Original Article

Enhancement of the mechanical properties of an aluminum metal matrix nanocomposite by the hybridization technique

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ABSTRACT

A uniform distribution of nanoparticles in the matrix plays a prominent role in improving the composite strength. In the present investigation, two types of launching vehicles, such as aluminum powder (primary) and CNTs (secondary), are considered to uniformly carry and launch ultra-fine nanoparticles (13 nm) into molten metal. The use of a secondary launching vehicle is identified to promote strengthening compared to a regular primary vehicle, as indicated by the good distribution observed from electron micrographs. CNTs are responsible for hybridizing the composite and also assist strengthening by anchoring to the matrix through the destroyed outer-walls and their axial orientation with the matrix. These results help us in attaining a strength of 197 MPa and a hardness of 93 BHN, with a minimal loss in ductility for the H-3 sample.

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1. Introduction

Clustering of the reinforcement particles is identified as a major cause of reducing the strength of cast metal matrix nanocomposites (MMnC) [1,2]. Pre-distribution of nanoreinforcement as a technique is revealed to circumvent the clustering of nanoreinforcements in the matrix [3]. However, pre-distribution of the nanoreinforcements by ball milling involves metal particles called launching vehicles that carry the nanoreinforcement into the molten matrix. Akbari et al. [4] ball milled Al and Cu particles with Al2O3 nanoparticles (1:1 weight ratio) independently and introduced the components into the metal melt by stir casting to achieve a uniform distribution. A similar launching vehicle methodology was used in Zeng et al. [5] and was revealed to assist in the fabrication of high strength composites of CNTs. Moreover, this technique of using a single launching vehicle to pre-distribute
nanoreinforcement has demonstrated a significant enhancement in the distribution of nanoparticles in the melt according to recent investigations [6–12]. Similarly, Haipeng et al. [13] proposed a novel method of alumina powder assisted CNTs that were reinforced in a magnesium matrix to improve the CNT distribution.

Moreover, reducing the size of nanoparticles to ultrafine nanoparticles promotes clustering in the matrix, which necessitates a better pre-distribution methodology unlike the regular use of a single launching vehicle (which is termed the primary vehicle in the investigation). In the present investigation, an attempt was made to distribute ultrafine nanoparticles (13 nm in size) in the cast sample by a stir casting route. We used two types of launching vehicles that were prepared by ball milling to launch the nanoparticles into the Al–Cu matrix [14], with an increase in the launching vehicle to a constant reinforcement (1.5 wt.% Al2O3) ratio, which is termed the launching vehicle to reinforcement ratio (LVRR, by weight). In addition to aluminum powder serving as the primary launching vehicle, CNTs are also considered to act as secondary launching vehicles for part of the study, and a comparative analysis in terms of the mechanical properties was conducted. Various electron micrographs and X-ray techniques were used to identify uniformity of distribution in the matrix and element/ phases involved in the composite.

2. Experimental procedure

The materials involved in the present investigation include the Al–Cu alloy (3.9% Cu, 1.2% Mg, 0.3% Mn, 0.2% Fe and balance Al) as the matrix material; aluminum powder (75 μm) and CNTs (9 nm in diameter and 5 μm in length) as the primary and secondary launching vehicles, respectively; and ultrafine nanoparticles of Al2O3 (13 nm) as the reinforcement.

<p>| Table 1 – Various LVRRs considered in the study. |</p>
<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Ingredients of sample (wt. in grams)</th>
<th>Sample name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture containing primary launching vehicles (A)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15 g Al, 15 g nano Al2O3</td>
<td>A-1</td>
</tr>
<tr>
<td>2</td>
<td>45 g Al, 15 g nano Al2O3</td>
<td>A-3</td>
</tr>
<tr>
<td>3</td>
<td>75 g Al, 15 g nano Al2O3</td>
<td>A-5</td>
</tr>
<tr>
<td>Mixture containing primary and secondary launching vehicles (H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15 g Al, 14 g nano Al2O3, 1 g CNTs</td>
<td>H-1</td>
</tr>
<tr>
<td>2</td>
<td>45 g Al, 14 g nano Al2O3, 1 g CNTs</td>
<td>H-3</td>
</tr>
<tr>
<td>3</td>
<td>75 g Al, 14 g nano Al2O3, 1 g CNTs</td>
<td>H-5</td>
</tr>
</tbody>
</table>

