

FORMATION OF CU-SIO₂ MULTILAYER COATING ON SiC PARTICLES

Lincy V.S.¹, Ginil Mon .S.²

Abstract— Multilayer coating on the surface of SiC particles by Sodium silicate and Cu metal using electroless method is done in this work. Several pretreatment steps such as cleaning, sensitization and activation are performed on the surface of SiC particles. Cerium (III) chloride, a less expensive activator which has the similar reaction mechanism like palladium chloride catalyst is used in the present study. After the cleaning step of the SiC particles, silica coating is made on the surface using sodium silicate which will improved the bond ability of metal ions to the surface of the particle. Then copper coating is done on the silicate using with and without heat treatment under varying bath pH which adversely affect the coating morphology on the substrate. Electroless Cu-SiO₂ multilayer coating has been successfully formed on the surface of SiC particles by using the activator CeCl₃ and the reducing agent formaldehyde which causes reduction of copper tartrate. This technique is feasible and efficient. The proposed mechanism of electroless coating over the surface is not only the chemical bonding but also mechanical bonding. In the present study, the multilayer coating is done with SiC particles in nano level and it is difficult to get a perfect coating in this nano level. Both heat treated and not heat treated samples are used in the present study and pH is adjusted to different values. The mechanism of electroless copper coating technique involves the reduction of Cu²⁺ to Cu⁰ in the presence of formaldehyde and gets coated on the SiO₂ coated SiC particles. The bath pH and agitation time have a major effect on electroless coating. There is an optimum pH for coating. Temperature is a factor which also affects the deposition rate. The nucleations of the coating process starts with globules in nano-size range and then grow laterally to cover the whole surface with high uniformity.

Keywords— multilayer coating

I. INTRODUCTION

‘Plating’ is a surface covering technology in which a metal is deposited on a conductive surface. Plating is also known as ‘Coating’. Plating has been done for hundreds of years, but it is also critical for modern technology. Plating is used to decorate objects, for corrosion inhibition, to improve solderability, to harden, to improve wearability, to reduce friction, to improve paint adhesion, to alter conductivity, for radiation shielding, and for other purposes. Thin film deposition has plated objects as small as an atom, therefore plating finds uses in nanotechnology.

There are several plating methods, for the deposition of metals. Electroless plating is a variety of chemical deposition technology. EL deposition is a process that has been used in practice for centuries. Electroless plating, also known as ‘Chemical’ or ‘Auto-catalytic plating’, is a non-galvanic type of plating method that involves several simultaneous reactions in an aqueous solution, which occur without the use of an external electric power.

Electroless plating involves the deposition of metals on a catalytic surface from the solution and was invented by A. Brenner and G. E. Riddell in 1940’s. Electroless coatings can be divided into three main categories like:

1. Alloy coatings.
2. Composite coatings.
3. Metallic coatings.

Electroless deposition is a self-sustaining process, in which reducing electrons are obtained from a separate electroless solution-derived compound, called the ‘reducing agent’. Electroless plating is based on the chemical reduction of metal ions in the solution to metallic atoms on the surface through the reducing agent and is not constrained by the shape, size or conductivity of the supporting substrate. Therefore, electroless plating is a highly effective means of plating metal onto non-conductive substrates. Electroless process uses redox reaction to deposit metal from aqueous solution and involves several simultaneous reactions.

Electroless coating technique is one of the elegant ways of coating by controlling the temperature and pH of the coating bath. Electroless deposition process occurs on a suitably prepared surface only, and does not occur in the bulk of the electroless solution. This technique gives coatings of uniform thickness and composition.

Electroless coating process involves several pretreatment steps such as cleaning of substrate, sensitization of surface and activation of surface. Several plating baths and reducing agents can be used for electroless process. Autocatalytic plating baths contain reducing agents, ready to react with the substrate. The catalyst is the metal to be deposited. The reaction is completed when hydrogen is released by the reducing agent.

Most materials can be electrolessly plated. Plastics can also be plated using electroless method. Some types of electroless plating methods are not suited to specific substrates due to temperature and other restraints. Electroless plating is well suited for parts with complex geometries and many fine features.

Electroless plating process has several advantages. Deposition of surface coatings is one of the important approaches in improving the friction and wear properties of surfaces. Coatings produced by electroless deposition are uniform and

¹ Department of Chemistry and Research, Nesamony Memorial Christian College, Marthandam, KK Dist., Tamil Nadu.

² Department of Chemistry and Research, Nesamony Memorial Christian College, Marthandam, KK Dist., Tamil Nadu.

continuous which makes this process very attractive for different applications. Selectivity and controllability of the process and adherence of the deposited layer to the substrate are the main advantages of electroless coating process. In EL deposition process, the material can be deposited onto areas that demonstrate appropriate electrochemical properties and EL deposition process can be selective. Therefore, local deposition can be performed more effectively onto metals that exhibit an affinity to the material being deposited or onto areas pretreated or pre-activated. Electroless deposition requires less expensive equipment.

