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Properties of Mg-based Metal Matrix Nanocomposites Processed by High Shear Dispersion Technique (HSDT) - A Review

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Abstract: Metal Matrix Nanocomposites (MMNCs) often show excellent properties as compared to their non-reinforced alloys due to either the achieved grain refinement or Orowan strengthening. Especially in light metals such as aluminium and magnesium as the matrix has the potential to be significantly improved in relation to mechanical properties. Functionalisation can also be achieved in some cases. However, the challenge lies in the homogeneous distribution of the ceramic nanoparticles in the melt if MMNCs have been processed via melt metallurgical processes. The large surface area of the nanoparticles generates large van der Waals forces, which need to be overcome. Furthermore, the wettability of the particles with molten metal is difficult. Additional forces can be applied by ultrasound, electromagnetic stirring, or even high-shearing. In this paper, properties of MMNCs with a light metal matrix, which have been produced with the High-Shearing Dispersion Technique are discussed. First, the process with its different characteristics and the underlying theory is presented, and then property improvements are discussed by comparing MMNCs to their matrix materials.

Keywords: Magnesium Alloys, nanoparticles, high shear dispersion technique, dispersion, creep, strength.

1. INTRODUCTION

The low density of magnesium alloys has made it a good choice for many years in lightweight metallic materials for the automotive and aviation industries. They combine low weight, very good castability, and also very good machinability. However, the flammability of the melt, moderate corrosion properties and the market dominance of China as the primary producer of the vast majority of magnesium have a negative impact. The mechanical and physical properties of magnesium alloys are excellent but can be improved to only a certain extent by alloying. Magnesium-based composite materials further expand this spectrum. A relatively new type of composites are metal matrix nanocomposites (MMNCs), in which reinforcing phases with a diameter of less than 500 nm in two dimensions are introduced into the magnesium alloy. These can be ceramic particles [1-5], CNTs [6, 7], C-dots, graphene [8, 9] or nanodiamonds [10-12]. It has been shown that strength and ductility could be increased at the same time, and in addition to Orowan strengthening, it is possible to achieve a grain refinement, which also increases strength [6, 13]. MMNCs can be produced using powder metallurgical processes or melt metallurgical ones. Concerning the latter, due to the small size of the particles, their surface area is very large, which leads to large van der Waals forces, resulting in agglomeration of the particles in molten metal. In addition, some of the ceramic or carbon-based phases have poor wettability with molten metal. For these reasons, additional forces must be applied to break up the agglomerates during the melt-metallurgical production of the nanocomposite [14]. This can be done by ultrasonic cavitation [15], electromagnetic stirring [16, 17], or additional shearing when stirring in the particles. Several review articles have already been published on the production, properties and potential applications of magnesium-based metal matrix nanocomposites (Mg-MMNCs) [7, 15-21]. In fields where magnesium alloys are already used, such as aerospace, automotive, medical and consumer electronics, magnesium-based nanocomposites can expand the range of applications. Higher strengths through grain refinement or through Orowan strengthening and ductility enhancement allow use in application fields where only aluminum alloys can be used today. But also the application in civil or military drones seems to be a potential field, as here lightweight construction is very significant because it in-
increases the operating range of the drones and, at the same time, the structural reliability.

In this review, magnesium-based nanocomposites and their properties produced by the High Shear Dispersion Technique (HSDT) process will be described.

2. THEORY OF HIGH SHEAR DISPERSION

The industrial prospect of mixing/dispersing was originated from chemical, pharmaceutical and pulp & paper industries to reduce the inhomogeneity of the product with two or more matter components, where the inhomogeneity can be the distribution of concentration, phase or temperature [22]. With the extensive technological development of mixing/dispersing, a large variety of the equipment and facilities has been commercialized and standardized in aspects of shear rate, energy dissipation, mixing time, processing environment and volume capacity. The adaption of the mixing/dispersing technology is conducted to other industries.

Metallurgy, a technique focused on the metal alloying process, has drawn attention on the addition of the foreign components into the metal since the oxide dispersion strengthened (ODS) superalloys in 1970s [23] with significantly enhanced high temperature performance, and then extensive metal matrix composites (MMCs) for aerospace application in late 1980s [24]. Extensive research interest was drawn to the material design through the addition of foreign components (reinforcement) into the matrix materials to achieve superior physical, chemical and mechanical properties. As a mixture of foreign components and metallic materials, the homogeneity of the MMCs are recognised as one of the critical factors to harness the advanced material performance. Thus, the treatment of mixing/dispersing converged into the metallic materials as a foundation of MMCs development.