The reinforcement mixture involving launching vehicles and nanoreinforcements, as stated in Table 1, were individually placed in a stainless steel jar containing 138 g of tungsten carbide balls (20 in number). Each mixture was milled in a planetary mill at 300 rpm for 2 h [4]. These mixtures were then preheated to 200 °C before their addition [3] into the Al–Cu metal melt maintained at 700 °C, i.e., above the liquidus temperature of the matrix alloy (584 °C) and primary launching vehicle (660 °C), followed by soaking for 30 min. After adding the reinforcement, the mixtures were stirred for 4 min at 200 rpm in a two-stage stirrer. The entire setup was maintained under an argon gas environment, as shown in Fig. 1. A boron nitrate coating was applied to all of the surfaces exposed to the casting environment to isolate the castings from iron contamination because this could show an adverse effect on composite strength according to Taylor et al. [15] and Sajjadi et al. [16].

The ball-milled mixtures were examined in terms of the reinforcement distribution among launching particles by transmission electron microscopy (TEM–Tecnai G2 FEI). The cast samples were qualitatively and quantitatively analyzed, and energy dispersive spectroscopy (EDS) was performed with a field-emission gun scanning electron microscope (FEG-SEM, Fig. 1 – Schematic representation of the experimental setup.
Zeiss Supra). The tensile properties of the cast samples, which were fabricated according to ASTM E8 standards, were determined using a TUE-C-600 universal testing machine (UTM).

3. Results and discussion

The addition of readily available nanoreinforcements into a metal melt decreases wettability and induces cluster formation, resulting in composites with low strengths. As mentioned earlier, investigations [1,2,4] suggest the pre-distribution of the nanoreinforcement by ball milling as an effective procedure to incorporate reinforcements in the metal melt, i.e., with the help of a single (primary) launching material with a fixed LVRR. In our recent investigation [17], the use of single launching vehicle with an increase in LVRR is noted to improve the distribution and hence the strength of the composite. Therefore, in the present study, the increase in LVRR by use of combined, i.e. primary and secondary launching vehicles was investigated and compared with our earlier study.

3.1. Pre-distribution

The distribution of the nanoreinforcements in the ball milled mixtures (with launching vehicles) before incorporation into the metal melt called as pre-distribution; is clearly revealed by means of dark field transmission electron microscope (TEM) images, as shown in Fig. 2(a)–(f) [18]. However, from our recent investigation [17], selected area diffraction (SAD) patterns obtained for the samples illustrate the good distribution of the nanoreinforcement by means of low intensity rings for sample with high LVRR, unlike spots observed in low LVRR sample, revealing either clusters of nanoreinforcement or reinforcements of micro-size.

This illustrates that the increase in LVRR during ball milling and the use of secondary vehicles are observed to further improve the distribution of nanoparticles. Among the different ball milled samples considered (Table 1), H-3 is noted to attain the best pre-distribution of Al₃O₅ among the rest of the samples of Fig. 2(a)–(f).

3.2. Experimental observations

In introducing the pre-distributed mixtures of increasing LVRR into the metal melt, some quantity of reinforcement rejection is noted to occur after attaining the cast samples. This rejection of particles is also identified by Valibeyglo et al. [12]. In his investigation, it is observed that the smallest Al₃O₅ nanoreinforcement rejection of 20 wt.% from the metal melt was observed for 1.5 wt.%; in contrast, the sample did not show the best compression strength. Therefore, it can be noted that the rejection of particles was mandatory, although no tangible relationship could be identified between the quantity of the rejected particles and the strength of the composite. Hence, a uniform distribution is the main factor influencing the composite strength irrespective of the quantity of particles rejected from the melt.

3.3. Distribution of the nanoreinforcement in cast samples

To understand the dispersion of nanoreinforcements in as-cast samples, FEG SEM micrographs are considered. As CNTs have melting temperatures above that of the casting temperatures used in the investigation, they also act as a secondary

![Fig. 2 – TEM images of the ball milled mixture showing a pre-distribution of (a) A-1, (b) A-3, (c) A-5, (d) H-1, (e) H-3, and (f) H-5.](image-url)
reinforcement, thus transforming the cast composite into a hybrid composite. Fig. 3(a)–(c) depicts FEG SEM images of H-1, H-3 and H-5, respectively, which illustrate a notable improvement in the distribution of nanoparticles and CNTs, with an increase in LVRR. Furthermore, H-5 is noted to attain the best distribution of CNTs as well as nanoparticles, unlike H-1, which possesses a poor distribution.

