Study of Polyacrylic Acid Dispersing Pb-Sn-CNTs Composite Plating Solution

ZHENGXI Hu[1, a *], XiAOHUA Jie [2, b]

[1] Hezhou University, Hezhou Guangxi China 542899

[2] Faculty of Materials and Energy, Guangdong University of Technology, Guangzhou China 510006

[a]huzhengxi588193@126.com, [b]xiaohuajie@126.com

Keywords: Polyacrylic Acid; composite-plating; CNTs

Abstract. Polyacrylic acid (PA) was used as dispersant to disperse carbon nanotubes(CNTs) composite plating solution. Dispersion effect was characterized by measuring the absorbance value of the suspension. The relationship between the volume percentage of PA and the suspension of absorbance value was remarked; the relationship between the ultrasonic vibration time and the absorbance value were studied too. The results indicated that PA could disperse CNTs suspension effectively. When the optimum amount of PA was added into the suspension, the experiments showed that it had some dispersion stability, the narrow particle size distribution and small average particle diameter. The surface quality of the slide bearings were significantly improved as well.

Introduction

Materials surfaces strengthened by Nano composite plating technology are better than single materials in abrasion, corrosion and high temperature properties[1-5].CNT composites such as resin–CNTs,[6] ceramic–CNTs,[7] and metal–CNTs[8] have been investigated extensively for practical applications.

Multi-walled CNTs, with the concentric hollow structure of enclosed surface graphite cylinders, have the privileged self-lubricating properties [9], if the CNTs were used as nano-reinforcements to add into Pb-Sn anti-friction alloy, the friction coefficient of the material would decrease and wear properties of the composite materials would be improved.

CNTs dispersion in the bath of Pb-Sn composite plating is the basis for obtaining uniform dispersion and high-quality coatings in the process of CNTs composite plating. In the paper, PA as dispersants was added into Pb-Sn-CNTs plating solution, the dispersion characteristics and optimum dispersion conditions were investigated in the work.

Experiments

Pb–Sn electroplating bath composition: Pb(BF4) 280 g/L, Sn(BF4) 220 g /L, HBF4160 g /L, H3BO3 25g /L, hydroquinone 1g / L. The reagents were of analytical grade, bath pH =1. Demonized water was used in the experiments. The multi-walled carbon nanotubes (CNTs) used in this study are commercially available (Shenzhen Nanotech Port Co., Ltd. China), have a specific diameter of 60–100 nm, a length of 5–15um, and a purity of greater than 95%. And polyacrylic acid(PA) of 3 mL L-1 used as dispersant.

UV-2100 spectrophotometer (made by Beijing Raleigh Analytical Company) was used to measure the absorbance value of the CNTs composite solution.

1 g CNTs and 500 ml Pb–Sn Plating solution were added into a beaker, mixed with dispersing agent, it was magnetically stirred. Then it was ultrasonic shocked 10 minutes by BILON92-Ⅱ type ultrasonic cell grinder (operating time: 5 seconds, gap time:5 seconds, working frequency:60 times), ultrasonic power was 600 watts. Then, the suspension was placed standing for 10 minutes.

Take the upper serum of the beakers, and it was moved to a cuvette, the absorbance value was measured at a certain wavelength, the absorbance value was used to characterize the dispersion

properties of CNTs suspension, the relationship between the absorbance value and the PA content was recorded.

After being dispersed by the optimum dispersant, CNTs suspension was shocked by ultrasonic cell crusher for 10 minutes, then it was shocked by ultrasonic oscillations instrument. At different time points, a few of CNTs suspension was taken into the cuvette, the absorbance values were measured, the absorbance values curve and the ultrasonic oscillations time were remarked.

Results and Discussion

Dispersant content on dispersion effect. When the volume percentage of PA was 0.1%, 0.3%, 0.5%, 0.7% and 0.9%, absorbance value was measured respectively. As it is showed in Fig.1, with the increase of PA volume percentage, absorbance value increase firstly then decrease.

