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Fabrication process of carbon nanotube/light metal matrix composites by squeeze casting

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Abstract

Multi-walled carbon nanotubes (MWCNTs) should be attractive for the reinforcement of metal-matrix composites, because of their high strength, high modulus and high thermal conductivity. However, the fiber diameter of MWCNTs is hundreds of times smaller than that of carbon fiber. This causes difficulty in infiltration into the MWCNT preform. Moreover, the threshold pressure which was applied to the preform will cause preform deformation. Therefore, knowledge of preform compressive properties which are the buckling strength and elastic modulus are necessary to fabricate the composites. In this study, at first, wettability of the basal plane of graphite by molten aluminum or magnesium was measured using the sessile drop method. Moreover, trial fabrication of MWCNT-reinforced aluminum or magnesium alloy composites was carried out by squeeze casting. As a result, these composites were fully infiltrated. An order-of-magnitude agreement was found between the estimated threshold pressure and the applied infiltration pressure to the MWCNT preform.

Keywords: Wettability; Multi-walled carbon nanotube; Aluminum; Magnesium; Composite; Infiltration process

1. Introduction

Since the first observation by Iijima [1], multi-walled carbon nanotubes (MWCNTs) have been at the focus of considerable research. MWCNTs have high strength, modulus and thermal conductivity, all superior to those of carbon fiber [2]. Therefore, they can be used as potential reinforcement for composites. Aluminum and magnesium alloys are attractive due to their light weight. MWCNT-reinforced aluminum or magnesium composites are expected to have superior high strength and high thermal conductivity.

Squeeze casting is often used as a composite fabrication method [3,4]. In the fabrication of composites, a threshold pressure must severally be overcome to infiltrate molten alloys into the preform. However, this often causes preform deformation [4]. The threshold pressure is a function of 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, the wettability between MWCNT and molten aluminum or magnesium has not been measured. A MWCNT can be imaged as some sheets of graphene rolled up to form a 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 by many researchers [6–10]. On the other hand, in the case of magnesium, the contact angle on graphite has been less extensively investigated [11,12], particularly as concerns the basal plane. In previous reports, the substrate was vitreous carbon or porous graphite or isotropic graphite.

In this study, the wettability of the basal plane of graphite by molten aluminum or magnesium was examined. After measurement of the contact angle, trial fabrication of MWCNT-reinforced aluminum or magnesium composites was carried out by squeeze casting. The diameter of MWNCT (20–70 nm)

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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, which should cause difficulty in infiltration into the preform.

By the measured contact angle between the basal plane of graphite and molten aluminum or magnesium, the threshold pressure was estimated. On the other hand, the applied pressure to the preform was estimated using the compressive deformation ratio of the preform in the obtained composite.

2. Experimental procedures

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. As shown in Fig. 1, the basal plane has peaks of (0 0 2), (0 0 4) and (0 0 6). The substrate has dimensions of 20 mm × 20 mm × 4 mm. The graphite substrate was polished using 0.04 μm diamond paste. In order to remove dust on the substrates, ultrasonic cleaning was conducted in ethanol and acetone.

Fig. 2 shows the sessile drop device [14,15]. 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 the substrate was confirmed by using steel ball after the substrate was set on a stand under the dropping tube. The dropping tube has ϕ 1.0 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 metal was dropped by means of a pressure difference between the chamber and the 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 the Bashforth and Adams [16], which is a numerical solution of Young-Laplace equation for a drop in gravity. When θ was less than 90°, 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.

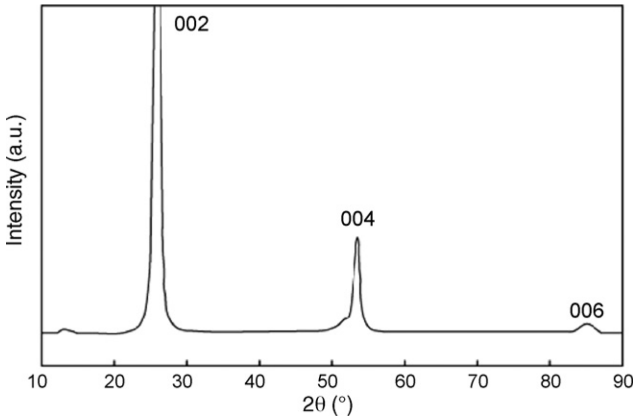

Fig. 1. X-ray diffraction profiles of basal plane of graphite.

