High Strength Magnesium Matrix Composites Reinforced with Carbon Nanotube

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1. Introduction

It has been increasingly important to develop lightweight and high-strength materials for improving energy-efficiency through the weight reduction of transportation carriers. Magnesium alloys have attracted lots of attentions[1-3], since the density of magnesium is approximately two thirds of that of aluminum and one fifth of steel. As a result, magnesium alloys offer a very high specific strength among conventional engineering alloys. In addition, magnesium alloys posses good damping capacity, excellent castability, and superior machinability. However, compared to other structural metals, magnesium alloys have a relatively low mechanical strength, especially at elevated temperature. The need for high-performance and lightweight materials for some demanding applications has led to extensive efforts in the development of magnesium matrix composites and cost-effective fabrication technologies. They are proved to have good mechanical properties through an incorporation of structural filler (e.g., ceramic whiskers such as silicon carbide whisker and others, aluminum oxide, graphite and other particles, carbon fibers and carbon nanotubes: CNTs) [4-7]. Within this context, the dimensionally nano-sized, mechanically strong CNTs [8-11], considered as the ideal reinforcing filler in various composite systems [12-15], have been incorporated into magnesium matrix [16-19]. This chapter put the spotlight into the very attractive new magnesium alloy matrix composites reinforced with CNTs.

2. Processing techniques for fabricate the metal matrix composite (MMC) with CNTs

The reinforcing phases such as powders, fibers and whiskers are generally incorporated into the metal matrices mostly by two typical techniques of liquid state fabrication and solid state fabrication [3,20]. The key techniques in the processing of MMC are how to realize the homogeneous distribution of reinforcement phases and to achieve a defect-free microstructure.

2.1 Liquid state fabrication of MMC

Liquid state fabrication of MMC involves incorporation of dispersed reinforcing phase into a molten matrix metal, followed by its solidification. There are many liquid state fabrication

methods such as stir casting, rheocasting, infiltration, gas pressure infiltration, squeeze casting infiltration, pressure die infiltration, etc., however, a few methods are applied for fabricating MMC with CNTs. Their features are written below. In order to provide high level of mechanical properties of the MMC, good interfacial bonding (procuring the wetting reaction) between CNTs and matrix should be obtained. Wetting improvement may be usually achieved by coating the reinforcing phases [21]. Unfortunately, proper coating for CNTs has not yet established.

2.1.1 Stir casting

Stir Casting is the simplest and the most cost effective method of liquid state fabrication. A dispersed phase (ceramic particles, short fibers) is mixed with a molten matrix metal by means of mechanical stirring. Liquid state composite material is then cast by conventional casting methods and may also be processed by conventional metal forming technologies. When CNTs are selected as a reinforcing phase, uniform distribution of CNTs in the matrix structure should be obtained since the CNT exhibits inherent deficiency of wetting for molten magnesium and magnesium alloy matrices.

2.1.2 Rheocasting

Rheocasting is a modified method using stirring metal composite materials in semi-solid state. Distribution of dispersed phase may be improved because the high viscosity of the semi-solid matrix material enables better mixing of the dispersed phase.

2.2 Solid state fabrication of MMC

Typical solid state fabrication method in which MMC is formed as a result of bonding matrix metal and dispersed phase due to mutual diffusion occurring between them. Raw powders of the matrix metal are mixed with the dispersed phase in form of particles or short fibers for subsequent compacting and sintering. Sintering involves consolidation of powder grains by heating the "green" compact part to the elevated temperature below melting point.

Relatively low process temperature as compared to Liquid state fabrication is expected to depress undesirable reaction generating fragile phase such as carbide on the boundary between the matrix and dispersed phase when carbon fiber or CNT are used as the reinforcing phase.

