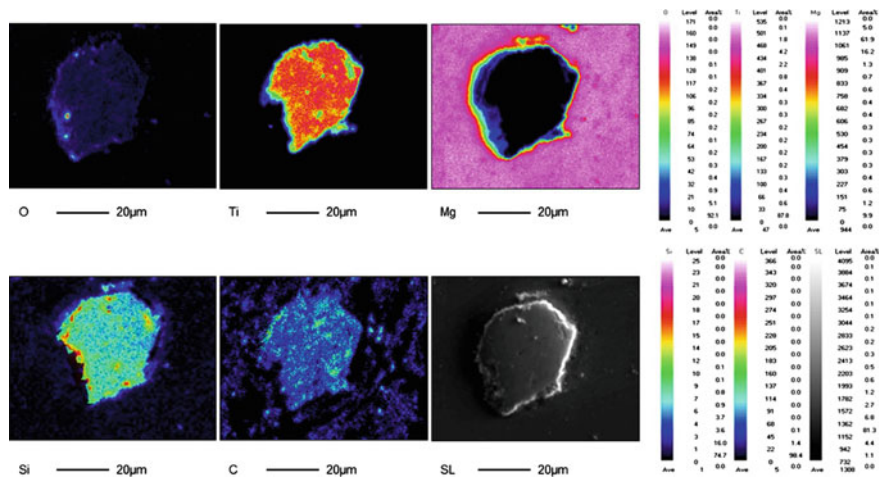


Fig. 3.46 EPMA results showing the compositional distribution around Mg/Ti interface in Mg–(5.6Ti + 1.0SiC)BM hybrid composite. Note the absence of high intensity of Si in the Mg–matrix that indicated absence of brittle Mg₂Si intermetallic [110]

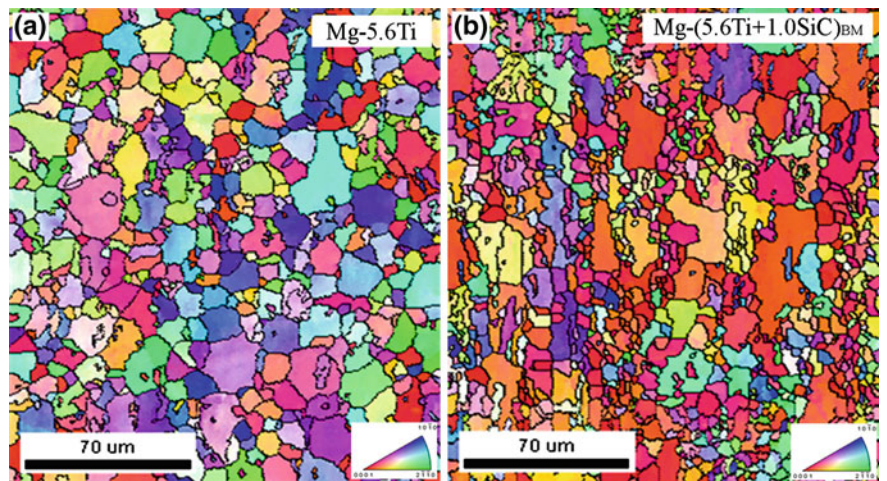


Fig. 3.47 EBSD generated inverse pole figure micrographs of (a) Mg–5.6Ti and (b) Mg–(5.6Ti + 1.0SiC)BM composite [110]

the presence of nanoparticles and microstructural evolution/texture characteristics (either individually or in combination), which can be further manipulated by parameters such as the base matrix composition, additional alloying/reinforcement elements, their combination, content and mode of addition.

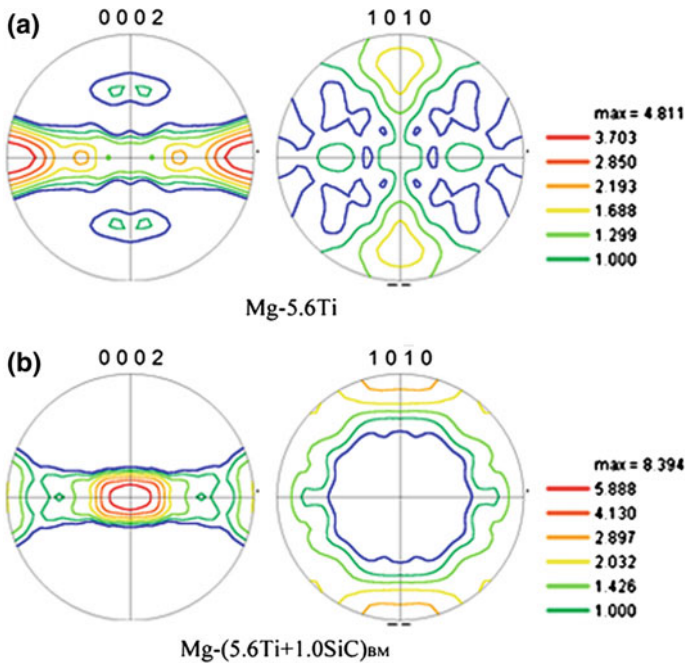


Fig. 3.48 (0002) and (10-10) pole figures of (a) Mg-5.6Ti and (b) Mg-(5.6Ti + 1.0SiC)_{BM} composite [110]

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Chapter 4

Mechanical Behavior of Al and Mg Based Nanocomposites

Abstract This chapter provides an insight into the mechanical properties of Al and Mg based nanocomposites. Tensile and compression properties, ductility and the influence of heat treatment on mechanical behavior of both aluminum and magnesium based nanocomposites are discussed. Experimental data (hardness, tensile/compression strength, ductility) reported in recent literature works is presented and compared, to highlight the effect of different processing techniques on the mechanical response of nanocomposites.

4.1 Al-Based Nanocomposites

4.1.1 Room Temperature Mechanical Properties

Mechanical properties of aluminium based nanocomposites are listed in Tables 4.1, 4.2, and 4.3, where experimental results have been summarized for different production routes. Mechanical properties of composites realized with traditional stir casting and compocasting are presented in Table 4.1 [1–7] while Tables 4.2 and 4.3 report mechanical properties of composites produced respectively with master powder feeding prior to stir or compo casting [8–16] and ultrasonic cavitation assisted casting [17–26]. Mechanical behaviour of nanocomposites obtained through other processing routes (i.e. high pressure die casting) is listed in Table 4.4 [27].

Tensile and compressive properties. A common result for the different production techniques is that mechanical properties are generally enhanced with respect to the corresponding unreinforced alloys by adding reinforcing nanoparticles (see representative curves in Fig. 4.1), and the improvement is generally superior to that obtained with micro-reinforcement at the same wt% fraction (Fig. 4.2). In particular, hardness, YS and UTS generally improve by increasing the reinforcement wt% content, by >100 % in some cases [1, 4, 8, 11, 14, 28]. Significant improvements in Young's modulus have been also reported [15, 16, 29], although they are usually limited by the low amount of reinforcing phase. As previously discussed, the strong enhancement in YS values observed in nanocomposites in comparison to the

Table 4.1 Hardness and tensile properties of Al-MMNCs obtained through stir casting (stir) and compocasting (compo)

Material	Hardness	Tensile Yield Strength (TYS), (MPa)	Ultimate Tensile/Compression (C) Strength (UTS), (MPa)	Ductility (%)
Stir/compo casting				
A356 + MgO (stir) [2]				
	HB	–	–	–
A356	45*			
A356 + 1.5 vol.% MgO	69*			
A356 + 2.5 vol.% MgO	70*			
A356 + 5 vol.% MgO	68*			
A206 + Al ₂ O ₃ (stir) [3]				
	HRF	–	–	–
A206 + 5 wt%Mg (10 min stir)	60.8 ± 5.79			
A206 + 5 wt% Mg + 2.5 wt%Al ₂ O ₃ (10 min stir)	67.7 ± 2.65			
A206 + 5 wt% Mg + 5 wt%Al ₂ O ₃ (10 min stir)	81.9 ± 0.57			
A206 + 5 wt%Mg (15 min stir)	61.4 ± 5.75			
A206 + 5 wt% Mg + 2.5 wt%Al ₂ O ₃ (15 min stir)	60.2 ± 2.96			
A206 + 5 wt% Mg + 5 wt%Al ₂ O ₃ (15 min stir)	64.6 ± 2.73			
A206 + 7 wt%Mg (10 min stir)	–			
A206 + 7 wt% Mg + 2.5 wt%Al ₂ O ₃ (10 min stir)	69.9 ± 1.71			
A206 + 7 wt% Mg + 5 wt%Al ₂ O ₃ (10 min stir)	72.4 ± 2.88			
A206 + 7 wt%Mg (15 min stir)	65.8 ± 8.63			
A206 + 7 wt% Mg + 2.5 wt%Al ₂ O ₃ (15 min stir)	57.7 ± 3.35			
A206 + 7 wt% Mg + 5 wt%Al ₂ O ₃ (15 min stir)	50.1 ± 2.34			

(continued)

Table 4.1 (continued)

Material	Hardness	Tensile Yield Strength (TYS), (MPa)	Ultimate Tensile/Compression (C) Strength (UTS), (MPa)	Ductility (%)
A356 + Al₂O₃ (stir) [4]				
	HB	–	234 _C	–
A356	53.1			
A356 + 1 wt% Al ₂ O ₃	67.8		551 _C	
			586 _C	
A356 + 2 wt% Al ₂ O ₃	70.6		610 _C	
A356 + 3 wt% Al ₂ O ₃	76.3			
A356 + Al₂O₃ (stir/compo) [1]				
A356 _{stir}	HB	82*	133*/234 _C	1.55
A356 _{compo}	53*	82*	133*/234 _C	1.55
A356 + 1 wt% m-Al ₂ O ₃ _{stir}	53*	89*	141*/272 _C	1.45
A356 + 1 wt% m-Al ₂ O ₃ _{compo}	63*	88*	146*/251 _C	1.48
A356 + 2 wt% m-Al ₂ O ₃ _{stir}	63*	92*	144*	–
A356 + 2 wt% m-Al ₂ O ₃ _{compo}	–	93*	148*	–
A356 + 3 wt% m-Al ₂ O ₃ _{stir}	–	95*	149*/348 _C	0.94
A356 + 3 wt% m-Al ₂ O ₃ _{compo}	65*	95*	148*/310 _C	1
A356 + 5 wt% m-Al ₂ O ₃ _{stir}	65*	101*	155*/423 _C	0.83
A356 + 5 wt% m-Al ₂ O ₃ _{compo}	74*	102*	157*/391 _C	0.87
A356 + 7.5 wt% m-Al ₂ O ₃ _{stir}	77*	93*	153*/450 _C	0.65
A356 + 7.5 wt% m-Al ₂ O ₃ _{compo}	78*	96*	150*/437 _C	0.7
A356 + 1 wt% n-Al ₂ O ₃ _{stir}	68*	87*	144*/580 _C	1.31
A356 + 1 wt% n-Al ₂ O ₃ _{compo}	67*	96*	149*/551 _C	1.37
A356 + 2 wt% n-Al ₂ O ₃ _{stir}	71*	102*	152*/602 _C	1.21
A356 + 2 wt% n-Al ₂ O ₃ _{compo}	71*	104*	154*/586 _C	1.29
A356 + 3 wt% n-Al ₂ O ₃ _{stir}	73*	102*	151*/625 _C	1.12

(continued)

Table 4.1 (continued)

Material	Hardness	Tensile Yield Strength (TYS), (MPa)	Ultimate Tensile/Compression (C) Strength (UTS), (MPa)	Ductility (%)
A356 + 3 wt% n-Al ₂ O ₃ compo	77*	112*	161*/595 _C	1.19
A356 + 4 wt% n-Al ₂ O ₃ compo	78*	107*	156*/630 _C	0.74
A356 + SiC (stir/compo) [5]				
	HB			
A356 stir	52*	122*	147*	6.0*
A356 compo	55*	130*	157*	8.0*
A356 + 0.5 vol.% SiC stir	64*	127*	227*	3.8*
A356 + 0.5 vol.% SiC compo	65*	138*	243*	5.6*
A356 + 1.5 vol.% SiC stir	67*	135*	240*	3.7*
A356 + 1.5 vol.% SiC compo	70*	143*	253*	5.0*
A356 + 2.5 vol.% SiC stir	73*	143*	260*	3.7*
A356 + 2.5 vol.% SiC compo	75*	147*	273*	4.5*
A356 + 3.5 vol.% SiC stir	76*	146*	290*	3.6*
A356 + 3.5 vol.% SiC compo	80*	149*	295*	4.3*
A356 + 4.5 vol.% SiC stir	75*	138	247*	3.3*
A356 + 4.5 vol.% SiC compo	82*	151*	303*	4.1*
A356 + Al₂O₃ (compocasting+T6) [6]				
	HB			
	After			
A356	Solution h.t.		117	2.1
A356 + 1 wt%Al ₂ O ₃	35		122	2.4
A356 + 2 wt%Al ₂ O ₃	30*		157	4
A356 + 3 wt%Al ₂ O ₃	36*		150	3.2
A356 T ₆	44		185	3.56
A356 + 1 wt%Al ₂ O ₃ T ₆			230	4
A356 + 2 wt%Al ₂ O ₃ T ₆			259	4.5
A356 + 3 wt%Al ₂ O ₃ T ₆			238	4.1

(continued)

Table 4.1 (continued)

Material	Hardness	Tensile Yield Strength (TYS), (MPa)	Ultimate Tensile/Compression (C) Strength (UTS), (MPa)	Ductility (%)
A356 + SiC (compocasting+CARB) [7]				
A356 + 2 vol.%SiC	–	58	110	2.1
A356 + 2 vol.%SiC (1 cycle)		69	210	3.3
A356 + 2 vol.%SiC (8 cycles)		121	354	6.9

*Estimated from graphs

monolithic aluminium matrix is mainly due to enhanced dislocation density, Orowan effect grain refinement, while direct load bearing by nanoparticles only plays a marginal role [30, 31]. Moreover, the enhancement in tensile strength is partly due to the higher work hardening rate due to the presence of nanoparticles [10]. However, it is generally observed that a critical volume/weight reinforcing fraction exists, beyond which a further addition of nanoparticles leads to a decline of mechanical properties [1, 8, 10, 32]. This behavior is mainly due the increasing presence of nanoparticles agglomerates and higher degree of micro-porosity [8], which lead to lower flow stress in the composite; moreover, debonding at the particle/matrix interface could be induced by excessive dislocation density and other defects around hard particles due to the difference in thermal expansion coefficient with respect to the matrix. As concerning the A356-Al₂O₃ system, the nanoparticle wt% giving rise to the maximum tensile yield strength was found to be 3 and 2 % respectively for compo and stir casting production techniques [1], also in line with other investigations [10, 32]. It was shown that porosity volume percent and grain size in compo-casting is generally lower than those in stir process due to the better wettability of particles in compo-casting in A356–Al₂O₃ composites [1], while stir casting gives less porosity and better mechanical properties than powder metallurgy methods in Al–MgO composites [33].

In the graphical data shown in Figs. 4.3 and 4.4, tensile properties (UTS, YS) and Brinell hardness are reported as a function of reinforcing volume fraction for A356-based nanocomposites from different studies [2, 5, 10, 15, 22]. Different liquid state techniques are compared, as well as different kind of reinforcing particles. In the considered works, cast composites produced both by melt stirring, as well as master powder milling prior to stir casting, achieved the maximum UTS between 2 and 3 vol.% reinforcement, while on the contrary, compocast composites present a constant increasing tendency for UTS with increasing volume fraction of nanoparticles up to 5 %, achieving the maximum value of the considered data, about 303 MPa, without T6 heat treatment [10]. Similar UTS values were achieved by the T6 ultrasonically treated A356–1.5 vol.% Al₂O₃ nanocomposite [22] which, as later discussed, presents a superior ductility. By comparing different casting techniques, it is generally found that given the same matrix, reinforcement type and

Table 4.2 Hardness and Tensile Properties of Al–MMNCs obtained through master powder feeding prior to stir casting

Material	Hardness	Tensile/Compressive (C) Yield Strength (TYS), (MPa)	Ultimate Tensile/Compressive (C) Strength (UTS), (MPa)	Ductility	E (GPa)
<i>Master powder feeding (MPF)</i>					
AA2024–Al₂O₃ (stir/MPF) [9]					
	HV				
AA2024	108	85	155	1.4	
AA2024 + 0.6 wt%Al ₂ O ₃ stir	112	97	135	0.6	
AA2024 + 0.6 wt%Al ₂ O ₃ MPF	130	154	213	1.0	
A356–Al₂O₃ (stir/MPF) [10]					
	HB				
A356	52*	93*	115 ± 3	2.9	
A356 + 1.5 vol.%Al ₂ O ₃ stir	–	–	126 ± 4	1.4	
A356 + 0.75 vol.%Al ₂ O ₃ (Al–Al ₂ O ₃)MPF	64*	112*	167 ± 2	2	
A356 + 1.5 vol.%Al ₂ O ₃ (Al–Al ₂ O ₃)MPF	71*	115*	182 ± 2	2.2	
A356 + 2.5 vol.% Al ₂ O ₃ (Al–Al ₂ O ₃)MPF	77*	113*	171 ± 2	2	
A356 + 3.5 vol.%Al ₂ O ₃ (Al–Al ₂ O ₃)MPF	74*	112*	163 ± 2	1.9	
A356 + 5 vol.%Al ₂ O ₃ (Al–Al ₂ O ₃)MPF	73*	111*	160 ± 3	1.7	
A206–Al₂O₃ (stir/compo, MPF, cold pressing) [11]					
A206		174*	259*	8.3*	
A206 + 5 vol.%Al ₂ O ₃ stir		180*	268*	4.4*	
A206 + 5 vol.%Al ₂ O ₃ compo		183*	278*	4.4*	
A206 + 5 vol.%Al ₂ O ₃ –(Al–Al ₂ O ₃)MPF, stir	–	231*	322*	6.1*	

(continued)

Table 4.2 (continued)

Material	Hardness	Tensile/Compressive (C) Yield Strength (TYS), (MPa)	Ultimate Tensile/Compressive (C) Strength (UTS), (MPa)	Ductility	E (GPa)
A206 + 5 vol.%Al ₂ O ₃ -(Al-Al ₂ O ₃) _{MPF} , compo		300*	388*		
A206 + 5 vol.%Al ₂ O ₃ -(Al-Al ₂ O ₃) _{MPF+CP} , stir		291*	382*	6.7*	
A206 + 5 vol.%Al ₂ O ₃ -(Al-Al ₂ O ₃) _{MPF+CP} , compo		401*	483*	7.2*	
A356-SiC (stir + MPF) [12]					
A356	–	90	140	6.1	
A356 + 1 wt%SiC-(Al-20 wt%SiC) _{MPF} -cast T 650 °C		95	125	3.18	
A356 + 1 wt%SiC-(Al-20 wt%SiC) _{MPF} -cast T 700 °C	–	110	168	6.19	
A356 + 1 wt%SiC-(Al-20 wt%SiC) _{MPF} -cast T 750 °C		137	173	5.38	
A356 + 1 wt%SiC-(Al-20 wt%SiC) _{MPF} -cast T 800 °C		107	118	2.93	
A356 + 1 wt%SiC-(Al-20 wt%SiC) _{MPF} -cast T 750 °C, 450 rpm		95 _C			
A356 + 1 wt%SiC-(Al-20 wt%SiC) _{MPF} -cast T 750 °C, 700 rpm		110 _C			