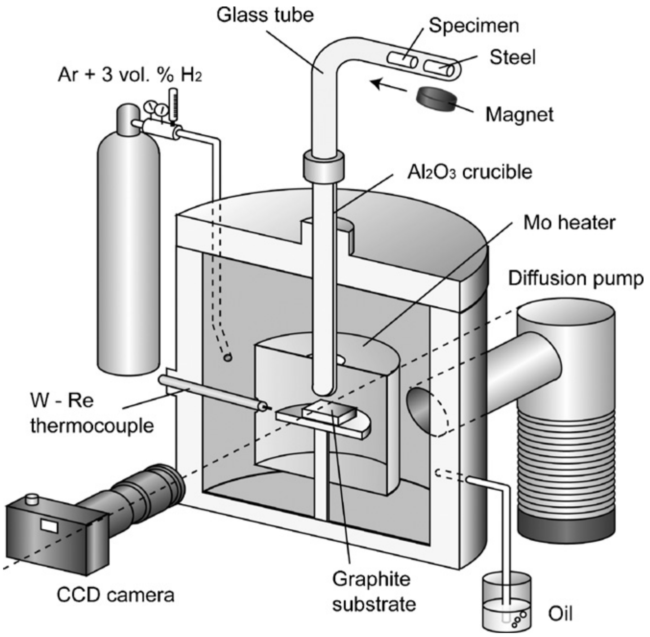

Fig. 2. Illustration of sessile drop device.

The MWCNT material was fabricated by Nano carbon technologies Co., Ltd. Fig. 3 and Table 1 show a scanning electron microscopy (SEM) image of MWCNT microstructure and structural properties, respectively [13]. Some regions of whiter color indicated by the arrow in Fig. 3 are not impurities but joining points between MWCNTs which were produced during the fabricating process of MWCNTs. In the fabrication process of the preform, after the MWCNT were mixed with an organic binder (50 wt.% versus weight of MWCNT addition), the preform was sintered at 2773 K for 20 min in Ar atmosphere. The fiber volume fraction of the preform was 25%.

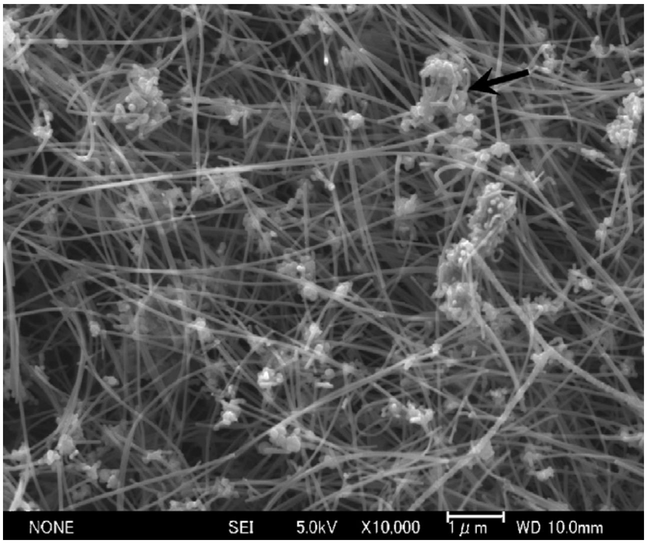

Fig. 3. Microstructure of MWCNT (as fabricated).

Table 1
Structural properties of MWCNTs

Diameter (nm)	20–70
Length (μm)	1–20
Density (g/cm^3)	1.89
Aspect ratio	>100

In the infiltration process, a finite threshold pressure often causes preform deformation. In order to estimate the applied pressure during infiltration, the preform compressive deformation ratio was compared with the compressive properties of the obtained preform, measured at room temperature using a compression testing apparatus (Shimadzu AG-250) on preform samples (40 mm diameter × 10 mm) at 10^{-1} min^{-1}.

The matrices used are JIS-A1050 (pure Al), JIS-AC8A (Al–12Si–Cu–Ni–Mg alloy) and AXE522 (Mg–5Al–2Ca–2RE alloy). The reason why AC8A and AXE522 were used was to obtain the composites which have superior high temperature strength. 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 parameters are shown in Table 3.

