Abstract:
In this study, we report the processing, microstructure, and microhardness of aluminum-copper composites reinforced with multi-walled carbon nanotubes (CNTs). Composite powders were prepared by a high energy ball (HEB) milling process then consolidated by vacuum sintering and hot isostatic pressing (HIP) techniques. The specimens show a uniform dispersion of CNTs in the Al–Cu matrix with CNT content up to 1 wt.% and a cluster formation observed with higher CNT content of 1.5 wt.%. The specimens have a relative density of 92% to 95% for composites sintered by vacuum sintering and 93% to 96% for composites sintered by HIP. Microhardness of specimens increases with increasing CNT content up to 1 wt.% and then decreases due to the formation of CNT clusters. Microhardness is enhanced both by the dispersion strengthening effect of CNTs and by precipitation hardening of Al-Cu matrix.

Keywords: Carbon nanotubes; Metal matrix composite; CNT/Al-Cu composite; Microhardness.

1. Introduction

Because of the combination of the outstanding properties of the metal matrix and reinforcement materials, metal matrix composite (MMC) is one of the most important materials mentioned recently. This is due to their application in many industry fields such as aerospace, defense and security, mechanical, electrical, and electronics etc. Since carbon nanotubes (CNTs) were discovered by S. Iijima [1], CNTs have attracted enormous interest among researchers globally due to their special properties such as unique structures, very high mechanical strength, good thermal and electrical conductivity as well as chemical stability. Because of the above properties, CNTs have been used for reinforcing polymers, ceramics
and MMC to combine the best properties of CNTs and matrix materials [2-4]. Recently, using CNTs as reinforcements have been investigated and developed for manufacturing lightweight, high strength and high-performance MMCs [4-6]. In particular, the study and preparation of CNT/Al composites have also received special attention of researchers with the goal to create new materials with better properties for more demanding potential applications [6-9]. Besides of using pure Al as matrix material, numbers of works have been done and presented, in which Al alloys such as Al6061, Al2124, A356 and Al-Cu were used as matrix materials [10-17]. Among them, CNT reinforced Al-Cu matrix (CNT/Al-Cu) composites have exhibited some potential properties but only a limited number of studies have been done and presented. For example, Nam et al have presented a route to prepare the CNT/Al-Cu composite. Firstly, a molecular-level mixing process was used to preparing a CNT/Cu powder; the obtained powder was then mixed with Al powder using a planetary mill to create a CNT/Al-Cu composite powder. The composite powder was consolidated by spark plasma sintering (SPS) system. The obtained composites show a uniform dispersion of CNTs within the matrix. Yield strength and hardness increase by a factor of 3.8 and 2.3, respectively compared to Al–Cu matrix [13, 14]. In similar, Maqbool et al. also used a molecular-level mixing process using copper coated CNTs to prepare the CNT/Al–Cu composite powders, in which the mixing of CNTs was accomplished by ultrasonic mixing and ball milling. The powders were then pressureless sintered under vacuum followed by hot rolling. The obtained composites showed a uniform microstructure and dispersion of CNTs and with 1.0 wt.% uncoated and Cu-coated CNT/Al composites, the microhardness increased by 44 % and 103 % respectively compared to pure Al [16]. Meng and co-workers have also reported the result of in-situ synthesized CNT reinforced Al–Cu composites prepared by powder metallurgy. Nano-sized Cu particles precipitated on CNTs/Al powders, which were in-situ synthesized by combining CVD with ball milling for a short time. After powder metallurgy process, the CNT/Al–Cu composites were achieved, which showed that CNTs were well dispersed in the matrix and mechanical properties were enhanced [15]. According to above comments, almost presented works concerning to CNT/Al-Cu composites were mainly focused on using either molecular-level mixing process or in-situ synthesis to prepare the composite powders. The presented methods exhibited an advantage in uniform dispersing of CNTs in the matrix and good enhancement in mechanical properties of composites. However, a disadvantage of the method could be the formation of some oxidized phases during the preparation process, in which many chemical and thermal treatments were applied.

