SECONDARY FORMING OF HYBRID REINFORCEMENTS METAL MATRIX COMPOSITE

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1 Introduction

Many material scientists and engineers have shifted their focus from monolithic materials to composite materials for the development of lightweight, environment friendly, and high performance appliances. Composite materials are a combination of at least two chemically distinct materials with a clear interface separating the components. Composites are replacing traditional materials because of their relative advantages in terms of high stiffness and strength. They can have metal or polymer matrices, and can be reinforced with continuous fibers, discontinuous fibers, or particles [1-3].

Since 1970, carbon fiber reinforcement has been extensively used in a wide array of applications in the automotive, aerospace, and military fields. Carbon nanotubes (CNTs) were discovered by Iijima [4] in 1991. Experiments have shown that CNTs have superior mechanical properties over carbon fibers; e.g., stiffness values up to 1000 GPa, strength on the order of 100 GPa [5-9], and thermal conductivity of up to 6000 Wm⁻¹K⁻¹. Since the discovery of CNTs, many interesting studies on composites with CNTs have been performed. Katsuyoshi et al. [10] considered a magnesium alloy powder composite with carbon nanotubes. They tried to uniformly disperse the CNTs in Mg alloy with a zwitterionic surfactant solution. The addition of very small quantities of un-bundled multi-wall carbon nanotubes (MWCNTs) (0.95–1.43 vol. %) to an Mg matrix composite causes a large increase in the tensile strength and yield stress, but a considerable decrease in elongation.

A review of the literature shows that only limited studies have been carried out on hybrid metal matrix composites using nano/micro-sized reinforcements. S. C. Okumus et al. [11] studied the thermal properties of Al-Si/SiC/graphite hybrid MCs fabricated by squeeze casting. Z. M. Du et al. [12] evaluated the wear-resisting properties of Al₂O₃/SiC/Al hybrid composites. No systematic attempt has yet been made to study the effects of the hybridization of CNTs and Al₂O₃sf on the mechanical properties of aluminium-based composites, particularly by the infiltration method. Moreover, the resulting mechanical changes and workability by secondary forming of Al₂O₃/CNTs/A356 has not been reported. Most of the industrial parts are followed by additional processing such as compression or extrusion or machining, etc. Therefore, we investigated the secondary formability of hybrid reinforcement composites in order to reduce trial and error. The goal of this study is to develop and characterise CNT/Al₂O₃sf preform-based aluminium hybrid composites after the extrusion process.

2 Experimental

2.1 Fabrication of preform with CNT/Al₂O₃sf reinforcements

MWCNTs and Al₂O₃sf were used as reinforcements to develop a hybrid preform. The properties of these fibers are listed in Table 1. Preform binders are resins that hold or bind pre-woven or chopped strands in position so that the resulting preforms can be handled easily before use. In this study, colloidal silica was used as a binder. Silica can improve the viscosity of the slurry and the hardness of the preform [13]. It is often used in the form of an aquatic dispersion. The silica colloid is
Table 1 Properties of Saffil alumina fibers (ICI, U.K.), GNF, and MWCNTs (Polyfield, Korea)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Density (g/cm$^3$)</th>
<th>Mean diameter (μm)</th>
<th>Mean length (μm)</th>
<th>Tensile strength (GPa)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.3</td>
<td>3</td>
<td>120</td>
<td>2</td>
<td>300</td>
</tr>
<tr>
<td>CNTs</td>
<td>2.1</td>
<td>0.1</td>
<td>50</td>
<td>150</td>
<td>1200</td>
</tr>
</tbody>
</table>

Table 2 Chemical composition of A356 aluminium alloy (all elements are in weight percent)

<table>
<thead>
<tr>
<th>Element</th>
<th>A356</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.01</td>
</tr>
<tr>
<td>Mg</td>
<td>0.33</td>
</tr>
<tr>
<td>Cu</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.13</td>
</tr>
<tr>
<td>Si</td>
<td>7.00</td>
</tr>
<tr>
<td>Mn</td>
<td>0.01</td>
</tr>
<tr>
<td>Ti</td>
<td>0.01</td>
</tr>
<tr>
<td>Al</td>
<td>Bal.</td>
</tr>
<tr>
<td>$T_l$</td>
<td>614 °C</td>
</tr>
<tr>
<td>$T_s$</td>
<td>554 °C</td>
</tr>
</tbody>
</table>