2.1. The Need for Particle Dispersion in the Metallurgy

The MMCs, with advanced properties, is one of the major material innovations of modern times [24]. The flexible combination of reinforcements, matrix materials and fabrication methods led to a large group of construction/functional composite materials being developed with different physical, chemical and mechanical properties for engineering applications [25]. The reinforcements are generally catalogued into three major types: continuous fibres, short fibres whiskers and particles. Compared to the fibre/short whiskers reinforced MMCs, the particle reinforcement provides uniform mechanical/physical properties of the composite materials, as they are free from fibre alignment directions to reduce the anisotropy of the material. The particle reinforcement has a wide choice of ceramic particles including oxides, nitrides, carbides, silicates, borides, sulfides, variety of metal and intermetallic particles [26-30]. More recently graphene, carbon nanotubes (CNT) [31, 32] have also become popular. In the pursuit of advanced MMCs properties, the dimensions of the reinforcing particles went from micron scale to the nanoscale. Such material is termed metal matrix nanocomposites.

It is well accepted that, the homogenous distribution of reinforcing particles is a necessity to maximise the performance of particulate reinforced composites [33]. The powder metallurgy was the most commercialized processing method to produce the MMCs with uniform distribution of reinforcement, as the homogeneity of the material was guaranteed through the powder tumble blending and a multi-pass thermal-mechanical process [34]. With the rising expectation of component complexity and material cost-effectiveness [35], the liquid metal processing route has a promising advantage for manufacturing the next generation MMCs. This technological route includes liquid mixing method, semi-solid casting, infiltration, spray deposition [33], and newly merged additive manufacturing [36]. The liquid mixing method shares a dominant volume of the production due to the low facility criteria, high flexibility of the volume capacity and component geometry. However, the reinforcing particle agglomeration, limited wetting of liquid metal on the ceramic particle, and thus consequent porosity defects are major obstacles that prevent the particulate reinforced MMCs from achieving advanced properties [37].

The reinforcing particle agglomeration in the liquid metal is a reflection of the nature of the particle cohesion. Such a phenomenon is caused by the particle surface characteristics, material bridges, and sometimes mechanical locking [38]. The van der Waals force [39] is recognised as the attracting force for the cluster/agglomerate formation in ceramic particles. A more dominant influence is expected with the particle size decreasing from fine (d<100 µm), ultrafine (d<10 µm) to nano-sized (d<100 nm). In some applications, electrostatic forces may be found in the particle addition of electric conductor and non-conductor [40]. Material bridges between the particle surfaces are formed through (i) the liquid bridges due to the low viscous wetting liquid through the capillary pressure and the surface tension, e.g. moisture on the particle; and (ii) the solid bridges by crystallization of solvents, solidification of viscous bond agents, contact fusion of the surface impurity, and the solid-state sintering of the reinforcing particles [41, 42].

The wetting of liquid metal to the non-metallic particle is normally poor due to the diversion of their interfacial characteristics, which causes difficulty to incorporate reinforcing particles into the molten metal and alloys, and the deterioration distribution of reinforcement by the agglomerate/cluster formation. Alloying elements with higher oxygen partial pressure tend to concentrate at the melt surface, which helps to reduce the surface energy and thereby improve the wetting of liquid metal on the ceramic particles. Mg is known to decrease the surface tension of the molten metal due to its low surface tension (0.599 N/m) [43]. With 3 wt.% Mg in the Al melt, the surface tension of the melt reduced from 0.760 N/m to 0.620 N/m [44]. Furthermore, surface modification of reinforcing particles by doping the metallic elements also reduces the surface tension between the reinforcement and the matrix melt. With the Ni or Cu doping [45, 46], the CNTs have successfully been introduced into the Al melt with a high reinforcement yield in the matrix. The improved wetting of the molten matrix to the reinforcement al-

...
so promotes the liquid metal to penetrate into the gaps between neighbouring particles and reduce the tendency of agglomeration.

Besides the above mentioned factors, interfacial reaction of the reinforcing particles and the interaction between the particle and the solidification front of matrix metal may also influence the MMCs production. The interfacial reaction can cause the particle bridging due to the particle growth under the thermodynamic reaction, which also results in changes to the composition of alloy matrix through the new phase formation and influence the basic properties such as the melting point and strength of the matrix [47]. In the solidification of particulate reinforced MMCs, the interaction between the particle and the solidification front of matrix metal will change the distribution of the reinforcing particles as a result of the development of the solidification microstructure. The majority of reinforcing particles experience the pushing at the solid-liquid interface during the solidification [48]. In commercial alloys, the redistribution of the reinforcement can be influenced by the solidification rate as the reinforcing particles are pushed into the network of inter-dendritic area. The finer network of the inter-dendritic region will result in a more uniform distribution of the reinforcing particles.

2.2. The Dispersion of Reinforcing Particles in the Liquid Metal

As a promising solution to improve the homogeneity of MMCs in the liquid metal mixing process, dispersion of solid powder particles in liquid is of great importance. The enhanced dispersion of reinforcement will substantially affect the physical, chemical and mechanical properties of the resulting products. The object of the dispersion is to break agglomerates to discrete particles and then distribute them uniformly throughout the liquid [38].