(continued)

Table 4.2 (continued)

Material	Hardness	Tensile/Compressive (C) Yield Strength (TYS), (MPa)	Ultimate Tensile/Compressive (C) Strength (UTS), (MPa)	Ductility	E (GPa)
A356 + 1 wt%SiC-(Al- 40 wt%SiC) _{MPF} - cast T 750 °C, 700 rpm		83.3 _C			
A356 + 1 wt%SiC-(Al-20 wt%SiC) _{MPF} - cast T 750 °C, 950 rpm		84 _C			
AA7xxx + CNF (Stir + MPF + T6 + Hot extrusion) [13]					
	Micro-HV				
A7xxx	98 ± 0.5	269 ± 4.1	313 ± 6.4	14.1 ± 1.5	77 ± 3
A7xxx + 0.43 wt%CNF	104 ± 1.5	294 ± 2.6	436 ± 8.7	11.2 ± 1.5	82 ± 0
A7xxx + 0.59 wt%CNF	108 ± 0.95	331 ± 3.1	483 ± 3.8	13.1 ± 1.4	85 ± 1
A7xxx + 0.76 wt%CNF	120 ± 1.2	357 ± 4.8	461 ± 1.6	6.0 ± 0.2	90 ± 1
AA1050 + CNF (Stir + MPF + Hot extrusion) [14]					
	HV				
AA1050	28 ± 1.6	117 ± 7.1	131 ± 8.2	25.5 ± 4.3	
	48 ± 3	108 ± 5	201 ± 7.4	24.6 ± 4.1	
AA1050 + 0.065 wt%CNF	55 ± 3.3	179 ± 7.3	241 ± 7.2	9.7 ± 3.4	
AA1050 + 0.58 wt%CNF	66 ± 1	169 ± 5.5	265 ± 12.1	9.9 ± 3.1	

(continued)

Table 4.2 (continued)

Material	Hardness	Tensile/Compressive (C) Yield Strength (TYS), (MPa)	Ultimate Tensile/Compressive (C) Strength (UTS), (MPa)	Ductility	E (GPa)
A356 + Al ₂ O ₃ (Stir + MPF + T6) [15]					
A356	See Fig. 4.7	128	137	0.7	60*
A356 + 1.5 vol.%Al ₂ O ₃ (Al–Al ₂ O ₃)MPF–4min _{stir}		196	213	0.91	79*
A356 + 1.5 vol.%Al ₂ O ₃ (Al–Al ₂ O ₃)MPF–8min _{stir}		149	182	1.2	69*
A356 + 1.5 vol.%Al ₂ O ₃ (Al–Al ₂ O ₃)MPF–12min _{stir}		151	168	0.58	68*
A356 + 1.5 vol.%Al ₂ O ₃ (Al–Al ₂ O ₃)MPF–16min _{stir}		120	142	0.5	61*
A356 + 1.5 vol.%Al ₂ O ₃ (Cu–Al ₂ O ₃)MPF–4min _{stir}		237	265	1.12	88*
A356 + 1.5 vol.%Al ₂ O ₃ (Cu–Al ₂ O ₃)MPF–8min _{stir}		191	197	0.7	78*
A356 + 1.5 vol.%Al ₂ O ₃ (Cu–Al ₂ O ₃)MPF–2min _{stir}		169	188	0.7	72*
A356 + 1.5 vol.%Al ₂ O ₃ (Cu–Al ₂ O ₃)MPF–16min _{stir}		125	139	0.5	61*
A356 + CNT (Stir + MPF/T6) [16]					
	HV				
A356	–	150 ± 3.6	229 ± 14	2.8 ± 0.56	39 ± 3.6
A356 + 1 wt%CNT (Si + CNT) _{MPF}	–	187 ± 3.7	265 ± 8.4	1.7 ± 0.15	70 ± 7.1
A356–T6 (sol.T = 470 °C)	69*				
A356–T6 (sol.T = 530 °C)	73*				
A356–T6 (sol.T = 560 °C)	69*				

(continued)

Table 4.2 (continued)

Material	Hardness	Tensile/Compressive (C) Yield Strength (TYS), (MPa)	Ultimate Tensile/Compressive (C) Strength (UTS), (MPa)	Ductility	E (GPa)
A356 + 2 wt% <i>CNT</i> (Si + <i>CNT</i>) _{MPP-T6} (sol.T = 470 °C)	56*	–	–		
A356 + 2 wt% <i>CNT</i> (Si + <i>CNT</i>) _{MPP-T6} (sol.T = 500 °C)	94*				
A356 + 2 wt% <i>CNT</i> (Si + <i>CNT</i>) _{MPP-T6} (sol.T = 530 °C)	96*			–	–
A356 + 2 wt% <i>CNT</i> (Si + <i>CNT</i>) _{MPP-T6} (sol.T=560 °C)	105*				
AA6061 + Al₂O₃ (stir + MPP/T6/extrusion) [8]					
	HB				
AA6061 _{T6}	49*	86*	109*	–	–
AA6061 _{Ex+T6}	61*	162*	188*		
AA6061 + 0.5wt% Al ₂ O ₃ _{T6}	61*	173*	213*		
AA6061 + 0.5wt% Al ₂ O ₃ _{Ex+T6}	76*	211*	247*		
AA6061 + 1wt% Al ₂ O ₃ _{T6}	78*	246*	256*		
AA6061 + 1wt% Al ₂ O ₃ _{Ex+T6}	108*	265*	306*		
AA6061 + 1.5wt% Al ₂ O ₃ _{T6}	67*	195*	206*		
AA6061 + 1.5wt% Al ₂ O ₃ _{Ex+T6}	151*	338*	372*		

MPP Master Powder Feeding
Stir Stir Casting
Compo Compo Casting
CP Cold Pressing
Ex Extrusion
T6 T6 heat treatment

Table 4.3 Hardness and tensile properties of Al–MMNCs obtained through ultrasonic assisted casting

Material	Hardness	Tensile Yield Strength (TYS), MPa	Ultimate Tensile Strength (UTS), MPa	% Ductility	E (GPa)
Ultrasonic treatment					
A356 + SiC (US) [19]					
	HV				
A356	65*				
A356 _{US}	62*	–	–	–	–
A356 + 2 vol.% SiC _{US}	77*				
A356 + SiC (US) [20]					
A356	–	110*	270*	2,7*	–
A356 + 0.5 wt% SiC		120*	290*	3,5*	
A356 + 1 wt% SiC		140*	275*	3*	
A356 + 2 wt% SiC		155*	300*	3,5*	
Al + Al ₂ O ₃ (NC-US/cold rolling) [21]					
	HV				–
Al cp	36				
Al cp _(NC-US)	51	30	62	47 %	
Al + 2 wt% Al ₂ O ₃ (NC-US)	102	47	92	36 %	
Al + 2 wt% Al ₂ O ₃ (NC-US)+ cold rolling R. R.1,1	118	–	–	–	
Al + 2 wt% Al ₂ O ₃ (NC-US)+ cold rolling R. R.2,0	139	–	–	–	
AlSi7Mg0.3 + Al ₂ O ₃ (Cu addition/US) [22]					
Al–7Si–0.3 Mg	–	94 ± 0	153 ± 10	4.7 ± 0.7	–
Al–7Si–0.3 Mg–T6		167 ± 0.5	256 ± 0	7.45 ± 0.2	
Al–7Si–0.3 Mg– 0.5Cu		97.0 ± 4	148.5 ± 2	3.0 ± 0.1	
Al–7Si–0.3 Mg– 0.5Cu–T6		197.0 ± 7	243.0 ± 3	1.7 ± 0.2	
Al–7Si–0.3 Mg– 0.5Cu–1 wt% Al ₂ O ₃		110.0 ± 3	197.5 ± 6	7.9 ± 0.6	

(continued)

Table 4.3 (continued)

Al–7Si–0.3 Mg– 0.5Cu–1 wt% Al ₂ O ₃ –T6				10.4 ± 4	
Al–7Si–0.3 Mg– 0.75Cu		103.0 ± 2	170.0 ± 10	4.4 ± 2	
Al–7Si–0.3 Mg– 0.75Cu–1 wt% Al ₂ O ₃		107.5 ± 4	190.5 ± 10	6.5 ± 0.8	
Al–7Si–0.3 Mg– 1.0Cu		112.5 ± 1	177.5 ± 8	3.7 ± 0.5	
Al–7Si–0.3 Mg– 1.0Cu–1 wt% Al ₂ O ₃		110.0 ± 5	195.5 ± 10	5.6 ± 1	
Al–20Si + Al ₂ O ₃ (US) [17]					
Al–20Si	–	94*	120*	0.375*	
Al–20Si _{US}		82*	130*	1.1*	
Al–20Si P-refined		90*	138*	0.65*	
Al–20Si–0.1 wt% Al ₂ O ₃ _{US}		96*	146*	1.3*	
Al–20Si–0.5 wt% Al ₂ O ₃ _{US}		98*	154*	1.7*	
Al–20Si–1 wt% Al ₂ O ₃ _{US}		100*	150*	1.4*	
Al + Al ₂ O ₃ (US) [23]					
	HV				
Al	36	–	–	–	69.3 ± 1.7
Al _{US}	51	30	62	50	72.6 ± 1.5
Al + 2 wt%Al ₂ O ₃ US	102	47	92	41	75.2 ± 2.0
Al + 3.57 wt% Al ₂ O ₃ _{US}	127	–	93	36	78.5 ± 2.9
Al + 4.69 wt% Al ₂ O ₃ _{US}	149	–	96	34	79.4 ± 3.5
AA2024 + fly ash (US) [24]					
	HV				
AA2024	75		289 _C		
AA2024 + 1 wt% fly ash	96		–		
AA2024 + 2 wt% fly ash	100		–		
AA2024 + 3 wt% fly ash	114		345 _C		

(continued)

Table 4.3 (continued)

AA2024 + Al ₂ O ₃ (US) [25]					
AA2024	–	83*	154*	1.4*	
AA2024 + 0.5 wt% Al ₂ O ₃		139*	194*	1.2*	
AA2024 + 1 wt% Al ₂ O ₃		154*	212*	1*	
AA2024 + 1.5 wt% Al ₂ O ₃		149*	208*	0.6*	
AA2024 + 2 wt% Al ₂ O ₃		144*	203*	0.5*	
Al-9 Mg + TiCN (US) [18]					
Al-9 Mg US	–	137 ± 3	167 ± 18	1.4 ± 0.8	
Al-9 Mg + 0.2 vol. % TiCN		140 ± 7	185 ± 18	2.0 ± 0.7	
		143 ± 3	200 ± 4	2.7 ± 0.4	
Al-9 Mg + 0.5 vol. %TiCN		146 ± 3	209 ± 9	2.9 ± 0.7	
Al-9 Mg + 1.5 vol. % TiCN					
A356 + SiC (US) [26]					
A356	–	As compared to	As compared to A356	5*	
A356 + 1 wt%SiC		A356	+63 %	2.5*	
A356 + 1.5 wt% SiC		+103 %	+86 %	3*	
A356 + 2 wt%SiC		+134 % +35 %	+45 %	5*	

US Ultrasonic treatment

NC-US Non contact ultrasonic treatment

Table 4.4 Hardness and tensile properties of Al-MMNCs obtained through high pressure die casting

Material	Hardness	Tensile Yield Strength (TYS), (MPa)	Ultimate Tensile Strength (UTS), (MPa)	% Ductility	E (GPa)
AlSi10 Mg + CNT (High pressure die casting) [27]					
AlSi10 Mg	–	–	229*	4.4*	–
AlSi10 Mg + 0.05 wt% CNT			250*	5.8*	

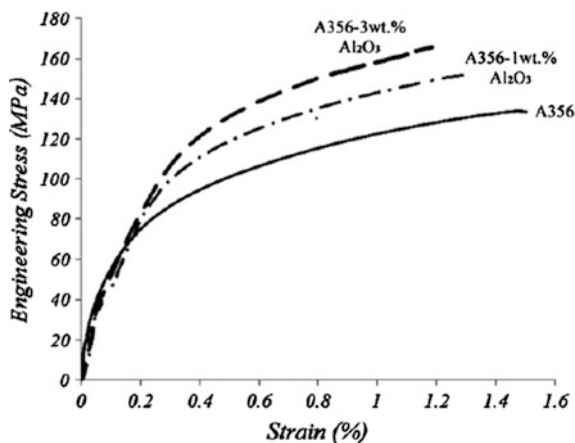


Fig. 4.1 Representative tensile engineering stress-strain curves under tension for A356–Al₂O₃ composites realized by compo casting [1]

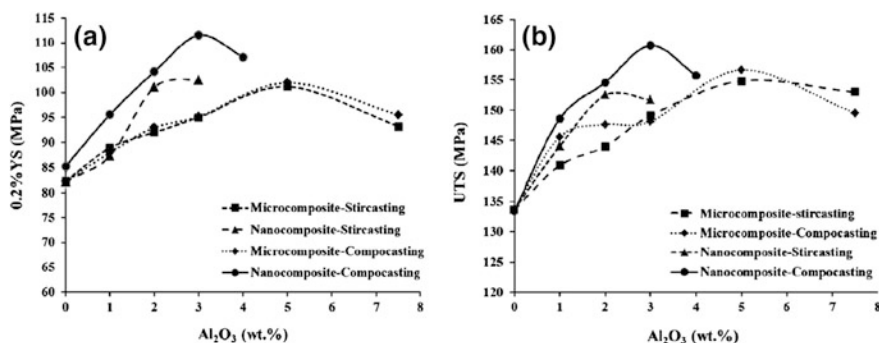


Fig. 4.2 The variation of (a) 0.2 % yield strength and (b) ultimate strength of the composites with different nano and micro-Al₂O₃ weight fractions fabricated by compo and stir casting processes [1]

volume/weight fraction, compocasting gives better mechanical properties than stir casting [1], and milling of mixed reinforcement and metallic powder prior to stir casting enhances mechanical properties with respect to base stir casting [11, 15]. By comparing the use of different reinforcement pre-mixed with aluminium to produce A356 nanocomposites through stir casting, adding 0.84 wt% Si powder and 1 wt% CNTs [16] allowed achieving, without heat treatment, YS similar to that obtained by adding 1.5 wt% of Al₂O₃ after T6 [15]. Furthermore, in the A356–CNT nanocomposite an improvement equal to 79 % of Young's modulus was reported [16].

Hardness data relating to different processing routes and different reinforcing particles are reported to be very similar to each other as a function of equal reinforcement volume fraction. Hardness increases with increasing particles content, while a decline is registered for high particles content (4.5–5 vol.%).

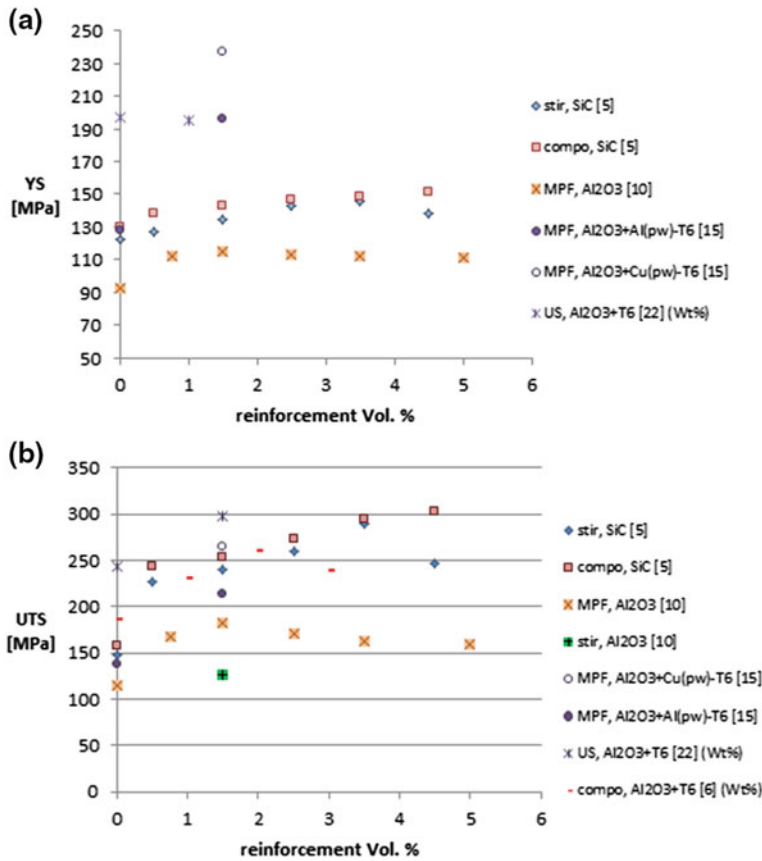


Fig. 4.3 YS (a) and UTS (b) as a function of vol.% for A356-based nanocomposites with different production techniques and reinforcement

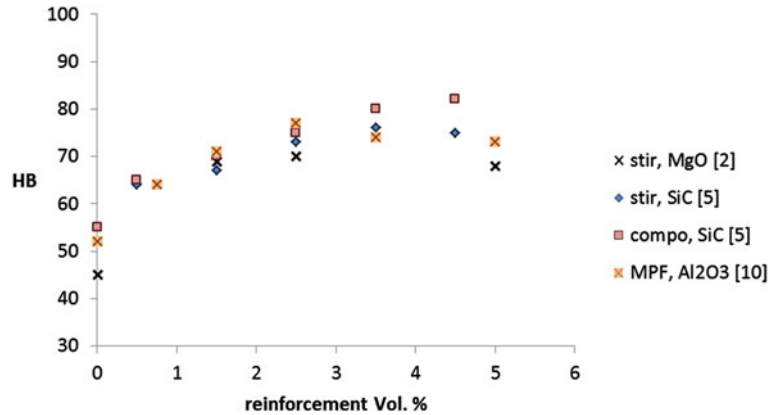


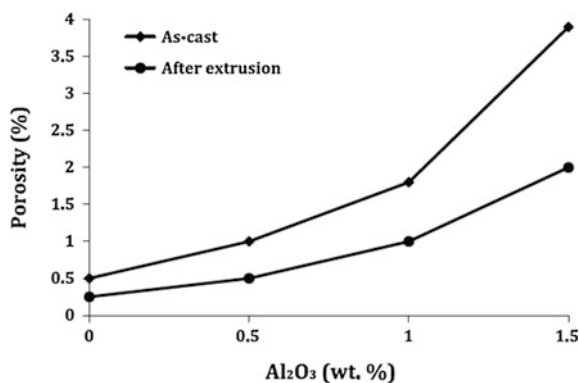
Fig. 4.4 Brinell hardness as a function of vol.% for A356-based nanocomposites with different production techniques and reinforcement

The increasing quantity of porosity seems to influence not only the tensile strength but also the compressive behavior of the composites produced by stir casting. The optimal reinforcement amount depends on process parameters: Abdizadeh [33], in particular, reported an ascending trend of the compressive strength from 0 to 1.5 vol.% of MgO nanoparticle reinforcement in A356 matrix, while a descending trend was detected from 1.5 to 5 vol.% when casting at 850 °C. It should be reported that casting at 800 °C enabled to increase the compressive strength up to 5 vol.% of MgO reinforcement, although the overall highest compressive strength was achieved when casting at 850° with 1.5 vol.% of MgO.

