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The Chemical Nature of Aluminum Corrosion:
I. Activation of Aluminum Surfaces by Aluminum Salts

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By:
K. Sotoudeh, R.T. Foley and B.F. Brown
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The activation of aluminum surfaces (alloys 1199-H14 and 7075-T6) by solutions of $Al(NO_3)_3$, $AlBr_3$, $AlCl_3$, $Al_2(SO_4)_3$, $Al(ClO_4)_3$, AlI_3 and NaCl of various concentrations has been measured. Experiments were also conducted in saturated solutions of aluminum acetate, benzoate, phosphate, chromate and fluoride. The dissolution rate of the alloys varies considerably with the salt, the nitrate and iodide being most aggressive. The corrosion rate in sulfate solutions is much less than the rate in bromide, chloride, or perchlorate. The pH of the various salt solutions is not the determining paramter but for a given salt

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(AlCl$_3$) the corrosion rate increases with decrease in pH. The experiments definitely demonstrate that the activation effect is not restricted to aluminum chloride and suggests a strong chemical effect in the pitting and stress cracking mechanism.

A

THE CHEMICAL NATURE OF ALUMINUM CORROSION: I ACTIVATION OF ALUMINUM SURFACES BY ALUMINUM SALTS

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Aluminum and its alloys are passive unless they are made active by either chemical environments or mechanical actions or by a combination of the two. Although water vapor has been shown in laboratory experiments to be capable of propagating stress corrosion cracks (which indicates a locally active state), it is known from both service experience and laboratory experiments on stress corrosion cracking (to be reported subsequently in this series) that there are effects involving ions other than those of water. It is also known from laboratory experiments that the corrodent in localized forms of corrosion (such as pitting and stress corrosion cracking) is chemically different from the bulk environment, though whether this change is a cause or rather a result of the localized corrosion has not been established.

It is generally recognized that the pH of the solution in a growing pit on an aluminum alloy or in a crack on a stress-cracking specimen of an aluminum alloy is approximately 3.5 and there appears to be a relatively high concentration of Al^{+++}. Experiments by Rosenfeld and Marshakov[1], Brown, et al.[2], Marek, et al.[3], Davis[4], and Hagyard and Santhiapillai[5] support this conclusion. The analytical studies on the nature of local corrodents by Brown, et al., by Marek, et al. and by Davis were conducted on small quantities of corrodent, with attendant uncertainties, and they involved only chloride as an anion (other than OH^-). Indeed, most of the experimental work in this field has been done in chloride solution and thus an attempt has been made to relate this corrosion to the hydrolysis of aluminum chloride. Almost without exception the thinking has been focused on aluminum chloride and as a result a complete understanding of the pitting mechanism or the stress cracking mechanism has not been realized. The fact is that, aluminum pits and cracks in a number of (non-chloride) environments.

The objective of this work was to measure the corrosion rate of aluminum alloy 1199 and alloy 7075 in various aluminum salt solutions to determine the ability of these various salts to activate the aluminum surface. The longer range intent is to relate this specific corrosion reaction to the initiation of pitting and the stress cracking process.

EXPERIMENTAL

The experimental work reported here consisted of immersion tests with two aluminum alloys, alloy 1199-H14 and alloy 7075-T6. Samples 38 x 26 x 0.81 mm were cleaned in the conventional manner. The strip was immersed in NaOH solution (5g/100ml) at 70°-80°C for one minute, rinsed thoroughly, dipped in HNO_3 (1:3) for one minute at room temperature, and thoroughly rinsed in distilled water and acetone. Samples were immersed in triplicate in solutions of $Al(NO_3)_3$, $AlBr_3$, $AlCl_3$, $Al_2(SO_4)_3$, $Al(ClO_4)_3$, AlI_3 and NaCl of various concentrations as well as in saturated solutions of aluminum acetate, aluminum benzoate, aluminum phosphate, aluminum chromate and aluminum fluoride. These samples were immersed for 7 to 9 day periods at room temperature, 23° ± 2°C. Following exposures, the corrosion products were removed with a stripping solution of 20 g of chromic acid and 32.25 ml of 85% phosphoric acid/liter. The weight loss reported was the difference in weight of the sample before the test and that after the stripping. The latter was corrected with the weight loss of an uncorroded metal specimen in the stripping solution.