The fragmentation theory [49, 50] is commonly used to refer a broader class of processes involving breakup of solid clusters/agglomerates. The two main processes considered in the theory are rupture and erosion [51]. The Fragmentation number (Fa) characterizes the breakup due to hydrodynamic forces. It is the ratio between the viscous shear stress and the strength of the agglomerate [52].

\[ Fa = \frac{\mu V}{T} \]  

(1)

where \( \gamma \) is the magnitude of the rate-of-deformation tensor which equals to \( \sqrt{2D: D} \). \( D \) equals to \( (V_e + (V_e)^T)/2 \), where \( V \) is the velocity of the flow. The term T denotes the characteristic cohesive strength of the agglomerate and plays a role analogous to the surface tension in the definition of the Capillary number of liquid drops [53].

The adhesive strength of agglomerates is a combination of the strength of inter-particle bonds due to van der Waals forces, moisture or electrostatic charges [39, 40]. Several models have been developed to describe the adhesive strength and the simplest model describes two neighbouring particles. Rumpf’s model considers the agglomerate as a collection of spherical particles with a radius \( a \), occupying a volume fraction \( \phi \), bonded to each other via cohesive forces. According to this model [54], the tensile strength of agglomerates are given as:

\[ T = \frac{9}{32} \frac{\eta a^2}{\pi b^2} n_b F \]  

(2)

where \( F \) is the average binding force of a single bond and \( n_b \) is the average number of bonds per particle. For the particle size of ~5 \( \mu \)m, the strength of SiC agglomerates could be in the range of 10^7 Pa [55].

Kendall proposed a model assuming that the breakage occurs at a strength limiting flaw, and the expression of the strength of the agglomerate [56] is given as:

\[ T = 11.03 \frac{\sigma_{c}^{1/2} \Gamma_{e}^{1/6}}{\sqrt{\eta a}} \]  

(3)

where \( \Gamma_e \) and \( \Gamma \) are the fracture surface energy and the equilibrium surface energy, respectively, and \( L_f \) is the flaw size. In this model, the influence of the fractal structures in the agglomerate has been considered compared to Rumpf’s theory.

The understanding of the cohesive bonding of particles in agglomerates makes it clear that sufficient forces are required to overcome the cohesive forces and break up the agglomerate into discrete particles to achieve a good dispersion of particles in the liquid.

The external forces required for uniform dispersion of the reinforcing particles in the solid-liquid system is provided by the mechanical energy input into the liquid-solid system. In the high shear process, the energy input creates a turbulent flow field in which solid particles are introduced from top/bottom of the vessel and subsequently dispersed and distributed in the liquid. The dispersion of solid particles is achieved by a combination of drag and lift forces of the moving fluid on the solid particles and the bursts of turbulent circulated eddied liquid originating from the bulk flow in the vessel [22], which is illustrated in Fig. (1).

The term high shear is normally referred to as the high shear rate generated by the specific dispersion device. By assuming the equal rotor tip velocity, the nominal shear rate \( \gamma \) in the rotor-stator gaps can be calculated [22] as:

\[ \gamma = \frac{nND}{\delta} \]  

(4)

where the \( N \) is the rotational speed of the rotor, \( D \) is the rotor diameter and \( \delta \) is the gap width between the rotor and stator. By combining the dynamic viscosity of the treated liquid flow \( \eta \), the shear stress \( \tau \) can be estimated as:

\[ \tau = \eta \frac{nND}{\delta} \]  

(5)

This equation is the criteria for the device design to concur the cohesive force of the targeted particle clusters, and lead to a well dispersion of the particles in the liquid flow.
After the mixture of the liquid flow and the particles are delivered into the gap between the rotor and stator, the liquid will be further ejected out through the apertures on the stator head at a high speed. The shear stress will be applied to the particle clusters by the large velocity gradient generated by the boundary layer effect between the inner wall surface of the aperture and the centre of the aperture. This shear phenomenon further breaks-up the agglomerate/cluster of the reinforcing particles. The shear stress on the mixture of liquid flow and the reinforcing particles flowing through the stator aperture can be calculated [59] as:

\[ \tau = f \rho v^2 / 2 \]  

where \( f \) is the flow friction factor, \( \rho \) is the fluid density of the mixture and \( v \) is the mean flow velocity.

From the physical analysis, it is clear that the shear rate is the key device parameter to increase the shear stress for agglomerate/cluster break-up. With the finer particle addition in the liquid flow, the higher shear rate by the increased rotating speed and reduced rotor-stator gap will be needed for the required dispersion effect.

The concept of high shear treatment in Al and Mg melts has been extensively studied and well understood in terms of solidification and application to industrial casting processes to solve some commonly associated fundamental problems. It has also proven to be applicable to different casting processes making it a ‘multi-purpose’ liquid metal treatment technology, which can be easily integrated to benefit various industrial casting processes.

### 3. EQUIPMENT FOR HSDT

In the initial times, the primary dispersing means in the MMCs production was the impeller stirring [37], which compile the variety of design of the impeller head and buffers, and the shear rate is in the range of \( 10^2 \) s\(^{-1} \) to \( 10^3 \) s\(^{-1} \). This was useful in the MMCs production with fine particle size. By the increasing understanding of the benefit of composites materials with finer reinforcing particle, more powerful dispersing technologies with higher shear rates and energy dissipation are expected to break-up the agglomerates/cluster of the reinforcing particles are introduced into the molten matrix.

