J Mater Sci (2007) 42:10040–10046
DOI 10.1007/s10853-007-2004-0

Development and characterization of magnesium composites containing nano-sized silicon carbide and carbon nanotubes as hybrid reinforcements

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Received: 30 March 2007 / Accepted: 17 July 2007 / Published online: 21 August 2007

Abstract Magnesium based hybrid composites containing nano-sized silicon carbide and carbon nanotubes reinforcements with minimal porosity were successfully fabricated using powder metallurgy technique with microwave sintering and hot extrusion. It was found that the addition of nano-sized silicon carbide and carbon nanotubes reinforcements lowered the coefficient of thermal expansion of magnesium. Moreover, increasing presence of silicon carbide particles led to a progressive reduction in coefficient of thermal expansion for a constant overall amount of reinforcements indicating that carbon nanotubes lowered the coefficient of thermal expansion to a lesser extent when compared to silicon carbide. Micro-hardness, 0.2% YS and UTS (except for Mg+1%CNT) showed improvement, while failure strain decreased when nano-sized silicon carbide and carbon nanotubes were added to magnesium. The failure mode of magnesium and magnesium composites was predominantly brittle exhibiting the presence of cleavage steps.

Introduction

Extensive research and rapid development of metal matrix composites (MMCs) in recent years have been fuelled by the demand of superior performance materials to meet the needs of scientific and technological advances. MMCs are combination of matrix materials which are metal based and reinforcements which are normally ceramic based. Many metallic matrices have been tried so far, however, aluminum, titanium and magnesium are the most widely studied due to their superior strength to weight ratio amongst all the structural metals [1]. Amongst these metals, magnesium has found quickly its niche in the base material family of MMCs due to lowest density (1.74 g/cm^3). Moreover, magnesium has been found to have superior damping resistance, EMI shielding and machinability characteristics [1]. However, due to limited formability, corrosion resistance and modulus of magnesium, its application in wider engineering areas has been restricted. In recent years, corrosion resistance of magnesium based materials has been overcome by development of proper coatings and new alloy developments whereas formability has been improved by addition of lithium to magnesium [2]. Improvement in mechanical properties of magnesium has been attempted by reinforcing magnesium by ceramics, e.g. alumina, silicon carbides, etc. in particle and fiber forms. So far, much of the developments have taken place by using singular reinforcements such as silicon carbide and carbon nanotubes (CNT) [3–6]. Results of literature search reveal that not many studies [7, 8] have been carried out where combination of nano-sized ceramic particles and carbon nanotubes were added as hybrid reinforcements and their effect on thermal and mechanical properties of magnesium were studied.

Processing of MMCs is a measure hurdle in popularizing the use of MMCs in cost effective way to obtain quality products for applications in industries such as automobiles, aerospace and electronics. Many techniques have been tried before such as liquid state route (melt infiltration

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technique) [9] and solid state route (powder metallurgy route) [10] to name a few. Powder metallurgy route looks more practical industrially, provided powder of the raw materials can be available at cheaper cost and in good quality as raw materials affect the final properties of the product. Powder metallurgy route can also be a more productive route if sintering can be faster, cheaper, cleaner and less prone to porosity and defects in the final product. Several techniques have been tried before for making MMCs through powder metallurgy route, however, microwave sintering [11] has proved to be a process fulfilling all the above mentioned conditions of lower cost, lower cycle time and environmental friendly process.

Accordingly, the primary aim of this study was to synthesize magnesium based composites with hybrid silicon carbide and carbon nanotubes reinforcements in nano length scale using a new rapid two-dimensional microwave sintering methodology. Particular emphasis has been placed on investigating the effects of relative proportions of the reinforcements on the physical, microstructural and mechanical characteristics of the magnesium.

Experimental details

Materials

Pure magnesium powder (98.5% purity and 60–300 μm size range) obtained from Merck KGAa, Germany, was used as the matrix material. Silicon carbide powder was used as one of the reinforcements with average particle size of 50 nm. Another reinforcement used was multi-wall carbon nanotubes with greater than 95% purity and outer diameter in the range of 40–70 nm. Both the reinforcements were obtained from Nanostructured and Amorphous Materials, Inc., USA.

Processing

The processing technology adopted in the present study is powder metallurgy with incorporation of microwave sintering, followed by hot extrusion. The details of the primary and secondary processing are described in the following sections.

