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RAPID COMMUNICATION

Design and preparation of amorphous carbon nanotubes reinforced copper

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Carbon nanotubes (CNTs) reinforced copper (CNTs/Cu) is one of the most promising and extensively researched materials for replacing traditional Cu-based materials in high-load and high-current applications, particularly within the aerospace industry. Amorphous carbon nanotubes (aCNTs) are a type of carbon nanotubes characterized by the presence of mesopores distributed across their amorphous sidewalls, facilitating connectivity between the hollow core and the external environment. Therefore, we propose utilizing aCNTs as a reinforcing agent for Cu. The mesoporous structure of aCNTs facilitates the interpenetration of Cu into the aCNTs, thereby maintaining the continuity of the matrix properties. Experimental results demonstrate that Cu effectively penetrates the mesoporous sidewalls of aCNTs. Both pure Cu and aCNTs-reinforced Cu exhibit comparable electrical conductivity, while the hardness of the aCNTs/Cu composite is significantly enhanced. Additionally, both the density and porosity of aCNTs/Cu are lower than those of pure Cu, and the introduction of aCNTs helps to reduce the sintering temperature.

Keywords: amorphous carbon nanotubes, copper-based composite, interpenetrating composites, mesoporous, conductivity

PACS: 61.43.Gt, 61.46.–w, 61.48.De, 62.23.Pq

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1. Introduction

Owing to their superior electrical and thermal conductivity, Cu-based materials have found extensive applications in various sectors, including national defense, railways, aerospace, communications, electricity, and machinery manufacturing. However, the suboptimal mechanical properties and high density of Cu-based materials have constrained their performance and application. Research has demonstrated that incorporating carbon nanotubes (CNTs) can significantly enhance the hardness and strength of Cu. For instance, the ultimate tensile strength and elongation of Cu reinforced with 0.5-vol% CNTs (CNTs/Cu) are 79.8% and 54.9% higher, respectively, compared to pure Cu.[1] Additionally, CNTs/Cu composite wires can achieve a conductivity of 145% IACS.[2]

To achieve CNTs/Cu composites with increasingly superior properties, significant efforts have been devoted to addressing the interface issues between CNTs and Cu and enhancing their interfacial bonding. Without surface modification of CNTs, the amorphous carbon layers and dangling graphene sheets of CNTs facilitate Cu–C interdiffusion during the formation of CNTs/Cu composites, which is beneficial for improving the interfacial bonding of CNTs-Cu.[3–5] Compared to unmodified CNTs, oxygen-containing group-modified CNTs (O-CNTs) exhibit a higher affinity for Cu, particularly those modified with –COOH groups. The presence of O-containing groups not only facilitates electronic exchange but also reacts with Cu to form Cu–O–C bonds or Cu_2O, thereby further enhancing the mechanical properties of CNTs/Cu composites.[6] Consequently, most research has focused on utilizing O-CNTs to improve the properties of Cu. The tensile strength, conductivity, and elongation of O-CNTs/Cu composites can reach up to 601 MPa (when reduced graphene oxide is used as a co-strengthening phase),[7] 96.9% IACS,[8] and 41.7%,[9] respectively.

Furthermore, based on O-CNTs, the pre-fabrication of a metallic transition layer on O-CNTs or the introduction of other strengthening phases can contribute to enhancing the mechanical properties of CNTs/Cu composites. Studies have shown that Ni or Cr transition layers significantly improve the conductivity, interfacial wettability, and strength of CNTs/Cu composites. Specifically, Al transition layers enhance the conductivity of CNTs/Cu more effectively than Cr, although Cr layers aid in improving the conductivity of the composite over a wide temperature range. Additionally, Ni on the CNTs surface transforms into Ni_3C, which is the most effective in enhancing the properties of CNTs/Cu.[10,11] Moreover, the incorporation of an Ni transition layer and Cu_2O on the CNTs surface results in a 52.15% increase in tensile strength and a 56.67% increase in yield strength, while reducing the friction coefficient and wear rate by 66.8% and 62.3%, respectively.[12] Furthermore, by leveraging the network struc-