Because CNTs wet surfaces with a surface tension between 100 and 200 mN/m, their wettability with relatively high surface tension liquid aluminum (865 mN) has a bias [19]. In understanding the wettability of CNTs in the matrix, the stem of CNTs was observed by FEG SEM. Fig. 4(a) depicts a CNT stem of H-3 cast samples, and Fig. 4(b) indicates a CNT pull-out region. This reveals that the CNT is surrounded by a void, indicating poor wettability with the matrix, which correlates to a negligible load transfer from the matrix to the CNT, and as a result, the strength of the nanocomposite is expected to deteriorate, as noted by Bustamante et al. [19]. Such surrounded voids are not observed in the other cast samples. This suggests that the H-5 cast sample would attain the best tensile strength as a result of the best distribution of nanoreinforcements in the matrix and due to absence of surrounded voids.

### 3.4 X-ray diffraction analysis

Fig. 5(a)–(c) presents XRD plots of H-1, H-3 and H-5 cast samples, respectively. From Fig. 5(a)–(c), it can be noted that all of the XRD plots of the cast samples contain peaks that are identical, with those of Al–Cu matrix, with an acceptable error of 5%, illustrating the absence of intermetallic phases. However, the H-3 cast sample in Fig. 5(b) contains an Al$_3$Cu peak, which is a regular peak seen in Al–Cu alloys [20].

As XRD gives average property of the phases present and if the amount of the phase/element is less than 5 wt.%, then on the average, collectively, it cannot give any diffraction (kinematical diffraction condition does not satisfy, where minimum number of planes are required to have diffraction) and thus very difficult to detect. Thus, grains coming across an incident beam of electrons to produce intensity in X-ray, is very much minimal and thus cannot be detected [21]. Thus, X-ray mapping analysis is conducted to identify phases below 5 wt.% of the sample.
3.5. **X-ray mapping analysis**

X-ray mapping analysis is employed in this investigation to identify the compounds that are involved in the H-5 nanocomposite. In correlating the Al, C and O maps of Fig. 6(a)–(g), it is clear that the intensity is highest for O and C. This illustrates that Al₂O₃ nanoparticles are coated on the periphery of CNT, which could assist in the good wettability of the CNT and Al₂O₃ with the matrix. Other intermetallic phases marked in Fig. 6(h) are regular phases of the matrix alloy [20]. The Fe map is produced from X-ray mapping; however, Fig. 7 indicates a 0 wt.% of Fe compared to 0.2 wt.% present in the received matrix alloy. Therefore, this does not represent Fe contamination, as it could degrade the composite strength [15].
Fig. 6 – Elemental X-ray maps of the H-5 composite.
3.6. Mechanical properties

From our previous publication as illustrated in Table 2, it can be noted that the A-5 sample attained the highest strength of 202 MPa through the expense of ductility (1.9%) by making use of single launching vehicle. However, the H-3 cast composite of the present investigation using combined launching vehicles, attained a 197 MPa of strength with a better ductility of 3.9% compared to the A-5 sample. However, in correlating the mechanical properties of the H-3 composite with Fig. 4(a) and (b), it can be concluded that the destroyed CNTs would assist in improving the composite strength. This destruction of CNTs during ball milling is also noted by Bustamante et al. [22]. These observations may be due to destroyed outer walls, resembling the petals of a flower, as illustrated in Fig. 4(a). These petals of CNTs create a highly uneven surface between CNTs and the matrix during solidification. This uneven surface (petals) could aid in pinning the CNTs to the matrix. Furthermore, during solidification, the matrix is expected to solidify between petals of CNTs, creating a small region of matrix bound between the petals, which is called a splat. During application, the load is transferred from the matrix to the CNTs via splat surfaces, as shown in Fig. 4(b). Thus, the load is supported by the nanocomposite until the splat fractures, i.e., splat delamination occurs; such splat delamination is also noted to occur in composites fabricated using the plasma spray forming technique, as revealed by some investigators [23,24].

