COMPRESSIVE DEFORMATION OF MWCNT POROUS PREFORM DURING INFILTRATION OF ALUMINUM OR MAGNESIUM ALLOY

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Abstract

Multi-walled carbon nanotube (MWCNT) has sperior high strength, high modulus and high thermal conductivity. The contact angle between MWCNT and molten metal is necessary to estimate the threshold pressure to infiltration. In this study, at first, wettability of the basal plane of graphite by molten aluminum or magnesium was measured using sessile drop method. As the result, the contact angle molten aluminum or magnesium was 127° or 120° respectively. Secondary, wettability of the MWCNT preform by molten aluminum or magnesium was measured. The both molten droplets bounced and rolled on the MWCNT preforms. By means of average values of droplet height, equatorial diameter and interfacial diameter, the contact angle was estimated. As a result, the contact angle between the MWCNT preform and molten aluminum or magnesium was 174° or 165° respectively. By using Cassie's rule of mixture, it was calculated that contact angle between MWCNT and molten aluminum or magnesium was 168° or 150° respectively. Moreover, trial fabrication of MWCNT reinforced aluminum or magnesium alloys composites was carried out by squeeze casting. As the result, these composites were obtained without non-infiltration.

1 Introduction

Since the first observation by Iijima [1], multi-walled carbon nanotube (MWCNT) has been a focus of considerable research. MWCNT has superior high strength, modulus and thermal conductivity than carbon fiber [2]. Therefore, they can be used as potential reinforcement for composites. Aluminum and magnesium alloys are attractive due to their lightweight. MWCNT reinforced aluminum or magnesium composites were expected to have superior high temperature strength and high thermal conductivity.

Squeeze casting method is often used as the composites fabrication method [3-4]. In fabrication process of composites, threshold pressure is necessary to infiltrate molten alloys into the preform. However, the threshold pressure often causes the preform deformation [4]. The threshold pressure is expressed by fiber volume fraction, fiber diameter, surface tension of molten metal and contact angle between fiber and molten metal [5]. Namely, the threshold pressure depends on wettability between fiber and molten metal. However, wettability between MWCNT and molten aluminum or magnesium has not been clarified. MWCNT can be imaged as some sheets of graphene rolled up to form seamless cylinder. Namely, the surface of MWCNT is covered with the basal plane of the graphite.

Previously, the contact angle between molten aluminum and graphite has been studied [6-9]. On the other hand, in the case of magnesium, the contact angle on graphite has been poorly investigated [10-11]. Furthermore, as to a particular plane of graphite, the basal plane, no attention has been paid to the contact angle of molten aluminum or magnesium.

In this study, wettability of the basal plane of graphite by molten aluminum or magnesium was examined. Secondary, the wettability of MWCNT preform (a porous body which consists of MWCNT and graphitized binder) by molten aluminum or magnesium was measured.

After measurement of the contact angle between MWCNT and molten aluminum or magnesium, trial fabrication of MWCNT reinforced aluminum or magnesium composites was carried out by squeeze casting. These kinds of composites fabricated by squeeze casting have not been reported. The diameter of MWNCT (20-70 nm) is hundreds of times smaller than that of carbon fiber (about 10 μm). Therefore, the threshold pressure to infiltration into MWCNT preform would be hundreds of times larger than that into carbon fiber preform. This would cause the difficulty in infiltration into the preform.

Moreover, by the measured contact angle between MWCNT and molten aluminum or magnesium, the threshold pressure was estimated. On the other hand, the applied pressure to the preform was calculated by compressive deformation ratio of the obtained composite. After that, the applied pressure to the preform was compared with the estimated threshold pressure.

