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FINAL REPORT

INTERNAL SACRIFICIAL ANODES IN HIGH STRENGTH ALUMINUM ALLOYS

U.S. ARMY GRANT NO: DAAG29-76-G-0061

NOVEMBER 1977

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Principal Investigators: A. J. McEvily, Professor J. E. Morral, Associate Professor Metallurgy Department University of Connecticut Storrs, Ct. 06268 (203) 486-4620

Submitted to: Department of the Army U.S. Army Research Office P.O. Box 12211 Research Triangle Park, N.C. 27709

Attn: Dr. P. Parrish

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FINAL REPORT

Statement of Problem Studied

Despite the fact that a great amount of qualitative information has been acquired about the nature of stress-corrosion cracking, no generally accepted quantitative treatment of the subject, even under specific given conditions, is available in the attempt to advance the state of the art. Our efforts have been directed toward the development and assessment of a quantitative approach of the stress-corrosion cracking of Al-Zn-Mg alloys in salt water environments. Initial work on this approach was carried out by Poulose, Morral, and McEvily and reported in Met. Trans., 5, 1974, pp. 1393-1400. The basic idea is that in the K-independent region (Stage II), where the velocity of crack growth is constant, the rate of crack advance is controlled by the rate of dissolution of the grain boundary precipitates. These precipitates are anodic with respect to the surrounding aluminum, and as such should preferentially dissolve. This fact was recognized years ago by Dix and coworkers, except that they considered the precipitate dissolution step to be very rapid, with the overall rate of crack advance being controlled by the rate of dissolution of the intervening aluminum. One might expect on this basis that the greater the amount of grain boundary precipitate, the greater should be the rate of crack growth. In our preliminary work however just the reverse was found, that is, the greater the amount of precipitate on the grain boundary the slower is the rate of crack growth. It appeared therefore for that the rate of dissolution of the precipitates is rate controlling White Section Buff Section rather than the rate of dissolution of aluminum, i.e., the precipitates n **JUSTIFICATION** act as sacrificial anodes.

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The purpose of the present investigation was to determine further the general validity of the sacrificial anode concept. The variables included specimen thickness to determine the sensitivity of the rate of cracking to either plane strain or plane stress conditions (in the first investigation specimens were 1.5 mm thick, in the present they were 6 mm), the extension of the range of K over which the data were obtained as compared to the previous investigation, and specimen potential. Initially we were interested in the possibility of modelling the double plateau that is found in the crack growth vs. stress-intensity (v-k plot) for Al-Zn-Mg alloys. In addition, as the work progressed the interest broadened to include consideration of the environment and alloy composition in order to provide further data to better understand the mechanisms involved, and also to contrast the above dissolution mechanism with the mechanism based upon hydrogen embrittlement.

Summary of Results

The experimental findings of this study lend further support to our sacrificial anode model of stress corrosion cracking of Al-Zn-Mg alloys in 3-1/2% NaCl solution. A wider range of K was investigated with no pronounced effect of thickness being observed, so that the results of this and our previous work were found to be in general agreement. Some experimental problems were encountered because of crack branching in the equiaxed alloy which was tested, and in further studies specimens containing side grooves as well as alloys with an elongated grain shape will be utilized in an effort to minimize this problem. It was also observed that, in contrast to findings reported in the literature, small amounts of cathodic polarization tended to accelerate rather than retard the rate of crack growth. This result is subject to at least two interpretations, one

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being that cathodic polarization leads to hydrogen embrittlement of the grain boundary which accelerates the rate of crack growth, the other being that cathodic polarization results in greater hydrogen evolution and contaminant stirring of the crack tip solution thereby accelerating the kinetics of the chemical interchanges. With respect to the cause of the double plateau, it was concluded that interfacial rupture of the grain boundary precipitate matrix interface was responsible for this behavior, and that the addition of copper to the alloy may lead to the elimination of the double plateau as a result of the strengthening of the particlematrix interface.

