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Influence of Bulk-Solution-Chemistry Conditions on Corrosion-Fatigue Crack-Growth Rate

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Metals Performance Branch
Material Science and Technology Division

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An exploratory study has been conducted to determine the influence of bulk-solution-chemistry conditions on corrosion-fatigue crack-growth rate in high-strength alloys. Various solutions commonly employed in studies relating to marine corrosion were evaluated for their relative severity in crack-growth-rate tests. Related aspects involving aeration and applied cathodic potential were included. The results indicate that bulk-solution-chemistry conditions can influence measured values of corrosion-fatigue crack-growth rate by as much as a factor of three; however, the relative severity of various solutions can vary, depending upon alloy composition.

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INFLUENCE OF BULK-SOLUTION-CHEMISTRY CONDITIONS ON CORROSION-FATIGUE CRACK-GROWTH RATE

INTRODUCTION

Materials-characterization data generated in corrosion-fatigue crack-growth-rate tests can be strongly influenced by experimental procedures [1]. In the absence of standard methods for such tests, specific procedures have evolved which vary from one laboratory to another. For instance, the literature indicates that in tests relating to marine corrosion, numerous environments are used more or less interchangeably, depending upon availability or preference. Current practices for such tests involve the use of natural seawater (both fresh and otherwise), ASTM substitute ocean water [2] which can have separate formulations relating to heavy-metal content, and aqueous NaCl solutions involving various concentrations of salt. Also, the conditions of contact between bulk solution and test metal vary between quiescent and flowing.

Little evidence exists either to support or to refute the validity of these varying practices. This investigation was undertaken as a step toward prescribing standard procedures for Navy tests involving fatigue-crack propagation in marine environments; it was also undertaken to provide a basis for assessing the differing practices currently employed by various Navy in-house and contractor laboratories which perform these tests.

EXPERIMENTAL DETAILS

This study was performed at NRL's Marine Corrosion Research Laboratory located in Key West, Fla. Fatigue crack-growth-rate tests were conducted on four high-strength alloys under various conditions involving corrosion. The alloys studied are shown in Table 1 along with their corresponding yield-strength levels.

Table 1 — Materials

Alloy	0.2% Yield Strength (MPa)
7475-T7351 Aluminum	433
HY-130 Steel	1015
Vacuum-Melted H1050 17-4 PH Steel	1060
Argon-Oxygen-Melted H1050 17-4 PH Steel	1125

Manuscript submitted July 14, 1978.

Each of these materials was received in the form of 25-mm-thick rolled-plate stock. A previous study of corrosion-fatigue crack growth in the three steels is described in Ref. 3.

Crack-growth-rate tests were conducted using single-edge-notch cantilever specimens, shown in Fig. 1. Fracture-mechanics crack-tip stress-intensity-factor values for the cantilever specimens were calculated by use of the Kies expression [4]. All specimens were oriented with the edge crack parallel to the final rolling direction of the material, in the ASTM-designated T-L orientation [5]. Specimens were cycled under constant load, zero-to-tension, with the stress ratio $R = 0$. All tests were conducted at a cyclic frequency of 10 cpm (0.167 Hz). The cyclic load-vs-time waveform was approximately triangular. A polyurethane enclosure cell was placed around the specimen test section in order to contain the corrosive environment. The corrosion cell had a Plexiglas viewing area for optical observation of crack growth. Periodic measurements of fatigue-crack length were performed by means of a slide-mounted optical micrometer focused on the root surface of one side groove of the specimen.

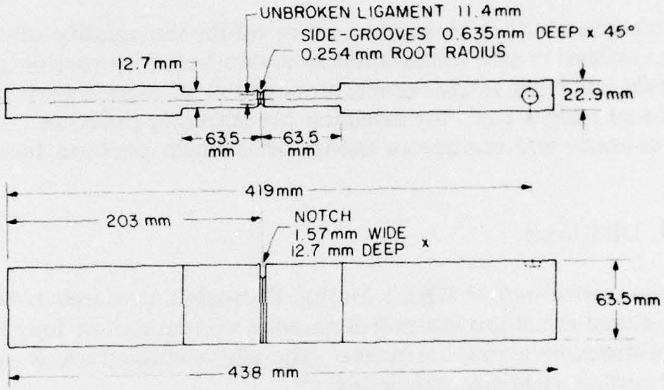

Fig. 1—Details of the single-edge-notch cantilever specimen

A total of four aqueous solutions were investigated in the course of this study: fresh natural seawater, 3.5% NaCl, and ASTM substitute ocean water [2] prepared both with and without heavy-metal additions. The latter three solutions were prepared using deionized water obtained from the Key West City Electric System generating station. Tests were conducted either in quiescent solutions, which were changed twice per daily 8-hour testing period, or under flowing conditions in a single-pass mode at a flow rate of approximately 200 ml/min.