Electroless plating process involves the deposition of metals on the catalytic surface of a variety of metallic and non-metallic objects and this process has extended applications. The research achievements in the area of electroless deposition have contributed to tremendous applications and developments in various industries. Electroless deposition is the process of depositing a coating with the aid of a chemical reducing agent in the solution. It is therefore applicable to non-conducting substrates, and has been used extensively for metallizing printed wiring boards (PWB). Electroless deposition is experiencing increased interest in micro electronics, in part due to its selectivity of deposition. Electroless platings have wide range of application in corrosion prevention and electronics. Applications of electroless deposition are also related to energy conversion, aerospace, biomedical and automotive industries. In addition, new applications in the area of metallization of polymers, ceramics, fabrics, etc.

Electroless coating technique can be used for multilayer coatings. Multilayer is a system of adjacent layers on monolayers. Coatings that consists of different properties can be prepared as multilayer coatings. These coatings can have different sequence of layers depending on the intended application of the material. Basis of multilayer coating is constituted by thousands of alternating properties nanosize and nanostructure layers of various composition, which take a priority place in the sphere of protective coatings investigation.

System of parameters that define the multilayer coating are,

1. Material
2. Deposition technique
3. Layer thickness
4. Number of periods

Microhardness is one of the key mechanical properties of hard protective coatings. The advantage of multilayer coatings is connected with the fact that alternation of nanosize layers prevents from the growth of phases and their size is limited by the thickness of the layer being formed. The reduction of the phase size considerably decreases inner tensions in the coatings and on the border with the substrate, which increases their exploitation properties. In multilayer coating, coverage and performance is built up in layers.

Cu-SiO₂ multilayer coating on SiC particle can be done by electroless method. In this coating process, SiC is coated with sodium silicate. The sodium silicate coated SiC is sensitized and activated, using Stannous chloride and Cerium chloride respectively. Then copper can be coated on the surface of the substrate by electroless coating process.

The study of copper deposition on the surface of the substrate can be done using several techniques such as Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). Microstructural analysis of multi-layer coatings can be done using certain techniques. Thickness of multilayer coating can be examined by the cross-sectional micrographs of FE-SEM. Each layer can be evidenced by EDS elemental analysis. X-ray diffraction can be used to identify the structural characteristics of coatings.

II. EXPERIMENTAL PROCEDURE

The major steps involved in the electroless method are,

1. Sensitization followed by activation of the surface of ceramic particles by deposition of metals.
2. Deposition of metal on the activated surface from a reducing bath containing metal ions.

Since the electroless coating is a result of chemical reduction reaction, proper pre-treatment of substrate, on to which coating has to be carried out, is essential. This can be achieved by using specific chemical solutions depending up on the physical and chemical properties of substrate. The major component of the electroless technique is the "bath". The bath consists of an aqueous solution of metal ion, a catalyst, reducing agent, complexing agent, bath stabilizer, etc., operating at a required metal ion concentration, temperature and pH ranges. Unlike the conventional electroplating, no electrical current is required for deposition. The pre-treatment of the substrate and the bath composition play a vital role in attaining the desired coating.

2.1 Materials

Silicon Carbide powder of micron size is the substrate used in this Cu-SiO₂ multilayer coating experiment by electroless method. Silicon carbide is also known as 'Carborundum', which is a compound of silicon and carbon with chemical formula, SiC. Colour of SiC is black, dark gray, or green. SiC is a semi conductor.

Physical Properties of SiC includes,

- Low density
- High strength
- Low thermal expansion
- High hardness
- High elastic modulus
- Excellent thermal shock resistance
- Superior chemical inertness



Fig. 1 Silicon Carbide

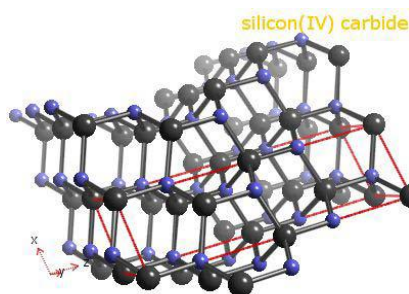


Fig. 2 Structure of SiC

Table 1: Properties of SiC

Molecular Formula	SiC
Molecular Weight	40.07g/mol
Colour	Dark Gray
Crystal Structure	Hexagonal
Density	3.21g/cm ³
Melting Point	2730 ⁰ C
Boiling Point	2815 ⁰ C
Solubility in Water	Insoluble
Dielectric Constant	10.8
Specific Heat	0.69J/g ⁰ C
Thermal Conductivity	350W/m ⁰ C
Temperature Coefficient of Expansion	4.8ppm/ ⁰ C

