Microstructure and Properties of Silver Matrix Composite Reinforced with Multi-walled Carbon Nanotubes

WANG Fei[1], LIU Jie[2 *], ZHANG Jiming[3 *], XIE Ming[3], LI Aikun[3], WANG Song[3]

(1. The Fourth Filial Company of 404 Company China National Nuclear Corporation, Lanzhou 732850, China;
2. Kunming Metallurgy College, Kunming 650033, China;
3. State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, Kunming 650106, China)

Abstract: Multi-walled carbon nanotubes/silver (CNTs/Ag) composite powders with 8% volume fraction of CNTs were prepared by chemical plating of Ag on the CNTs. CNTs/Ag composite was fabricated by powder metallurgy through high-energy ball milling, pressing and sintering, hot pressing and hot extrusion. The microstructure, electrical conductivity, tensile strength and hardness of the composite were measured. The results show that the interface bonding between the CNTs and the Ag substrate is improved by the chemical plating process, ensuring good processing performance of the resulting composite. The tensile strength of the composite increases by 65% and the hardness doubles, indicating a good reinforcement effect of CNTs.

Key words: carbon nanotubes; CNTs/Ag; microstructure; hardness; tensile strength
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多壁碳纳米管增强银基复合材料的组织与性能

王 飞[1]，刘 捷[2*]，张吉明[3*]，谢 明[3]，李爱坤[3]，王 松[3]

(1. 中核四〇四有限公司第四分公司，兰州 732850；2. 昆明冶金高等专科学校，昆明 650033；
3. 稀贵金属综合利用新技术国家重点实验室，昆明 650106)

摘 要：采用化学镀方法将银沉积在碳纳米管上，获得体积分数为 8%的多壁碳纳米管/银(CNTs/Ag)复合粉末，通过高能球磨、压制烧结、热挤压粉末冶金手段制备了 CNTs/Ag 复合材料，并研究了复合材料的微观组织、导电率、抗拉强度及硬度。结果表明，化学沉积工艺能够显著改善 CNTs 和 Ag 之间的界面结合，进而提高 CNTs/Ag 复合材料的加工性能。与纯银比较，CNTs/Ag 复合材料的抗拉强度增加了 65%，硬度增加了近 2 倍，表明 CNTs 对银具有较好的强化作用。

关键词：碳纳米管；CNTs/Ag；微观结构；硬度；抗拉强度

Since their discovery by Iijima in 1991[1], carbon nanotubes (CNTs) have been known as ideal reinforcement in composite materials for its high aspect ratios, large specific surface area and low density[2]. Large amount of literatures indicated that CNTs reinforced metal matrix composites, such as CNTs reinforced Cu[3-5], Al[6-8] composite, show high strength and electrical conductivity, good corrosion, wear resistance and processability, and are widely used.

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第一作者：王 飞，男，工程师，研究方向：有色金属合金。E-mail：tangseng_2156@qq.com
2*通讯作者：刘 婕，女，硕士，工程师，研究方向：稀有及贵金属材料加工，E-mail：114987164@qq.com
3*通讯作者：张吉明，男，硕士，高级工程师，研究方向：贵金属合金及特种合金粉末，E-mail：zjm_zane@ipm.com.cn

Silver matrix contact materials present good wear, welding resistance, high electrical conductivity, as well as low and stable contact resistance, thus are widely used in low-voltage apparatus, household appliances, auto electric and aerospace electronics[9-12]. Silver-graphite composites are widely used as contact materials currently. Silver in the composite presents good electrical and thermal conductivity. At the same time, graphite shows goods self lubrication with a lamellar structure, which contributes to improving the wear and welding resistance under high electrical current. However, application of the Ag-graphite composite is limited due to its severe arc erosion and poor processability caused by the low strength and poor bonding with silver matrix of graphite. Considering the advantages of CNTs, CNTs reinforced Ag composites have been fabricated using CNTs as the replacement of graphite [13-15].

In this study, CNTs were coated by Ag via electroless deposition method. Sintered CNTs/Ag body was fabricated by high-energy ball-milling and powder metallurgy using Ag-coated CNTs and Ag powder as raw materials. CNTs/Ag composite with high compactness was then obtained by extrusion and drawing of the sintered body, and the microstructure and properties of the composite were studied in detail.

