PREPARATION OF AL_2O_3/CU CORE–SHELL STRUCTURAL COMPOSITES BY ELECTROLESS PLATING AND DETERMINATION OF OPTIMUM BATH COMPOSITION USING TAGUCHI EXPERIMENTAL DESIGN

H. Beygi[1]*, S.A. Sajjadi[1], S.M. Zebarjad[1], A. Babakhani[1]
[1] Department of Materials Science, Engineering Faculty, Ferdowsi University of Mashhad, Mashhad, Iran
* Corresponding author (Babakhani@um.ac.ir)

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Abstract

In this study Al2O3/Cu core-shell structural composites are fabricated through two step electroless coating process of pretreatment and Electroless deposition. The influence of various electroless parameters on the thickness and uniformity of coated layer are investigated and because of numerous experiments needed an experiment design based on Taguchi robust design method is applied. The morphology, uniformity, and chemical composition of the Cu coated Al2O3 particles were characterized and it is concluded that the 3step pretreatment method, 10ml/l HCHO, 20g/l CuSO4.5H2O, 60g/l C4H4O6KNa.4H2O, PH=11and Pouring rate of 5ml/min are the best condition for Electroless deposition of Cu. During the electroless plating of activated Al2O3 particles, nucleation of nano-sized copper particles was started from the Pd clusters and subsequently more nucleation and growth of copper was performed onto the catalyst Cu nucleies and surface of Al2O3 particle and caused to coat the surface of Al2O3 particle and form a uniform Cu shell with thickness of 500nm around the Al2O3 core.

1 Introduction

Core/shell structural composites, thin metallic films coated ceramic particles, are an attractive kind of ceramic matrix composites due to their combined characteristics of metals and ceramic matrix with improved functional and mechanical properties of particles[1].

This kind of composites are fabricated by solid state methods such as ball milling, liquid state methods such as sol gel, Electroless deposition (ED) and precipitation deposition, and vapor deposition such as PVD and CVD[2-3]. Among these methods, the electroless coating has been recognized as one of the most effective techniques for preparing metal-coated ceramics powders due to the its advantages such as even dispersion of the metal coating, uniformity of deposits on complex shapes, lower cost with simple processing, easy control of the coating thickness and nondependence on the electrical properties of the substrate [4-6].

Electroless plating is an autocatalytic electrochemical reaction, used to surface metallization of conductive or nonconductive substrates without any external current. The method consisted of pretreatment of inert substrate, in order to obtain catalytic activity, and then dipping the pretreated substrate in a bath of metal ions, complexing agents, reducing agents and stabilizers [6-7].

However, in electroless deposition it is difficult to obtain uniform and nano-sized metallic coating on the ceramic powders because Powder electroless plating is a complex chemical reaction, which is affected not only by bath composition of electroless plating, but by lots of process parameters such as pretreatment type, mixing method, bath temperature, dipping time, pH ranges, particle size of substrate, etc [6, 8]. However, effects of some parameters on the deposition rate, uniformity and chemical composition of coated layers were studied by some researchers, although there are some inconsistent results because of complicated ED system, but it is essential to understand the effect of other important factors, contribution percent of each one and relationship between them to optimize the fabrication condition with minimum thickness and maximum uniformity of coated layer.

In this study, the Al2O3/Cu core-shell nanocomposite was fabricated by electroless plating of Cu on Al2O3 particles. This kind of nanocomposites can be used as the catalysts, electromagnetic wave absorbing materials, electrodes in fuel cells, thermal protective coatings of air engines, contact materials in relays, contactors, switches, circuit breaks, electronic packaging, high current brush and etc, because of its excellent properties such as significant improvement of the fracture toughness of the particles, improving the wetting property between metal and ceramics materials, good electrical and thermal conductivities, excellent resistance to high temperature annealing, excellent corrosion and wear resistance, high bonding strength, excellent weldability, and controllable magnetic properties through suitable heat treatment[5, 9-11].