Thus, the aim of this study is to present the results of preparation of CNT/Al–Cu composites by using HEB milling process to mix of CNTs, Cu and Al powders followed by consolidation by using vacuum sintering and hot isostatic pressing techniques. Microstructure, density and microhardness of specimens were investigated and presented.

2. Experimental procedure

2.1. Materials

A commercial Al powder (99.5 % purity) with average particle size about 30 μm was used as matrix material (Fig. 1a). Cu powder (99.8 % purity) with an average particle size of 5 μm was used as sintering aid material (Fig. 1b). Carboxyl-functionalized multi-wall carbon nanotubes (MWCNT-COOH) (95 % purity), average outer diameter about 17 nm, length of 10-30 μm and calculated density of 1.85 g/cm³, were used as reinforcement material (Fig. 1c) [18].
2.2. CNT/Al-Cu composite preparation

Composite powders were prepared by mechanical alloying using high energy ball (HEB) milling technique as presented in our previous study [18]. Firstly, a uniform CNT solution was prepared by dispersing the MWCNT-COOH in ethanol by using ultrasonic vibration, after which the desired content of Al and Cu powder were added into the solution. The solution containing CNT, Al and Cu was continuously mixed by mechanical stirring with a speed of 400 rpm at 80 °C in order to remove slowly a part of ethanol to achieve a slurry state. Finally, the slurry was mixed and milled in a planetary ball milling machine for 6 h at a speed of 300 rpm, then followed by drying process at a temperature of 80 °C in vacuum to obtain the composite powders. Composite powders were noted as P0, P0.5, P1, and P1.5 with different compositions as presented in Table I. The composite powders were consolidated by vacuum sintering and HIP techniques at 620 °C for 1 h to prepare the pellet specimens 10 mm in diameter and 5 mm in thickness. In the sintering cycle for CNT/Al-Cu composite by HIP using the American Isostatic Press Inc’s equipment AIP6-30H the same conditions as presented in our previous study for CNT/Al composite were applied [18]. Firstly, the sample was heated to 400 °C and remained for 30 min to remove the organic content or vapour and then heated to the sintering temperature of 620 °C. Finally, the pressing process was carried out for 60 min under a pressure of 100 MPa. The sintered specimens are noted as S0, S0.5, S1 and S1.5 for specimens sintered by vacuum sintering and H0, H0.5, H1 and H1.5 specimens sintered by HIP corresponding to powders P0, P0.5, P1, and P1.5, respectively.

<table>
<thead>
<tr>
<th>Powder s</th>
<th>Composites (vacuum sintering)</th>
<th>Composites (HIP)</th>
<th>Al content (wt. %)</th>
<th>Cu content (wt. %)</th>
<th>CNT content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>S0</td>
<td>H0</td>
<td>96.5</td>
<td>3.5</td>
<td>0</td>
</tr>
<tr>
<td>P0.5</td>
<td>S0.5</td>
<td>H0.5</td>
<td>96.5</td>
<td>3.5</td>
<td>0.5</td>
</tr>
<tr>
<td>P1</td>
<td>S1</td>
<td>H1</td>
<td>95.5</td>
<td>3.5</td>
<td>1</td>
</tr>
<tr>
<td>P1.5</td>
<td>S1.5</td>
<td>H1.5</td>
<td>95</td>
<td>3.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

2.3. Characterization

The morphologies of starting materials, composite powders and sintered specimens were characterized using a field emission scanning electron microscope (FESEM, Hitachi S-4800). To investigate microstructure, the specimens were polished and etched by Weak reagent with composition of KMnO₄ 0.25M and NaOH 0.25M in 6 seconds to reveal the grain boundaries, then tested by an optical microscope (3D KEYENCE VHX-1000). The distribution of CNTs within Al-Cu matrix was performed on specimens sintered by HIP, specimens were polished and etched by solution of NaOH 0.5M + Na₂CO₃ 0.4M to dissolve part of the Al matrix and leave inert CNTs on the surface, then characterized by FESEM. X-ray diffraction (XRD) patterns of samples were recorded using a XRD, Bruker D4 Endeavor. The density of the specimens was determined by a densitometer based on the Archimedes principles. Microhardness tester (Shimadzu HMV 2000) was used to measure microhardness of sintered specimens under an applied load of 50 g for 10 s.
3. Results and discussion