Fig. 1 Schematic diagram showing fabrication of the hybrid preform.

particularly attractive due to its high temperature resistance. The average size of the silica particles is in the colloidal range from 10 to 80 nm. Sodium dodecylbenzene sulfonate (NaDDBs) was used as a surfactant because of its ability to generate a uniform dispersion of the MWCNT hybrid fiber network [13]. Cationic starch was used for the flocking effect between the binder and the reinforcements [14]. Flocculation is a process by which fine particles are suspended in a liquid, and form an aggregate or a clumped mass. Cationic polyacrylamide was used as a flocculant to increase the fiber-fiber flocculation and shear strength of the fiber flocs [15]. It can also increase the pore size of the preform. A commercial casting-grade aluminium alloy (A356) was used as the matrix material. Its chemical composition is given in Table 2. This alloy was selected because of good fluidity and the presence of silicon and magnesium. Since the silicon content of A356 alloy is high, it can be maintained in the liquid state at typical casting temperatures.

The presence of Mg improves the wettability of the reinforcement by the matrix.

Initially, hybrid preforms were developed from CNTs and Al$_2$O$_3$sf. The volume percentages of the CNTs and Al$_2$O$_3$sf were maintained at 3% and 97%, respectively. To examine the effect of the quantity of binder, three quantities (10%, 15%, and 20%) were used. A schematic diagram representing the fabrication of the preform is given in Fig. 1. A punch was attached to a hydraulic cylinder, and an electric motor operated the cylinder. The speed of the cylinder, measured by a velocity meter, was continuously controlled by regulating an oil flux. For the extraction of water from the prepared preforms, a vacuum pump and a drain box were attached to the equipment.

Figure 2 shows an overview of the manufacturing process for the hybrid preform. In the first stage, Al$_2$O$_3$sf and CNTs were mixed in a selected ratio with water and the required amount of binder (10%, 15%, or 20% of the total weight of the fibers). The
were pressed by a punch to the desired height. The pressed preforms were removed from the mould and baked at 100, 150, or 200 °C. Laboratory-scale hybrid fiber preforms (55 mm in length, 20 mm in width, and 15 mm in thickness) were developed. In order to prepare the specimens for microstructural studies, the samples were mounted on an epoxy mounting media and subjected to a dry grinding sequence using 1200 grit silicon carbide papers. The samples were coated with platinum and then subjected to scanning electron microscope (SEM) analysis (JEOL 2000-FX, JEOL Ltd., Tokyo, Japan).

2.2 Fabrication of hybrid MMCs with CNT/Al2O3sf preform using the infiltration method

The MMCs used in this study were made using the infiltration method. A schematic diagram of the infiltration method is shown in Fig. 3. The mould was 70 mm long, 20 mm wide, and 50 mm deep. This allowed the fabrication of 20 mm-thick MMCs without encountering problems of melt overflows prior to the entry of the ram into the mould. For developing aluminium-based hybrid MMCs, we used hybrid preforms, fabricated as described in Section 2.1. Initially, the hybrid preform was heated to a temperature of 400 °C. The mould used to make the MMCs was pre-heated to 300 °C. The metal ingots, prior to melting, were treated with alkaline solution and washed with acid in order to eliminate surface impurities. A mould lubricant was sprayed into the inner surface of the mould so that it would be easy to release the cast sample. The pre-heated hybrid preform was placed in the mould, and then molten aluminium alloy was poured into the preform. The pouring temperature of the aluminium alloy was 700 °C. A pressure of 3 MPa was then applied with a punch velocity of 7 KN/s for a holding time of 30 s. In this way, the molten aluminium was successfully infiltrated into the hybrid preform.