RESULTS

The weight losses for alloy 1199 immersed in 0.1M solutions of aluminum nitrate, bromide, chloride, sulfate, perchlorate and iodide are given in Table I. The activating effect of the nitrate and iodide is approximately three times that of the bromide, chloride and perchlorate, the sulfate one-half. This order is approximately followed in 0.2N solutions in a 7-day experiment reported in Table II. In neither set of experiments is there a correlation between corrosion rate and pH. The pH of these solutions fell in the 3.0-4.0 range with the exception of the aluminum perchlorate solution which had a pH of 2.6-2.7.

Dissolution rates for alloy 7075 in 0.5M solutions of the salts (Table III) were appreciably higher. Aluminum iodide produced a very high corrosion rate as did the nitrate and chloride solutions. The bromide and perchlorate effects were about about one-third of the latter and the sulfate solution an order of magnitude lower. Again, the pH of the solution was not a significant factor.

A number of aluminum salts, mainly those formed from weak acids, were used as saturated solutions. These included aluminum acetate, benzoate, phosphate, chromate, and fluoride.

The weight losses exhibited by samples of 1199 in these saturated solutions over a 7 to 9 day period are tabulated in Table IV. Chromate and phosphate solutions gave very little corrosion but the acetate and benzoate gave low but appreciable corrosion rates. The coupons immersed in aluminum

TABLE I

WEIGHT LOSS OF ALUMINUM ALLOY 1199 IN 0.1M SOLUTIONS OF VARIOUS ALUMINUM SALT SOLUTIONS

Solution	Duration of Test (days)	pH	Loss in Weight Average (mg/cm^2)
$Al(NO_3)_3$	7	3.30	1.69
	8	3.33	1.22
$AlBr_3$	7	3.76	0.60
	9	3.64	0.79
$AlCl_3$	7	3.23	0.58
	9	3.28	0.80
$Al_2(SO_4)_3$	7	3.40	0.33
	8	3.28	0.42
$Al(ClO_4)_3$	7	2.60	0.60
	9	2.60	0.72
AlI_3	7	3.62	1.83

TABLE II

WEIGHT LOSS OF ALUMINUM ALLOY 1199 IN 0.2N SOLUTIONS OF VARIOUS ALUMINUM SALTS

Solution	Duration of Test (days)	pH	Loss in Weight Average (mg/cm^2)
$Al(NO_3)_3$	7	3.32	1.79
$AlBr_3$	7	3.68	0.74
$AlCl_3$	7	3.26	0.53
$Al_2(SO_4)_3$	7	3.46	0.27
$Al(ClO_4)_3$	7	2.70	0.65
AlI_3	7	3.77	1.16

TABLE III

WEIGHT LOSS OF ALUMINUM ALLOY 7075 IN 0.5M SOLUTIONS OF ALUMINUM SALTS

Solution	Duration of Test (days)	pH	Loss in Weight Average (mg/cm^2)
$Al(NO_3)_3$	7	2.63	10.6
	7	2.60	11.2
$AlBr_3$	7	3.36	3.04
	10	2.94	7.07
$AlCl_3$	7	2.66	9.69
	7	2.53	9.66
$Al_2(SO_4)_3$	7	2.90	0.83
	7	2.81	0.97
$Al(ClO_4)_3$	7	1.32	3.17
	7	1.10	4.82
AlI_3	7	3.49	44.9
	7	3.30	51.6

TABLE IV

WEIGHT LOSS OF ALUMINUM ALLOY 1199 IN SATURATED SOLUTIONS OF VARIOUS ALUMINUM SALTS

Solution	Duration of Test (days)	pH	Loss in Weight Average (mg/cm^2)
$Al(CH_3COO)_3$	7	4.78	0.22
	9	4.92	0.10
	7	4.53	0.16
$Al(C_6H_5COO)_3$	7	3.32	0.15
	9	3.31	0.17
	7	3.54	0.17
$Al\ PO_4$	7	3.00	0.07
	8	2.84	0.09
	7	3.39	0.01
$Al(CrO_4)_3$	7	3.49	0.005
	8	3.12	0.03
	7	3.37	0.005
AlF_3	7	5.30	(+0.22)
	8	5.05	(+0.23)
	7	5.22	(+0.56)

fluoride solution gave a weight increase indicating that the standard stripping solution did not remove the precipitated corrosion product. Again, there was no correlation between the corrosion rate and pH of the solution. Similar results were obtained with alloy 7075 (Table V), with the exception that the rate in aluminum acetate solution at a pH, 4.7-4.9, was higher than the other solutions.