3. Microstructure of the composite with CNTs

3.1 Characteristics of the CNTs introduced into matrix

Kroto *et al*. discovered fullerene (C60) in 1985 [22] and won Nobel Prize in Chemistry in 1996. After their discovery, Iijima found that carbon nanotube (CNT) generated on the electrode of the generation device of C60 in 1991and opened the beginning to the CNT generation [23]. As it should be noted that CNTs are sorted into two main groups by their structure and size. Fig.1 shows the illustration sorting the carbon fiber and CNTs [24]. The first group of CNTs is single-layered carbon nanotube (SWCNT) having wondrous strength such as 1 TPa in Young's modulus and 140 GPa in Yield strength [25]. However, SWCNT is too expensive for normal industrial application. The second CNT group is multilayered

carbon nanotube (MWCNT). Table 1 presents the characteristics of an example of MWCNT called as a vapor grown carbon fiber (VGCF)[26] made by SHOWA DENKO K.K. in Japan. In late years mass production of MWCNT has been achieved and enabled to use it with relatively low cost.

Density	(kg/m³)	2000
Bulk density	(kg/m³)	40
Fiber diameter	(nm)	150
Fiber length	(μm)	10~20
Aspect ratio		10~500
Elastic modulus [28]	(GPa)	100~700
Tensile strength [28]	(GPa)	0.5~2.2
Thermal conductivity	(W/mK)	1260

Table 1. Characteristics of the MWCNT(VGCF) [26]
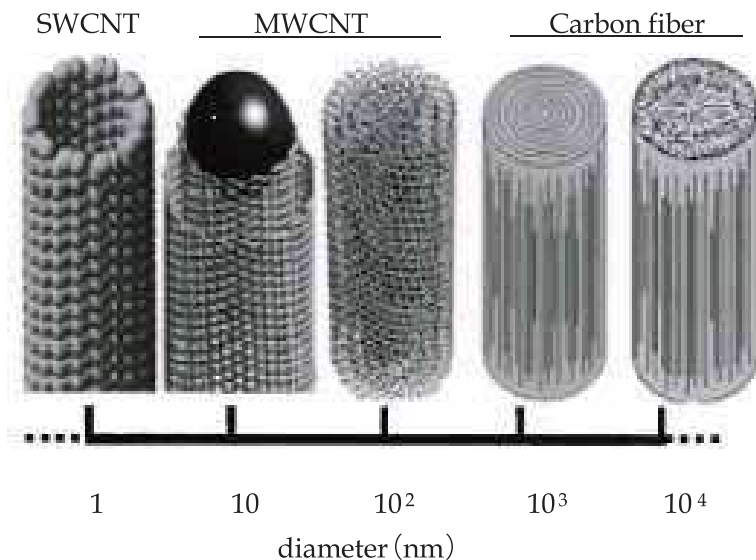
Fig. 1. Illustration sorting carbon fiber and CNTs[24]

3.2 Distribution of CNTs in the matrix

Scanning electron microscopies of the composite showing distribution state are presented for instance in Fig.3(a) and (b). These microstructure were observed on the tensile fracture surface of the test specimens prepared by the following powder metallurgical process[27], i.e. at first, AZ91D magnesium alloy powders of 100 μm or less in diameter were prepared by tri-axial ball

milling process from lathe cutting chips of AZ91D raw ingot. Then, the AZ91D powders and MWCNTs were physically blended with zirconia balls (diameter = 1 mm) in a container using the same ball miller in argon atmosphere. The absence of the aggregated MWCNTs for the magnesium alloy powder containing 1 mass% MWCNTs indicates that the short MWCNTs are homogeneously impinged on the near surface of magnesium alloy particles
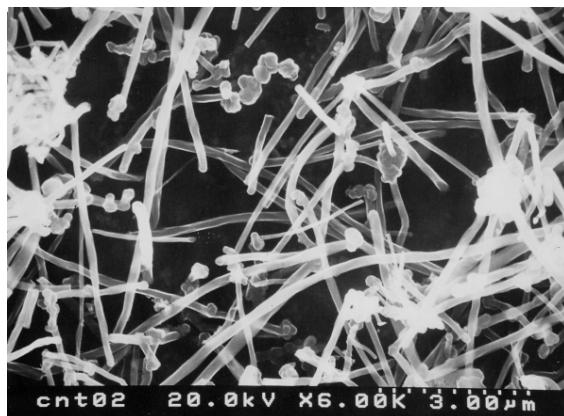

Fig. 2. Scanning microscopy of MWCNTs

(Fig.4(a)). In the case of the powders containing 5 % MWCNTs, aggregated MWCNTs were indicative of non-homogeneous distribution (Fig.4(b)). Next, the magnesium powders containing 0.5 to 5mass % MWCNTs were hot-pressed in a molder to form precursor at 823 K for 5 hrs by applying a pressure of 25.5 MPa in a vacuum below 10 Pa. Then finally composites obtained in a form of rod (Fig.4(c)) (diameter = 6 mm, length = 120 mm) by extruding precursors at 723 K with an extrusion ratio of 9. There was no distinctive defect in appearance.