2 Experimental procedures

2.1 Materials

As specimens for sessile drop, 99.99 mass% pure aluminum and 99.98 mass% pure magnesium were used. The surface of graphite substrate (Pfizer Inc) was the basal plane as confirmed in Fig. 1. The substrate has dimensions of 20 mm × 20 mm × 4 mm. The graphite substrate were rubbed using 0.04 μm diamond paste. In order to remove dust on the substrates, ultrasonic cleaning was conducted in ethanol and acetone. In order to measure contact angle between MWCNT and molten aluminum or magnesium, MWCNT preform was fabricated. Because it was impossible to measure the contact angle between MWCNT and molten aluminum or magnesium directly. The MWCNT was fabricated by Nano carbon technologies Co., Ltd.. Fig. 2 and Table 1 show SEM image of MWCNT microstructure and structural properties respectively [12]. After MWCNT was mixed with an organic binder, the preform was sintered at 2773K for 20 min. in Ar atmosphere. The fiber volume fraction of the preform was 25%

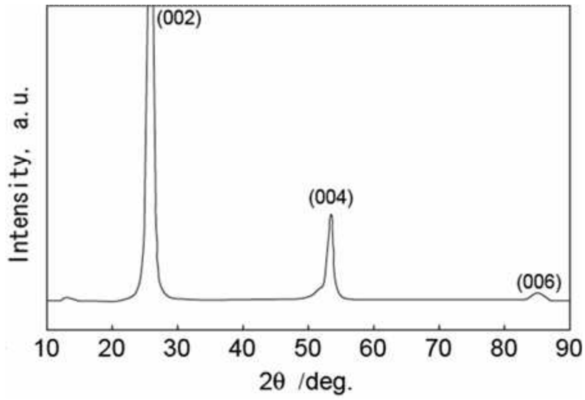

Fig. 1 X-ray diffraction of the graphite substrate

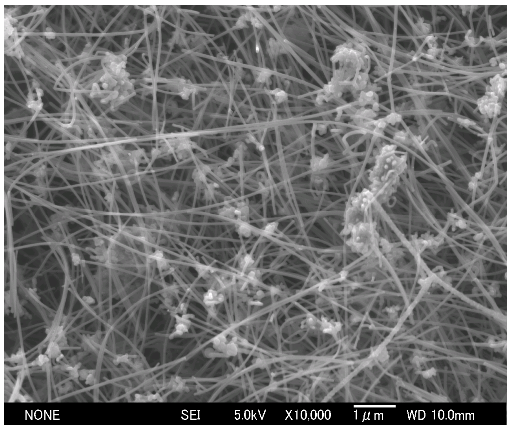

Fig. 2 Microstructure of MWCNT

Table 1 Structural properties of the MWCNT

Diameter [nm]	20 - 70
Length [μm]	1 - 20
Density [g/cm^3]	1.89
Aspect ratio	> 100

2.2 Wettability measurement by sessile drop method

Fig. 3 shows sessile drop device [13-14]. The system was composed of a sealed chamber, a bottle of Ar + 3 vol. % H_2 inert gas, a set of vacuum pumps, dropping tube and a CCD video camera or a high speed video camera. The level of substrate was confirmed by using steel ball after the substrate was set on a stand under dropping tube. The dropping tube has φ1.0 mm aperture at the bottom to drop molten metal. The chamber was evacuated to 1.3 × 10^{-3} Pa and heated at 1189 K. Ar + 3 vol. % H_2 inert gas was introduced at the rate of 1.67 × 10^{-5} m^3/s up to 1.0 × 10^5 Pa. The specimen was moved to the bottom of dropping tube. After 180 s, the chamber was evacuated. Molten aluminum or magnesium was dropped by pressure difference between chamber and dropping tube. The droplet was observed with a CCD camera or a high speed video camera for 1 ks after dropping or until the droplet was not observed. The surface tension (γ_{LV}) and the contact angle were estimated by using table of Bashforth and Adams [15]. The table of Bashforth and Adams is numerical solution of Young-Laplace equation. When θ was less than 90º, the contact angles were measured directly by the CCD camera images because the contact angle defined by the table had a large margin of error.