Table 2 – Mechanical properties of the various cast composite samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relatives density (%)</th>
<th>Brinel hardness number (BHN)</th>
<th>UTS (MPa)</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–Cu</td>
<td>98.89</td>
<td>58</td>
<td>96</td>
<td>6.5</td>
</tr>
<tr>
<td>Al/Al2O3 (direct)</td>
<td>94.58</td>
<td>68</td>
<td>106</td>
<td>1.2</td>
</tr>
<tr>
<td>A-1</td>
<td>98.24</td>
<td>72</td>
<td>169</td>
<td>4.9</td>
</tr>
<tr>
<td>A-3</td>
<td>98.17</td>
<td>85</td>
<td>185</td>
<td>3.2</td>
</tr>
<tr>
<td>A-5</td>
<td>98.08</td>
<td>94</td>
<td>202</td>
<td>1.9</td>
</tr>
<tr>
<td>H-1</td>
<td>97.2</td>
<td>106</td>
<td>173</td>
<td>4.2</td>
</tr>
<tr>
<td>H-3</td>
<td>97.8</td>
<td>93</td>
<td>197</td>
<td>3.9</td>
</tr>
<tr>
<td>H-5</td>
<td>98.1</td>
<td>86</td>
<td>192</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Hence, the interface is observed to partially improve due to destroyed outer walls assisting in the marginal transfer of the load from the matrix to CNTs, which reduces the prominent strength of the CNTs. Thus, these low strength CNTs participating in the load transfer mechanism tend to marginally increase the strength of the composite. The Al2O3 interface between the CNTs and the aluminum matrix is noted to aid in improving wettability and, as a consequence, enhances the composite strength [25]. However, some investigations illustrated enhanced strength in the absence of Al2O3 interface [26] as these destroyed CNTs that assist in the strengthening of the composite may be the cause of some conflicting observations made between researchers [22,25].

From Figs. 8 and 9, it is clear that the relative density and ultimate tensile strengths are observed to increase with the increase in LVRR. Larger voids are noted only in the H-3 cast sample. The theory behind such inconsistent results is the coating of Al2O3 on the periphery of CNTs. For the H-3 sample, Al2O3 reinforcement is uniformly distributed on the primary launching vehicle, as noted from the TEM image of Fig. 2(e), unlike H-1, where the Al2O3 reinforcement and CNTs are clustered, as in Fig. 2(e). This indicates that in the H-1 cast sample, due to the Al2O3 clusters on the CNTs, the wettability of the...
CNTs in the matrix is expected to improve, whereas in the H-3 sample, the very marginal coating of Al2O3 on CNTs is revealed, leading to poor wettability. Because the wettability is poor in the H-3 cast sample, a weak interface between the CNT and matrix is noted by the void formation, unlike in the H-1 sample. Uniformly distributed Al2O3 in H-3 and the CNTs (with good wettability or interface) in H-1 are noted to contribute to the composite strength. Moreover, the destroyed CNTs observed in the H-3 sample are noted to anchor to the matrix, which further enhances the composite strength, i.e., a higher strength compared to the H-1 cast sample is noted. The tensile results obtained are observed to be superior to some investigations, as indicated in Table 3.

A decrease in hardness and ductility with increasing LVRR is noted from Figs. 10 and 11 for the composite samples fabricated using secondary reinforcements. Although there is a significant loss in the strength of H-1 compared to H-3, the ductility is observed to improve as a consequence of the good wettability of CNT with the matrix, as also observed by Thakur et al. [27]. The marginal decrease in strength of the H-5 nanocomposite is attributed to the orientation difference in CNTs observed from Fig. 3. The orientation of CNTs in H-1 and H-3 is noted to run parallel to the loading direction, whereas sample H-5 illustrates a radial orientation, as shown in Fig. 3(c). According to Bakshi et al. [26], low CNT additions lead to their arbitrary orientation in the axial direction following iso-strain or the Voigt model, whereas a higher CNT addition results in the radial orientation in the matrix obeying iso-stress or the Reuss model. In accordance to this theory, the H-1 and H-3 samples obey the Voigt equation, illustrating high strength, contrary to the extremely low CNT contents (highest LVRR) in H-5, which are observed to obey the Reuss equation and possess low strength composites.

4. Conclusions

Ultra-fine nanoparticles possess a high tendency to cluster compared to nanoparticles, resulting in the fading of the composite strength. Here, in our study, ultra-fine nanoparticles are successfully distributed in the Al–Cu matrix using a stir casting route with CNTs as secondary launching vehicles. The key observations are as follows:

- The launching vehicle methodology is noted to significantly enhance the distribution of reinforcements and hence the composite strength.
- The use of a secondary launching vehicle (CNTs) is observed to be a better technique compared to a primary vehicle in strengthening the composite. Additionally, ductility is noted to improve using secondary vehicles.
- CNTs are revealed to play a dual role, i.e., as a launching vehicle and as a secondary nanoreinforcement, which transforms the composite to a hybrid composite.
- CNTs destroyed during ball milling are illustrated to assist in improving the strength of the composite by anchoring to the matrix via a splat surface.
- In addition to the destroyed CNTs, their arbitrary alignment in axial direction with the matrix is noted to further promote composite strength according to the Voigt model.
• The H-3 sample is identified to be an optimal ratio for attaining enhanced strength and hardness with minimal loss in ductility compared to other nanocomposite samples.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES