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Copper thin coating deposition on natural pollen particles

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Abstract

We have deposited thin copper coatings on micro-sized natural pollen particles by electroless plating, using palladium as the catalyst, copper sulfate as the source of deposited metal, and formaldehyde as the reducing agent. A two-step pretreatment process is used to activate the pollen surface with stannous chloride and palladium chloride. The results of XRD, SEM, AES, and cross-section metallography show that the pollen particles are completely coated by a pure and porous FCC-structured crystalline copper film about 1 μm thick. The film is composed of spherical and some needle-shaped metallic copper particles. The latter are attributed to the strong aggregation tendency among neighboring nano-sized copper particles grown with rapid hydrogen release. We find that lightweighted pollen particles are good candidates for fabricating metallic composite microspheres with core-shell structures. © 2001 Elsevier Science B.V. All rights reserved.

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Keywords: Electroless plating technique; Copper; Pollen; Core-shell structure

1. Introduction

Metal powders possess good conductivity and have wide applications in various fields. However, in some practical cases applications are limited by their heavy weight. For this reason among others the development of metal composites is being investigated.

Electroless plating is a promising method for fabricating uniform metal coatings on any kind of substrate, such as glass, ceramic, plastic, or metal [1–4]. It is based on controlled autocatalytic redox reactions in aqueous solutions [5], does not need a current supply, and has no limitations on the type or shapes of substrates. Consequently, it has attracted considerable attention over the last few years in depositing metal coatings on particles and shows promise in fabricating metal composite powders.

Up to now, many metal–ceramic composites have been successfully prepared by electroless plating, with the ceramics as the core substrates and deposited metal films as the coating [6–11]. These composites

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have been widely used as strengthened and electro-contact materials. Organic polymer particles were also used as the core template for metal coatings to produce cellular intelligent materials [12,13].

Pollen is a kind of very lightweight natural organic powder. It possesses special structure with bioactivated nutrition components inside and firm sculptured ektexine outside. Conventionally, much effort is invested to breach the firm outside walls and extract the inside components for nutriments. However, here we pay more attention to utilizing the firm ektexine as a core template to produce lightweight metal composites for special applications.

The present study is concerned with depositing metallic copper coatings on natural pollen by copper electroless plating using palladium as the catalyst, copper sulfate as the source of deposited metal, and formaldehyde as the reducing agent. The pollen-cored copper composite spheres so obtained may be a novel kind of lightweight materials with good conductivity, similar to that of metallic copper.

2. Experimental

The surface-activation procedure was performed as follows. Pollen particles were first pretreated for good dispersibility in aqueous solution and for good mechanical adhesion for the following deposited metal particles. After that, the particles were sensitized by dispersing them in a 40 ml/l hydrochloric acid solution containing 7.5 g/l stannous chloride for 5 min. The particles were then isolated and activated by immersing them into a solution containing 0.25 g/l palladium chloride for 10 min, followed by reduction pretreatment using formaldehyde aqueous solution of low concentration.

Copper electroless plating was carried out by introducing the activated pollen particles into a blue copper electroless plating bath under magnetic stirring at ambient temperature. The bath was composed of 26 g/l $CuSO_4{\cdot}5H_2O$, 17.5 ml/l HCHO (37% aqueous solution), 43 g/l $KNaC_4H_4O_6{\cdot}4H_2O$, 21 g/l NaOH and a very small amount of composite stabilizer. Twenty minutes later the suspension was separated by filtration and rinsed with water three times. Finally, the dark brown product was dried at 40°C in a vacuum oven.

The morphology and structure of the obtained products were characterized by XRD, SEM, AES, and cross-section metallography, respectively. XRD patterns were recorded using a D/max RA X-ray diffractometer, SEM analysis of the product was carried out on a Hitachi S-450 type scanning electron microscope. Cross-section images were obtained with MEF-3 type optical microscopy. AES spectra were obtained on an AES-350 type spectrometer.

3. Results and discussions

Catalytic sites usually containing palladium nuclei should be created on the surface to be metallized for initiating electroless plating on nonmetallic species [14]. Natural pollen is not catalytic in nature and needs appropriate surface-activation before electroless plating. Pollen ektexine is mainly composed of sporopollenin, which has no hydrophilic or active groups on its surfaces. Stannous chloride sensitization is indispensable for palladium chemisorption on it. Therefore, we chose the empirical two-step pretreatment process for surface-activation with stannous chloride and palladium chloride.

