Simple and efficient preparation of uniformly dispersed Carbon nanotubes reinforced Copper matrix composite powders by *in situ* chemical vapor deposition without additional catalyst

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Abstract
Carbon nanotubes (CNTs) reinforced Copper (Cu) matrix composite powders have been successfully prepared by *in situ* chemical vapor deposition (CVD) using Cu-0.6 wt% Al alloy powders without additional catalyst. The catalyst for CNTs growth is nano-copper particle (∼28 nm), and the interaction between Cu and Al2O3 would promote the formation of nano-copper particles (∼28 nm). The high quality multi-walled CNTs obtained dispersed uniformly on and well bonded to the composite powders. And the formation mechanism was discussed, the results show that part of the growth of CNTs follows tip-growth mode and the others without catalyst particles at the top follow the base-growth mode. This providing a simple and effective method for *in situ* preparation of CNTs/Cu composite powder with uniform dispersion of CNTs.

1. Introduction

CNTs are an ideal reinforcement to improve the properties of Cu due to their unique structure and exceptional mechanical, electrical and thermal characteristics [1–3]. CNTs reinforced Cu matrix composite is usually prepared by powder metallurgy [4, 5]. However, CNTs tend to aggregate and hardly bond to Cu due to strong van der Waals’ force among CNTs and poor wettability with Cu [6]. Therefore, it is critical to prepare the composite powders in which CNTs are uniformly dispersed and well combined to the powders before sintering, which will determine the properties of the bulk composite.

In order to remedy those problems, several approaches have been developed such as ball milling [7, 8], molecular level mixing [9, 10], and chemical vapor deposition (CVD) [11]. But ball milling will destroy the complete structure of CNTs to a certain extent and weaken the properties of the composite [8]. The amount of composite powder prepared by molecular level method is limited and costly. Comprehensive consideration, CVD is a better choice to solve those problems because uniformly dispersed CNTs can be obtained on the surface of the powders by this method. But first of all, it is necessary to introduce catalyst particles such as Fe, Co, Ni for the growth of CNTs and make them disperse uniformly on the surface of the powders [11–13], which is not easy to achieve.

In this study, a simple, efficient and large-scale CVD method for preparing CNTs/Cu composite powders has been proposed without additional catalyst (such as Fe, Co, Ni). Copper nanoparticles, which are catalysts for the growth of CNTs by CVD, precipitated uniformly on the surface of the powders through simple pretreatment of Cu-Al alloy powders. The obtained CNTs not only distributed uniformly on the surface of the powders but also well bonded to the powders. We have solved the problem of easy agglomeration of CNTs and poor wettability between CNTs and copper. Moreover, the method can ensure the integrity structure of CNTs,

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making the excellent performance of CNTs can be fully released. This method provides a new idea for in situ CVD synthesis of CNTs/Cu composite powders.

2. Experimental

2.1. Fabrication of the CNTs/Cu composite powders

Figure 1 shows the typical preparation process for the CNTs/Cu composite powders in this study. The gas atomized Cu-wt0.6% Al alloy powders (about 15 μm, Chinalco Luoyang Copper Co., Ltd.) were dispersed on a quartz sheet and placed in the tube furnace of the CVD apparatus. Then the powders were heated to 850 °C at 10 °C per minute in the flow of Ar (1000 ml min⁻¹) and H₂ (500 ml min⁻¹) and held for 30 min. Subsequently, the Ar flow was shut off and a mixture of H₂/C₂H₄ (1500/80 ml min⁻¹, v/v) was introduced into the quartz tube for 30 min. Then, the C₂H₄ flow and the power of tube furnace were shut off, when the powders cool down to room temperature under H₂ (1500 ml min⁻¹) atmosphere protection, the CNTs/Cu composite powders were obtained.

2.2. Characterization

Scanning electron microscope (SEM, FEI Quanta 450) and Energy dispersive spectroscopy (EDS, Philips Tecnai G2 F20) were used to observe morphology and analyse elements of the powders. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi) was conducted to analyze elemental composition on powder surface. A Bruker RFS 100/S Raman spectrometer (excitation wavelength: 532 nm) was used to investigate the quality of the CNTs. The detailed structure of the CNTs was characterized by a TEM.