1 Experiment

1.1 CNTs/Ag composites preparation

Multiwalls carbon nanotube grade of 20~80 μm length and 20~30 nm diameter was selected as raw materials in the experiment. Concentrated hydrochloric, nitric, sulphoric acid, were used for CNTs surface cleaning and acid treatment. The concentrated hydrochloric acid was used for dissolving any metallic contaminants in the CNTs powder by sonication of CNTs in hydrochloric acid for 5 h followed by soaking for 10 h and then filtration and drying in vacuum dryer for 1 h at 80°C. The produced CNTs powder undergoes further acid treatment by sonication in nitric acid and sulphoric acid mixture of the ratio (1:3) for 10 h followed by soaking for 10 h and then filtered and dried in vacuum dryer at 80°C for 1 h.

CNTs/Ag composite powders with 8% CNTs volume fraction were prepared by electroless Ag deposition on the CNTs. The chemical plating was conducted by adding silver-ammonia and VC solution into the delation solution with CNTs dispersed in. After stirring for 15 min, the CNTs were then filtered out and dried with Ag-coated CNTs obtained.

The coated CNTs and the Ag powder were mixed through a high-energy ball milling process using a planetary miller for 20 h at 150 r/min. The milled powder was pressed into a cylinder body with a diameter of 27 mm and then sintered at 850°C for 2 h. The sintered body was hot extruded at 800°C, then drawn into a wire with diameter of 2 mm and annealed at 600°C for 1 h. The complete process of fabrication of CNTs/Ag composites was illustrated in Fig.1. Also a comparative pure silver powder was prepared by the same electroless deposition method as mentioned before.

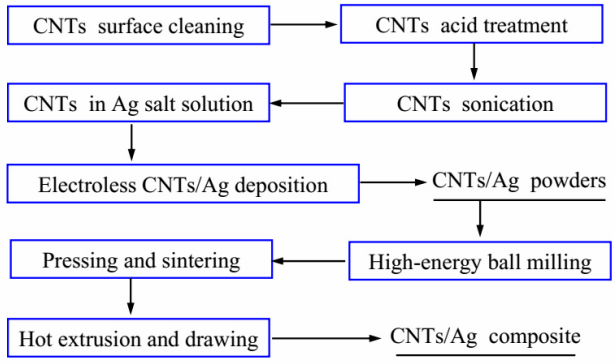


Fig.1 Schematic fabrication process for chemical plating preparations of CNTs/Ag composite

图 1 化学镀法制备碳纳米管/银(CNTs/Ag)复合材料的流程

1.2 Characterization method

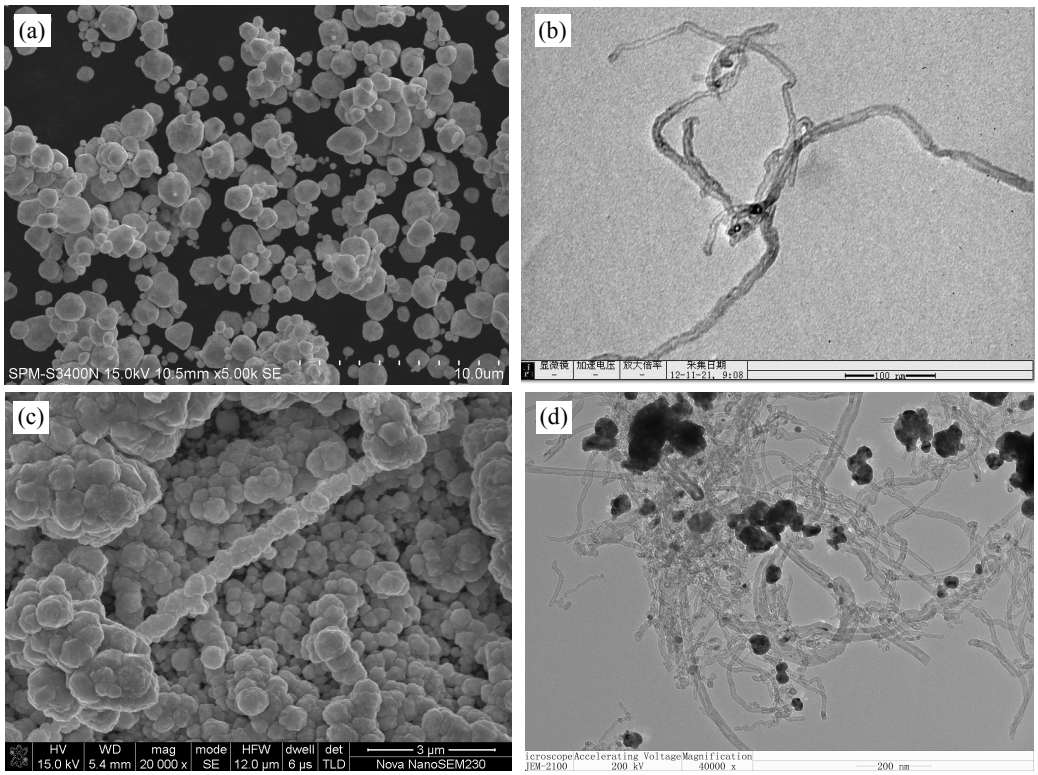
Density of the CNTs/Ag composite was obtained according to the Archimedes' principle. Tensile strength was tested using the mechanical testing machine on the wire with length of 120 mm. Hardness of the sintered body was tested under the condition of $HV_{0.1}$/15 s. Phase composition of the composite was analyzed by X-ray diffraction (XRD, RIGAKU-3014 X). Morphology of the powder, microstructure of the