3.3 Chemical reaction between the alloy matrix and CNTs

It should be noted that the interfacial state between magnesium alloy matrix and CNTs because the formation of carbide (Al_2MgC_2) was reported when the temperature was above 773 K and the aluminum level in magnesium alloy compositions was above 0.6 % and below 19 % [25]. Therefore, TEM (JEOL, JEM-2100F) observations and EDS mappings for the samples, prepared by ion milling technique, were carried out. As shown in elemental mappings in Figure 5, magnesium alloys containing homogeneously distributed aluminum elements occupied around carbon elements. Also, it is confirmed that there are the absence of void (Fig.5(e)) and new phase (Fig.5(f)) between MWCNT and magnesium alloys. From the viewpoint of bonding nature for the samples, it is rational to say that magnesium alloys have high capability to move on the outer surface of MWCNTs, and they don't have chemical reactivity to form new products like carbides.

4. Mechanical properties of the composites

Mechanical properties such as Young's modulus, yield strength, tensile strength and fatigue elongation are usually the major attraction for the composite materials. Very small particles (less than 0.25 micron in diameter) finely distributed in the matrix impede movement of
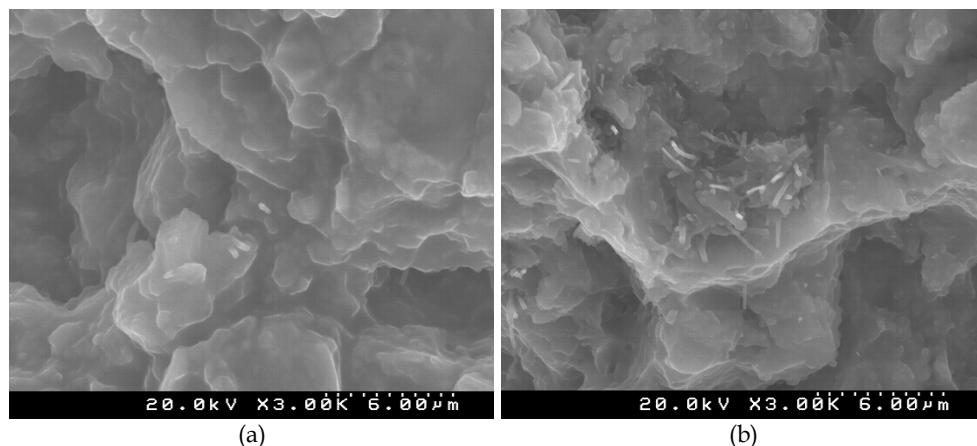
Fig. 3. Scanning microstructure of the tensile fracture surface observed on the composite specimens. (a)AZ91D-1mass%MWCNT, (b) AZ91D-5mass%MWCNT, in which the aggregation of MWCNTs was observed.

dislocations and deformation of the material. Such strengthening effect is similar to the precipitation hardening. In contrast to the precipitation hardening, which disappears at elevated temperatures when the precipitated particles dissolve in the matrix, dispersed phase of MWCNT and/or particulate composites (ceramic particles) is usually stable at high temperatures, so the strengthening effect is expected to be retained.

Remarkable studies on the mechanical properties of the composites reinforced with any of MWCNTs and other fillers are reviewed in Table 2.

Magnesium matrix composites investigated by S. F. Hassen *et al*. [29] and C. S. Goh *et al*. [18] are strengthened with fine particles or MWCNTs as well as magnesium alloy matrix composites. However, it is interesting phenomenon that the breaking elongation is also increased. It was explained that the MWCNT fillers act as an obstacle to prevent cleavage fracture and increase fracture energy.