The negative effect of porosity may be suppressed or mitigated by secondary processes such as hot extrusion [8, 34]. As observed by Ezatpour in AA6061- Al_2O_3 composites [8] in the as-cast state, hardness, YS and UTS of the composites increased by increasing reinforcement weight fraction up to 1 % but then decreased, due to uneven distribution of nanoparticles and high porosity content (Figs. 4.5 and 4.6). Hot extrusion process, however, allowed obtaining a continuous increase in mechanical properties beyond the threshold weight fraction, owing to decrease the amount of porosity in the extruded samples and a more homogenous distribution of Al_2O_3 nanoparticles, a better interface bonding between particles and matrix, as well as microstructural densification. 1.5 wt% reinforced hot extruded nanocomposites showed YS and UTS approximately doubled with respect to the unreinforced hot extruded material.

Grain refining is a common outcome of ceramic nanoparticle addition [15, 18, 25]. It is therefore needed, to evaluate if nanoparticles strengthening is a direct effect or an indirect effect related to the induced microstructural refinement. Wang [18] reported a sensible decrease of grain size of the ultrasonic processed Al-9 Mg + $\text{TiC}_{0.7}\text{N}_{0.3}$ composites as compared to the unreinforced matrix (165 μm versus 36, 42 and 73 μm of the 1.5, 0.5 and 0.2 vol.% reinforced nanocomposites). Besides Hall-Petch strengthening mechanism, nanoparticles were reported to play a direct effect in strengthening the composites, as the same alloy refined through Al-5Ti-1B achieved similar grain sizes without as significant enhancement in UTS and ductility.

Fig. 4.5 The variation of porosity with nano- Al_2O_3 particle content in as-cast state and in extruded condition [8]



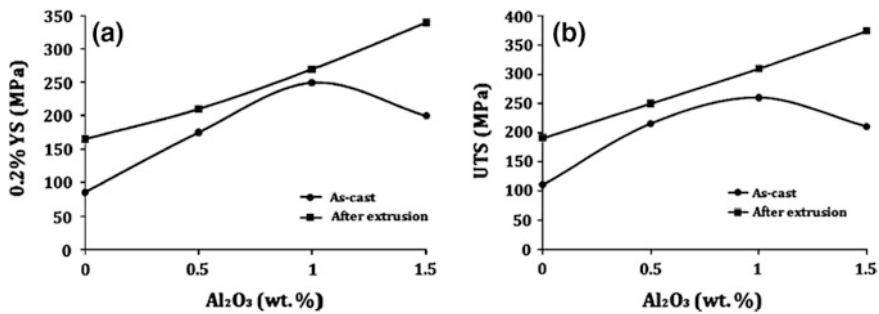


Fig. 4.6 The variation of (a) 0.2 % yield strength; and (b) ultimate strength of the composites with different nano-Al₂O₃ content in as-cast state and in extruded condition [8]

Influence of the heat treatment. Improvement in Al-nanocomposite mechanical properties can be achieved by age hardening. However, it should be noted that the presence of nano-reinforcement may change the aging kinetics, so that aging conditions should be optimized for each specific matrix-reinforcement system. Segregation of elements such as Mg at the n-SiC_p-Al interfaces and at the grain boundaries have been reported in powder metallurgy 7005 alloys subjected to HIP and T6 heat treatment [35], resulting in reduced precipitation hardening of the Al matrix and deterioration of its properties. In particular, in addition to equilibrium segregation, which is thermodynamically governed as to minimize grain boundary energy, interface energy, or free surface energy of the system [36], reinforcing particles could magnify non-equilibrium segregation [37]. In the latter, solute atoms are being driven to vacancies or point defects, and the reinforcement-matrix interface could represent a good sink for the solute atoms during heat treatment [35].

El Mahallawi et al. [6] reported that in the A356-Al₂O_{3-np} system synthesized by compocasting, the hardness of the aged A356 unreinforced alloy remained higher than the aged A356 based nanocomposite. Since the eutectic plates in the A356 nanocomposite did not show the presence of Mg peaks, it was inferred that the addition of Al₂O₃ nanoparticles to the A356 alloy prevents the formation of Mg₂Si precipitates. On the other hand, adding the nanoparticles with T6 heat treatment caused an increase in both tensile strength and elongation % of the nano-composites with respect to the T6 matrix (39.5 % increase in strength and 26.4 % ductility with 2 wt% reinforcement). Based on microstructural analysis reported in Fig. 4.7, it was concluded that the T6 heat treatment was effective in fragmenting and spheroidising eutectic silicon lamellae and this change in morphology could explain the significant strengthening and increase in ductility.

The enhancement of yield strength in T6 heat-treated Al-7Si-0.3 Mg-0.5 Cu-1 wt% Al₂O₃ nanocomposite was also shown to be limited by the reaction between Mg and Al₂O₃ nanoparticles during the heat treating process in nanocomposites produced by ultrasonic cavitation based dispersion [22]. However, the same study showed a positive effect on ductility induced by the refining of the

Fig. 4.7 Microstructure of A356–1 % Al_2O_3 , stirring time 1 min, cast in semi-solid state in the T6 heat treated condition (b) [6]. (See Fig. 3.18b for comparison with the as cast condition)

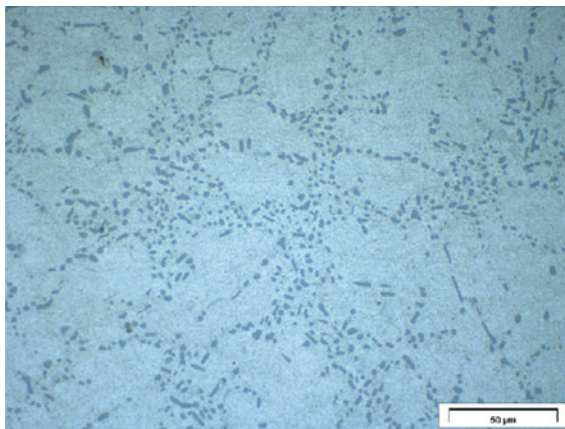
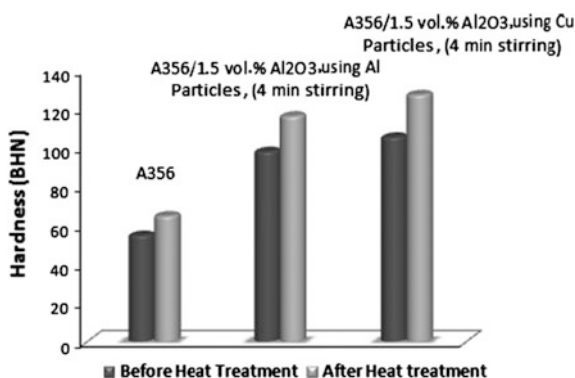


Fig. 4.8 T6 heat treatment effects on A356– nAl_2O_3 composites [15]



Si eutectic phase due to the presence of $\text{n-Al}_2\text{O}_3$. On the other hand, the beneficial effect of T6 heat treatment was shown in the Al_2O_3 –A356 system, processed by stir casting [15] and then heat-treated (T6) via a two steps solubilisation (8 h at 495 °C, followed by 2 h at 520 °C), water quenching (40 °C) and artificially aging (8 h at 180 °C). Figure 4.8 clearly show the effect of both the dispersion and age hardening strengthening mechanisms.

The hardness value of A356.2 reinforced by SiC and CNTs (2.4 and 2 wt%, respectively) using stir casting was measured after T6, after varying solution treatment temperatures between 470 and 560 °C (4 h) and fixing the aging conditions at 130 °C (3 h). Hardness was found to decrease after aging when 470 °C solution treatment was employed however, the hardness increased as the solution treatment temperature increased (50 % improvement with 560 °C solution treatment), suggesting that nano-sized reinforcement could prevent solute dissolution, thus requiring higher temperature to obtain uniform solution treatment [16].

A study aiming at evaluating the different contributions has been conducted by Lim [13], who produced AA7xxx-based composite reinforced with CNFs.

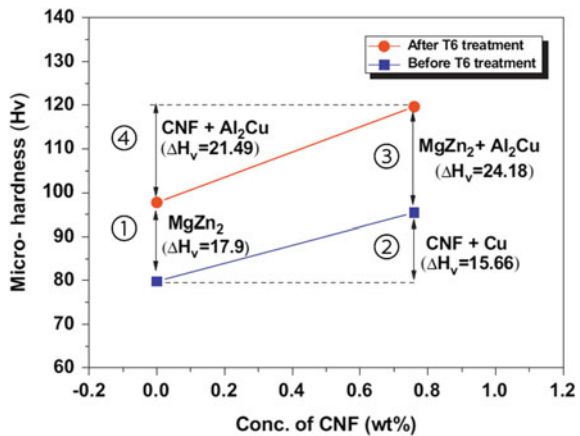
The strengthening factors taken into account were the Cu solid solution strengthening induced by the Cu layer on the CNFs, the precipitation hardening related to $MgZn_2$ and Al_2Cu precipitates induced by T6 heat treatment and the dispersion hardening due to CNFs. Micro-hardness tests on A7xxx alloy and CNF/A7xxx composite were performed before and after T6 treatment.

The precipitation of $MgZn_2$ particles due to T6 heat treatment in the unreinforced matrix induced an increase of about 18 HV; with the addition of 0.67 wt% Cu-coated CNFs, an increase of 16 HV was registered, due to both Cu solid solution strengthening effect and CNFs dispersion hardening. After T6 treatment, further increment of ~ 24 HV were attained, due to $MgZn_2$ and Al_2Cu precipitates. As a result, in the T6 heat treated condition, CNFs (and Cu atoms in solution, whose effect is negligible (ΔH_v 0.45) induced an increase in hardness of 21.5HV (Fig. 4.9). The authors concluded that the contribution of CNFs to the strengthening of CNF/A7xxx nanocomposite was about 38 %, which was less than that induced by precipitation hardening of $MgZn_2$ and Al_2Cu phases (61 %). The slight effectiveness of dispersion hardening was related by the researchers to the sub-optimal distribution of CNFs in the matrix.

Studies suggest that in Al-based nanocomposite, dispersion and age hardening strengthening can be additive, although parameters optimization is required with respect to the unreinforced alloys as to take into account the effect of nano-reinforcements on the solubilization and aging kinetics.

Ductility. Ductility of Al-based nanocomposites strongly depends on nanoparticle distribution. Unless an excellent distribution is achieved through proper dispersing technique, it can be generally stated that elongation to failure of Al-based nanocomposite is usually comparable or lower to the one of the unreinforced matrix. This is due to the presence of particle clusters which may act as preferential crack initiation or propagation sites. At the same time, ductility of nanocomposites is generally superior to the one of micro-size reinforced composites. The effect of particle size on ductility has been investigated by Sajjadi, who compared micro to

Fig. 4.9 Hardness of the A7xxx alloy and the 0.67 wt % CNF/A7xxx nanocomposite before and after T6 heat treatment [13]



nano composites based on A356 alloy, reinforced with Al_2O_3 particles [1]. With the exception of 1 wt% reinforced composite, microparticles induced a lower ductility as compared to the nano-sized ones. Compocast processed specimens, moreover, exhibited higher ductility than the ones obtained through stir casting. The increase of ductility in nanocomposites was related by the authors to the increase in grain boundary area due to grain refinement, the strong multidirectional thermal stress at the $\text{Al}/\text{Al}_2\text{O}_3$ particles interface, and to the load transfer between the matrix and the huge number of well-bonded nano- Al_2O_3 particulates. Higher ductility related to compocast specimens was also observed by Mazahery in A356 based composites containing SiC particles [5].

Figure 4.10 reports ductility data collected from works related on A356-based nanocomposites [5, 10, 15, 22]. As a common trend, ductility of the composites decreases by increasing the volume fraction of nanoparticles. Good level of ductility was maintained by master powder feeding technique [11, 12], especially in semi-solid state processed specimens. Carbon based reinforcement such as CNFs may induce relevant UTS and YS increase as compared to the unreinforced matrix while maintaining high ductility, as in the case of the hot rolled CNF-AA1050 composite [14], or in the hot rolled and T6 treated AA7xxx-based composites [13]. Both these studies, however, reported that for a further addition of CNFs, even though higher mechanical properties were obtained, a decrease in ductility was observed when achieving CNF vol.% of respectively 0.65 and 0.76 %.

An increase of ductility was observed when compared to the matrix in ultrasonic treated composites containing SiC, Al_2O_3 and TiCN particles [15, 18, 20, 22, 29]. Akbari related the combined enhancement in UTS and ductility of A356 alloy to the strengthening effects of uniformly distributed Al_2O_3 nanoparticles, grain refinement of aluminium matrix, thermal stress at the matrix/reinforcement interface and the effective transfer of applied tensile load [15, 29]. Choi related the strong enhancement of ductility (+512 % comparing to the T6 matrix) obtained in the

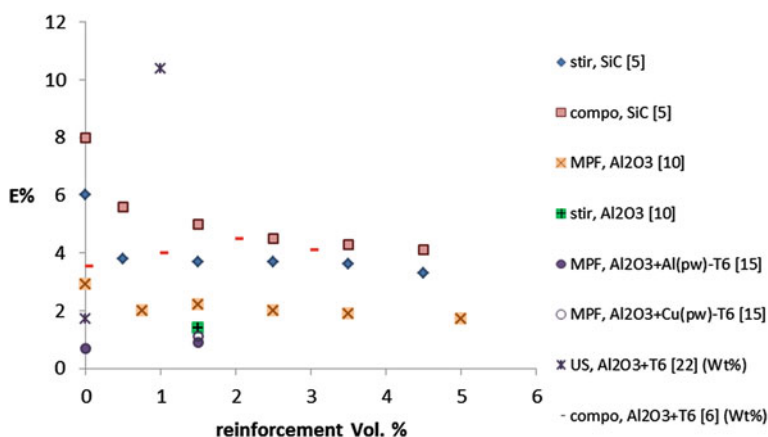


Fig. 4.10 Ductility (elongation to failure) as a function of vol.% fraction (V_f) for A356-based nanocomposites with different production techniques and reinforcement

1 wt%–T6 composite to the decrease of porosity (from 2.1 to 0.5 %) and modification of eutectic Si phases due to the addition of Al_2O_3 nanoparticles [22], as also reported in [6]. In particular, it was inferred that nucleation of eutectic Si is enhanced with the addition of Al_2O_3 nanoparticles during T6, resulting in rounder and smaller eutectic Si phases (size reduction of 49 %). When ultrasonic dispersion was used, an increase in ductility (+26.4 %) was also reported in compocast and T6 heat treated A356–2 wt% Al_2O_3 [6].

Fractography. The good ductility of Al-based nanocomposites is confirmed by fracture surface morphologies. Tensile fracture surfaces of the A356– Al_2O_3 system were found to be characterized by dispersed shallows and small dimples with varying sizes in the matrix, confirming the high ductility observed in the tensile tests [32]. Larger dimples were also found, mainly linked together along the boundaries, as a result of the increased degree of clustering along the grain boundary. By observing compression test specimens, the authors also reported the interdendritic region to be the weaker one in the composite structure, as the cracks find here their preferential growing path [32].

Interdendritic cracking was observed by Akbari et al. [15] as the main mechanism of failure in A356/ Al_2O_3 composites, which is the same as that of the unreinforced A356 matrix. Dendrites were observed in wide areas of fracture surfaces (Fig. 4.11a) and micro-cracks were reported to propagate along interdendritic region, within the eutectic structure, where nanoparticles are rejected by the solid-liquid interface and segregate [15, 29]. Dimples were found in some areas of fracture surfaces (Fig. 4.11b, c), as a possible result of void nucleation at eutectic silicon particles and coalescence by shear deformation and fracture process. In stir cast composites, porosities in the matrix due to air entrapment were observed (Fig. 4.11d), especially in composites stirred for the longest duration of time (16 min). The presence of big pores in the matrix is related by the authors to the decrease in mechanical properties (UTS, YS, ductility, elastic modulus) of 16 min stirred samples as compared to the 4, 8 and 12 min samples. Fracture path, was preferential along the regions containing localized and clustered pores [29].

