# Electroplating of Copper on Annular Zirconium Alloy Billets

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Copper has been electroplated on the inner and outer surfaces of cylindrical annular zirconium alloy billets, prior to hot extrusion. A copper rod served as internal anode and a copper pipe served as external anode. Two separate power supplies were used, one for coating the billet inner surface and the other for the billet outer surface, enabling independent current control. A cathode current density of 2.0 A/dm<sup>2</sup> (18.6 A/ft<sup>2</sup>) for the outer surface and 1.3 A/dm<sup>2</sup> (12.1 A/ft<sup>2</sup>) for the inner surface of the annular billet were found to have given the specified thicknesses of copper in a plating bath without agitation. The current density voltage relationship with concentric cylindrical anode-cathode geometry has been examined and compared to that of parallel plate geometry. The polarization (nonohmic) voltage drop at the electrode was found to be higher for the inner electrode than for the outer one, which was in turn, more than that observed for horizontal parallel plate electrodes.

Zirconium alloy billets are clad in copper sheets before hot extrusion. The copper acts as a lubricant during high temperature extrusion, prevents the sticking of zirconium alloy to the extrusion container and die and protects the highly reactive zirconium alloy from oxidation. Before hot extrusion, the billets are mechanically jacketed, using 1.6 mm (0.63 in.) thick copper sheet. An alternative to mechanical jacketing is electroplating, which has the advantage of giving a very adherent coating. In addition, only a 0.3 mm (0.12 in.) thickness of the adherent deposit is sufficient for the purpose of extrusion, resulting in considerable savings in copper. It is seen from literature

## Nuts & Bolts: What This Paper Means to You

This paper brings together two rather interesting thrusts. The first involves the challenges of plating copper on cylindrical annular zirconium alloy billets prior to hot extrusion. The advantages and savings over copper cladding are significant. The second thrust is a geometric one, involving the steps necessary to assure quality plating on the inner and outer surfaces of these cylinders. that nickel has been plated on zirconium alloys<sup>1-8</sup> and copper has been plated on titanium alloys.<sup>9,10</sup> However, published work on electroplating copper on zirconium alloys could not be located. The present paper deals with copper electroplating of annular billets of zirconium-tin and zirconium-niobium alloy that will be subjected to high extrusion ratios of about 14.

Zirconium alloy billets of different sizes are sandblasted, water washed, alkaline cleaned and mild-acid etched before immersion into the electroplating bath and switching on the current. A copper rod serves as anode for coating the inner surface of the billet. A copper pipe serves as anode for coating the outer surface of the billet. The aim of this work is to establish the viability of copper electrodeposition with two power sources with independent control for coating zirconium alloy annular billets to be subjected to high extrusion ratios.

## Choice of plating bath and parameters

### Nature of zirconium

The electrochemical behavior of zirconium is characterized by the anodic formation of an oxide film. Because the standard potential of zirconium is very negative, the bare metal never exists in aqueous solution and a thin oxide film is always present. Previous work on zirconium, especially on thick oxide films, has shown that the oxide is of the socalled "high-field" type because the potential drop from the metal to the solution has a magnitude of 107 V/cm.<sup>11</sup> The film insulates anodically but not cathodically.<sup>12</sup> Zirconium has been found to be suitable as cathode in copper electrowinning.<sup>13</sup> The electrodeposition of copper on zirconium or its alloys should therefore be practicable.

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## Surface preparation

Cox, *et al*<sup>14</sup> found that copper deposits preferentially on scratches on zirconium alloy clad tubes. We chose sand blasting for surface preparation, which causes uniform surface roughening, thereby providing a multitude of possible sites for preferential copper deposition. When plated without sand blasting, the deposition was non-uniform and non-adherent.

*Alkaline cleaner solution.* A mixture of 0.5% sodium carbonate, 0.75% trisodium phosphate and 1% sodium metasilicate solution in distilled water was used for cleaning.

*Etching solution.* It is known from the literature that zirconium was etched in a solution of ammonium fluoride and hydrofluoric acid, before plating with nickel.<sup>4</sup> We chose an etching solution consisting of hydrofluoric acid which dissociates weakly and sulfuric acid which dissociates strongly. The presence of the strong acid further reduces the concentration of the fluoride ion by common ion effect, enabling better control of the etching reaction. Specifically, a mixture of 2% hydrofluoric acid (of 48% strength) and 10% concentrated sulfuric acid was used as etching reagent. When plated without etching, the deposit was not as adherent as with etching.

