

Electrodeposition of Co–Mo–P barrier coatings for Cu/Au coated systems

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Abstract

By using citrate as the complexing agent, cobalt–molybdenum–phosphorus (Co–Mo–P) alloy coatings were successfully developed and electrodeposited. Coatings containing up to about 10% Mo have been produced. Coating containing 8% Mo, 20% phosphorus and Co balance have been investigated further as barrier coating. To study the diffusion property, the apparent interdiffusion coefficients of Cu/Co–Mo–P/Ni were determined. The micro-profiling and Boltzmann–Matano Method were used to obtain the interdiffusion coefficients. It was found that the interdiffusion coefficients for nickel are higher than that the apparent interdiffusion coefficients of the Cu/Co–Mo–P alloys. The results have indicated the potentials of Co–Mo–P alloy as effective substitutes for nickel.

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1. Introduction

Solid state diffusion at the interface of metal substrate and the coating deposit can result in the degradation of the properties of a deposit. In a gold/copper system, intermetallics form at room temperature over time and bulk lattice diffusion occurs at 200 to 250 °C. For example, 1 month of exposure at 250 °C is sufficient to allow copper to diffuse extensively through 2.5 µm of gold overplate, and at 500 °C, only 3 days is required for similar penetration of 25 µm of gold [1]. In the case of gold plated jewellery and watches, underlying copper can diffuse through the thin gold deposit to the surface where it oxidizes, and lose their aesthetic appearance. An effective way to retard diffusion is to use a barrier coating. Traditionally, nickel and its alloys were used as the electroplated barrier coating. However, when the gold-plated jewellery or watches are in direct contact with human skin, body perspiration migrates through crystal boundaries of the gold coating and interacts with the nickel

layer and as a result nickel ions are released. Nickel ions cause dermatitis and nickel allergy. In view of the allergic effect of nickel in skin, the Commission of the European Union (EU) has implemented controls, on the use of nickel for products directly in contact with the human body. For articles with direct contact to human bodies which have Ni²⁺ ions, the release rates of the Ni²⁺ ions of more than 0.5 µg/cm²/week are prohibited [2].

To meet the control for the use of nickel in skin contact object, many laboratories and manufacturers are searching for substitute for nickel. Palladium [3] and copper/tin [4] coatings have been investigated and used in the last few years as nickel replacement. Palladium is one of the precious metals, which has higher corrosion resistance. Chow [5] observed that palladium barrier is not as effective as nickel. Moreover, the large fluctuation on the cost of palladium in the last couple of years has plagued the manufacturers to adopt it. Copper/tin alloy coating is another developed nickel-free barrier. However, at over 80°C, the interdiffusion of copper, tin and gold become dominated [6]. Other problems such as high internal stress and sublimation in high vacuum-temperature during the ion plating process limit their application.

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Table 1
Variation of cobalt (II) sulfate on the coating contents in Co–Mo–P bath

CoSO ₄ concentration (g/l)	Co (wt.%)	Mo (wt.%)	P (wt.%)
30	62.9	12.5	24.6
45	68.3	10.2	21.5
60	72.0	8.0	20.1
75	76.1	6.5	17.4
90	82.3	5.1	15.6

Cobalt and cobalt–tungsten have been suggested as a good substitute for, and even better than nickel as the diffusion barrier material between copper and gold [5]. Cobalt was found to be at least 100 time less allergic to the skin as that of nickel [7] and so far it does not have any legislative control for its applications for products that have direct contact with the skin. Although cobalt has excellent barrier property and better skin compatibility, the cobalt is more costly and less resistant to corrosion than nickel. Molybdenum co-deposited with cobalt can form amorphous coatings. Addition of phosphorus increases the possibility of forming amorphous coating. The amorphous coatings have high corrosion resistance and good barrier coating because they are free of crystal defects.

This paper reports the results on the study of the platings using Co–Mo–P bath. The diffusion barrier properties for bright Ni and Co–Mo–P alloys electro-deposits are compared.