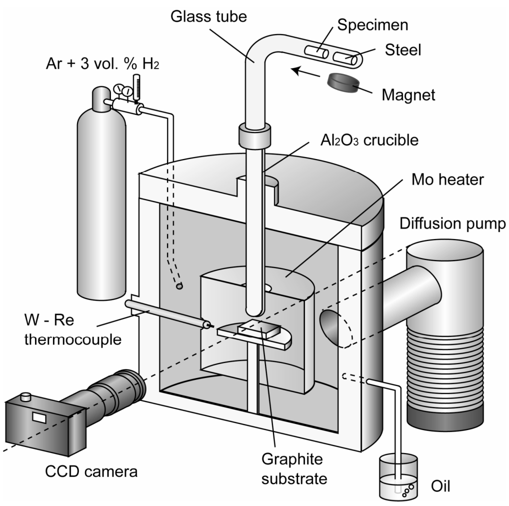

Fig. 3 Schematic illustration of the sessile drop device

2.3 MWCNT preform compression test

In infiltration process, the buckling strength and elastic modulus of the MWCNT preform are important factor in order to prevent buckle by threshold pressure and minimize compressive deformation of the MWCNT preform.

Relationship between compressive stress and compressive strain of the obtained preforms were measured at room temperature with an autograph (Shimadzu AG-250). The sample preform (φ40×10mm) was compressed at the rate of 1mm/min.

2.4 Squeeze casting

The matrices used are JIS-A1050 (Pure Al), JIS-AC8A (Al-12Si-Cu-Ni-Mg alloy) and AXE522 (Mg-5Al-2Ca-2RE alloy). Chemical compositions of matrix metals are shown in Table 2. The preheated preform is placed in the die and is infiltrated with the molten metal. Squeeze casting condition is shown in Table 3.

Table 2 Chemical compositions of matrices [mass%]

	Si	Cu	Fe	Mg	Ni	Mn	Ti	Al
JIS-A1050	0.05	0	0.13	0.01	-	0.01	0.01	Bal.
JIS-AC8A	12.5	1.3	0.2	1.3	1.2	0.01	0.11	Bal.
	Al	Ca	Fe	La	Ce	Pr	Nd	Mg
AXE522	5.5	2.1	0.0005	0.8	1.2	0.13	0.15	Bal.

Table 3 Condition of squeeze casting

	A1050	AC8A	AXE522
Melt pouring Temperature[K]	1053±10	963±10	963±10
Preform preheating [K]		773~873	
Preform preheating atmosphere		Ar + 3vol.%H_2	
Die temperature [K]		473～523	
Pressure [MPa]		100	
Pressure time [min]		3	

3. Results and discussion

3.1 Wettability between the basal plane of graphite and molten aluminum or magnesium

Fig. 4 shows the shape of the aluminum droplet on the basal plane of the graphite at one second after dropping. The measured surface tension was 1.0 (N/m). It is confirmed that this value is nearly equal to previous reported values [9,16-17]. Fig. 5 shows change in contact angle between the basal plane and molten aluminum. The number of experiments was more than three. The contact angle between the basal plane and molten aluminum was constant for 1 ks. The initial contact angle at 1 s after dropping was 127º on the basal plane of graphite.

In the case of magnesium, wettability of the basal plane of graphite by molten magnesium has not been reported. W. Shi et al. [10] examined the contact angle between molten magnesium and graphite substrates in a chamber filled with magnesium vapor. The initial contact angle between the molten magnesium and porous graphite was 74º in this report. If the equilibrium contact angle is less than 90º, i.e. so-called "good wettability state", spontaneous infiltration of molten magnesium into the porous preform should be expected.

