ELECTRODEPOSITION OF DISPERSION—HARDENED CU—Al_2O_3 COMPOSITES

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Acid Copper Sulphate baths containing 25 to 125 gpl Al_2O_3 gave Cu-Al_2O_3 deposits containing 0.75 to 2.92 wt.%Al_2O_3. The highest ultimate tensile strength and microhardness of as-deposited composite foils were 36.2Kg/mm^2 and 166 VHN respectively, compared with 20.50Kg/mm^2 and 72 VHN respectively for electrodeposited copper. A stress relieving heat treatment at 500°C for 30 minutes resulted in a drop in tensile strength and microhardness. Electrical conductivity measurements of vacuum annealed Cu-Al_2O_3 foils have shown that the presence of inert alumina has not degraded the electrical conductivity. Addition of Cs^+ and Tl^+ ions to the bath has no effect on the amount of alumina codeposited with copper. Adsorption studies of radioactive Cs-137 and Tl-204 ions on Al_2O_3 have shown that these ions are not adsorbed on inert particles.

It has been well established that composite coatings containing hard ceramic particles in a soft metal matrix can be produced by electrolytic co-deposition [15]. The process differes from the conventional electrodeposition in that fine insoluble ceramic particles are suspended in the plating bath. It has, however, been reported that finely dispersed particles of Al_2O_3, SiC, $BaSO_4$, etc. do not readily co-deposit from acid copper sulphate bath unlike from acidic nickel baths and cyanide copper bath [6,7]. Addition of cationic promoters such as heavy monovalent cations like Cs^+, Tl^+ and Rb^+ to the plating solution has been reported to promote the co-deposition of these inert particles with copper [1]. Chen et al[16] have reported the possibility of co-deposition of Al_2O_3 and TiO_2 with copper from acid-sulphate bath, provided the oxide particles are of favourable crystalline form as α-Al_2O_3 and rutile-TiO_2. There has been a little or no data available in literature on the physical and mechanical properties of electrodeposited Cu-Al_2O_3 composites, though tensile and creep rupture properties as a function of temperature have been reported for Cu-Al_2O_3 and Cu-SiO_2 composites prepared by mechanical mixing method[11]. Recently Lakshminarayan et al[10] have studied the physical and mechanical properties of electrodeposited Cu-Al_2O_3 composites containing 1.2 to 2.3 v/o Al_2O_3. The possibility of electro-codeposition of sub-micron grade alumina particles with copper, to the extent of 3.3 w/o from acid-sulphate bath have been indicated[12]. The present work relates to the study of plating parameters on electrodeposition of Cu-Al_2O_3 composites from acid-sulphate bath and the physical and mechanical properties of these electrodeposited Cu-Al_2O_3 composites in the as-plated and annealed conditions.

Experimental

Electroplates of varying thickness have been obtained from acid-sulphate bath of the following composition: $CuSO_4.5H_2O$ (G.R. Grade), 200gpl; H_2SO_4 (A.R. Grade), 70 gpl.

The dispersoid, Linde Alumina type 5175, which is α-Al_2O_3 of particle size 0.3μ, was added to the bath to provide concentrations of 25–125 gpl. The addition was made by first blending Al_2O_3 powder with a small amount of electrolyte (50 ml) in a mortar, thus preventing the agglomeration of particles. The bath was prepared in distilled water. Alumina was kept in suspension by mechanical stirring.

Copper plates (3mm thick) were used as the anode. The cathode was a S.S. plate (1.5 mm thick). The deposits were separated from the substrate by trimming the edges and peeling off the substrate. The electrodeposition was carried out at 25–27°C at cathode current densities varying from 3 amp/dm^2 to 10 amp/dm^2 for 2-4 hours. A fully regulated power supply was used to provide direct current.

The oxide content in the deposits was analysed by dissolving the deposit in warm 50% nitric acid and then estimating the undissolved oxide gravimetrically.

Copper and copper-alumina deposits were mechanically tested in the as-plated condition and after annealing at different temperatures (200 to 500°C) for 30 minutes. For tensile testing 12.5 mm gauge specimens were cut from the deposits, and their room temperature yield (0.2% offset) and ultimate tensile strengths were measured using an Instron tensile testing machine. Microhardness of the deposits was determined by Leitz mini-load hardness tester with 200 gm load. A minimum of six indentations were made on the sample mounted in bakelite.

