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Ellipsometric Measurements On the Passive Film Prior to the Initiation of Breakdown in Aluminum

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The presence of chlorides in aqueous solutions causes pitting attack or stress corrosion cracking in many metals if the oxidation potential is high enough.

While a considerable amount of work has been devoted in the literature to the mechanisms of penetration of corrosion pits and propagation of stress-corrosion cracks, little is known on the events which occur in the film during the incubation period which proceeds breakdown.

It has recently been reported[1] that subtle changes occur in the ellipsometric parameter of the passive film on iron during the incubation period. These changes in the parameters were found for iron only at a few particular wavelengths.

In order to check whether similar changes occur in the surface film on aluminum, a series of experiments was carried out on 99.99% pure aluminum.

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The breakdown conditions for aluminum in chloride solutions were studied by Galvele and DeMicheli[2]. They found that the "pitting potential" decreases linearily with the logarithm of NaCl concentration. Their results could not however be readily used in the present investigation due to differences in the polarization procedure and to short (if any) incubation periods in their results.

Since in the present experiments the incubation period, prior to breakdown, was studied, an attempt was made to get at conditions which bring about a delayed breakdown with an incubation period sufficient to run ellipsometry measurements across the visible spectrum. The incubation period was found to be dependent on the polarization potential, the preliminary polarization time in a non-chloride environment and on the chloride concentration. All experiments were done at ambient temperature (24° C). The range of possible combinations of conditions leading to a sufficiently long incubation period is very narrow. The conditions finally selected were the following, a preliminary potentiostatic polarization in a 3% ammonium tartrate solution at +1240 mV (SHE) for between 40 and 90 min. at +1240 mV (SHE) followed by the addition of .0062 M NaCl while keeping the specimen at the above potential. This resulted in an incubation period of between 30 and 90 min. prior to breakdown. In one case, a fresh non-chloride solution was introduced after the polarization in chloride in order to check the effect of removing chloride. Ellipsometric-spectroscopic measurements were done in-situ during all the stages of polarization.

Fig. 1 shows the variation of the ellipsometric parameters Δ and Ψ with wavelength during two periods of the 90 min. pre-polarization stage in the non-chloride solution, as well as two periods after NaCl had been added. The first obvious feature in Fig. 1 is the smoothness of the curve in contrast to the discontinuous curves reported previously for iron[1]. The variations in Ψ are slight, taking into consideration the measurement reading accuracy of ±0.1°. The variations in Δ are, however, significant. At any measured wavelength the value of Δ was found to be lower in the later stage of pre-polarization. This could be interpreted as a thickening of the film (assuming no changes in the optical constants during the polarization). The results leading to the lower curve of polarization were obtaine about 35 min. later than those for the upper curve.

The effect of added NaCl to the solution is, as shown in Fig. 1, again, in contrast to the results reported for iron[1] in that Δ was affected uniforml across the spectrum. The slight narrowing of the curve at the longer wavelengths is presumably due to the tapering of the growth curve with time (the sequence of taking readings was from shorter to longer wavelengths). The values of Δ are increased by the addition of chloride to values closer to those obtained during the begining of the preliminary polarization. This is apparently due to thinning of the film in the presence of chloride probably by dissolution. A subsequent further growth occurs later as indicated by the final decrease of Δ. Such further growth is possible if it is a porous and/or conductive film.

When chloride was added to a thinner film formed during a shorter polarization period of 40 min., Δ decreased as shown in Fig. 2 reaching values clo to those attained by adding chloride after longer pre-polarization (Fig. 1). Again the changes in Ψ were insignificant. Since breakdown occurred earlier after the shorter polarization period, ellipsometric readings were taken in this experiment only for a part of the spectrum. If the changes in Δ are attributed to changes in thickness, the results indicate thickening of the film to some value determined by a balance between dissolution and oxidation rates. This value is similar to that attained during the chloride polarization in Fig. 1.

It is interesting to note that the film thickness attained during an intermediate pre-polarization period of 60 min. is closer to the thickness attained in chloride solutions, as can be judged by the smaller changes of Δ in Fig. 3. However, removal of the chloride environment clearly resulted in a renewed growth of the film as indicated by the changes in Δ in Fig. 3.

It is concluded that in the case of aluminum, breakdown by chloride usually occurs either instantaneously or does not occur at all (at least for several hours) depending upon the potential, chloride concentration and duration of the preliminary polarization in a non-chloride environment. Only under specific intermediate conditions does a noticable incubation period precede breakdown. During the incubation period, the film attains a thickness which is controlled by a balance between dissolution and oxidation rates. The pre-formed film will thicken or thin during this period depending on whether it is above or below the value attained in chloride. Further thickening which occurs during the incubation period indicates a film of a porous or conductive nature. The ellipsometric parameters for the surface film on pure aluminum change smoothly with wavelength in the visible spectrum. Changes in the film due to chloride are noticable across the spectrum and at no particular wavelength is the chloride effect more pronounced than in others. This should enable more detailed ellipsometric study of the transient behavior of films in chloride using one wavelength.