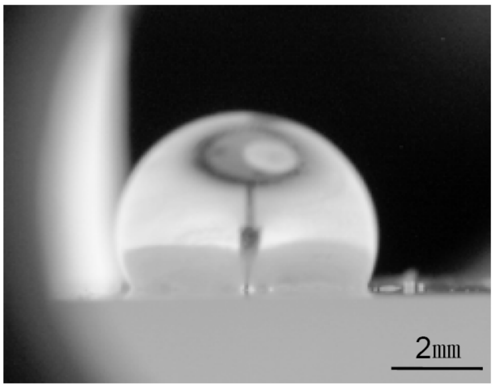

Fig. 4 Shape of the molten aluminum droplet on the basal plane of graphite

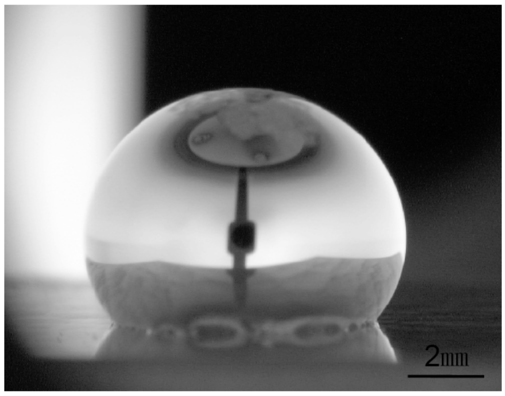

Fig. 6 Shape of the molten magnesium droplet on the basal plane of graphite

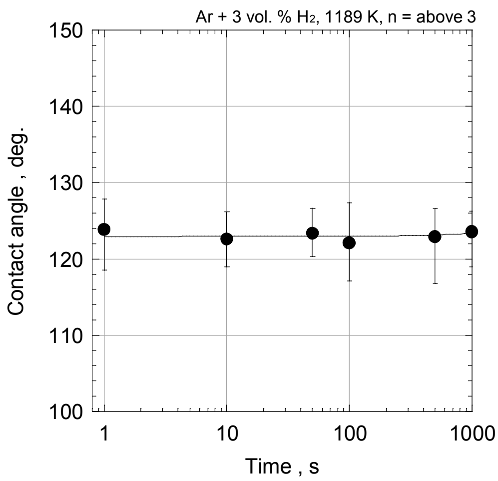

Fig. 5 Change in the contact angle between the basal plane of graphite and molten aluminum

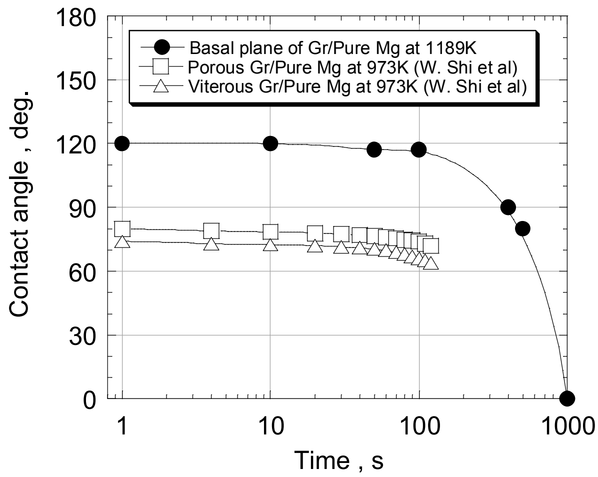

Fig. 7 Change in the contact angle between the basal plane of graphite and molten magnesium

Fig. 6 shows the shape of the magnesium droplet on the basal plane of the graphite at one second after dropping. The measured surface tension was 0.56 (N/m). It is confirmed that this value is nearly equal to previous reported values [18-21]. Fig. 7 shows change in the contact angle between the basal plane and molten magnesium compared with the data of previous report [10]. The initial contact angle was 120º and then the contact angle decreased gradually. In this experiment, the atmosphere around the sessile drop was not filled with equilibrium vapor pressure to the molten magnesium. Thus, the observed contact angle has to be the receding contact angle with holding time. The observed contact angle was larger than 90º for 200 s after dropping. Therefore, equilibrium contact angle between the molten magnesium and the basal plane of graphite at 1189K has to be larger than 90º. Moreover, in our previous study [22], AZ91D magnesium alloy did not infiltrate into 3D woven carbon fiber preform spontaneously. When the contact angle is more than 90º, external force is necessary to infiltrate molten aluminum or magnesium into space between carbonaceous fibers. The work per unit area of external force, W, can be estimated by using Young's equation [23]. The work of adhesion wetting was calculated by

$$W = \gamma_{SL} - \gamma_{SV} = -\gamma_{LV} \cos\theta \qquad (1)$$

As to the surface energy, aluminum or magnesium was 0.914, 0.559 (J/m^2) respectively [24]. For the work of adhesion wetting, aluminum or magnesium was 0.550, 0.280 (J/m^2) respectively. As compared, the wetting work of aluminum is higher than that of magnesium. Namely, in fabricating composites, infiltration of molten magnesium is easier than that of aluminum.