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ture of CNT aggregates, CNTs/Cu composites have achieved conductivity, current-carrying capacity, thermal conductivity, tensile strength, and elastic modulus values of 81.4% IACS, 2.5×10^5 A·cm^{-2}, 418 W·m^{-1}·K^{-1}, 392 MPa, and 40.2 GPa, respectively.[13]

The amorphous carbon nanotubes (aCNTs), whose sidewalls are adorned with mesoporous structures, can encapsulate materials without compromising their integrity. Therefore, this paper proposes the application of aCNTs as a reinforcing phase to enhance the overall properties of copper-based materials, utilizing the mesopores of aCNTs to help Cu penetrate into the interior of the aCNTs, forming an interpenetrating composite. This composite is expected to exhibit significant improvements in both the electrical and mechanical properties of the CNTs/Cu system.

2. Experimental methods

Hydroxy-modified, self-prepared aCNTs[14] were utilized as the reinforcing phase in Cu, whose mesoporous on the sidewall is circa 4 nm.[15] These aCNTs were dispersed in $Cu(NO_3)_2$ solution (40 g, 50 g, 60 g, 70 g, 80 g, 90 g, and 100 g in 100-mL deionized water), followed by thorough mixing through stirring (24 h). The resulting mixture of aCNTs and $Cu(NO_3)_2$, along with additional $Cu(NO_3)_2$, was then reduced using hydrazine hydrate. Subsequently, the composite powder (aCNTs content is 1 wt%) and pure Cu powder were sintered via spark plasma sintering at 750 °C under 45 MPa for 5 min, respectively. The structural and compositional characteristics of the aCNTs/Cu composite were analyzed using x-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). Electrical conductivity was measured using a four-probe resistance meter.

3. Results and discussion

Based on the principle of capillary adsorption, when the mesoporous structure of aCNTs sidewall is utilized to impregnate an aqueous solution containing a significant amount of copper precursors, the mesoporous solution can be effectively adsorbed into the cavity and mesoporous wall of the aCNTs, where it remains. As illustrated in Fig. 1, as the concentration of $Cu(NO_3)_2$ gradually increases, the filling efficiency improves. However, at excessively high concentrations, the filling efficiency may decline due to the influence of surface tension. Consequently, a moderate concentration of 0.8-g/mL $Cu(NO_3)_2$ has been chosen for further experimentation.

To further validate the integration of aCNTs with the precursors, an elemental mapping analysis was conducted on the composite powder of precursor@aCNTs after stirring and impregnation, as illustrated in Fig. 2. Figures 2(b) and 2(c) provide evidence that Cu is extensively embedded on the surface of the aCNTs in the presence of a substantial amount of carbon.

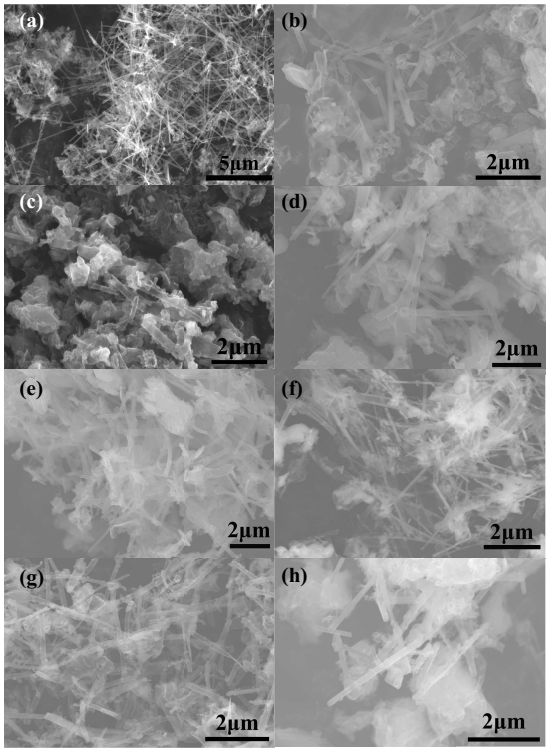


Fig. 1. Scanning electron microscopy analysis of the effect of different concentrations of $Cu(NO_3)_2$ solutions encapsulated by amorphous carbon nanotubes, raw aCNTs (a), 0.4 g/ml–1 g/ml of $Cu(NO_3)_2$ solutions encapsulated by amorphous carbon nanotubes [(b)–(h)].