Choi conducted fractographic study [17] in Al-Si hypereutectic alloys based nanocomposites (Al–20Si/ Al_2O_3 nanocomposite), as shown in Fig. 4.12. While the unreinforced matrix presented intergranular brittle failure due to the presence of coarse primary Si particles, Al_2O_3 nanocomposite presented a much finer fracture surface, as a result of primary Si particles refinement and modification of the eutectic structure induced by Al_2O_3 particles. The primary Si particles were refined from the star shape to a polygon or blocky shape, while their edges and corners were smoother. The refining effect was reported to be more relevant with increasing Al_2O_3 nanoparticle fraction up to 1 wt%. As concerning eutectic Si particles, the large plate morphology changed into fine coralline-like. These microstructural effects not only show an increase in mechanical properties when compared to the unreinforced and refined matrix, but also enhanced the ductility, which improved from 0.37 to 1.72 %. Al_2O_3 nanoparticles appear to be more effective for the

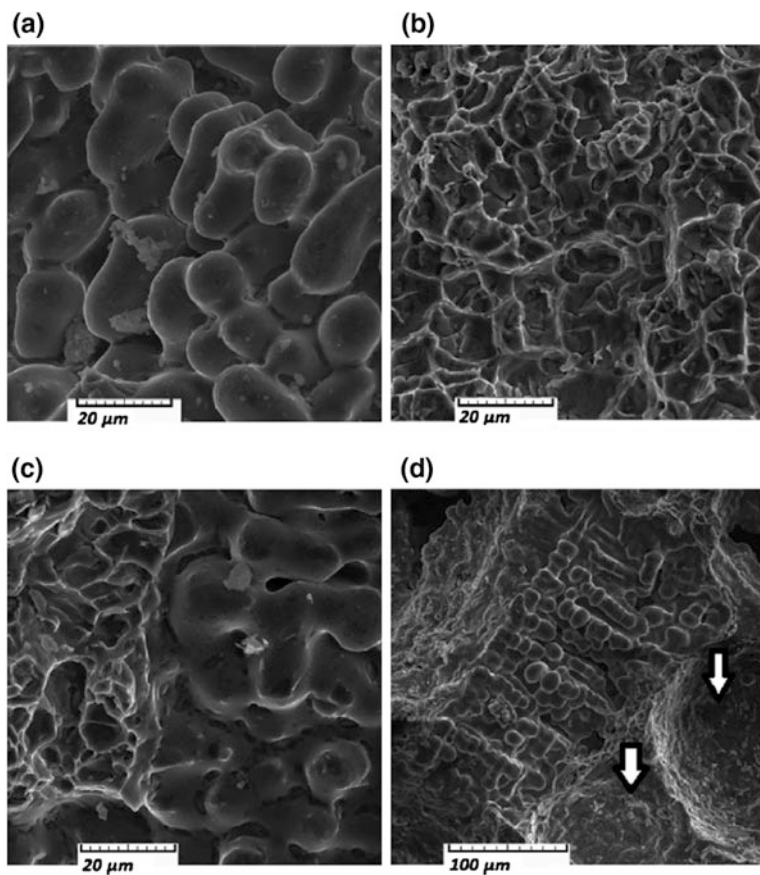


Fig. 4.11 SEM micrographs of tensile fracture surface of a A356–Al₂O₃ nanocomposite: (a) dendrites, and (b) dimples, (c) border between two structures, and (d) trace of gas bubbles in fracture surface [15]

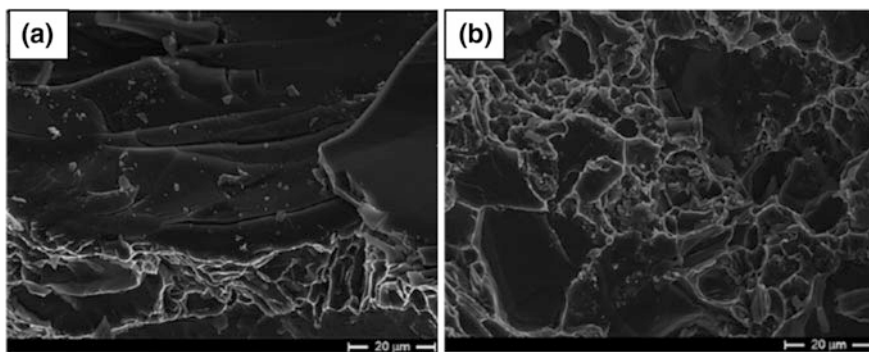


Fig. 4.12 SEM fractographs of (a) monolithic Al–20Si alloy and (b) its 0.5 wt% Al₂O₃ nanocomposite [17]

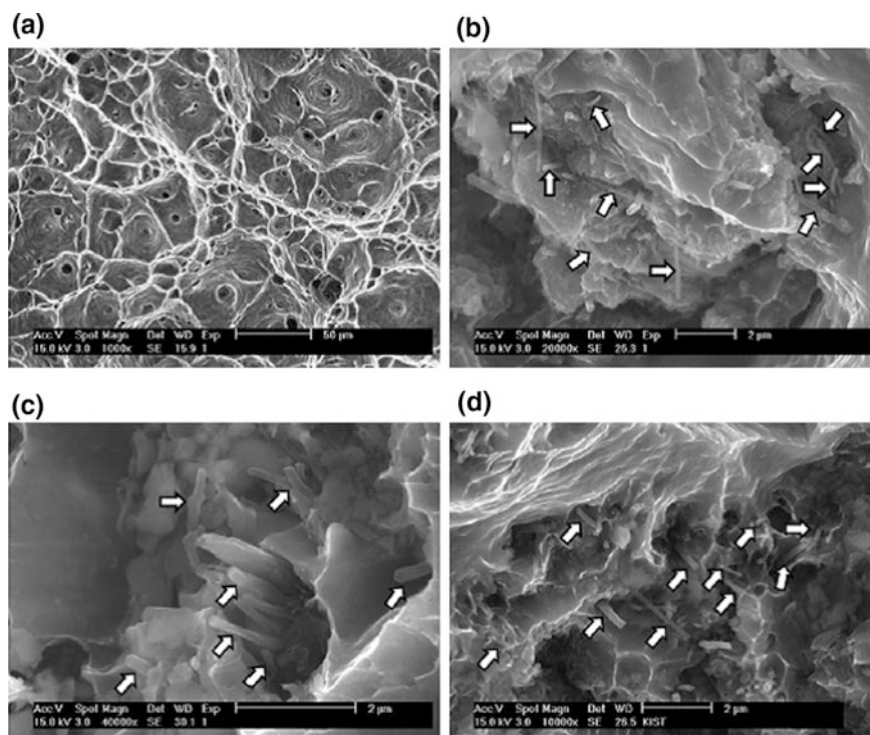


Fig. 4.13 Fracture surfaces of A1050 alloy (a) and composites containing 0.065, 0.38 and 0.58 wt% of CNF (b, c, d). CNF were randomly oriented in the 0.065 wt% composite, while evenly dispersed in 0.38 and 0.58 wt% composites [14]

enhancement of mechanical properties and microstructure refinement than conventional methods for hypereutectic Al–Si alloys. A similar eutectic refining effect of nano-reinforcing particles was highlighted also by Choi in the hypoeutectic Al–7Si–0.3 Mg–0.5Cu–Al₂O₃ composite [22].

Oh et al. [14] reported the tensile fracture surface of AA1050/CNF composite realized by stir casting and subsequent extrusion, that showed a dimpled structure (Fig. 4.13a), which became less pronounced by increasing CNF concentration. A correlation between mechanical properties and distribution of CNF was highlighted by SEM images. The lower yield strength of the 0.065 wt% composite as compared to the unreinforced matrix was related to the uneven dispersion and agglomeration of CNF within the matrix (Fig. 4.13b). On the contrary, a good and uniform distribution, such as in the case of 0.38 and 0.58 wt% composites, led to enhancement of strength, hardness and stiffness (Fig. 4.13c, d).

4.1.2 High Temperature Mechanical Properties

Despite their expected potential, very few data are available in the peer-reviewed literature concerning the high temperature mechanical properties of Al-based nanocomposites prepared by liquid routes. It was recently shown that the addition of Ni-P coated CNT either by stir casting or compocasting can improve mechanical properties of the unreinforced alloy either at room and high temperature [38]. In particular, adding 2 vol.% of MWCNT and stirring the semisolid slurry with a solid fraction of 30 % resulted in nanocomposites able to retain 90 % of YS at 300 °C (142 MPa) as compared to room temperature (158 MPa), while the unreinforced alloy prepared with the same compocasting route showed a YS of 79 MPa at 300 °C (60 % of the room temperature value).

The introduction of incoherent non-shearable second-phase particles in the aluminium matrix also improves the creep resistance by restricting the dislocation climb or gliding processes [39] and/or carrying higher load than the matrix [40], as reported for oxide or carbide microparticles [41]. Particles with smaller sizes are expected to further improve the creep resistance because of the shorter interparticle spacing, while stiffer reinforcement may carry greater stress. In fact, it was shown that the creep resistance of pure aluminium is greatly enhanced by incorporating 4.5 vol.% MWCNTs by hot rolling ball milled powders [42]. Furthermore, a threshold creep-stress was found in hot extruded Al–Al₂O₃ nanocomposite powder [43]. The threshold was related to the detachment of dislocations from the Al₂O₃ nanoparticles during the high-temperature extrusion and its magnitude was found to decrease with increasing the testing temperature, from 8.3 MPa at 648 K to 2.7 MPa at 723 K. Al–Al₂O₃ nanocomposite showed a change in the creep behaviour with increasing temperature, passing from invariant substructure model to dislocation glide. No threshold stress should be seen at $T > 765$ K, a critical temperature higher than the one of Al-based composites reinforced with micrometric ceramic particles [44]. Since the dislocations detachment-stress required for micrometric reinforcement particles is very small to be accounted in estimation of the threshold stress [45], it can then be inferred that nanometric particles are more effective in dislocation pinning with respect to micrometric particles.

4.2 Mg-Based Nanocomposites

4.2.1 Room Temperature Mechanical Properties

The room temperature mechanical properties of Mg-based MMNCs are given in Tables 4.5 and 4.6. Table 4.5 lists the microhardness and tensile response of Mg–MMNCs with varying Mg-matrices and nanoparticles, [46–68, 69–76], while Table 4.6 lists the properties under compressive loading [49, 50, 53, 56, 58, 60, 61,

Table 4.5 Microhardness and tensile properties of Mg–MMNCs

Material	Micro Hardness, Hv	Tensile Yield Strength (TYS), (MPa)	Ultimate Tensile Strength (UTS), (MPa)	% Ductility	Improvement in ductility
Processing Method: DMD + Hot Extrusion					
Mg [46]	40	97 ± 2	173 ± 1	7.4 ± 0.2	
Mg + 1.1 V _f n-Al ₂ O ₃ [46]	65	175 ± 3	246 ± 3	14 ± 2.4	89 %
Mg [63, 64]	45	126 ± 7	192 ± 5	8 ± 1.6	
Mg + 1.3 wt% CNT [63, 64]	46	146 ± 2	210 ± 4	13.5 ± 2.7	69 %
Mg [47]	40	97 ± 2	173 ± 1	7.4 ± 0.2	
Mg + 0.22 V _f n-Y ₂ O ₃ [47]	51	218 ± 2	277 ± 5	12.7 ± 1.3	72 %
Mg [65]	–	126 ± 7	192 ± 5	8.0 ± 1.6	
Mg + 0.5 V _f n-Y ₂ O ₃ [65]	–	141 ± 7	223 ± 5	8.5 ± 1.6	6.25 %
Mg [48]	40	97 ± 2	173 ± 1	7.4 ± 0.2	
Mg + 0.66 V _f n-ZrO ₂ [48]	51	221 ± 6	271 ± 6	0.7	–35 %
Mg [79]	48	120 ± 9	169 ± 11	6.2 ± 0.7	
Mg–5.6Ti (wt%) [79]	71	158 ± 6	226 ± 6	8 ± 1.5	29 %
Mg–5.6Ti–1.5 B ₄ C (wt %) [79]	85	180 ± 5	238 ± 6	9.8 ± 0.7	58 %
Mg [49]	48	125 ± 9	169 ± 11	6.2 ± 0.7	
Mg–5.6 Ti–2.5 n-Al ₂ O ₃ (wt%) [49]	74	175 ± 4	227 ± 10	3.3 ± 0.2	–46 %
Mg–5.6 Ti–2.5 n-Al ₂ O ₃ (BM) [49]	69	168 ± 8	214 ± 8	6.8 ± 0.8	9 %
Mg [50]	48	120 ± 9	169 ± 11	6.2 ± 0.7	
Mg–5.6Ti (wt%) [50]	71	158 ± 6	226 ± 6	8 ± 1.5	33 %
Mg–5.6Ti–1 SiC–BM (wt%) [50]	83	204 ± 7	260 ± 3	9.2 ± 1.1	53 %
AZ31B [51]	63	201 ± 7	270 ± 6	5.6 ± 1.4	
AZ31B +1.5 V _f n-Al ₂ O ₃ [51]	86	144 ± 9	214 ± 16	29.5 ± 1.9	426 %
AZ31B [52]	63	201 ± 7	270 ± 6	5.6 ± 1.4	
AZ31B + 1.5 V _f n-Al ₂ O ₃ + 3Ca [52]	113	235 ± 7	285 ± 14	7.3 ± 0.2	31 %
AZ31 [66]	64	172 ± 15	263 ± 12	10.4 ± 3.9	
AZ31 + 1.5 V _f n-Al ₂ O ₃ [66]	83	204 ± 10	317 ± 5	22.2 ± 2.4	114 %
AZ31 [53]	64	172 ± 15	263 ± 12	10.4 ± 3.9	

(continued)

Table 4.5 (continued)

Material	Micro Hardness, Hv	Tensile Yield Strength (TYS), (MPa)	Ultimate Tensile Strength (UTS), (MPa)	% Ductility	Improvement in ductility
AZ31 + 1 V _f CNT [53]	95	190 ± 13	307 ± 10	18.0 ± 2.6	68 %
AZ31B [54]	63	201 ± 7	270 ± 6	5.6 ± 1.4	
AZ31B + 3.3 V _f n-Al ₂ O ₃ + 10 Cu [54]	103	241 ± 8	313 ± 9	5.6 ± 0.5	–
AZ31B [55]	63	201 ± 7	270 ± 6	5.6 ± 1.4	
AZ31B + 1.5 V _f n-Al ₂ O ₃ + 1.5 Ni [55]	93	227 ± 4	298 ± 5	5.7 ± 0.7	1.7 %
AZ31/AZ91 [56]	111	207 ± 4	316 ± 6	8 ± 0.1	
AZ31/AZ91 + 1.5 V _f n-Al ₂ O ₃ [56]	140	232 ± 13	339 ± 10	15.9 ± 0.5	98.75 %
AZ31 [57]	67	180 ± 4	265 ± 7	10.9 ± 2.4	
AZ31 + 1.5 V _f n-Al ₂ O ₃ + 2 Cu [57]	76	250 ± 11	301 ± 11	13.5 ± 2.1	23.85 %
AZ31/AZ91 [58]	111	207 ± 4	316 ± 6	8 ± 0.1	
AZ31/AZ91 + 1.5 V _f n-TiC [58]	129	236 ± 8	337 ± 7	14.5 ± 0.1	81.25 %
AZ51 [59]	85	222 ± 4	302 ± 4	9 ± 0.4	
AZ51 + 1.5 V _f n-Al ₂ O ₃ + 2 Ca [59]	119	248 ± 2	338 ± 3	10 ± 0.3	11 %
ZK60A [62]	97	139 ± 4	246 ± 4	20.2 ± 2	
ZK60A + 1.5 V _f n-Al ₂ O ₃ [62]	92	147 ± 8	252 ± 5	26.0 ± 1	5.75 %
ZK60A [61]	138	163 ± 3	268 ± 3	6.6 ± 0.6	127 %
ZK60A + 1 V _f CNT [61]	114	180 ± 6	295 ± 8	15 ± 0.7	
ZK60A [60]	117	182 ± 4	271 ± 1	6.7 ± 1	170 %
ZK60A + 1.5 V _f n-Al ₂ O ₃ [60]	135	175 ± 2	305 ± 2	18.1 ± 0.9	
ZK60A [67]	138	163 ± 3	268 ± 3	6.6 ± 0.6	76 %
ZK60A + 1.5 V _f n-TiC [67]	116	184 ± 2	309 ± 3	11.6 ± 1.4	
ZK60A [68]	138	163 ± 3	268 ± 3	6.6 ± 0.6	85 %
ZK60A + 1.5 V _f n-Si ₃ N ₄ [68]	121	198 ± 6	313 ± 4	12.2 ± 0.8	
AZ91/ZK60A [58]	137	225 ± 4	321 ± 4	16.1 ± 0.3	–14 %
AZ91/ZK60A + 1.5 V _f n-AlN [58]	160	236 ± 6	336 ± 4	13.8 ± 1	

(continued)

Table 4.5 (continued)

Material	Micro Hardness, Hv	Tensile Yield Strength (TYS), (MPa)	Ultimate Tensile Strength (UTS), (MPa)	% Ductility	Improvement in ductility
Other Processes					
Mg-(2,4)Al-1Si (USC ^a) [72]	–	62	145	8.8	
Mg-(2,4)Al-1Si-2 n-SiC (USC ^a) [72]	–	82	178	9.5	8 %
Mg-n-SiC (6 vol.%) [73] (Semi-solid + Ultrasonic)	180				
AZ31 (ECAP ^b) [73]	57	–	–	–	
AZ31-nAl ₂ O ₃ (ECAP ^b) [73]	61	–	–	–	
AZ63 (FSP ^c) [74]	80	–	150	6	83 %
AZ63-n-SiC (FSP ^c) [74]	110	–	300	11	
Mg (USC ^a) [69]	–	47 ± 3	120 ± 4	12.3 ± 1.1	–48 %
Mg-1n-SiC (wt%) (USC ^a) [69]	–	67 ± 4	133 ± 5	6.3 ± 0.8	
AZ61 (FSP ^c) [71]	60	140	190	13	
AZ61 (4P) (FSP ^c) [71]	72	147	242	11	–15 %
AZ61(4P)-5 n-SiO ₂ (FSP ^c) [71]	97	214	233	8	–27 %
AZ31-Hot Rolled [70]	–	170	265	–	
AZ31-Annealed [70]	–	103	210	–	
AZ31-n-Al ₂ O ₃ (wt%) Hot Rolled [70]	–	260	296	–	
AZ31-1.0 n-Al ₂ O ₃ (wt %) Anneal [70]	–	153	255	–	
AZ91 (Semi-solid stirring + USC ^a) [75]	–	70	125	2	
AZ91-nSiCp (Semi-solid + USC ^a) [75]	–	85	180	5.7	185 %
AZ91 (Semi-solid + USC ^a) [76]	–	125	200	6	
AZ91-0.7V _f CNT-0.3V _f n-SiC (Semi-solid stirring + USC ^a) [76]	–	200	300	9	50 %

^aUltrasonic cavitation, ^bEqui-channel angular pressing, ^cFriction stir process

Table 4.6 Compressive properties of Mg–MMNCs

Material	Compressive Yield Strength (CYS), MPa	Ultimate Compressive Strength (UCS), MPa	% Ductility	Yield Asymmetry, (R) (CYS/TYS)
Processing Method: DMD + Hot Extrusion				
Mg [79]	65 ± 4	248 ± 8	19.2 ± 1.1	0.54
Mg–5.6Ti (wt%) [79]	77 ± 3	347 ± 5	13.5 ± 0.8	0.48
Mg–5.6Ti–1.5 B ₄ C (wt%) [79]	96 ± 7	395 ± 5	15.6 ± 1.3	0.53
Mg [50]	65 ± 4	240 ± 8	19.2 ± 0.7	0.54
Mg–5.6Ti (wt%) [50]	77 ± 3	424 ± 5	14.4 ± 1.2	0.48
Mg–5.6Ti–1 SiC–BM (wt%) [50]	117 ± 6	349 ± 7	15.2 ± 1.1	0.57
Mg [49]	87 ± 4	169 ± 9	6.2 ± 0.7	0.69
Mg–5.6 Ti–2.5 n-Al ₂ O ₃ (wt%) [49]	106 ± 0	227 ± 15	3.3 ± 0.2	0.60
Mg–5.6 Ti–2.5 n-Al ₂ O ₃ (BM) [49]	106 ± 3	214 ± 9	6.8 ± 1.7	0.63
AZ31B [77]	133 ± 4	444 ± 10	12.6 ± 1.0	0.66
AZ31B + 1.5 V _r n-Al ₂ O ₃ [77]	176 ± 7	486 ± 5	14.3 ± 1.2	1.22
AZ31 [66]	93 ± 9	485 ± 4	19.7 ± 7.2	0.54
AZ31 + 1.5 V _r n-Al ₂ O ₃ [66]	92 ± 2	509 ± 12	19.0 ± 2.7	0.48
AZ31 [53]	93 ± 9	485 ± 12	19.7 ± 7.2	0.54
AZ31 + 1 V _r CNT [53]	147 ± 13	501 ± 10	20.6 ± 2.8	0.77
AZ31B [78]	133 ± 4	444 ± 10	12.6 ± 1.0	0.66
AZ31B + 3.3 V _r n-Al ₂ O ₃ + 10 Cu [78]	235 ± 8	530 ± 11	10.7 ± 1.5	0.97
AZ31/AZ91 [56]	117 ± 15	495 ± 13	19.6 ± 1.9	0.56

(continued)

Table 4.6 (continued)

Material	Compressive Yield Strength (CYS), MPa	Ultimate Compressive Strength (UCS), MPa	% Ductility	Yield Asymmetry, (R) (CYS/TYS)
AZ31/AZ91 + 1.5 V _f n-Al ₂ O ₃ [56]	123 ± 16	512 ± 3	18.2 ± 0.7	0.53
AZ31/AZ91 [58]	117 ± 15	495 ± 13	19.6 ± 1.9	0.56
AZ31/AZ91 + 1.5 V _f n-TiC [58]	104 ± 13	531 ± 11	20.3 ± 2.7	0.44
ZK60A [61]	136 ± 11	522 ± 11	19.6 ± 0.9	0.97
ZK60A + 1 V _f CNT [61]	152 ± 5	547 ± 3	33.2 ± 6.2	0.61
ZK60A [60]	93 ± 8	498 ± 16	23.2 ± 4.6	0.97
ZK60A + 1.5 V _f n-Al ₂ O ₃ [60]	88 ± 7	530 ± 9	32.6 ± 3.3	0.50
ZK60A [67]	128 ± 11	522 ± 11	19.6 ± 0.9	0.97
ZK60A + 1.5 V _f n-TiC [67]	106 ± 7	577 ± 6	25.3 ± 1.6	0.57
ZK60A [68]	128 ± 11	522 ± 11	19.6 ± 0.6	0.97
ZK60A + 1.5 V _f n-Si ₃ N ₄ [68]	86 ± 11	605 ± 5	29.9 ± 3.1	0.43
AZ91/ZK60A [58]	106 ± 5	508 ± 17	19.5 ± 1.7	0.47
AZ91/ZK60A + 1.5 V _f n-AlN [58]	107 ± 12	541 ± 19	24.1 ± 6.5	0.45

66–68, 77–79]. The methods used to produce these nanocomposites are also given in the tables.