3.2 Wettability between the MWCNT preform and molten aluminum or magnesium

Fig. 8 and Fig. 9 show the shape of aluminum or magnesium droplet on the MWCNT preform respectively as sequential photographs. The photograph was shot at the rate of 125 shots per second. Regardless of molten metals, the droplets rolled and bounced on the MWCNT preform nevertheless the level of substrate was confirmed by using steel ball. The number of experiments was more than five. For measurements of contact angle and surface tension, Young-Laplace equation should be applied in static state. However, in this study, the droplet in static state has never been obtained for five times. The equilibrium shape of the droplet should exist between the droplet at the highest position and the lowest position. Namely, the equilibrium contact angle should exist between the advancing contact angle and the receding contact angle. Hence, for the droplet in dynamic state, the average values of the height, equatorial diameter and interfacial diameter of the droplets were calculated. For example, the size of each droplet in the picture numbers from one to twelve in Fig. 8 was measured and the average values were calculated. By means of the average value of the size of the droplet, the surface tension of molten aluminum or magnesium was calculated by Young-Laplace equation. As the result, the surface tension of molten aluminum or magnesium was 0.95±0.02 N/m (n=3), 0.58±0.01 N/m (n=4) respectively. It is confirmed that this calculated surface tension is close to the previous reported values [9,16-21]. For the droplet which surface tension was calculated, the contact angle between the MWCNT preform and molten aluminum or magnesium was estimated. As the result, contact angle between MWCNT preform and molten aluminum or magnesium was 174±2° (n=3) or 165±1° (n=4) respectively.

The MWCNT preform could be regarded as heterogeneous surface which consists of MWCNT and gas. Cassie's equation (2) can be applied to this heterogeneous surface [25].

$$\cos\theta' = A_1 \cos\theta_1 + A_2 \cos\theta_2 \qquad (2)$$

where $\theta'$is contact angle of a heterogeneous surface, θ_1 or θ_2 is the contact angle of material 1 or 2, respectively. A_1 or A_2 is the area ratio of material 1 or 2, respectively.

For θ_2=180° [26], the equation is

$$\cos\theta' = A_1 \cos\theta_1 - A_2 \qquad (3)$$

As to the θ', aluminum or magnesium was 174° or 165° respectively. For the fiber volume fraction of the preform is 25 %, A_1 = 0.25, A_2 = 0.75.

Thus, it is estimated that contact angle between the MWCNT and molten aluminum or magnesium is 168° or 150° respectively. It is found that wettability of MWCNT by molten aluminum or magnesium is poorer than that of graphite.

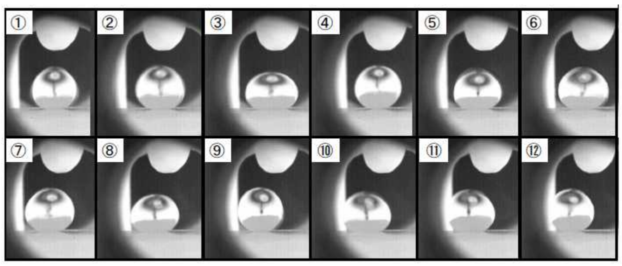

Fig. 8 Change in the shape of the droplet of molten aluminum on the MWCNT preform

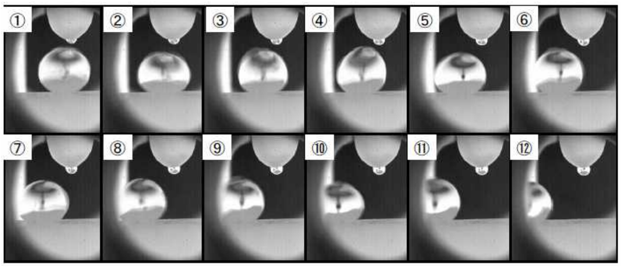

Fig. 9 Change in the shape of the droplet of molten magnesium on the MWCNT preform

