Sequential deposition of copper/alumina composites

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Ceramic-metal composites have drawn considerable interest due to their mechanical, thermal and wear resistant capabilities. High temperature processing of these materials when they are employed in electronic circuitry is not desirable, since elevated temperatures can irreversibly affect physical properties of the produced components. Wet chemical methods have potential advantages because they do not require thermal processing. Co-deposition of ceramic particles in metal plating baths has been extensively investigated during the past decades [1, 2]. However, the ceramic particle concentration in co-deposited materials was usually limited to below 30 vol.%.

Electrophoretic Deposition (EPD) is a technique, which is capable of producing ceramic coatings. Various ceramics and metals have been deposited from aqueous and organic suspensions [1]. Due to the hydrolysis of water, bubbles are formed on the electrodes during the aqueous EPD process. Using an organic suspension solves this problem. Ceramic coatings have been prepared in organic solvents, such as alcohol and acetone. Since the coatings produced by EPD are porous, it is possible to impregnate the ceramic skeleton with metals by a post-EPD electroplating (EP) process. Only a few publications have described this approach. Shrestha *et al*. [2] have prepared Ni/Al_2O_3 and Ni/BN coatings by this method, forming composites with particle concentration as high as 67 vol.%.

In the present work, the authors studied Cu/Al_2O_3 coatings by the sequential EPD-EP deposition method. First, a layer of Al_2O_3 was produced by the EPD method. The kinetics of the EPD was studied to control the thickness of the deposited ceramic layer. After EPD, the ceramic coating was dipped into a copper plating bath for impregnation. The resultant deposited coatings were characterized by Scanning Electron Microscope (SEM).

Al_2O_3 particles (Alcoa A-16SG) of 0.4 μm typical size were used for EPD. The acetone-based suspension solvent contained *n*-butylamine, which was added to increase particle charging. The suspension was made by mixing 220 ml of acetone (Fisher Scientific), 20 g Al_2O_3 and differing amounts of *n*-butylamine (Fisher Scientific). A Brookfield DV PRO II+ viscometer was used to measure the viscosity in order to evaluate the influence of the *n*-butylamine concentration on viscosity. The spindle shear rate was set to 100 rpm, while the temperature was maintained at 19.8 °C. The experimental results demonstrating the dependence of viscosity on the *n*-butylamine volume concentration are shown in Fig. 1. According to Zhao [33], 8 vol.% concentration of *n*-butylamine gives the highest deposition rate. In order to ensure both fast deposition rate and low suspension viscosity, 8 vol.% concentration of *n*-butylamine was used to produce EPD deposit.

Due to the agglomeration, after mixing powders with the solvent, particle sedimentation was observed to occur. It was found that an ultrasonic vibration step can effectively breakup the agglomerates. During our experiment, after 10 min of the ultrasonic vibration by an ultrasonic system (L&R Manufacturing Company, Q90), the suspension was very stable by visual inspection. Two stainless steel pieces were used as electrodes. Table I lists the parameters used in the EPD experiment. Fig. 2 shows a plan view SEM picture of an alumina coating obtained by EPD.

In order to control the thickness of the EPD layer, the kinetics needs to be determined experimentally. The deposits were weighed and the yield was calculated. The thickness was measured by laser profilometer (Zygo Newview 5000, USA). A scratch has been made in the coatings at the half height of the substrate to enable the thickness measurement. Fig. 3 shows the deposit thickness measured by this method of the sample after 15 sec of the deposition time. The thickness was also measured based on the SEM pictures of a green deposit's cross section. Fig. 4 shows the SEM picture of deposit's cross section after 15 sec of deposition time. The results, plotted in Fig. 5, show the deposition kinetics, which follows Hamaker's law [4]. From Fig. 5, one can determine the time of EPD required to obtain a coating with desired thickness.