Microstructures of the obtained preform and composites were observed by optical and field-emission SEM (FE-SEM) (JSM-6500F) in order to examine existence of porosity and distribution of the MWCNTs in the preform and composites.

3. Results and discussion

3.1. Wettability between the basal plane of graphite and molten magnesium

In the case of magnesium, wettability of the basal plane of graphite by molten magnesium has not been reported. Shi et al. [11] examined the contact angle θ between molten magnesium and porous graphite in a chamber filled with magnesium vapor. The initial contact angle between the molten magnesium and porous graphite was 74° in this report. If the equilibrium contact angle is less than 90°, i.e. so-called “good wettability state”, spontaneous infiltration of molten magnesium into the porous preform should be expected.

Fig. 4 shows the shape of the magnesium droplet on the basal plane of the graphite at 1 s after dropping. The measured surface tension was 0.56 (N/m). It is confirmed that this value is nearly equal to previous reported values [18–22]. Fig. 5 shows the change in the contact angle between the basal plane and molten magnesium compared with the data of previous report [11]. The initial contact angle was 120° and then the contact angle decreased gradually. In this experiment, the atmosphere around the sessile drop was not at the equilibrium vapor pressure with molten magnesium. Thus, the observed contact angle has to be the receding contact angle with holding time. The observed contact angle was larger than 90° for 200 s after dropping. Therefore, the equilibrium contact angle between molten magnesium and the basal plane of graphite at 1189 K has to be larger than

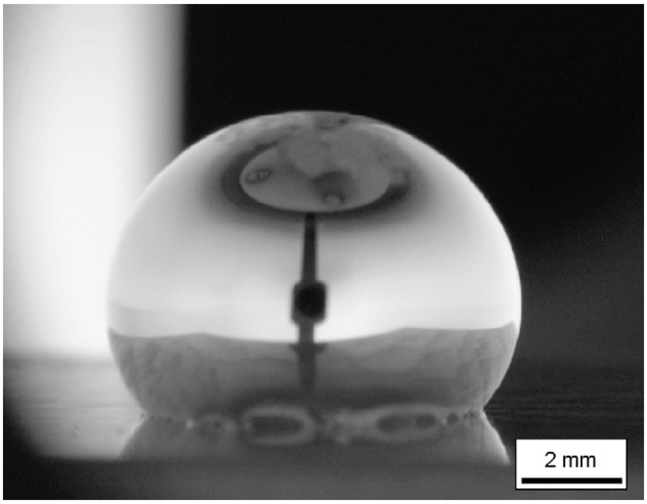

Fig. 4. The droplet of molten pure magnesium on the basal plane of graphite 1 s after dropping.

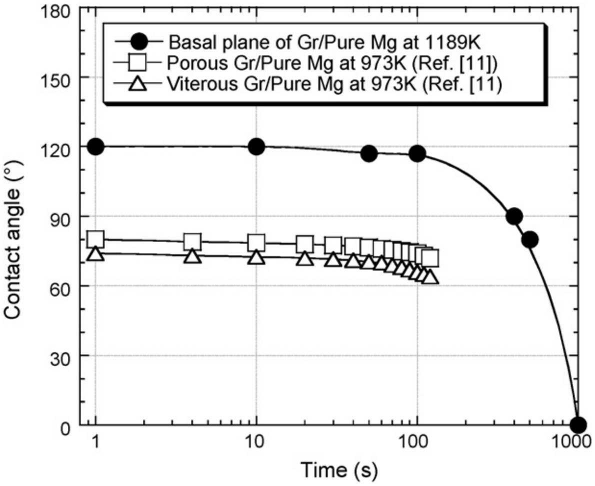

Fig. 5. Change in the contact angle between the basal plane of graphite and molten pure magnesium.