The chemicals used in this experiment are,

- Sodium Silicate: The chemical formula is Na₂SiO₃. It is a white powder that is readily soluble in water, producing an alkaline solution. It is stable in neutral and alkaline solutions. In acidic solutions, the silicate ion reacts with hydrogen ion to form silicic acid.
- Stannous Chloride: Stannous chloride is also known as tin (II) chloride. It is a white crystalline solid with the formula, SnCl₂. It is widely used as a reducing agent in acid solutions.
- Cerium (III) Chloride Heptahydrate: It is also known as Cerous chloride or Cerium trichloride, is a compound of cerium and chlorine. The chemical formula is CeCl₃.7H₂O. It is a white, hygroscopic solid. It rapidly absorbs water on exposure to moist air to form a hydrate. It is highly soluble in water.
- Hydrochloric Acid: The chemical formula is HCl. It is a solution of hydrogen chloride (HCl) in water that is a highly corrosive, strong mineral acid with many industrial uses. It is found naturally in gastric acid.
- Cupric Sulphate Pentahydrate: It is also known as Copper (II) sulphate and the chemical formula is CuSO₄.5H₂O. It is bright blue in colour. Other names of this compound are, 'blue vitriol' and 'bluestone'.
- Sodium Potassium Tartrate: It is also known as 'Rochelle salt'. The chemical formula is NaKC₄H₄O₆.4H₂O. Another name of this compound is 'Seignette's salt'. It is a colourless to blue-white salt crystallizing in the orthorhombic system. It is completely soluble in water and slightly soluble in alcohol.
- Formaldehyde: It is an organic compound with the chemical formula, HCHO. It is the simplest aldehyde and it is colourless.
- Sodium Hydroxide: It is also known as 'Lye' and 'Caustic soda'. The chemical formula is NaOH. Pure NaOH is a white solid. It is hygroscopic and dissolves in water with the liberation of heat.
- Distilled Ethanol: It is a straight - chain alcohol, and its molecular formula is C₂H₅OH. It is a volatile, colourless liquid that has a slight odor.

2.2 Method of Coating

The pre-treatment of commercially available ceramic SiC powder involve the cleaning, sensitizing with SnCl₂ and activation with CeCl₃ steps. After the pre-treatment step and silica coating, Cu coating is done on the surface of the SiC particles.

2.2.1 Cleaning Step

About 10g of SiC is washed in distilled water, mechanically stirred in a magnetic stirrer and kept aside until the particles settle. Then the supernatant solution is decanted. The procedure is done thrice so that the surface impurities and the small size particles can be effectively removed. Then the cleaned SiC is dried in vacuum.

2.2.2 Sodium Silicate Coating

2g of sodium silicate is dissolved in 100ml distilled water and mechanically stirred. Then 10g of the cleaned SiC is to this solution mechanically stirred and dried.

2.2.3 Sensitization by SnCl₂

5g of the SiO₂ coated SiC is heated to 6000C and then it is subjected to sensitization process by immersing the substrate to the sensitizing bath. The sensitization bath is prepared by mixing 4g of SnCl₂ and 10ml of con.HCl. This mixture is made up to 100ml with distilled water. From this 50ml is used for preparing the sensitizing bath. The sensitizing bath containing SiO₂coated SiC is thoroughly stirred by the magnetic stirrer for 30 minutes. Then the substrate is filtered and dried.

The remaining 5g of the SiO₂ coated SiC, which is not heat treated is then subjected to the sensitization process. Here, the remaining 50ml of the mixture of solution (SnCl₂, Con.HCl & Distilled water) is used for preparing the sensitization bath. Then the process is repeated as above and the substrate is filtered and dried.

2.2.4 Activation by CeCl₃

The sensitized particles are then subjected to activation step. The SiO₂ coated SiC particles are dipped into activation bath which is composed of 0.1g CeCl₃ (0.1%) in 100ml distilled water. From this solution, 50ml is used for preparing activation bath for the heat treated substrate particles and the remaining 50ml is used for the ordinary substrate particles which are not heat treated. Then these two activation baths with ordinary and heat treated substrates are stirred for 30 minutes and dried at 100-105 °C.

Table 2: Details of the chemicals used for the pre-treatment of SiC

Bath	Chemicals	Formula	Concentration
Sensitization Bath	Stannous chloride solution (Sensitizer)	SnCl ₂ .2H ₂ O	4g in 100 ml distilled water
	Hydrochloric acid	HCl	10 ml in 100 ml distilled water
Activation Bath	Cerium chloride	CeCl ₃ .7H ₂ O	0.1g in 100 ml distilled water

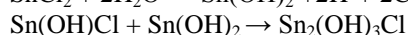
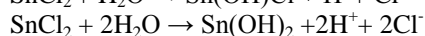
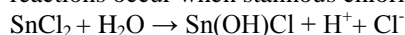
2.3 Mechanism of Coating Process

2.3.1 Silica Coating

SiO₂ is coated on the surface of the cleaned SiC particles by using sodium silicate (Na₂SiO₃).

2.3.2 Sensitization Process Details

The stannous chloride (SnCl₂) solution is used as the sensitization bath. In the sensitization process, the following reactions occur when stannous chloride dissolves in water.



The compound Sn₂(OH)₃Cl is finally attached to the surface of silica coated SiC powder. The acid present in the sensitization bath increases the oxygen content.

2.3.3 Activation Process Details

In this work, Cerium (III) Chloride (CeCl₃. 7H₂O) is used as the catalyst for the activation process. The catalyst provides large surface area in order to adsorb the metal atom.

2.3.4 Catalytic Action Of Cerium (III) Chloride

Cerium (III) chloride is economically less expensive catalyst as compared with conventional PdCl₂ catalyst. Similar to all lanthanides, Ce shows +3 oxidation state and +4 oxidation state is also possible. But Ce⁴⁺ in aqueous solution have a tendency to change readily to Ce³⁺ ion. There is only one possible mechanism for Cerium adsorption on SiC surface, i.e. Ce is adsorbed as Ce³⁺ (CeCl₃).