Because of the use of a single-pass mode for the tests conducted under flowing conditions, sizeable quantities of solutions were required. Testing durations of a week or more were not uncommon, thus a large storage-and-delivery system was necessary. For the fresh natural seawater, this requirement created no special problems; the Marine Corrosion Research Laboratory is specially situated and equipped for exactly this purpose. However, for the 3.5%-NaCl solution and the ASTM substitute ocean water additional facilities were needed. This was accomplished by constructing a storage-and-delivery system consisting of ordinary plastic refuse cans, on an elevated platform for gravity flow, connected to the corrosion cells via plastic tubing.

For tests involving applied potential, a commercial potentiostat device was employed. Potentials were measured against a Ag/AgCl reference electrode.

RESULTS AND DISCUSSION

The results of this investigation are presented in a cyclic crack-growth-rate (*da/dN*) vs stress-intensity-range (ΔK) format in Figs. 2 through 7.

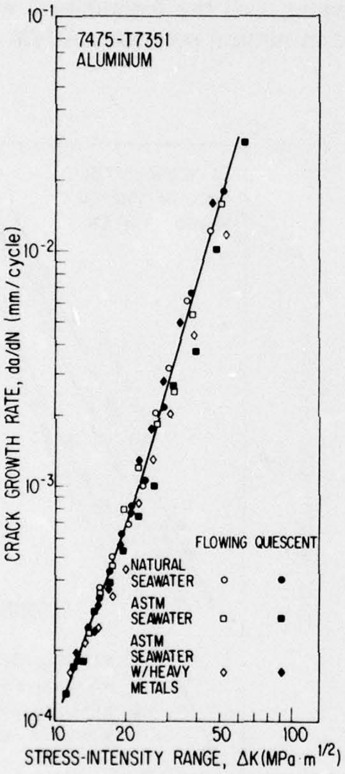

Fig. 2 — Crack-growth-rate data for 7475-T7351 aluminum alloy in natural seawater and in ASTM substitute ocean water, with and without heavy metals, under both flowing and quiescent conditions

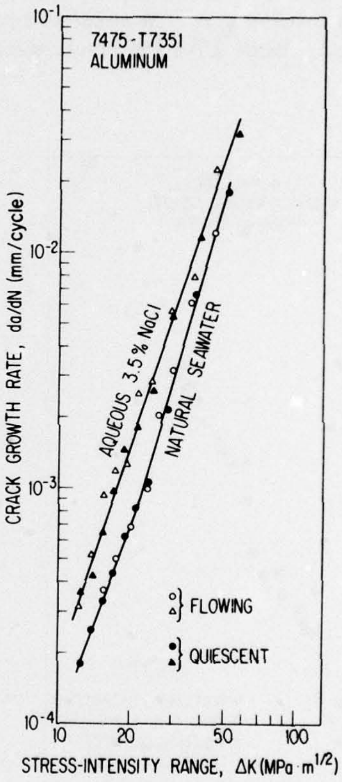

Fig. 3 — Crack-growth-rate data for 7475-T73571 aluminum alloy in natural seawater and in aqueous 3.5%-NaCl solution under both flowing and quiescent conditions

The first phase of this investigation consisted of testing the 7475-T7351 aluminum alloy under eight separate conditions of bulk-solution chemistry. Fresh natural seawater, 3.5%-NaCl solution, and ASTM substitute ocean water, with and without heavy-metal additions, were each studied separately under quiescent and flowing conditions. No effect of quiescent vs flowing solutions could be detected, and no differences between natural seawater and either formulation of ASTM substitute ocean water were apparent (Fig. 2). However, *da/dN* values were observed to be approximately twice as great in 3.5%-NaCl solution as in natural seawater (Fig. 3).