In order to reach to the uniform and submicron shells effect of pretreatment type and Electroless bath composition will be investigated. Due to the lots of experiment needed, an experiment design based on Taguchi robust design method is applied. Finally, analysis of variance (ANOVA) is used to study the effects of each factor on the thickness of coated layers and determination of experimental condition having the least variability as the optimum condition.

2 Experimental procedure

2.1 Electroless deposition

Copper was coated on the surface of micron size Al2O3 particles (50µm) through two step electroless coating process. At first, Because of chemical inertness of Al2O3 particles, 100gr Al2O3 powders were pretreated to obtain catalytic activity. The pretreatment had been performed in stages of washing, coarsening, Sensitization and activation using magnetic stirrer. Details of these stages are reported in table1. Subsequently, Electroless deposition was performed in a described bath in table 1, while magnetic stirrer was used to stir the bath and avoid particle agglomeration. Finally the powders were washed in distilled water for several times; they were filtrated and dried in a vacuum oven at 80 ºC for 3 h.

2.2. Experiments design

The influence of various electroless parameters on the thickness and uniformity of coated layer are investigated. The main controlling electroless parameters and their levels are reported in table 2. Because of numerous experiments needed and interaction between the parameters, special design of experiments was applied.

At first, the individual effects of pretreatment type on the deposition of copper on the micron sized Al2O3 particles are studied. Based on research done, pretreatment can be performed by different manner of 1step (only coarsening), 2step (coarsening and activation) and 3step (coarsening, Sensitization and activation). Effect of each process on the morphology, catalytic activity and deposition of copper on the Al2O3 surface are investigated and the best condition is selected.

In the second part, parameters of bath composition were chosen as the independent parameters. The parameters are HCHO/CuSO4.5H2O ratio (10/10, 10/15, and 10/20ml/g), C4H4O6KNa.4H2O concentration (40, 50 and 60g/l), PH (11,12 and 13) and Pouring rate (3 and 5ml/min). Normally, in this case, 33 *2= 54 experiments should be conducted. In order to decreasing in number of experiments and understanding the contribution percent of each factor on the thickness, plating rate and uniformity of coated layer an experiment design based on Taguchi method was applied. According to the Taguchi method, the standard orthogonal array, namely L9 that reduces the number of experiments to 9 was used and the optimized situation for deposition of Cu on the micron sized Al2O3 particles was determined by analysis of variance (ANOVA).

2.3 Structural characterization

The morphology, uniformity, and chemical composition of the Cu coated Al2O3 particles were characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). In order to measuring the thickness of coated layers, some amount of Cu coated particles mounted and then carefully polished. The cross section views of coated particles are used and high magnification OM micrographs were taken and thickness of layers was calculated using Celemex image analyzer software. The average of 5-10 measurements has been reported as the thickness of the coated layers. Also plating rate was determined by measuring the weight gain of powder after plating.

3 Result and discussion

3.1 Effect of Pretreatment

As mentioned before, Because of chemical inertness of Al2O3 particles direct copper growth on alumina surfaces are not observed[9] and the particles first should be activated to obtain catalytic activity. On the other hand, the electroless coating process was divided in two stages of pretreatment and Electroless plating. Based on research done, pretreatment can be performed by different manner, and the most accepted methods are 3step method (coarsening, Sensitization and activation), 2step method (coarsening and activation) and 1step method (without conventional sensitization and activation steps[6]). Respected to other routs, the 3step pretreatment method is most accepted between the researchers because of its more tendencies in increasing the adhesion properties. The method consisted 3stage of coarsening, Sensitization and activation. Fig 1 shows the schematics of processes. Coarsening process was applied in a Hydrophilic etcher (fig1b) in order obtain a rough surface and increase the specific surface area and hydrophilic property of the particles[6]. During the Sensitization stage, when the coarsed particles dispersed in a sensitization hydrochloric acid solution of $SnCl_2$ and HCl, the surface of Al_2O_3 particles sensitized due to the chemisorption of Sn on the surface of Al_2O_3 particles (fig 1c) and after this step the surfaces of Al2o3 particles are ready to be activated. Among lots of catalytic agents, Pd was known the most efficient[5]. However activation process was performed in a hydrochloric acid solution of $PdCl_2$ and HCl. In consequence of Pd activation, the Pd^{2+} ions translate into electroneutral atoms when they are encountering with the Sn^{2+} ions. It is observed that by chemisorption of Pd onto Sn clusters (fig 1d) passive condition of the al2o3 particles eliminated and they were suitable for electroless plating due to the promotion of chemical absorption phenomena.