Electrical conductivity of the deposits was measured by the standard four probe technique with current reversal, using Keithley digital Nanovoltmeter. The deposits were vacuum annealed at 500°C for 30 minutes prior to electrical conductivity measurements.

Results and Discussion

Composition :

The amount of alumina incorporated in the deposit increases uniformly with the alumina concentration of

the bath (Fig 1); however, it remains almost constant at concentrations greater than 75 gpl, probably due to inefficient stirring with mechanical agitation. The photomicrographs (Fig.2) of the composites show the increase in the amount of alumina co-deposited.

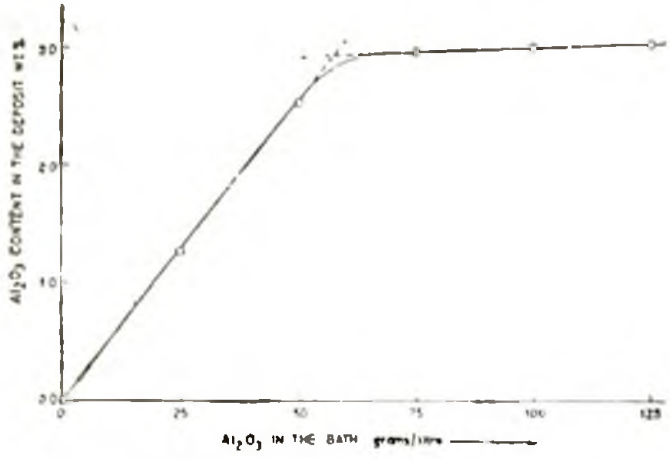


FIG 1 VARIATION OF THE AMOUNT OF Al_2O_3 INCORPORATED IN THE DEPOSIT WITH THE AMOUNT OF Al_2O_3 IN THE BATH. ELECTRODEPOSITION CARRIED OUT AT CATHODE CURRENT DENSITY 3.3–3.6 amp/dm²

Cathode current density has no perceptible influence on the alumina content of the deposits, except in cases where the alumina bath concentration was 25 gpl, in which case an increase in cathode current density from 2.75 to 10.00 amp/dm² decreases the alumina content of the deposits from 1.25% to 0.75%. This observation is in agreement with Foster and Kariapper[13] who have pointed out that at higher bath loadings, cathode current density has little or no effect on the extent of co-deposition.

Alumina content of the deposits has been observed to increase slightly with plating time up to 30 minutes; for an increase in plating time from 10 minutes, to 30 minitus the value has been observed to increase from 2.56 w/o to 2.92 w/o for electrodeposit at 3.3 amp/dm² from a bath containing 75 gpl alumina. In all plating tests, a plating time of 2 to 4 hours has been kept.

The pH of the bath has no significant effect on the amount of alumina in the deposit.

Effect of addition of cesium and thallium ions on co-deposition:

It has been reported in literature[3] that addition of certain heavy monovalent cations like cesium, thallium and rubidium ions to the acidic copper sulphate bath promotes co-deposition of fine inert particles such as Al_2O_3, SiC, $BaSO_4$, etc. The effect of addition of Cs^+ ions (1 to 4 gpl) and Tl^+ ions (0.004 to 0.24 gpl), both as sulphate, on the co-deposition of α-alumina with copper has been studied in detail; the addition of either Cs^+ or Tl^+ ions has practically no effect on the co-deposition of alumina with copper.

Table 1 Effect ofAddition of Cr and Ti (3hr plating 25°)

75 gpl Al_2O_3 in bath			12.5 gpl Al_2O_3 in bath		
Cs Conc. gpl	c.c.d. amp/dm²	w/o Al_2O_3 indeposit	Tl Conc. gpl	c.c.d. amp/dm²	w/o Al_2O_3 in deposit
0	3.54	2.93	0.0	4.0	3.22
1	3.51	2.89	0.04	4.0	3.34
2	3.35	2.86	0.06	3.31	3.24
3	3.35	2.81	0.12	3.25	3.32
4	3.35	2.82	0.12	6.6	2.44
			0.18	3.25	3.22
			0.24	3.31	3.21

It has been suggested that the cation adsorption on the fine particles is an important factor in its ability to be co-deposited [1,8,10-16]. These cation (Cs^+ or Tl^+) may be adsorbed on the inert particles, thus promoting the co-deposition of these particles. Our studies on the adsorption of Cs^{137} ions (by radioactive tracer technique– Cs^{137} being r-ray emitter) on α-alumina particles in the acid sulphate bath have however indicated that Cs^+ ions are not adsorbed onto the oxide particles.