2.3.5 Action Of Reducing Agent

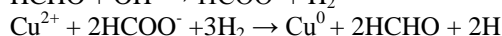
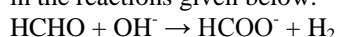
Reducing agents are used in order to reduce the Cu-T complex which is adsorbed on the surface of the SiO₂ coated SiC powder. Formaldehyde solution is used for this purpose.

During the electroless metal coating, it is found that the silica coated SiC particles adsorb water soluble metal complexes. It has also been noted that the nature of adsorption depends on the stereochemistry of the complexes. Metal complexes with planar configuration are adsorbed on the surface of the silica coated SiC particles more rapidly and they are not washed away when stirred in water.

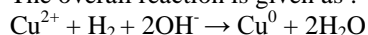
The size of the metal complex molecule also plays a prominent role, i.e. complexes with large size are adsorbed to a lesser extent than smaller molecules within a prescribed time interval.

The adsorbed Cu-T complex can be reduced to metallic copper which, in turn, will activate the surface of the particles for deposition of copper from the reducing bath. The stability of Cu-T complex is lower and hence formaldehyde (HCHO) is essential to reduce the adsorbed complex. The deposition of copper from the reducing bath is catalyzed by the initially deposited activating agent, and the rate of deposition is dependent up on the catalytic surface area.

Copper cations gets deposited on to the surface by capturing electron furnished from the reducing agent, HCHO as shown in the reactions given below:



The overall reaction is given as :



2.4 Electroless Copper Coating

The electroless coating of Cu on the pretreated, SiO₂ coated SiC ceramic powder involves mainly two steps.

(i) Formation of Cu-T complex on SiC

(ii) Reduction of Cu-T complex to Cu

2.4.1 Formation of Cu-T Complex

At first, copper tartrate (Cu T) solution was prepared by mixing 1.25g of sodium potassium tartrate in 20 ml distilled water and 0.5g cupric sulphate in 20 ml distilled water.

1g of the pretreated, SiO₂ coated, dried SiC powder without preheating was added to the Cu-T solution and subjected to continuous stirring at room temperature for 1 hour. During this process, the Cu-T complexes are adsorbed on the surface of SiC. The deposition of Cu-T from the Cu-T bath was catalysed by the initially deposited Ce activation layer and the rate of deposition is dependent on the catalytic surface area. The above process was repeated for 1g each of other two samples of pretreated, SiO₂ coated SiC. The whole procedure was done also for the SiO₂ heated samples at 500°C. (i.e. three samples of pretreated, SiO₂ coated SiC, each of 1g).

2.4.2 Reduction of Cu-T Complex

In order to reduce the Cu-T complex, a good reducing agent is needed. The reducing agent used in this work is formaldehyde (HCHO). 0.7 ml formaldehyde was added to the SiO₂ coated SiC-Cu-T complex with and without heating at 500°C for 3hrs and stirred continuously for half an hour. Then pH of the bath was adjusted by adding 5% NaOH solution (i.e. 5g NaOH in 100 ml distilled water) dropwise and stirred for half an hour at room temperature. Then this mixture is filtered, washed with distilled water and distilled ethanol and finally dried at 105°C. The process is done for pH=10,11 and 12 and the whole process is repeated for the heat treated samples.

Table 3: Composition Of Electroless Bath For Copper Coating

Electroless bath solution	Formula	Role in bath	Concentration
Cupric sulphate	CuSO ₄ .5H ₂ O	Metallic ions of coating	0.5g in 20 ml distilled water
Rochelle salt	NaKC ₄ H ₄ O ₆ .4H ₂ O	Complexing agent	1.25g in 20 ml distilled water
Formaldehyde	HCHO	Reducing agent	0.7 ml
Sodium hydroxide	NaOH	Buffering solution	5g in 100 ml distilled water

2.5 Characterisation Studies

2.5.1 Scanning Electron Microscopy (SEM)

The JEOL scanning electron microscope (SEM) is used for the analysis of Cu-SiO₂ multilayer coated SiC particles. SEM uses a focused beam of high –energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron sample interactions reveal informations about the sample, including external morphology, (texture), chemical composition, crystalline structure and orientation of materials making up the sample. Areas ranging from 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). Coating prevents the accumulation of static electric charge on the specimen during electron irradiation.

III. RESULTS AND DISCUSSION

In this work, the efficiency of electroless Cu-SiO₂ coating on SiC powder is studied using CeCl₃ activation bath. Heat treated and not heat treated samples are used for the coating process and the process is done at different pH. The multilayer coating on SiC can be seen through SEM photographs.