From Tables 4.5 and 4.6, it could be seen that the tensile and compressive properties improve significantly upon the addition of nanoparticles. It is interesting to note that unlike in micron-size MMCs wherein strength improvement alone is observed [80–90], in the case of nanocomposites, not only does the yield and tensile strengths increase, but also that the ductility is significantly enhanced in most of the composites. This gives rise to enhanced toughness of the nanocomposites, the absence of which is a major drawback in the case of micron-composites. Further, the results indicate that hybrid processes such as intermediate solid-state processing prior to casting, has a marked effect on the mechanical properties, as shown in the representative stress-strain curves in Fig. 4.14a, b [49]. Another example that highlights the effect of hybrid process in influencing the properties was reported by Chen et al. [91]. In this work, combination of semi-solid processing and ultrasonic processing enabled incorporation of very high volume fraction of n-SiC particles (6 vol.%) in a Mg–Zn matrix, which eventually resulted in very high hardness. Figure 4.15 shows the hardness comparison based on the work by Chen et al. [91] and those Mg-based nanocomposites produced by various other techniques. In this work, the authors have compared the hardness data of their material with those of Mg-nanocomposites containing other reinforcements with noticeably lower volume fractions. While the advantage of their processing method to reinforce high volume fraction of nano reinforcements cannot be disputed, a more valid comparison of hardness increase would have been to make a comparison with systems having similar reinforcement volume fractions and type.

As mentioned in the introduction section, the strengthening mechanisms in nanocomposites are usually attributed to the combined effects of: (i) grain refinement by which increase in strength occur due to the piling up of dislocations at

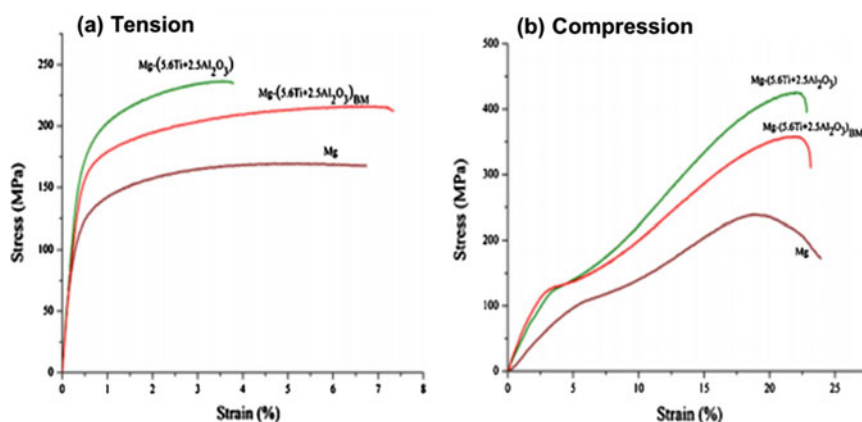


Fig. 4.14 Representative engineering stress-strain curves under (a) tension and (b) compression [49]

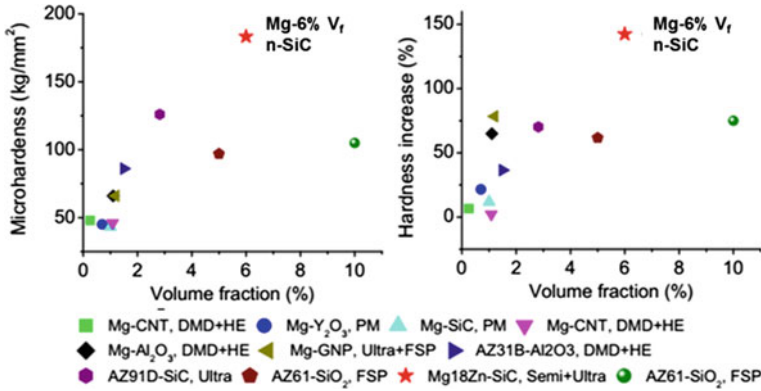


Fig. 4.15 Hardness of Mg-based metal matrix nanocomposites (Mg–6 vol.% n-SiC) produced by hybrid processing of semi-solid + ultrasonic processes. The microhardness value and the hardness increase are compared with those hardness values of Mg-composites prepared by other processes (DMD disintegrated metal deposition; HE hot extrusion; PM powder metallurgy; Ultra ultrasonic processing; FSP friction stir processing; Semi-semisolid mixing; CNT carbon nanotube; GNP grapheme nanoplatelets [91])

grain boundaries (Hall-Petch effect) [92–94], (ii) Orowan strengthening that occurs due to the impeding of dislocation motion by the nanoparticles [92, 93, 95], (iii) increase in the dislocation density due to thermal mismatch (difference in thermal expansion coefficients of the reinforcements and matrix) [96, 97] and (iv) effective load transfer from matrix to hard nanoparticles [98]. Among these mechanisms, the strengthening effect due to grain refinement is widely accepted to be the major phenomenon, with relatively less contribution from the rest of the factors [93].

In a different view point, Fergusson and co-workers [99] performed analyses regarding the enhancement of yield strength and failure strain of unimodal Mg–MMNCs in order to understand the mechanisms of strengthening, in particular the effect of grain refinement and subsequent nanocomposite strengthening by Orowan mechanism. Based on the analysis made, these authors reported that the direct effect of nanoparticle addition on properties was effective only for few materials and that Orowan strengthening was absent in nanocomposites [99]. They also claimed that using traditional methods (post-processing such as rolling), significant grain refinements and Orowan strengthening can be easily achieved (to give rise to increased dislocation density that is usually accompanied by increase in yield strength and decrease in ductility), rather than by nanoparticle addition. According to these authors, the presence of nanoparticle is not a necessary factor for work-hardening. Based on their analysis, they concluded that traditional alloys have better properties than nanocomposites [99].

However, considering the above-mentioned study by Fergusson and co-authors, it could be seen that the entire analysis (Figs. 1 to 7 in Ref. [99]) was performed based on grain refinement, i.e. pertained to investigating the effect of nanoparticle

on the yield strength and failure strain with reference to ‘change in grain size alone’. Such an interpretation may be misleading, as particularly in wrought Mg-materials, the deformation characteristics are governed by slip and twinning, and hence on the crystal orientation and direction of application of the load [100]. Hence, the change (or reduction) in grain size due to nanoparticles by itself may not be directly related to the improvement in properties; rather the nanoparticles and fine grain-sized matrix together or individually would control/contribute towards: (i) evolution of crystallographic texture before and during deformation, (ii) activation of additional non-basal slip systems, (iii) facilitation of cross-slip, (iv) induction/restriction of twins/twinning activity, and (v) in influencing slip-twin interaction during deformation, with one or more of these factors determining the deformation characteristics [101–106]. Other factors controlling the mechanical properties include the orientation and interfacial coherency of the nanoparticles with respect to the Mg-matrix [107, 108]. Some of the reports that have identified the evidences relating to some of these factors are mentioned below.

Most of the reported literature data indicate that the significant improvement/retention in ductility in Mg–MMNCs is due to the nanoparticles aiding the activation of non-basal slip system or cross-slip [46, 51, 64, 109]. Some representative features in tensile fracture surfaces of liquid-state processed Mg–MMNCs are briefly mentioned here. Hassan et al. [46] reported that in the case of pure Mg, dominant cleavage feature was observed with slip in the basal planes (Fig. 4.16a, b). In contrast when nano- Al_2O_3 particles were incorporated, mixed mode fracture with dominant dimple features were observed (Fig. 4.17a). The increased non-basal slip activity (Fig. 4.17b) observed in the nanocomposite conforms with the very high ductility observed in the system (~ 90 % improvement when compared to pure Mg). Under compression, intense shear fracture with increased shear band activity is usually observed which is attributed to heterogeneous deformation, as seen in the fracture surfaces of Refs. [49, 50, 77, 78].

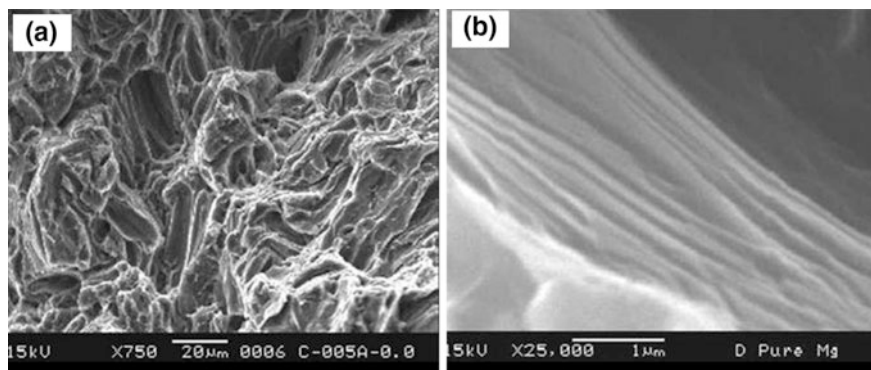


Fig. 4.16 SEM tensile fracture surface in pure Mg showing dominant cleavage feature with slip in the basal planes [46]

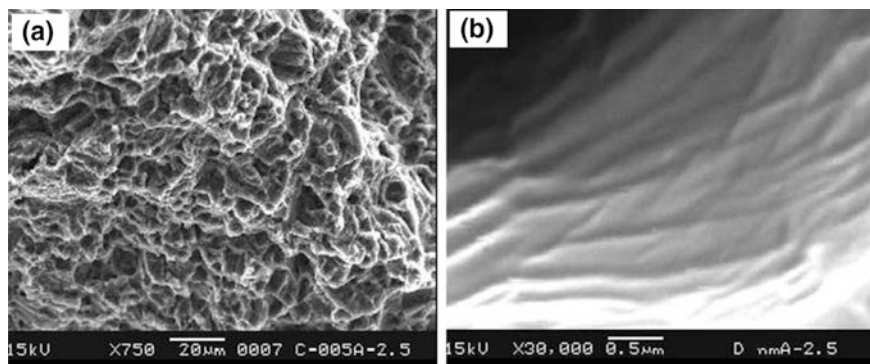


Fig. 4.17 SEM tensile fracture surface in Mg-nAl₂O₃ composite showing mixed mode fracture with (a) dominant ductile morphology and (b) increased non-basal slip activity [46]

Very few research works have used TEM to investigate fracture surfaces after deformation (under tensile loading). TEM analyses of tensile fracture surfaces of pure Mg and Mg-CNT composite conducted by Goh et al. [63] showed the following interesting features (Fig. 4.18a-d). In pure Mg, limited amounts of basal dislocations were observed, with no pyramidal $\langle c + a \rangle$ dislocations. However, extensive prismatic dislocations were found to be more active than the basal slip

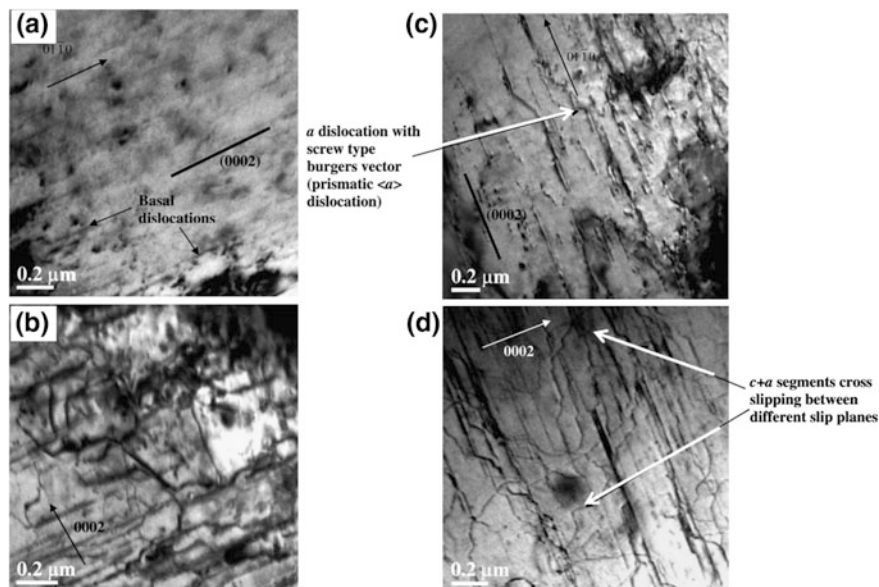


Fig. 4.18 TEM analyses of tensile fracture surfaces: (a, b) pure Mg with limited amounts of basal dislocations and (c, d) Mg-CNT composite showing cross-slip of basal dislocation with prismatic slip [63]

systems. On the other hand, in the Mg–1.3CNT nanocomposite, cross-slipping of basal dislocation with prismatic slip was clearly observed after tensile deformation (Fig. 4.18c), and that the pyramidal $\langle c + a \rangle$ dislocations traverse between the basal and non-basal slip planes [63]. Based on the investigation, it was reported that while tensile deformation resulted in a substantial increase in non-basal dislocations in both the pure Mg and Mg–CNT specimens, the occurrence of dislocation cross-slip was also found to be prevalent in the nanocomposite (Fig. 4.18d), thus attributing for the increased ductility observed in the CNT incorporated composite. Similar features were observed in Mg–Y₂O₃ nanocomposite [65]. In Mg–Y₂O₃ nanocomposite [65], the composite showed improved strength values with retention in ductility. TEM investigations revealed that the activity of basal slip is relatively less, thus causing no improvement in tensile ductility [65]. However with regard to strength improvement, considering that no significant reduction in grain size was observed when compared to pure Mg, the effect of grain refinement on strengthening will be minimal. Hence, the improvement in yield strength will be governed by other factors rather than grain size effect, in contrast to the grain refinement based analysis by Fergusson et al. [99]. TEM studies in Mg–Y₂O₃ nanocomposite [65] revealed that non-basal dislocations were found to originate at the twin interface prior to tensile deformation (Fig. 4.19a). Further, dislocations originating in clustered nanoparticles were also observed indicating contribution from Orowan-type strengthening. Upon tensile deformation, non-basal slip/cross-slip and slip-twin interactions occur (Fig. 4.19b) resulting in improvement in the strength properties [65]. These observations reinforce the fact that in Mg–MMNCs, multiple strengthening mechanisms operate to bring forth improvement in properties, and that the interpretation of properties improvement (strengthening) should not be restricted to grain refinement effect alone.

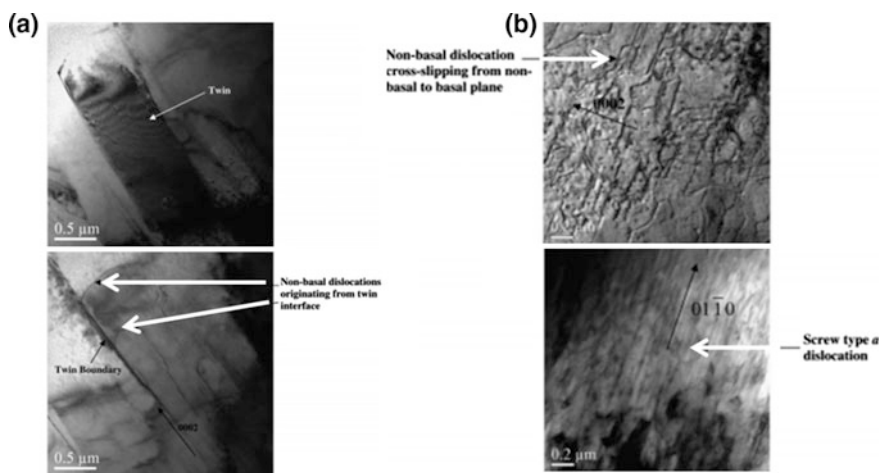


Fig. 4.19 TEM analyses of Mg–nY₂O₃ composite showing (a) non-basal dislocations originating at the twin interface prior to tensile deformation and (b) occurrence of non-basal slip/cross-slip and slip-twin interactions after tensile deformation [65]

Another feature that should be observed is the difference in the shape of the stress-strain curve under tensile and compressive loading conditions, which is typical of extruded Mg-materials (Fig. 4.14 [49]). As explained earlier, in wrought Mg-materials, such as in extruded Mg-rods, the basal planes of the grains tend to be strongly aligned parallel to the axis of the rod (i.e. perpendicular to the c-axis) [100]. Under such conditions, a compressive stress applied nearly parallel to the basal planes favours twinning, whereas a similarly-directed tensile stress cannot induce such twins. As a consequence, the stress-strain curves in tension and compression obtained from specimens made from extruded Mg-rods would appear very different (tension-compression asymmetry) [100, 102, 105]. In both the unreinforced and reinforced materials, the tensile curve (Fig. 4.14a) exhibits a higher yielding stress with low work hardening until close to the peak stress and fracture. Unlike the tensile curve, the stress-strain curve under compression displays an upward concave profile after yield. This initial upward concave hardening then progresses into a convex profile, resulting in a sigmoid-shaped response in the hardening phase (Fig. 4.14b). Under tension, the higher yield stress and relatively low work hardening is due to slip being the dominant deformation mode, and that there are fewer slip systems in Mg-materials [102, 104]; under compression, the low initial yield is indicative of dominant deformation by twinning and the significant work hardening is due to factors such as activation of non-basal slip systems, cross slip, slip-twin interactions [102, 104]. As mentioned earlier, when nanoparticles are incorporated, other mechanisms such as those due to the evolution of crystallographic texture during deformation, twin boundaries, activation of non-basal slip systems, cross slip, slip-twin interactions increasingly occur. Further, the yield asymmetry, R , listed in Table 4.6 (R is the ratio of compressive yield to tensile yield; $R = 1$, no yield asymmetry [102, 110]) indicates that while in most Mg-MMNCs there is a decrease in asymmetry when compared to the unreinforced Mg-material, in few nanocomposite systems, the asymmetry increased after nanoparticle addition. This is prominent in non-Al containing Mg-alloy matrix nanocomposites (such as ZK60A based Mg-MMNCs) [60, 61, 67, 68]. This is probably due to the fact that unlike pure Mg or Al-containing Mg-alloys which exhibited dominant basal texture, the unreinforced ZK60A alloy exhibited pyramidal bulk texture [67] (with $R \sim 0.97$, low asymmetry). Hence, when nanoparticles were added, asymmetry tended to increase. This was reported to be due to the nanoparticles which facilitated the compressive shear buckling of Mg-Zn based nano-rod/disc intermetallic present in these systems during deformation (Fig. 9 in [67]), thereby increasing the tensile-compressive yield asymmetry.