### 3.1. The Material Consideration

Due to the significant difference in the service conditions, the design of high shear devices for chemical engineering cannot be easily transplanted to the scenario of liquid metal treatment. The properties of the suitable material must match the design of the components, but at the same time take into account the harsh environment.

The graphite and the metallic materials with refractory coating are the typical materials for the conventional impellers as the impeller rigidity and the high temperature durability was sufficient under the low shear rate condition [60]. With the increasing shear rate and dynamic fluid flow, the materials with high temperature stiffness, toughness, fatigue and wear resistance, and limited thermal expansion coefficient is desired to build the high shear dispersion device for a chemically harsh and stress complexed environment.

Superior to these desired characteristics of materials, the durability of the device candidate materials in the molten metal is the essential factor determining its engineering practicality for the high shear dispersion device [61]. It is generally accepted the material’s life in the molten metal and alloys can be affected by the chemical corrosion and physical erosion. From a systematic study of a variety of the engineering materials under liquid Al, Yan and Fan [62] proposed a selection guidance for high durable materials for high shear dispersion. Here quoted as: “(i) low solubility in liquid metal; (ii) limited thickness and dissolution rate of the interfacial layer; (iii) the interfacial layer should be dense and well...
bonded to the substrate; (iv) a high hardness layer is required to protect the substrate from wear and erosion under dynamic condition”.

Using an extensive trial and a long period test, a narrowed range of a candidate material is framed for Al and Mg melt treatment. At the current state, the ceramics such as, the silicon carbide, aluminium oxides, boron nitride, silicon nitride, sialon and metallic materials, such as tool steel and NbTiW alloys [63, 64], are shortlisted for molten Al. The nickel-free high temperature steels are the preferred materials for liquid Mg application [65].

3.2. The Type of High Shear Dispersion Equipment

There are two mechanisms of twin-screw and rotor-stator, which were utilised to design and prototype the high shear dispersion devices for liquid Al and Mg which have been produced. During the R&D activities in the last two decades [66, 67]. High shear treatment of Al and Mg melts in liquid and semisolid states, using a twin-screw device, was first developed to refine the microstructure and improve the mechanical properties of both cast and wrought alloys [68, 69]. Due to the size of the twin-screw device, the incorporation of this method into the existing processing chain is difficult. Thus, a simpler design to incorporate the high shear treatment into a process is required, leading to the development of a new technology based on a rotor-stator shearing mechanism [64].

3.2.1. Twin-screw Design

Twin-screw mixer is popular in the plastics industry to obtain good mixing of polymer powder/granular with various additives [70]. The main advantages of the twin-screw device are the excellent dispersive mixing of materials with high viscosity, continuous processing and multistage capability.

In 2000, Fan and co-workers developed the prototype of twin-screw device for application to liquid metal for melt conditioning of various melts [71, 72]. The device is constructed with five main sub-systems [65], (i) a driving motor to rotate twin-screws, (ii) the feeder and treatment barrel to host melt flow, (iii) the C shape heating elements embracing treatment barrel and thermocouple to maintain melt temperature, (iv) a pair of co-rotating and intermeshing screws applying high shear to the alloy melt, and (v) a control valve to release the treated melt to down-stream process.

The process starts with the liquid metal fed into the treatment chamber with a pre-set temperature, and then the twin-screws rotate at speed up to 1000 rpm using the driving force from the motor. The control valve releases the treated melt after twin-screw high shear at an accurate temperature and a given time. From the schematics of the twin-screw device, it shows that the high shear stress is applied on the melt where the screws are in contact with each other and screw tip reaching to the barrel wall.

With the distinct advantage for viscous liquid applications, the twin-screw device is capable of being operated at temperatures above or below the liquidus of the liquid feed to provide treated liquid metal or highly sheared semi-solid slurry. Previous research showed that the well dispersed nano-size native MgO oxide films resulted in a refined microstructure, uniform distribution of solute elements through the enhanced heterogeneous nucleation [68]. Moreover, excellent dispersion of SiC particles from micron to nano scale has been obtained in Al metal matrix composites through the twin-screw based high shear treatment [67, 73].

3.2.2. Rotor-stator Mechanism High Shear Dispersion

High shear mixers, also known as high shear reactors, rotor-stator mixers, and high shear homogenizers have been widely used in chemical, pharmaceutical and food industries for emulsification, suspension and chemical reaction purpose [22]. They are characterised by high rotor tip speeds (10-50 m/s), high shear rate (10^4-10^5 s^-1) and highly localized energy dissipation rates near the mixing head.