Fig. 3 SEM of SiC

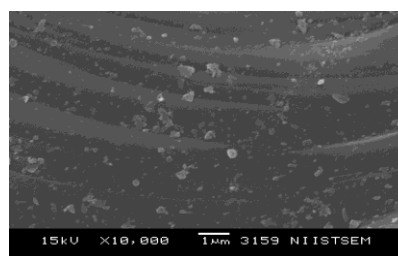
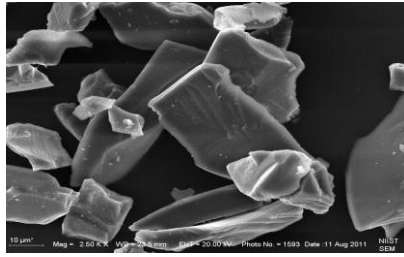
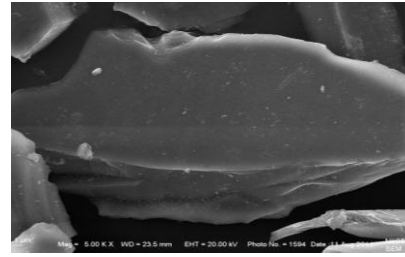


Fig. 4 Silica coated SiC

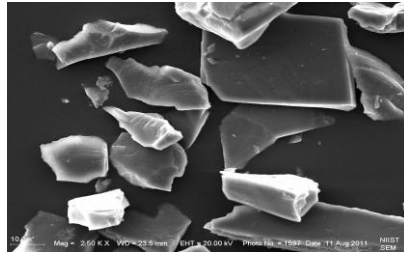


(a)

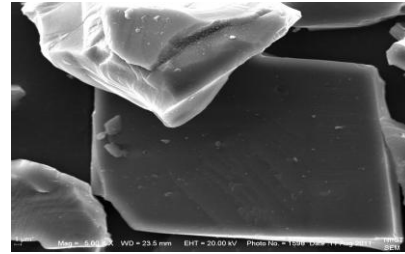


(b)

Fig. 5 SEM of Sample 1

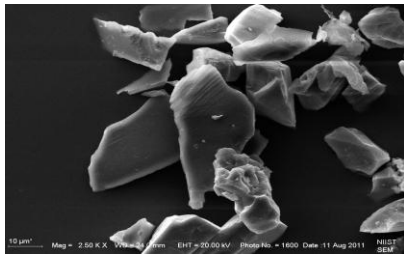


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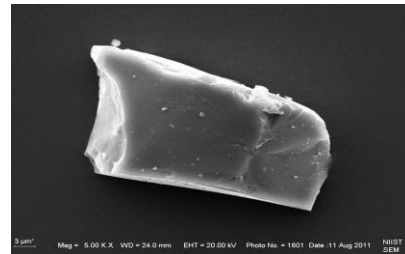


(b)

Fig. 6 SEM of Sample 2

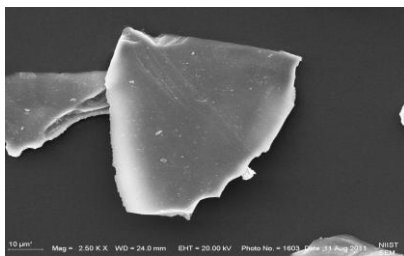


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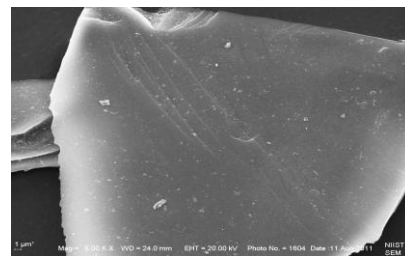


(b)

Fig. 7 SEM of Sample 3



(a)

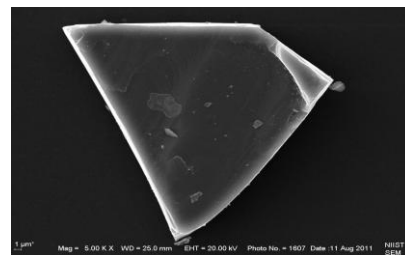


(b)

Fig. 8 SEM of Sample 4



(a)



(b)

Fig. 9 SEM of Sample 5

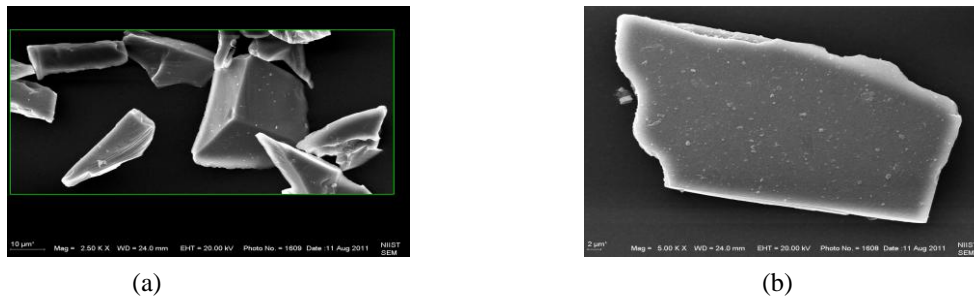


Fig 10 SEM of Sample 6

Figure 3 shows the SEM micrograph of uncoated silicon carbide particles. The uncoated SiC particles are polyhedral in shape and the surface shows many small particles absorbed on the surface of SiC particles. The absorbed particles are the contaminants which will adversely affect coating on the particles. The studies on the directly coated particles without any treatment show low coating. The present studies were done by coating a ceramic oxide layer which has a greater tendency to absorb the metal ions more towards itself and can provide better properties than the single layer coating. Figure 4 shows the SEM of silica-coated SiC. The SEM picture clearly shows that on treating the particles without silica sol, the surface of the particle gets coated with silica to some extent.