### Plating bath

The sulfates of Cu(II) and Cu(I) readily hydrolyze with the formation of copper oxide which, if codeposited, would embrittle the copper deposit. The presence of sulfuric acid prevents the formation of basic salts (from hydrolysis of cuprous sulfate), decreases the resistivity of the bath and decreases the copper ion concentration, yielding finer crystal structure in the plate.<sup>15,16</sup> Several plating bath formulations are available in literature.17-20 A concentration of less than 60 g/L (8.0 oz/gal) of copper sulfate results in decreased cathode efficiency.<sup>21</sup> The addition of potassium aluminum sulfate is beneficial in producing a fine, dense grained structure in the deposit and in enhancing the conductivity of the plating bath.<sup>22</sup> Lee, et al<sup>23</sup> found that copper films plated with low acidity electrolyte [CuSO, = 40 to 70 g/L (5.3 to 9.3 oz/gal);  $H_2SO_4 = 10$  to 20 g/L (1.3 to 2.7 oz/gal)] were more reliable and void-free compared to those with higher acidity [CuSO<sub>4</sub> = 10 to 20 g/L (1.3 to 2.7 oz/gal);  $H_2SO_4$  = 150 to 200 g/L (20.0 to 26.7 oz/gal)].

We chose the acid copper bath for its simplicity of preparation, good throwing power needed to fill depressions in the workpiece, relative ability to tolerate ionic impurities and low voltage requirements. Specifically, the compositions "A" and "B" shown in Table 1 were used.

Table 1
Composition of electroplating baths

Chaminal	Composition		
Chemical	Bath A	Bath B	
Copper sulfate [CuSO <sub>4</sub> ·5H <sub>2</sub> O], g/L (oz/gal)	165 (22.0)	200 (26.7)	
Sulfuric acid [H <sub>2</sub> SO <sub>4</sub> ], g/L (oz/gal)	24.5 (3.3)	56.0 (7.5)	
Potash alum [KAl $(SO_4)_2$ ·12H <sub>2</sub> O], g/L (oz/gal)		12.0 (1.6)	

## Cathodic current density

According to the Canning Handbook,<sup>19</sup> for still solutions, the cathodic current density to be employed is 1.0 to 1.6 A/dm<sup>2</sup> (9.3 to 14.9 A/ft<sup>2</sup>). According to Fraunhofer,<sup>8</sup> the limit is 3.0 A/dm<sup>2</sup> (27.9 A/ft<sup>2</sup>). Very high current densities would lead to greater polarization, hydrogen evolution and codeposition of impurities. High current densities are usable when the bath is agitated, when the cathode (such as a printing cylinder) is rotated, when bath temperature is increased or when periodic reverse current is used. As a general rule, the distribution of the deposit is more uniform at low current densities. However, low current densities need longer plating times to achieve a reasonable deposit thickness. High current densities however, cause the deposit to build up excessively on prominent edges or extremities of the article while recessed areas may receive less than adequate coverage.<sup>19</sup> When electrotyping or electroforming molds are started, it is well to plate at a very low current density until enough copper has been deposited to conduct the current evenly over the surface of the object being plated.<sup>21</sup>

Since we provided no agitation, the cathodic current density was restricted to a maximum of 2.5 A/dm<sup>2</sup> (23.2 A/ft<sup>2</sup>). A non-agitated plating bath has the advantage that there is no agitation of solid particles from the bottom of the tank that could get occluded in the deposit and filtration can be less frequent. The use of low current density also means greater deposit purity and less non-ohmic voltage losses.

#### Anodic current density

Too high a current density at the anode may render it passive and too low a current density may cause the metal to dissolve in an unwanted valence state. Passivation is caused by cuprous chloride (CuCl) formation at low anode current densities and cuprous oxide (Cu<sub>2</sub>O) formation at high current densities, when oxygen is evolved at the anode surface. The formation of Cu<sub>2</sub>O is very common under normal process conditions and usually not a serious problem. Chloride ions in the electrolyte "punch" holes in the Cu<sub>2</sub>O layer (cathode polarizer) to keep the copper surface available for dissolution. However, when the anode surface becomes excessively passivated by the Cu<sub>2</sub>O, and the set current density can no longer be maintained by dissolving copper, the potential will rise and oxygen gas formation will take over to meet the set current density. Then the anodes will ultimately become completely passivated.<sup>24</sup>