It was reported that ultrasonic homogenization is very effective in electroless plating due to the physical effects of ultrasonic energy, such as effective stirring, microjet streaming, and the development of shock waves during the collapse of cavitation bubbles [15,16]. However, we did not find it to be effective. Under ultrasonic activation the lightweight pollen particles were subjected to floating and aggregating on the solution surface and could not be uniformly coated by the deposited copper. Many pollen particles remained bare and free copper particles were produced in the suspension. However, with magnetic stirring the pollen could be well dispersed in the solution without any break or damage. Copper deposition only occurred on the pollen surfaces. Free copper particles were hardly observed. Thus all particles could be uniformly coated by a copper layer. Therefore, magnetic stirring is selected for homogenization in this paper.

Fig. 1 shows the XRD patterns of pollen powders and the products. The "hill-like" peak in Fig. 1(a) indicates that pollen is amorphous. By comparing Fig. 1(a) with Fig. 1(b), we could see that there are

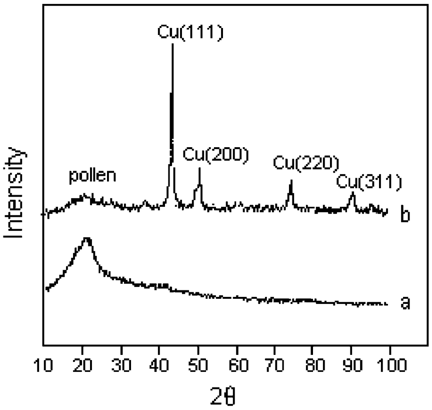

Fig. 1. XRD patterns of: (a) pollen; (b) the products.

diffraction peaks of FCC-structured crystalline copper in addition to that of pollen in Fig. 1(b). We could educe that the products are of copper–pollen composites. Based on Scherrer formula, the size of the copper particles is calculated to be 15.2 nm according to the Cu(1 1 1) main peak.

Fig. 2 shows the SEM micrographs of pollen and the products. In order to obtain the undamaged original image of the pollen, we did not coat the particles with gold to improve the conductivity. Therefore, the SEM micrograph of pollen in Fig. 2(a) is vague, since the non-metallized organic pollen was easily charged under the high electron accelerated voltage of the SEM. Fig. 2(b) and (c) shows that the copper coated quasi-spheres have narrow dimensional distribution ranging from 32 to 45 μm. Besides, they are similar to pollen in shape. All these suggest that a single metal-coated sphere is cored with a single pollen particle. The enlarged image of the product in Fig. 2(c) also indicates that the copper coating is porous and is composed of spherical and some needle-shaped copper particles.

The formation of needle-shaped particles may be explained as follows. As is known, the copper electroless plating reaction may be represented by

$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu\downarrow + 2HCOO^- + 2H_2O + H_2\uparrow \quad (1)$$

Reaction (1) indicates that copper ions are reduced to metallic copper with high purity by formaldehyde in the alkaline solution, accompanying with the hydrogen gas release. The nano-sized spherical copper particles, which are originally produced at the pollen/solution interface, possess high surface energy and have strong tendency to aggregate while depositing on the surfaces. With the influence of the rapid hydrogen release at the interface, some neighboring copper particles tend to aggregate along the gas flow and grow in lines. Thereby, needle-shaped particles were formed.

The cross-section image of the product is shown in Fig. 3. As can be seen, the 40 μm sized pollen particles are coated by a layer of bright copper about 1 μm thick. The copper coatings can be confirmed by the surface element analysis of the product. AES results in Fig. 4 illustrate that the unetched surface contains three kinds of elements: Cu, C, O; while that undergoing etching for 15 min only contains Cu, without C

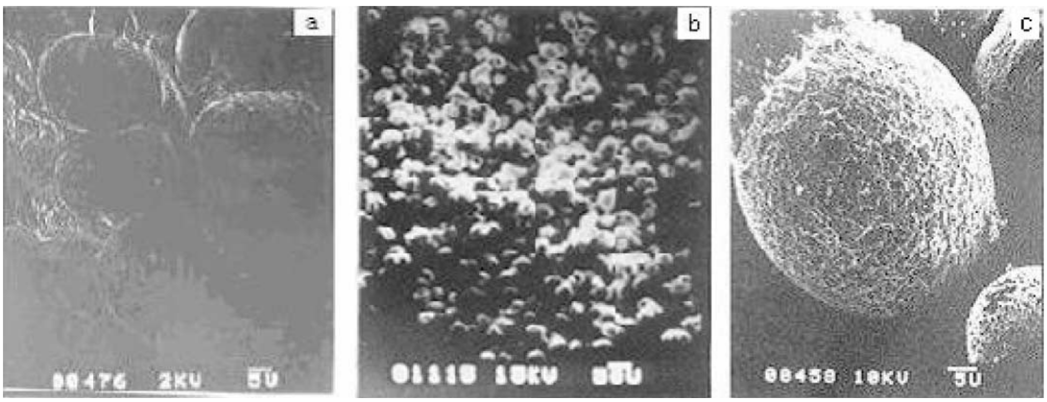

Fig. 2. SEM micrographs of: (a) pollen; (b) more product; (c) enlarged microstructure of the products.