Figure 5 (a) and (b) shows the Cu-SiO₂ coating on SiC particles which are not heat treated and pH is maintained at 10 for 2 hours. The figures show the coating under low magnification and high magnification. From the SEM micrographs it was observed that at pH 10 the surface of the particle gets cleaned and there was no observable coating on the surface of the particles. The surface smoothness of the particles gets improved showing that at this pH the bath has either removed the surface-absorbed silica and contaminants or a smooth nano-layer of coating which cannot be observed was formed on the surface of the particles.

Figure 6 (a) and (b) shows the Cu-SiO₂ coating on heat-treated SiC particles at pH 10. The figures under low and high magnification show some difference in the appearance of coating than figure 5. The SEM micrographs show spots of deposition on the rough surface and on the deep cracks present in the particles showing that these areas get better activated than the other areas. The SEM also shows some narrow layer-like appearance on the surface of the particles showing a nano-layer of coating is formed on the activated particles and likely to grow with variation in bath parameters.

Figure 7 (a) and (b) shows the Cu-SiO₂ coating on SiC particles which are not heat treated and pH is 11. These figures also show similarities to that of coated particles without any heat treatment at pH 10. The surface seems to be smoother and patches of deposition were observed on certain regions of the sample. On comparing the heat and unheated samples it was observed that heat treatment has a greater effect on coating. On heating the samples amorphous silica formed on the surface of the particles gets converted to crystalline form and favors the formation of a coating layer on the particles. The metal ions have more tendencies to get absorbed on the surface of particles in the crystalline form than the amorphous form. The amorphous silica has a tendency to get dissolved in the reaction bath during the coating process carried out under magnetic stirring for 2 hours which is effective to get observable coating on the surface of particles.

Figure 8 (a) and (b) shows the Cu-SiO₂ coating on heat-treated SiC particles at pH 11. From the SEM micrographs it is clear that heat treatment has a major effect on coating. The particles show better coating than that at pH 10 and pH 11 without any heat treatment of the silica-coated particles.

Figure 9 (a) and (b) shows the Cu-SiO₂ coating on SiC particles which are not heat treated and pH is 12. From the SEM micrographs it was observed that even on increasing the pH the silica-coated particles with silica coating in the amorphous state show similar coating properties as that of silica-uncoated particles. The surface of the particles gets cleaned and seemed to have some surface absorption which is in nano-layer.

Figure 10 (a) and (b) shows the Cu-SiO₂ coating on heat-treated SiC particles at pH 12. The high magnification figure shows almost uniform coating. The SEM micrographs clearly show at pH 12 with heat treatment at 500°C for three hours effective coating over the entire surface of the particle occurs. The coating on the particle was observed to be uniform throughout on the entire particles and there was no hump-like growth on the surface of the particle. This shows that copper coating on silica-coated SiC particles with treatment provides better coating and such coated particles find application in high-tech areas which require the combined application of both metal and ceramic-coated particles with smooth uniform coating over the entire surface.

In the present study, the Cu-SiO₂ multilayer coating on SiC particles is done at nano level and it is observed that it is difficult to get a perfect multilayer coating at this level.

IV. CONCLUSION

Electroless Cu-SiO₂ multilayer coating has been successfully formed on the surface of SiC particles by using the activator CeCl₃ and the reducing agent formaldehyde which causes reduction of copper tartrate. This technique is feasible and efficient. The proposed mechanism of electroless coating over the surface is not only the chemical bonding but also mechanical bonding. In the present study, the multilayer coating is done with SiC particles in nano level and it is difficult to get a perfect coating in this nano level. Both heat-treated and not heat-treated samples are used in the present study and pH is adjusted to different values. The mechanism of electroless copper coating technique involves the reduction of Cu²⁺ to Cu⁰ in the presence of formaldehyde and gets coated on the SiO₂-coated SiC particles. The bath pH and agitation time have a major effect on electroless coating. There is an optimum pH for coating. Temperature is a factor which also

affects the deposition rate. The nucleations of the coating process starts with globules in nano-size range and then grow laterally to cover the whole surface with high uniformity.