References

1. C. L. McBee and J. Kruger, Nature Physical Science, <u>230</u> 194 (1971).

2. J. R. Galvele and S. M. DeMicheli, 4th International Congress on Met. Corrosion, Amsterdam (1969).

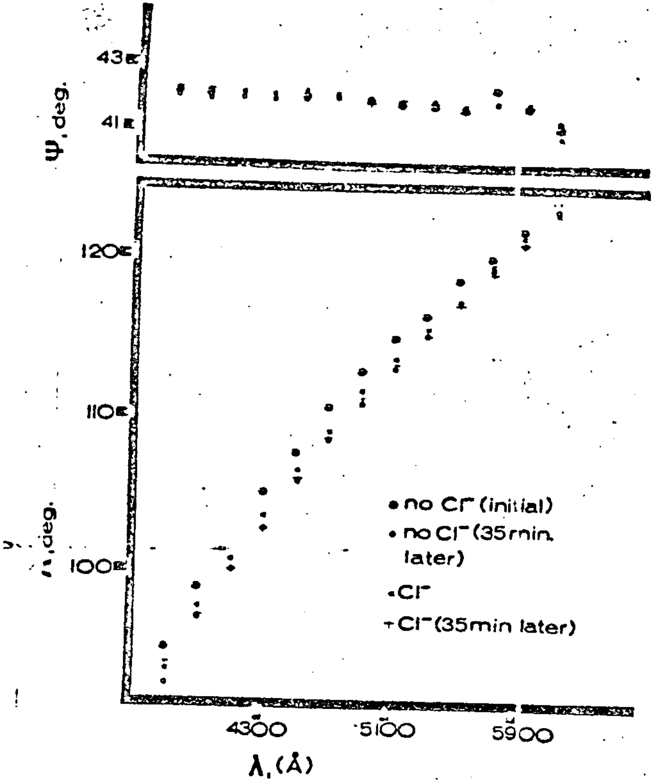

Figure 1. Δ and Ψ vs. λ for two periods of pre-polarization totalling 90 min. and two subsequent periods of polarization in 0.0062 <u>M</u> NaCl.

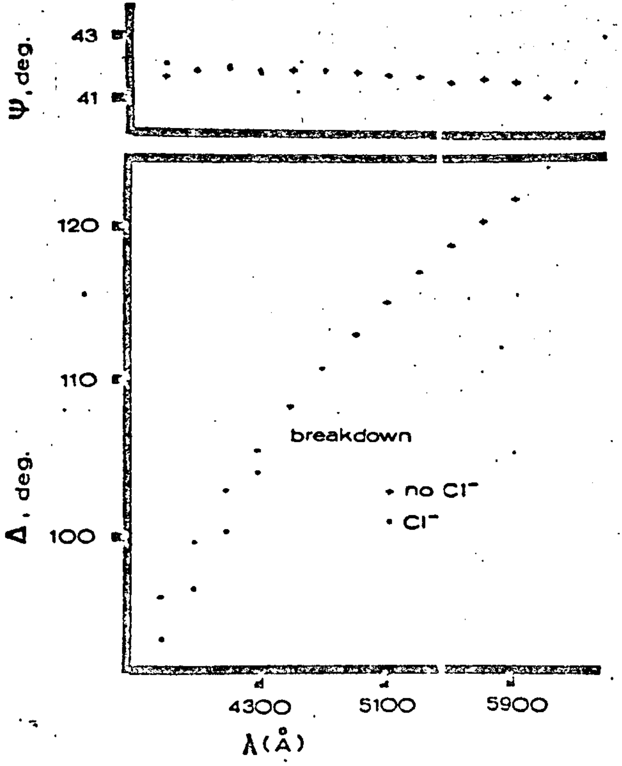

Figure 2. Δ and Ψ vs. λ for a pre-polarization period of 40 min. followed by polarization in 0.062 M NaCl.

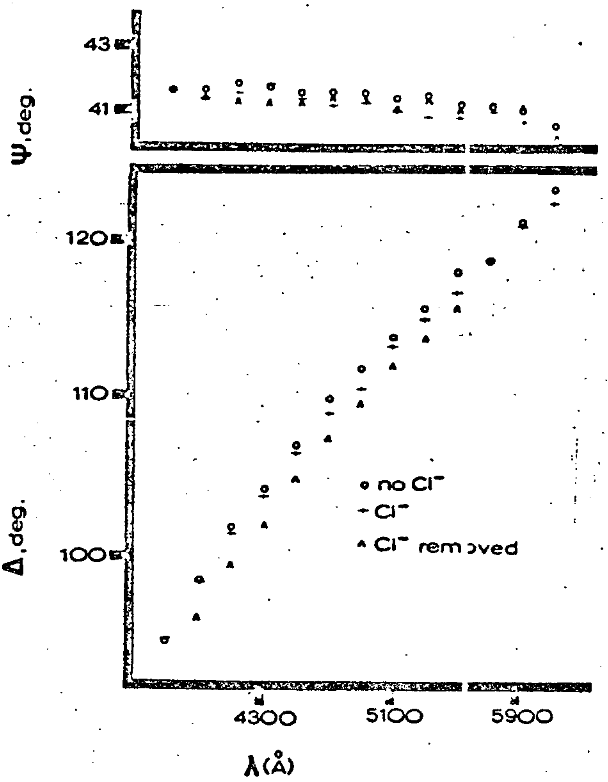

Figure 3. Δ and Ψ vs. λ for polarization for 60 min. followed by polarization in 0.062 M NaCl and subsequent removal of NaCl.