2.3 Extrusion process of hybrid MMCs

For the extrusion process, we used hybrid reinforcement MMCs, fabricated as described in Section 2.2. High temperature extrusions were conducted using an MTS testing machine (MTS 810, MTS, USA). Extrusion specimens with a diameter of
Table 3 Variable conditions of extrusion test and specimens

<table>
<thead>
<tr>
<th>Value</th>
<th>Extrusion temperature (°C)</th>
<th>Ram velocity (mm/min)</th>
<th>Al₂O₃ volume fraction (%)</th>
<th>CNT weight fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350, 400, 450</td>
<td></td>
<td>2</td>
<td>10, 15, 20</td>
<td>1, 2, 3</td>
</tr>
</tbody>
</table>

Fig. 4. Schematic diagram of secondary forming.

Fig. 5. The position of microstructure observation.

10 mm and a height of 20 mm were used. The extrusion ratio and angle is 2.04 and 45°, respectively. The extrusion ratio R is defined as follows:

\[ R = \frac{A_0}{A_f} \quad (1) \]

where \( A_0 \) and \( A_f \) are the billet area before and after hot extrusion, respectively. The forming process parameters include temperature, strain, and strain rate. The main factors that influence successful extrusion in metal are as follows [16]:

- Temperature
- Extrusion ratio
- Extrusion speed
- Chemistry of the alloy
- Friction between the material and die

All process parameters were fixed to minimise the variables except for temperature and reinforcement composition factors, as described in Table 3. A boron nitride lubricant was used to prevent sticking, and for lubrication. Figure 4 shows a schematic diagram of the extrusion process. The extrusion processes were conducted in a hot chamber. Before forming, each specimen was kept in the hot chamber for a minimum of 30 min to heat the specimen. The dies and ram were also heated in the chamber to prevent heat transfer between the dies and the hybrid material billet.

A microstructure observation was conducted to expect the mechanical change of the hybrid material after extrusion, as shown Fig. 5.

3. Results and Discussion

3.1 Analysis of CNT/Al₂O₃sf hybrid preform

SEM examinations of the hybrid preforms were conducted for different volume fractions of fibers. The SEM images are shown in Figs. 6(a)-(d). These figures indicate that the Al₂O₃sf and CNTs were well-dispersed in the preform. The array of the Al₂O₃sf network helped the CNTs become well distributed within the preform. In the case of the preform with a 15% volume fraction of fiber (Fig. 6(b)), most of the CNTs were found to be dispersed as clusters as compared to the preform shown in Fig. 6(a). In the case of the preform with a 20% volume fraction of fibers (Fig. 6(c)), a higher level of clustering of CNTs in the short fiber network was observed. However, CNTs and Al₂O₃sf were bonded in a better manner within the preform, as shown in Fig. 6(d). Thus, we note that with a 20% colloidal silica binder, better binding between the CNTs and
Al₂O₃sf occurred. This better bonding helped the preform withstand the operating pressure during the infiltration of the metal melts.

3.2 Surface investigation of CNT/Al₂O₃sf hybrid MMCs by using SEM

An SEM investigation was conducted to determine whether or not CNTs existed in the A356 matrix after infiltration. Therefore, we needed to find the form of the CNTs in the material directly by using SEM. Figures 7(a) and (b) show images on the fracture surface after compression of the Al₂O₃/CNT/A356 material. Overall, the Al₂O₃ fibers were well distributed as short fibers in the matrix. The CNT clusters were attached to the Al₂O₃ surface like branches, as shown in Fig. 7(b). Generally, CNTs do not mix well with aluminium due to poor wettability. When pouring the molten aluminium onto the CNTs, the aluminium immediately floats due to the difference in specific gravity and poor wettability. Therefore, using a hybrid preform is an effective method for fabricating CNT/Al₂O₃/A356 aluminium alloy hybrid MMCs.

Fig. 6. SEM micrographs of hybrid preform with various volume fractions of fibers.

(a) 10% Al₂O₃, 2% CNTs.
(b) 15% Al₂O₃, 2% CNTs.
(c) 20% Al₂O₃, 2% CNTs.
(d) Cluster of CNTs are bonded with Al₂O₃sf, (15% Al₂O₃, 2% CNTs).

