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PITTING IN ALUMINUM.(U)
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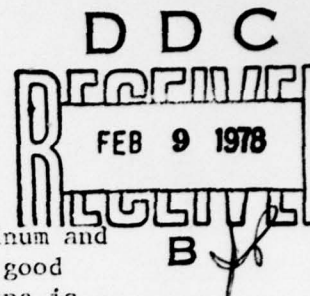
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PITTING IN ALUMINUM

19 AUGUST 1977

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STATEMENT OF THE PROBLEM



Pitting and crevice corrosion limit the serviceability of aluminum and some other alloys in many environments in which they have otherwise good resistance to corrosion. Our present understanding of these phenomena is quite inadequate to guide control efforts in diagnosis, prediction and alloy design. Recent work in this laboratory has dealt with electronmicroscopic and electrochemical studies of the nature of the passive state and the question why and how the passive film on high-purity aluminum breaks down in the presence of chloride and certain other ions, with some specific attention to the role of grain boundaries. This report covers a terminal year in which two projects were completed to the extent possible.

8

I. Electronmicroscopic Study of Film Breakdown

Study of film breakdown by electronmicroscopic observations of the structure of anodic films represents a different approach and yields significant insights into breakdown phenomena. Earlier, extensive work in this laboratory was done at potentials high enough (mainly ~7V vs. SCE) to ensure that the films were not too fragile for handling. This work has been extended to a lower potential and thinner films by making a survey of films formed in 2.4M sulfuric acid (without chloride additions) at 1.0 V vs SCE. This films showed breakdown-pitting-repair events similar to those observed earlier. The results provide further support for the view presented in our earlier work that film breakdown and transient pitting - the "micropitting phenomenon" - is a characteristic of the passive state in the absence of chloride and thus that this ion is not needed to produce breakdown; its role must be the stabilization of pit growth. These results are significant as a further step in the long-term process of obtaining new insights into pitting which will evaluate the various views now held and reach an understanding of mechanisms.

II. Pitting of Aluminum Containing Copper

Copper is an ubiquitous alloying element or impurity in aluminum and is known in a general way to diminish its corrosion resistance (apart from its association with intergranular corrosion in two-phase alloys). The approach in this study started from the judgment that systematic understanding of the role of copper in pitting was most likely to be gained by starting with low concentrations in otherwise high-purity material. That copper can have potent effects on the rate of pit growth at ppm levels was demonstrated in this laboratory some years ago in gasvolumetric studies of autocatalytic pitting in hydrochloric acid. In this corrodent the range of potentials experimentally accessible is restricted and the present electrochemical studies were made in 2.4M sulfuric acid (as used for the microscopic studies) with chloride additions from 0.01 to 1M.

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Potential scan experiments showed that copper had little or no effect on anode polarization or pit initiation at 600 ppm, the highest copper content examined. Further efforts were concentrated on cathode processes. Copper has a strong influence on these because pure aluminum is a poor cathode due to the low electronic conductivity of the passive film, and copper originally in solid solution concentrates on the surface yielding low overpotential cathodes of copper. This can cause the corrosion potential in solutions containing chloride to rise with time to potentials sufficiently noble for pitting, and the continued buildup of cathodes causes the rate of pit growth to rise. The present work paid particular attention to the time dependence.

1. The change in cathode behavior with time was demonstrated explicitly by making periodic cathode polarization scans as the corrosion potential of a specimen rose with time.

2. It was shown that the rise of corrosion potential with time was a systematic function of copper content, that the process was accelerated by chloride, and that the effect was exhibited at very low copper levels. For example, in sulfuric acid containing $1M Cl^-$, the corrosion potential of material with only 1 ppm Cu rose in 125 hours to a potential sufficiently noble for pitting while at 0.1 ppm Cu the potential was still 200 mV lower.

The mechanisms involve complex questions. The large effects of low copper contents indicate the copper cathodes are formed in metallic contact with the aluminum (rather than on the external surface of the passive film). It must then be concluded that in the passive state the effective cathodes form within the micropitting events referred to earlier where the metal surface is transiently exposed. The effect of chloride on cathode buildup can be seen as the result of an action to extend the lifetimes of the transient pits, in line with the view of its role as the stabilization of pit growth. A detailed scheme for the electrochemical processes involved and their relation to the microtopography of a transient or stable pit has not yet been achieved. However, a qualitative framework has been provided for interpreting the effects of copper on the passive state and pitting. Apart from insight into mechanisms, this work is considered important for the demonstration of the macroscopic aspects of the effect of copper on cathode processes, thus allowing this effect to be more readily identified and distinguished from other effects on cathode processes due to intermetallic constituents in commercial aluminum alloys.

Manuscript Published

"Intergranular Corrosion of Single-Phase Aluminum as a Pitting Phenomenon,"
M. Metzger, *Journal de Physique* 10, C-4-387-93 (1975).

Manuscripts in Preparation

"Further Observations of Transient Pitting of Aluminum in the Passive State,"
J. Zahavi, I. D. Ward and M. Metzger.

"Cathode Behavior and Pitting of Aluminum Containing Copper," T. R. Odom and
M. Metzger.

PARTICIPATING SCIENTIFIC PERSONNEL

M. Metzger (Principal Investigator)
T. R. Odom (Research Assistant)
N. S. Berke (Research Assistant)
J. Zahavi (Visiting Associate Professor)

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ADVANCED DEGREE AWARDED

T. R. Odom, M.S. (1976)

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18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Pitting Corrosion Film Breakdown Aluminum Cathode Behavior

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

1. Observations by electron microscopy of transient pitting during film growth in the passive state were extended to a lower potential. 2. Electrochemical studies in sulfuric acid of the effect on cathode behavior of copper contents from 0.1 to 600 ppm showed that cathode polarization decreases with time, that corrosion potential rises with time and that the effect is accelerated by chloride additions and can be substantial even at 1 ppm Cu. It is proposed that the formation of cathodes of copper during corrosion occurs in transient pits.

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