As soon as activated particles are dispersed in an electroless bath of metal ions, complexing agents, reducing agents and stabilizers, an autocatalytic electrochemical reaction is performed as follow:

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

As the reaction started, the solution turned to be orange-color, shows deposition of Cu, and lots of bubble appeared in the solution. fig 1e shows that during the electroless plating of activated Al_2O_3 particles, nucleation of nano-sized copper particles was started from the Pd clusters and subsequently (fig 1f) more nucleation and growth of copper was performed onto the catalyst Cu nucleies and surface of Al_2O_3 particle and caused to coat the surface of Al_2O_3 particle and form a uniform Cu shell around the Al_2O_3 core.

Comparing morphology of cu coated powders pretreated by different method, it is revealed that all of methods have tendency to promote the chemical activity of passive Al_2O_3 particles. However, the uniformity and adhesion property of coated layers pretreated by 3step method is more than the others.

In 1step method the surfaces of particles were activated by coarsening treatment and without conventional sensitization and activation steps. Specific surface area of the particles increased in this method, and nano-sized voids observed on the surface of particles that caused to create suitable parts for nucleation of copper. However the nucleation locations are less in amount and the cu coated layers seems to be non uniform with weak adhesion to substrate. In other method, pretreatment performed after coarsening in a unique chemical bath of $SnCl_2$ and $PdCl_2$ (2step method). The method was not efficient compared to 3step method to create nucleation locations on the surface of Al_2O_3 particles; therefore the resulted coated layer was not dense and uniform[9].

3.2 Optimization of bath composition parameters

The structure of Taguchi orthogonal robust design, the results of measurement for thickness of coated layer and corresponding S/N ratios are shown in Table 2.

The structure of Taguchi orthogonal robust design, the results of measurement for thickness of coated layer and corresponding S/N ratios are shown in Table 2.

Fig. 3 shows the mean of S/N ratio values versus levels of parameters for thickness of coated layer. The graph applied in order to understanding effects of parameters and their levels on the output. Using fig 3 the parameter with most variability is significant parameter and also, in each parameter the levels with minimum S/N ratio were selected as the optimal condition.

In Electroless plating characteristics of coated layers are very much dependent on the composition of electroless bath. However, there is a little theoretical study of the plating composition and in all studies choosing the appropriate bath composition is determined through experimental. For example, it is well known that the concentration of copper salt in the bath has little influence on plating rate, whereas increasing in reducing agent caused to increasing in plating rate and thickness of coated layer. The result of our experiments also confirmed the observations. Fig 3 shows that by increasing the HCHO concentration (decreasing the $CuSo_4.5H_2O$/HCHO ratio), the thickness of coated layers decreased significantly. Also it is revealed that, more increasing in HCHO concentration caused to increasing the plating time and hydrogen evolution,