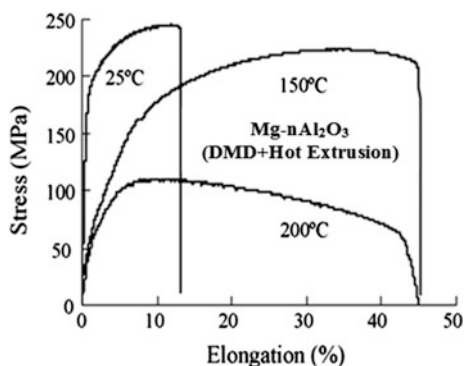
4.2.2 High Temperature Mechanical Properties

The development of Mg-nanocomposites with various nano-sized reinforcements and the subsequent evaluation of their room temperature mechanical properties have been widely studied. However, only few research works have reported the

high temperature characteristics. Hassan et al. [111] studied the high temperature tensile properties of extruded n-Al₂O₃ reinforced Mg–MMNCs produced by DMD. It was found that the nano-size Al₂O₃ reinforced composite showed strain matrix hardening up to 150 °C and beyond that temperature (i.e., 200 °C) strain softening occurred (Fig. 4.20). When compared to room temperature strength, strength retention was observed at 150 °C, whereas large reduction in strength occurred at 200 °C. Nie et al. [112, 113] studied the high temperature tensile behaviour of AZ91/SiC nanocomposites produced through semisolid stirring and subsequent ultrasonic treatment followed by hot extrusion. The high temperature tensile tests (75, 125, 175 and 225 °C) showed that both tensile strength and elongation to fracture were enhanced when compared to the AZ91 extruded alloy at the same temperatures.

Srinivasan and co-workers [114] investigated the hot compressive deformation behaviour and microstructural evolution of AZ31B–nAl₂O₃ composite by using processing maps, in the temperature range of 250–400 °C and strain rate range of 0.01 to 1.0 s^{−1}. The optimal region for hot working was observed at a strain rate of 0.01 s^{−1} and the temperature of 400 °C for both Mg–alloy and nanocomposite. The instability regimes were identified at higher strain rate and temperature characterized by shear bands, flow localization and twinning in TEM analyses, whereas the stable domains were identified in the lower strain rate regimes with dominant dynamic recrystallization [114]. Sankaranarayanan et al. [115] in their study on Mg–Ti–Al–nAl₂O₃ composites, highlighted the effect of heat treatment on the ductility of Mg–nanocomposites [115]. In this work, Mg–Ti–Al–nAl₂O₃ composites were heat-treated at 200 °C for 5 h which led to significant enhancement in ductility (210 % or ~3 times increase under tension and 45 % increase under compression) with slight or no reduction in yield strength under both tensile and compressive loading conditions. This was attributed to the stress relaxation at matrix–reinforcement interface, and it was identified that the best combination of strength and ductility can be obtained after heat treatment [115].

Fig. 4.20 High temperature tensile properties of extruded n-Al₂O₃ reinforced Mg–MMNCs produced by DMD [111]



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Chapter 5

Tribological Characteristics of Al and Mg Nanocomposites

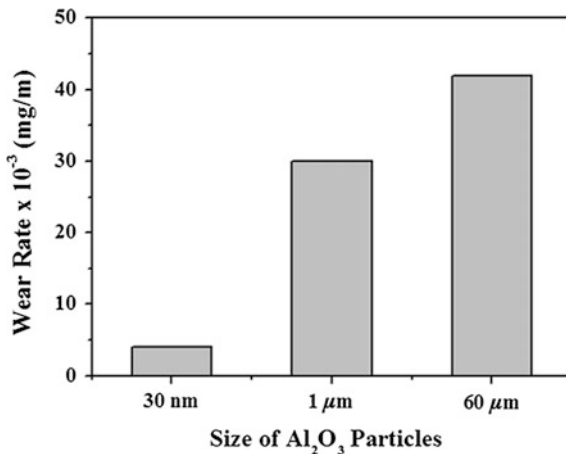
Abstract Al and Mg nanocomposites have good mechanical properties and are potential tribological candidates for applications where weight-reduction is a critical factor, such as in automotive, aerospace and sports. This chapter presents the tribological characteristics of various Al and Mg nanocomposites. The tribological properties of wear and friction of the light-metals nanocomposites are influenced by several factors such as: process and process parameters, composition and microstructure, mechanical properties, heat treatment to enhance mechanical properties, applied external parameters of velocity and load, and formation of in situ protective films/layers. Examples of tribological investigations of nanocomposites that highlight these influencing factors are presented in the view of providing a comprehensive outlook on the tribology of light-metals nanocomposites. Some suggestions for future work are also mentioned.

5.1 Al-Based Nanocomposites

Al based metal matrix composites exhibit better mechanical and tribological properties than their Al metal/alloys counterparts and therefore have been used as tribological parts in some vehicles [1, 2]. To note, Al nanocomposites display enhanced mechanical properties when compared to Al metal matrix composites, and hence Al nanocomposites are being investigated for their tribological performance.

Wear behaviour of Al6061 alloy reinforced with micron-sized (1 μm , 60 μm) and nano-sized (30 nm) Al_2O_3 particles (3 vol%, mechanical milling and hot press) was evaluated by Hosseini et al. [3]. Wear test specimens were taken in the form of discs (hot pressed samples) and AISI 52100 carbon steel pins were slid against the discs (sliding velocity: 0.08 m/s, applied load: 20 N). Figure 5.1 shows the wear rate (mg/m) of the composites as the function of Al_2O_3 particulate size [3]. It could be seen from the figure that the nanocomposite showed a wear rate that was about an order of magnitude lower than the micrometric composites. Better dispersion of Al_2O_3 nano-particles, higher relative density and hardness when compared to the

Fig. 5.1 Wear rate (mg/m) of the Al6061 alloy based composite as the function of the size of the reinforced Al_2O_3 particles [3]. The composite with nano-particles has a wear rate that is about an order of magnitude lower than the micrometric counterparts [3] (Regenerated from [3])



composites with micron-reinforcements together contributed towards the superior wear performance of the nanocomposites. Wear mechanisms of abrasion in nanocomposites and delamination in composites with micron-reinforcements were observed. They also reported that (i) milling of nano-particles with matrix material for longer durations of time resulted in improved relative density and hardness, which promotes the wear resistance, and (ii) lower volume fractions of nano-sized reinforcement is sufficient to achieve better mechanical properties when compared to higher volume fractions needed for micron-sized reinforcements. Hosseini et al. [4] further investigated the influence of volume percent (vol%) of Al_2O_3 nano-particles in the range of 1–5 % on the wear and friction characteristics of Al6061 alloy based nanocomposites. The composites were taken in the form of discs and AISI 52100 carbon steel pins as the sliding counterface (sliding velocity: 0.08 m/s, applied load: 20 N). They observed that the wear was controlled by hardness. An increase in hardness was seen by the addition of nano-particles up to 3 vol% consistently, and correspondingly the wear decreased. At higher volume percents of 4 and 5 % agglomeration of nano-particles led to the lowering of relative density (increase in porosity) that reduced the hardness and thereby increased the wear. The coefficient of friction (μ) value was ~ 0.3 – 0.4 for nanocomposites with 1 and 3 vol% Al_2O_3 , whereas for the composites with 5 vol% Al_2O_3 , the μ value was ~ 0.5 . Large fluctuations in the μ values were seen in the friction traces of composites with the highest vol% of nano-particles, which was attributed to the higher roughness of the material. Akbari et al. [5] studied the wear performance of A356 alloy with Al and Cu additions having Al_2O_3 nano-particles. The nanocomposites were produced by stir casting method. Al and Cu powders were separately milled with Al_2O_3 nano-particles (20 nm), and were incorporated into A356 alloy matrix by vortex method at stirring time varying from 4 to 16 min, followed by T6 heat treatment. Nanocomposite pins were slid against DIN 100Cr6 steel discs at 180 rpm speed and 7 N applied load. It was found that the wear rate was lowest for the Al_2O_3 -Al reinforced composite and Al_2O_3 -Cu reinforced composite stirred at the duration of 4 min. The better

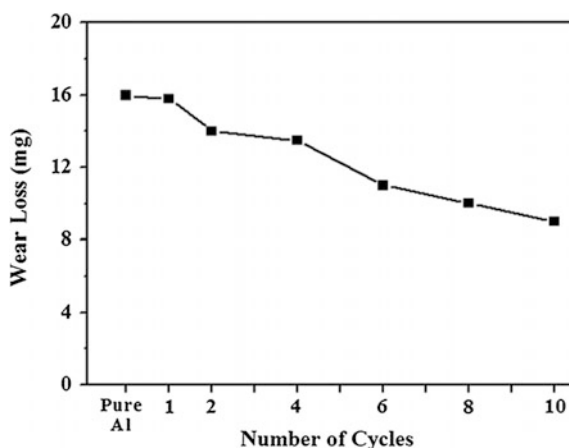
performance of these composites was attributed to their higher hardness, compressive strength and lower porosity. It was observed that the increase in stirring time leads to uniform distribution of Al_2O_3 nano-particles. However, it also caused increase in porosity that became detrimental in terms of hardness and compressive strength, which in turn increased the material wear. The Al_2O_3 nano-particles were seen to be well dispersed in the Al_2O_3 -Cu reinforced composites, and these nanocomposites outperformed the Al_2O_3 -Al reinforced composites in terms of wear resistance. Cu strengthens Al, which is improved by the T6 heat treatment. This study is a good example as to how by the proper selection of metallic additions, wear resistance of Al MMNCs can be considerably enhanced.

Alumina (Al_2O_3) proves to be an effective reinforcement for Al/Al-alloys. Similarly, titanium carbide (TiC) and silicon carbide (SiC) are also effective reinforcements due to their inherent mechanical strength and thermal stability. Nemati et al. [6] investigated the tribological performance of Al-Cu composites with different fractions of nano and micron-sized TiC particles (0–10 wt%) produced by ball milling and sintering. The composites were tested in the form of pins slid against AISI 52100 steel disc. Results showed that the nanocomposites exhibited higher hardness and exhibited lower wear when compared to those of the composites with micron-sized TiC particles. For nanocomposites, it was found that 5 wt % was the critical volume fraction and any addition of TiC nano-particles beyond 5 wt% leads to particle agglomeration that causes deleterious effect on hardness and material wear. Jeyasimman et al. [7] prepared hybrid AA 6061 nanocomposites with TiC + Al_2O_3 nano-particles by mechanical alloying route. Tribological investigation of the test materials revealed that the nanocomposite with hybrid inclusions had superior wear resistance and lower friction coefficients compared to the nanocomposites reinforced with TiC and Al_2O_3 separately. Mostafapour Asl and Khandani [8] evaluated the wear performance of surface hybrid nanocomposite of Al5083/graphite/alumina fabricated by friction stir processing method. They found that the nanocomposite with graphite hybrid ratio of 75 % shows highest wear resistance. Increasing the graphite hybrid ratio further increased the wear rate due to deterioration in mechanical properties. Bathula et al. [9] investigated wear and friction characteristics of Al5083 composites reinforced with nano-SiC particles (20 nm; 10 wt%), made by ball milling and consolidated via spark plasma sintering method (SPS). Wear tests were conducted for the composites in the form of pins slid against EN-31 steel discs (sliding velocity: 1 and 2 m/s, applied load: 9.81 N and 49.05 N). It was observed that the wear rate increased with the increase in the applied load. Al5083 alloy showed higher wear rate than its nanocomposite. The nanocomposite undergoes abrasive wear, whereas the alloy experiences a change in wear mechanism from abrasion to adhesion with the increase in the applied load. Homogenous distribution of SiC particulates in the alloy matrix and associated networked dislocations after the SPS process enhanced the hardness and strength properties, which induced superior wear resistance to the nanocomposites. The lower wear rates in the case of nanocomposites were accompanied with lower values of coefficient of friction, when compared to the alloy. Darmiani et al. [10] produced Al-SiC nanocomposites by the accumulative roll bonding (ARB) process

and demonstrated the influence of the number of cycles on the mechanical property (micro-hardness) and tribological properties of the materials. SiC particles ($<75\text{ }\mu\text{m}$) of 0.26 g were added during each rolling cycle (up to 5 cycles). It was observed that the micro-hardness of the nanocomposite increased with an increase in the number of cycles. Dry sliding wear tests were conducted using AISI 52100 steel pins against the nanocomposite counterfaces (speed: 38 rpm, applied load: 50 N). Figure 5.2 shows the wear loss (mg) of pure Al and that of the nanocomposite as a function of number of cycles [10]. As can be seen from the figure, the wear loss of the nanocomposite reduces considerably with the increase in the number of cycles, which is due to the increase in the micro-hardness. With the increase in the ARB cycles, the coefficient of friction also decreases.

Boron carbide (B_4C) is the third hardest material after diamond and boron nitride. It is an excellent reinforcement material for Al matrices due to its low density, high hardness, high strength and chemical stability. Sharifi et al. [11], conducted tribological investigation of B_4C nano-particles (10–60 nm) reinforced Al matrix. Al- B_4C powders containing of 5, 10 and 15 wt% of B_4C were ball milled and hot pressed to produce the Al- B_4C nanocomposites. Tribological tests were conducted with AISI 52100 steel pins against nanocomposite discs (sliding velocity: 0.08 m/s, applied load: 20 N). Figure 5.3a shows the variation of the hardness of the B_4C reinforced Al matrix nanocomposites as a function of B_4C wt%. Figure 5.3b shows the wear rate (mg/m) of the nanocomposites with varying wt% of B_4C reinforcements [11]. It can be seen from the figure that the hardness of the nanocomposites increases with the increase in the content of nano-particles, and thereby the wear rate decreases correspondingly. The nanocomposite with the highest content of B_4C nano-particles (15 wt%) showed the lowest wear rate. Scanning electron microscopy (SEM)/EDAX cross-sectional analysis showed the formation of a stable mechanically mixed layer (MML) on the wear tracks of the nanocomposites (Fig. 5.4) [11]. During sliding, material removed from the contacting surfaces gets mechanically mixed and transferred to the surface of the nanocomposite discs, which results in the

Fig. 5.2 Wear loss (mg) of the pure Al and that of the Al-SiC nanocomposite produced by the process of accumulative roll bonding process, as a function of number of cycles [10] (Regenerated from [10])



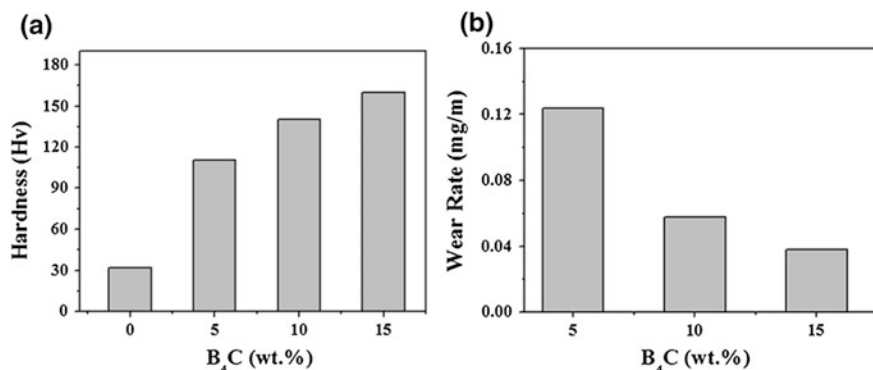


Fig. 5.3 (a) Hardness of B₄C reinforced Al matrix nanocomposites as a function of B₄C wt% [10]. The hardness of the nanocomposites increases with the increase in the content of nano-particles. (b) Wear rate (mg/m) of the nanocomposites with varying wt% of B₄C reinforcements [11] (Regenerated from [11])

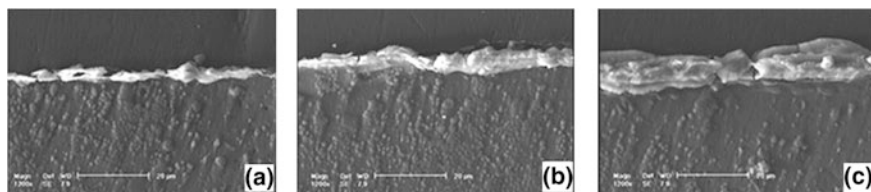


Fig. 5.4 Cross-sectional SEM images of the Al-B₄C discs showing the formation of stable mechanically mixed layer (MML) on the wear tracks of (a) nanocomposite with 5 wt% B₄C, (b) nanocomposite with 10 wt% B₄C and (c) nanocomposite with 15 wt% B₄C [11]

formation of the protective MML that is hard due to the presence of Al oxide and Fe oxide. As can also be seen from the figure, the thickness of the protective layer increases with the amount of the reinforcement in wt%. With the increase in the amount of B₄C, the amount of hard oxide compounds also increases. This reduces the wear rate and friction values correspondingly. Under tribological conditions, whereas MML forms, the formation of this layer determines the tribological response of the material. Alizadeh and Taheri-Nassaj [12] studied the wear behaviour of Al-Cu alloy reinforced with B₄C nano-particles (80 nm, 2 wt%) produced by mechanical milling and extrusion. Test specimens included coarse grained Al, nanostructured Al and Al-B₄C nanocomposites with 2 and 4 wt% B₄C nano-particles. These test materials taken in the form of pins were slid against AISI-01 tool steel discs (sliding velocity: 0.6 m/s, applied load: 20–50 N). The ranking in the microhardness values of the test materials was in the order: Al-B₄C 4 wt% > Al-B₄C 2 wt% > nanostructured Al > coarse grained Al. Wear tests revealed that the nanocomposites outperformed the Al materials, such that the wear resistance of test materials was in the order: Al-B₄C 4 wt% > Al-B₄C 2 wt% > nanostructured Al > coarse grained

Al. These results show that the wear behaviour is dominantly controlled by the hardness of the test materials. Figure 5.5 shows deformed layer at/near surface of the test materials. The thickness of the deformed layers was ~ 150 , 70 and 50 μm for the coarse grained Al, nanostructured Al and Al-2 wt% B_4C nanocomposite, respectively [12]. This evidence clearly shows the wear resistant capability of the nanocomposite materials brought forth by their excellent mechanical properties. Recently, Ramachandra et al. [13] produced aluminium nanocomposites by introducing nano-particles of zirconium dioxide (n-ZrO_2) using powder metallurgy technique. They observed increase in wear resistance with increase in the content of the n-ZrO_2 reinforcement. Oxidation, micro-cutting and thermal softening were reported as the predominant wear mechanisms in the test materials.