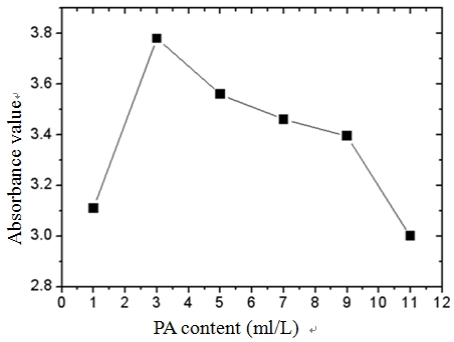


Fig. 1 PA content on dispersion stability

When the volume percentage content was 0.3%, the absorbance value of the CNTs suspension reached the maximum of 3.78. The image of the highest point absorbance value is showed in Fig.2; the optimum volume percentage of PA is 0.3%.

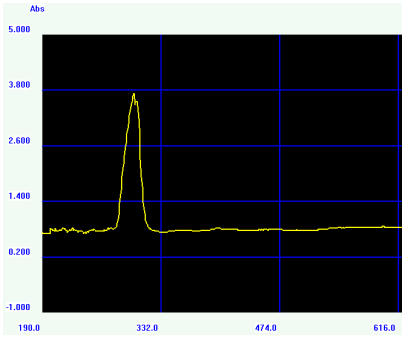


Fig.2 The UV absorption spectra of the optimal content of PA in the solution

PA is polycarboxylic acid electrolyte anion; By Coulomb (charge-charge), dipole- dipole interactions, hydrogen bonding and van der Waals forces and so on, PA were adsorbed on the surface of CNTs, which formed elastic layers covering around the nanotubes. Its interaction was limited; free energy was increased, so the repulsive force was generated. carbon atoms on the main chain of PA could also combined with carbon tube by few π bond [10], thus contributing to the PA absorbed on the surface of CNTs, the adsorbed hydrophilic molecules groups –COOH of PA could also produce partial ionization. Not only it could effectively improve the hydrophobic of CNTs, but also could reduce their CNTs reunion, In addition, PA macromolecules dissolved in the water form a hydrated gel undoubtedly, it increased the density of the solution in the continuous phase, thereby effectively prevented the sinking motion of the dispersed phase particles due to gravity, which also played the stability role.

Ultrasonic shock time on dispersion effect. As it can be seen from Figure 3, when the ultrasonic vibration time is 10 minutes, the absorbance value of CNTs suspension is about 3.78. When it was

shocked for 20 minutes, the absorbance value of the suspension obvious decreased. With the increase of the ultrasonic time, the absorbance value of the suspension decreased further, it indicated the CNTs suspension was unstable.

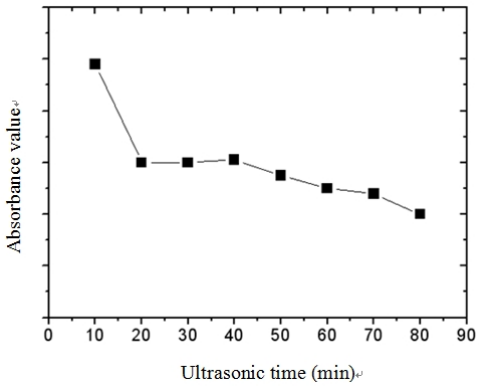
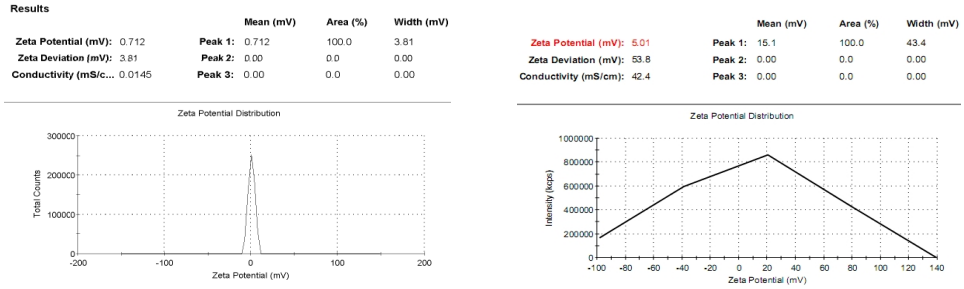


Fig. 3 The curve of absorbance value VS ultrasonic time

With the increase of ultrasonic time, it did not show an optimal ultrasonic dispersion time, and the absorbance value decreased gradually. Probably in the process of ultrasonic dispersion, there was the temperature factor of ultrasound medium. The ultrasonic time growth will lead to the increase of the suspension, for this reason, the particles in the suspension also increases the probability of collisions, and will further cause the second reunion of the c CNTs. Further, since the dispersion is unstable, the CNTs would sink for the gravity, resulting in the decreasing of the number of CNTs in the suspension. Therefore, the absorbance value decreased with the increase of ultrasonic time.