Table 2
Chemical compositions of matrices (mass%)

	Si	Cu	Fe	Mn	Mg	Ni	Ti	Al
JIS-A1050	0.05	0	0.13	0.01	0.01	–	0.01	Balance
JIS-AC8A	12.5	1.3	0.2	0.01	1.3	1.2	0.11	Balance

	Al	Ca	Mn	Fe	La	Ce	Pr	Nd	Mg
AXE522	5.5	2.1	0.15	0.0005	0.8	1.2	0.13	0.15	Balance

Table 3
Conditions of squeeze casting

Parameter	Matrix		
	A1050	AC8A	AXE522
Melt pouring temperature (K)	1053 ± 10	963 ± 10	963 ± 10
Preform preheating (K)	773∼873		
Preform preheating atmosphere	Ar + 3 vol.% H_2		
Die temperature (K)	473–523		
Pressure (MPa)	100		
Pressure time (min)	3		

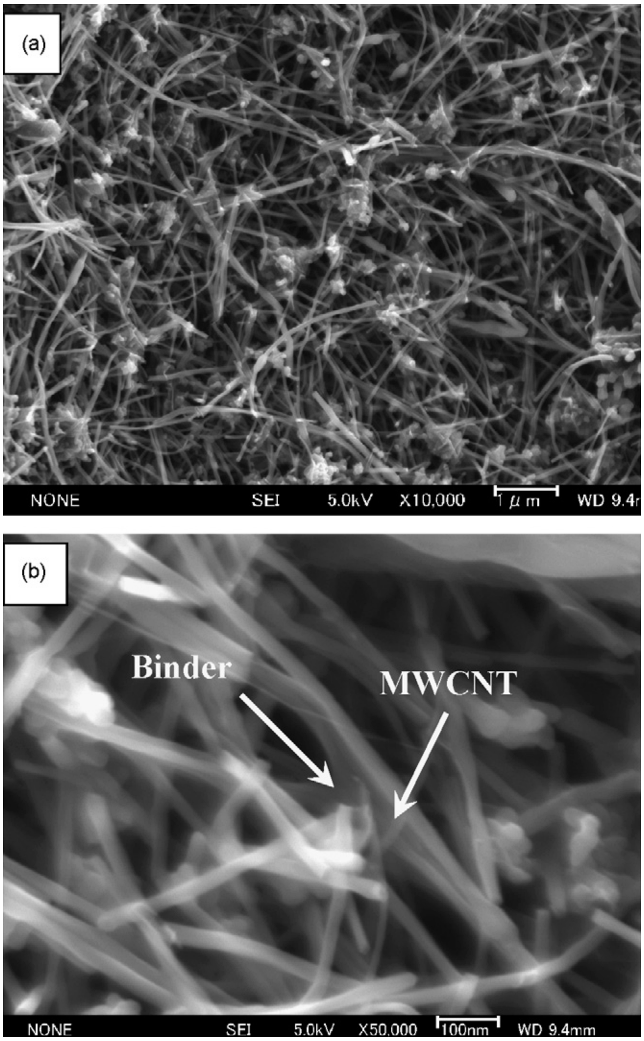

Fig. 6. Microstructure of the MWCNT perform. (a) Lower magnification and (b) higher magnification.

90°. Moreover, in our previous study [23], AZ91D magnesium alloy did not infiltrate into a three-dimensional woven carbon fiber preform spontaneously.

As to the aluminum, the contact angle on the basal plane of graphite has been examined by various researchers. Therefore, as a comparison, the contact angle between the basal plane of graphite and molten aluminum was measured (see Appendix A).

When the contact angle is more than 90°, 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 [24]. The work of adhesion wetting was calculated by

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

For the surface energy γ_{LV} of liquid aluminum and magnesium, values are 0.914 and 0.559 J/m^2, respectively [25]. For the contact angle, the experimental value ($\theta = 127°$ or $120°$) was used. Thus, the work of adhesion values for aluminum and magnesium are 0.550 and 0.280 J/m^2, respectively. The wetting work of aluminum is higher than that of magnesium. Thus, in fabricating composites, infiltration of molten magnesium will be easier than that of aluminum.

3.2. Microstructure and compressive properties of MWNCT preform

Fig. 6 shows the microstructure of a MWCNT preform. The MWCNTs as dispersed in the preform are three-dimensionally random. As shown in Fig. 6b, it was found that MWCNTs were jointed by the binder. Fig. 7 shows compressive stress–strain curve of the MWCNT preform. It is known that monofilament MWCNTs are not buckled or broken but bent elastically when several 10 MPa compressive stress are applied in a direction transverse to MWCNT [26]. Therefore, at the first peak of obtained compressive stress–strain curve (indicated by the arrow in Fig. 7), the jointed points between MWCNTs would be broken. Then the preform could be bulked by compressive stress.