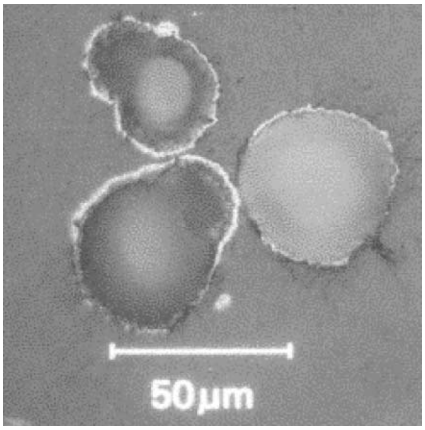

Fig. 3. Cross-section image of the product.

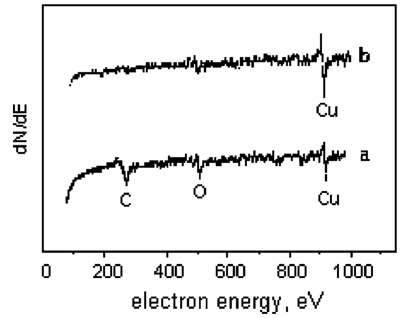

Fig. 4. AES patterns of products: (a) unetched; (b) etched for 15 min.

and O. It indicates that the copper coating freshly prepared has high purity. C and O existing on the unetched surface stand for contamination and are not from the pollen cores. Randomly selecting the analytical zone of the sample, we obtained similar results. That is, the pollen particles were completely covered by a copper layer.

4. Conclusions

In summary, we have successfully deposited thin metallic copper coatings on micro-sized natural pollen particles by copper electroless plating. Analysis results of XRD, SEM, AES and cross-section metallography show that the single pollen particles are completely coated by a pure crystalline copper film about 1 μm thick. The film is porous and is composed of spherical and some needle-shaped copper particles. Thus we find that pollen is a good candidate as a core template for fabricating lightweight metal composites with core-shell structure.

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References

[1] Y.A. Yang, Y.B. Wei, B.H. Loo, J.N. Yao, J. Electroanal. Chem. 462 (1999) 259.
[2] A. Li, G. Xiong, J. Gu, L. Zheng, J. Membr. Sci. 110 (1996) 257.
[3] A. Moebius, E. Tolls, Trans. IMF 77 (1999) B9.
[4] J. Shu, B.P.A. Grandjean, E. Ghali, S. Kaliaguine, J. Membr. Sci. 77 (1993) 181.
[5] J.R. Henry, Met. Finish. 97 (1999) 431.
[6] G.W. Wen, Z.X. Guo, C.K.L. Davies, Scripta Mater. 43 (2000) 307.
[7] W.S. Chung, S.Y. Chang, S.J. Lin, Plat. Surf. Finish. 83 (1996) 68.
[8] C.A. Leon, R.A.L. Drew, J. Mater. Sci. 35 (2000) 4763.
[9] S.Y. Chang, J.H. Lin, S.J. Lin, T.Z. Kattamis, Metall. Mater. Trans. A 30 (1999) 1119.
[10] O.A. Harizanov, P.L. Stefchev, A. Iossifova, Mater. Lett. 33 (1998) 297.
[11] P.B. Joshi, N.S.S. Murti, V.L. Gadgeel, V.K. Kaushik, P. Ramakrishnan, J. Mater. Sci. Lett. 14 (1995) 1099.
[12] S. Kishimoto, N. Shinya, Mater. Des. 21 (2000) 575.
[13] Y.M. Wang, C.Y. Pan, Eur. Polym. J. 37 (2001) 699.
[14] J.R. Henry, Met. Finish. 97 (1999) 431.
[15] J. Zhou, Y.Y. Zhao, W. Mo, C.G. Bao, R. Feng, Chin. J. Appl. Chem. 16 (1999) 99.
[16] M. Abe, Electrochim. Acta 45 (2000) 3337.