

EFFECT OF MAGNESIUM SURFACTANT ON WETTABILITY OF CARBON NANOTUBE IN A356 ALLOY COMPOSITE

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ABSTRACT: MWCNT-A356 alloy composite is a promising material for automotive applications owing to its excellent casting fluidity, good mechanical properties, high corrosion resistance and low density. However, wettability problem between the reinforced particles and alloy matrix is the major concerns. Poor wetting also caused inhomogeneity dispersion of the particles in the matrix. The present study investigated the effects of additional pure magnesium surfactant into the liquid state processing method on the mechanical properties of the composite. A thixoforming and short T6 heat treatment have also been applied to the composite. The composites were characterized using optical microscopy, field emission secondary electron microscopy and mechanical testing. As results, the weight fraction of 0.5 wt% of Mg, added into the 0.5 wt% MWCNT-A356 alloy composite improves the hardness, yield strength, and ultimate tensile strength by 1.4%, 9.2% and 4.0%, respectively. Some agglomeration of MWCNT was also detected in the 1.0 wt% MWCNT-A356 alloy composite. Evidences of bridging and pull-out structures of MWCNT were clearly observed indicating good wettability and load transfer strengthening mechanism. The results prove that the additional of small weight fraction of magnesium into the alloy matrix has positive impact to the mechanical strength of the composite.

KEYWORDS: *Semisolid Metal Processing; Aluminum Alloy Composite; Wettability; Thixoforming; T6 Heat Treatment*

1.0 INTRODUCTION

A356 casting alloy is widely used in the automotive industry due to its excellent casting fluidity, good mechanical properties, high corrosion resistance and low density [1]. Recently, the interest in enhancing this alloy's properties has been increased tremendously. In fact, the development of carbon nanotube (CNT) reinforced aluminum alloy composite is one of the active studies explored by many researchers [2]. The CNT has superior strength (~150 GPa) and Young's modulus (E) (~1TPa) is desirable to be imparted in the aluminum alloy matrix [3-4]. In addition, a multiwalled carbon nanotube (MWCNT) consists of several layers of graphene sheet, exhibits the high strength and E values of 63 GPa and 1.8 TPa, respectively [5].

However, many factors need to be considered in the production of the MWCNT-A356 alloy composite by the liquid casting route. One of the major issues in producing the cast aluminum matrix composites is a wettability problem between the reinforced particles and matrix. Wettability is the ability of the metal liquid to spread on a solid surface of the reinforcement [6]. Several considerations can be made in order to improve the wettability, for instances, by increasing the surface energy of the MWCNT, decreasing the surface energy of the liquid alloy matrix or the solid-liquid interfacial energy. An addition of alloying element such as magnesium (Mg), Zirconium (Zr), Titanium (Ti), Bismuth (Bi), Zinc (Zn), and Copper (Cu) into the matrix alloy during the processing stage acts as surfactant to promote the wetting.

In addition, the Mg is a powerful surfactant to remove the oxide layer from the surface of the matrix, which resulted in widely used in the liquid casting fabrication of the aluminum composite. According to Hashim et al. [7], magnesium has lower surface tension of 0.599 N/m than the aluminum silicon alloy matrix of 0.800 N/m. This will help to improve the wettability between the MWCNT reinforced particles in the matrix. Besides, Landry et al. [8] reported the formation of aluminum carbide Al₄C₃ at the interfacial regions will also help in enhancing the wettability of MWCNT. In addition, without the good wetting, to obtain an effective load transfer between the two materials is very difficult.

Another concern in liquid casting processing is the dispersion of the MWCNT in the matrix, because of the strong Van der Waals forces between the carbon atoms will pull them together and form clusters or agglomerates of the MWCNT. The homogeneous dispersion of the MWCNT in the alloy matrix is required for high mechanical properties of the alloy composite [9]. Therefore, on top of the wettability improvement, a mechanical stirring process is one of the many techniques being introduced during the liquid mixing of the composite. A vortex condition created in the liquid while stirring produces the convection forces that help to distribute the reinforced particles into the matrix [10].

Furthermore, a thixoforming and heat treatment processes can also be applied to the composite to further the strengthening the mechanical properties [11]. The thixoforming is a reheating process of a thixotropic as-cast composite billet up to certain solid-liquid fraction conditions and compacting into a near net-shape mold. Thus, it helps to reduce or eliminate some defects especially porosity [12]. The thixotropic billet with non-dendritic microstructures can be achieved through several methods, including the mechanical stirring process. On the other hand, the heat treatment of solution treatment, quenching and aging processes will help to further deformation of the α -Al and eutectic-Si, redistribute and stabilize the phases in the alloy matrix. As a result, the highest strength can be achieved and preventing a catastrophic failure of the composite.