Perhaps the most significant outcome of the study is a paper "On the Mechanisms of Stress-Corrosion Cracking in Al-Zn-Mg Alloys" by R. Haag, J. E. Morral, and A. J. McEvily. This paper includes the new information mentioned above and discusses the results in the light of three different approaches to the understanding of stress corrosion cracking, namely, the sacrificial anode theory, the theory that the rate of cracking is a dissolution controlled by the cathodic polarization characteristics, and hydrogen embrittlement. As might be expected, the sacrificial anode theory is able to account quantitatively for the variation in crack growth rate with the amount of grain boundary precipitates. Neither of the other current approaches can provide a quantitative explanation for the observed trends and even qualitative explanations are at least speculative. This conclusion must be stated with care, for it may well be that with other environments, other mechanisms may be operative. For example, in moist air or in distilled water hydrogen embrittlement may be the operative mechanism.

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Although the program is no longer sponsored by ARO, the research is continuing along several lines which were initiated in the ARO program, and one new result of interest should be mentioned. In determining the pH at the crack tip of a Al-Zn-Mg specimen tested in 3-1/2% NaCl, we obtained a pH reading of about 3. On the other hand, for the same alloy tested in distilled water the pH reading was approximately 4.5. Such a result might not be expected based upon published NRL results, which as reported appear to indicate that in both salt water and distilled water environments the pH for the crack tips of all aluminum alloys is about 3. However on checking further with NRL researchers it was ascertained that this result for aluminum alloy was obtained only in salt water environments. Our results indicate that the crack tip reactions in the two environments are different, and are consistent with a shift in cracking mechanism from precipitate dissolution to hydrogen embrittlement as the amount of chloride in solution is reduced, a possibility raised in the above mentioned report.

In addition to pH and crack tip chemistry studies presently underway the initial ARO program has led to further studies in two areas. One of these is concerned with the effect of the amount of grain boundary precipitate on cracking rate in distilled water and moist air. It is possible that the pronounced sensitivity to the amount of grain boundary precipitate when the alloy is tested in salt water will be absent when the alloy is tested in distilled water since the dissolution mechanism may not be operative. We are also studying the cracking behavior of Al-Cu alloys in various environments in order to learn more of the cracking behavior of an alloy in which the grain boundary precipitate is cathodic rather than anodic to the surrounding matrix.

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In conclusion we know we have a research program underway which will contribute to the understanding of a complex subject, and are appreciative of the support given to the program by ARO.

List of Publications

 "On the Mechanisms of Stress Corrosion Cracking in Al-Zn-Mg Alloys," R. Haag, J. E. Morral, and A. J. McEvily in Environmental Degradation of Engineering Materials, ed. by M. R. Louthan, Jr., and R. P. McNitt, Virginia Tech. Printing Dept., 19-40, 1977, (an invited paper; a modified version of this paper will be submitted to Corrosion).

Participating Scientific Personnel

- 1. Professor A. J. McEvily
- 2. Associate Professor J. E. Morral
- 3. Graduate Assistants: R. Haag, L. Luini, V. Singh

Advanced Degrees Awarded

 R. Haag - M. S. 1977, Thesis Title: "Stress Corrosion Cracking of Al-Zn-Mg Alloys."

INSTITUTE OF MATERIALS SCIENCE

The Institute of Materials Science was established at The University of Connecticut in 1966 in order to promote the various fields of materials science. To this end, the State of Connecticut appropriated \$5,000,000 to set up new laboratory facilities, including approximately \$2,150,000 for scientific equipment. In addition, an annual budget of several hundred thousand dollars is provided by the State Legislature to support faculty and graduate student salaries, supplies and commodities, and supporting facilities such as various shops, technicians, secretaries, etc.

IMS fosters interdisciplinary graduate programs on the Storrs campus and at present is supporting five such programs in Alloy Physics, Biomaterials, Crystal Science, Metallurgy, and Polymer Science. These programs are directed toward training graduate students while advancing the frontiers of our knowledge in technically important areas.