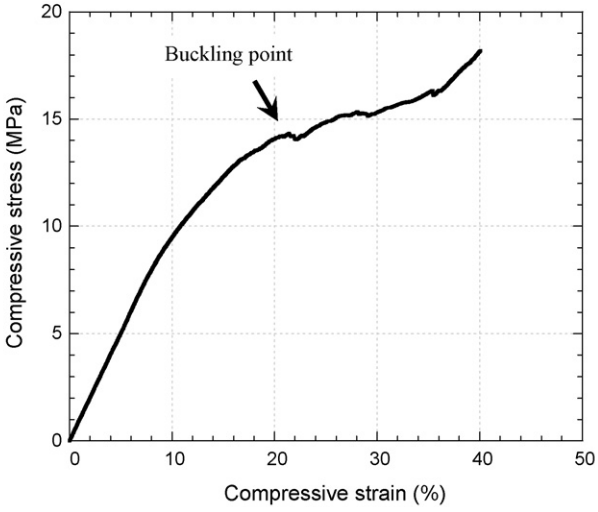

Fig. 7. Compressive stress–strain curve of the MWCNT perform.

3.3. Fabrication of MWCNT-reinforced aluminum or magnesium composites

Fig. 8 shows the appearance of cross-sections and microstructures of MWCNT composites. All matrices infiltrated into the MWCNT preforms completely. Thus, fabrication of pore-

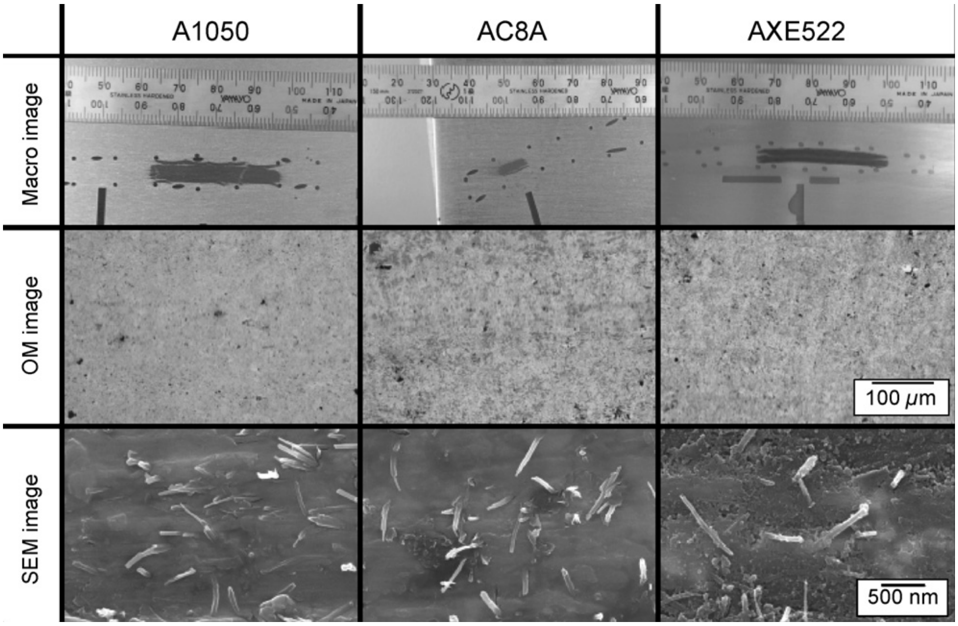

Fig. 8. Appearance of cross-sections and microstructures of MWCNT-reinforced aluminum or magnesium alloy composites.

free MWCNT-reinforced aluminum or magnesium composites by squeeze casting was achieved. 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%.

The threshold pressure for infiltration, P_c can be estimated as

$$P_c = -\frac{4V_f\gamma_{LV}\cos\theta}{d(1-V_f)} \tag{2}$$

where V_f (%) is fiber volume fraction of preform, and d (m) is the fiber diameter [5]. For the surface tension of pure aluminum or pure magnesium, 0.914 or 0.559 N/m was used for a first approximation [25]. For the contact angle, experimental values of contact angle on the basal plane of graphite ($\theta = 127°$ and $120°$) were used. For γ_{LV} note that these values for the alloys should be somewhat different from those for the pure metal [23,27].