3.3 Compressive property of MWCNT preform

Fig. 10 shows compressive stress - strain curve of the MWCNT preform. The compressive strength of the MWCNT preform increased with quantity of the binder addition. Fig. 11 and 12 show relationship between the buckling strength and elastic modulus

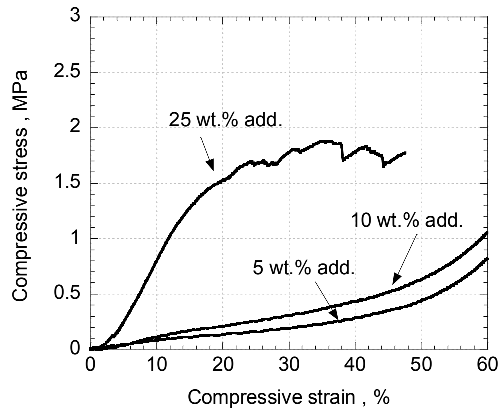

Fig. 10 Compressive stress - strain curve of the obtained MWCNT preform

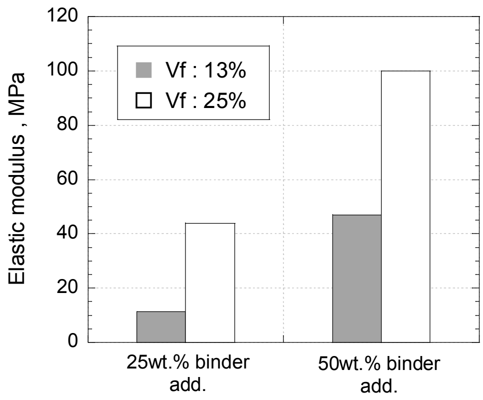

Fig. 12 Relationship between the elastic modulus of the MWCNT preform and quantity of the binder addition

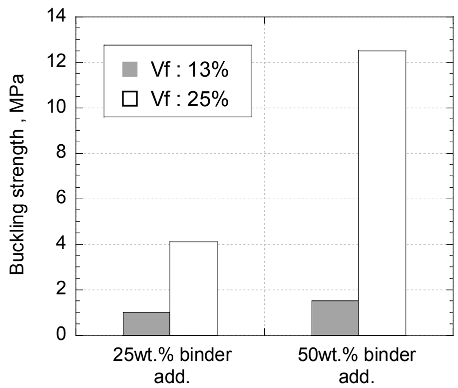

Fig. 11 Relationship between the buckling strength of the MWCNT preform and quantity of the binder addition

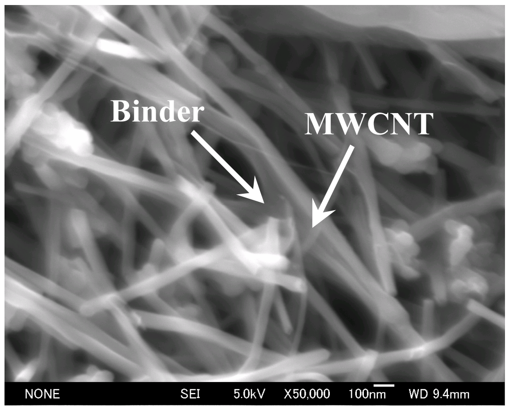

Fig. 13 Microstructure of the MWCNT preform (Vf : 25%, Binder addition: 50wt.%)

of the MWCNT preform and quantity of the binder addition. The buckling strength of the MWCNT preform increased with the MWCNT volume fraction. This would be caused by increasing joint points between MWCNTs. Fig. 13 shows microstructure of MWCNT preform. It is found that binder joints the MWCNTs. The 50wt.% binder addition preform with 25% MWCNT volume fraction had the highest buckling strength and elastic modulus in the obtained preforms. Therefore, for this preform, squeeze casting was carried out.

3.3 Fabrication of MWCNT reinforced aluminum or magnesium composites

Fig. 14 shows appearance of cross sections and microstructures of MWCNT composites. All matrices infiltrated into the MWCNT preforms completely. Thus, fabrication of MWCNT reinforced aluminium or magnesium composites by squeeze casting were succeeded. These kinds of composites fabricated by squeeze casting have not been reported. However, compressive deformation of MWCNT preforms was found in the obtained composites. The compressive deformation ratio was defined as compressive deformation ratio of thickness direction. The compressive deformation of the MWCMT preform ratio was 15-35 %.