Primary processing

The monolithic magnesium and magnesium based composites were synthesized by using powder metallurgy technique according to the following procedure. Pure magnesium, nano-sized silicon carbide and carbon nanotube, all available in the form of powder, were carefully weighed to the specified weight percentage of each composition as presented in Table 1. Handling of powders was done in a glove box to minimize the exposure to moisture and contamination which would be detrimental to the mechanical properties of the composites [12]. The weighed powders were then blended in a RETSCH PM-400 high speed planetary ball mill at 200 rpm for 1 h. After blending, the powders were inspected to ensure that there was no visible clustering which would lead to inhomogeneous distribution of the reinforcements in the matrix. The blended mixture was further compacted under a pressure of 50 tons to fabricate billets of 35 mm diameter and 40 mm height. After compaction, the green compact was checked to ensure that the surface was free of cracks or scales. Thereafter, each billet was placed in a graphite crucible, surrounded by silicon carbide powder as susceptor and fiberfax as insulation as shown in Fig. 1. Subsequently, each billet was placed in a 900 W, 2.45 GHz frequency microwave oven and sintered at a temperature of 640 °C without any soaking time. Once the temperature was reached (25 min), microwave was switched off and the whole assembly was cooled to room temperature under normal conditions. Prior to the sintering stage, the microwave oven was calibrated by using the dummy block of the same material as a function of time to ensure that the desired temperature could be achieved. The calibration chart was used to decide the time that would be needed for the compact to reach the sintering temperature. The higher sintering temperature was chosen

Table 1 Formulation of the materials investigated in the present study

Material	Matrix		Reinforcement 1		Reinforcement 2	
	Mg (60–300 μm)		CNT (40–70 nm)		SiC (50 nm)	
	wt.%	vol.%	wt.%	vol.%	wt.%	vol.%
Mg	100.0	100.0	–	–	–	–
Mg+0.3%CNT+0.7%SiC	99.0	99.3	0.3	0.3	0.7	0.4
Mg+0.5%CNT+0.5%SiC	99.0	99.2	0.5	0.5	0.5	0.3
Mg+0.7%CNT+0.3%SiC	99.0	99.1	0.7	0.7	0.3	0.2
Mg+1%CNT	99.0	99.1	1.0	0.9	–	–

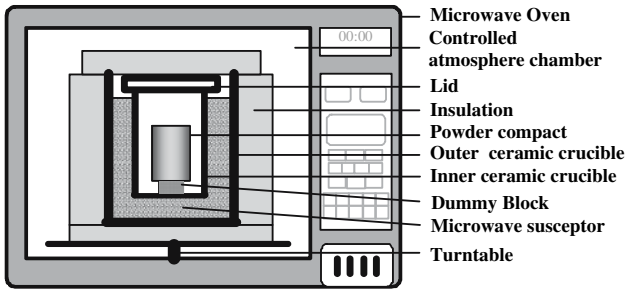

Fig. 1 Schematic diagram of the experimental set up

to improve sintering kinetics and to effectively minimize sintering time [13]. It may be noted that at higher sintering temperature, diffusion, which is a time and temperature dependent phenomenon, would be more, thus the holding time can be completely eliminated [11]. The unique experimental set up shown in Fig. 1 used silicon carbide as susceptor to provide microwave coupled heating in addition to the direct microwave heating of the compacted billet. The two-directional heating enables rapid sintering and provides overall superior microstructural characteristics and improved properties [11].

Secondary processing

The sintered compacts were soaked in a resistance furnace at a temperature of 400 °C for an hour and hot extruded. Hot extrusion was carried out at 350 °C by using a 150 ton hydraulic press with an extrusion ratio of 25:1 to obtain rods of 7 mm diameter. Colloidal graphite was used as lubricant for hot-extrusion.

Specimen preparation

Representative transverse sections about 10 mm in length were obtained from the rods using a precision diamond cutting machine. The composite samples were further mirror-polished by using conventional metallographic techniques and ultrasonically cleaned in ethanol for subsequent tests.

Density and porosity measurement

Density measurements were performed on polished samples by using an electronic balance (AND HF-3000D) to weigh the samples in air and in distilled water. The density measurements were carried out in accordance with Archimedes' principle. The porosity of the samples was calculated from theoretical density obtained from the rule of mixture and experimental density.