For a single salt, aluminum chloride, initially at 0.5N concentration, the corrosion rate varies with pH. This effect is shown in Table VI wherein the dissolution rate drops appreciably in going from a pH of 2.0 to 4.5.

The unexpected results obtained with aluminum nitrate, chloride, and sulfate suggested performing experiments wherein the salts were compared at approximately equivalent activity. The comparison, of necessity, was rather rough because the activity coefficients for these salts over a range of concentrations, particularly in dilute solutions, are not available. To approximate equivalent activities, solutions 0.69M in $Al_2(SO_4)_3$, 0.014M in $AlCl_3$, and 0.020M in $AlNO_3$ were compared. However, the order of activation was still the same for the three salts (Table VII).

DISCUSSION

The idea that aluminum surfaces may be activated by aluminum chloride has been advanced by several other investigators. The "autocatalytic" nature of aluminum pitting seems to have been first suggested by Edeleanu and Evans[6] but explored in more detail by Hagyard and Santhiapillai[5]. The latter investigators measured the pH and electrode potential inside an artificial pit on an aluminum electrode undergoing corrosion by short circuit to a graphite cathode in a solution 0.0141M in chloride. The pH in the artificial pit ranged from a minimum of 3.18 to 3.8. The $AlCl_3$ concen-

TABLE V

WEIGHT LOSS OF ALUMINUM ALLOY IN 7075 IN SATURATED SOLUTIONS OF VARIOUS ALUMINUM SALTS

Solution	Duration of Test (days)	pH	Loss in Weight Average (mg/cm^2)
$Al(CH_3COO)_3$	7	4.67	0.54
	10	4.92	0.42
$Al(C_6H_5COO)_3$	7	3.40	0.13
	10	3.13	0.26
$AlPO_4$	7	3.11	0.075
	7	2.84	0.11
$Al(CrO_4)_3$	7	3.52	0.005
	7	3.12	0.005
AlF_3	7	4.90	(0.25)
	7		(0.24)

TABLE VI

WEIGHT LOSS OF ALUMINUM ALLOY 1199 in 0.5N SOLUTION OF $AlCl_3$ AT DIFFERENT pH's

pH	Duration of Test (days)	Loss in Weight Average (mg/cm^2)
2.0	7	0.64
3.0	7	0.49
3.5	7	0.46
4.0	7	0.34
4.5	7	0.24

TABLE VII

WEIGHT LOSS OF ALUMINUM ALLOY 1199 IN SOLUTIONS OF APPROXIMATELY EQUIVALENT ACTIVITY

Solution	Duration of Test (days)	Molarity	Loss in Weight Average (mg/cm^2)
$Al_2(SO_4)_3$	7	0.69	0.20
$AlCl_3$	7	0.014	0.68
$Al(NO_3)_3$	7	0.020	0.85

tration at a pH of 3.2 conforms to 0.24 eq/l $AlCl_3$. They concluded that a NaCl solution did not activate the Al surface but highly basic $AlCl_3$ at the same pH (3.79) did. Solutions of $AlCl_3$ in concentrations of 0.1 and 1.0 eq/l activated Al in times decreasing with increased concentration while NaCl solutions at the same pH did not. Thus the "autocatalytic" nature of the process is not due to the pH or the Cl^- but the ability of the $AlCl_3$ solution to react with the oxide. The activation can be followed by the potential going negative, e.g. to -0.65 to -0.69 v (vs. Ag-AgCl reference) and the negative potential is due to the Al-$AlCl_3$ couple.

The present results support the concept that it is the nature of the aluminum salt rather than the pH of the solution produced by the hydrolysis of the aluminum cation. Thus, consistently aluminum sulfate solutions are non-corrosive and aluminum nitrate solutions accelerate corrosion. The results of these experiments emphasize the chemical nature of the process as opposed to strictly physical or electrochemical approaches. The results are inconsistent with some of the mechanisms proposed in the past particularly these that give to the chloride ion unique properties of adsorption and penetration of the oxide film.[7]

This approach is also inconsistent with those models that put a heavy emphasis on flaws and dislocations in the film.[8] Presumably, all of the samples of a given alloy would have the same surface structure.

These experiments definitely demonstrate that aluminum salts in the 3.0-4.0 pH range are accelerators for aluminum corrosion. This effect is not restricted to <u>aluminum chloride</u> solutions. Whether or not they are <u>the</u> accelerators for aluminum pitting and aluminum stress cracking for these processes occurring in neutral salt solutions remains to be demonstrated.

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