Mechanical Properties :

Both yield and ultimate tensile strengths increase with the amount of oxide in the deposit, (Fig 2). Like the strength values, microhardness also increases with the amount of alumina in the deposits (Fig. 2). An increase in the oxide content of deposits, on the other hand decreases the ductility of the deposits, the percent elongation being reduced from 31.5 for pure copper to 11.5 for deposits containing 2.92 w/o alumina.

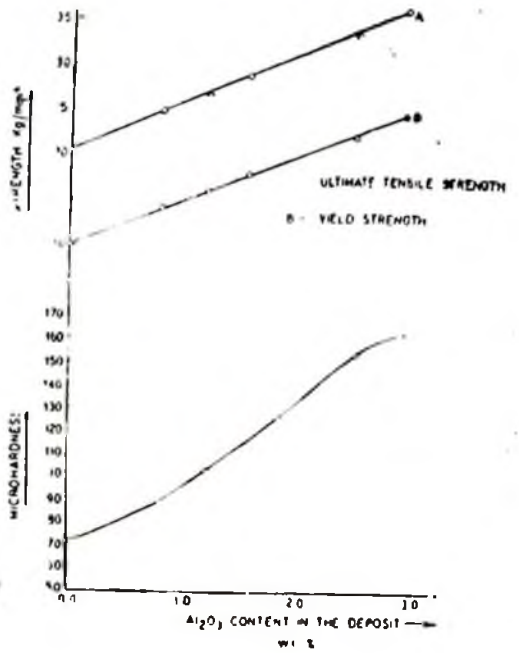
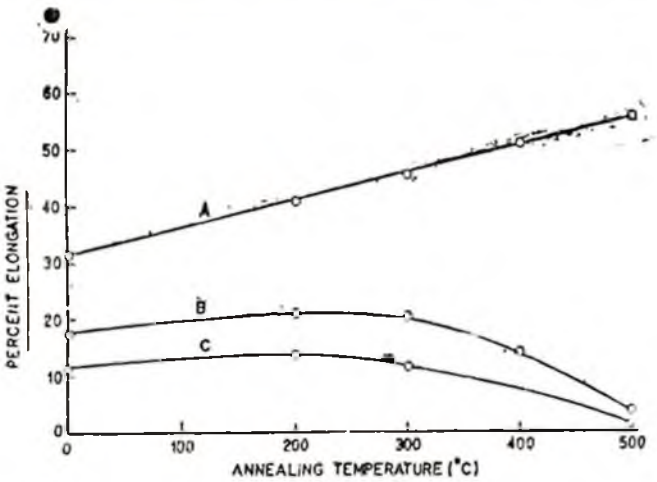


FIG 2 VARIATION OF ULTIMATE TENSILE STRENGTH, YIELD STRENGTH AND MICROHARDNESS WITH THE OXIDE CONTENT OF THE DEPOSITS

Annealing the deposits has been found to greatly their modify mechanical properties. Figs 3 and 4 illustrate



A- ELECTRODEPOSITED COPPER.
B- Cu-Al_2O_3 ALLOY 1.62% Al_2O_3
C- Cu-Al_2O_3 ALLOY 2.92% Al_2O_3

FIG 4 VARIATION OF PERCENT ELONGATION WITH ANNEALING TEMPERATURE

the effect of annealing at 200 to 500°C on yield and ultimate tensile strengths and on percent elongation respectively of the electrodeposited copper and copper-alumina deposits. It is evident from Fig.3 that whereas the electrodeposited copper shows a slight increase in both yield and ultimate tensile strengths if annealed at temperatures below about 450-480°C, the copper-alumina deposits show a decrease in these mechanical properties on annealing at temperatures above 200°C. However, the strength of these deposits is better as compared to electrodeposited copper, if annealed at temperatures below 430°C. On annealing at 500°C the deposits do not show any sign of blistering or cracking; their strength is, however, very much low, lower than even pure copper electrodeposit. The microstructure of the deposits Fig.2 (e) shows particle agglomeration and non-uniform distribution in the copper matrix, with the result that large non-

