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CORROSION OF 1100 ALUMINUM IN BOILING H_2O AND D_2O

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TABLE OF CONTENTS

	<u>Page</u>
Abstract	3
Introduction.	3
Experimental.	4
Materials	4
Apparatus	4
Procedure	4
Results.	5
Acknowledgements	8
References	8

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ABSTRACT

After an initial exposure period, corrosion rates of 1100 aluminum are approximately the same in H_2O and D_2O at 100°C . More corrosion was observed during the initial exposure period in H_2O , but it is possible that this is only a reflection of the difference in control of the purity of the test water.

INTRODUCTION

There is little information about the corrosion of aluminum alloys as a function of time in pure water. Until a few years ago, results from the laboratory of one of us (JED)^(1,2) indicated that after an initial period of rapid reaction the corrosion rate was small and constant. Our recent experiments, however, have shown that the rate for 1100 aluminum continuously decreases with time, and this will be the subject of another report. Dillon⁽³⁾ has reported a parabolic dependence of the amount of corrosion for at least certain alloys at 100°C and above. The basic cause of these discrepancies is probably the very low rate of corrosion, after the initial reaction, and the consequent requirement for precise measurement of the amount of corrosion.

There is no known work of this sort reported for corrosion in heavy water. However, operating experience in D_2O has shown no gross unusual behavior.

The present work was not done with the objective of determining the kinetics of the reaction between 1100 aluminum and water, but rather to study the difference between behavior in H_2O and in D_2O .

There are two basic reasons for the study. First, the corrosion of aluminum in D_2O is of considerable importance to the designers of nuclear reactors. Second, the information is valuable in interpreting the results of studies of the exchange of deuterium with hydrogen in the corrosion product formed on 1100 aluminum in boiling water. Part of this work has been reported by R. B. Bernstein⁽⁴⁾.

EXPERIMENTAL

Materials: All specimens, $3 \times 3/4$ in., were cut from one sheet of 16 gauge 1100 aluminum with the following composition by weight: Fe, 0.47%; Cu, 0.11%; Si, 0.14%; Zn, 0.01%; and Zr, 0.01%; balance aluminum. A $1/8$ -in. hole was drilled near one end of each specimen. All samples were annealed before use.

Samples were prepared for testing by wet grinding to a uniform surface, finishing on 400 grit Durite paper on a metallurgical polisher. They were examined under the microscope and any samples showing inclusions of foreign material or abrasive were discarded. The samples were then washed in distilled water and degreased in freshly distilled methyl alcohol.

The H_2O was double distilled. Previous analyses of similar samples showed the presence of sodium to the extent of the order of 50 parts per billion; nearly all other metals were undetectable.

The D_2O was distilled before use. Its high specific resistance was an indication of purity (see RESULTS).

Apparatus: A constant-boiling refreshed system was used, as shown in Figure 1. Twelve specimens could be supported on insulated (Pyrex) aluminum hangers. Freshly boiled water (or steam) was continuously fed into the test chamber at a rate of about 5 ml per minute, and the excess water from the chamber overflowed back into the boiler. A reflux condenser prevented excessive loss of water to the atmosphere. Two identical models of the test apparatus were used: one for the H_2O test and the other for the D_2O test. In the case of the D_2O experiment the exit from the reflux condenser was connected through a trap to a vented "Drierite" drying tube to reduce contamination by moisture from the air, and to collect the valuable D_2O in the event the condenser water supply failed. Except for the sample support, the entire apparatus was constructed of Pyrex glass.

Procedure: All samples were weighed to the nearest 10 micrograms, using a Grammatic microbalance in a balance room where the temperature and humidity were controlled (23.5 - $24.5^\circ C$, 39-41% rel. hum.). Before weighing, samples were dried in a vacuum desiccator for 20 minutes (measured pressure about 20 microns), then exposed to the balance room air for one hour.

At intervals, samples were removed, weighed, and replaced in test. At the conclusion of exposure, each sample was stripped of its corrosion product by cathodic treatment at $90^\circ C$ in a solution containing 4% CrO_3 and 10% H_3PO_4 , by weight. Protective current was supplied to the sample from insulated contact points at a current density of 6 - 10 ma/cm² for 2 to 6 hours, depending on efficiency of corrosion product removal. This stripping procedure has been indicated by other studies to be reproducible within about

100 μg for samples of this size. Visual observation with a microscope is a sensitive means of determining complete removal of corrosion product.

Expected precision of weight gains during corrosion is thus about $\pm 0.03 \text{ mg/dm}^2$, although reproducibility in excess moisture content of the corrosion product is not as good as this. Expected precision of values of metal corroded is about $\pm 0.3 \text{ mg/dm}^2$.

FIGURE 1
CORROSION TESTING APPARATUS

RESULTS

Soon after the samples were immersed in boiling H_2O or D_2O a copious amount of hydrogen or deuterium was released. After the first half-hour the rate of gas evolution decreased rapidly. After the second day, the boiler water in both systems contained a white, finely divided, flocculent corrosion product. Samples in the H_2O system lost more product to the water than did the D_2O samples, as judged by the amount of product in the boiler.