If the copper oxide becomes detached from the anode and physically contacts the part being plated, it is reduced to copper metal and becomes welded to the surface. This creates high current density points and produces serious particle roughness.<sup>25</sup>

$$Cu_2O + 2 H^+ + 2e^- \rightarrow 2 Cu + H_2O$$

In a concentric cylindrical electrode configuration, the anodic current density of the internal anode is very much higher than that of the external anode because of the much smaller surface area of the internal anode. In the configuration used for this work, the limiting internal anodic current density was taken to be 3.0 A/dm<sup>2</sup> (27.9 A/ft<sup>2</sup>). The corresponding limit on the internal cathode current density would be 1.35 A/dm<sup>2</sup> (12.5 A/ft<sup>2</sup>), taking into account the difference between cathode and anode areas. The current density limit for the external cathode also is assumed as 3.0 A/dm<sup>2</sup> (27.9 A/ ft<sup>2</sup>). By using separate power sources for the internal and external anodes, the current density of the internal anode can be independently controlled within the acceptable range. If on the other hand, a single power source is used and the two anodes are connected in parallel, the currents in the branches will depend on the interelectrode distances, which will vary for differently sized billets. A rheostat may be incorporated in the electrical circuit of the inner anode to get the appropriate voltage but only at the cost of energy efficiency of the plating process.

#### Polarization

Figure 1 shows the nature of potential drop between electrodes in an electrolyte.<sup>26</sup> Failure to maintain good electrical contact between the bus bars and the anodes probably represents the greatest single factor in excessive or abnormal polarization. This can lead to variations in the thickness of deposits, especially in manually-operated installations.<sup>25</sup> Depletion of metal ions results in depletion in the solution adjacent to the surface. These ions must be replenished if the deposition process is to continue. Replenishment can be accomplished by (1) ionic migration, (2) convection or (3) diffusion. Ionic migration is least effective as it depends on current and transport number. When conducting salts are added, these conduct most of the current, reducing the metal ion migration to nearly zero. Convection is most effective (stirring and agitation). Diffusion is the effective mechanism for ionic migration in the vicinity of the electrode surface itself where convection is negligible.<sup>27</sup>

The copper ions move by convection in the bulk of the electrolyte and by diffusion in the diffusion layer. The charge transport is by the migration of the ions of the supporting electrolyte, in this case sulfuric acid. However, for low current densities, the concentration polarization at both electrodes is negligible. On the other hand, activation polarization is significant, the polarization of the cathode being greater than that of the anode, and the gap widens further as the current density is increased.<sup>28</sup>

#### Plating rate

In the case of nanocrystalline copper on a silicon wafer, the plating rate was found to increase linearly with current density for the same bath composition.<sup>29</sup>

### Nature of the deposit

It is known that the properties of electrodeposits depend on their microstructure, which can be substantially influenced by the deposition conditions. It has also been established that the deposit microstructure can be controlled by the current density. Using atomic force microscopy, Grujicic and Pesic<sup>30</sup> found that copper concentration, deposition potential, solution pH and the presence of a background electrolyte all had profound effects on the nucleation mechanism of copper. According to the  $E_{Cu/Cu^{+2}}$  - pH diagram, the cupric ion predominance area is confined to a narrow region between pH 0 and 4.2 and above the solution potential of -20 mV.<sup>31</sup> The soluble copper concentration rapidly decreases by two orders of magnitude for a unit increase of pH, yielding the copper hydroxy sulfate. An increase of pH and copper concentration produced nuclei with a coarser texture and lower population density. An increase of deposition potential and addition of background electrolyte had the opposite effect.<sup>32</sup> The grain size of as-deposited copper films is usually not a normal distribution and often is bimodal, indicating that some abnormal grain growth occurs during the deposition process.<sup>33</sup> In the case of nanocrystalline copper on silicon wafers, the grain size of the copper deposit decreased from 1.0 to 0.1  $\mu$ m as the current density was increased from 1.0 to 6.0 A/dm<sup>2</sup> (9.3 to 55.7 A/ft<sup>2</sup>).<sup>29</sup>

## **Experimental**

Zirconium alloy billets of inner diameter 40 mm (1.57 in.), outer diameter 118 mm (4.65 in.) and height 246 mm (9.69 in.) were sand-blasted, alkaline rinsed, acid etched and water washed, before immersion into the plating bath. The arrangement of the anode, cathode and power sources is shown in Fig. 2 along with the



Figure 1-Variation of potential from anode to cathode in electrolysis.

equivalent electrical circuit. The thickness of the plated deposit was determined by measuring the diameter before and after plating. Applied voltage and current were noted for inner and outer surfaces of the billet, for Bath A and B.