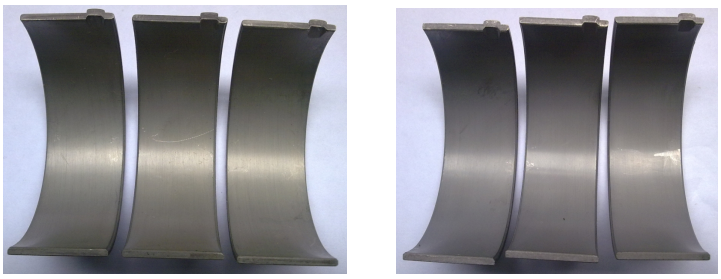
Zeta potential measurement. Figure 4 (a) is the Zeta potential of CNTs composite bath without PA; the result shows that its Zeta potential is 0.712mV. It is very unstable suspension status. If the suspension was placed standing for some time, the suspension would soon aggregate and form sediments. The main reason is the high surface area of the CNTs can intertwine from each other, depositing to the bottom of the container by the gravity. The composite bath is unfavorable for plating. If using the bath for composite electrode position, the coatings was rough, its surface roughness can not reach Ra6.3.



(a) No PA (b) Plus PA

Fig.4 Zeta potential of the Pb-Sn-CNTs composite solution

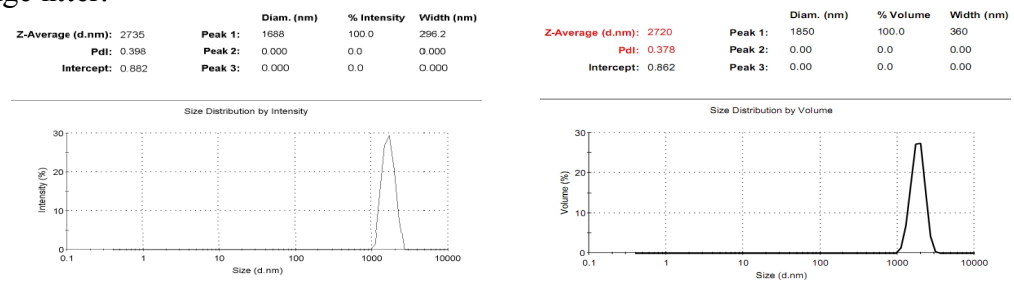
When 0.3% PA solution was added to the composite bath, Zeta potential has been improved from 0.712 mV to 5.01 mV, so the stability of dispersion has been improved, as it is shown in Figure 4 (b), Although Zeta potential did not reach the relatively stable range, when the bath was used for composite electrode position, the surface roughness of coatings decreased significantly, it can reach Ra6.3 or more, the result is shown in Figure 5.



(a) No CNTs (b) Plus CNTs

Fig.5 Images of sliding bearings

Measurements of Nan particles size. The Nan particles size in the bath was measured by dynamic light scattering method. Figure 6 (a) is the test picture without PA, its particle size is 2.735um, while PA Volume percentage is 0.3%, particle size is 2.720 um, it is shown in Figure 6 (b), and particle size value change litter.



(a) No PA (b) Plus PA

Fig. 6 size of the particles in the Pb-Sn-CNTs composite solution

There are a lot of aggregates in Pb-Sn-CNTs composite solution; these aggregates were opened due to the mechanical forces in the dispersion process, and the independent primary particles or small aggregates were formed. Crushing process is accompanied by the increase of particles surface area and the surface energy. While particles have been split smaller granule, they have strong tendency to reunite again. Without the dispersing agent and the mechanical force, the primary particles or small particles would aggregate again; consequently, the average particle diameter becomes large.

