Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 37 (2011) 2181–2184

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

The preparation of Cu-coated Al_2O_3 composite powders by electroless plating

Hui Wang, Jianfeng Jia, Hongzhang Song, Xing Hu, Hongwei Sun, Delin Yang *

School of Physical Engineering and Laboratory of Material Physics, Zhengzhou University, Zhengzhou 450052, China

Received 18 January 2011; received in revised form 23 February 2011; accepted 3 March 2011
Available online 9 March 2011

Abstract

Cu-coated Al_2O_3 composite powders were synthesized by using the electroless plating method. The influence of the components proportion and the pH value of the plating solution on the Cu layer were analyzed with XRD and SEM. The results showed that the proportion of the plating solution components plays an important role for synthesizing the Al_2O_3/Cu composite powders. The content of copper in the composite powders could be effectively controlled by adjusting the content of copper sulfate and formaldehyde in the plating solution. Furthermore, the pretreatment of the Al_2O_3 powders is also a key factor to form a uniform Cu layer coating Al_2O_3 particles. The optimum technical parameters for producing Al_2O_3/Cu composite powders with uniform Cu coat were obtained.

© 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Key words : Cu coat; Electroless plating; Al_2O_3/Cu composite powders

1. Introduction

Al_2O_3 has been widely used in many fields due to its excellent mechanical properties, high hardness, excellent anti-corrosion and wearable characteristic. However, in some situations, the toughness, the electric conductivity and thermo-conductivity of the ceramic need to be enhanced [1–3]. Making suitable Al_2O_3/metal composite powders is a key step to solve the problems. However, one difficulty of fabricating Al_2O_3/metal composite powders is the poor wettability between the Al_2O_3 particles and metals [4,5]. Metal-coated ceramics particles with a ceramics core and a metallic shell can improve the wettability between the metal and the ceramics [6,7]. Among the preparation of metal-coated ceramic powders, Al_2O_3/Cu composites have attracted considerable researcher's attentions [8,9]. In general, metal coating can be prepared by many ways, such as precipitation, ball milling, electroless plating and reduction [10]. As for these methods, electroless plating has been recognized as one of the most effective techniques [11], which is based on the controlled autocatalytic reduction of metallic salt on target surface [12–16]. The composite powders prepared by this method have good dispersivity and the metal content in the powders can be also controlled effectively [17,18]. In our study, the electroless plating method was used to synthesize Cu-coated Al_2O_3 particles. According to the analyses of the samples we found out a promising pretreatment and plating process, which could result in a uniform coat of Cu particles on each Al_2O_3 particle.

2. Experimental

2.1. Pretreatment of Al_2O_3 particles

Al_2O_3 particles (Al_2O_3 powder from market) were used as the cores of the composite powders in the electroless plating. SEM (Fig. 1) examination revealed an irregular and polyhedral shape of the ceramics crystal with a clean and smooth surface of grains. The particles have a size distribution in the range of 3–5 μm, approximately. XRD pattern indicated the powder is pure α-Al_2O_3. In order to activate the surfaces of the particles, the particles must be pretreated. In this work, the Al_2O_3 particles were pretreated as follows:

(a) **Surface cleaning**: The Al_2O_3 particles were immersed into sodium hydroxide solution for 10 min to clean their surfaces.

---

* Corresponding author.
E-mail address: dlyang@zzu.edu.cn (D. Yang).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.03.013

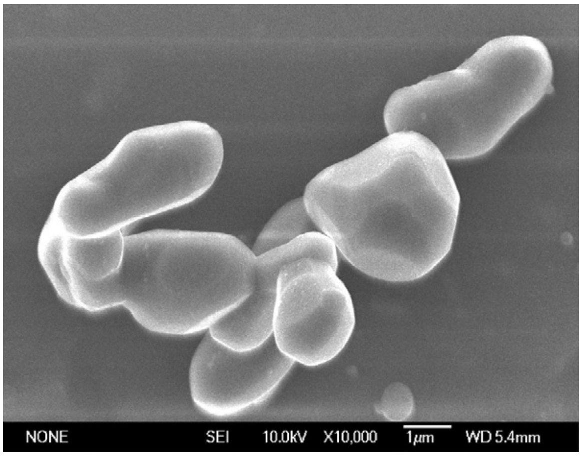


Fig. 1. SEM images of the Al_2O_3 powder.