Thermo-mechanical analysis

The thermo-mechanical analysis was carried out to measure the coefficient of thermal expansion (CTE) of the composites. The samples were polished to remove any surface contamination, especially, carbon deposits inherited from extrusion. The CTE of the polished samples was determined by using an automated SETARAM 92-16/18 thermo-mechanical analyzer. The tests were carried out in accordance to ASTM E831-00. The samples were machined to an approximate length of 10 mm and were polished to 10 micron surface finish by using the Amet polishing alumina to provide a clean and flat surface. The displacement of the specimens as a function of temperature (in the range of 50–400 °C) was measured by using a 5 mm spherical ended alumina probe, under an argon atmosphere and the data was subsequently processed to determine the average CTE of the composites. The temperature was measured by a K-type, co-axial thermocouple and the heating rate was maintained at 5 °C/min. The experimental values of the CTE were correlated with rule-of-mixture (ROM) model, Turner model and Kerner model [14, 15].

Microstructural characterization

The grain size and morphology were determined by using the technique of image analysis performed on images captured from polished and etched samples using Olympus BH2-UMA microscope. The samples were metallurgically polished up to 0.05 micron finish and etched by using acetic glycol (1.0 mL nitric acid, 19.0 mL distilled water, 2.0 mL acetic acid and 60 mL ethylene glycol) to reveal grain boundaries. Scion Image Analyzer software was used in the present study. The distribution of the reinforcements was determined by using Hitachi S4100 Field Emission Scanning Electron Microscope (FESEM).

Micro-hardness measurement

The micro-hardness tests were carried out by using an automated digital micro-hardness tester (Matsuzawa MXT50). The measurements were made by using: (1) a pyramidal diamond indenter with a facing angle of 136°, (2) 25 gf indentation load and (3) a load dwell time of 20 s. Testing was performed in accordance with ASTM standards E384-99.

Tensile testing

Tensile tests were carried out to obtain ultimate tensile strength (UTS), 0.2% yield strength and failure strain of the monolithic magnesium and composite samples. To carry out tensile tests, the extruded rods were machined by using the Okuma CNC lathe machine to produce cylindrical specimens of diameter 5 mm and gauge length 25 mm. Tensile tests to failure were performed on the machined specimens at room temperature by using MTS Servo-hydraulic Testing Machine (Model 810), in accordance with ASTM standard E8M-01 at a strain rate of 0.254 mm/min.

Fractography

Fracture surface characterization was carried out on the tensile fractured samples to provide an insight into the fracture mechanisms operative during tensile loading of the samples. The fractography was carried out by using JEOL JSM-5600LV scanning electron microscope (SEM).

Results and discussion

Processing, density and porosity measurements

The fabrication of monolithic magnesium and magnesium based hybrid composites was carried out successfully by using powder metallurgy technique with microwave sintering, followed by hot extrusion. The extruded rods were inspected and found to have minimal surface defects that show that the blending, compaction, sintering and hot-extrusion parameters were adequate and optimal for the magnesium and composite samples. No oxidation was observed and XRD results also revealed the absence of oxides in Mg-based systems (monolithic and composites). The experimental density determined by the Archimedes' principle was closer to the theoretically calculated density, with low standard deviation (see Table 2). This indicates that the final product after processing had uniform distribution of reinforcements as the three representative samples were taken from different locations of the extruded rod. However, the experimental density was lower than the theoretically calculated density due to the presence of porosity.

The porosity values measured for all the samples were found to be very low (Table 2). This can be attributed to the judicious selection of processing parameters for the microwave sintering and extrusion process. Magnesium composites showed slightly higher porosity values and this can be attributed to the presence of reinforcement [16]. Considering standard deviation, the difference in porosity between monolithic and composite samples can be considered statistically insignificant.

Thermo-mechanical analysis

The experimental CTE results shown in Table 3, indicates that the addition of silicon carbide and carbon nanotube reinforcements lowered the CTE value of the magnesium matrix. The decreased CTE of the composites can be attributed to much lower CTE of the dispersed nano-particles. Silicon carbide reinforcement appears to have the greatest effect in lowering the CTE values of magnesium composites, as denoted by the lowest experimental CTE