The second phase of this investigation consisted of testing the three high-strength steels. All of the tests on steels were conducted under flowing conditions, and all of the tests on steels involving ASTM substitute ocean water used the formulation with heavy metals included. Both 17-4 PH steels were tested in natural seawater, ASTM substitute

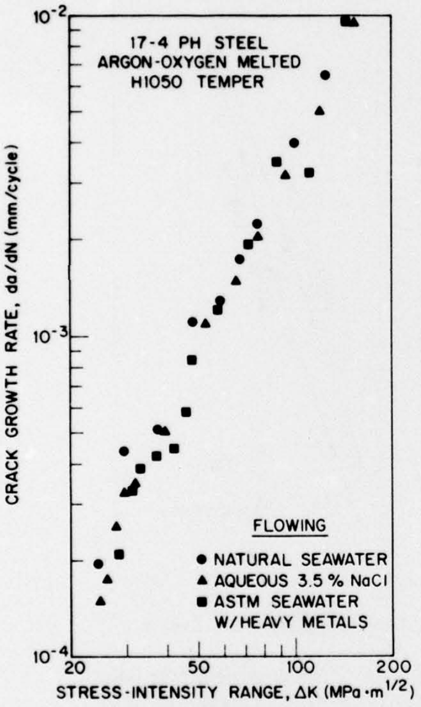

Fig. 4 — Crack-growth-rate data for argon-oxygen-melted H1050 17-4 PH steel in natural seawater, in aqueous 3.5%-NaCl solution, and in ASTM substitute ocean water with heavy metals under flowing conditions

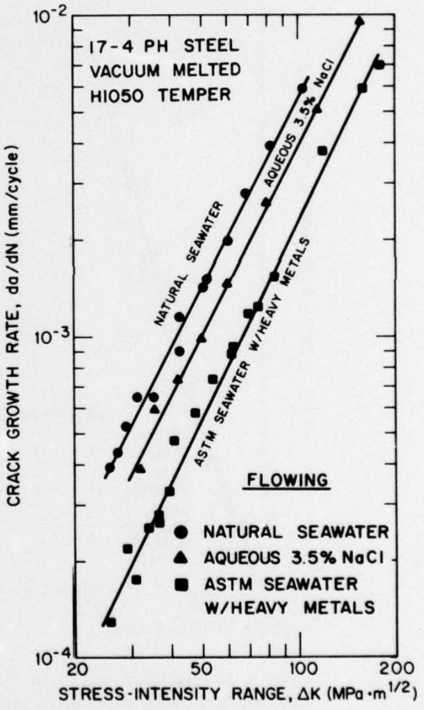

Fig. 5 — Crack-growth-rate data for vacuum-melted H1050 17-4 PH steel in natural seawater, in aqueous 3.5%-NaCl solution, and in ASTM substitute ocean water with heavy metals under flowing conditions

ocean water and 3.5%-NaCl solution. These data are shown in Figs. 4 and 5. The *da/dN*-vs-ΔK data for the argon-oxygen-melted 17-4 PH steel are virtually identical for the three environments. However, similar data for the vacuum-melted 17-4 PH steel exhibit *da/dN* values which differ among the various environments by as much as a factor of three. In this instance, significant differences were apparent; the most aggressive environment was natural seawater, the least aggressive was ASTM substitute ocean water, and 3.5%-NaCl solution lies between the two extremes.

The HY-130 steel was tested in natural seawater and in 3.5%-NaCl solution at two electrochemical potentials, freely corroding (~ -0.665 V) and an applied cathodic potential of -1.05 V. The *da/dN*-vs-ΔK data for the HY-130 steel are shown in Figs. 6 and 7. In both cases, *da/dN* values were approximately 1.5 to 2 times greater in natural seawater than in the 3.5%-NaCl solution. Applied cathodic potential appeared to moderately accentuate the environmental differences.