Although many papers have been published in the fabrication of the alloy composite, little work on liquid state processing of MWCNT-aluminum alloy was carried out. So far, there are not enough analyzed data on the effect of surfactant to the mechanical properties enhancement of the composite. Moreover, it appears that there are less previous investigations which adopting the thixoforming and heat treatment processes in fabricating the aluminum alloy composite. In this work, the effects of surfactant Mg on the microstructures and mechanical properties of the composite were determined based on two sets of experimental setups. Further analysis of the influences of the thixoforming and a short T6 heat treatment process was also being discussed.

2.0 METHODOLOGY

In this study, MWCNT-A356 alloy composite was fabricated by a mechanical stirring prior to a liquid casting process. A commercially

available A356 aluminum alloy matrix as shown in Table 1, and an industrial-grade MWCNT (purity>88%, outside φ 20–40 nm, inside φ 5–10 nm and length 10–30 nm) as the reinforcement. A pure Mg in granule formed (φ 1 mm) was added to the mixture as wettability agent. Figure 1 shows the scanning electron microscopy (SEM) image of the as-received MWCNT.

Table 1: A356 alloy matrix composition by weight fraction (wt.%)

Al	Si	Cu	Mg	Mn	Zn	Ni	Fe	Pb	Ti
Bal. %	6.5	0.2	0.2	0.3	0.1	0.1	0.5	0.1	0.2

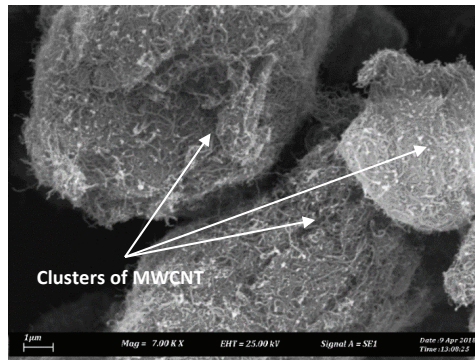


Figure 1: SEM image of as-received MWCNT

A 400 g of the alloy matrix was fully melted in an induction furnace at temperatures up to 700 °C. The liquid temperature was then reduced and maintained at 650 °C. The MWCNT powder and Mg according to weight fractions as shown in Table 2 were wrapped in an aluminum foil and placed inside a plunger. The wrapped was then injected into the liquid matrix at the bottom of the crucible and stirred mechanically at 500 rpm by using three-blade propeller for 10 minutes. The liquid composite was poured immediately into a mold to form the thixotropic feedstock billet.

Table 2: Experimental setup

MWCNT (wt.%)	Mg (wt.%)
0.5	0.25
0.5	0.50
1.0	0.25
1.0	0.50

Thixoforming process was carried out using the T30-80KHz machine as shown in Figure 2. The feedstock billet was placed on a pneumatic cylinder ram inside the induction coil and reheated up to 580°C of 50%

of solid-liquid fraction. Then, the billet was rammed into a top mold with a forging load (5 tons) and speed (1 m/s) and cool down at room temperature.

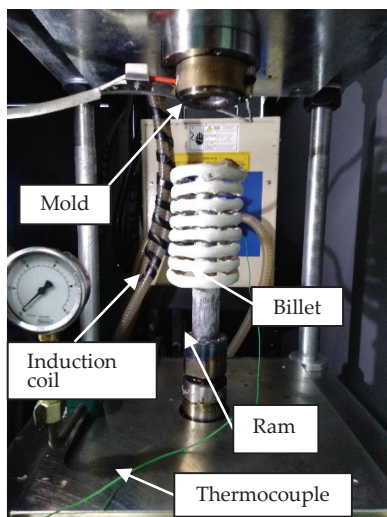


Figure 2: Schematic of the thixoforming machine [10]

A short T6 (ST6) heat treatment was applied to the samples in the Nabertherm 30°C-30000°C furnace according to the ST6 setting in Table 3. Previous studies in [13] have shown that the short solution treatment of 1 hour is sufficient to form a spheroid microstructure of silicon particle after 5 min and the highest hardness can be achieved after 20 min. In addition, since the samples have undergone the thixoforming process, the shorter treatment duration was believed to be sufficient.

