

Passive Film Growth Kinetics for Stainless Steel

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The kinetics of growth of passive oxide films have long been studied in order to understand and quantify the ability of films to protect alloys from aqueous corrosion. Bare metal surfaces are highly reactive, but formation of only a few monolayers of oxide can reduce the reactivity by orders of magnitude. It is generally observed that the current density flowing decays exponentially with the electric field in the film. This was formulated into a model by Cabrera and Mott (1), who proposed that the limiting step was movement of an ion into the film at one of the interfaces.

Cabrera and Mott's film growth model leads to the prediction of a relationship between the logarithm of the current density and the reciprocal of the charge passed (inverse logarithmic kinetics) for film growth under conditions where the decay is measured from a bare metal surface and negligible dissolution takes place. Other workers have observed a "direct logarithmic" relationship. However, one of us (2) has shown that for measurements under potentiostatic conditions, these two kinetic forms are very close, and the difference can be further obscured by the change in iR drop as the current changes. The iR drop is a particular issue for measurements in resistive solutions. This problem can be avoided by growing the film galvanostatically. In this work, we will examine new data for galvanostatic growth of the passive film on stainless steel in the context of a review of film growth kinetics.

The growth of passive films under conditions of negligible dissolution can be approximated to

$$i = A \exp\left(\frac{B'V}{q}\right) \quad [1]$$

where i is the current density, V is the voltage across the film, q is the charge density passed in growing the film, and A and B' are constants. For potentiostatic data, it is necessary to know the absolute value of q . However, relative changes in thickness can be monitored through changes in potential (E) during galvanostatic experiments, in which a change in charge density in the film can be equated to $i\Delta t$, where Δt is the time passed, leading to:

$$\frac{dE}{dt} = \frac{i}{B'} \ln\left(\frac{i}{A}\right) \quad [2]$$

Thus the voltage-time relationship during galvanostatic growth of the film should be approximately linear, with a slope related to the applied current density.

We have used this approach to investigate the growth of the passive film on 304 stainless steel (Fe-18Cr-10Ni) in a borate buffer (in which negligible dissolution takes place (3)), and simulated potable water, a poorly-conducting solution in which conventional potentiostatic film growth measurements are difficult.

Measurements were made in a "flat cell", where the sample is pressed against an o-ring that defines the electrode area. The cell also contained a saturated calomel reference electrode, and was in some cases

de-aerated with argon. Type 304 stainless steel was abraded, finishing with 1200 grit SiC paper. Samples were ultrasonically cleaned in ethanol, and an air-formed film allowed to thicken for 0.5 hours.

Figure 1 shows a series of voltage-time transients measured for stainless steel in borate and in simulated potable water at several different current densities. The data show some lateral displacement as a consequence of variation in initial film thickness, but they approximate to linearity after initial curvature, and show similar gradients for the two solutions (Figure 2).

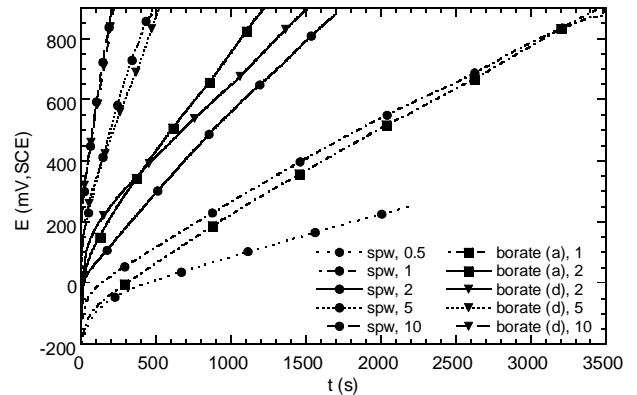


Figure 1: potential (E) vs. time (t) for galvanostatic growth of the passive film on stainless steel in aerated simulated potable water (spw), and aerated (a) and de-aerated (d) borate buffer. The applied current density is shown in units of $\mu\text{A cm}^{-2}$.

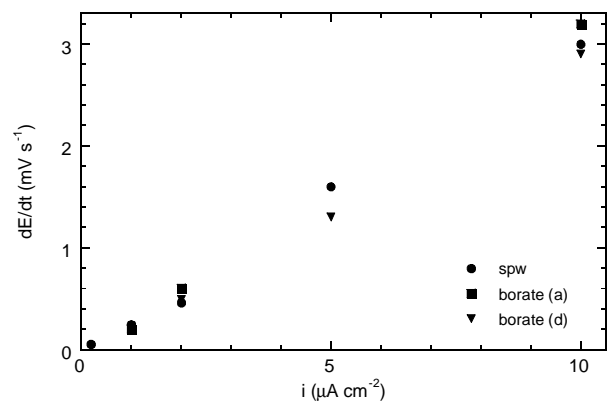


Figure 2: gradients of the data shown in Figure 1 plotted as a function of applied current density (i).

Conclusions

- Passive film growth kinetics can readily be measured galvanostatically in resistive solutions.
- The growth of the passive film on Type 304 stainless steel shows very similar kinetics in a borate buffer and in simulated potable water.

Acknowledgements

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References

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