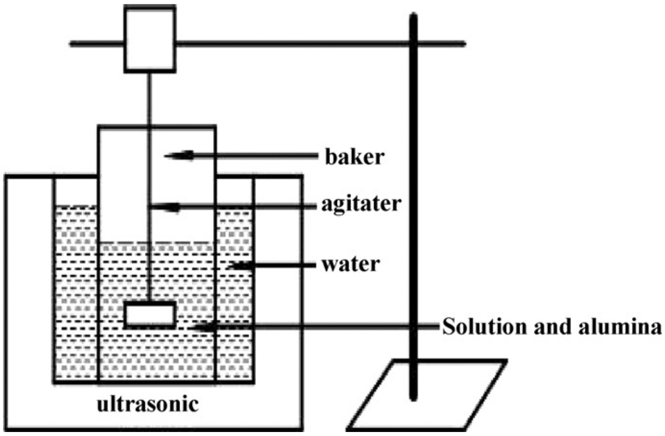


Fig. 2. Experiment set for the ultrasonic electroless plating.

(b) **Etching**: The cleaned Al_2O_3 particles were immersed in boiling hydrochloric acid for 15 min to coarsen their surfaces to improve the adhesion between the Al_2O_3 and copper particles.

(c) **Activation**: The Al_2O_3 particle surface is non-conducting, so the activation is necessary to improve its catalytic property. One-step sensitization-activation was introduced in this work. The etched Al_2O_3 particles were immersed in a palladium activation solution consisting of palladium chloride $PdCl_2$(0.3 g/l), stannous chloride $SnCl_2\cdot 2H_2O$ (16 g/l), sodium chloride NaCl (150 g/l) and hydrochloric acid HCl (60 ml/l), and stirred strongly at room temperature for 15–20 min.

(d) **Peptization**: The powder after activation was put into sodium hypophosphite solution and stirred for 15 min to remove the bivalent tin on the surface of micelle and make the palladium atoms expose, which would become the catalytic activity in the future electroless plating process.

After each step mentioned above, the powder was repeatedly washed using distilled water until pH = 7, and was dried after last step in an oven at 80 °C for 12 h.

2.2. Eletroless plating process

The copper plating solution is composed of copper sulfate solution (20–28 g/l $CuSO_4\cdot 5H_2O$, 30 g/l EDTA-2Na, 14 g/l $C_4H_4O_6KNa\cdot 4H_2O$ and 10 mg/l $K_4[Fe(CN_6)]\cdot 3H_2O$) and formaldehyde solution (24–30 ml/l HCHO, 100 ml/l CH_3OH and 16 g/l NaOH). Plating was carried out at 30 °C in a container with ultrasonic wave generator (CQF-50 CSIC Corp.). During the reaction process, the pH value of the system was kept as a constant by adding NaOH solution. The experiment set is shown in Fig. 2. Mechanical rabble and ultrasonic are necessary to make Al_2O_3 particles suspend in the solution and make the hydrogen produced during plating easily escape. After plating, the power was washed with distilled water and then dried in an oven at 80 °C for 12 h. The weight increment was determined by the calculation $\Delta W = W_2 - W_1$, where W_2 is the mass of Cu-coated powder and W_1 is the mass of Al_2O_3 powder before coating. The experiment was repeated several times to check the repeatability of the results and data of 5 experiments result were statistic.

The phase composition was analyzed by X-ray diffraction (XRD, PANalytical, Holland). The morphology of the powder was observed by using scanning electron microscope (SEM, JEM, Japan).

3. Results and discussion

3.1. Effect of the plating solution prescription

Fig. 3 shows the influence of $CuSO_4\cdot 5H_2O$ content in the plating solution on the copper content in the produced Al_2O_3/Cu powder. It shows that the weight increment increased with the increase of the content of $CuSO_4\cdot 5H_2O$. So the Cu content in the composite Al_2O_3/Cu powder can be controlled by controlling that of $CuSO_4\cdot 5H_2O$. It was also found that the gestating time became shorter with the increase of the content of $CuSO_4\cdot 5H_2O$. However, if the content of $CuSO_4\cdot 5H_2O$ was very high (this is commonly called as spontaneous decomposition of the solution) copper particles would not well coated the surface of the Al_2O_3 particles, which was unfavorable for obtaining a uniform Cu coating layer. Therefore, the content of

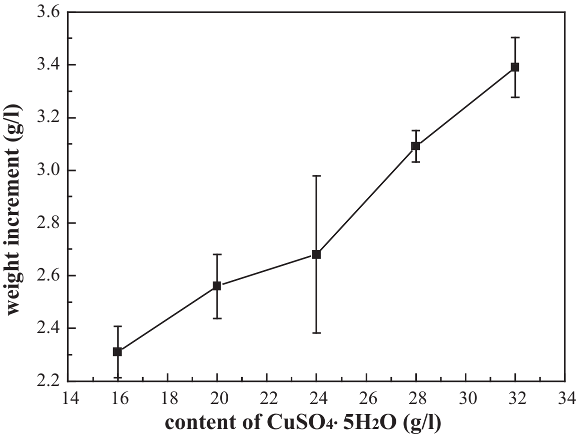


Fig. 3. Effect of the content of $CuSO_4\cdot 5H_2O$ on the weight increment.