The rotor-stator based high shear melt conditioning (HSMC) device developed within Brunel Centre for Advanced Solidification Technology (BCAST) provides intensive melt shearing, dispersing inclusions into finer scale particles that enhance the number of nucleation sites [64]. It is comprised of a set of rotor and stator attached to an electrical motor with a speed control. During its operation, the motor transfers the power to the rotor by the shaft and drives the rotor to spin and shear the melt in the gap between the rotor and the inside of the stator and also in the openings of the stator (Fig. 2). The rotation speed can be in the order of 1,000-10,000 rpm providing an extremely high shear rate. Since the rotor is spinning at high speed, this creates a centrifugal force that displaces the melt upwards in a pumping action, followed by squeezing the same volume of melt through the stator holes. The HSMC technique provides macro-flow in a volume of melt for distributive mixing and intensive shearing near the tip of the device for dispersive mixing.

The main advantages include; significantly enhanced kinetics for chemical reactions or phase transformations, uniform dispersion, distribution and size reduction of solid particles and gas bubbles, improved homogenisation of chemical composition and temperature fields and also forced wetting of usually difficult-to-wet solid particles in the liquid metal. Hence, the HSMC technology can be used for: physical grain refinement by dispersing naturally occurring oxides [69], for degassing of melts [74], for the preparation of metal matrix (nano) composites [75, 76] and also for preparation of semi-solid slurries [66]. In turn, these characteristics can be applied to benefit various conventional casting processes, in order to improve the quality of cast products.

4. MAGNESIUM BASED MMNCs

Since HSDT could offer an ideal combination of refined microstructures and homogeneous spatial distribution of particles, many investigations have been made to fabricate metal matrix based nanocomposites (MMNCs), particularly on light metals, such as Mg alloys due to its high strength-to-weight ratio compared to other structural metals.
The nanoparticles (NPs) usually incorporated in Mg alloys include but are not limited to ceramic reinforcements, such as Al₂O₃, AlN, SiC, Y₂O₃, etc. [18-79]. In order to combine the suitable mechanical properties with excellent corrosion resistance, many studies selected ceramic nanoparticles containing human bone compositions such as hydroxyapatite (HA), beta-tricalcium phosphate (β-TCP) and MgO, to fabrication MMNCs. In the following sections, the Mg based MMNCs will be reviewed according to different types of NPs incorporated by HSDT.

4.1. AlN

AlN NPs were considered as promising nucleation sites for Mg alloys due to their same hexagonal closed packed (hcp) structure with similar lattice parameters [80, 81]. Many efforts have been made to reveal the influence of AlN NPs on the creep resistance of Mg based MMNCs, Yang et al. [82] employed HSDT to fabricate the mixture of 0.75% AlN NPs and 0.25% metallic Al (AlN/Al, 80 nm) to Mg-2.85Nd-0.92Gd-0.41Zr-0.29Zn (El21) alloy. Shearing speed was fixed at 500 and 3000 rpm for 1 min. It was shown that the creep resistance of El21 was improved by approximately one order of magnitude with the addition of 0.5% AlN/Al NPs by HSDT at 3000 rpm, (Figs. 3a and b). Moreover, El21 with 0.5% AlN/Al NPs showed even higher creep resistance with assistance of HSDT than that incorporated using US-assisted treatment with more addition (1%).
[78], which further indicated HSRT was more effective to disperse the NPs than the latter, (Fig. 3c and d). They proposed that high speed turbulence generated from HSRT was helpful for promoting the physical contact between AlN NPs and matrix and increased their wetting, leading to a uniform distribution of AlN NPs. The addition of AlN/Al NPs in E21 by HSRT also led to a refined, thinner and homogeneous eutectic phase, which was beneficial for alleviating the grain boundary sliding and dislocation movement during creep.

Since the superiority of HSRT for the fabrication of Mg-based MMNCs was demonstrated in [82], further research was focused on the optimum content of AlN/Al on the improvement of creep resistance in E21 alloy [83]. 0, 0.25, 0.5 and 1% contents of AlN/Al NPs were added to E21 alloy using HSRT, respectively. The grains were coarsened by adding AlN/Al NPs due to the loss of grain refiner Zr, which for the formation of Al-Zr phase. Table 1 summarises the grain size and hardness of the nanocomposites with different contents of AlN/Al particles prepared at a shear speed of 3000 rpm and a duration of shearing of one minute.

Table 1. Grain size and hardness of AlN/Al-particle reinforced nanocomposites with Elektron21 matrix [83].

<table>
<thead>
<tr>
<th>AlN/Al Content [wt.%]</th>
<th>Grain Size [µm]</th>
<th>Hardness [HV5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>80.1 ± 5.0</td>
<td>45.0 ± 1.2</td>
</tr>
<tr>
<td>0.25</td>
<td>86.4 ± 2.7</td>
<td>46.3 ± 2.6</td>
</tr>
<tr>
<td>0.5</td>
<td>144.5 ± 4.0</td>
<td>45.7 ± 2.4</td>
</tr>
<tr>
<td>1</td>
<td>463.5 ± 17.5</td>
<td>51.1 ± 3.6</td>
</tr>
</tbody>
</table>

Tension and compression tests at room temperature were carried out on the Elektron21 and the 0.5% NP nanocomposite [84]. Two different shear rates of 500 and 3000 rpm were used. Tables 2 and 3 show the results of the tests. It is clear that the room temperature properties cannot be improved by shearing and addition of NP. This is mainly due to the reduction of the grain refining effect of the Zr, which is inhibited by the addition of Al.

