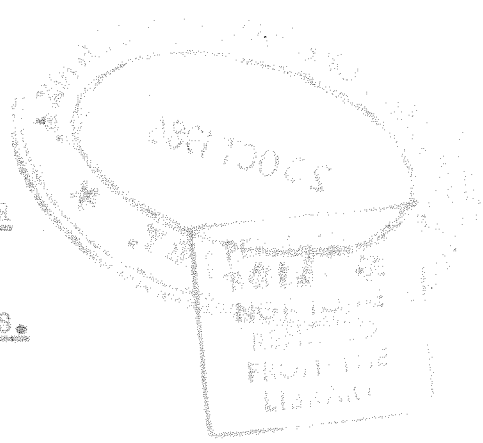


KINETICS OF CHARGE TRANSFER

AT STRAINED COPPER ELECTRODES.



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## ABSTRACT

In the first part of the thesis, the importance of dislocation in the study of stress-strain behaviour of metals is emphasised and in the second part an attempt is made to introduce 'strain' into electrode-kinetic phenomena so as to elucidate the mechanisms of electro crystallization and electro-dissolution. A brief summary of the more important aspects of plastic behaviour of metals, crystal growth, metal deposition and anodic processes is given. Attempts are also made to interpret the experimental evidence as much as possible.

Stress-strain curves obtained experimentally under dynamic conditions for different rates of strain are reported. By introducing factors for healing of dislocations during strain and rate of strain into the Taylor-Mott theory for the plastic behaviour of metals, it is possible to obtain a linear relationship by plotting corrected stress ( $\tau$ ) vs (corrected strain)<sup>1/2</sup>. These straight lines appear to coincide when  $h = 0.05$  and beyond a certain critical value of strain rate. A reasonably good value for the dislocation density ( $N$ ) averaged over the bulk of the material is given. The value for  $N$  is an intermediate value between those obtained by etch pit studies and electron microscopy. Further it is shown that about 300 dislocations cluster to form a "multi dislocation" which is generally observed in etch pit counts.

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An equation based on the dislocation density taking into account the entire range of elasticity and plasticity has been suggested for the strength of metals. By one simple equation it is possible to determine the ultimate strength of a metal, the minimum strength of a metal and the possible strength that could be achieved by work hardening. The strength of a metal whisker can be easily deduced.

Easy glide region which is not generally explained properly becomes more meaningful on the simple equation proposed. The temperature effect on stress-strain curves particularly with respect to the minimum stress is satisfactorily explained.

Current theories for the mechanism of metal deposition and dissolution are briefly surveyed. It is shown that existing experimental evidence experimental technique is reported which permits the identification of the correct model and its quantitative verification. This technique consists in registering under potentiostatic control, the change in current when a copper wire is strained at a predetermined rate upto the breaking point. The results are presented for anodic dissolution and cathodic deposition covering an overpotential range + 15 mv to -25 mv.

Studies have been carried out on the effect of rates of strain in the range of 0.047 strain min<sup>-1</sup> (26 rpm) to 0.3105 strain

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$\text{min}^{-1}$  (500 rpm.). Equations have been derived for the slow diffusion model and the direct discharge model which relate current to the strain. It is shown that for the former the current is directly proportional to the square root of the corrected strain and for the latter the dependence is more complex, the gradient increasing with increasing strain. The results show that the surface diffusion model is correct. The effect of rate of strain has been discussed quantitatively. The expression shows that for each  $\eta$  there is a limiting law which applies at high rates of strain for all strains and at sufficiently low strains for all rates of strain. The deviation from this limiting law has been attributed to thermal healing or annealing effects and quantitatively verified for the anodic graphs. For the cathodic polarization the healing effect is found to be very large and this has been traced to the combined effect of thermal healing and electrolytic healing.

It is shown that the gradient of  $i$  vs.  $\epsilon^{\frac{1}{2}}$  graph at constant  $\eta$  is proportional to the function  $G$  where  $G = e^{\frac{x}{4}} \text{Sinh } x$  where  $x$  is  $\frac{ZF}{RT} \eta$ . The constant of proportionality has characteristic values for the anodic and cathodic polarisations. From the anodic gradient, the density of dislocations has been calculated using established values for the various electrode-kinetic parameters. The value thus determined is in close agreement with that obtained from etch-pit counts. The corresponding factor for the cathodic region is approximately an order of magnitude lower and this difference has been shown to be due

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to the greater effectiveness of dislocations for anodic dissolution.

From the value of  $N$  obtained from purely stress-strain curves, it is clear that one in about 300 dislocations are effective for anodic dissolution whereas one in about 3000 dislocations can be regarded as active sites for metal deposition.

The often assumed inverse dependence of  $i$  on  $\eta$  is critically examined. It is shown that experimental data obtained here provides no evidence for this assumption. The zero strain current has been found to show a similar potential dependence. This current is primarily due to the same electrode process operating in the vicinity of grain boundaries which appear to act as line sinks in the same way as growth steps. From the gradients of zero strain current vs.  $G$ , the grain size has been estimated to be approximately  $10 \mu$  square.

The condition for the transition from the surface diffusion control to charge transfer control with solid electrodes are examined. It is shown that asymmetry of  $i - \eta$  curves is a characteristic of surface diffusion control and that Faradaic rectification would be a diagnostic criterion for the same. The process of activation is also discussed.

The potentialities of this new technique are outlined and the main conclusions from this work are summarized.

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