3. Results and discussion

Figure 2(a) shows the SEM morphology of the raw Cu-Al alloy powders with sizes of 5–30 μm. There are only the peaks corresponding to elementary Cu matrix and no peaks to Al in XRD pattern of the powders as shown in figure 2(b). The reason is that the aluminium content is too low to be detected [14]. The Cu-Al alloy powders heated to 850 °C and held for 30 min in the flow of Ar and H₂ (figure 2(c)) have been studied. As can be seen in figure 2(d), Cu, Al and O elements had been detected on the surface of the powder by EDS. Further analysis by XPS (figures 2(e), (f)) showed aluminum exists in the form of alumina. Because there is trace oxygen in Ar and H₂ atmosphere, the external oxidation process of Cu-Al alloy powder would occur, that is, the aluminum element dissolved in the Cu-Al alloy powders diffused to surface and combined with oxygen to form Al₂O₃ [15]. It has been reported the Cu/Al₂O₃ system would promote the precipitation of Cu nanoparticles [16], which is necessary for subsequent growth of CNTs. Figures 2(g)–(i) shows the distribution of Cu, Al and O element. It can be found that Al and O elements are uniformly distributed on the alloy surface, indicating that aluminum oxide is uniformly distributed on the alloy surface.

Figures 3(a)–3(c) illustrate the SEM morphology of the CNTs/Cu composite powders as obtained. Since the high temperature calcination of CNTs in H₂ can effectively remove amorphous carbon without destroying the structure of CNTs, we use this method to calculate that the mass percentage of CNTs in the composite powders.
is 1%[17]. As shown in figure 3(a), the average grain size of Cu-Al particles is about 16.5μm, so we can calculate the mass of one Cu-Al particle and the mass of all the CNTs formed for each copper alloy particle. From figure 3(b) and 3(c), we can see that the surface of composite powder is covered by uniformly dispersed CNTs. Raman spectra measurements were performed on the CNTs synthesized at different temperatures in CVD reaction stage. The intensity ratio of the D-band and G-band peaks (ID/IG) can semi-qualitatively reveal that the CNTs are in good quality and they contain almost no defects [18]. As shown in figure 3(d), The ID/IG ratio of

Figure 2. (a) SEM image; (b) XRD patterns of the Cu-Al powders; (c) SEM image, (d) EDS element analysis; (e), (f) XPS core level spectra of the Cu-Al powders heated at 850 °C for 30 min; distribution of (g) Cu, (h) Al and (i) O element.

Figure 3. SEM images (a), (b), (c) of the CNTs/Cu composite powders; (d) Raman spectra of as-received CNTs; (e), (f) SEM images of the CNTs/Cu composite powders prepared using Cu-0.1wt%Al alloy powders.
CNTs obtained at 850 °C is less than 800 °C and 900 °C, which indicates that 850 °C is the most suitable for the growth of CNTs, and higher or lower temperatures will increase the defects of CNTs. No CNTs were found when the temperature was below 700 °C.

In addition, we found that the content of the CNTs on the composite powders could be tuned by adjusting the Al content in the initial Cu-Al alloy powders. Figure 3(e), 3(f) shows the SEM morphology of the CNTs/Cu composite powder prepared using Cu-0.1%Al alloy powder, it can be clearly seen that the amount of CNTs is significantly less than that prepared using Cu-0.6%Al alloy powder under the same conditions. This indicates that the growth of CNTs is closely related to aluminum element.

To reveal the formation mechanism of CNTs in this process, the detailed structure of the CNTs was characterized by TEM. As shown in figures 4(a)–(c), CNTs are multi-walled hollow tubular structures with a diameter of about 20 nm. Some nanoparticle catalysts were found in the samples. EDS analysis and Selected area electron diffraction (SAED) pattern (figure 4(d)) indicated that the nanoparticle coated by CNTs are nano-copper, and its size is about 28nm (region A). It indicates that the catalyst for CNTs growth in this study is nano-copper particle. But the prior related work was mainly to add catalyst particle elements into the alloy, such as Fe, Co, Ni and so on [11–13], whose process is complex and the stability was difficult to control.

As shown in figure 4(e), the aluminum element dissolved in the Cu-Al alloy powders diffused to surface and combined with oxygen to form Al2O3 at 850 °C, and the interaction between Cu and Al2O3 on the surface of powder promoted the formation of nano-copper particles, which had been verified by density functional theory [16]. No CNTs were obtained using pure copper powders and the amount of CNTs obtained using Cu-Al alloy powder is positively correlated to the content of Al, which also indicates that the interaction between Cu and Al2O3 would promote the formation of nano–copper particles for CNTs growth. Not all catalysts are present at the top of the CNTs obtained in this study, because part of the growth of CNTs follows tip-growth mode and the others without catalyst particles at the top follow the base-growth mode [19].

