ANL-5889 Addendum
Chemistry
(TID-4500, 16th Ed.)
AEC Research and
Development Report

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Argonne, Illinois

DEUTERIUM-HYDROGEN EXCHANGE IN BOEHMITE CORROSION PRODUCT FORMED ON PURE ALUMINUM IN BOILING WATER

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Work completed February 1959
Report written December 1960

Published April 1961

Operated by The University of Chicago
under
Contract W-31-109-eng-38

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ABSTRACT

Proton-deuteron exchange is rapid in boehmite corrosion product formed on pure aluminum in boiling water. In addition, deuterated boehmite films undergo rapid exchange with the humidity of the atmosphere. This explains the previously reported[1] anomaly in the H-D exchange rate for the growing corrosion product on 1100 aluminum.

In the first report,[1] studies of the exchange of deuterium for hydrogen and of O^{18} for O^{16} in boehmite (alpha alumina monohydrate) were described. The exchange of deuterium with hydrogen in the corrosion product growing on 1100 aluminum in boiling water was considered anomalous for two reasons: (1) the amount of exchange was less than had been anticipated from results with relatively pure boehmite powder (see also Ref. 2), and (2) the estimated amount of deuterium exchanged for hydrogen decreased with time after an initial period.

In order to check the possibility that the impurities in the corrosion product on 1100 aluminum (0.5% Fe, ~0.2% Si) were responsible for the first anomaly, the experiment was essentially repeated using 99.99% pure aluminum. Six specimens, each 10 cm square, were cut from a sheet of 0.010-inch thickness. Their measured surface areas were 207.3 ± 0.5 cm^2. These were etched for 1 minute in a warm nitric-hydrofluoric acid mixture (50 cc H_2O, 50 cc 70% HNO_3 reagent, 10 cc 49% HF reagent), rinsed, dried, and weighed on an analytical balance. All were then exposed for 19.5 hours in continuously distilled boiling water, using the glass apparatus described by Draley, Mori and Loess.[3] The six specimens were then weighed and further exposed, in pairs, to boiling D_2O (99.6% D) for periods from 0.5 to 21.5 hours.

After corrosion in D_2O, all specimens were dried by evacuation for $\frac{1}{2}$ hour, weighed after $\frac{1}{2}$ hour in the controlled atmosphere balance room (24°C, 40% RH), and kept in stoppered glass tubes for analysis. They were pumped out at room temperature, and then heated to 450°C to remove the water from the hydrated corrosion product. This water was then converted to hydrogen by passage over zinc at 675°C, and the hydrogen was analyzed for isotopic content by the ANL Chemistry Analytical Group, using the mass spectrometer.

Results are shown in Table I. The last column was calculated from corrosion weight gains, assuming that the corrosion products were AlOOH and AlOOD, and that all were retained on the specimens. The latter is not strictly true, but the errors due to the assumption are quite small and would not significantly change results.

Table I

HYDROGEN-DEUTERIUM EXCHANGE IN BOEHMITE CORROSION PRODUCT AT 100°C

All Specimens Initially Exposed to Boiling H_2O for 19.5 Hours

Sample No.	Time in D_2O, hours	Weight Gain in H_2O, mg	Weight Gain in D_2O, mg	%D in Gas Removed	Calculated % D if No Exchange Occurred
0	0.5	32.4	0.5	6.1	1.6
3	0.5		0.4	5.9	
1	4.5	42.6	1.6	7.4	3.5
4	4.5	42.7	1.8	6.8	3.9
5	21.5	11.3(1)	6.0	10.7	
6	21.5	37.6	6.0	10.0	13.4

(1)Weighing error suspected

The numbers in the next-to-last column are of about the same magnitude as those in the top line of Figure 4 of ANL-5889, indicating that the alloy impurities had not controlled the exchange rate.

Comparison of the last two columns of Table I indicates that the amount of deuterium exchanged for hydrogen in the boehmite present before D_2O exposure decreased with time, becoming negative at 21.5 hours! Thus the second anomaly of the original experiment with 1100 aluminum was repeated.

The negative amount of exchange is manifestly impossible, and such results suggest that some of the deuterium content of the product formed in D_2O was exchanged with H_2O from the air during handling. It is recalled that such handling included $\frac{1}{2}$ hour in the balance room and a longer time in stoppered tubes.

Accordingly, a test was run to observe exchange of deuterated corrosion product with hydrogen from normal air humidity. The same six specimens were re-etched and corroded in the boiling D_2O for 24 hours.

Two specimens were then transferred to glass tubes in as short a time as practicable, which were then pumped down and sealed off. The remaining specimens were dried by evacuating, exposed for somewhat over an hour in the balance room, and weighed. Two of these were then evacuated and sealed in glass tubes (total air exposure 2 hours); the remaining two were corroded for 24 hours in boiling H_2O. These were finally weighed, evacuated, and sealed off as for the others. Isotopic deuterium analyses were run as before, without further exposure to air.

From the results in Table II it can be concluded that the boehmite corrosion film on pure aluminum was readily exchangeable with water. Approximately 25% of the deuterium ions were exchanged in the initial 20 minutes of exposure to low-humidity room air. The experiment was done about the end of December; although the relative humidity was not measured, it can be estimated to be below 10% (absolute humidity is normally about that of outside air). Approximately 85% exchanged during a total of 2 hours in the balance room at 40% RH and the normal low-humidity laboratory air; nearly complete exchange occurred during 24 hours of immersion in boiling H_2O.

It is also clear that our earlier experiments did not provide reliable measure of exchange rates because of accidental exchange during handling.

Table II

HYDROGEN-DEUTERIUM EXCHANGE IN A1OOD

Sample No.	Weight Gain (mg) During 24 Hr in Boiling D_2O	Further Treatment	Weight Gain (mg), 24 Hr in Boiling H_2O	% D in Final Boehmite Film
0	(a)	Evacuated; sealed off		75.4[b]
1	(a)	Evacuated; sealed off		41.0[c]
3	40.6	Exposed to air for 2 hr, then evacuated and sealed off		15.5
4	41.8			13.0
5	41.9	Same as 3 and 4; plus 24 hr boiling H_2O exposure	29.0[d]	2.2
6	43.2		10.7	2.6

(a) No weighings made; rapid seal off.
(b) Two attempts were required to effect seal: total air exposure about 20 minutes.
(c) Tube was cracked near the seal; some leakage to atmosphere, probably accounting for exchange to lower D content.
(d) Seems high in comparison with previous series.

REFERENCES

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3. J. E. Draley, S. Mori and R. E. Loess, Corrosion of 1100 Aluminum in Boiling H_2O and D_2O, ANL-6015 (July 1959).