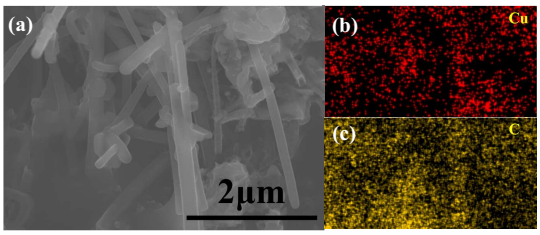


Fig. 2. Scanning electron microscopy (a) and mapping analysis of the $Cu(NO_3)_2$@aCNTs nanopowder [(b) and (c)].

The $Cu(NO_3)_2$@aCNTs nano-powders have been successfully reduced to Cu@aCNTs using hydrazine hydrate (Fig. 3). Additionally, the sintered bulks also consist of Cu. Due to the limited size of the obtained sample, a tensile test could not be conducted. Instead, the sample was directly fractured to examine its fracture morphology. As illustrated in Figs. 4(a) and 4(b), a significant number of dimples are present in the fractures of both samples. However, after the addition of aCNTs, no particles were observed within these dimples, and their shapes were irregular compared to those in pure Cu, with more uneven sizes. The particles observed in the fracture of the pure Cu sample are likely due to incomplete sintering, suggesting that the addition of aCNTs can improve sintering conditions. The presence of Cu@aCNTs at the fracture surface, as shown in Figs. 4(c) and 4(d), indicates that the incorporation of aCNTs alters the tensile properties of the matrix. The specific mechanisms behind this phenomenon will be explored

in future studies. Additionally, the distribution of nano-copper on the walls of the aCNTs/Cu composite (Figs. 4(e) and 4(f)) was noted, particularly concentrated in the mesopores, thus validating the hypothesis of mesopore filling.

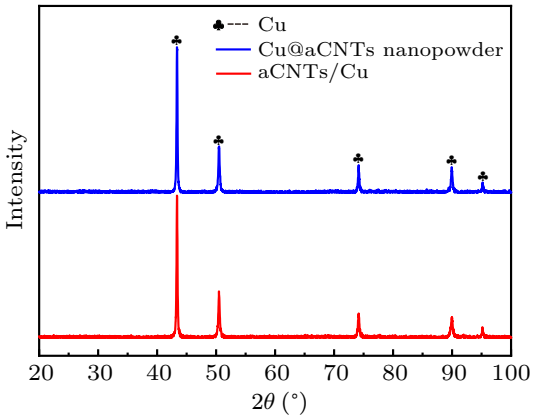


Fig. 3. XRD result of the Cu@aCNTs nanopowder and aCNTs/Cu composite.

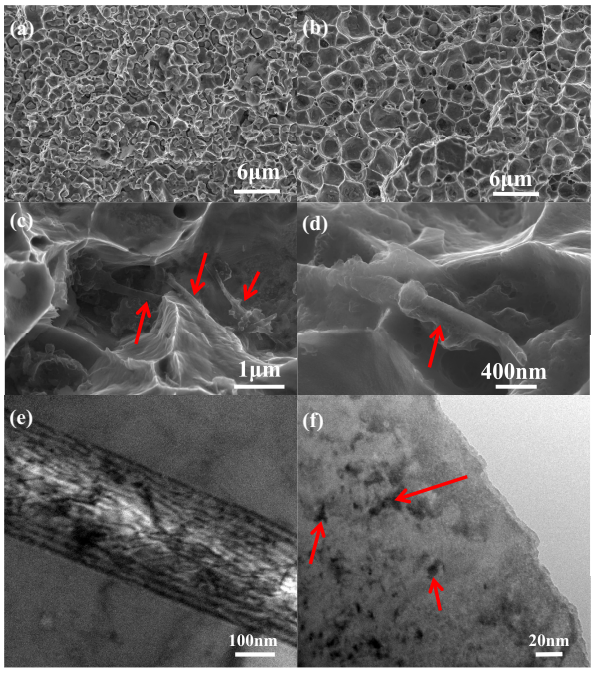


Fig. 4. Fracture analysis of pure Cu (a) and aCNTs/Cu (b), aCNTs at the dimples [(c) and (d)], and aCNT in Cu matrix analysis by transmission electron microscopy [(e) and (f)].