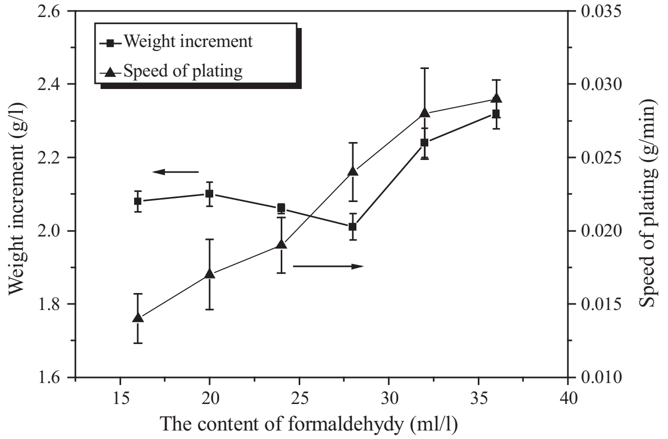


Fig. 4. Effects of the formaldehyde content on the weight increment and plating speed.

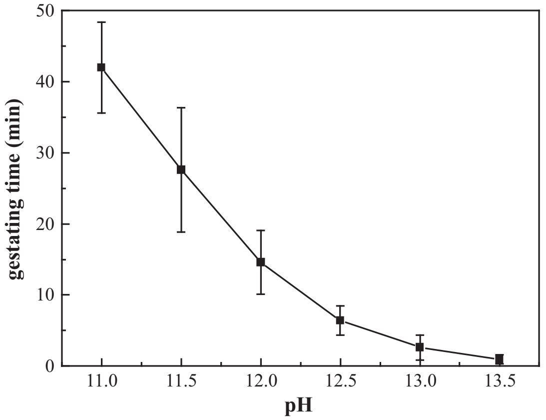


Fig. 5. Effect of different pH on the gestating time.

$CuSO_4{\cdot}5H_2O$ should be controlled in an appropriate range. Our result indicated that the suitable content of $CuSO_4{\cdot}5H_2O$ is about 30 g/l.

Fig. 4 shows the influences of formaldehyde content in the plating solution on the weight increment and on the plating speed respectively. From Fig. 4 we can see that changing the content of formaldehyde will not obviously affect the weight increment. However, we can also see that before the formaldehyde content reach 30 ml/l the plating speed increases greatly with the increase of the formaldehyde content. After the formaldehyde content beyond 30 ml/l, the increment of the plating speed becomes slower with the increase of the formaldehyde content. The reason of this phenomenon is possibly as follows: during the electroless plating process, the overall reaction is

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

It can be seen from the reaction that the high concentrations of formaldehyde can increase the driving force of reaction and result in the increase of the plating speed. On the other hand, the reaction speed is also controlled by the concentration of $CuSO_4{\cdot}5H_2O$ and pH. In our experiments the initial pH value and the concentration of $CuSO_4{\cdot}5H_2O$ were fixed. When the formaldehyde content is low, the reaction speed is controlled mainly by formaldehyde. With the increasing amount of formaldehyde more electrons will be provided, so the reaction speed increases. But the spontaneous decomposition of the solution would become more intense with increasing formaldehyde content, which prolongs the reaction time and reduces the weight increment. This, in turn, results in a depression of the plating speed. We think that is why adding more formaldehyde will not obviously increase the plating speed when the formaldehyde content exceeds a certain value (30 ml/l in our cases). The most suitable content of formaldehyde in our experiments is about 24 ml/l.