PA is ionic polymer dispersant. It can dissociate into charged groups. It was adsorbed on the particles surface, which may bring about electrostatic stabilization effect and the steric hindrance effect, and in some concentration range, the stabilizing effect strengthen as the amount of the dispersant increases.

The stabilizing effect of PA prevented solid particles from aggregate smaller particles, so the average particle size of the suspension was reduced; dispersion performance was improved inadequately, there may be two reasons, one was that the pH value of the bath was 1, the bath contains large amounts of hydrogen ions, inhibiting the dissociation of PA, which electrostatic stabilization mechanism has not been fully brought into play, on the other hand, the bath contained a large amount of metal ions, it was high concentration electrolyte solution, the thickness of the electric double layer depended on the type and concentration of ions. High concentrations of electrolyte would shrink the double electric layer; “double electrical layer compression effect”maked electrostatic stabilization mechanism could not fully play, so particle size did not change significantly.

Conclusions

(1)PA as dispersant was used to disperse the Pb-Sn-CNTs suspension, when the volume percentage content was 0.3%, the absorbance value of the CNTs suspension reached the maximum of 3.78. The absorbance value decreased with the increase of ultrasonic time. So, when the Pb-Sn-CNTs coatings were prepared, in order to get excellent coatings, magnetic stirring is necessary.

(2)When the carbon nanotubes were added into the Pb-Sn-CNTs plating bath in the best dosage, the suspension are unsteady, it had a narrow particle size distribution, and a small average particle diameter.

(3)Adding dispersants in carbon Pb-Sn-CNTs bath, though the stability of nano-suspensions had not been improved obviously, the surface roughness of the coatings could be significantly improved.

Acknowledgments

This work was supported by "Guangxi Education Department Key Laboratory of Symbolic Computation and Engineering Data Processing", and also supported by Guangxi Department of Education Program (Grant No. 200911MS248) and Guangxi Higher Education Undergraduate Teaching Reform Project (Grant No. 2015JGA360).

References

[1] Vanek D． An update on brush plating[J].Metal Finishing，2002，100(7):18～20.

[2] Straffrd K N，Subramanian C．Surface engineering: an enabling technology for manufacturing industry[J].Journal of Materials Processing Technology, 1995,53(8):393～403.

[3] Xu Jiang, Zhuo chengzhi, Han dezhong, et.al., Corrosion and erosion performance nano-particle reinforced Ni-based nitrided layer [J] plated Metal Materials and Engineering, 2010,39 (2): 318–324.

[4] Allahkaram S Ｒ，Golroh S，Mohammadalipour M．Properties of Al2O3 nano -particle reinforced copper matrix compositecoatings prepared by pulse and direct current electroplating[J]．Materials & Design,2011,32(8):4478-4484.

[5] Xu Bin Shi, Shi Yun Dong, Ma Shining, et al. Friction and wear properties of n-Al2O3P /Ni composite brush plating coatings [J] Materials Protection, 2002, 35 (6): 6-8.

[6] Chen, WX, Li, F, Han, G, Xia, JB, Wang, LY, Tu, JP, Xu,ZD, ‘‘Tribological Behavior of Carbon Nanotube-Filled PTFE Composites.’’ Tribol. Lett., 15 275–278 (2003)

[7] Flahaut, E, Peigney, A, Laurent, C, Marliere, C, Chastel, F, Rousset, A, ‘‘Carbon Nanotube–Metal–Oxide Nanocomposites: Microstructure, Electrical Conductivity, and Mechanical Properties.’’ Acta Mater, 48 3803–3812 (2000)

[8]Tu,JP ,Yang YZ, Wang, LY, Ma, XC, Zhang, XB, ‘‘Tribological Properties of Carbon-Nanotube-Reinforced Copper Composites.’’ Tribol. Lett., 10 225–228 (2001)

[9] Zhang Haiyan, Chen Yiming, et al. The effect of laser power on the formation of carbon Nan tubes prepared in CO2 continuous wave laser ablation at room temperature [J].PhysB: Condens Matter, 2003, 325: 224.

[10] Gong Shusheng, Tang Yiwen, Xu Liang, et al., Preparation and Characterization of multi-walled CNTs / polypropylene acid composites [J], Central China Normal University Learned Journal (Natural Science), 2008,42 (1): 77 -80.