Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 27 (2007) 3983–3986
www.elsevier.com/locate/jeurceramsoc

Electroless multilayer coatings on aluminium–silicon carbide composites for electronics packaging

A. Ureña*, M.V. Utrilla, J. Rams, P. Rodrigo, M. Ferrer

Departamento de Ciencia e Ingeniería de Materiales, ESCET, Universidad Rey Juan Carlos, 28933 Móstoles, Madrid, Spain

Abstract

Present research studies the deposition of electrical conductive coatings on aluminium matrix composites that have 75 vol% of SiC particles (AlSiC composites) to be used for electronics packaging. Ni(P)–Au multilayer coatings were produced by electroless plating, and continuous and well adhered coatings have been developed. Coatings were characterised using microstructural and micromechanical techniques (microhardness and nanoindentation). Corrosion tests in aggressive environments were also applied to analyse the durability of the coatings under extreme service conditions.

Keywords: Films; Composites; Interfaces; Corrosion; SiC

1. Introduction

A driving force for the electronic industry is the necessity of increasing the packaging density and the power of electronic and microwave devices. This has brought up the necessity of implementing new materials to be used in form of hermetic boxes or as carriers that allow handling higher powers while fitting well into current technology.[1] These materials must have coefficients of thermal expansion (CTE) close to those of ceramic substrates used nowadays (alumina, beryllium oxide or aluminium nitride), or to Si or GaAs semiconductors. In addition, materials with higher thermal conductivity are needed to maintain the component within its service temperatures.

Kovar, i.e. a nickel–cobalt ferrous alloy, is the most used material because of its low CTEs and acceptable weldability, in spite of its reduced thermal conductivity and high density. Molybdenum and tungsten or metal–metal composites, such as W–Cu and Mo–Cu, have compatible CTEs and higher thermal conductivities, although they are dense. The application of metal matrix composites (MMCs) with high content of ceramic particles is being investigated.[2] In particular, aluminium matrix composites with silicon carbide particles (AlSiC) are those that better combine adequate CTE values (controlled by means of the percentage of ceramic phase), with high thermal conductivity, reduced density and outstanding values of specific strength and stiffness.[3,4]

To achieve environmental durability against corrosion and to facilitate joining with other electronic stages, electronic carriers must be coated with Au and/or Ni alloys. Since the discovery of autocatalytic electroless nickel (EN) plating, this technology has been extensively applied in avionics and electronics[5] as it provides excellent corrosion resistance, solderability, thermal stability and electrical properties.[6,7]

In this study, we have focused on the EN plating technologies of aluminium matrix composites with 75 vol% SiC particles. Nickel–phosphorus coatings have been laid on substrates, and on them gold coatings have been deposited using a cyanide-free bath. The aim of this research is to determine the optimum EN plating conditions that give place to continuous and well adhered coatings on the AlSiC substrate that ensure environmental durability.

2. Experimental procedure

AlSiC substrates used (Electrovac, Austria) were fabricated through a pressure infiltration method of a cast aluminium alloy (AA356) on SiC particle preforms constituted with bimodal size particle distribution (average sizes of 46.7 and 5.9 μm) to 75 vol% SiC. Samples were cut down to 24 mm × 20 mm × 2 mm, and were washed with ethanol and acetone in an ultrasonic bath and rinsed with deionised water.

---

* Corresponding author. Tel.: +34 914887015; fax: +34 914888150.
E-mail address: alejandro.urena@urjc.es (A. Ureña).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.02.079

Table 1
Conditions of AlSiC substrate pre-treatment

Stage	Aqueous solution composition	Procedure (at 25 °C)
Sensitization	$SnCl_2 \cdot 2H_2O$ (12 g/L) HCl (40 mL/L)	Ultrasonic bath Time: 15–30 min
Activation	$PdCl_2$ (0.2 g/L) HCl (2.5 mL/L)	Ultrasonic bath Time: 10 min

Before metallization, ceramics require a sensitizing stage. However, the presence of a metallic phase in the substrate could allow avoiding the application of this pre-treatment, so sensitized and non-sensitized AlSiC surfaces were studied. Both were activated in a solution containing $PdCl_2$ and HCl, forming Pd sites on the substrate to allow the later metallization with Ni; Table 1 resumes the conditions used.

