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CREVICE-GALVANIC CORROSION OF ALUMINUM

by

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ABSTRACT

In water at 50°C, localized attack occurred on 1100 aluminum in the crevice formed by coupling to copper, but not outside the crevice. More severe attack occurred where copper deposited from a copper sulfate solution onto aluminum alloy surfaces. Pure aluminum was not susceptible to this type of attack.

INTRODUCTION

As noted in previous communications,^{1,2} accelerated attack of 1100 aluminum sometimes occurs in crevices during immersion in distilled water. The attack can be made worse by forming the crevice with materials cathodic to the aluminum, such as graphite or stainless steel. It was believed that the attack is stimulated by a pH increase in the crevice caused by reactions such as

The presence of oxygen in the water reduces the attack, perhaps by oxidizing the iron to the almost insoluble ferric oxide. The existence of the galvanic driving force in itself is not sufficient to produce the accelerated attack, as indicated by the lack of effect at contiguous surfaces in free contact with the bulk water.

In the work described in this report, experimental conditions are extended to include aluminum alloys other than 1100, and to include copper and nickel as cathodic elements. As a special case, copper deposited on aluminum surfaces from a copper sulfate solution produces the galvanic couple.

EXPERIMENTAL PROCEDURE

Aluminum-Copper and Aluminum-Nickel Couples

Couples were assembled from 3/8-in.-diam 1100 aluminum (99.3% pure), electrolytic tough pitch copper (99.9%), and Grade A nickel (99.4%).

Matching screw threads on the mating members allowed attachment by screwing together, as shown in Fig. 1. Half the couples were left unsealed and half were sealed watertight at the joints with a high-melting-point inert wax (Unichrome 330). Adequacy of electrical contact was checked with an ohmmeter before and after test.

106-3149

Crevice Not Sealed

Sealed

Crevice Not Sealed

Sealed

Al-Cu Couple

Al-Ni Couple

Medium: Distilled Water, O₂-saturated, 50°C

Exposure Time: 100 days

Materials: 1100 Aluminum, Electrolytic Copper, and Grade "A" Nickel

Fig. 1. Appearance of Couples after Corrosion Test

All specimens were wet-ground to 400-grit Durite paper and degreased before immersion in refreshed, oxygenated, distilled water at 50°C. During the 100 days exposure, specimens were suspended on Pyrex glass.

Corrosion in Copper Sulfate Solution

The four sample materials were as follows:

Aluminum Alloy

Swiss High Purity

1100

X8001

A288C

Composition, w/o

99.999 Al

99.3 Al, 0.5 Fe, 0.1 Cu, 0.1 Si

98.3 Al, 1.0 Ni, 0.5 Fe, 0.1 Cu, 0.1 Si

98.4 Al, 1.0 Ni, 0.5 Fe, 0.1 Ti, 0.003 Si

Specimens were cut to 3/4- by 3- by 1/16-in. sheet. In the "standard" condition, unannealed specimens were wet-ground to 400 grit. They were suspended on Pyrex glass hangers, and separated by spacers of the same material. Most exposures were made in an oxygenated solution of reagent-grade cupric sulfate containing 5 mg of copper, per liter. The solution was continuously passed through the test chamber (6 ml/min), at 50°C.

To evaluate the importance of some obvious variables, some exposures were made with annealed specimens, with different surface preparations, with reduced oxygen content, and with nickel sulfate added to the solution.

RESULTS

Couples

Hydrogen bubbles were first seen at the crevice joints of the unsealed aluminum-nickel couple after 8 days; 69 days passed before hydrogen was seen at the joint of the unsealed aluminum-copper couple. White barnacle-like corrosion product formed at the joint of only the unsealed copper couple. After 100 days corrosion, the couples were taken apart and inspected, particularly at the internal aluminum surfaces.

The sealed couples showed no signs of corrosion in the crevice, indicating that the seals were effective. There was only a thin film of corrosion product on these exposed aluminum surfaces, even where contiguous to copper or nickel surface. For the unsealed specimens, the aluminum screw, where in contact with nickel, showed only the presence of a thin oxide and a little tarnishing; in contact with copper, considerable corrosion had occurred, with a copious amount of white corrosion product (see Fig. 1).

It is judged that the crevice was essential for severe attack in the presence of copper. The severe attack was not produced on 1100 aluminum by contact with nickel, even within the crevice.

Alloys in Copper Sulfate Solution

The high-purity metal formed no pits during the (seven) tests, although microscopic copper particles were deposited. Corrosion appeared typical of the essentially uniform attack ordinarily noted in distilled water.

Typical attack on the alloys is illustrated in Fig. 2. Pitting was most prevalent in the support hole and where the spacers were in contact with the metal (crevice areas). Additional pits within the dark-colored region appeared to have resulted from downward flow of a dense solution from the region of the support holes.

27831

A288C

SWISS H.P.

X8001

1100

Pretreatment: Unannealed and Wet-ground to 400 Grit

Fig. 2. Aluminum Samples after Corrosion for $11\frac{3}{4}$ days in Oxygen-saturated Copper Sulfate Solution at 50°C . (Magnification 1.33X)

Some pits were completely covered with a fragile white mound of oxide. Many were partly broken, as shown in Fig. 3. Red copper deposits were also found near each pit. Specimens with the greatest number of pits generally had the largest amount of copper deposition on their surface.

Under most test conditions, the two nickel-bearing alloys, X8001 and A288C, were most susceptible to galvanic attack in copper solution. In a few cases, the attack on 1100 aluminum was equally severe.

Annealed specimens were observed to accumulate less deposited copper than the as-rolled specimens; in one test (out of two), this was accompanied by less severe pitting, while in the other there was no discernible difference in the degree of pitting.

In the study of surface preparation, alloy X8001, wet-ground to 240-grit finish, formed more pits than specimens ground to 400-grit finish. Further decrease in roughness by electropolishing resulted in the most severe localized attack.

27836

Fig. 3. Corrosion Product and Pit on A288C Sample, Corroded in 50°C, Oxygen-saturated Copper Sulfate Solution. (Magnification 40X)

Replacement of oxygen with helium in the copper sulfate solution diminished pitting on the open surface, but not in the crevices. Addition of 5 ppm nickel ion to the copper sulfate solution had no effect on corrosion behavior.

All experiments verify the importance of crevices in the development of local attack of aluminum. There is no evidence that a differential concentration cell is important. In fact, this seems unlikely in the distilled-water tests, due to the low solution conductivity. It appears likely that contamination of the water in the crevice by a harmful contaminant is important in the mechanism. The lack of pitting of pure aluminum, even under copper deposits, supports the old proposal of alkali formation from impurity reaction.

Copper that has been deposited from solution apparently can form effective crevices, as judged by the attack occurring in such places, but not on exposed aluminum surfaces contiguous to coupled copper surfaces.

Nickel-bearing alloys are notable for the ease with which hydrogen is liberated locally on their surface, i.e., the ease with which cathodic reactions occur on the cathodic phase precipitates.^{1,3} It is not clear whether their special susceptibility to pitting in copper sulfate solution is due to the ready development of sizable copper deposits (and hence effective crevices) or to high current densities for alkali-producing cathodic reactions at such locations.

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