Table 2. Results of tensile tests at RT performed on Elektron21 as cast and sheared with 500 and 3000 rpm, and the 0.5AlIN nanocomposite [84].

<table>
<thead>
<tr>
<th>Material</th>
<th>YS [MPa]</th>
<th>UTS [MPa]</th>
<th>E [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E21 as cast</td>
<td>102.3 ± 1.5</td>
<td>197.4 ± 4.2</td>
<td>10.1 ± 1.9</td>
</tr>
<tr>
<td>E21 500 rpm</td>
<td>94.0 ± 1.2</td>
<td>169.1 ± 12.9</td>
<td>6.9 ± 1.5</td>
</tr>
<tr>
<td>E21 3000 rpm</td>
<td>97.4 ± 2.2</td>
<td>189.1 ± 3.4</td>
<td>8.4 ± 1.1</td>
</tr>
<tr>
<td>E21+0.5AlN 500 rpm</td>
<td>92.1 ± 1.5</td>
<td>167.4 ± 10.1</td>
<td>5.8 ± 1.6</td>
</tr>
<tr>
<td>E21+0.5AlN 3000 rpm</td>
<td>95.4 ± 2.1</td>
<td>167.8 ± 2.3</td>
<td>5.9 ± 0.5</td>
</tr>
</tbody>
</table>

(YS: Yield Strength; UTS: Ultimate Tensile Strength; E: Elongation)

However, the intermetallic phase was sheared to be more homogeneous in the matrix with reduced size. Such phase and AlN NPs could act as reinforcements on the grain boundaries and matrix to enhance the creep resistance of E21, thus E21+1% AlN/Al showed the best creep resistance among all the materials.

It is noticed that the aforementioned NPs contain 75% AlN and 25% Al. Therefore it is of interest to differentiate the individual/synergistic roles of AlN and Al NPs on the creep resistance of E21 by HSRT. Yang et al. [85] further compared the creep resistance of E21 alloy with additions of pure 0.25 Al%, 0.75% AlN and 1% AlN/Al NPs sheared by HSRT. They claimed that the simultaneous addition of Al and AlN NPs played a synergistic strengthening effect on the creep resistance of E21 alloy. HSRT was not only beneficial for dispersing the NPs uniformly in the matrix, but also promoted the chemical reactions between Al and RE for the formation of Al3REE. Such structure was more thermally stable to inhibit the dislocation movement and transfer the load from matrix to NPs.

Since E21 alloy is a heat treatable alloy [86], Yang et al. [87] investigated the influence of T6 heat treatment on the creep resistance of E21+1% AlN/Al NPs stirred by HSRT. They found additional plate-like Al3REE precipitates were formed after T6 heat treatment (green arrows in Fig. 4f), while there were no such precipitates in NP-free E21 alloy (Fig. 4e). This formation of plate-like Al3REE precipitates consumed certain amount of RE solutes and decreased the amount of γ” precipitates in the subsequent ageing process. Therefore, they provided a reduced the precipitation strengthening during creep and were detrimental to the creep resistance of E21+1% AlN/Al (T6) MMNCs (Figs. 4a-f).

Table 3. Results of tensile tests at RT performed on Elektron21 as cast and sheared with 500 and 3000 rpm, and the 0.5AlIN nanocomposite [84].

<table>
<thead>
<tr>
<th>Material</th>
<th>CVS [MPa]</th>
<th>UCS [MPa]</th>
<th>C [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E21 as cast</td>
<td>113.3 ± 1.4</td>
<td>333.8 ± 1.4</td>
<td>16.4 ± 0</td>
</tr>
<tr>
<td>E21 500 rpm</td>
<td>103.4 ± 1.2</td>
<td>322.3 ± 0.9</td>
<td>17.7 ± 0.6</td>
</tr>
<tr>
<td>E21 3000 rpm</td>
<td>110.0 ± 0.7</td>
<td>330.0 ± 0.5</td>
<td>16.8 ± 1.3</td>
</tr>
<tr>
<td>E21+0.5AlN 500 rpm</td>
<td>98.5 ± 0.4</td>
<td>320.6 ± 1.5</td>
<td>19.4 ± 0.5</td>
</tr>
<tr>
<td>E21+0.5AlN 3000 rpm</td>
<td>102.8 ± 0.7</td>
<td>328.8 ± 2.0</td>
<td>17.0 ± 0.6</td>
</tr>
</tbody>
</table>

(YS: Compressive Yield Strength; UCS: Ultimate Compressive Strength; C: Creep)

4.2. Hydroxyapatite

Hydroxyapatite (HA) NPs have been extensively utilized for bone grafting and biomimetic coatings, which were capable of improving corrosion resistance and strength of materials [88]. This made them promising for tailoring both the corrosion resistance and mechanical properties simultaneously in Mg based MMNCs. Razavi et al. [89] fabricated an Mg-1.61Zn-0.18Mn-0.5Ca+1% HA (Compositions in wt.% throughout unless specified) nanocomposites by a novel route combining HSRT and equal channel angular extrusion (ECAE) technique, followed by heat treatment. It is found that the combination of HSRT and ECAE effectively decreased its biodegradation rate with a marginal corrosion rate of 0.12 mm/year. This is ascribed to the improvement of
wettability between reinforcements and matrix with the assistance of HSDT and ECAE.