For EN plating, samples were vertically rotated (100 rpm) inside the metallization solution (Table 2). The influence of metallization temperature (70, 75 and 80 °C) and time (10, 20 and 25 min) on the thickness and properties of coatings was also evaluated. After EN plating, specimens were rinsed in deionised water for 1 min and dried at 60 °C for 1 h.

Gold plating was carried out on the same equipment as EN using Table 3 solution at 60 °C and pH 8.8 for 10–30 min time. Plating was carried out without adding any reducing agent that would favour the direct Au deposition by a displacement mechanism (cementation) on EN plated substrates. After plating specimens were rinsed in deionised water and dried.

Surfaces and cross-sections of different samples were characterised by scanning electronic microscope (SEM) Philips XL30 ESEM with an energy dispersive spectroscopy (EDS). Vickers microhardness measurements (Micromet 2103) were carried out on the coatings with 1 N loads for 15 s. A nanomechanical test instrument from Hysitron installed on a Digital Instruments Multimode IIIa AFM with a diamond tip was used for nanoindentation tests. The full load–displacement curve was acquired, and from it hardness and elastic modulus were determined.

To evaluate the corrosion resistance and possible passivation behaviour of the EN coated AlSiC substrates, potentiodynamic anodic polarization curves were acquired in 0.5 M H_2SO_4 solution at room temperature with a potentiostat/galvanostat (EG&G 273A) in a three electrode cell with a graphite bar as counter electrode and a saturated calomel electrode as reference. After a 10 min immersion to stabilize the open-circuit potential (E_{corr}), potentiodynamic curves were recorded by sweeping the electrode potential from −250 to 1200 mV (with respect to E_{corr}), at 2 mV/s rate.

Table 2
Chemical composition of the aqueous solution used for electroless nickel plating

Chemical	Concentration
$NaH_2PO_2 \cdot H_2O$	20 g/L
$NiSO_4 \cdot 6H_2O$	40 g/L
$Na_3C_6H_5O_7 \cdot 2H_2O$	100 g/L
NH_4Cl	50 g/L
$NH_3 \cdot H_2O$	To keep pH 8.5

Table 3
Chemical composition of the aqueous solution used for gold plating

Chemicals	Concentration (g/100 mL)
$NaAuCl_4$	0.54
Na_2SO_3	1.51
$Na_2S_2O_3 \cdot 5H_2O$	9.92
$Na_2B_4O_7 \cdot 10H_2O$	3.81

3. Results and discussion

One objective of this study was to determine the relevance of the sensitizing stage with $SnCl_2$ of AlSiC composites. During sensitization, the adsorption of Sn^{2+} ions occurs and they directly react during activation reducing Pd^{2+} ions into Pd^0. Cross-sections of EN coated specimens obtained on unsensitized substrates are similar to sensitized ones. This indicates that the aluminium of the substrates, which covers 25% of sample surface, can reduce Pd^{2+} (Eq. (1)) and deposit Pd^0. For this reason, this initial pre-treatment was obviated in the following.

$$2Al^0 + 3Pd^{2+} \leftrightarrow 2Al^{3+} + 3Pd^0 \qquad (1)$$

Activation and metallization conditions were optimized to obtain a continuous and well adhered coating with about 6 μm thickness, standard values for electronic devices coating. The layers obtained after metallizing for 20 min at 80 °C and pH 8.5 showed homogeneous coating thicknesses (6.20 ± 0.60 μm) and reproduced the AlSiC surface defects and discontinuities. However, some differences were observed among the Ni coatings deposited on Al matrix/small SiC particle zones and those produced on large SiC particles. In both cases, the coating thicknesses are homogeneous, but higher continuity is observed on surfaces with higher Al matrix proportions (Fig. 1(a)), while lower continuity is observed when the EN coating grows on large ceramic particles (Fig. 1(b)).