Mechanical properties of the magnesium alloy composites are similarly improved by reinforcing fillers of MWCNTs or various ceramic materials, on the contrary to the magnesium matrix composite, the breaking elongation decreases due to the peculiar brittleness of reinforcing fillers. K. Osada *et al*. [31] developed the AZ91D alloy composite reinforced with 14.8 vol.% SiC particles reaching highest tensile strength of 485MPa, whereas breaking elongation decreased less than 1 %. T. Honma *et al*. [33] recently reported that the AZ91D alloy composite with 7.5 mass % MWCNTs improved its wettability by surface coating of Si was gained 470MPa in tensile strength and breaking elongation of 2%.

By the way, when the additive amount of MWCNT was increased too much, MWCNT could not be uniformly distributed and partially aggregated. The aggregation of MWCNTs act like a cave defect, consequently the performance of the Composite are degraded.

Technological development to improve the limit of an effective MWCNT additive amount is important. Recently, author *et al*. [34] fabricated new AZ91D alloy composite with simultaneous additions of 2mass%MWCNTs and 1mass% graphite particles by means of the

ball milling method. This new method resulted higher properties of 51GPa in elastic modulus, 464MPa in tensile strength, 420MPa in 0.2% proof stress and 4% in breaking elongation respectively. These results were explained by the Hall Petch effect related to crystal grain refining.
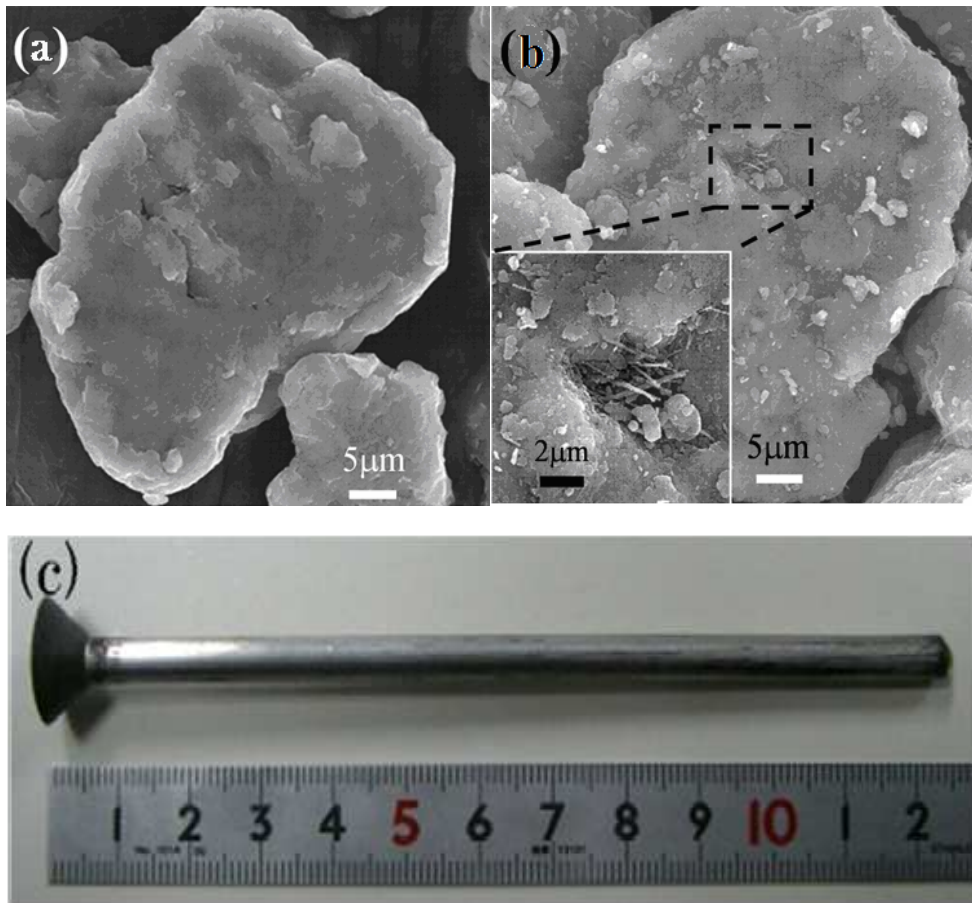

Fig. 4. SEM images (a, b) mechanically mixed magnesium powders containing 1 mass % and 5 mass % MWCNTs, respectively. Note that the aggregated MWCNTs were observed in magnesium powders containing 5 mass% of MWCNTs (inset is a magnified SEM image). (c) Photo of carbon nanotube-reinforced magnesium composite-based rod exhibiting clean appearance without any macro-morphological defects).