Fig. 1d-f shows the SEM images taken on composite powders with different CNT contents obtained by the end of high energy milling stage. It can be seen that CNTs were dispersed separately for the content up to 1 wt.% in Al-Cu powders (Fig. 1d and 1e). For higher CNT content of 1.5 wt.%, some CNT clusters have formed as shown in Fig. 1f. As a result, good dispersion of CNTs within Al-Cu powders using HEB method was achieved only for the CNT contents up to 1 wt.%. This result is consistent with the results of previous work done by Chen et al [19], and Saheb [20], in which HEB milling was mainly used for CNT dispersion. The formation of CNT clusters with high CNT content will reflect in the microstructure, density and microhardness of sintered specimens that will be discussed in the next section.

![Fig. 1. SEM images of a) Al powder, b) Cu powder, c) CNTs and composite powder d) P0.5, e) P1, and f) P1.5](image)

![Fig. 2. Optical images of sintered specimens a) S0, b) S1, c) H0 and d) H1](image)
Fig. 2 a-d) shows the microstructure of specimens S0, S1, H0 and H1. The images show that the shape and size of Al particles after sintering by both HIP and vacuum sintering are nearly the same. However, as CNT content increases, a number of pores (black points) were found. It could be due to fact that the presence of CNTs impedes the densification process. The increase of pores was also observed in the specimens sintered by vacuum sintering compared to the specimens sintered by HIP. The existence of pores could be affected to relative density of specimens and will be further discussed in next section.

Fig. 3. SEM images of specimens a) H0.5, b) H1, and c) H1.5.

The presence of CNTs was observed within all specimens. The distribution of CNTs in specimen H0.5, H1 and H1.5 was shown in Fig. 3. Fig. 3a and 3b shows the distribution of CNTs within specimen H0.5 and H1, in which CNTs were well dispersed and good bonding with matrix. For specimen H1.5, some CNT clusters were observed at the boundary of Al particles and be consistent with the morphological study in the composite powders. The obtained results confirmed again that HEB method allows to uniformly disperse of CNT content up to 1 wt.% and the distribution of CNTs within matrix, and strongly depend on initial state of CNT dispersion in composite powder. In addition, the dispersion of CNTs
could not be improved during sintering process for both by vacuum sintering and by HIP.

XRD patterns of powder P1, specimen S1 and specimen H1 were shown in Fig. 4. The presence of Al peaks were detected and indicated at $2\theta = 38.473^\circ$, $44.74^\circ$, $65.135^\circ$, $78.229^\circ$ and $82.438^\circ$ corresponding to (111), (200), (220), (311) and (222) planes, respectively. No oxidation and carbide phases were identified in both composite powders and sintered specimens. Two typical peaks of Cu were detected in powder P1 at $2\theta = 43.298^\circ$, $50.434^\circ$ corresponding to (111), (200) planes, respectively. However, Cu peaks were not detected both in S1 and H1, instead of Cu, some peaks of CuAl$_2$ intermetallic phase were identified at $2\theta = 20.677^\circ$, $42.070^\circ$, $42.518^\circ$, $47.319^\circ$, and $47.728^\circ$ corresponding to (110), (220), (112), (310) and (202), respectively. This means that Cu content in powder P1 was transferred completely to the CuAl$_2$ intermetallic phase. Probably Cu has diffuses into the Al matrix, and then interacts with Al to form the CuAl$_2$ during the sintering process [15].

