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FILM BREAKDOWN AND PITTING

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Aluminum was studied in sulfuric acid, with chloride to 0.1M, by electron microscopy, polarization and gravimetric methods. Film breakdown and transient pitting occurred in the absence of chloride. Chloride was not found to alter the film; its role was to stabilize pit embryo growth. Stable pit nucleation was conceived as requiring a pit embryo persistent enough to produce sufficient chloride enrichment within the pit. The observed absence of a sharp potential threshold for pit nucleation at low chloride levels was consistent with these views.

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STATEMENT OF THE PROBLEM

There is at present inadequate fundamental knowledge concerning the processes involved in pit initiation and growth. Such knowledge provides guidance for efforts in diagnosis, prediction and alloy design for control of pitting and crevice corrosion, problems which limit the use of aluminum and some other alloys in many environments in which they have otherwise good corrosion resistance. One of the greatest areas of uncertainty and discord is the basic question why the film is stable in the passive state and why and how it apparently breaks down in the presence of chloride and certain other ions. A part of this question is the mechanisms by which film breakdown may be influenced by the metallurgical structure and composition of the substrate. The present work was directed to these problems of film breakdown and pit nucleation and was designed for two objectives and two types of experimental approach. I. High magnification transmission microscopy of films and surface replicas was performed to look for breakdown events in their very earliest stages and to deduce appropriate models and approach relatively unexploited up to now. II. More conventional anode polarization studies, supported by scanning electron microscopy, were performed to examine whether the results obtained through microscopy were applicable to the interpretation of macroscopic electrochemical measurements.

RESULTS

This work was performed on high-purity aluminum for which previous corrosion studies of other types in this laboratory provided well-characterized material and techniques for control of its surface state. The only metallurgical effects examined were those of grain boundaries. The work employed an electrolyte of 2.4M H_2SO_4, with additions of chloride from 0.003M to 0.1M, to take advantage of certain information on film growth and properties obtained from the extensive literature on thick film sulfuric acid anodizing. An electron-opacity technique was developed for obtaining a measure of film mass-thickness in the electron microscope studies, and a theory of the electron-opacity of a porous amorphous film was formulated for analysis of film growth versus time.[4]

I. Electronmicroscopic Studies of Film Breakdown

A. The structure of films grown galvanostatically in sulfuric acid showed, even without chloride additions, numerous "events" representing forms of local breakdown-repair or breakdown-pitting-repair occurring concurrently with film growth. These were considered to be mainly tiny embryonic pits growing briefly at the base of the main film before being themselves filmed over. Their small size (0.1μm and less) and the fact that the event was subsequently buried in the growing film explains in part why these had not been noted previously. Some geometrical models were proposed. Checks of the effect of surface preparation and of the behavior of zone-refined material indicated that the breakdowns were not due to extraneous factors, so that it could be concluded that the stability of the passive film in the absence of chloride was due not to the absence of breakdown events but to the effectiveness of repair.[1,4] No convincing explanation has emerged for the mechanism of the original breakdown, but a supplementary effort is being made to explain some details of the transient pitting processes.[7]

B. Electron-opacity measurements of film growth were analyzed to determine the efficiency of film formation. It was found that a significant part of the external current never went to form film but was consumed in direct-dissolution of aluminum in the acid. Two other groups have recently reached a similar conclusion by other methods. This supported the microscopy results indicating that transient pitting accompanies film growth.[4]

C. Chloride was added to the acid in quantities sufficient to produce stable pitting but (usually) only after a certain interval so that its effect on film growth and structure could be examined in the initial period. It was found that, at the same cell voltage, the structure and the thickness of the film were the same whether it had been grown in the presence of chloride or not. No evidence was found to indicate that chloride damaged the film. Its action was considered to be a stimulation of the growth of the pit embryos which on the average grew larger before repassivation and so yielded a larger transient pitting current.[4] The implications for the nucleation of stable pits are as follows. There is no film breakdown stage, pit embryos always being provided even in the passive state; the role of chloride is to stabilize pit growth, and stable pit nucleation is a pit growth question.[4,3]

II. Electrochemical Studies

A. Film-growth measurements were made in this case gravimetrically, which was better suited to the lower potentials and more fragile films of this part of the work. These led to the conclusions, similar to those of IB and C, that a) even in the absence of chloride a substantial part of the anodic current went to direct dissolution of aluminum and b) chloride did not directly influence the rate of film growth.[5]

B. Anode polarization studies by potential step scanning showed stable pit nucleation at 0.01M Cl^- to be very variable without the sharp potential threshold found by other workers in straight chloride solutions at higher concentrations. It was proposed that stable pit initiation can be viewed as follows. A pit embryo will repassivate unless it can become sufficiently concentrated in chloride (as to form the chloride salt layer envisioned in certain theories of pit growth). This requires that the embryo have a sufficient lifetime, which needs to be greater the lower the chloride concentration in the bulk solution. In the present work, pit nucleation required an unusually persistent pit embryo the occurrence of which was variable and a gradual rather than a discontinuous function of potential. Our interpretation is that, although it was not involved in the present work, there is a characteristic potential in pitting, as noted by other workers, but it is associated not with pit nucleation but with electrochemical requirements for pit growth. Of course these questions need much further investigation.[5]

C. From investigation of the role of grain boundaries in the transmission and the scanning electron microscopy, the conclusion was that pit embryos which formed at the boundaries had slightly more probability of growing, but there were so many embryos providing potential nucleation sites within the grains that grain boundaries generally did not play a significant part in pitting under these experimental conditions.[1,3,6]

LIST OF PUBLICATIONS SUBMITTED OR IN PREPARATION

Manuscripts Published

1. "Electron Microscope Study of Breakdown and Repair of Anodic Films on Aluminum," J. Zahavi and M. Metzger, Jnl. Electrochem. Soc. 119, 1479-85 (1972).
2. "Electron Opacity Measurements Applied to Film Growth Kinetics," J. Zahavi and M. Metzger, Proceedings of the 30th Annual Meeting, Electron Microscope Society of America, 1972, pp. 504-5.
3. "Breakdown of Films and Initiation of Pits on Aluminum," J. Zahavi and M. Metzger, Localized Corrosion, NACE-3, 1974, pp. 547-55.
4. "Effect of Chloride on Growth of an Anodic Film," J. Zahavi and M. Metzger, Jnl. Electrochem. Soc. 121, 268-79 (1974).

Manuscripts in Preparation

5. "Pit Initiation on Aluminum in Sulfuric Acid Containing Chloride," J. A. Smaga and M. Metzger, to be submitted to Jnl. Electrochem. Soc.
6. "Scanning Electron Microscope Study of Pits Formed in Aluminum at Various Potentials," J. G. Scheltens and M. Metzger, to be submitted to Jnl. Electrochem. Soc.
7. "Additional Observations on Film Breakdown Structures on Aluminum," J. Zahavi and M. Metzger, to be submitted to Jnl. Electrochem. Soc.

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