SOME POLISHING EXPERIMENTS ON COPPER IN A HYPERBOLIC CELL

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ABSTRACT

Some polishing experiments have been carried out on copper anodes in a hyperbolic cell designed by Gilmont and Walton, using orthophosphoric acid as the electrolyte. The results obtained have been compared to those obtained in similar experiments in a Hull cell. It has been found that very similar bands of different reflectivity and polishes are found to form in both the cells. These bands shift with time and a study of such displacements has been made. The results are briefly discussed.

INTRODUCTION

Of late various workers have tried to design and work out the theory of different types of electrolytic cells which would give a uniformly varying current density along an electrode assuming that there is no polarization, a condition normally not attainable in practice. The use of the Hull cell for studying electro-plating phenomena is well known. The construction of the Hull cell is fairly simple, but a theoretical and mathematical analysis of the current distribution is not so easy. Although recently Skwirzynski and Huttly have given a mathematical solution of the current distribution for a trapezoidal cell very much similar to Hull cell, yet they found that the current distribution is linear only on about \( \frac{1}{2} \) of the electrode, there being a singularity at the high current density end. According to Kasper, the proper choice of electrode geometry should give a sufficiently linear current distribution with simple mathematical solutions which would eliminate the need for empirical methods. Recently, Gilmont and Walton, on the basis of Kasper's ideas, have designed a new cell, usually referred to as hyperbolic cell, in which the current density function along an electrode is almost linear and can be predicted by a simple equation. The correct geometrical shape of the new cell was obtained by applying the fundamental principles of the theory of electro-potentials, according to which the current density lines are orthogonal to the equi-potential surfaces.
Briefly stating, the hyperbolic cell (Fig. 1) as designed by Gilmont and Walton consists of 4 sides, two of which are straight and equal intersecting at 45°. The other two sides are rectangular hyperbolas orthogonal to each other and each in turn orthogonal to one of the straight sides. One of the straight sides and its opposite curved surface are used as electrodes. The straight side is used as the anode while the curved side as the cathode. Recently, we have reported\textsuperscript{8,7} some of our experimental findings on the electrolytic polishing of copper in a Hull cell using orthophosphoric acid as electrolyte. There we observed highly different finishes on one and the same specimen, with sharp contrasts and discontinuities between these finishes or bands. Also, it was found that two almost equally polished bands were always separated by a small unpolished band. The position of the various bands was also found to shift with the time of polishing. As no definite and clear insight into these phenomena is so far available and as the current distribution in the Hull cell is rather complex, it was considered worth while to compare these observations with similar experiments using the hyperbolic cell. The results of these comparative experiments in a hyperbolic cell are reported below.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{Fig. 1}
\end{figure}

\textbf{Experimental}

In order to facilitate comparison, the hyperbolic cell was also made of perspex and the electrolyte used was of the same concentration (756 g/l of \(\text{H}_3\text{PO}_4\)) as employed in our Hull cell studies. The experimental details and copper (high purity 99.98%) electrodes were similar to those used in our previous study.

\textbf{Results and Discussion}

Figs. 2, 3, 4 and 5 show the various effects produced on copper electro-polished in the hyperbolic cell for varying times. It will be seen that in
all the figures there are 5 well-defined regions showing different reflectivity, colour, structure etc. The same are briefly described and shown in Fig. 6. The above results were found to be quite reproducible both as regards their nature and their relative position. The bands are also found to be slightly curved at the top towards the high current density end and straight at the bottom. The most interesting observation was that although this type of cell is known theoretically to have a very linear current distribution, yet, the two well polished regions (II and IV, Fig. 6) were always found to be separated by a small unpolished or frittered region (III), exactly as was the case in Hull cell experiments.

![Fig. 6](image)

The shift in the position of bands with varying time also similarly compares with that observed with Hull cell, i.e., as the polishing time increases, the different bands are found to shift towards the low current density end up to a certain extent of time after which they tend to retrace and shift back towards the high current density end. For example, during polishing at a total cell current of 6 A, the bands shift towards the low current density end up to a period of about 6 min. If the polishing time is further increased beyond 6 min. the shifts are in the opposite direction (see Figs. 4 and 5) as the time of polishing increases. Similarly, for Hull cell, it was found that at a total cell current of 4 A, the retracing of the band-shifts occurs after about 8 min.

Thus, we see that on the whole the results obtained both in a hyperbolic cell and in a Hull cell resemble each other quite closely. The full logic of these observations is not yet clear. It appears that for understanding the
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above phenomena, we must look for a detailed knowledge of (a) the progressive effect of the anodic reaction on the composition of the film of liquid near the anode, (b) the formation of solid films on the anode and their electrical properties, (c) the effect of the resulting intense polarization on the current density pattern on the anode as a function of time, (d) the current density values necessary for getting polishing effect under the particular hydrodynamic conditions obtaining at the anode, and (e) short-circuiting effect by the anode on the regions of different potentials and the consequent effect of current density pattern.

It appears that the actual conditions existing in such cells are very different from those initially assumed for working out the cell design. In electropolishing, in particular, there is a high degree of polarization due to the production of poorly conducting anodic films. This leads to complete deviation of the current distribution on the electrode, from the theoretical function. Since, moreover, the polarization is a function of time and depends on the hydrodynamic conditions, the whole pattern of current density distribution would considerably change with time.

No detailed study of the above factors has so far been reported and further work is required for a correct elucidation of our observations.

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REFERENCES

7. .......... "Polarization and Polishing studies on copper in a Hull cell"—(under publication).