![Fig. 4. XRD patterns of powder P1, specimen S1 and specimen H1.](image)

A densitometer based on the Archimedes principles was used to determine the experimental density of the specimens and the theoretical densities were calculated using 1.85 g cm$^{-3}$ for MWCNT, 2.7 g cm$^{-3}$ and 8.9 g cm$^{-3}$ for Al and Cu. The dependence of relative density of specimens on CNT contents is shown in Fig. 5. The relative densities range from 92 % to 95 % for composites sintered by vacuum sintering and 93 % to 96 % for composites sintered by HIP. The relative density of specimens decreases if higher CNT contents added. Considering at higher CNT content, the uniform dispersion of CNT is more difficult to obtain. They tend to tangle together, hinder the mass transportation of diffusion and plastic flowing in the sintering and thus impede the densification process resulting in the decrease of the relative density of composites [21-23]. In addition, the presence of CuAl$_2$ is also a reason leading to reduce the relative density of composite. The density of CuAl$_2$ is 4.36 g cm$^{-3}$ and thus less than a half that of Cu [24]. When Cu phase is transferred completely into CuAl$_2$ phase by sintering as demonstrated by XRD study, the relative density of composites (referring to the initial phase relations) will decrease. As can be also seen in Fig. 5, the relative density of CNT/Al-Cu composite is lower than that of the CNT/Al composite prepared by HIP at the same conditions [18].
Fig. 5. Relative density of specimens with CNT contents and sintering temperatures.

Fig. 6 shows the microhardness of specimens consolidated by both vacuum sintering and HIP as a function of CNT contents. The microhardness is higher in the specimens containing higher CNT contents. The microhardness of the nanocomposites increased with CNT content up to 1 wt% and then decreased significantly. The microhardness increased by a factor of 1.9 and 2.1 for specimen S1 (109 HV) and H1 (130 HV) in compared with specimen S0 and H0, respectively. The microhardness of specimen H1 is considerably higher than that of the composite reported by Maqbool et al. [25]. This is attributed to the grain refinement and strain hardening introduced into the composite powders during ball milling. Maqbool et al. applied a milling time of 1 h to disperse CNTs in the matrix. This is a much shorter time compared to our work where a longer milling time of 6 h was used.

The enhancement of microhardness could be explained by either the dispersion strengthening and or the dislocation motion effects. If CNTs are well dispersed in the matrix,
we may assume a load transfer from Al-Cu matrix to CNTs resulting in a strain. CNTs own unique properties thus lead to an increase of the microhardness of the nanocomposite [18]. Besides, CNTs also act as the keys hindering the movements of dislocations and resisting the deformation and thus increase the microhardness of nanocomposite [18]. In addition, the precipitation hardening effect also helped to enhance the microhardness of Al-Cu matrix composites as evidenced by Nam and coworkers [14, 15]. The formation of CuAl2 phase boundaries resists the dislocations motions which leads to increase the material strength. This is made clear by the comparison of the microhardness of CNT/Al-Cu composites with that of CNT/Al composite without Cu prepared by HIP at the same condition. The microhardness of CNT/Al-Cu composites is significantly higher than that of the CNT/Al composite even though the latter has lower relative density. With 1 wt.% CNT content, the relative density of H1 (93.5 %) is lower in comparison with that of composite without Cu (94.6%), but microhardness of specimen H1 is nearly 2.3 times higher. The decrease in microhardness when CNT content higher 1.5 % could be due to the porosity formed by CNT clusters as evidenced by many authors [7, 18, 26-28]. In conclusion, the high microhardness of CNT/Al-Cu composite is due to the synergistic effect of CNTs reinforcement and precipitation hardening of Al–Cu matrix and also affected by the defect and uniform dispersion of CNTs during the preparation process.

4. Conclusions

The CNT/Al-Cu composites were successfully prepared by powder metallurgy method. The specimens showed a homogeneous dispersion of CNTs in the Al–Cu matrix with CNT contents up to 1 wt.% and a cluster formation with higher CNT content of 1.5 wt.% The specimens had a relative density of 92 % to 95 % for composites sintered by vacuum sintering and 93 % to 96 % for composites sintered by HIP. Microhardness of specimens increased with increasing CNT contents up to 1wt% and then decreased due to formation of CNT clusters. The microhardness increased by a factor of 1.9 and 2.1 for specimens containing 1 wt.% CNT sintered by vacuum sintering and by HIP compared to specimens without CNTs sintered by the same technique, respectively. The enhancement of microhardness is attributed to both by the dispersion strengthening effect of CNTs and to precipitation hardening of Al-Cu matrix.

5. References