However, HSDT/ECAE showed diverse responses to corrosion resistance depending on the shapes of HA NPs. Razavi et al. [90] added two commercial available HA NPs as reinforcements to Mg-2Zn-0.2Mn-0.5Ca fabricated with HSDT and ECAE (Fig. 5a), which have spherical and needle morphologies with an average size of 40 nm (Fig. 5b). It was found that spherical HA NPs showed better corrosion resistance than needle morphology ones. This was attributed to the relatively worse wettability between needle HA NPs and matrix than that of spherical ones. It was more difficulty for needle HA NPs to physically contact with the alloy matrix due to their sharp corners, which made their bonding loose. Meanwhile, residual stress concentrations around the needle HA NPs were readily created, which might result in pitting corrosions and promote local corrosion.

Li et al. [88, 91] used HSDT to fabricate the Mg-3Zn-0.5Zr+HA NPs MMNCs followed by ECAE technique. Spherical HA NPs with an average size of 35 nm were selected as reinforcements at different amounts of weight percentage, i.e. 1, 3, 5 and 10 wt. %. The shearing speed of HSDT was controlled at several speeds up to 10000 rpm for 5-20 min. The optimum shearing speed was found to be approximately 5000 rpm for 10 min and holding for less than 3 min prior to solidification. Fig. (6) exhibited the comparisons of as cast microstructures of Mg-3Zn-0.5Zr+5% HA with and without high shearing. HSDT led to a refined microstructure with a uniform spatial dispersion of HA NPs (Fig. 6a), while Fig. (6b) showed coarse grains and HA NPs aggregated randomly as large clusters in the matrix. They claimed that the grain size of high-sheared MMNCs was only about one tenth to that of non-sheared ones, which was distinctly smaller than those fabricated by PM process. HSDT enhanced the wettability between HA NPs and the matrix and effectively broke down the HA clusters in the molten metal, which led to an obvious improvement on the mechanical properties. It is shown that Mg-3Zn-0.5Zr with
addition of 3-5% HA NPs showed a better combination of strength and ductility than those of commercial Mg wrought alloys.

4.3. β-TCP

TCP (Ca$_3$(PO$_4$)$_2$) NPs were capable of offering superior biocompatibility, bioactivity and osteoconductive performances, which make them possible as bone graft substitute. It is reported that Ca$_3$(PO$_4$)$_2$ group acted as the largest inorganic constituent in human bone tissue and had wide applications in orthopedic and dental usage [92, 93]. Meanwhile, compared with HA particles, TCP exhibits higher dissolution rate, which makes them promising as complete degradation implant materials. Liu et al. [76] employed HSDT to incorporate β-TCP NPs in Mg-3Zn-Ca matrix. Such β-TCP powder has spheroid-like morphology with a diameter of less than 100 nm. After adding 1% β-TCP NPs in the melt, the mixer of HSDT was controlled over a range of 6000-8000 rpm at 640°C melt temperature for 4-5 min before being subjected to another rheo-diecasting process (MCAST) process [94]. Fig. (7a) exhibits severe agglomeration of β-TCP NPs located in the matrix after conventional stirring. After intensive shearing by HSDT, β-TCP clusters were homogeneously dispersed as smaller-sized ones (Fig. 7b). With combination of HSDT and MCAST, the agglomeratation of β-TCP NPs were further alleviated in Fig. (7c). They proposed that with the assistance of HSDT β-TCP NPs were effectively to break up and wet with Mg-3Zn-Ca matrix due to an extremely high shear area generated by HSDT.

Huang et al. [95] combined HSDT with ECAE process to fabricate a biodegradable Mg based MMNCs with β-TCP NPs. Its corrosion resistance was determined via electrochemical test. 1% β-TCP NPs with a diameter range of 100-200 nm were incorporated by HSDT at a shearing speed of 1200 rpm for 5 min at 650°C prior to ECAE process. It is claimed that a refined uniform grain structure were obtained with the addition of β-TCP NPs after intensive shearing by HSDT. This was a result of HSDT providing an equilibrium temperature and uniform chemical compositions in the melt, which spread the nucleation agents homogeneously throughout the melt to make the most of their effects. Such microstructures given by HSDT and ECAE contributed to the improvement of both the hardness and corrosion resistance of Mg-2Zn-1Ca+1% β-TCP. Vickers-hardness values are given in Table 4.