REFERENCES

- [1] Aldo. R. Boccaccini, Johann Cho, Judith A. Roether, Boris J.C. Thomas, E. Jane Minay, Milo S.P. Shaffer: Electrophoretic deposition of carbon nanotubes; 12 June 2006
- [2] Creighton, J.R and P.Ho: Chemical Vapor Deposition; edited by Jong Hee Park & T.S.Sudarsan, 2001.
- [3] Daniel.M.Dodlein & Michael.Z.Zuraw: Chemical Vapour Deposition; Kluwer Academic Publishers, 2003.
- [4] Ian Mc Donald & Fredrick gumm: Catalytic methods; Chemical Company, Lyndhurst, 1984.
- [5] Jan B Talbot: Fundamentals and Applications of Electrophoretic Deposition; Department of Nano Engineering University of California, San Diego La Jolla, CA 2002.
- [6] Jayanta.S.Kapat: Intermetallic and Ceramic Coatings edited by Narendra.B.Dahotree & T.S.Sudarsan, Marcel Dekker, WC, 1999.
- [7] Lenoid.P.Dorfmann, Michael.J.Scheithour: Electroless Mo coating on copper particles, United states Patent; May 16, 2006.
- [8] Li. J. & P.A. Kohl, Complex Chemistry & the Electroless Copper Plating Process: Plating and surface chemistry, Feb 2004.
- [9] Louis Kosarek: Electroless Nickel conference of 1989 held in Cincinnati Ohio, Titled "Solderability Parameters of Electroless Nickel Bearing Electronic Finishes" in 2003.
- [10] Makowski M.P: Electroless cobalt plating bath; Wilowick, Ohio, US Patent-3416955, 1968.
- [11] Meenu Srivastava, V.K. William Grips, K.S. Rajam: Applied Surface Science 253 Surface Engineering Division, National Aerospace Laboratories, 3814–3824, 2007.
- [12] Nathan Feldstein: Composite Plating- Electroless plating fundamentals and application, 1990.
- [13] Natividad E., Lataste E., Lahaye M., Heintz J. M. and Silvain J. F.; Chemical and morphological study of the sensitisation, activation and Cu electroless plating of Al₂O₃ polycrystalline substrate, Surface Science Volume 557, Issues 1-3, 20 May 2004, Pages 129-143
- [14] Perminder Bindra, James.R.White: Fundamental aspects of electroless copper plating.
- [15] Satyajith Shukla and Sudipta Seal: Electroless Copper Coating of Zirconia utilizing Palladium as catalyst; Journal Ceram. Soc. 86[2] (2003)279-285.
- [16] Silvian J. F, J. L. Bobet, and J. M. Heintz: Electroless deposition of copper onto alumina sub- micronic powders and sintering; Composites: part A 33 (2002) 1387-1390
- [17] Teija Laine-Ma, Pekka Ruuskanen, Satu Kortet and Mikko Karttunen: Electroless copper plating and surface characterization of thermoplastic PPO based printed circuit boards; Pori Unit, Tampere University of Technology, Pori, Finland,
- [18] Thomas Nissen: Electroless nickel plating; Torben Lenau, March 1997.
- [19] Tetsuya Osakaa, Yutaka Okinakab, Junji Sasanoc, Masaru Katod: Development of new electrolytic and electroless gold plating processesfor electronics applications; Science and Technology of Advanced Materials 425– 437, 18 July 2006
- [20] Vansant E.F, P.Vander Voort, K.C. Vrancken: Characterization and chemical modification of the Silica Surface; Elsevier Science, 1995
- [21] WANG Guang-jun, WANG De-zhi: Schools of Materials Science and Engineering; Central South University, Changsha 410083, China. Trans-Nonferrous Met. Soc. China 17, 2007, (803-807)
- [22] Agarwala R C, Ray S, 1988 Z. Metallkde. 79: 472-475
- [23] Agarwala R C, Ray S, 1992 Z. Metallkde. 83: 203-207
- [24] Agarwala R C, Ph D thesis, Department of Metallurgical and Materials Engineering, University of Roorkee (presently IIT, Roorke),1987
- [25] Agarwala R C, Agarwala V, Singhal V, Stress corrosion studies of electroless silver coating with Al-3.8 wt% Mg alloy. Proc. National Seminar on Surface Eng. Jaipur, pp 54-64, 1997
- [26] Agarwala R C, Agarwala V, Sharma S B, 1999, Article presented at Institute Industry Interaction Meet, held on Oct. 9, 1999 at University of Roorkee (presently IIT, Roorkee), pp 32-40
- [27] Apachitei I, Duszczyk J, 2000, Surface Coating Technol. 132: 89-98
- [28] Apachitei I, Duszczyk J, Katgerman L, Overkamp P J B, 1998a Scr. Mater. 38: 1347-1353
- [29] Apachitei I, Duszyk J, Katgerman L, Overkamp P J B, 1998b Scr. Mater. 38: 1383-1389
- [30] Bakonyi I, Czirkai A, Nagy I, Hosso M, 1986 Z. Metallkd. 77: 425-432
- [31] Balaraju J N, Sheshadri S K, Metal Finishing 1999, 97 (7): 8-13
- [32] Bin-Sudin M, Leyland A, James A S, Matthew A, Housden J, Garside B, Surface Coating Technol., 1996, 81 (2-3) 215-224
- [33] Boudrand D W, Electroless Plating. ASM Handbook, 1994, Surface Eng. 15: 200
- [34] Bozzini B, Boniardi M,1997 Z. Metallkde 88: 493-497
- [35] Bozzini B, Cavallotti P L, Scr. Mater., 1997, 36: 1245-1248
- [36] Bozzini B, Martin C, Cavallotti P L, Lanzoni E, Wear, 1999, 225: 806-813
- [37] Brenner A, Electrodeposition of alloys, principles and practice (Academic Press), 1963
- [38] Brenner A, Riddell G, 1946, Res. Natl. US Bur. Stand. 37: 31
- [39] Brenner A, Riddell G, 1947, Res. Natl. US Bur. Stand. 39: 389
- [40] Brenner A, Couch d. E, Williams E K, 1950 J. Res. Nat. Bur. Stand. 44: 109
- [41] Datta P K, Bedingfield P B, Lewis D B, Wells P B, Structure and phase changes accompanying treatment of electroless Ni-B alloy coating, 1991, Conf. Proc. 2nd Int. Electroless Nickel Conference Solihull pp. 139-153
- [42] Dini J W, Coronado D R, Plating, 1967, 38: 385
- [43] Feldstein M D, Metal Finishing, 1999, 97: 87-90
- [44] Gaurilow G G, Chemical (electroless) nickel plating, 1979, (Redhill: Porticullis)
- [45] Gawne D T, Ma U, Wear, 1987, 120: 125-149
- [46] Ge J P, Che R X, Wang X Z, Plating Surface Finishing, 1987, 85: 69-73
- [47] Gorbunova K M, Nikiforova A A, Sadkov G A, Electrochemistry (ed.), 1966, M M Melnikova, p.41
- [48] Graham A H, Lindsay R W, Read H J 1965 J. Electrochem. Soc. 112: 401-413
- [49] Graham A H, Lindsay R W, Read H J 1962 J. Electrochem. Soc. 109: 1200-1201
- [50] Grosjean A, Rezzazi M, Tachez M, Surface Coating Technol., 1997, 96: 300-304
- [51] Gutzeit G, Plating Surface Finishing, 1959, 46: 1158, 1275, 1377
- [52] Gutzeit G, Plating Surface Finishing,1960, 47: 63
- [53] Gutziet G, London R, 1954a Met. Progr. 66:113
- [54] Gutziet G, London R, 1954b Plating 41: 1416
- [55] Heinz G S, Heinrich K, Plating Surface Finishing, 1990, 77: 50-54
- [56] Henry J, Metal Finishing, 1984a, 82: 17-18
- [57] Henry J, Metal Finishing, 1984b, 82: 45-47
- [58] Hur K H, Jeong J H, Lee D N, 1990, J. Mater. Sci. 25: 2573-2584
- [59] Husheng G, Haicheng G, Huijiu Z, Wear, 1991, 142: 291-301
- [60] Jun L, Hu X, Wang D, Plating Surface Finishing,1996, 83: 62-64
- [61] Kim D H, Aoki K, Takano O, 1995, J. Electrochem. Soc. 142: 3763-3767