Metallization times shorter than 20 min, and bath temperatures below 80 °C reduce the coating thickness, causing local discontinuities and irregular deposits. Longer metallization times and higher temperatures have been tested, but baths get unstable and Ni homogenously precipitates.

Deposited EN coatings are made of Ni–P mixtures with a phosphorous content that depends on plating conditions and coating thickness. Quantitative EDS microanalysis made across the EN thickness show that there is a linear P increase from the coating/surface interface (10.2 wt%) to the outer zone of the coating (13.1 wt% P). The following reactions explain nickel and phosphorus deposition with hypophosphite:

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \leftrightarrow Ni + 2H_2PO_3^- + H_2 + 2H^+ \qquad (2)$$

$$Ni_{cat} + H_2PO_2^- \leftrightarrow P + NiOH_{ads} + OH^- \qquad (3)$$

Reaction (3) explains the higher P content at the outer zone of the coating, where the precipitation of catalytic Ni progressively increases favouring P co-deposition. This process causes the lamellar morphology of the deposits that has been observed on transversal sections etched with a mixture of HNO_3 and

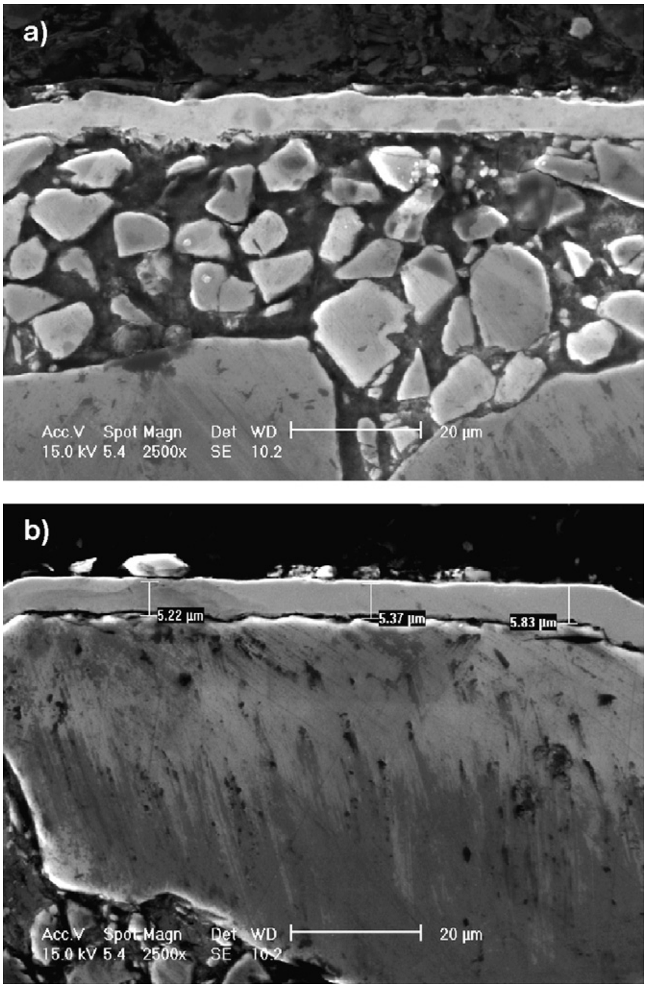

Fig. 1. Electroless Ni coating produced by $PdCl_2$ activation followed by 20 min of metallization (80 °C, pH 8.5) deposited on: (a) a SiC–Al zone and (b) a coarse SiC particle.