Table 3: Short T6 (ST6) heat treatment

Solution Treatment	Quenching	Artificial Aging
540°C 1 hr	27°C (room temp)	180°C 2 hours

The characterizations of the alloy composite of the microstructures evolution and mechanical properties were determined. The samples were sectioned and prepared with standard metallographic procedures of grinding (400, 600, 800 and 1200 grits), polishing and etching with Keller’s solution. The microstructures and distribution of MWCNT were examined through optical microscopy (OM) and field emission secondary dispersive x-ray (FESEM/EDX) analyses using the Hitachi SU5000 machine. The hardness of the composite was tested using the Vickers Hardness Matsuzawa machine (load=1 kgf and dwell time=10 s), yield strength at 0.2% strain rate (YS) and ultimate tensile strength

(UTS) tests was performed using the Autograph Universal Testing machine. The samples for the tensile test were machined according to the ASTM E8M standard.

3.0 RESULTS AND DISCUSSION

3.1 Effects of Mg Amount on MWCNT Distribution

The FESEM morphologies of the MWCNT distribution in the tensile fracture surfaces of A356 alloy matrix for 0.5 wt% and 0.25 wt% Mg amounts are shown in Figure 3a and b, respectively. Based on the homogeneous dispersion of MWCNT in the void fracture surface (Figure 3a), the addition of Mg into the composite during the liquid casting process helps to break up the entanglement of the MWCNT. However, some agglomerations of MWCNT have also been observed (Figure 3b) in the 0.25 wt% of Mg. The agglomeration may cause some defects formation and decrease the tribology performance of the alloy composite [14]. Therefore, it appears that besides, the mechanical stirring and amount of MWCNT parameters, the right amount of wetting agent was also influential in improving the distribution of the MWCNT in the composite samples.

The reactive Mg helps to create a transient layer around the reinforcement particle and simultaneously decreases the surface tension of the matrix alloy [15]. Hence, this layer allows better dispensability of the particles throughout the matrix. According to Elshalakany et al. [16], without the addition of 0.75 wt% of Mg into A356 alloy matrix, some rejection of the MWCNT was observed during the mixing process. Rashad et al. [17] has added 0.5 wt% of pure Mg into the MWCNT-A356 alloy composite to improve the wettability between the materials. Therefore, the present of Mg in the composite during liquid processing not only improves the wettability between the reinforcement particles and enhance the distribution of MWCNT in the matrix [3, 18].

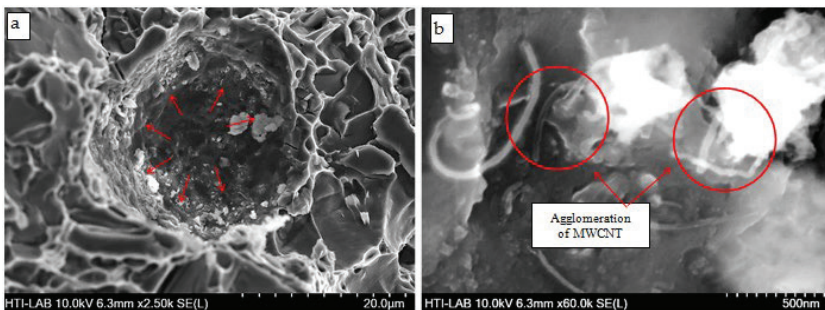


Figure 3: Distribution of MWCNT in the tensile fracture surface (a) 0.5 wt% Mg and (b) 0.25 wt% Mg

3.2 Effects of Mg on Wettability

The tensile fracture surfaces of MWCNT-A356 alloy composite produced by the method are demonstrated in Figure 4 (a and b), at two varied magnifications. The evidence of bridging of MWCNT structures (arrow marks) crossing the aluminum grains are clearly observed. Moreover, the pull-out structures of MWCNT (circle marks) within the cracks could also be visible in the FESEM fracture analysis. Previous studies have found similar conditions of bridging and pull-out MWCNT structures, indicating the wettability of MWCNT in the matrix [19-21]. The Mg is also believed to increase the surface contact area to assist the formation of aluminum carbide (Al_4C_3) between the grains matrix. This interfacial compound of Al_4C_3 is necessary for effective load transfer strengthening mechanism [22-23].