Carbon nanotubes (CNTs) exhibit excellent mechanical and thermal properties and because of which they have found their niche in various material systems for diverse engineering applications, including tribological applications as additives in lubricants and coatings. CNTs have also been proved effective as reinforcements for improving tribological performance of Al matrices in the form of Al-CNT nanocomposites. Bastwros et al. [14] prepared Al-CNT composites by incorporating Al with CNT of vol% 1, 2.5 and 5 %. These composites were produced by cold compaction and hot extrusion processes. Wear and friction performance of the nanocomposites were evaluated by taking the composites in the form of pins and were slid against En31 high Cr tool steel (sliding velocity: 1.1 m/s, applied load: 20 N). To investigate the effect of sliding velocity and applied load, the Al-5 % CNT material was subjected to wear tests at sliding velocities of 0.18, 1.1 and 7.3 m/s (constant load: 20 N) and at varying loads of 10, 15 and 20 N (constant velocity: 1.1 m/s). With the increase in the CNT content, their hardness increases directly and correspondingly the wear resistance of the composites also increases. The wear rate (mg/km) of the Al-5 %CNT composite showed a significant

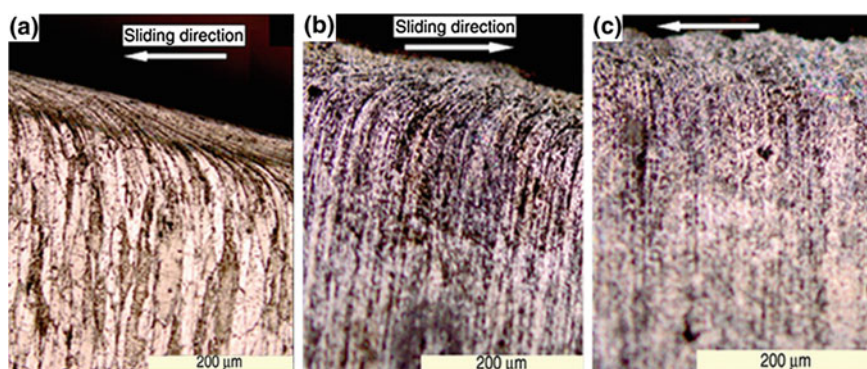


Fig. 5.5 Optical images of the cross-sectioned worn surfaces of (a) coarse grained Al, (b) nanostructured Al and (c) Al-2 wt% B_4C nanocomposite [12]. The coarse grained Al shows heavy deformation at/near the surface when compared to the nanostructured Al. Compared to both the Al types, the nanocomposite shows less deformation [12]

reduction by $\sim 78\%$ when compared to the un-reinforced metal. The reduction in wear rate and the coefficient of friction (μ) (Fig. 5.6) were also attributed to the formation of lubricious carbon film at the surfaces of the composites that consisted of crushed loose/detached CNTs [14]. The Al-5 %CNT composite showed increase in the wear rate with increase in applied load, and a decrease in the wear rate with increase in velocity. Al-Qutub et al. [15] investigated the wear and friction performance of Al6061 alloy reinforced with 1 wt% CNTs produced by ball milling and spark plasma sintering. They conducted wear tests of the composites, taken in the form of pins slid against AISI 4140 steel discs (sliding velocity: 0.5 m/s, applied load: 5–30 N). Results showed that the applied load significantly influenced the wear and friction behaviour. Within the range of applied load, it was found that the composite exhibited lower wear rates and lower friction property until 15 N. At loads above 15 N, the wear rates and friction values of the composites increased drastically. Below the critical load of 15 N, abrasion was seen to be the operating wear mechanism and above the critical load of 15 N sub-surface fracturing led to severe wear and friction.

Heat treatment of materials is another route to improve the hardness and mechanical properties. Sameezadeh et al. [16] prepared AA 2024 Al matrix reinforced with MoSi_2 nano-particles (71 ± 20 nm) by mechanical alloying and consolidated by cold and hot pressing. The prepared samples were then heat treated to solution and aged condition (T6). They conducted wear tests of the materials taken in two different conditions: (i) hot-pressed, and (ii) after solution and aging heat treatment (T6: 8 h at 495 °C, 2 h at 520 °C, water quenching at 40 °C and artificially aging for 8 h at 180 °C). Two important observations were made in this investigation, namely: (i) T6 heat treatment increased the hardness of the samples in

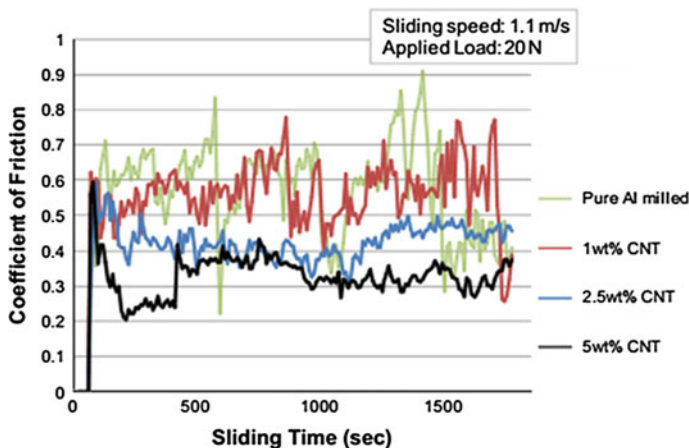


Fig. 5.6 Coefficient of friction of pure Al (milled) and Al-CNT nanocomposites [14]. The friction property decreases as the vol% of the CNT increases in the composites. Formation of lubricious layer of carbon reduces friction

comparison to that of the hot pressed, because of which the wear resistance of the samples in the T6 condition significantly enhanced and (ii) there exists a critical volume fraction of 4 %, beyond which any addition of MoSi_2 nano-particles leads to particle agglomeration which causes adverse effects on hardness and wear resistance. Another investigation also reveals the importance of heat treatment in improving tribological properties of nanocomposites [17]. In this investigation, Sahu et al. [17] prepared aluminium alloy nanocomposite by incorporating nano-sized alumina particles in Al 6061 alloy by using ultrasonic assisted stir casting technique. Wear tests showed that the heat treated Al- Al_2O_3 heat treated nanocomposites showed significant wear resistance when compared to their un-heat treated counterparts. Selective heat treatment of nanocomposites enhances mechanical and tribological properties. Nemati et al. [18] prepared Al composites with $\text{Al}_{13}\text{Fe}_4$ complex metallic alloys (CMA) nano-particles (1 to 10 wt%), by conventional powder metallurgy and hot extrusion process. Wear tests were conducted for the nanocomposites under reciprocating motion at the temperature range of 25–350 °C. The composites exhibited superior wear resistance such that their wear rate reduced by a factor of 25 when compared to that of the base un-reinforced metal. Factors that contributed towards the superior performance of the composites include: (i) microstructure refinement due to incorporation of CMA nano-particles, (ii) increase in hardness (up to 2 GPa) and (iii) nano-particles aided formation of hard and temperature resistant tribo-layers.

To summarize, many factors influence the wear and friction properties of Al nanocomposites. Some important factors include: (i) process and process parameters: selection of process/technique to prepare nanocomposites plays a very important role, as the microstructure and properties of the produced material depend on it. Process parameters (e.g. milling time to control relative density and hardness [3], number of cycles in accumulative roll bonding [10]) have to be optimized to obtain materials with beneficial microstructure and properties; (ii) composition and microstructure: proper selection of metallic additions [5], critical volume fraction (vol%) of reinforcement particles [6, 16], right hybrid ratio [8] and most importantly uniform distribution of reinforcement particles; (iii) heat treatment: choice of heat treatment to enhance mechanical properties [5, 16]; (iv) mechanical properties: hardness and strength directly enhance wear resistance, (v) velocity and load: usually there exist critical levels of velocity, and especially load below which nanocomposites exhibit good wear resistance [15]. The range of velocity and load within which the tribological properties of a material is good has an important implication in their selection for suitable applications; and (vi) in situ tribo-layers: formation of protective tribo-layers/films such as MML [10] and lubricious carbon film [14] is desirable as they promote wear resistance and lower friction. Regarding wear analysis, it is evident from the works of Sharifi et al. [11] and Alizadeh et al. [12], that observation/examination of sub-surfaces of worn materials are very useful and can provide important insights on the underlying wear mechanisms. For future work, it is suggested that tribological investigations of Al nanocomposites under lubrication be undertaken as they will provide better information on the materials behavior in the context of broader applications. Al nanocomposites are potential

candidates for automotive application for components such as pistons, cylinder block/liners, brake discs and connecting rods [6, 13].

5.2 Mg-Based Nanocomposites

Mg-based materials are attractive for tribological applications. Investigations on tribological properties of Mg nanocomposites are very few when compared to those on Al nanocomposites.

Mg based nanocomposites investigated for tribology have Al_2O_3 nano-particles as second phase reinforcements. Lim et al. [19] prepared Mg nanocomposites with alumina nano-particles (50 nm, vol% of 0.22, 0.66, 1.11 %). The materials were made using the liquid-state processing method of disintegrated melt deposition (DMD). Wear tests of the nanocomposites taken in the form of pins were conducted against AISI-01 tool steel discs (sliding velocity: 1–10 m/s, applied load: 10 N). Results showed that the wear rate of the nanocomposites decreased with an increase in the reinforcement content. This was attributed to the increase in the hardness and strength of the materials with the increase in the vol% of the Al_2O_3 nano-particles. The trend in wear was seen to be consistent with the Archard's wear equation, which states that the wear of a material is inversely related to its hardness [20]. Archard's wear equation gives the relation between the amount of wear and the hardness of a material as $Q = kW/H$ (where, Q is volume worn per unit sliding distance, W the applied load, H the hardness and k the wear coefficient) [20]. It was observed that the wear resistance of the nanocomposite with the highest vol% of alumina reinforcement (1.11 vol%) was about 1.3 times at the lowest velocity (1 m/s) and about 1.8 times at the highest velocity (10 m/s), when compared to the unreinforced metal. It was also seen that the wear rate of all the test materials decreased with the increase in velocity from 1 to 7 m/s, beyond which at the speed of 10 m/s the wear rate increased. Scanning electron microscopy (SEM) was used to observe the worn surfaces of the test specimens and to identify the wear mechanisms. At the lowest velocity (1 m/s), the worn surfaces showed evidence of abrasion of grooves parallel to the sliding direction, caused by the hard and rough steel counterface (Fig. 5.7a) [19]. As the velocity increased to/more than 3 m/s, adhesion was seen to dominate (Fig. 5.7b) [19]. Increase in the velocity causes frictional heating which increases ductility by the activation of additional slip planes. Increase in ductility leads to plastic deformation, and the wear i.e. material loss, occurs by adhesion. At the highest test velocity of 10 m/s, due to the increased frictional heating, thermal softening and localized melting caused the material to flow/protrude at the trailing edge. To note, here the intensity of the operating wear mechanisms was observed to be high in the unreinforced material when compared to the nanocomposites, thereby indicating the benefit of making nanocomposites for tribological applications. The main observations made in this study are: (i) wear of Mg based materials and the underlying wear mechanisms depend on sliding velocity and (ii) wear of nanocomposites is influenced by the content of

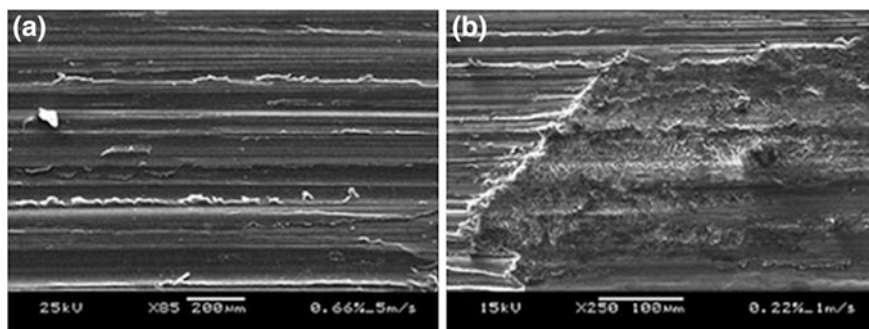
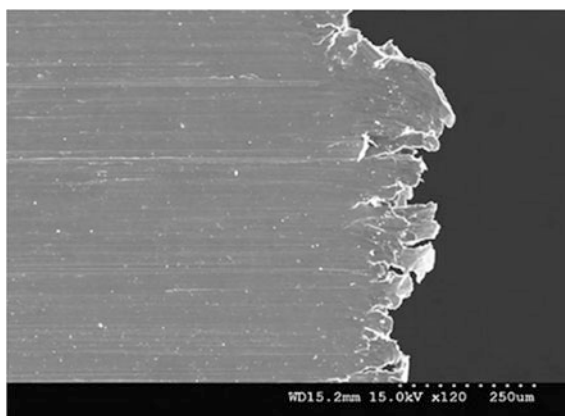


Fig. 5.7 Worn surfaces of Mg-Al₂O₃ nanocomposites tested at different sliding velocities [19]. (a) Grooves parallel to the sliding direction seen on the worn surface of the nanocomposite slid at 1 m/s indicating abrasion. (b) Adhesion seen on the worn surface of the nanocomposite slid at 3 m/s [19]

nano-particle reinforcement (vol%). Shanthi et al. [21] prepared AZ31B based nanocomposites with Al₂O₃ nano-particles (50 nm, 1.5 vol%) by the DMD process. Wear tests of the nanocomposites was conducted against AISI-01 tool steel discs (sliding velocity: 1–10 m/s, applied load: 10 N). SEM images of worn surfaces showed transition of wear mechanism from abrasion to adhesion with increase in velocity. At higher velocity (10 m/s) due to thermal softening the unreinforced alloy showed extruded layer at the trailing edge (Fig. 5.8), and such an occurrence was not seen in the case of the nanocomposites [21]. In this investigation, the effect of calcium (Ca) addition to the matrix on the mechanical properties and wear behaviour was also evaluated. With the addition of Ca, hardness and strength considerably increased due to the formation of (MgAl)₂Ca intermetallic phase. The enhancement in the mechanical properties due to the addition of Ca led to increased wear resistance of the nanocomposites. It has been reported by Srinivasan et al. [22]

Fig. 5.8 Extruded layer at the trailing edge of the AZ31B alloy wear pin when slid against AISI-01 tool steel discs at high velocity (10 m/s) [21]. Such an occurrence due to thermal softening was not evident in the case of AZ31B-Al₂O₃ nanocomposites [21]



that these nanocomposites, at relatively low sliding velocity (≤ 1 m/s) undergoes oxidative wear.

Habibnejad-Korayem et al. [23] in their investigation of Mg/AZ31-Al₂O₃ (2 wt%) nanocomposites identified the importance of work-hardening capacity on the wear behaviour of the materials. Wear tests were conducted on test materials namely, Mg, AZ31 alloy, Mg-Al₂O₃ nanocomposite and AZ31-Al₂O₃ nanocomposite. The test materials were taken in the form of pins and were slid against AISI 52100 steel discs (sliding velocity: 0.5 and 5 m/s, applied load: 12, 24 and 36 N). Figure 5.9 shows the wear rate (g/m) of the test materials (sliding velocity: 1.5 m/s, stress: 1.5 MPa) [23]. Mg shows the highest wear rate, whereas the AZ31-Al₂O₃ nanocomposite shows the lowest wear rate due to increased work-hardening capacity (because of the interaction of dislocations with nano-particles). Further, the wear rate of materials decreased as the function of sliding velocity, while the wear rate increased as the function of applied load. To identify the influence of work-hardening on the wear behaviour, compression flow curves were obtained. Results from these tests showed that the nanocomposites retained their work-hardening capability even at higher stress levels. Given this fact, with increase in applied load the nanocomposites exhibited lower wear rates in comparison with those of the pure metal and alloy. Transition in the wear mechanism from abrasion to oxidation with increase in applied load was observed. Figure 5.10 shows the friction coefficient of Mg, AZ31 alloy, Mg-Al₂O₃ nanocomposite and AZ31-Al₂O₃ nanocomposite as a function of stress level (sliding velocity: 1.5 m/s, stress: 1.5 MPa) [23]. It can be seen that the AZ31-Al₂O₃ nanocomposite shows the lowest friction coefficient.

It is to be noted that in the context of tribology, nanocomposites provide better performance than composites with micron-sized reinforcements. Conventional composites having micron-sized reinforcements are known to: (i) abrade the counterface, (ii) cause counter-abrasion by the wear debris (third-body abrasive wear) and (iii) undergo material loss (i.e. wear) by delamination, due to mismatch in

Fig. 5.9 Wear rate (g/m) of Mg, AZ31 alloy, Mg-Al₂O₃ nanocomposite and AZ31-Al₂O₃ nanocomposite against AISI 52100 steel discs (sliding velocity: 1.5 m/s, stress: 1.5 MPa) [23]. Pure Mg metal shows the highest wear rate, whereas the AZ31-Al₂O₃ nanocomposite shows the lowest wear rate due to increased work-hardening capacity [23] (Regenerated from [23])

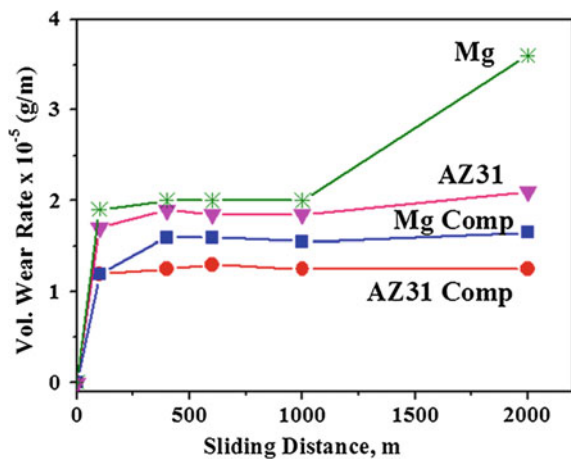
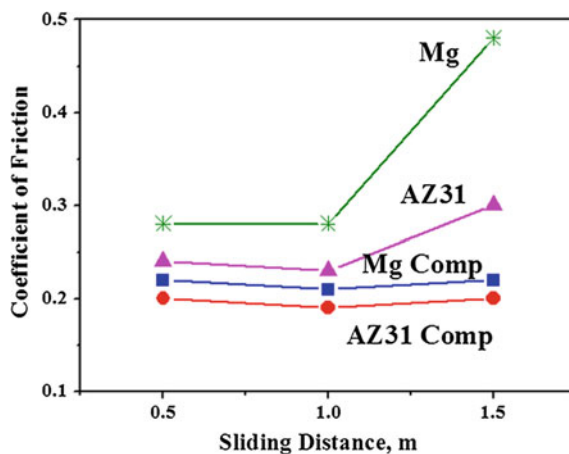


Fig. 5.10 Friction coefficient of Mg, AZ31 alloy, Mg-Al₂O₃ nanocomposite and AZ31-Al₂O₃ nanocomposite against AISI 52100 steel discs, as a function of stress level (sliding velocity: 1.5 m/s, stress: 1.5 MPa) [23] (Regenerated from [23])



strains under external load. (i) and (ii) also lead to higher friction property. In the case of nanocomposites, all these aspects are absent because of which they exhibit superior tribological properties. In addition, lower volume fractions of nano-sized reinforcement is adequate to achieve enhancement of mechanical properties when compared to higher volume fractions of micron-sized reinforcements needed to achieve the same.