5. Application and problem of the composites

Promising developments are carried out, however, few applications using CNT reinforced magnesium and magnesium alloy matrix composite materials has been realized. Mechanical
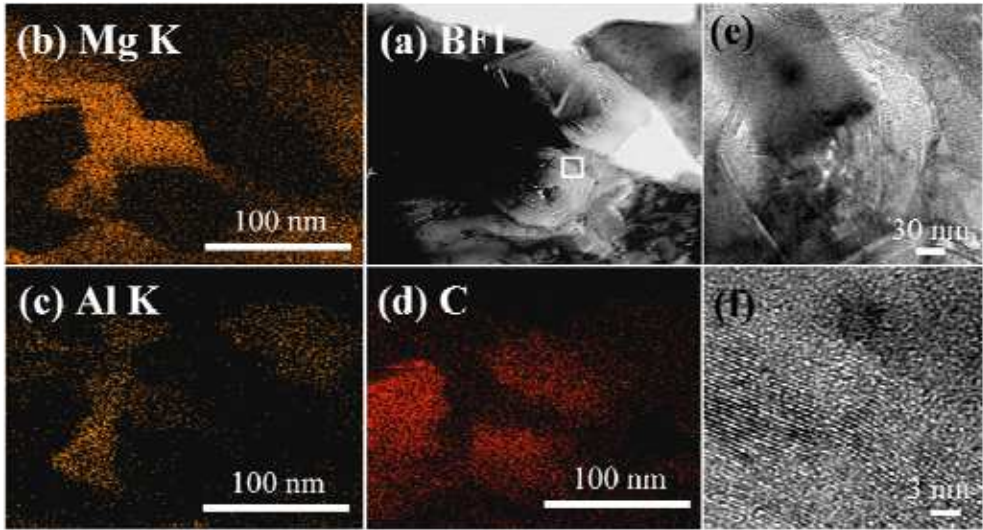
Fig. 5. TEM image of 1mass% MWCNT-reinforced AZ91D-type magnesium alloy composite; (a) bright field image, (b) elemental Mg mapping (in yellow) , (c) elemental Al mapping (in light yellow) , (d) elemental C mapping (in light red). TEM images showing the characteristic facetted cross sectional MWCNT (e) and linear lattices (f) contacted with magnesium alloy matrix, revealing that there was the absence of void and new phase between MWCNT and magnesium alloy matrix.
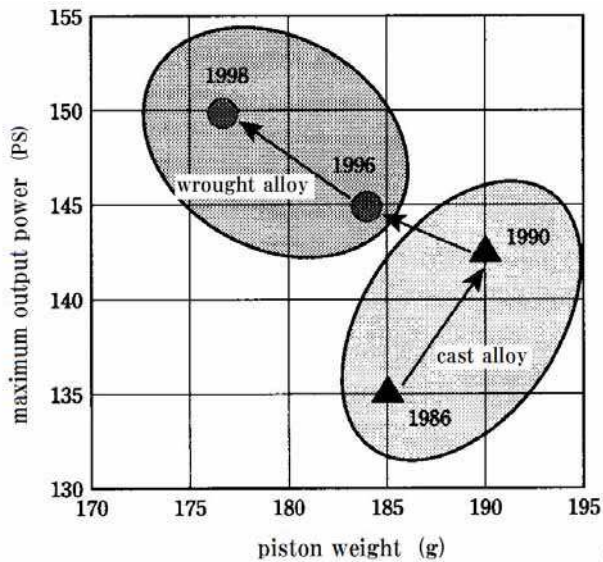

Fig. 6. Historical review of the relation between maximum output power and aluminum alloy piston weight for 1,000cm^3 engine[35)]