composite and fracture morphology of the composite was observed using SEM (Nova Nano SEM 230) and transmission electron microscope (FEI Tecnai G-2 TF30 S-Twin).

2 Results and discussion

2.1 Electroless CNTs/Ag deposition

CNTs/Ag composite powders with 8% CNTs volume fractions are prepared by electroless Ag deposition on the CNTs. Fig.2(a) shows SEM micrograph of the electroless deposited Ag powder has spheroid particle shape with size of 100~200 nm. The CNTs were functionalized by acid treatment with sonication to modify the surface of the graphene structure by introducing functional groups such as carboxylic, carbonyl and hydroxyl groups on the CNTs surfaces. This process enhances the shortening of the CNTs length as well as the functionalized CNTs can be suspended in the solution. Fig.2(b) shows the TEM micrographs for the acid treated CNTs. After the acid treatment and sonication the agglomerated filaments were destroyed and the CNTs length was descended by shortening of the CNTs chains. Fig.2(c) shows SEM micrographs for the coated CNTs by Ag metal. Also the prepared CNT/Ag composite powders were investigated by TEM as shown in Fig.2(d). It was observed from these microstructures, the silver was deposited on the CNTs surface in coated type morphology.



(a). SEM - electroless Ag powder (化学镀 Ag 粉末-SEM); (b) TEM - CNTs (CNTs 的 TEM); (c). SEM - electroless deposited CNT/Ag powder (化学镀 CNTs/Ag 粉末-SEM); (d). TEM - electroless deposited CNT/Ag powder (化学镀 CNTs/Ag 粉末-TEM)

Fig.2 Images of CNTs/Ag powders　　图 2　CNTs/Ag 复合粉末图像

XRD pattern of the CNTs/Ag composite powders are shown in Fig.3, in which only peaks of Ag and CNTs can be seen. The results indicate there is no impurity in the coated CNTs and that part of the CNTs is not coated completely. Ag coating on the surface of the CNTs can improve the interface bonding between CNTs and Ag matrix and the dispersibility of CNTs in the CNTs/Ag composite.