The current voltage relationship was determined for a flat copper anode and zirconium cathode. The inter-electrode distance was 100 mm and the immersed area of each electrode was  $220 \times 180$  mm (8.66  $\times$  7.09 in.). Bath A was used in this experiment.

## **Results and discussion**

#### Electrolyte resistance

The ohmic resistance of the electrolyte lying between the cylindrical copper rod and the inner surface of the annular billet may be estimated as follows:

Consider a circular ring of electrolyte with radius r and thickness dr, as shown in Fig. 3.



Figure 2-Schematic arrangement of electrodes and equivalent circuit.



Figure 3—Geometry of circular electrodes.

Resistance of the element = (resistivity) × (length) / (area) =  $\rho dr / (2 \pi r H)$ 

Resistance of the inner electrolyte between radii  $R_1$  and  $R_2$  is given by

$$\Omega_{\text{inner}} = [\rho/(2 \pi \text{H})] \int dr/r = \rho/(2 \pi \text{H}) \ln (\text{R}_2/\text{R}_1)$$
(1)

Similarly, the ohmic resistance of the outer electrolyte between radii  $R_4$  and  $R_3$  is given by

$$\Omega_{\text{outer}} = \rho/(2 \pi \text{ H}) \ln (\text{R}_4/\text{R}_3)$$
<sup>(2)</sup>

The resistivity of the copper sulfate electrolyte increased strongly with a decrease in sulfuric acid content and decreased weakly with an increase in copper sulfate content. The conductivity values were tabulated<sup>34</sup> as a function of sulfuric acid content for different copper sulfate contents. Curve fitting of the corresponding resistivity values for a CuSO<sub>4</sub>·5H<sub>2</sub>O content of 200 g/L (26.7 oz/gal) gives the expression:

$$y_{200} = 7.2489 e^{-0.0067 x}$$
 (3)

where  $y_{200}$  is the resistivity in  $\Omega$ -cm and "x" is the sulfuric acid content in g/L. For a copper sulfate concentration of 150 g/L (20.0 oz/gal), the resistivity is similarly given by:

$$y_{150} = 7.2158 \ e^{-0.0071 \ x} \tag{4}$$

Based on the above expressions, the resistivity of Bath A (low acidity) is 7.1  $\Omega$ -cm and that of Bath B (normal) is 5.2  $\Omega$ -cm.

The ohmic resistance of the electrolyte between parallel flat plate electrodes was calculated for Bath A using a resistivity value 7.1  $\Omega$ -cm. The ohmic voltage drop was obtained by multiplying the resistance by current or current density. The non-ohmic component was determined by subtracting the ohmic voltage drop from the measured total voltage drop between the anode and cathode.

#### Polarization

Figure 4 gives the current density - voltage relationship for the electrolyte with parallel flat vertical plates of copper and zirconium alloy, determined experimentally. The figure also shows the voltage versus current density for the ohmic resistance of the electrolyte contained between the flat plates. For a resistivity of 7.1  $\Omega$ -cm, the ohmic resistance of the electrolyte contained between the flat plates in bath A was 0.1768  $\Omega$ . The difference between the applied voltage and the ohmic voltage is taken to be the polarization component of the voltage. It can be seen that the polarization increased



Figure 4-Total and ohmic voltage vs. current density for flat electrodes.

as the current density increased. The slope of the line changed to a lower value above a current density of  $2.5 \text{ A/dm}^2$  ( $23.2 \text{ A/ft}^2$ ) and again at 7.0 A/dm<sup>2</sup> ( $65.0 \text{ A/ft}^2$ ). It appears that diffusion control begins at this current density. The non-ohmic component of the voltage drop was similarly determined for the inner anode-cathode as well as the outer anode-cathode in the cylindrical electrode configuration, both for Bath A.