3.2. Effect of the pH value on the process of plating

The action of formaldehyde is affected by the pH value of the plating solution. When the pH value was less than 11, the reaction was not observed in 4 h in our experiments. Only if the pH value of the solution was greater than 11 it had the reduction ability. The pH value was adjusted by the sodium hydroxide solution in the experiments. With the increase of the pH value the driving force of reaction and the nucleation rate increase, and the reaction becomes much easy, which will shorten the gestating time. Fig. 5 shows the effect of different pH values on the gestating time. When the pH value was between 11.5 and 12.5, the gestating time was in the range of 10–20 min. And the following reaction would take place smoothly and spontaneous decomposition of the solution did not appear during the whole process. No free copper particles and uncoated Al_2O_3 particles were found in the composite powder.

At the higher pH value (12.5–13.5) the gestating time shortened. But the side reaction accelerated. Fig. 6 shows the XRD patterns of Al_2O_3/Cu at different pH values. The results indicated that the Cu_2O was formed when the pH value was higher than 12.8. The solution color became darkening after reaction and there was elemental copper attached to the beaker wall. Fig. 7(a) shows the SEM photograph of Al_2O_3/Cu powder at the pH = 13.6. The small particles were the segregation of free copper. It is clear that most of the Al_2O_3 particles were uncoated. When the pH = 14, the gestating time was nearly

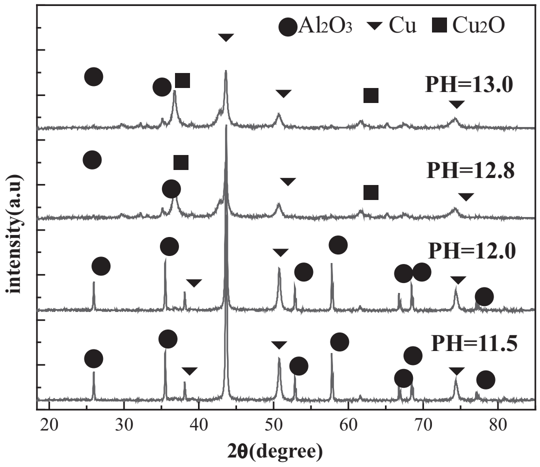
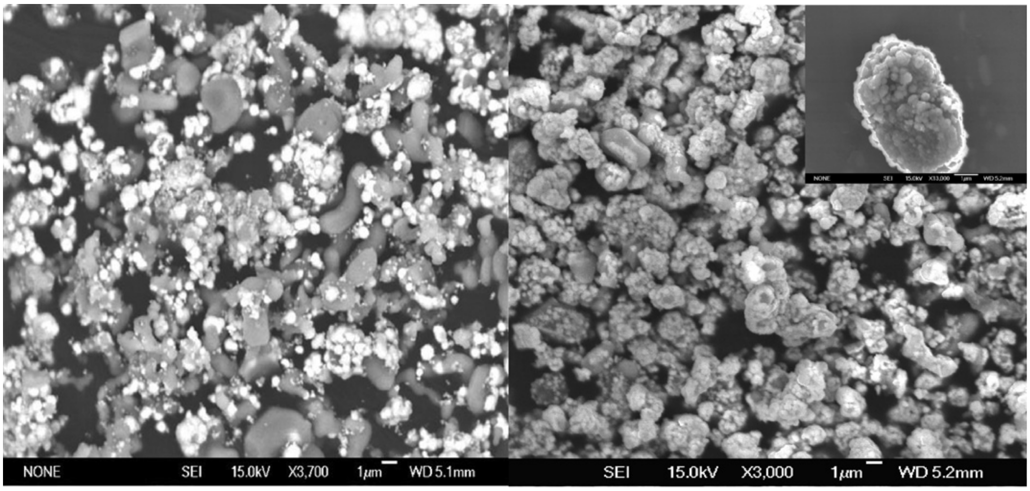


Fig. 6. XRD patterns of Al_2O_3/Cu at different pH values.



(a) pH=13.6 (b) pH=11.5

Fig. 7. SEM images of the composite powders (a) pH = 13.6 and (b) pH = 11.5.

zero. The plating solution spontaneously and completely decomposed, and the reaction lasted only a very short time. Because of the continuous depletion of sodium hydroxide in the whole reaction process the pH value became gradually lower. It was necessary to add the sodium hydroxide solution constantly during the plating process in order to maintain the pH value between 11.5 and 12.5.

Fig. 7(b) shows the overall morphologies of Al_2O_3/Cu powder produced by our optimum process with pH = 11.5. It shows that there are almost no free copper particles and no uncoated Al_2O_3 particles. Meanwhile, the powder produced by the optimum process also shows a good dispersivity.