Table 2 Results of density and porosity measurements

Material	Theoretical density (g/cm^3)	Experimental density (g/cm^3)	Porosity (%)
Mg	1.74	1.737 ± 0.002	0.17 ± 0.11
Mg+0.3%CNT+0.7%SiC	1.746	1.742 ± 0.003	0.23 ± 0.15
Mg+0.5%CNT+0.5%SiC	1.744	1.740 ± 0.001	0.24 ± 0.04
Mg+0.7%CNT+0.3%SiC	1.743	1.739 ± 0.002	0.23 ± 0.09
Mg+1%CNT	1.741	1.736 ± 0.002	0.29 ± 0.10

Table 3 Results of CTE determination and image analysis

Material	Average CTE ($\times 10^{-6}$/°C)	Grain size (μm)	Aspect ratio	Roundness
Mg	29.04 ± 1.05	25.9 ± 4.0	1.5 ± 0.2	1.5 ± 0.4
Mg+0.3%CNT+0.7%SiC	28.03 ± 0.38	21.8 ± 1.4	1.5 ± 0.1	1.4 ± 0.3
Mg+0.5%CNT+0.5%SiC	28.13 ± 0.53	21.9 ± 1.3	1.4 ± 0.2	1.4 ± 0.3
Mg+0.7%CNT+0.3%SiC	28.25 ± 0.63	22.1 ± 2.7	1.5 ± 0.2	1.5 ± 0.4
Mg+1%CNT	28.67 ± 0.29	22.3 ± 2.0	1.5 ± 0.3	1.6 ± 0.5

value of Mg+0.3%CNT+0.7%SiC as 28.03×10^{-6}/°C, when compared to the experimental CTE value of monolithic Mg as 29.04×10^{-6}/°C. Hybrid composites with increasing amounts of CNT showed a general increase in the absolute CTE values that could be due to poorer CNT/Mg bonding [17]. It was found that the CTE value obtained experimentally for Mg+1%CNT was the highest among composites. The results suggest the superior ability of SiC nano-particles to constrain the matrix expansion when compared to CNT.

Microstructural characterization

Analysis of the grain morphology as shown in Table 3, revealed that the magnesium matrix grain structure was predominantly equiaxed and this can be attributed to the recrystallization of grains during hot-extrusion [18]. The equiaxed grain structure indicates that the extrusion temperature was sufficient to allow the recrystallization of strain-free grains. Addition of CNT and nano-sized SiC reinforcements caused marginal grain size reduction of the Mg matrix. Within composite samples the difference in grain size was statistically insignificant. The results revealed inability of singular and hybrid reinforcements to affect the grain size and shape within 1 wt.% range.

The microstructural features of Mg based composites at high magnification are shown in Fig. 2(a) and (b). The nano-sized reinforcements were found to be uniformly distributed within matrix for all the composites. This indicates that the processing parameters for blending and extrusion are capable of producing composites of homogeneous distribution of reinforcements in magnesium matrix. The uniform distribution of reinforcements is critical for obtaining good mechanical properties of the composites. The quality of interfacial integrity could not be determined due to limitations of the FESEM.

Micro-hardness characterization

Table 4 shows the results of micro-hardness measurements. Monolithic Mg displayed the lowest micro-hardness value when compared to composite samples. Mg+0.3%CNT+0.7%SiC showed the highest micro-hardness value and there was a trend of decreasing micro-hardness with a decrease in amount of SiC. The increase in the micro-hardness of reinforced Mg can be attributed to the presence of harder SiC and CNT particles; as well as to a higher constraint to the localized matrix deformation during indentation due to the restraining effect of the reinforcements. This effect was insignificant for CNT due to its poorer interfacial adhesion with Mg [17].