Composite system (mass%, vol%)	Fabrication Method (r:extrusion ratio)	Heat treatment	Elastic Modulus (GPa)	0.2%Proof Stress (MPa)	Tensile Strength (MPa)	Fracture Elongation (%)
Mg(≧98.59 mass%)[29]	Powder Metallurgy + Hot Extrusion (extrusion ratio: r=20.25)	None	41.2	132±7	193±2	4.2 ±0.1
Mg-2.5mass% Al_2O_3(p)[29]	Powder Metallurgy + Hot Extrusion (r=20.25)	None	44.5	194±5	250±3	6.9±1.0
Mg (99.9mass%)[18]	DMD* + Hot Extrusion (r=20.25)	None	—	126±7	192±5	8.0±1.6
Mg-1.3mass %MWCNT[18]	DMD* + Hot Extrusion (r=20.25)	None	—	140±2	210±4	13.5±2.7
AZ91A[30]	DMD* + Hot Extrusion (r=20.25)	T6	43±3	263±12	358±5	7± 4
AZ91A- 15.54%Cu(p)[30]	DMD* + Hot Extrusion (r=20.25)	T6	54±1	299±5	382±6	6±1
AD91D[31]	Melt Stiring + High Pressure casting + Hot Extrusion (r=54)	T6	—	240	370	12
AD91D- 14.8vol%SiC(p)[31]	Melt Stiring + High Pressure casting + Hot Extrusion (r=54)	T6	—	449	485	1
AZ91D- 11vol%Al_2O_3(f)[32]	Squeeze casting	T6	—	—	260	1
AZ91D[27]	Powder Metallurgy + Hot Extrusion (r=9)	T6	40±2	225±4	320±4	17±3
AD91D- 1.0%MWCNT[27]	Powder Metallurgy + Hot Extrusion (r=9)	T6	49±3	288±5	395±4	6±1
AD91D- 5.0%MWCNT[27]	Powder Metallurgy + Hot Extrusion (r=9)	T6	51±4	267±6	305±8	1.6±0.4
AZ91D[33]	Rheocastig + Hot Extrusion (r=25)	None	—	250	340	12
AD91D- 7.5mass%Si- MWCT[33]	Rheocastig + Hot Extrusion (r=25)	None	—	416	470	2
AD91D- 2mass%Graphite (P) + 1mass%MW CNT[34]	Powder Metallurgy + Hot Extrusion (r=9)	None	51	420	464	4

※ DMD: Disintegrated Melt Deposition Method

Table 2. Remarkable results on the mechanical properties of the magnesium and magnesium alloy matrix composites reinforced with any of MWCNTs and other fillers.

strength of magnesium alloy composites with MWCNTs is highly improved today and comparable to that of the generally utilized mild steel in automobiles. Fig.6 shows the historical review of the relation between maximum output power and aluminum alloy piston weight for 1,000cm^3 engine [35]. Although the magnesium alloy has not been applied, it is clearly suggests that the effort to reduce the piston weight is very effective to enhance the engine performance, therefore the magnesium alloy composite with MWCNTs will be increasingly promising material.

The lying problems on the magnesium and magnesium alloy matrix composites with CNTs should be overcome is not only to promote the performance advantages but also to develop the cost-effective processing technologies.

6. Acknowledgement

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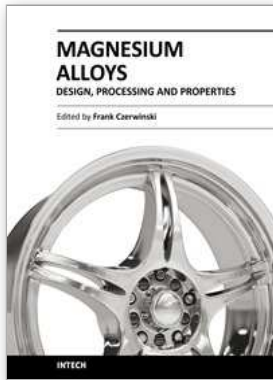
Magnesium Alloys - Design, Processing and Properties

Edited by Frank Czerwinski

Scientists and engineers for decades searched to utilize magnesium, known of its low density, for light-weighting in many industrial sectors. This book provides a broad review of recent global developments in theory and practice of modern magnesium alloys. It covers fundamental aspects of alloy strengthening, recrystallization, details of microstructure and a unique role of grain refinement. The theory is linked with elements of alloy design and specific properties, including fatigue and creep resistance. Also technologies of alloy formation and processing, such as sheet rolling, semi-solid forming, welding and joining are considered. An opportunity of creation the metal matrix composite based on magnesium matrix is described along with carbon nanotubes as an effective reinforcement. A mixture of science and technology makes this book very useful for professionals from academia and industry.

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