The EPD coatings have to be dried prior to electroplating. Cracks were formed due to the non-uniform drying of a green deposit. During electroplating, the water pressure can delaminate the coating from the electrode. We found that adding polyvinylbutyral (PVB) as a binder can solve this problem. However, adding too much PVB can significantly decrease the EPD rate. In our experiments, the concentraion of PVB

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TABLE I Parameters used in EPD experiment

Parameter	Value
Voltage	50 V
Distance between Electrodes	30 mm
Particle loading	100 g/l
Drying time	10 min
Mixing time before EPD	5 min

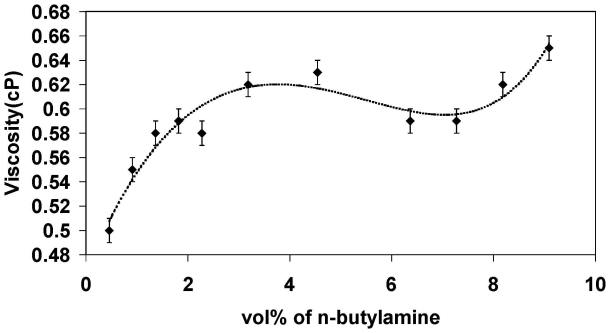

Figure 1 Viscosity of suspension as a function of the amount of *n*-butylamine.

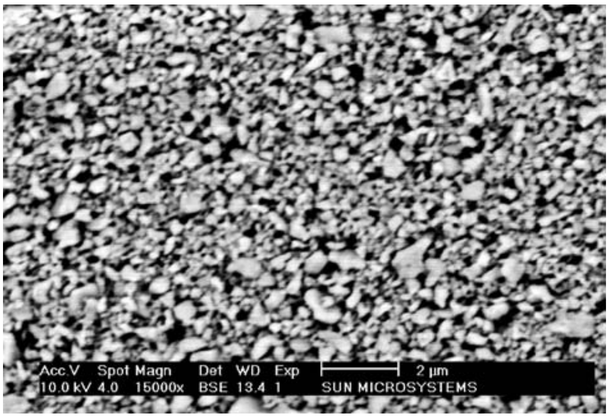

Figure 2 Plan view of scanning electron micrograph of an alumina deposit produced by EPD.

TABLE II Main composition of copper FB plating bath

Composition	Concentration
Cu^{2+}	25–29 g/l
Cl^-	45–75 ppm
H_2SO_4	12–15 vol.%

was 0.0004 g/l. After adding PVB, the suspension was magnetically stirred to make it homogeneous. The sequence in which the suspension was mixed is also very important. If PVB, acetone, *n*-butylamine and alumina powders were mixed at the same time, the EPD rate decreased down to zero. This is caused apparently by the attraction of the PVB to the surface of ceramic particles. As a result, the particles' charging is not sufficient. If acetone, *n*-butylamine and particles are mixed together, and then PVB is added, the EPD rate stabilizes.

After the EPD coating had dried completely, it was plated in a copper plating bath (Copper FB plating bath, Technic Inc., USA) to impregnate copper into the alumina matrix. The EPD deposit for following electroplating is deposited for 90 seconds (the other parameters are given in Table I). The chemical composition of the plating bath was determined by titration. The results are given in Table II. A piece of copper served as the anode. The bright current density was determined to be 21–64 mA/cm^2 from Hull cell experiments. The current density was chosen as 21 mA/cm^2 in our electroplating process. During electroplating, it was observed that gas bubbles formed on the surface of the EPD coating. This is due to the residual *n*-butylamine reacting with the electroplating bath. In order to solve this problem, the EPD coating was first rinsed in deionized water for 10 min to wash out the residual *n*-butylamine after drying. Following 27 h of electroplating, the coating was cross-sectioned and polished. After the mechanical polishing, the alumina particles were covered by soft copper making it impossible to observe the alumina particles. To remove the copper, the sample was chemically etched in the etchant (20 ml NH_4OH, 8 ml H_2O_2 and 10 ml water) for 1 min.

The results of the SEM analysis for the composite coating obtained by EPD-EP sequence are shown in Fig. 6, which shows an intermediate cross-section (located at the distance of 30 μm from the substrate) of the film. Al_2O_3 partricles are embedded as inclusions inside the copper matrix. The small white dots in Fig. 6 correspond to Al_2O_3 particles with a typical size of 0.4 μm. The pores in the Al_2O_3 skeleton provide channels for copper ions to impregnate. Copper deposited quite well during the impregnation process.

