Materials Characterization 105 (2015) 30–46

Contents lists available at ScienceDirect

Materials Characterization

journal homepage: www.elsevier.com/locate/matchar

Tutorial review

Magnesium-based nanocomposites: Lightweight materials of the future

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ARTICLE INFO

Article history:
Received 3 January 2015
Received in revised form 16 April 2015
Accepted 17 April 2015
Available online 19 April 2015

Keywords:
Magnesium nanocomposites
Microstructure
Tensile properties
Compressive properties
Hardness

ABSTRACT

Magnesium and its alloys reinforced with nano-size reinforcements display improved mechanical properties without significant reduction in the ductility that is usually associated with the addition of micron size reinforcements, making them an attractive choice for lightweight structural applications. This paper provides a review of magnesium nanocomposites containing ceramic and metallic reinforcements synthesized using liquid based (Disintegrated Melt Deposition Technique) and solid based (Powder Metallurgy and Microwave Sintering) processing techniques. The properties of these nanocomposites will be discussed in terms of microstructure, grain size, hardness, tensile, compressive, dynamic, high temperature, corrosion, fatigue and wear.

1. Introduction

Magnesium is the lightest structural metal. Magnesium alloys are 33% lighter than aluminium, 61% lighter than titanium and 77% lighter than stainless steel making them promising candidates as replacement material for these metals. In terms of availability, magnesium is the sixth most abundant element in the earth's crust comprising of 2% by mass and third most dissolved mineral in seawater with an availability of 1.1 kg/m^3 [1]. Other than its low density, cast magnesium alloys display similar melting temperature, specific strength and elongation with cast aluminium alloys as shown in Table 1 [2]. Magnesium possesses several other benefits including excellent castability, high damping capacity, good electromagnetic shielding, most easily machinable of all structural metals and less energy requirement in the production of magnesium compared to aluminium. The limitations of magnesium include its low elastic modulus and ductility, poor creep and abrasion resistance and high corrosion rate. These limitations have been circumvented by the development of new magnesium alloys and the addition of reinforcements to create magnesium composites [3–5].

Commercial exploitation of magnesium started in Germany in 1886 and has been used traditionally in flares, tracer bullets and pyrotechnics [5]. During the Second World War, magnesium was used to make fuselages, engine parts and wheels in Messerschmitt and Stuka dive bombers [6]. In the 1950s, Volkswagen Beetle car used almost 25 kg of magnesium castings in its transmission housing and air-cooled engine and U.S. Convair B-36 bomber planes contained 8600 kg of magnesium [5,6]. Currently, magnesium and its alloys find limited use in major commercial aircraft structural components but are used in gearboxes and transmission casings for helicopters. Increasing demands for lightweighting also drives the interest for magnesium to be used in automotive, sports and consumer electronics which are discussed in later section. In recent years, magnesium is also increasingly attractive for biomedical applications due to its biocompatibility, biodegradability and similar density, elastic modulus and tensile strength to human cortical bone [7,8].

The addition of ceramic and metallic particulate as reinforcements is one of the possible methods, in addition to precipitation hardening, grain size strengthening and solid solution strengthening (alloying), used to improve the mechanical properties of magnesium. The types of micron size particulate reinforcements include oxides (Al_2O_3, TiO_2), nitrides (BN, AlN, TiN, ZrN), carbides (B_4C, SiC, TiC, ZrC), borides (TiB_2, ZrB_2) and metals (Ti, Mo, Cu, Ni) [3–5,9–12]. However, the addition of micron-size reinforcements generally leads to substantial reduction in the ductility of the magnesium matrix due to particle cracking and void formation at particle-matrix interface leading to accelerated failure [13]. In micron-size reinforcements, there is a higher probability of it containing fracture initiating defects due to the larger size, making particle fracture more prevalent. Secondary processing such as extrusion is often used to improve the properties of composites by further consolidation of the composite and homogenization of the distribution of reinforcements but may further increase the likelihood of particle fracture [13].

Recent studies on magnesium nanocomposites have revealed that the addition of nano-reinforcements helped to improve the mechanical properties of magnesium without any adverse effect on the ductility

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http://dx.doi.org/10.1016/j.matchar.2015.04.015
1044-5803/

Table 1
Selected properties for cast magnesium alloys, cast aluminium alloys, titanium alloys and stainless steel based on values from CES EduPack 2014 [2].

Property	Cast Mg alloys	Cast Al alloys	Titanium alloys	Stainless steel
Density (g/cm^3)[a]	1.75–1.87	2.5–2.9 (33%)	4.4–4.8 (61%)	7.6–8.1 (77%)
Price (SGD/kg)	4.71–5.17	2.71–2.98	28.7–31.6	7.04–7.75
Melting point (°C)	447–649	475–677	1480–1680	1370–1450
Elastic modulus (GPa)	42–47	72–89	110–120	189–210
Specific stiffness	22–27	25–36	23–27	23–28
Yield strength (MPa)	70–215	50–330	750–1200	170–1000
Specific strength	37–123	17–132	156–273	21–132
Elongation (% strain)	1–10	0.4–10	5–10	5–70

[a] Number in parenthesis indicates the percentage difference in density between magnesium and the metal.