Using equations (1) and (2) above, and the resistivity value of 5.2  $\Omega$ -cm for Bath A, the ohmic resistance of the inner electrolyte (between radius R<sub>1</sub> and R<sub>2</sub>) and that of the outer electrolyte (between radius R<sub>3</sub> and R<sub>4</sub>) were calculated to be 0.026863 and 0.031615  $\Omega$  for Bath B. Figure 5 shows the variation of current density with applied voltage with the outer anode for the cylindrical configuration. Figure 6 shows the same for the inner electrolytes with the cylindrical configuration. The polarization component of the applied voltage is shown as a percent of the total in Table 2 for the outer and inner electrolytes with the cylindrical configuration. The polarization component is indicative of unused energy with cost implications and clearly underlines the need for agitation. It can be seen that the polarization component of the applied voltage is at a minimum for the flat plates. In the cylindrical configuration, the polarization is higher for the inner electrolyte than for the outer one.

#### Plating rate

Table 3 gives the plating rates obtained under the two different conditions in Bath A. It can be seen that the plating rate on the inner diameter of the billet cathode is lower than that on the outer diameter.

It is generally expected that the plating rate increases as the cathodic current density is increased as per Faraday's Law. However, after a critical value is exceeded, the plating rate decreases as other cathodic reactions start taking place or as the anode becomes passivated. In the case of the cylindrical electrode configuration, the plating rate doubled when the internal anodic current density was decreased from 4.21 to 2.73 A/dm<sup>2</sup> (39.1 to 25.4 A/ft<sup>2</sup>). The lower the anodic current density, the lower is the probability of passivation and the greater the availability of metallic ions from anodic dissolution.

#### Summary and conclusion

The electroplating of cylindrical annular zirconium alloy billets is proposed as an economical alternative to mechanical cladding by copper sheets prior to hot extrusion. Internal and external copper anodes have been used to deposit copper on the inner and outer surfaces of the zirconium alloy billet. Two separate power sources





Figure 5-Total and ohmic voltage vs. current density for outer circular electrodes.

Figure 6-Total and ohmic voltage vs. current density for inner circular electrodes.

Table 2Polarization for inner and outer surfaces of the billet versus cathodic current density (Bath B)

	Inner Surface			Outer Surface		
Cathode current density, A/dm <sup>2</sup> (A/ft <sup>2</sup> )	1.5 (13.9)	2.0 (18.6)	2.5 (23.2)	1.5 (13.9)	2.0 (18.6)	2.5 (23.2)
Total Volts	0.44	0.80	0.89	0.75	1.26	1.50
Ohmic Volts	0.13	0.17	0.21	0.43	0.58	0.72
Non-ohmic Volts (%)	0.31 (72%)	0.63 (79%)	0.68 (77%)	0.32 (42%)	0.68 (54%)	0.78 (52%)

have been employed for the inner and outer anodes, thereby facilitating current densities independent of electrode areas and inter-electrode distances. The ohmic and non-ohmic components of the voltage drops between anode and cathode have been determined for the cylindrical electrode geometry. For comparison, the voltage drop between parallel plate electrodes of copper and zirconium alloy was also determined. The non-ohmic component of the voltage drop was greater for the cylindrical electrodes than for the parallel plate electrodes. In the cylindrical configuration, the non-ohmic drop was larger for the inner electrodes. The configuration dictates restriction of the inner anodic current density, to avoid anode passivation and consequent lowering of the plating rate.

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# Table 3Plating conditions and plating thickness (Bath A)

	Condition #1	Condition #2				
Plating Time, hr	11.34	16.0				
Outer Diameter						
Voltage, V	1.65	1.78				
Cathodic current density, A/dm <sup>2</sup> (A/ft <sup>2</sup> )	2.0 (18.6)	2.0 (18.6)				
Anodic current density, A/dm <sup>2</sup> (A/ft <sup>2</sup> )	0.7445 (6.9)	0.7445 (6.9)				
Achieved thickness, $\mu m$ (mils)	300 (11.8)	460 (18.1)				
Plating Rate, µm/hr (mil/hr)	25.00 (0.98)	28.75 (1.13)				
Inner Diameter						
Voltage, V	0.74	0.65				
Cathodic current density, A/dm <sup>2</sup> (A/ft <sup>2</sup> )	2.0 (18.6)	1.3 (12.1)				
Anodic current density, A/dm <sup>2</sup> (A/ft <sup>2</sup> )	4.205 (39.1)	2.730 (25.4)				
Achieved thickness, $\mu m$ (mils)	100 (3.9)	265 (10.4)				
Plating Rate, $\mu$ m/hr (mil/hr)	8.333 (0.33)	16.5625 (0.65)				

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