Our experiments indicate that on top of the composite ceramic-metal coating there is a layer of alumina coating obtained from the previous EPD step. This indicates that the electroplating has not been

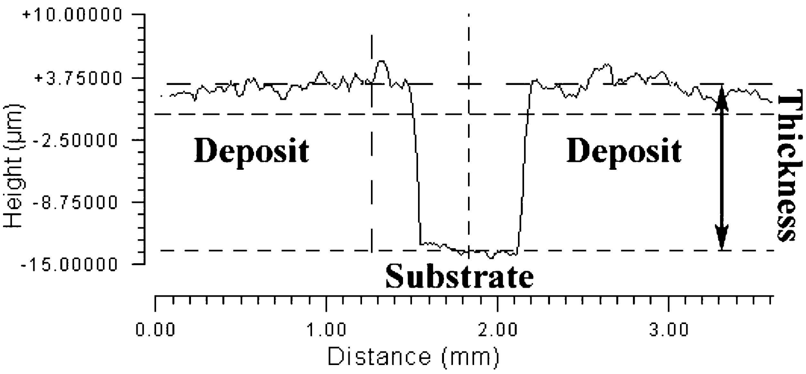

Figure 3 Thickness measured by laser profilometer (corresponding to 15 s electrophoretic deposition).

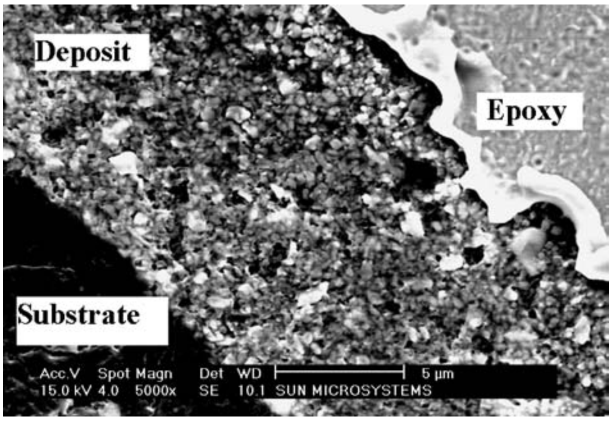

Figure 4 Cross-section of deposit after 15 sec of electrophoretic deposition.

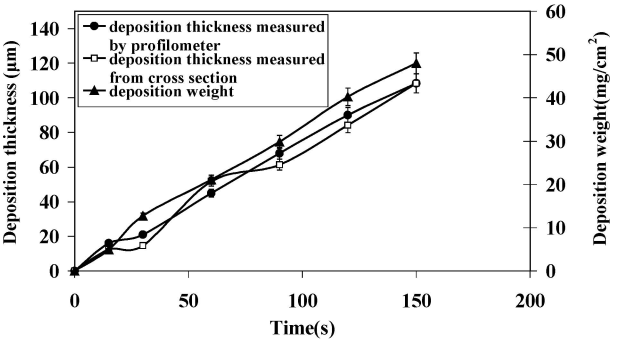

Figure 5 Deposition weight and thickness as a function of time of EPD experiment.

completedthroughout the depth of the EPD film. Since the copper impregnates pores of the alumina skeleton during electroplating, stresses develop in the composite layer. Due to the low strength of the obtained EPD coating, as the composite layer grows, the surface of the EPD coating, which is free of copper, was separated from the composite coating.

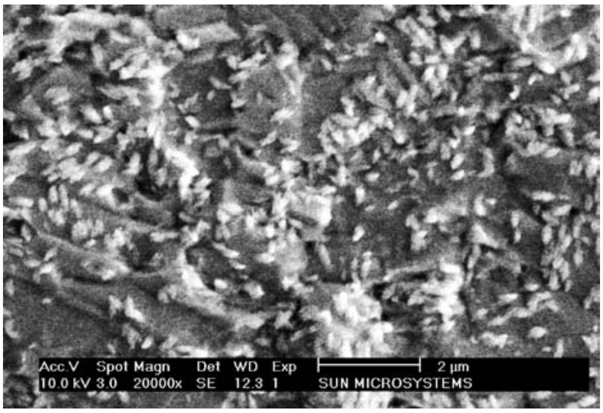

Figure 6 Cross-section of Al_2O_3-Cu composite coating produced by EPD-EP sequential deposition.

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