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Chapter 6

Future Directions

Abstract Most of the work carried out on microstructural and mechanical characterization of Al and Mg based nanocomposites is currently based on laboratory-scale research activities. Aiming to fully exploit the potential of MMNCs at a larger scale, however, the feasibility of the manufacturing processes to produce nanocomposite components should be investigated at a much larger-scale. In this chapter, industrial scaling-up issues related to casting processes are highlighted and discussed, as well as the translation of MMNCs to the product level. Critical aspects still partially unexplored in the literature, such as fatigue properties, corrosion behavior and recycling of MMNCs will be also presented.

6.1 Industry-Level Translation

In the earlier sections, the various liquid-state and solid-state processes have been discussed. As mentioned, the prominent liquid-state routes for producing MMNCs include stir casting, compocasting, ultrasonic assisted casting, infiltration and disintegrated melt deposition techniques. Most of the microstructural and mechanical properties discussed in the previous sections are based on laboratory-scale research works. In order to utilize the full potential of the developed MMNCs, the feasibility of the processes to produce nanocomposites at a much larger-scale should be investigated. Important factors such as matrix-particle bonding, easier control of matrix structure, simplicity and low cost of processing should be considered.

Considering the stir casting process, although it has been established as a suitable method for micron-size reinforcements, however, in the case of nano-sized reinforcements, it is extremely difficult to distribute and disperse nanoscale particles uniformly (by mechanical stirring) in industrial-scale melts due to the large surface-to-volume ratio [1]. Similarly to stir casting, pressure/vacuum infiltration is already a promising technique for composites with micron-size reinforcements, and is especially used for selective infiltration. The process itself being a near-net shape process - can be easily automated and is widely considered as a promising method for manufacturing small-sized MMC components. However, the challenge to use

the process for large-scale MMNCs production depends on the preparation of the nanoparticle or nanofiber preforms and the subsequent process parameters involved in the infiltration process. For example, the uniform distribution of nano-particles/fibers in the preform is an important factor, as the presence of clusters in the preform will give rise to variation in volume fraction within the preform. Eventually, during molten metal infiltration, this would result in: (i) preform breakage due to applied squeeze pressure and (ii) variation in solidification rate within the material, giving rise to increased porosity and/or undesirable intermetallic phases/segregation. Due to these reasons, the large-scale production of MMNCs by stir and squeeze casting demands a highly standardized process procedure with accurate control of process parameters.

On the other hand, the disintegrated melt deposition (DMD) technique has several advantages (as mentioned in Sect. 6.2) and gives rise to MMNCs with fine grain size, uniform nanoparticle distribution, minimum porosity (high density) and superior mechanical properties [2]. Recently Gupta & co-workers, in collaboration with a Singapore government enterprise successfully up-scaled the DMD technique to produce >20 kg of Mg-MMNCs per casting (deposition). While this effort can be considered as a successful attempt of industry-level production of Mg-MMNCs, it should be noted that the improvement in properties reported on MMNCs produced by DMD method (as mentioned in the earlier sections) are all on wrought forms and not in the cast/deposited state. In the DMD method, the microstructural and mechanical properties depend on parameters such as the disintegrating gas velocity, distance between the melt exit stream and the substrate etc. which have to be varied according to the dimension of the final product. Hence, the DMD process is more suitable to produce MMNC ingots to be used as precursors for making wrought products. Also, due to its set-up (see Sect. 6.2), the DMD process is difficult to be automated and to be used for continuous casting operations [2], unless further modifications are made judiciously.

The ultrasonic-assisted casting is widely considered as a method which provides better matrix-particle bonding, breaks nano-particle clusters and removes impurities from the particles surface, resulting in MMNCs with high microstructural properties [3]. Despite these advantages, the ultrasonic technique is quite difficult to be scaled up for industrial applications as the volumes of castings are limited to the dimension of the ultrasonic probe and power of the ultrasonic source, which determine the ultrasonically processed volume.

To overcome these limitations, ultrasonic flow processing could be adopted. This concept was used in developing a scaled-up ultrasonic processing system, aimed at producing MMNCs at industrial scale, which was recently presented [4]. The developed system comprises a simple mechanical pumping component with a radial impeller as to force a large volume of melt to flow into a ultrasonic cavitation zone, enabling large scale production of MMNCs with small ultrasonic devices. The ultrasonic cavitation system includes a chamber defining the volume of the molten metal which conforms to the volume of the ultrasonic cavitation zone generated by the ultrasonic probe used in the system. The scale-up ultrasonic processing system was used to successfully fabricate 2500 g (5.5 lb) of A206-1 wt% Al_2O_3

nanocomposite. Based on the same concept, a larger scale of the processing system was designed and built for producing about 27 kg of Al-based MMNCs. To overcome or limit corrosion issues, all components in prolonged contact with the melt were made with Ti alloy (grade 5) with boron nitride coating.

Among semi-solid state technologies, it was demonstrated that compocasting with energetic mechanical stirring has the potential of facilitating nanoparticle incorporation owing a better wettability of nano-reinforcement in the semisolid matrix as compared to the liquid metal. Rheoprocesses are industrially attractive as no special feedstock is required, and the semi-solid slurry is generated starting from the liquid state by cooling the molten metal during the casting process itself, thus involving standard foundry equipment. Nevertheless, the need of achieving excellent particle distribution and hence superior strength and ductility generally requires the subsequent application of ultrasonic cavitation in liquid state and/or secondary processes such as extrusion or forging of cast components.

Given that one clear benefit of MMNCs is that significant effects on properties can be obtained at low volume fractions of particles, thixoprocessing appears to be a key technology for the industrial scaling up of MMNCs production. The use of prewetted feedstock, which can be prepared in several methods, allows handling nano-reinforcement on a smaller volume scale before diluting the master composite in larger metal volume. Further than the several methods described in this review as to dilute nanoparticles feedstock, including DMD, stir casting an ultrasonic assisted casting, future production routes could exploit actual thixoprocesses such as thixocasting, thixoforging or thixomolding [5, 6], although particle pushing during solidification still would need to be resolved.

Given that most of the MMNCs produced by the various techniques mentioned in this review have given rise to nanocomposites with excellent properties, henceforth, further research is required towards synthesizing these materials in bulk, in an industrial-friendly process at lower cost, with little or no voids/defects and with retained microstructural and mechanical characteristics, so as to utilize these promising materials in various real-time applications.

6.2 Product-Level Translation

Similar to the requirements for designing industrial level processing methods, the need of the hour is to translate the developed MMNCs into components/products (finished/semi-finished) and to understand/manipulate their microstructural and mechanical characteristics under real-time loading/operating conditions. In this aspect, when compared to conventional MMCs, the major advantages of nanocomposites include incorporation of as little as 1 vol% of nano-sized particles that can result in a significant enhancement in strength properties coupled with large improvements in ductility, along with high temperature stability and wear resistance. Hence, most of the cast products proposed for conventional composites can be substituted by MMNCs.

For example, in aerospace applications such as ventral fins for aircrafts and for exit guide vanes, the materials are required to possess high stiffness and strength, low weight as well as resistance to erosion from rain, airborne particulates and hail, and Al- and Mg- MMNCs are the best choices [1]. In the automotive industry, potential applications include brake system components (high wear resistance and thermal conductivity), piston liners (high wear resistance, good thermal conductivity and low coefficient of thermal expansion) etc. MMNCs are ideal candidates in thermal management and electronic packaging systems such as radiator panels and battery sleeves, power semiconductor packages, black box enclosures and printed circuit board heat sinks, due to their high thermal conductivity, low density, and near-matching coefficient of thermal expansion with the substrate materials [7]. MMNCs are also suitable for space structures (presence of extreme environment), wherein light-weight, high strength/ductility and dimensional stability are crucial factors [7]. For wrought MMNCs, focus should be directed towards various product-oriented wrought forms such as tubings, pipings, sheets etc. Some of the prospective automotive applications for wrought MMNCs would include bumper beam and connectors (extruded), inner hood (stamped), steering knuckle (forged), crash support beams (extruded), wheels (forged) etc. Further, in-depth studies on hot deformation processes (secondary processes such as rolling/forging/sheet metal forming etc.) are necessitated so as to identify regimes (processing window) for ease of hot workability.

It is to be noted that both these focus areas (industrial-level and product-level translations) needs to be complemented by theoretical/mathematical simulations so as to identify efficient, cost-effective processing methods and MMNCs product design with superior performance suitable to rising demands.

6.3 Other Critical Properties to be Investigated

As reported in Chap. 4, properties under tensile and compressive loading have been widely reported. Considering the above mentioned applications, and that most of the real-time component failures occur due to fatigue/creep, corrosion and wear, the behaviour of MMNCs under these conditions should be investigated. Several research works have investigated these properties and a few are mentioned here. Other properties of importance include creep resistance, thermal conductivity, machinability and castability. As concerning Al-based MMNCs, it was discussed that high temperature mechanical properties still needs to be widely investigated.

6.3.1 Fatigue

Fatigue is the most common source of failures of engineered components, and in particular in the context of applications that demand high performance. However,

investigations pertaining to the fatigue behavior of metal matrix nanocomposites are very limited.

The effect of SiC nanoparticles on the low and high cycle fatigue behaviour of pure aluminium was investigated by Ghasemi Yazdabadi et al. [8] through tensile-compression axial fatigue testing. At a low cycle fatigue regime, SiC nanoreinforcement was reported to enable an improvement of the cyclic hardening rate (the number of cycles required to reach steady-state strain amplitude), due to the locking effect of non-shearable particles on moving dislocations. Furthermore, despite the higher porosity of the nanocomposites, the high cycle (10^7) fatigue (HCF) strength was improved with increasing the volume fraction of the reinforcement nanoparticles (30 % increase with 6 wt% reinforcement). It was demonstrated that the cyclic response of micro-reinforced MMCs with commercially pure matrix is mainly controlled by the structure of the matrix [9]. However, since the distance between the inclusions in nanocomposites could be comparable with the self-trapping distance for dislocations, it can be inferred that the particles can influence the cyclic fatigue behaviour of the composite [8]. A mixture of ductile-brittle fracture surfaces were detected, with the amount of ductile fracture area increasing with higher content of ceramic particles.

Srivatsan et al. [10] conducted stress-amplitude controlled high cycle fatigue tests of AZ(12)1 matrix (an alloy with 3 % higher Al-content when compared to AZ91 alloy) reinforced with n- Al_2O_3 particles, and observed that the unreinforced AZ91 alloy exhibited higher endurance limit when compared to the nanocomposite. The lower fatigue resistance of the composite was due to presence of nanoparticles that facilitated early initiation of fatigue crack and subsequent rapid growth/coalescence into macroscopic cracks. A similar work by the same authors on AZ31-CNT nanocomposite [11] indicated superior fatigue resistance of the composite, with a 40 % improvement in the endurance limit for 10^6 cycles. Fracture studies highlighted the positive role played by the CNT reinforcement in enhancing the resistance to crack initiation during cyclic stress-controlled fatigue and suppressing, or delaying, crack growth [11]. Goh et al. [12] studied the high cycle fatigue test of Mg-CNT composites, which revealed that the cycles to failure for the Mg-1.3 wt% CNT nanocomposite was lower than that of pure Mg, and was attributed to the presence of voids and the clusters of CNTs present in the nanocomposite. Given that fatigue behaviour is highly statistical in nature, these results indicate that the behaviour of nanocomposites varies significantly with the matrix and reinforcements, and should be critically investigated.

6.3.2 Corrosion/Oxidation

Composites are comprised of two or more materials characterized by different corrosion potential and properties. The chemical, physical, and galvanic interaction between matrix and reinforcement could accelerate the corrosion process. In

particular, preferential corrosion can occur at the particle-matrix interface. Its rapid penetration into the material could result in higher corrosion rate in comparison to the respective monolithic matrix alloys [13, 14]. The study of the corrosion behavior is vital especially for structural components, as corrosion decreases the load bearing capacity and could result in catastrophic failures. However, investigation on the corrosion behaviour of metal matrix nanocomposites are extremely limited.

Mahmoud et al. [15] studied the corrosion behaviour of several Al/SiC and Al/Al₂O₃ metal matrix nanocomposites (MMNCs), produced by a powder metal-lurgy route. Composites were tested in NaCl aqueous solution under several corrosion conditions. It was found that both Al/SiC and Al/Al₂O₃ MMNCs are characterized by better corrosion resistance than the pure Al matrix in NaCl aqueous solution; further, the Al/Al₂O₃ MMNCs exhibited lower corrosion rates than the Al/SiC MMNCs. Interestingly, it was reported that the corrosion resistance of MMNCs in NaCl solution decreases with the increase in the size of the SiC and Al₂O₃ nanoparticles (from 60 to 200 nm). Furthermore, the corrosion rate of the MMNCs increases when the volume fraction of the nanoparticles is increased beyond 3 vol%, possibly due to the increased agglomeration of the nanoparticles which reduces the corrosion resistance of the composite.

El-Mahallawi et al. [16] also reported the improvement of the corrosion resistance of the Al matrix due to the dispersion of Al₂O₃ sub-micron particles (nanoparticle size <500 nm) in a A356 matrix using the rheocasting technique. In particular, the A356 monolithic was reported to present higher corrosion rates in 3.5 %NaCl solution at room temperature when compared with the A356/Al₂O₃ nanocomposite. Although the improvement in corrosion resistance of MMNC needs to be further investigated, it opens up applications of such techniques able to produce surface matrix composites (i.e. FSP).

The corrosion resistance of pure Mg and its composites reinforced with CNT reinforcements was studied by Aung et al. [17] in 3.5 wt% NaCl solution using immersion testing and electrochemical measurements. It was found that the corrosion rate was increased considerably by the presence of CNTs because of microgalvanic action between the cathodic CNTs and the anodic Mg matrix. Kukreja et al. [18] studied the effect of n-Al₂O₃ reinforcements on the corrosion behaviour of AZ31B Mg alloy using polarisation and electrochemical impedance measurements. They reported that the corrosion resistance of the composite was superior to that of the monolithic alloy, which was attributed to the beneficial effect of n-Al₂O₃ particles in reducing the volume fraction of the beta phase (Mg₁₇Al₁₂ phase that act as cathodic sites) in the microstructure [18]. The oxidation behavior of AZ31B-n-Al₂O₃ composite was reported by Nguyen et al. [19] at temperatures ranging from 300 to 470 °C, for ~7 h. The significant increase in the oxidation resistance of the composite was reported to be due to the presence of n-Al₂O₃ particles that retarded the transient stage of oxidation.

6.4 Recycling Issues

Material recyclability is one of the most critical issues that need to be addressed before the widespread commercialization of MMNCs. Recycling is driven by the need to preserve the natural environment, conserve energy and reduce wastage. Further, stricter environmental requirements (such as in the automotive industry) means recyclability is a prerequisite for the use of these advanced materials. In addition, recyclability is a key cost-saving parameter in the processing of MMNCs, as it consumes only a fraction of energy when compared to that required to produce a new material. It should be noted that, recycling refers to processing of MMNCs for reuse. It is different from reclamation, which refers to the separation of the reinforcement particles and matrix material [20]. Reclamation is carried out only when the material cannot be recycled back to useful composite, and it involves dewetting of the nanoparticles from the metal matrix [20]. In the recycling of MMNCs, the main issue is whether or not the scrap can be restored to the same condition (microstructure and properties) as that of the original material. Due to the high temperatures employed and the extended contact between the matrix and reinforcement during multiple recycling, some of the main concerns are the excessive reactivity which may have a significant effect on their interfacial characteristics and the retention of volume fraction/distribution of reinforcements. These variations/reactions would likely result in metallurgical changes in the matrix, which would in turn affect the composite properties. Recently, AZ31-n-Al₂O₃ composites were re-melted (recycled once) using the DMD technique followed by hot extrusion [21]. The recycled nanocomposite did not show any significant change in microstructure and mechanical properties. More studies pertaining to recycling of MMNCs should be investigated and recycling process techniques with accurate control of process parameters that is cost-effective, energy efficient and reliable should be developed.

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Concluding Remarks

Light-metal matrix nanocomposites are promising materials to replace conventional metal alloys and their metal matrix composites (with micron-size reinforcements) particularly for applications wherein specific strength, high temperature microstructural and mechanical stability, wear resistance and retention of ductility are critical. While Al- and Mg- based nanocomposites can be produced by both via liquid-state and solid-state processes, in this book a detailed report on those produced using liquid-state processing have been presented. Liquid-state processing methods are simple, cost-effective and have high degree of process flexibility when compared to solid-state processes. This book highlights the fact that most of the liquid-state processes used for composites with micron-size reinforcements can also be adopted for making nanocomposites. Considering that uniform dispersion of nano reinforcements devoid of agglomeration/clustering is the major requirement to achieve high quality nanocomposites, various intermediary processes have been utilised to bring forth efficient incorporation of the reinforcements. Ultrasonic cavitation, effective stirring followed by disintegration of the melt using bottom pouring or pre-mixing of reinforcement elements have proved to be effective as to obtain uniform dispersion. Alternative methods such as friction stir process and various semi-solid processing methods have also been investigated, although the studies are in the infant stage.

The Al- and Mg- based nanocomposites reported in this book have been discussed in terms of their microstructural and mechanical properties (hardness, tensile and compressive). Microstructural studies reveal that in most cases, the processes employed have successfully resulted in uniform dispersion of nano reinforcements with minimum porosity. The nanoscale reinforcements have also been successful in obtaining fine, equi-axed matrix grains. Mechanical properties evaluation highlights that in most cases, the nano reinforcements exactly perform the role that they were selected for in the first instance, i.e. production of composites with significantly high yield point with retention/enhancement of ductility, which gives rise to higher toughness. The absence of these critical properties had been the major drawback in conventional micron-sized reinforced metal matrix composites. The microstructural characteristics and the occurrence of prominent yield/ductility are strongly dependent on the volume/weight fraction and the process parameters. The improvement

in mechanical properties, viz, hardness, yield and ultimate strength and ductility are usually governed by strengthening mechanisms such as the Hall-Petch effect, Orowan strengthening, load-bearing capacity and increased dislocation density due to matrix/reinforcement CTE mismatch, brought forth by the addition of nano reinforcements. While this is true for cast Al- and Mg- nanocomposites, in wrought Mg-nanocomposites, texture modification effects also play a dominant and additive role in defining the strengthening/deformation characteristics.

In this book, several topics that can provide impetus for future research have also been addressed. It was stressed the need to investigate other properties such as fatigue, wear, corrosion and oxidation behaviour, as the studies pertaining to these critical, industrial application-oriented properties are meagre. Likewise, the requirement to study products other than castings/extrusions of nanocomposites such as rolling, sheet metal, forgings is mentioned. While most of the discussed processes are very suitable and robust in producing nanocomposites at the laboratory scale, the need to translate these processes towards industrial-scale and component-level production are emphasized by examining the various requirements that should be met during such translation. A brief remark has also been made on the importance of nanocomposite recycling.

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