In order to compare the threshold pressure with the applied pressure to the MWCNT preform, the threshold pressure was estimated. The threshold pressure P_c [5] was described by

$$P_c = -\frac{4V_f \gamma_{lv} \cos\theta}{d(1-V_f)} \qquad (4)$$

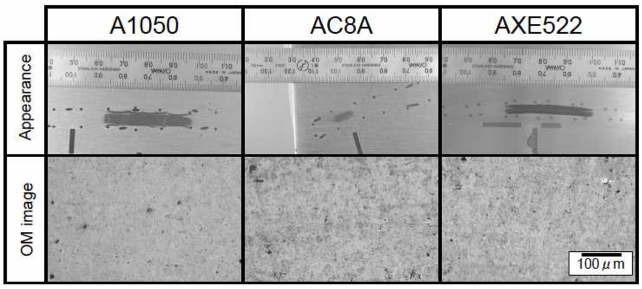

Fig. 14 Appearance of cross section of the MWCNT reinforced aluminum, magnesium alloy composites

where V_f (%) is fiber volume fraction of preform, γ_{LV} (N/m) is surface tension of molten metal, θ (deg.) is contact angle between fiber and molten metal, d (m) is fiber diameter. As to the surface tension of pure aluminum or pure magnesium, 0.914 or 0.559 was used for a first approximation [24]. As to the contact angle, experimental value ($\theta = 173°$ or $163°$) was used.

Fig. 11 shows the estimated threshold pressure by using contact angle on the basal plane of the graphite $P_{c\text{-}Gr}$ and MWCNT $P_{c\text{-}CNT}$ compared to the applied pressure to the preform P_{appl}. P_{appl} was calculated by S-S curve of preforms and the compressibility of the composites. As the result, an order agreement was found between the estimated threshold pressure and P_{appl}. In our previous study [27], the applied pressure to the carbon fiber preform was less than 0.1 MPa. Therefore, compared to the carbon fiber, hundreds of times larger pressure was applied to the MWCNT preform. It is experimentally demonstrated that the smaller fiber diameter leads to the larger infiltration pressure.

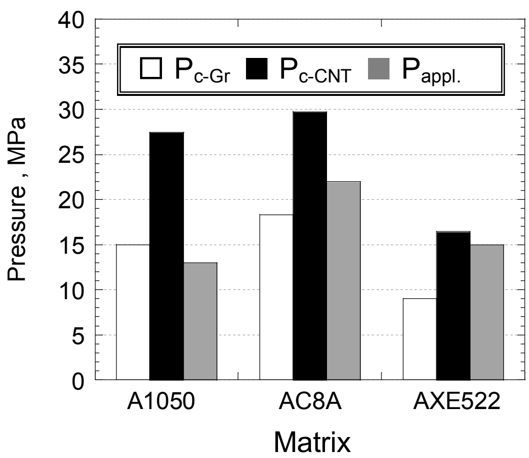

Fig. 11 Relationship between the estimated threshold pressure and the applied pressure to the MWCNT preform

4. Conclusions

For fabricating CNT/light metal matrix composites, wettability of graphite materials (the basal plane of graphite, MWCNT) by molten Al, Mg was examined. Moreover, trial fabrication of MWCNT reinforced aluminum or magnesium alloy composites was carried out by squeeze casting. The applied pressure to the preform was compared with the estimated threshold pressure. Consequently, we concluded that as follow;

1. The contact angle between the basal plane of the graphite and Al or Mg was 127° or 1 20° respectively. On the other hand, it was calculated that the contact angle between MWCNT and molten Al or Mg would be 168° or 150° respectively.

2. MWCNT reinforced aluminium or magnesium alloy composites were obtained by squeeze casting without non-infiltration area.

3. An order agreement was found between the estimated threshold pressure and the applied pressure to the MWCNT preform.

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