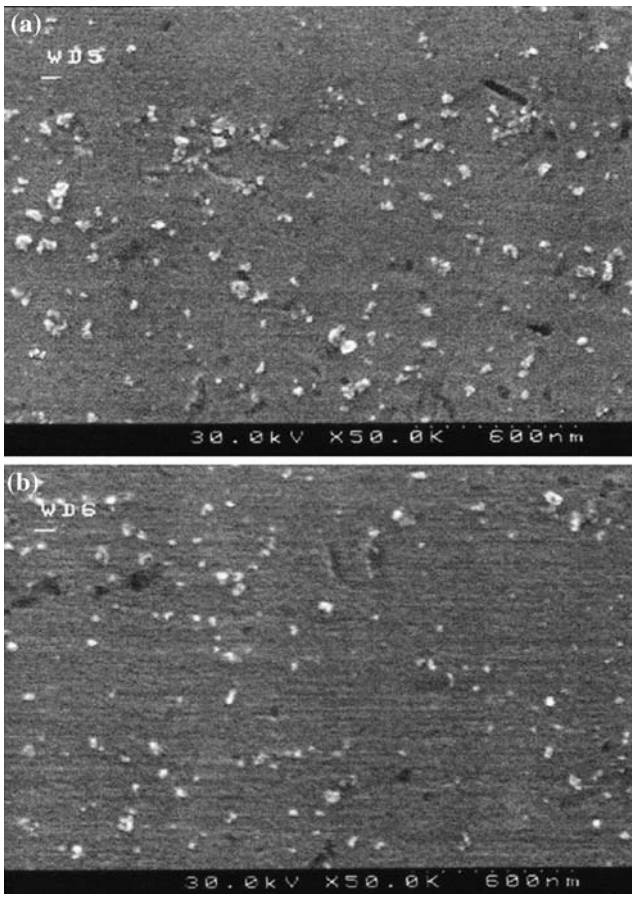

Fig. 2 Representative micrograph showing distribution of nano-sized reinforcements in (**a**) Mg+0.5%CNT+0.5%SiC and (**b**) Mg+0.7% CNT+0.3%SiC

Table 4 Results of micro-hardness and tensile properties

Materials	Micro-hardness (HV)	0.2% YS (MPa)	UTS (MPa)	Failure strain (%)
Mg	41 ± 1	111.9 ± 7.7	155.8 ± 2.1	5.9 ± 1.2
Mg+0.3%CNT+0.7%SiC	46 ± 1	152.9 ± 4.1	195.4 ± 4.7	3.3 ± 0.7
Mg+0.5%CNT+0.5%SiC	45 ± 1	152.1 ± 1.2	188.5 ± 2.7	2.3 ± 0.6
Mg+0.7%CNT+0.3%SiC	44 ± 1	139.5 ± 6.5	182.9 ± 7.5	2.1 ± 0.5
Mg+1%CNT	43 ± 1	117 ± 6.2	153.8 ± 2.8	1.5 ± 0.3

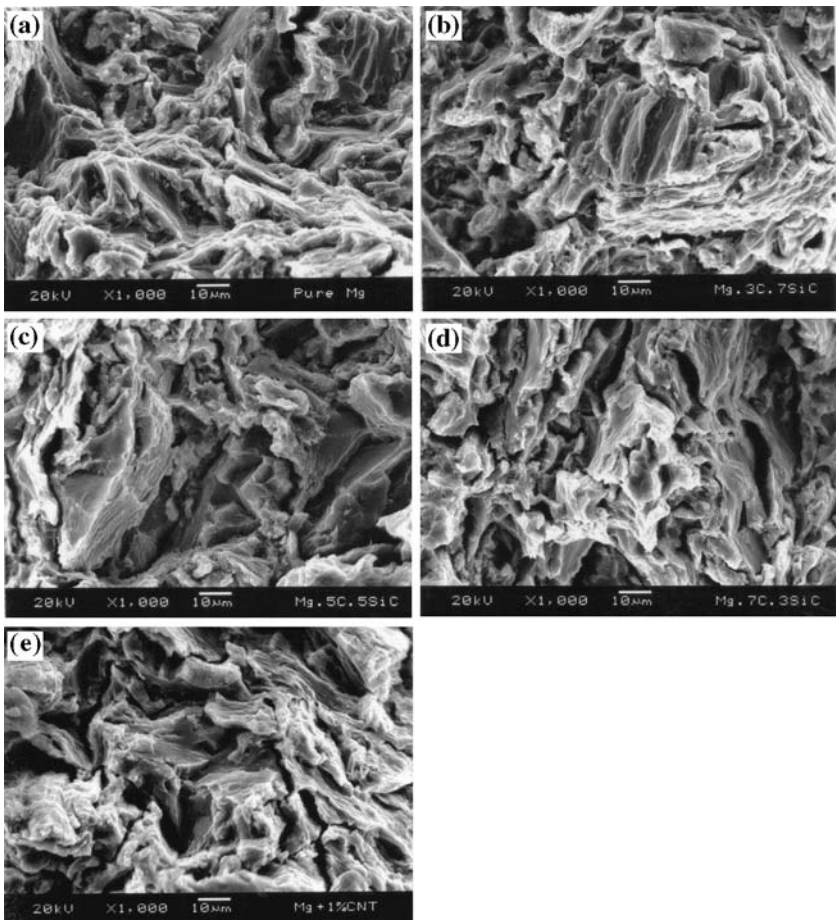

Fig. 3 Representative micrograph showing brittle cleavage in (**a**) monolithic Mg, (**b**) Mg+0.3%CNT+0.7%SiC, (**c**) Mg+0.5%CNT+0.5%SiC, (**d**) Mg+0.7%CNT+0.3%SiC and (**e**) Mg+1%CNT