4. Conclusions

In summary, a simple and effective approach was developed to synthesize CNTs/Cu composite powders by in situ CVD using Cu-Al alloy powders without additional catalyst. In this study, the aluminum element dissolved in the Cu-Al alloy powders diffused to surface and form Al2O3, and the Al2O3 on Cu matrix promoted the formation of nano–copper catalytic particles for CNTs growth on the surface of powder. The obtained CNTs dispersed uniformly and well bonded to the powders. In addition, the content of the CNTs on the composite powders could be tuned by adjusting the Al content in the initial Cu-Al powders.
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References

[1] Long X, Bai Y J, Algarri M, Choi Y and Chen Q F 2015 Study on the strengthening mechanisms of Cu/CNT nano-composites Mater. Sci. Eng. A 645 347–56
[2] Xiong N, Bao R, Yi J H, Tao J M, Liu Y C and Fang D 2019 Interface evolution and its influence on mechanical properties of CNTs/CuTi composite Mater. Sci. Eng. A 755 75–84
[3] Radhamani A V, Lai H C and Ramakrishna S 2018 CNT-reinforced metal and steel nanocomposites: a comprehensive assessment of progress and future directions Composites Part A 114 170–87
[4] Wang X H, Guo B S, Ni S, Yi J H and Song M 2018 Acquiring well balanced strength and ductility of Cu/CNTs composites with uniform dispersion of CNTs and strong interfacial bonding Mater. Sci. Eng. A 733 144–52
[5] Chen X F, Tao J M, Yi J H, Li C J, Bao R, Liu Y C, You X and Tan S L 2018 Balancing the strength and ductility of carbon nanotubes reinforced copper matrix composites with microlaminated structure and interdiffusion interface Mater. Sci. Eng. A 712 790–3
[6] Chen X F, Tao J M, Yi J H, Li C J and Bao R 2018 Strengthening behavior of carbon nanotube-graphene hybrids in copper matrix composites Mater. Sci. Eng. A 718 427–36
[7] Yoo S J, Han S H and Kim W J 2013 A combination of ball milling and high-ratio differential speed rolling for synthesizing carbon nanotube/copper composites Carbon 61 487–500
[8] Bor A, Ichinkhorloo R, Uyanga B, Lee J and Choi H 2018 Cu/CNT nanocomposite fabrication with different raw material properties using a planetary ball milling process Powder Technol. 323 563–73
[9] Cha S I, Kim K T, Arshad S N, Mo C B and Hong S H 2005 Extraordinary strengthening effect of carbon nanotubes in metal-matrix nanocomposites processed by molecular-level mixing Adv. Mater. 17 1377–81
[10] Liu L, Bao R, Yi J, Li C, Tao J, Liu Y, Tan S and You X 2017 Well-dispersion of CNTs and enhanced mechanical properties in CNTs/Cu Ti composites fabricated by Molecular Level Mixing J. Alloy. Comp. 726 61–7
[11] Kang J L, Nash P, Li J J, Shi C S and Zhao N G 2009 Achieving highly dispersed nanofibres at high loading in carbon nanofibre-metal composites Nanotechnology 20 235607
[12] Yang X D, Liu E Z, Shi C S, He C N, Li J J, Zhao N Q and Kondoh K 2013 Fabrication of carbon nanotube reinforced Al composites with well-balanced strength and ductility J. Alloy. Comp. 563 216–20
[13] Meng X, Liu T, Shi C S, Liu E Z, He C N and Zhao N Q 2015 Synergistic effect of CNTs reinforcement and precipitation hardening in in situ CNTs/Al–Cu composites Mater. Sci. Eng. A 633 103–11
[14] Zhang X H, Li X X, Chen H, Li T B, Su W and Guo S D 2016 Investigation on microstructure and properties of Cu-Al2O3 composites fabricated by a novel in situ reactive synthesis Mater. Des. 92 58–63
[15] Correia J B, Caldas M P and Shohoji N 1996 Dependence of internal oxidation rate of water atomized Cu-Al alloy powders on oxygen partial pressure J. Mater. Sci. Lett. 15 463–8
[16] Shi L, Wang D S, Yu X H, Li L, Lu Z H, Feng C, Zhang R B, Qing S J, Gao Z X and Luo Q Q 2019 Adsorption of Cu2+ (n = 1–4) clusters on CuAl2O4 spinel surface: a DFT study Mol. Catal. 468 29–35
[17] Das N C, Yang K K, Liu Y Y, Sokol P E, Wang Z G and Wang H 2011 Quantitative characterization of vertically aligned multi-walled carbon nanotube arrays using small angle x-ray scattering J. Nanosci. Nanotechnol. 11 4995–5000
[18] Gohier A, Ewels C P, Minea T M and Djoudia M A 2008 Carbon nanotube growth mechanism switches from tip- to base-growth with decreasing catalyst particle size Carbon 46 1331–8
[19] Yang Y, Zhang H P and Yan Y 2019 Synthesis of CNTs on stainless steel microfibrous composite by CVD: Effect of synthesis condition on carbon nanotube growth and structure Composites Part B 160 369–83