meanwhile the uniformity of coated layers becomes better.
In this study $C_4H_4O_6KNa.4H_2O$ was choose as the complexing agent. The result from fig 3 shows that increasing in mount of complexing agent can be caused to decreasing in thickness of coated layers.
Another influencing parameter of bath composition is NaOH concentration. But during the electroless, the $OH\_$ ions are consumed rapidly, which leads to the decrease of pH value of the plating bath. When the pH decreases to a level that is low enough, the HCHO will lose its reducing capability and the copper deposition will terminate automatically. In order to maintain the plating reaction, the NaOH must be supplied continuously. Therefore concentration of NaOH in plating bath is not constant and PH of the bath was choosing as the other independent factor. It is known that only in the solution whose pH value is greater than 11, the HCHO has the reducing capability. However effect of bath PH investigated and it is indicated that increasing the pH range of the solution from 11 to 13 caused to increasing the thickness of coated layers.
Ling and Li studied the various feeding modes in electroless powder deposition and reported that, when the copper-complex solution was fed into suspending solution of formaldehyde, NaOH and activated particles, more uniformity of copper coating was appeared[5]. According to this method, two different feeding rates were examined and it is revealed that, there is not any big difference in thickness of coated layer in both rates; however 5ml/min feeding rate caused to less thickness of coating layers.
Statistical analysis of variance (ANOVA) was performed to identify the effect of individual factors on the process response and understanding which process parameters are statistically significant. In the present study, ANOVA is performed using Minitab. Table 3 shows the ANOVA result for the thickness of coated layer. The results show that PH of the bath solution with 41.77% contribution has the most effect on thickness of coated Cu layer, $C_4H_4O_6KNa.4H_2O$ concentration with 26.98% contribution has the next largest effect, and $HCHO/CuSO_4.5H_2O$ ratio is third (24.88%).
At the final step of Taguchi method optimal combination of the process parameters and response of this situation will be predicted using ANOVA. A3, B3, C1 and D2 are predicted as the best levels for parameters to achieve minimum thickness of coated layer and the estimated value for thickness is 645nm. The verification experiment is conducted and the thickness of coated layer is measured to be 500nm, which is significantly lower than the calculated amount.
Fig 3 shows cross sectional image of Al_2O_3 core-shell structural composites prepared though 3step pretreatment procedure and coated by the optimized composition of electroless bath. As received Al_2O_3 particles were recognized polygonal in shape with particle size of 50µm. However after the activation procedure (fig. 3a), no difference in the morphology of Al_2O_3 particles observed and only the Pd nucleies are identified on the surface of Al_2O_3 particles. Fig 3b shows the first stage of electroless plating that is related to nucleation of Cu particles at palladium activated locations. It is indicated that, Cu particles were deposited on the surface of Al_2O_3 cores as nanospherical particles. The microscopy experiments of coated particles at the end of electroless deposition procedure (fig 3c), mention that by growing of copper on the surface of the cu nucleies, a continuous coating around the Al_2O_3 particle form a thin and uniform shell within about 500nm thickness. However in some places agglomerates of spherical particles observes. Same events cause to change the shape of particles from polyhedral to semispherical, with diameters of about 53 µm.

4 Conclusion

1- In this study, Al_2O_3–Cu core-shell nanocomposite was fabricated by electroless plating of Cu on Al_2O_3 particles.
2- Copper was coated on the surface of micron size Al_2O_3 particles (50µm) through two step electroless coating process of pretreatment and Electroless deposition.
3- The influence of various electroless parameters on the thickness and uniformity of coated layer are investigated and because of numerous experiments needed an experiment design based on Taguchi robust design method is applied.
4- Comparing morphology of cu coated powders pretreated by different method, uniformity and adhesion property of coated layers pretreated by 3step method is more than the others. The method consisted 3stage of coarsening, Sensitization and activation.
5- PH of the bath solution with 41.77% contribution has the most effect on thickness of coated Cu layer, $C_4H_4O_6KNa.4H_2O$ concentration with 26.98%

contribution has the next largest effect, and HCHO/CuSO4.5H2O ratio is third (24.88%).

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Table 2: Main controlling factors and their levels

Factor	Levels		
	1	2	3
(A) Pretreatment type	1step	2 step	3step
(B) CuSO4.5H2O/HCHO ratio (g/ml)	10/10	10/15	10/20
(C) C4H4O6KNa.4H2O concentration (g/l)	40	50	60
(D) PH (NaOH concentration)	11	12	13
(E) Pouring rate (ml/min)	3	5	-

Table 4: ANOVA for S/N ratio of the micron size Cu(Al2O3) particle size.