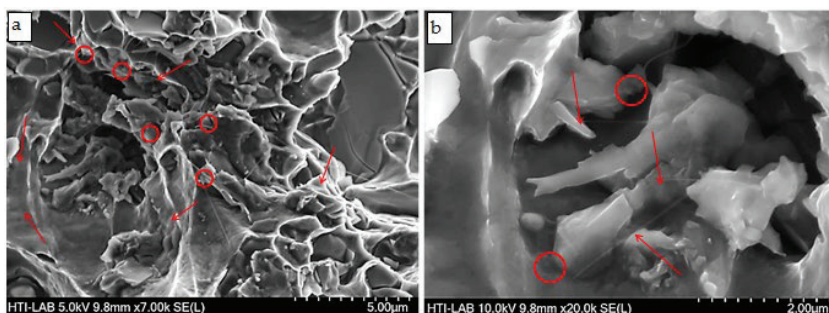


Figure 4: FESEM images of tensile fracture surfaces: (a) 5 μ m and (b) 2 μ m

3.3 Effects of Mg on Mechanical Properties of the Composite

Previous research has established that multiple strengthening mechanism, including grain refinement, load transfer, Orowan looping and thermal mismatch dislocations taken place in the alloy composite [23-24]. However, these mechanisms are largely dependent on the good dispersion of reinforcements and wettability in the matrix. Figure 5 indicates the hardness of the MWCNT-A356 alloy composites increased with increasing the Mg weight fraction. The hardness improved by 1.4% for 0.5 wt% MWCNT and 3.8% for 1.0 wt% MWCNT-A356 alloy composites, respectively when the additional of Mg has been increased from 0.25 wt% to 0.5 wt%.

A combination of strengthening of MWCNT and grain refinement of the matrix microstructure is the main attribution to the hardness of the alloy composite [25-26]. Similar observation also been made for the UTS data obtained from the experiment as shown in Figure 6. The yield

strength (YS) and UTS raised by 9.2% and 4.0% for 0.5 wt% MWCNT, respectively. Moreover, the yield strength (YS) and UTS increased by 2.9% and 5.9% for 1.0 wt% MWCNT, respectively for the MWCNT-A356 alloy composites when the Mg increased from 0.25 wt% to 0.5 wt%.

Another important finding is that 1.0 wt% MWCNT-A356 alloy composite has significantly lower values of hardness, YS and UTS as compared with the 0.5 wt% MWCNT. This was the result of more reinforced particles of MWCNT in the alloy matrix tend to promote more agglomeration and weaken the mechanical properties of the composites [27]. According to Chayong et al. [28], the commercial of A356 and A357 thixoformed alloys mechanical strength between 220-260 MPa. Therefore, the present of the correct amount of Mg as surfactant in the between the MWCNT and matrix is crucial in order to optimize the mechanical properties of the alloy composite.

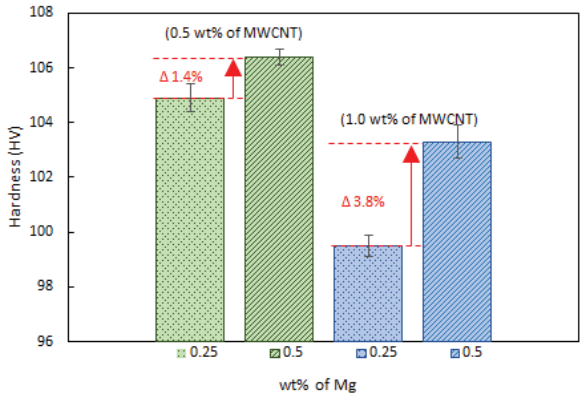


Figure 5: Effect of Mg different weight fractions on hardness

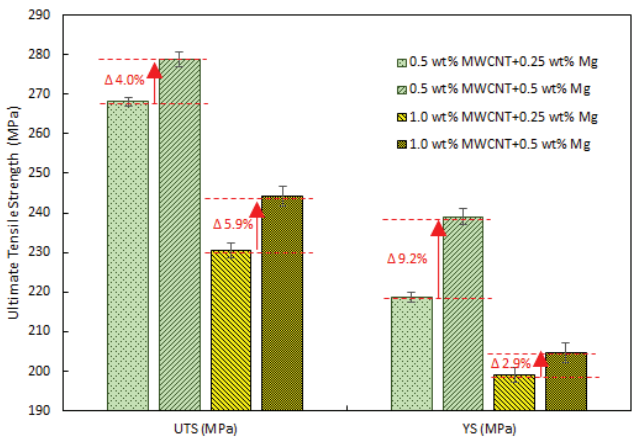


Figure 6: Effect of Mg different weight fractions on ultimate tensile strength

4.0 CONCLUSION

It can be concluded that the Mg surfactant has played the significant role in solving the wettability issue between MWCNT and A356 alloy matrix. Simultaneously, it also helps to enhance the distribution of the reinforced particles in the alloy matrix. The evidences for this improvement can be observed by the FESEM images of scattered and uniformed distributions and pull-out structures of MWCNT in the matrix. Furthermore, the mechanical properties of the hardness and ultimate tensile strength of the MWCNT-A356 alloy composite have also indicated the importance of the optimum amount of the surfactant in the composite to achieve the highest strength. By just doubling the amount of Mg into the composite from 0.25 wt% to 0.5 wt%, significant improvements by more than 1.4% and 5.1% to the hardness and UTS of the alloy composite. However, further investigation is needed to verify the behavior of the reinforced particles in the matrix under thixoforming and heat treatment process.

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