- [62] R C Agarwala, Vijaya Agarwala, Electroless alloy/composite coatings: A review, Metallurgical and Materials Engineering Department, IIT, Roorkee, June/August 2003, Vol.28, Parts 3 & 4, pp.475-493
- [63] Xiaolu Pang, Kewei Gao, Fei Luo, Yusuf Emirov, Alexandr A. Levin, Alex A. Volinsky, Investigation of microstructure and mechanical properties of multi-layer Cr/Cr₂O₃ coatings, Thin Solid Films, 517 (2009), 1922-1927
- [64] Lanzoni E, Martini C, Ruggeri O, Bertocello R, Glisenti A, European Federation of Corrosion Publications (London: The Institute of Metals), 1997, No. 20, pp. 232-243
- [65] Levy D J, Electrochem. Technol., 1963, 1: 38
- [66] Li Y, Plating Surface Finishing, 1997, 84: 77-81
- [67] Mallory G O, Plating, 1974, 61: 1005
- [68] Mallory G O, Products finishing magazine, Presented at Electroless Nickel Conference, Cincinnati, OH, Nov. 6-7, 1979
- [69] Moonir- Vaghefi S M, Saatchi A, Hedjazi J, Metallkde, 1997 Z, 88: 498-501
- [70] Narayan R, Pandey A, Electroless Ni PTFE composite coatings, 1997, Proc. of 12th National Convention of Metallurgists and Material Scientists, at Jaipur, pp. 98-106
- [71] Odekerken, 1996, Brit. Pat. 1,041, 753, U.S. Pat. 3,644, 183 and DDR Pat. 41,406
- [72] Parker K, Shah H, Plating, 1971, 108: 230
- [73] Parker K, Recent advances in electroless nickel deposits, 8th Interfinish Conference Basel, 1972
- [74] Pena-Munoz E, Bercot P, Grosjean A, Rezrazi M, Pagetti J, Surface coating technol., 1998, 107: 85-93
- [75] Ramasubramanian M, Popov B N, White R E, Chen K S, J. Electrochem. Soc., 1999, 146: 111-116
- [76] Sharma S B, Agarwala R C, Agarwala V, Ray S, Wear and Friction behaviour of Ni-P-ZrO₂-Al₂O₃ composite electroless coatings, 2001
- [77] Staia M H, Castillo E J, Puchi E S, Surface Coatings Technol., 1997, 94-95: 43-48
- [78] Shehdeh Jodeh, Tribological Properties of Composite Multi-layer Coating
- [79] P. Sai, Venkata Pramod, Krishna Valleti, M. Ramakrishna K. V. Rajulapati, Ravi. C. Gundakaram, S.V. Joshi, Structure-Property Correlation of Multi-layer coatings
- [80] A. Urena, J. Rams, M.D. Escalera, M. Sanchez, Effect of copper electroless coatings on the interaction between a molten Al-Si-Mg alloy and coated short carbon fibres, 2007.