The water in the test chambers was sampled immediately preceding the tests and at their conclusion. Specific resistances were 1.0 and 0.28 megohm-cm for H_2O , and 1.3 and 0.19 megohm-cm for D_2O . The isotopic content for the heavy water showed 99.3% D (remainder H) at the beginning of the test and 98.9% D at its conclusion.

All weight-gain data are shown in Figure 2. For all pairs of specimens the exposure period (during the operation of the equipment) is given. The weight gains plotted are the averages of the 2 specimens for these cases. One curve for D_2O and one for H_2O were averaged somewhat differently. Eight (H_2O) and 12 (D_2O) specimens were loaded at one time. Some of these were permanently removed at intervals. For each exposure period the incremental weight gains were determined for the remaining specimens. The incremental weight gains were averaged for these specimens and added to the preceding average weight gains. In effect, this procedure assumes that those samples which had been removed from test would have continued to corrode in the same fashion as those which remained on test.

FIGURE 2
AVERAGE WEIGHT GAINS FOR 1100 ALUMINUM
IN BOILING H_2O AND D_2O

During initial operation of the H_2O system the water flow to the reflux condenser failed and a considerable fraction of the water in the system was lost, resulting in only partial immersion of the specimens then in use. The test chamber was rinsed and filled with fresh water and the test started again, using new specimens. However, the water in the boiler was not changed; for this reason the initial exposure period in the H_2O tests is recorded as beginning at 6.7 days.

In general, it is observed that different weight-gain curves were obtained for samples started at different times. This is an indication of changing quality of the test water, since duplicate samples gave reproducible results. The effect of the water quality seems to have been the most influential during the initial stages of corrosion, since all but one of the curves show approximately the same slope after the first few days of exposure. There is no consistent difference in these slopes (or corrosion rates) between H_2O and D_2O .

There appears to be a significant difference between the amount of corrosion experienced during initial exposure in H_2O and D_2O . However, the control of water quality was quite doubtful, and the greater amount of contamination in the H_2O boiler makes spray or carry-back contamination during the H_2O test more likely than during the D_2O test. It is thus possible that the greater initial corrosion in H_2O is simply a reflection of poorer quality of H_2O . It is noted that the lowest H_2O curve (within the range of the D_2O curves) was obtained for samples tested during the last part of the operation, when water quality should have been best. No resistivities were measured during the corrosion tests, so this point cannot be determined.

For the cases where eight and twelve specimens were loaded at one time, the amount of metal corroded at various exposure times was determined from stripped metal weights. These data are plotted in Figure 3. Each point represents an individual sample.

FIGURE 3
CORROSION OF 1100 ALUMINUM IN BOILING H_2O AND D_2O

Roughly parallel curves are shown, with the one for water exposure displaced upward from that for D₂O exposure. The same comment applies as was made for the weight-gain data, namely, that quality control was not sufficient to determine whether the difference is intrinsic to the different hydrogen isotope or whether it simply reflects a difference in impurity contents.

DISCUSSION

Water quality was not maintained to the degree that had been hoped. Corrosion products of 1100 aluminum in oxygen-free water generally decrease the specific resistance of the water and increase its pH, resulting in a greater amount of initial corrosion. In these tests it was hoped that refreshment with pure water would avoid the contamination problem in the test chambers. Observation of considerable amounts of milky corrosion product (in the boilers only) indicated that some purification of the test water was effected. However, resistivity measurements of the water in the sample chambers after testing showed that it was much less pure than had been sought. In view of the relatively low corrosion rate (thus low contamination rate) towards the end of the tests, it is suspected that this contamination occurred either by spray carried over from the boiler or by occasional accidental backflow through the overflow tube, caused by the agitation in the boiler.

A little further insight into water quality might be afforded by comparison of the amount of corrosion observed here with that previously reported. G. C. English⁽¹⁾ found about 10 mg/dm² of corrosion during the initial period in H₂O at 95°C, while the present work showed of the order of 10 mg/dm² in D₂O and 14 mg/dm² in H₂O. Draley and Ruther⁽²⁾ observed about the same amount of corrosion in boiling H₂O as described herein; however, their subsequent corrosion rate was somewhat smaller. Troutner⁵ has observed corrosion, after about 13 days of exposure at 92°C, ranging from 2 to 37 mg/dm², apparently depending on the pH of the "distilled water" used.

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References

1. G. C. English, in CT-3027: The Corrosion of Aluminum in Dilute Solutions: Laboratory Studies, by J. E. Draley, J. W. Arendt, G. C. English, E. F. Story, M. M. Wainscott and R. W. Berger (June 19, 1945).
2. J. E. Draley and W. E. Ruther, Aqueous Corrosion of 2S Aluminum at Elevated Temperatures, ANL-5001 (February 1953). See also J. E. Draley and W. E. Ruther, Corrosion, 12, 441t (1956).
3. R. L. Dillon and V. H. Troutner, Observations on the Mechanisms and Kinetics of Aqueous Aluminum Corrosion, HW-51849 (Sept. 30, 1957).
4. R. B. Bernstein, Hydrogen and Oxygen Isotopes Applied to the Study of Water-Metal Reactions. Exchange of D_2O^{18} with Alpha Alumina Monohydrate, ANL-5889 (August 1958).
5. V. H. Troutner, Uniform Aqueous Corrosion of Aluminum -- Effects of Various Ions, HW-50133 (June 10, 1957).