2. Experimental procedure

The plating conditions of Co–Mo–P bath were tested by the Hull Cell tests. The composition of Co–Mo–P layer is depended on the deposition parameters as well as on the variation of electrolyte concentrations. The cobalt (II) sulphate content was varied from 5 to 30 g/l. Sodium molybdate content was varied from 5 to 30 g/l. Sodium

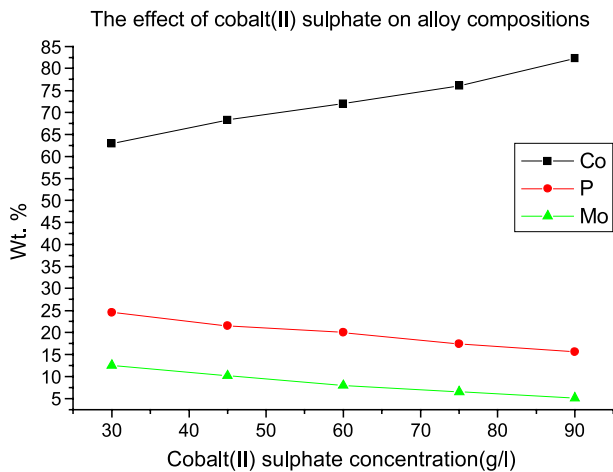


Fig. 1. Effect of bath cobalt (II) sulphate concentration on alloy compositions in Co–Mo–P bath.

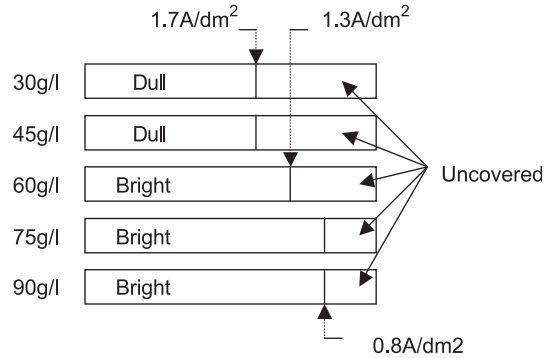


Fig. 2. The appearance of Hull cell panels in the test of bath cobalt (II) sulfate concentration in Co–Mo–P bath.

hypophosphite content was varied from 5 to 30 g/l. The citric acid content keeps at 180 g/l, respectively. The solution pH was adjusted by aqueous ammonia to 3. The plating temperature was kept at 60 °C and platinized titanium was used as anode. The alloy compositions were then determined by Energy Dispersive X-ray Spectroscopy.

In order to evaluate the performance of cobalt–molybdenum–phosphorus (Co–Mo–P) being a diffusion barrier for copper, alloy layers of thickness 0.5 and 1.0 μm were electroplated respectively on the copper substrates. The electroplated samples were then activated and plated with 20-μm bright nickel. Diffusion experiments of Cu/Co–Mo–P(barrier)/Ni and Cu/Ni systems were conducted for samples at temperatures ranging from 400 to 800 °C. Concentration–distance profiles were obtained by EDS and the results were compared with the Cu/Ni system. The chemical interdiffusion coefficients, *D*, were calculated using Boltmann–Matano method. With this analysis, the value of *D* is determined as a function of concentration and is given as:

$$D_{c=c_1} = -\frac{1}{2t} \frac{dx}{dc} \Big|_{c=c_1} \int_0^{c_1} xdc$$

where *t*=time of diffusion, (dx/dc)_{c₁}=reciprocal slope of the concentration–distance profile evaluated at *c*₁, ∫₀^{c₁} *x*dc=area between the profile and the Matano interface from *c*=0 to *c*=*c*₁ concentration lines and *c*₁=any concentration between 0 to 100%.

Concentration–distance data points with different diffusion times were fitted into a polynomial curve using computer software Table Curve produced by AISN Soft-

Table 2
Variation of sodium molybdate on the coating contents in Co–Mo–P bath

Na ₂ MoO ₄ concentration (g/l)	Co (wt.%)	Mo (wt.%)	P (wt.%)
10	73.8	5.2	21.0
20	72.0	7.2	20.8
30	71.6	7.9	20.5
35	72.0	8.0	20.0
40	64.4	15.0	20.6

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