HABIT MODIFICATION DUE TO CAESIUM IONS DURING THE ELECTRODEPOSITION OF COPPER ON A COPPER (111) FACE

The morphology of copper electrodeposited on the (111) plane of copper deposited from highly purified solution of acidified copper sulphate containing known concentrations of caesium sulphate was studied. Pyramids observed on (111) plane of copper when deposited from pure solution changed to layers, ridges and polycrystalline type of growth as concentration of caesium sulphate increased.

It is seen from the literature\(^1\)\(^2\) that there are very few reports on the effect of cations on the morphological and kinetic aspects during the prolonged deposition. Arsenic and antimony cause brittle and rough deposits when added to acid copper sulphate bath. The present experimental work was carried out to study the habit modification of copper electrodeposited, deposited on (111) plane of copper from acid copper sulphate bath in presence of caesium sulphate.

The cathode was (111) face of copper single crystal and the anode, a polycrystalline A.R. copper foil of area about 40 times larger than that of the cathode. The surface of the cathode was coated with araldite except the (111) plane of the crystal. This plane was mechanically polished on 400 emery paper using ethyl alcohol as a lubricant and electropolished in 50% of orthophosphoric acid at a constant cell potential of 1.2 volts in hydrogen atmosphere\(^6\). The electropolished surface of copper (111) face was washed with 10% orthophosphoric acid and finally with conductivity water and quickly transferred to the electrolytic cell. The electrolytic bath was a solution of 0.25 M pure copper sulphate and 0.1 M sulphuric acid\(^4\). A known concentration of caesium sulphate solution was added to the electrolytic bath and deposition was carried out at 10 mA/cm\(^2\) to a thickness of 10 Coulombs/cm\(^2\) at 25 ± 1°C. For each experiment fresh solution was used. The over-potentials were measured with respect to a freshly prepared copper electrode acting as a reference electrode, with the help of vacuum tube voltmeter (± 2 mv). The surface morphology was examined under a metallurgical microscope, and photomicrographs were taken.

A pyramidal type of growth was obtained when copper was deposited from purified copper sulphate at 10 mA/cm\(^2\), as noticed by earlier workers\(^5\)\(^6\) (Fig. 1). It was observed that the height of the triangular pyramids decreased as the concentration of caesium sulphate was increased from 10\(^{-10}\) to 10\(^{-4}\) m/l. When the concentration of caesium sulphate was 10\(^{-7}\) m/l, the pyramidal type of growth completely changed to layer type of growth (Fig. 2). The layer type of deposit was completely transferred to ridge type of growth at 10\(^{-5}\) m/l of caesium sulphate as illustrated in Fig. 3. The overpotential value decreased on the (111) plane as observed by earlier workers. The trend of decreasing and attaining a steady state remained but the initial as well as final values of overpotentials were always lower than in pure solution at the corresponding current density.

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**TABLE I**

<table>
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<th>3-aminopyridine</th>
<th>Taken, molar</th>
<th>Found, molar</th>
<th>Error (%)</th>
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<td>0.0757</td>
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<tr>
<td>0.0500</td>
<td>0.0505</td>
<td>+1.0</td>
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<tr>
<td>Potentiometric</td>
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<tr>
<td>0.0250</td>
<td>0.0248</td>
<td>-0.8</td>
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</tr>
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</table>

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**Fig. 1.** Hexagonal pyramids and occasional triangular pyramids of copper deposited on copper (111) plane from pure copper sulphate bath at 10 mA/cm\(^2\), × 625.
The above results indicate the remarkable effect of caesium ions on the habit modification of copper electrodeposited and on the overpotential during deposition. The mechanism of habit modification due to the caesium ions is under detailed study.

Fig. 2. Layer type of growth aligned in (110) direction when copper is deposited from acid copper sulphate bath in presence of $10^{-7}$ m/1 of caesium sulphate at 10 mA/cm$^2$, $\times$ 625.

Fig. 3. Ridge type of growth on copper (111) plane from acid copper sulphate bath at 10 mA/cm$^2$ in presence of $10^{-5}$ m/1 of caesium sulphate, $\times$ 625.

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EFFECT OF SIMULATED HIGH ALTITUDE ON RED CELL MEMBRANE PERMEABILITY AS REVEALED BY INFUX OF $^{86}$Rb AND $^{22}$Na

Potassium homeostasis in acute hypoxia is controversial. Decreased plasma potassium ($K^+$) has been reported in hypoxic animals\textsuperscript{1,2}, while in human beings under similar conditions, concentration of $K^+$ in plasma either increases\textsuperscript{3} or remains unchanged\textsuperscript{4}. In the present investigation, transerythrocytic availability of sodium ($^{22}$Na) and potassium [using rubidium-86 ($^{86}$Rb) as a marker] in hypoxic rats have been characterised and the results have been correlated with red cell membrane Adenosine triphosphatase (ATPase) activity.

**Materials and Methods**

Adult male Sprague–Dawley rats, 4 months old, were fed with Hindleaver Rat and Mice Feed and exposed to simulated altitude of 6100 m in a standard decompression chamber\textsuperscript{5} at 26°C for 4 hours. Red Blood cell counts were made by standard haematological procedures. Infux of $^{86}$Rb and $^{22}$Na in erythrocytes in vitro was studied as per literature\textsuperscript{6}, using Nuclear Chicago Autogamma Spectrometer Model 4219. Potassium in plasma\textsuperscript{7} and ATPase activity (basal and sodium potassium activated)\textsuperscript{8} in red cell membranes were estimated colorimetrically. Protein was estimated by biuret reaction\textsuperscript{9}.

**Results and Discussion**

Acute hypoxic condition was indicated by significant increase ($p < 0.001$) in red cell counts of experimental rats (Table I). Results of Table I also reveal increase in the concentration of potassium in plasma ($p < 0.001$) an observation which is not in agreement with the previous findings\textsuperscript{1,2}. Probably the drainage of intracellular potassium due to diminished oxygen supply\textsuperscript{10,12} was responsible for greater availability of potassium in plasma. In the present series of experiments, influx of $^{22}$Na in erythrocytes of experimental rats was the same as in control, while hypoxia led to 36% increase in influx of $^{86}$Rb in red blood cells in vitro. This might be due to loss of red cell potassium in vivo. Both basal and sodium potassium activated ATPase activity in red cell membranes have increased ($p < 0.01$) in hypoxic rats (Table I) which is not in agreement with the