4. Conclusions

The surface of each Al_2O_3 particle has been successfully coated by Cu particles by using eletroless plating. The Cu layer covering an Al_2O_3 particle was controlled by the content of $CuSO_4{\cdot}5H_2O$. The proportion between $CuSO_4{\cdot}5H_2O$ and formaldehyde as well as the pH value were found to play an important role in the uniformity of copper layer coating Al_2O_3 particles. The most suitable content of $CuSO_4{\cdot}5H_2O$ and formaldehyde are 30 g/l and 24 ml/l respectively. The preferable pH value scale ranges from 11.5 to 12.5. With these optimum conditions fine and uniformly Cu coated Al_2O_3 composite powder can been obtained.

References

[1] G.M. Shi, J.K. Han, Z.D. Zhang, H.Y. Song, B.T. Lee, Pretreatment effect on the synthesis of Ag-coated Al_2O_3 powders by electroless deposition process, Surf. Coat. Technol. 185 (2005) 333–337.

[2] P.F. Shi, X.Q. Cheng, Electroless Cu-plated Ni_3Sn_4 alloy used as anode material for lithium ion battery, J. Alloys Compd. 391 (2005) 241–244.

[3] A. Leon, G. Rodriguez-Ortiz, E.A. Aguilar-Reyes, Cold compaction of metal-ceramic powders in the preparation of copper base hybrid, Mater. Sci. Eng. A526 (2009) 106–112.

[4] O.A. Harizanov, P.L. Stefchev, A. Iossifora, Metal coated alumina powder for metalloceramics, Mater. Lett. 33 (1998) 297–299.

[5] W.B. He, B.L. Zhang, H.R. Zhuang, W.L. Li, Preparation and sintering of Ni-coated SiN_4 composite powders, Ceram. Int. 21 (2005) 811–815.

[6] C. Zhang, G.P. Ling, J.H. He, Co-Al_2O_3 nanocomposites powder prepared by eletroless plating, Mater. Lett. 58 (2003) 200–204.

[7] L.S. Sigl, P.A. Mataga, B.J. Dalgleish, et al., On the toughness of brittle materials reinforced with a ductile phase, Acta Metall. 36 (4) (1988) 945–953.

[8] J.H. Dai, X.Z. Liu, H.Z. Zhai, Z.F. Liu, J.T. Tian, Preparation of Ni-coated Si_3N_4 powders via electroless plating method, Ceram. Int. 35 (2009) 3407–3410.

[9] J.K. Han, F. Saito, B.T. Lee, Synthesis and characterization of nano-Ag spot-coated polymethylmethacrylate power by hydrothermal-assisted attachment method, Mater. Lett. 61 (2007) 4177–4180.

[10] G.J. Li, X.X. Huang, J.K. Guo, Fabrication of Ni-coated Al_2O_3 powders by the heterogeneous precipitation method, Mater. Res. Bull. 36 (7–8) (2001) 1307–1315.

[11] T. Puclin, W.A. Kaczmarek, Synthesis of alumina-nitride nanocomposites by successive reduction-nitridation in mechanochemically activated reactions, J. Alloys Compd. 266 (1–2) (1998) 283–292.

[12] W.H. Lin, H.F. Chang, Effect of chelating agents on the structure of electroless copper coating on alumina powder, Surf. Coat. Technol. 107 (1998) 48–54.

[13] H.J. Hwang, M. Toriyama, T. Sekino, et al., In-situ fabrication of ceramic/metal nanocomposites by reduction reaction in barium titanate–metal oxide systems, J. Eur. Ceram. Soc. 18 (14) (1998) 2193–2199.

[14] D.Y. Wang, C.L. Chang, K.W. Wong, Y.W. Li, W.Y. Ho, Improvement of the interfacial integrity of (TiAl)N hard coatings deposited on high speed steel cutting tools, Surf. Coat. Technol. 120–121 (1999) 388–394.

[15] K.M. Shu, G.C. Tu, The microstructure and the thermal expansion characteristics of Cu/SiCp composites, Mater. Sci. Eng. A 349 (2003) 236–247.

[16] G.P. Ling, Y. Li, Influencing factors on the uniformity of copper coated nano-Al_2O_3 powders prepared by electroless plating, Mater. Lett. 59 (2005) 1610–1613.

[17] Y.W. Li, H.D. Ding, H.Q. Hao, et al., Electroless plating improving the bending strength of copper graphite material, Rare Met. Mater. Eng. 27 (3) (1998) 182–185.

[18] R.Z.L. Gao, J. Guo, Preparation and characterization of coated nanoscale Cu-SiCp composite particles, Ceram. Int. 30 (2004) 401–404.