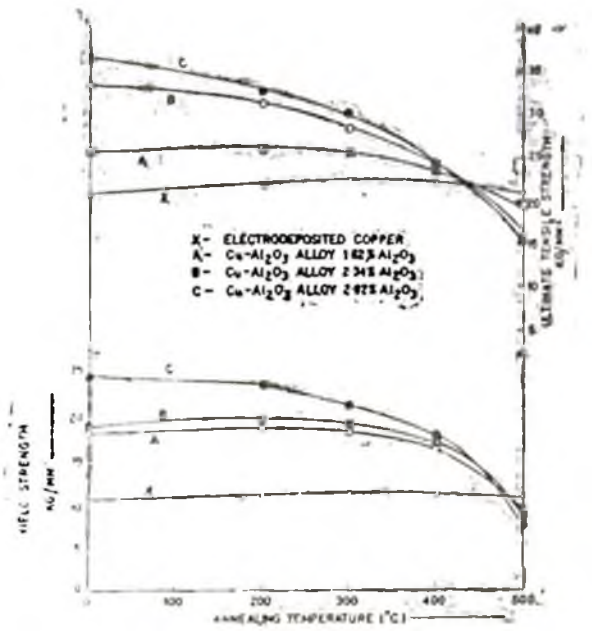


FIG 3 VARIATION OF YIELD STRENGTH AND ULTIMATE TENSILE STRENGTH WITH ANNEALING TEMPERATURE

uniform dislocation stress fields are formed around the agglomerated particles with a resultant shearing of the particles before effective hardening can occur[17-19].

Percent elongation of the deposits has been observed to increase slightly on annealing at temperatures up to 300°C (Fig.4). At higher annealing temperatures, elongation, however, decreases considerably to a very low value of 2.5 to 4.5 percent (at 500°C), as compared with about 56% for pure copper.

On the other hand, microhardness values for both copper and copper-alumina deposits decrease on annealing. The decrease is however small for copper, from 72 to 53.5, as compared with copper-alumina deposits whose values decrease from 118 to 74.8 for deposits containing 1.62 w/o alumina and from 166 to 85 for deposits containing 2.92 w/o alumina at 500°C.

Electrical Conductivity of Cu and Cu-Al_2O_3 Deposits

Room temperature electrical coductivity of electrodeposited copper and copper-alumina deposits is summarized in Table-II. The value for copper (0.51×10^6 mhos/cm) is in good agreement with that reported by

Lamb et al [17]. The electrical conductivity of copper-alumina deposits decreases with the amount of alumina incorporated in the copper matrix. It decreases by about 6% for deposits containing 1.25 w/o alumina and by about 16% for deposits containing about 2.0 w/o alumina. A decrease of about 8-10% for deposits containing 2.0 to 2.2 v/o has been reported by Lakshminarayan et al [10]. In their studies on copper-silica deposits (prepared by mechanical mixing of powders, pressing, sintering and hot extrusion) Zwilsky et al [11] have reported an increase of 6 to 25% in electrical resistivity over pure copper, for deposits containing 3w/o silica.



Fig.5 Photomicrographs of the Cu-Al_2O_3 deposits in the as-plated (a-d) as well as in annealed (at 500°C for 30 minutes) condition(e) obtained at c.c.d's of 3.3 to 3.6 amp/dm^2 ; Al_2O_3 bath concentration being a-20 gpl, b-30 gpl, c-40 gpl d-and e-50 gpl (x 225)

TABLE - II **Electrical Conductivity at Room Temperature**

w/oAl_2O_3 in deposit	Electrical conductivity mhos/cm($\times 10^6$)
0	0.51
1.25	0.48
1.97	0.35
2.04	0.33
2.71	0.28
2.80	0.29

Conclusion

Copper-alumina composites containing 3.2 w/o alumina can be easily produced by electro-codeposition of sub-micron α-alumina particles with copper from an acid-sulphate bath.

Addition of cesium and thallium ions have practically no effect on the co-deposition of α-alumina particles with copper.

The incorporation of oxide with copper increases the room temperature yield strength, ultimate tensile strength and microhardness and decreases the ductility of the as-plated deposits.

The electrical conductivity decreases slightly with the incorporation of oxide with copper.

Annealed deposits can retain higher strength (as compared to pure copper deposit) if annealed below 430°C; there being a decrease in strength values if annealed at temperatures above 430°C. The optimum annealing temperature, from ductility point of view, however, is between 250 and 300°C.

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