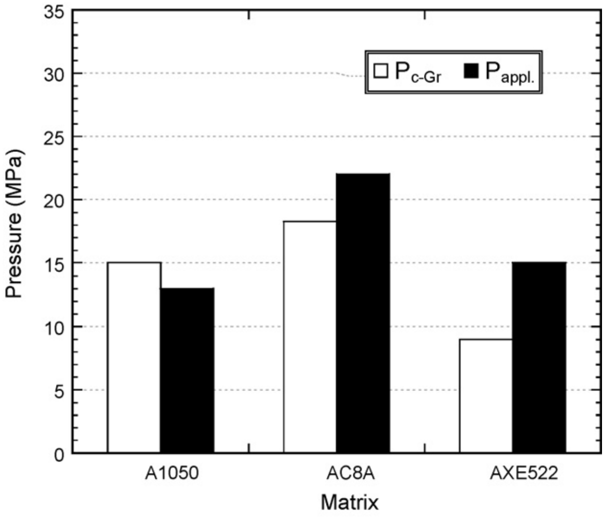

Fig. 9. The estimated threshold pressure by using contact angle on the basal of the graphite $P_{c\text{–}Gr}$ and compared to the applied pressure to the preform P_{appl}.

Fig. 9 shows the estimated threshold pressure by using contact angle on the basal plane of the graphite $P_{c\text{–}Gr}$ compared to the applied pressure to the preform P_{appl}. P_{appl} was calculated from stress–strain curves of preforms and the compressive deformation ratio of the preform in the composite. As seen, an order-of-magnitude agreement is found between the estimated threshold pressure and P_{appl}. It is known that the applied pressure on the preform is the sum of the threshold pressure P_c and viscous resistance in infiltration P_v [28]. Therefore, P_{appl} should

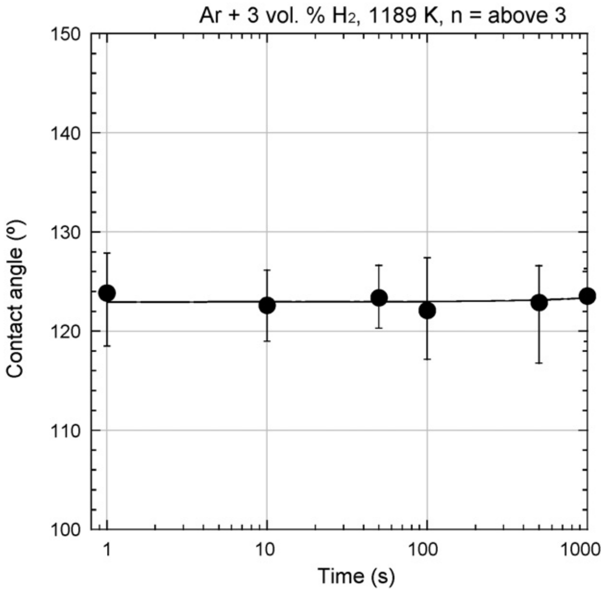

Fig. 10. Change in the contact angle between the basal plane of graphite and molten pure aluminum.

be more than P_c, which would explain measured values higher than estimated values.

In our previous study [29], the applied pressure to the carbon fiber preform was less than 0.1 MPa. Therefore, compared with the carbon fiber, it is confirmed that a pressure hundreds of times larger must be applied with the MWCNT preform.

4. Conclusions

For fabricating CNT/light metal matrix composites, the wettability of the basal plane of graphite by molten Al, Mg was examined. Moreover, trial fabrication of MWCNT-reinforced aluminum or magnesium alloy composites was carried out by squeeze casting. In order to examine whether an order-of-magnitude estimation of infiltration pressure was possible or not, the preform compression ration was compared with the estimated threshold pressure. Data show the following:

(i) The contact angle between the basal plane of the graphite and molten Al or Mg was 127° or 120°, respectively.
(ii) 25 vol.% MWCNT-reinforced aluminum or magnesium alloy pore-free composites were obtained by squeeze casting without non-infiltration area.
(iii) An order-of-magnitude agreement was found between the estimated threshold pressure and the applied pressure to the MWCNT preform.

Appendix A

Wettability between the basal plane of graphite and molten aluminum.Landry et al. [7] reported wettability between the basal plane of graphite and molten aluminum at 1100 K in He atmosphere. In this work, as described in Section 2, the wettability between the basal plane of graphite and molten aluminum was measured.

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. 10 shows the evolution of the 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 127° on the basal plane of graphite. Compared with previous data [6–10], a close agreement is found.

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