Table 4. Vickers micro-hardness of materials [95].

<table>
<thead>
<tr>
<th>Process</th>
<th>As-cast</th>
<th>1ECAE</th>
<th>2ECAE</th>
<th>4ECAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>HV0.1</td>
<td>55.1 ± 3.7</td>
<td>72.4 ± 6.8</td>
<td>77.8 ± 2.4</td>
<td>80.6 ± 1.9</td>
</tr>
</tbody>
</table>
4.4. MgO

Previous studies reported that HA particles exhibited a poor interface with Mg matrix [96] and showed very low solubility in vivo. [97]. MgO particles were one of the important constituents in bioglass, which were bioactive, antibacterial and capable of full degradation. These advantages make them as one of the promising reinforcements for the fabrication of biomedical MMNCs.

Lin et al. [98] used MgO NPs with spherical morphology with an average diameter of 50-100 nm to reinforce the Mg-3Zn-0.2Ca matrix. Four different amounts of weight percentage, i.e. 0.1, 0.2, 0.3 and 0.5%, were incorporated by HS-DT at a shearing speed of 4000 rpm for 5 min at 680°C before extrusion. The microstructural analysis showed that a relatively good dispersion of MgO particles were achieved by HS-DT. A good interface between MgO NPs and matrix was observed where no cracks or voids were formed. Mg-3Zn-0.2Ca with 0.5% MgO NPs exhibited the best mechanical properties in terms of tensile yield stress and ultimate tensile stress. The refined grain size and good interface between MgO NPs and Mg matrix, which resulted from the assistance of HS-DT, contributed to the improvement of corrosion resistance, Table 5. Moreover, MgO was helpful for the generation of Mg(OH)₂ films in the early stage of immersion.

Table 5. Grain size and corrosion rate of materials [98].

<table>
<thead>
<tr>
<th>Material</th>
<th>Grain Size [µm]</th>
<th>Corrosion Rate [mm/y]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-cast</td>
<td>As-extr.</td>
</tr>
<tr>
<td>MZC</td>
<td>90 ± 5</td>
<td>2 ± 0.5</td>
</tr>
<tr>
<td>MZCs</td>
<td>125 ± 5</td>
<td>10 ± 0.8</td>
</tr>
<tr>
<td>MZC0.1s</td>
<td>55 ± 4</td>
<td>5.1 ± 0.3</td>
</tr>
<tr>
<td>MZC0.2s</td>
<td>50 ± 3</td>
<td>3.1 ± 0.4</td>
</tr>
<tr>
<td>MZC0.3s</td>
<td>46 ± 3</td>
<td>2.2 ± 0.4</td>
</tr>
<tr>
<td>MZC0.5s</td>
<td>37 ± 2</td>
<td>1.5 ± 0.2</td>
</tr>
</tbody>
</table>

CONCLUSION

The following nanoparticles used as reinforcement materials in Mg based MMNCs were presented: AlN, HA, β-TCP and MgO. AlN nanoparticles in El21+1% AlN/Al NPs stirred by HS-DT tended to form Al₃RE phase which has higher thermal stability than that of Mg₃RE thus improved creep resistance. Following HS-DT, HA nanoparticles had greater wettability to the Mg matrix due to the breaking up of HA clusters. This led to an obvious improvement to mechanical properties. The intensive shearing by HS-DT and ECÆ contributed to the improvement of both the hardness and corrosion resistance of Mg-22Zn-1Ca+1% β-TCP as a result of the refinement of grain structures in β-TCP nanoparticles. Finally, MgO NPs, initially selected for their biocompatibility properties, were incorporated in Mg-3Zn-0.2Ca via HS-DT. Good grain refinement was achieved which contributed to improve corrosion resistance and ultimately allowed MgO to generate Mg(OH)₂ films in early stages of immersion.

FUTURE OUTLOOK

In order to be able to dare an outlook into the future of magnesium-based nanocomposites, this hybrid material must certainly be investigated in more detail. The effect of various nanoparticles on the solidification behaviour of different magnesium melts is not yet fully understood, and the processes for their production can still be optimised. The in-situ production of the nanoparticles during a chemical reaction prior to solidification is another interesting way to control the quantity, size and distribution of the particles.

Functionalisation through incorporated nanoparticles is also conceivable in the future. This is possible, for example, in medical applications in which degradable magnesium implants release fluorescent nanoparticles during degradation, the detection of which in the blood can then provide information about the degradation rate of the implant. But also nanoparticles that lead to repeated grain refinement after melting of the nanocomposite and subsequent solidification are of interest. They can be used in powders or wires that are used in additive manufacturing. In the additively manufactured component, the fine-grained material has a strength and ductility advantage compared to conventional magnesium alloys.

AUTHORS’ CONTRIBUTION

HY, JP, XY, SG, and HD contributed to collecting, writing, reviewing the text. HD contributed the idea for the review.

CONSENT FOR PUBLICATION

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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