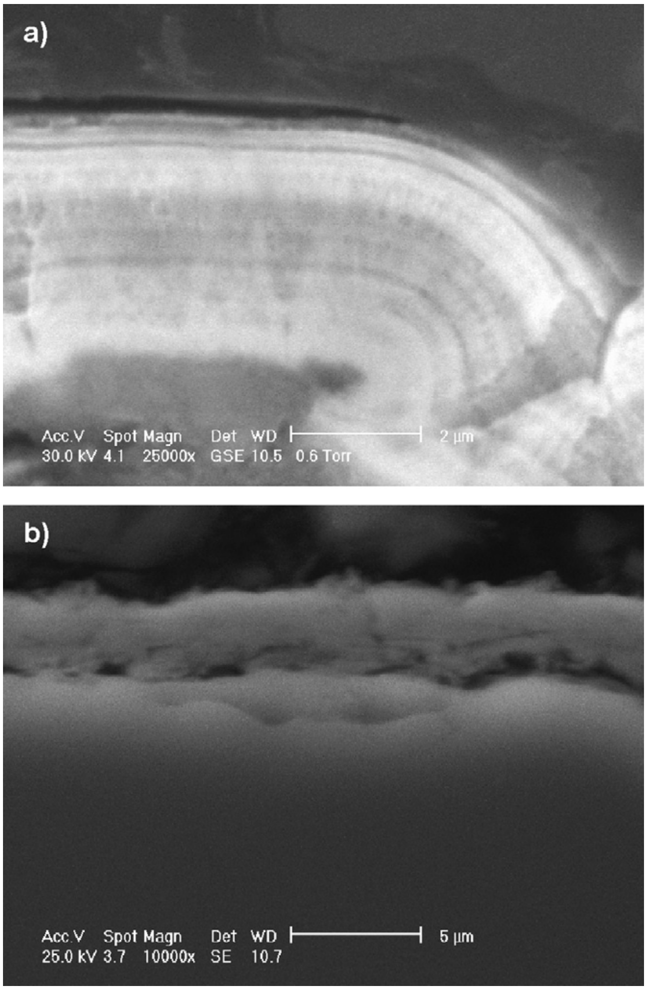

Fig. 2. SEM images of Ni–P electroless coatings: (a) lamellar structure of an etched coating and (b) coating deposited on non-activated substrate.

CH_3COOH (50/50) (Fig. 2(a)). The structure has a columnar growth mode which is more evident in the most internal layers, where the lower phosphorus content favours a higher crystalline structure.

Some authors[8] have suggested that Ni could dissociate P–H bonds, as Pd does, to produce the H_2 needed in the Ni^{2+} reduction, so that the activation treatment would be avoided. Our results indicate that coatings on non-activated substrates also grow with a lamellar microstructure, but they are more porous and heterogeneous (Fig. 2(b)).

Gold plating procedure was optimized to get 1.5 μm thick coatings on the EN plated substrates in a cyanide-free based solution. Because of the low deposition rate of Au when autocatalytic deposition is used, a heterogeneous galvanic process without reducing agents was used. This treatment originates a 1.5 μm Au film on the Ni–P coating by a displacement mechanism after a 30 min immersion. Cross-sections of golden specimens show that Au films are homogeneous and free from discontinuities at the Au/Ni–P interfaces.

Ni–P coatings were mechanically tested before the gold metallization. Vickers hardness measured is in the 280–415 H_v range, showing an almost linear decrease with the coating thickness. The thinnest coating shows the highest hardness because of the greater influence of the hard substrate on the measurements. For this reason, nanoindentation was used as it is not influenced by the substrate. Elastic modulus and hardness measured on the surface of a 6 μm thick coating are 210 ± 30 and 12.0 ± 1.0 GPa, respectively. Local variations of both properties are associated with the heterogeneous structure of the Ni–P coatings.

When comparing potentiodynamic polarization curves (Fig. 3), EN coated under optimal conditions, i.e. 20 min metallization time at 80 °C (dotted line), shows an increase of the corrosion potential (E_{corr}) as compared with uncoated substrate, indicating a nobler behaviour. In addition, the corrosion density (i_{corr}) decreases one order of magnitude, confirming the better behaviour of EN coatings under sulphuric dissolutions. In this kind of environment, pure nickel forms a stable nickel oxide film which behaves as passive layer; the absence of a vertical anodic branch indicates that EN coatings do not show a passive behaviour.