[14–17]. In addition, the use of a small volume fraction of nano-size reinforcements has been shown to produce results comparable or even superior to that of MMCs reinforced with similar or higher volume fraction of micron size reinforcements. Examples of the mechanical properties for pure magnesium reinforced with different sizes of SiC and Al_2O_3 particles are provided in Table 2 [18,19] showing the overall improvement in both strength and ductility of magnesium with the addition of nanoparticles while micron size particles are able to improve strength of the matrix only. In recent years, studies related to magnesium nanocomposites have increased rapidly from less than 10 publications in 1995 to approximately 540 publications in 2014 based on data extracted from ScienceDirect website [20]. The addition of nanosize reinforcements is therefore an attractive solution to improve the mechanical properties without substantially affecting the ductility of magnesium.

This paper provides a tutorial on magnesium nanocomposites, providing an introduction to the processing techniques, microstructures and the enhancements in mechanical properties observed.

2. Processing techniques

Magnesium composites containing nano-size particulates are typically processed using similar methodologies as composites reinforced with micron size reinforcements, either by liquid based or solid based processing techniques.

For liquid based processing, the reinforcement can be added together with the magnesium metal into the crucible prior to heating or added later to the molten magnesium melt. Upon reaching the molten stage, various methods are used to disperse the reinforcements to achieve a uniform distribution before casting. The most common method involves agitating the molten melt with a mechanical impeller [3–5,14] while others have made use of ultrasonic energy to disperse the nano-size particles [21]. Alternatively, the molten melt is infiltrated into a preform containing the reinforcements under pressure (squeeze casting) [22]. For the synthesis of nanocomposites using liquid based processing, the main problem lies in achieving a uniform distribution of the nanoparticles since the nanoparticles tend to cluster and form agglomerates due to their high surface energy. The formation of clusters and agglomerates tends to reduce the strengthening effect. Another problem with casting is the increased viscosity of the molten melt with the addition of finer particle size [13,17], thereby limiting the volume fraction of nano-size particles (typically around 2–3 vol.%) that can be added.

Table 2
Mechanical properties for MgSiC and MgAl_2O_3 composites [18,19].

Materials	Microhardness (HV)	0.2% YS (MPa)	UTS (MPa)	Ductility (%)
Pure Mg (PM)	38.6 ± 1.5	125 ± 15	172 ± 12	5.8 ± 0.9
Mg/10 vol.% 25 μm SiC	44.3 ± 0.5	140 ± 2	165 ± 2	1.5 ± 0.8
Mg/1 vol.% 50 nm SiC	43.2 ± 2.0	157 ± 22	203 ± 22	7.6 ± 1.5
Pure Mg (DMD)	40.0 ± 0.2	97 ± 2	173 ± 1	7.4 ± 0.2
Mg/1.1 vol.% 1 μm Al_2O_3	58.8 ± 0.5	209 ± 1	242 ± 3	3.5 ± 0.3
Mg/1.1 vol.% 0.3 μm Al_2O_3	52.0 ± 0.8	200 ± 1	256 ± 1	8.6 ± 1.1
Mg/1.1 vol.% 50 nm Al_2O_3	65.9 ± 0.9	175 ± 3	246 ± 3	14.0 ± 2.4

Solid based processing or powder metallurgy (PM) technique typically involves mixing the metal powders and nano-reinforcements in the desired composition by simple blending or by mechanical alloying. To disperse the nanoparticles, blending at high rotational speed for extended period of time or mechanical alloying using high energy ball milling can be employed. The mixed powders are pressed to form green compacts and then sintered using resistance heating or microwave heating [23]. Secondary processing such as extrusion or rolling may be employed to further consolidate or shape the composite materials.

Other methods that have been employed to produce magnesium-based nanocomposites include friction stir processing [24] and semisolid stirring [25]. Further details on different processing methodologies can be found in several review papers and books on magnesium composites [3–5,15–17,26].

This paper will focus in detail on two processing techniques developed by the research group: 1) Disintegrated Melt Deposition (DMD) and 2) Blend-Press-Sinter using Hybrid Microwave Sintering that have been employed to successfully synthesize lightweight aluminium and magnesium nanocomposites with enhanced properties.

2.1. Disintegrated Melt Deposition (DMD) technique

DMD is a unique cost-effective technique that brings together the advantages of spray processing and conventional casting, utilizing higher superheat temperatures and lower impinging gas jet velocities to produce bulk composite material. Synthesis of nano-particulate reinforced magnesium composites using DMD technique involves heating the magnesium chips/turnings and the reinforcement powder in a multi-layered arrangement to a superheated temperature (>650 °C) under an inert argon gas atmosphere in a graphite crucible with a resistance heating furnace. The crucible is equipped with an arrangement for bottom pouring. Upon reaching the superheat temperature, the molten slurry is stirred for 5 min at approximately 450 rpm using a twin blade (pitch 45°) mild steel impeller to facilitate the incorporation and uniform distribution of reinforcement particulates in the metallic matrix and to ensure temperature homogeneity. The impeller is coated with 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 avoid iron contamination of the molten metal. The melt is then released through a 10 mm diameter orifice at the base of the crucible. The composite melt is disintegrated by two jets of argon gas orientated normal to the melt stream before being deposited onto a metallic substrate. Preform of 40 mm diameter is obtained following the deposition stage. A schematic diagram of the DMD setup is shown in Fig. 1. The synthesis of pure magnesium and magnesium alloys has been successfully carried out using steps similar to those employed for the reinforced materials except that no reinforcement particulates were added [27].

The deposited magnesium ingot is machined to 35 mm diameter and hot extruded at 350 °C using an extrusion ratio ranging from 12.25:1 to 25:1 on a 150 ton hydraulic press to produce rods of diameter of 10 mm to 7 mm, respectively. The extruded rods are subsequently prepared according to the respective ASTM standards for further