Tensile tests

The results of the tensile properties of the magnesium based composites are presented in Table 4. It is clear that 0.2% YS and UTS significantly increase with increase in SiC particles in Mg matrix. The largest increase for 0.2%YS and UTS has been observed when 0.3%CNT+0.7%SiC was added to the matrix. The increase in strength can be attributed to the following:

(a) The presence of uniformly distributed (as can be seen in the micrographs of Fig. 2) hard and fine reinforcements which strengthen the material by pinning the dislocation motion in matrix.
(b) The strain mismatch between the matrix and the reinforcement which lead to a high density of dislocation in matrix around the reinforcements. The strain mismatch could have resulted from large disparity in CTE values of the reinforcements and the Mg matrix [15]. Under applied stress, the high dislocation density requires higher initial stress to operate the dislocations [19].
(c) Good bonding between the reinforcements (especially SiC) and the matrix that resulted in efficient load transfer of the applied stress from the soft matrix to the harder reinforcements.
(d) Marginal grain refinement of the Mg matrix as shown in Table 3 that increases the number of grain boundaries present to act as barriers to dislocation motion. Earlier study has shown that magnesium strength is highly sensitive to its grain size [12].

Addition of CNT did not seem to improve 0.2% YS and UTS of the Mg composites as shown by the values obtained for Mg+1%CNT, which are similar to those obtained for monolithic Mg and is in agreement with previous study [5]. This can be attributed to the poor interfacial adhesion [17] between Mg and CNT to facilitate effective stress transfer to the reinforcement, thus no strengthening was achieved.

From Table 4, it is also clear that the failure strain reduced with addition of reinforcements. Reinforcement particles serve as crack nucleation sites, leading to reduction in ductility under the action of uni-axial tensile load [20, 21]. This is consistent with previous works in which addition of reinforcing particles caused the tensile elongation to decrease [22]. The lowest reduction in failure strain is exhibited by Mg+0.3%CNT+0.7%SiC which has a

failure strain half of that of unreinforced Mg. Table 4 shows that decrease in amount of SiC and increase in amount of CNT cause a significant reduction in failure strain. This decrease in failure strain could have been caused by poor interfacial integrity between Mg and CNT. Further work is continuing in this area.

Fracture behavior

The tensile fractured surfaces of monolithic Mg and composite samples are shown in Fig. 3(a–e). The results of fracture surface analysis revealed a typical brittle fracture for monolithic Mg and its composites. This can be attributed to the hexagonal close-packed crystal structure of magnesium that restricts the slip to the basal plane. The presence of small steps and microscopically rough fracture surface indicates the inability of magnesium to cleave on any single plane consistent with the findings reported elsewhere [23]. The microscopic responses exhibited by Mg composites during tensile deformation could be due to particle cracking, interfacial debonding and matrix crystal structure. Due to limitations of the conventional SEM, presence of nano SiC and CNT particles could not be captured on the fractured surfaces.

Conclusions

1. Powder metallurgy technique with microwave sintering and hot extrusion can be successfully utilized to fabricate Mg based hybrid composites with uniform distribution of nano-sized SiC and CNT reinforcements with minimal porosity.
2. Addition of nano-sized SiC and CNT reinforcements lowered the CTE value of Mg. Increasing presence of SiC particles led to a progressive reduction in CTE value whilst CNT reinforcements lowered the CTE to a lesser extent as compared to SiC.
3. Micro-hardness shows an increase when nano-sized SiC and CNT reinforcements were added. 0.2% YS and UTS showed improvement, while failure strain decreased when nano-sized SiC and CNT were added to Mg. The failure mode of Mg and Mg composites was brittle fracture as evidenced by the presence of cleavage steps.

Acknowledgements The authors acknowledge the help rendered by Adlin Idris, NUS and Delphi Automotive Systems (Singapore) Pte Ltd. for carrying out the present work.

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