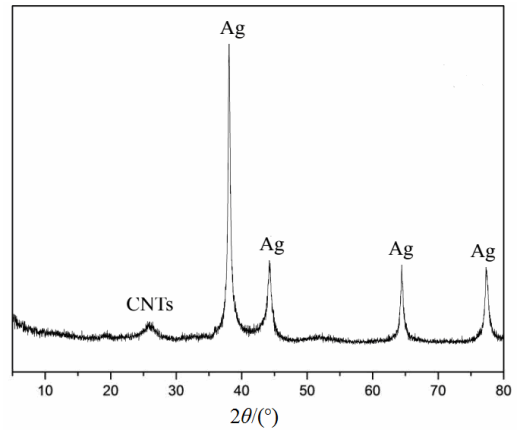


Fig.3 XRD patterns for CNTs/Ag composite powders

图 3 CNTs/Ag 复合材料粉末的 XRD 图谱

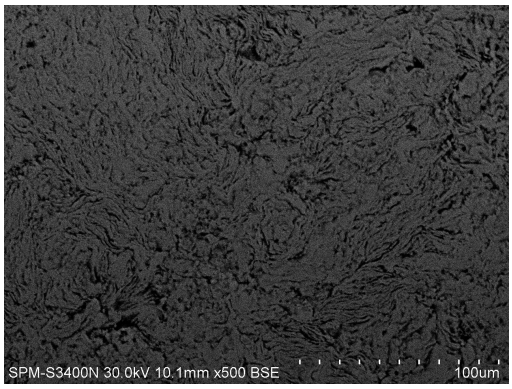


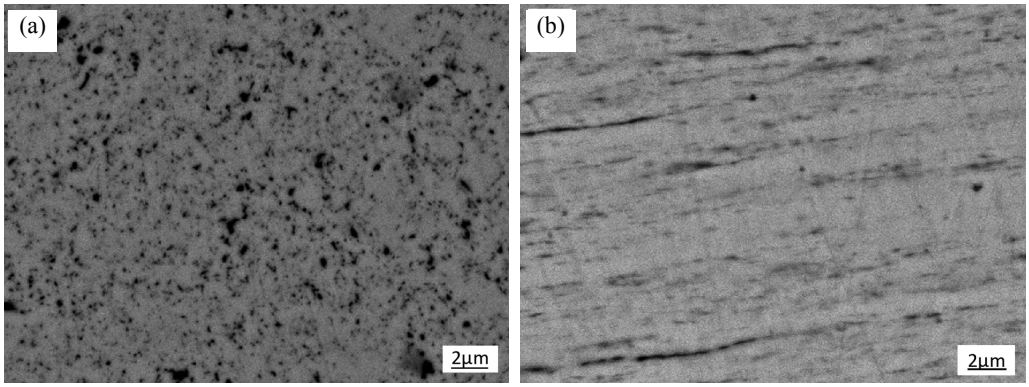
Fig.4 SEM images for sintered CNTs/Ag composites

图 4 烧结态 CNTs/Ag 复合材料 SEM 图像

2.2 Microstructure of sintered CNTs/Ag composites

Fig.4 presents microstructure of the CNTs/Ag composites after sintering. The second phase distributes uniformly in the composite and there is no obvious aggregation of CNTs. It means that the coating on the CNTs is benefit for reducing pores caused by non-wetting and enhancing compactness of the composite.

Fig.5 shows the microstructure of the composite after drawing.

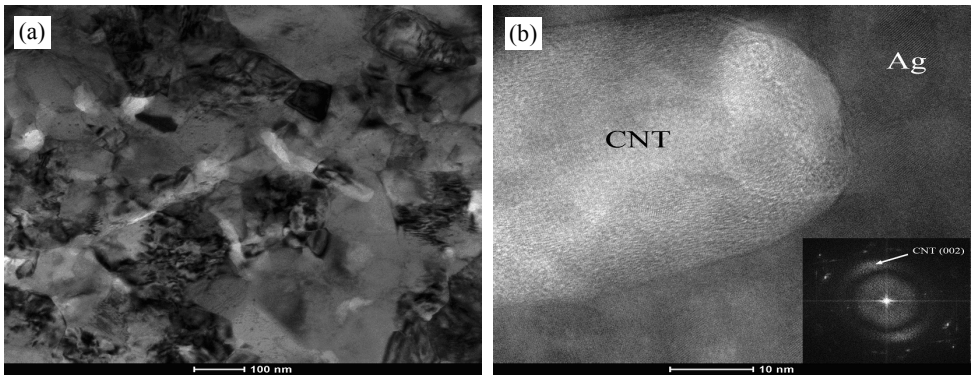


(a). Cross section (纵截面); (b). Longitudinal section (横截面)

Fig.5 SEM images for CNTs/Ag composite after drawing 图 5 拉拔后 CNTs/Ag 复合材料 SEM 图像

Compared with that before drawing as shown in Fig.4, CNTs exhibit less aggregation and more uniform distribution in the cross section. As seen from the longitudinal section in Fig.5(b), CNTs present orientation along the machining direction. Therefore, the machining process helps the dispersion of CNTs. Meanwhile, the orientated CNTs can improve the mechanical performance of the composite effectively.

TEM micrograph of the CNTs/Ag composite is shown in Fig.6. Fig.6(a) presents the good dispersity of the CNTs and Fig.6(b) exhibits the good interfacial bonding between CNTs and Ag, which is benefit for the reinforcement effect of CNTs.



(a). Low magnification (低放大倍数) /100 nm; (b). High magnification (高放大倍数) /10 nm

Fig.6 TEM images for CNTs/Ag composite　　图 6　CNTs/Ag 复合材料 TEM 图像

2.3 Physical and mechanical properties of CNTs/Ag composites

Stress-strain curves of CNTs/Ag composite and pure Ag as shown in Fig.7 indicate that the composite presents obvious characteristic of ductile fracture. Properties of the CNTs/Ag composite and pure Ag are listed in Table1. It can be seen that tensile strength and hardness of the composite reach 296 MPa and $HV_{0.1}$=80.1, which is approximately 1.65 times and 2 times higher than that of pure Ag, respectively.