Factors	df	SS	MS	F	p(%)
(B) HCHO/CuSO4.5H2O ratio (ml/g)	2	24.78	12.39	508	24.88
(C) C4H4O6KNa.4H2O concentration (g/l)	2	26.86	13.43	551	26.98
(D) PH (NaOH concentration)	2	41.56	20.78	853	41.77
(E) Pouring rate (ml/min)	1	6.15	6.15	252	6.17
Error	1	0.02	0.02	***	0.20
Total	8	99.39	***	***	100

Stage		Chemical	Composition	Temperature (°C)	Time (min)	Ultimate process
1- pretreatment	Washing	Cleaner	200 ml Acetone	25	15	Washing in de-ionized water for several times
	Coarsening	Hydrophilic etcher	100 ml/l HNO_3	25	15	Washing in de-ionized water for several times
	Sensitization	Sensitization hydrochloric acid solution	15 g/l $SnCl_2$ and 60 ml/l HCl	25	15	Washing in de-ionized water for several times
	Activation	Activation hydrochloric acid solution	0. 5 g/l $PdCl_2$ and 10 ml/l HCl	25	30	Washing in de-ionized water for several times/ filtering/ drying in an oven at 110 ºC and 1h
2- Electroless deposition		Main salt Reducing agent Buffering agent Complexing agent	Copper sulphate ($CuSO_4.5H_2O$) Formaldehyde (HCHO) Sodium hydroxide (NaOH) Pottasium sodium tartrate ($C_4H_4O_6KNa.4H_2O$)	60	30	Washing in de-ionized water for several times/ filtering/ drying in an vacuum oven at 80 ºC and 3h

Table3: experimental measured values and S/N ratio for thickness of coated layer

Exp. No.	(B) CuSO4.5H2O/ HCHO ratio (g/ml)	(C) C4H4O6KNa.4H2O concentration (g/l)	(D) PH (NaOH concentration)	(E) Pouring rate (ml/min)	Thickness of coated layer (µm)	S/N
1	1	1	1	1	2	6.0205
2	1	2	2	2	1.8	5.1054
3	1	3	3	1	2.3	7.2345
4	2	1	2	1	1.9	5.5750
5	2	2	3	1	2.3	7.2345
6	2	3	1	2	0.75	-2.4987
7	3	1	3	2	1.9	5.5750
8	3	2	1	1	1.1	0.8278
9	3	3	2	1	1	0