Following an initial analysis of the characteristics of the acquired sample (Fig. 5), it was observed that the density of the sample decreased while the porosity increased upon the incorporation of aCNTs (Figs. 5(a) and 5(b)). However, the conductivity remained superior to that of pure Cu (Fig. 5(d)), suggesting that the introduction of aCNTs imparted a degree of lightweighting to the Cu-based composites. Nonetheless, due to suboptimal sintering conditions, the compactness of the samples was not 100%, and the compactness of aCNTs/Cu was lower than that of pure Cu. Despite this, the aCNTs/Cu's conductivity exceeded that of pure Cu, indicating that the mesoporous structure of the aCNTs' sidewalls facilitates the preservation of matrix continuity, enhances electron conduction, and ensures electrical conductivity. Furthermore, the nanohardness of the aCNTs/Cu composite is greater than that of pure Cu (Fig. 5(c)), suggesting that aCNTs also contribute to enhancing the hardness of the matrix.

In addition, the authors in Ref. [16] has reported that the conductivity of CNTs/Cu composites decreases as the CNTs content increases. In this study, the doped aCNTs contained a higher proportion, leading to relatively lower electrical conductivity (Fig. 5(d)). When the CNTs content was comparable to that used in this study, enhancing the sintering conditions (80 MPa, at 900 °C for 5 min[17]) could yield CNTs/Cu composites with higher electrical conductivity than the aCNTs/Cu obtained here (Fig. 5(d)). Hot pressing sintering[18] resulted in CNTs/Cu composite with an electrical conductivity of 66.8% IACS, which is comparable to the electrical conductivity of aCNTs/Cu obtained in this study, but under more stringent sintering conditions (30 MPa, at 950 °C for 1.5 h). Therefore, the reinforced structure proposed in this paper holds promise for achieving composite materials with superior overall properties through further optimization.

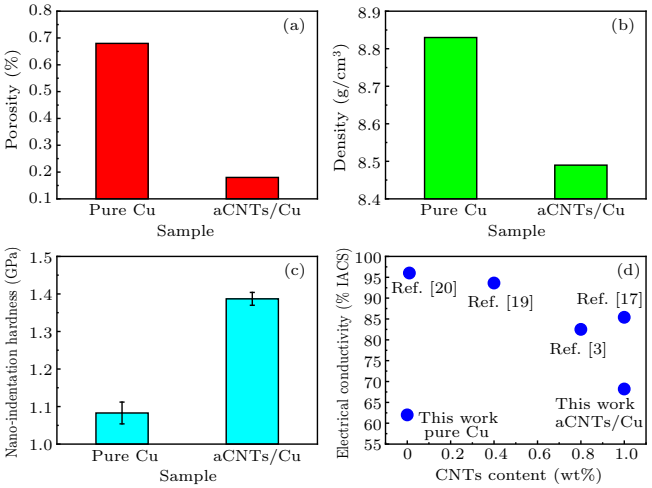


Fig. 5. Comparative analysis of porosity (a), density (b), and nano-indentation hardness (c) between pure Cu and aCNTs/Cu composite, samples' electrical conductivity of this work and reported works[3,17,19,20] (d).

4. Conclusion

In this paper, we proposed the concept of maintaining the matrix continuity of CNTs/Cu composites through the utilization of the mesoporous structure of aCNTs. Furthermore, by leveraging capillary forces, the $Cu(NO_3)_2$ solution was absorbed into the sidewalls of aCNTs, followed by SPS after reduction with hydrazine hydrate. The electrical conductivity and nanohardness of the resulting sample exceeded those of pure Cu processed under identical conditions, while its density was lower than that of pure Cu. This outcome confirms the successful realization of our proposed concept. The research presented herein offers a novel approach to the development of

CNTs/Cu composites, as well as CNTs-reinforced metal matrix composites in general.

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