Polarization curves for coated substrates with shorter metallization times (thin line) or without activation pre-treatment (dashed line) show poorer corrosion behaviours (lower E_{corr} and higher i_{corr}) in relation with the optimal EN plated substrate but

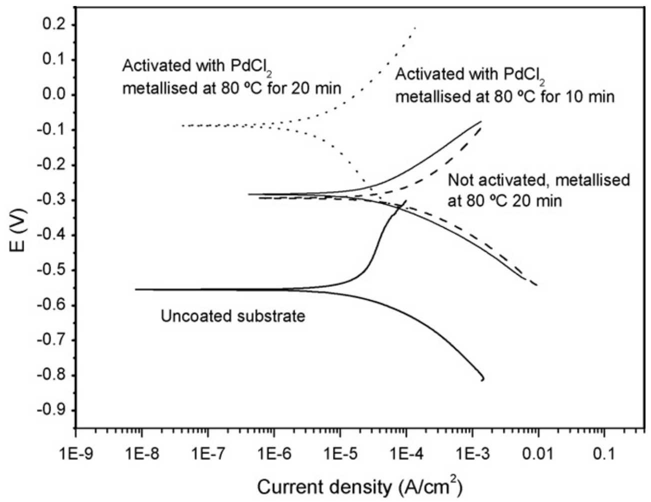

Fig. 3. Polarization curves in H_2SO_4 of different tested samples.

also regarding the uncoated one. This lower corrosion resistance can be attributed to the physical discontinuities that characterise these coatings (with higher porosity and lower adherence), and the higher P content in the thinner EN ones.

4. Conclusions

1. Electroless nickel plating of AlSiC substrates with 70 vol% ceramic contents has been obtained without sensitizing with $SnCl_2$ because aluminium from the matrix reduces Pd^{2+} in the activation stage.
2. Coatings obtained without any activation with $PdCl_2$ have lower thicknesses and higher porosity than on activated substrates, for the same metallization conditions.
3. EN coatings obtained are constituted by a Ni–P alloy that presents a lamellar structure. Phosphorous content increases from the coating–substrate interface to the outer layer of the coating.
4. Gold coatings (1.5 μm thick) have been obtained on the previously EN plated AlSiC composite by a cementation process using a cyanide-free based solution after 30 min of immersion.
5. EN plating increases the corrosion resistance of AlSiC substrates, only if coatings are thick (above 6 μm), free from porosity and well adhered to the substrate.

Acknowledgements

Authors wish to thank the financial support from MEC (MAT2004-06018) and from the CAM (ESTRUMAT-CM-MAT/77) to carry out this investigation.

References

1. Moores, K. A. and Joshi, Y. K., High performance packaging materials for improved thermal managements of power electronic. *Future Circuits Int.*, 2001, **7**, 45–49.
2. Datta, S. K., Tewari, S. N., Gatica, J. E., Shih, W. and Bentsen, L., Copper alloy-impregnated carbon–carbon hybrid composites for electronic packaging applications. *Metall. Mater. Trans. A*, 1999, **30**, 175–181.
3. Wu, G., Zhang, Q., Chen, G., Jiang, L. and Xiu, Z., Properties of high reinforcement-content aluminum matrix composite for electronic packages. *J. Mater. Sci. Mater. Electron.*, 2003, **14**, 9–12.
4. Davidson, A. M. and Regener, D., A comparison of aluminium-based metal-matrix composites reinforced with coated and uncoated particulate silicon carbide. *Compos. Sci. Technol.*, 2000, **60**, 865–869.
5. Jin, J. G., Lee, S. K. and Kim, Y. H., Adhesion improvements of electroless plated Ni layer by ultrasonic agitation during zincating process. *Thin Solid Films*, 2004, **466**, 272–278.
6. Tsai, T. K. and Chao, C. G., The growth morphology and crystallinity of electroless NiP deposition on silicon. *Appl. Surf. Sci.*, 2004, **233**, 180–190.
7. Lostetter, A. B., Barlow, F. and Elshabini, A., An overview to Integrated Power Module (IPM) design for high power electronics packaging. *Microelectron. Reliab.*, 2000, 365–379.
8. Li, L., An, M. and Wu, G., A new electroless nickel deposition technique to metallise SiCp/Al composites. *Surf. Coat. Technol.*, 2006, **200**, 5102–5112.