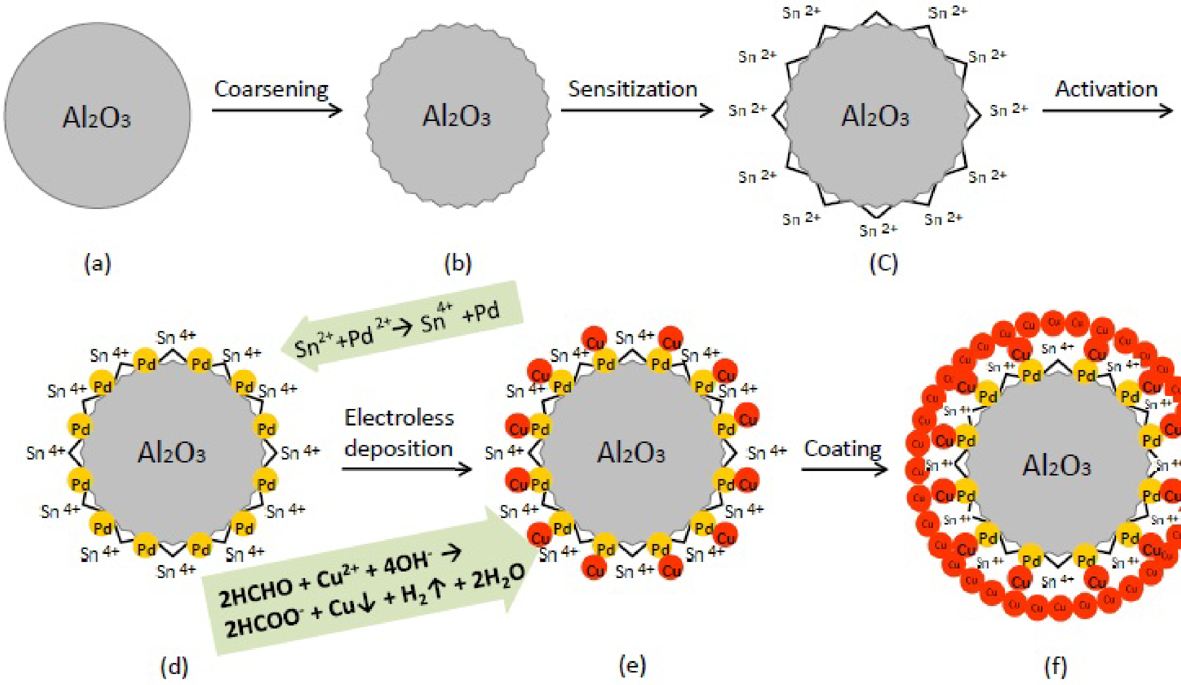

Fig. 1. Schematic of 3step activation and electroless Cu plating of Al2O3 powders.

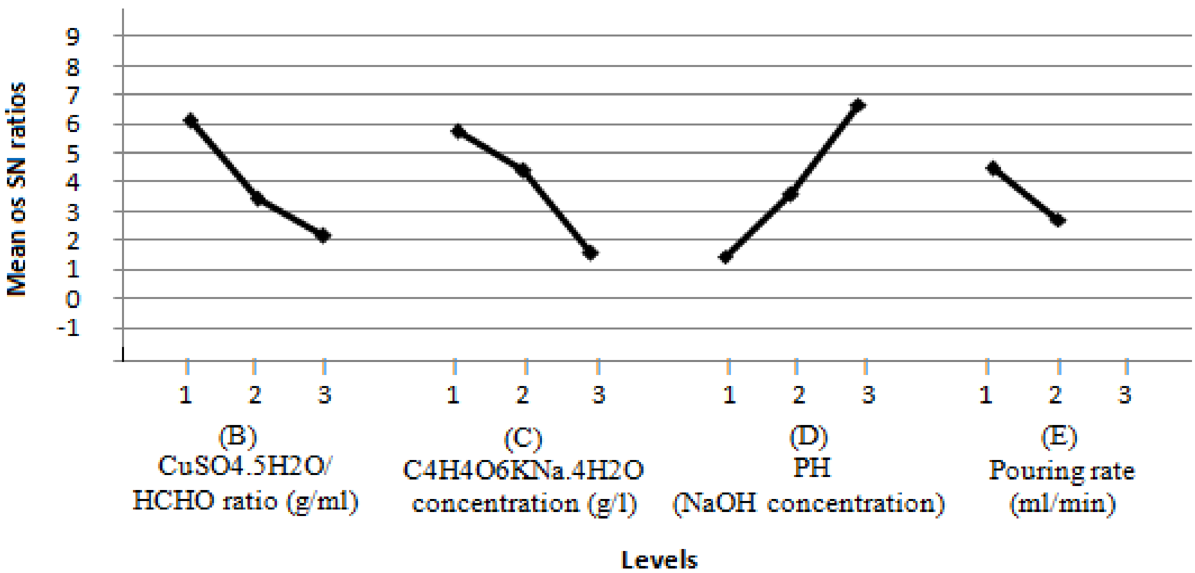

Fig 2: Mean of S/N ratios for different levels of the parameters

Fig. 3. OM micrograph of a) 3step activated powders, b) early stages of electroless plated powders; c) Cu coated powders at the end of plating