

POROSITY TESTING OF SILVER ELECTROPLATES

SOBHA JAYAKRISHNAN, B S SUMATHI, K R TAMILARASI, RM KRISHNAN
S SRIVEERARAGHAVAN, R SEKAR AND VISALAKSHI RAVINDRAN

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

Porosity testing is an important quality control test when a noble metal like silver is plated over a less noble basis metal. The present paper deals with an evaluation of chemical and electrographic test procedures to determine the porosity of silver electroplated over copper/nickel plated copper. A suitable electrographic test procedure has been identified.

Keywords: Porosity testing, chemical method, electrographic test.

INTRODUCTION

Silver plating offers barrier layer protection to less noble basis metals. Porosity in silver plates will result in localised corrosion of base metal at pores as they act as anodic centres. Creeping films on silver plated copper [1] is a result of pores in the silver layer. Hence porosity testing of silver electroplates is an important quality control procedure.

Porosity testing method depends on the base metal - plating metal combination. Testing methods can be of various types [2-4] and they are based on physical, chemical or electrochemical testing procedures. The present paper deals with the standardisation of a test procedure for measuring the porosity of electroplated silver on copper or nickel plated copper.

EXPERIMENTAL

Preparation of plated test specimens

Copper plates (2.5 x 7.5 x 0.03 cm) were mechanically polished, degreased using trichloroethylene, electrocleaned and then electroplated. Electroplating of silver was done either directly on copper or after applying a nickel (5 µm) undercoat. The composition of plating solutions and the operating conditions used are described in Table I. The duration of silver plating was so adjusted to obtain plates of varying thickness.

Porosity testing

In the chemical method of porosity testing, Whatman 40 filter paper strips (3.0 x 8.0 cm area) were soaked in test solution and left on the sample for a fixed duration. Filter paper was removed and suitable developer solutions applied over it to observe color changes at the areas corresponding to pores in the coating.

TABLE I: Composition of plating solutions and operating conditions used

	Bath composition	Temp K	C D A/dm ²	Duration (mts)
Nickel plating	Nickel sulphate 240 g/l	323	2.0	10
	Nickel chloride 30 g/l			
	Boric acid 30 g/l			
Silver strike	Silver cyanide 5 g/l	305	1.0	1
	Potassium cyanide 75 g/l			
Silver plating	Silver cyanide 40 g/l	305	0.5	---
	Potassium cyanide 60 g/l			
	Potassium carbonate 30 g/l			

In the electrochemical method of porosity testing, electrographic test was conducted as follows. Filter paper was taken in bunches of 5 strips, soaked in test solution and kept on the sample to be tested, which is connected to positive terminal of a regulated power supply unit. Aluminium plate (2.5 x 7.5 x 0.05 cm), kept pressed over it using a load of 1 Kg, was connected to the negative terminal. Suitable current was passed for a definite duration. Filter paper was removed and developer solution applied over it to observe colour changes indicating coating porosity.

RESULTS AND DISCUSSION

Porosity testing by chemical method

In the initial trials on porosity testing the test solution contained 10 g/l potassium ferricyanide and 50 g/l sodium chloride a composition similar to the modified ferroxyl test solution of ASTM test method B 765 [5]. Testing was done on nickel plated (1 μm) copper, silver plated (0.3 μm) copper, silver (0.3 μm) plated over a nickel (5 μm)

TABLE II: Results of trials on porosity testing by chemical method

Specimen details	Test solution	Duration (mts)	Developer solution	Observation
Ni 1 μm	Potassium ferricyanide 10 g/l + NaCl 50 g/l	30	Potassium ferrocyanide 20 g/l	Brown spots
Ag strike + Ag plating 1 mt	"	10	"	Blackening of silver
	"	30	"	Blackening of silver + Brown areas
	NaCl 50 g/l	10	Potassium ferricyanide 10 g/l	No visible change
	"	30	"	"
	NaCl 50 g/l (ammoniacal)	10	"	"
Ni 5 μm + Ag strike + Ag plating 1 mt.	Potassium ferricyanide 10 g/l + NaCl 50 g/l	10	Ammoniacal dimethyl glyoxime	Blackening of silver
	"	30	"	Blackening of silver + red areas
	NaCl 50 g/l	10	"	No visible change
	"	30	"	"

undercoat on copper. Test results are shown in Table II. When potassium ferrocyanide (20 g/l) solution was used as the developer solution, porosity in nickel coated over copper could be easily identified from the brown spots. But in the case of silver plated over copper, blackening of silver was observed making the identification of brown spots very difficult. Similar problem was observed in the case of silver plated over copper with nickel undercoat also. Though the use of ammoniacal dimethyl glyoxime as developer solution shows some reddish areas, blackening of silver results in difficulties in identifying the spots.