The strengthening mechanism of CNTs reinforcement is thought to be related to the excellent mechanical properties and the unique structured characteristics of CNTs, and good bonding interfaces between CNTs and Ag matrix, shown in Fig.6(b). Orowan looping strengthening mechanism is important in CNTs/Ag composite, which is about fine precipitates strengthening. CNTs with nanometers dimension and good bonding interface with Ag matrix may effectively represent fine precipitates to strengthen the Ag matrix. With high aspect ratios and large specific surface area compared with graphite, CNTs are expected having more effectively impacts on the restrain the dislocation motion and crack propagation during tensile testing[16-18].

Fig.8 shows the fracture morphology of the CNTs/Ag composite. Large amount of small dimples can be seen in Fig.8(a). Fig.8(b) shows there are many pulling-out CNTs, indicating the loading-bearing effect of the CNTs due to its good interfacial bonding with matrix. Holes appeared at the binding site between CNTs and Ag due to the plastic deformation of Ag. With the increasing of stress, Ag fractured and CNTs presented pulling-out. It was also observed from the fracture surface some particles were found in the grain boundaries of the Ag matrix. The characteristic of fracture and the comparison of strength in Tab.1 demonstrate that CNTs improve the mechanical performance of CNTs/Ag composite effectively.

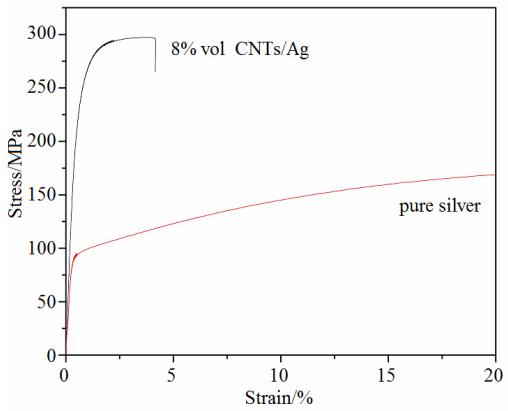


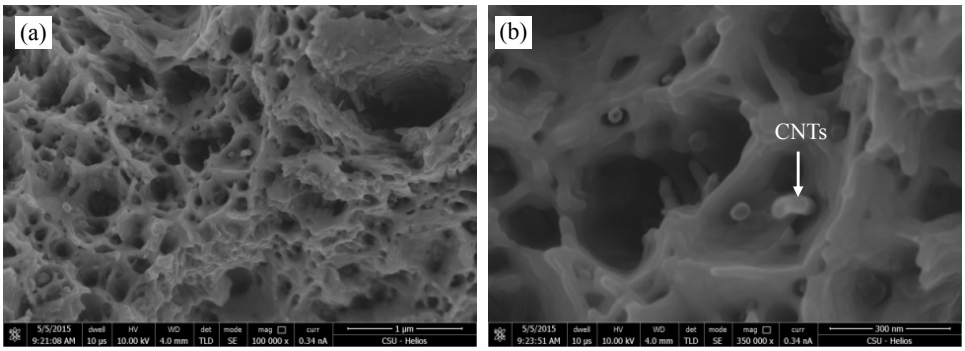
Fig.7 Stress-strain curves of CNTs/Ag composite and pure Ag

图 7　CNTs/Ag 复合材料和纯银的应力-应变曲线

Tab.1 Comparison of the physical properties of CNTs/Ag composite with pure Ag

表 1　CNTs/Ag 复合材料和纯银物理性能比较

Material	Density/ ($g \cdot cm^{-3}$)	Electrical resistivity/ ($\mu\Omega \cdot cm$)	Tensile strength/ MPa	Yield strength/ MPa	$HV_{0.1}$
CNTs/Ag	9.65	2.24	297	245	80.1
Pure Ag	10.49	1.59	180	25	36.2



(a). Low magnification (低放大倍数)/1 μm; (b). High magnification (高放大倍数)/300 nm

Fig.8 SEM images of fracture surfaces for CNTs/Ag composite

图 8 CNTs/Ag 复合材料断口表面 TEM 图像

3 Conclusions

In present investigation, the 8% volume fraction CNTs/Ag composite was successfully fabricated by high-energy ball milling and powder metallurgy method. The microstructure showed the CNTs distributes uniformly in the Ag matrix without aggregation of CNTs and the good interfacial bonding between CNTs and Ag. The tensile strength of the composite reaches 296 MPa, which is approximately double times of that of pure Ag. The fracture morphology of the CNTs/Ag composite showed a large amount of small dimples and pulling-out CNTs, indicating the good reinforcement effect of CNTs.

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