(a) 1,000X magnification.
3.3 Analysis of CNT/Al2O3sf hybrid MMCs by hot extrusion

3.3.1 Extrusion pressure curve

Strain rate is a very sensitive parameter in hot forming. However, we fixed the strain rate parameter in order to minimise the variable, as previously mentioned in section 2.3. The strain rate was calculated using Eq. (2), and the value is 0.0217 s⁻¹. The mean effective strain rate is given by [17, 18]

\[
\dot{\varepsilon} = \frac{6V}{(D_C^2 - D_E^2)} \tan \frac{\alpha}{2} \ln \frac{D_C}{D_E}
\]  (2)

where \(\dot{\varepsilon}\) is the mean strain rate, \(V\) is the average ram speed, \(D_C\) is the container bore, \(D_E\) is the diameter of the extruded rod, and \(\alpha\) is the dead metal zone semi-angle.

Figure 8 shows the displacement-extrusion pressure curve according to the composition of reinforcements MMCs. In the overall curve trend, the extrusion pressure increased with increasing \(\text{Al}_2\text{O}_3\) and CNTs fraction as shown Figs. 8(a) and (b). Especially, the required pressure for the extrusion process of hybrid material is significantly higher than for A356 aluminium alloy, as shown Fig. 8(a). The deformation resistance of the hybrid material is over two times that of the A356 original material due to the strengthening effect of \(\text{Al}_2\text{O}_3\)/CNT reinforcements. Another unusual trend is that the primary transition region was located in the hybrid material pressure-displacement curve as shown in Figs. 8(a)-(b). \(\text{Al}_2\text{O}_3\)/CNTs can lead to strengthening if they are well infiltrated with the matrix and there is sufficient stress transfer to the reinforcements. The first slopes are shown in the primary transition region (Fig. 8(a)) corresponds to the reinforcement-dominant Young's modulus \((E_f)\), and the second slope corresponded to the matrix-dominant Young's modulus \((E_m)\). Typically, elongations of reinforcements (below 4%) were limited as compared with A356 aluminium matrix elongation (over 10%). Therefore, over a limited strain value of about 4%, either reinforcements fracture or interfacial fracture will occur. In addition, excessive CNT content can cause unwanted effects such as the formation of carbide \((\text{Al}_2\text{MgC}_2)\) [19]. Carbide in the matrix can degrade the ductility of a hybrid material.
In our empirical findings, many extrusion specimens (Al$_2$O$_3$ 20%, CNT 3%) could be considered as failed specimens due to breakage during extrusion, as shown Fig. 9(b). Thus, the over-containing of reinforcements (Al$_2$O$_3$ 20%, CNT 3%) is not recommended.

3.3.2 Microstructures

Figure 10 shows the microstructure with respect to the temperature variable. The primary alpha phase changes were more coarsening and agglomerative with increasing temperature. During recrystallization, some of the stored internal strain energy was relieved due to dislocation motion [21]. The advantage of fine microstructure is described by the Hall-Petch law [21]:

$$\sigma_y = \sigma_0 + \kappa_y d^{1/2}$$  (4)

where $\sigma_y$ is the yield strength, $\sigma_0$ and $\kappa_y$ are constants for a given material, and $d$ is the average grain diameter. Residual thermal stresses can be produced at the CNT/Al$_2$O$_3$ and matrix interfaces due to the thermal mismatch between the reinforcement and the matrix. This can also contribute to a reduction in the extrusion formability.

Fig. 10 Microstructure of hybrid MMCs after compression.
4. Conclusion

Aluminium-based hybrid composites were fabricated using the infiltration method and characterised using hot extrusion and hardness tests. Based on our results, the following conclusions are drawn.

(1) The Al$_2$O$_3$sf and CNTs were well-dispersed within the hybrid material. The array of the Al$_2$O$_3$sf network helped the well-dispersed CNT distribution within the preform. This can also improve the infiltration behaviour of the hybrid preform by a metal melt.

(2) The deformation resistance of the hybrid material is over two times that of the A356 original material due to the strengthening effect of Al$_2$O$_3$/CNT reinforcements. Another unusual trend is that the primary transition region was located in the hybrid material pressure-displacement curve

(3) CNT/Al$_2$O$_3$/A356 hybrid material softening could easily be realized due to recrystallization at a temperature of over 400 °C. The softening of the material can help to increase the formability.

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