Trials with sodium chloride solution (50 g/l) as test solution either neutral or ammoniacal, showed no visible identification of pores in the coating, blackening of silver also was not noticed.

Porosity tests by electrochemical method

Results of trials on porosity testing by electrographic method are shown in Table III. Use of ferroxyl solution as test

TABLE III: Results of trials on porosity testing by electrochemical method

Specimen details	Test solution	Current used (mA/cm ²)	Duration (mts)	Developer solution	Observation
Silver strike + silver plating for 1 mt.	Potassium ferricyanide 10 g/l + NaCl 50 g/l	2	5	Potassium ferrocyanide 20 g/l	Blackening of silver + brown areas
	Sodium carbonate 40 g/l + Sodium nitrate 10 g/l	2	5	Potassium ferrocyanide 20 g/l	Blackening of silver + brown areas
	NaCl 50 g/l	2	5	"	Brown areas
	"	5	2	"	"
Nickel 5 μm + silver strike + silver plating for 1 mt	Potassium ferricyanide 10 g/l + NaCl 50 g/l	2	5	Ammoniacal dimethyl glyoxime (1%)	Blackening of silver + red areas
	Sodium carbonate 40 g/l + Sodium nitrate 10 g/l	2	5	"	Blackening of silver + red areas
	NaCl 50 g/l	2	5	"	Red areas
	"	5	2	"	"
	"	10	1	"	Blackening of silver

TABLE IV: Results of electrochemical tests with silver electroplates of varying thickness

Basis surface	Thickness of silver plating	Pore area % or number of pores/10 cm ²
Copper	0.0	100%
	0.1	100%
	0.3	90%
	0.7	84%
	1.5	8
	3.0	3
	5.0	2
	7.0	0
	10.0	0
Ni 10 µm over copper	0.0	100%
	0.1	199%
	0.3	80%
	0.7	70%
	1.5	9
	3.0	4
	5.0	1
	7.0	0
	10.0	0

solution followed by anodic treatment at 2 mA/cm² and development with either potassium ferrocyanide or dimethylglyoxime resulted in blackening of silver as in the case of chemical method. Similar results were observed when a test solution consisting of sodium carbonate 40 g/l and sodium nitrate 10 g/l was used.

But the use of sodium chloride (50 g/l) as the test solution and anodising at 2 mA/cm² or 5 mA/cm² for 5 and 2 mts respectively followed by use of suitable developer solution was found to be effective in producing identifiable brown spots without blackening of silver. Use of potassium ferrocyanide solution (20 g/l) showed brown areas revealing porosity of silver coated over copper whereas ammoniacal dimethyl glyoxime solution (1%) showed red areas revealing porosity of silver over nickel undercoat. Electrochemical treatment at 10 mA/cm², however, showed blackening of silver.

To assess the suitability of above method to test electroplates of varying thickness, experiments were repeated with silver plates of varying thickness. Results (Table IV) show that at low thickness of silver upto 0.7 µm on copper or nickel surface, brown or red areas extending to 70-100% of total area visible showing that coverage with silver was very poor. But at 1.5-5.0 µm silver, spots were visible indicating the presence of porosity in plating. At higher thicknesses plating was found to be nonporous as there was no coloured areas or spots.

On the basis of the above results the following electrographic methods to test the porosity of silver plated over copper or nickel plated copper was identified. A bunch of filter paper strips soaked in sodium chloride 50 g/l is to be pressed between test specimen and aluminium sheet. Specimen is to be made anode and Al as cathode and a current of 2 mA/cm² applied for 5 mts. Then the filter paper is to be removed carefully and colour developed using developer solution. The solution for silver plated copper is potassium ferricyanide 10 g/l solution and pores are visible as brown spots. The developer solution for silver plated over a nickel undercoat is dimethylglyoxime (1%) solution made ammoniacal and pores are visible as red spots.

CONCLUSION

An electrochemical method for detecting porosity of silver electroplated over copper either directly or with nickel undercoats has been optimised using sodium chloride solution as test solution and potassium ferricyanide/dimethylglyoxime solution as developer solution.

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