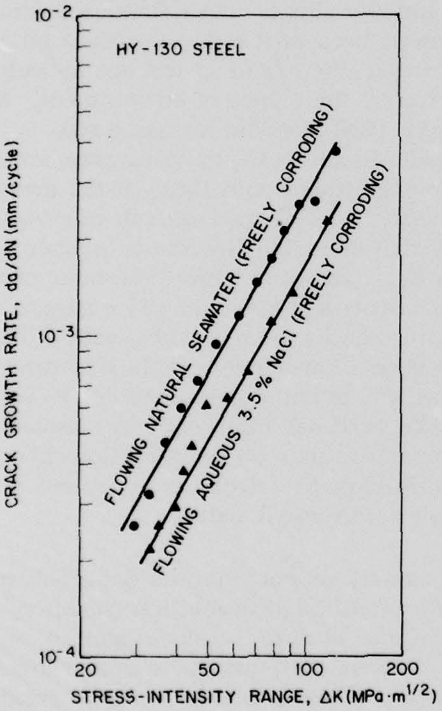

Fig. 6 — Crack-growth-rate data for HY-130 steel in flowing natural seawater and in flowing aqueous 3.5%-NaCl solution under freely corroding conditions (~ -0.665 V vs Ag/AgCl)

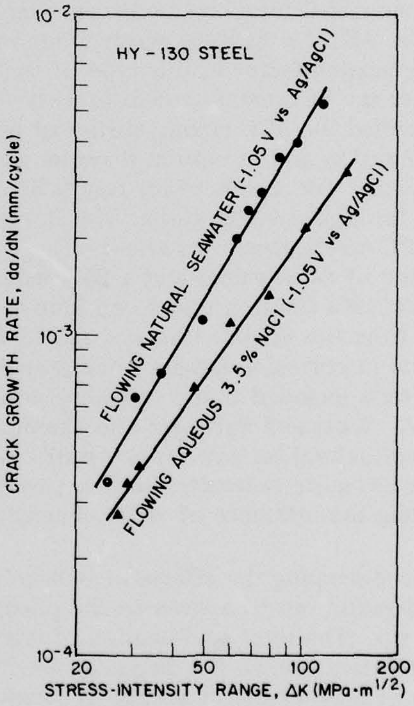

Fig. 7 — Crack-growth-rate data for HY-130 steel in flowing natural seawater and in flowing aqueous 3.5%-NaCl solution under cathodic potential of -1.05 V vs Ag/AgCl

These results indicate that differences in bulk-solution chemistry can have a significant effect on corrosion-fatigue crack-growth-rate-test results for marine environments. However, no consistent trend is apparent among these observed differences, and no single environment is clearly preferable for laboratory testing purposes. Since fresh natural seawater is not widely available, except at a few scattered field-site laboratories, the question resolves itself to a choice between ASTM substitute ocean water and 3.5%-NaCl solution for the majority of laboratory studies. Nothing among these results suggests that ASTM substitute ocean water possesses any demonstrable advantage over 3.5%-NaCl solution for these purposes. Additional factors favoring the use of 3.5%-NaCl solution are its relative economy, availability, and ease of preparation as compared to the ASTM substitute ocean water.

The literature provides little in the way of background information against which the results of this investigation can be judged. Only three other studies involving similar comparative evaluations among aqueous environments are known to the authors, and two of these involve stress-corrosion cracking (SCC) rather than corrosion fatigue. Humphries and Nelson [6] compared ASTM substitute ocean water vs 3.5%-NaCl solution for alternate immersion SCC tests on smooth specimens of aluminum alloys. Their findings indicated that the ASTM substitute ocean water was preferable because it reduced surface pitting, a complicating factor in this type of testing. However, their findings did not indicate whether the SCC crack-growth process was affected by the choice of environment. Novak [7] studied the SCC characteristics of high-strength 12Ni-5Cr-3Mo maraging steel in 3.5%-NaCl solution and in natural seawater at Wrightsville Beach, N.C., by using precracked specimens. The trends of his results are in general agreement with those of the present study for high-strength steels. Novak measured values of SCC crack-growth rate (da/dt) and SCC crack-growth threshold (K_{Iscc}) in both environments. His results indicate a doubling of da/dt values and a 25% reduction in K_{Iscc} values in natural seawater relative to 3.5%-NaCl solution under continuous aeration. Scott and Sylvester [8] compared seawater from the English Channel, stored for up to 6 months in large tanks, with 3.5%-NaCl solution in corrosion-fatigue crack-growth-rate tests on a low-strength C-Mn structural steel. Their tests included freely corroding conditions as well as cathodic potentials of -0.8 and -1.0 V. Scott and Sylvester also examined the effects of half-dilute natural seawater and acidified natural seawater (pH = 6.5). Their comparative data on bulk-solution-chemistry effects are quite extensive; however, overall, it is difficult to detect any consistent trends regarding the influence of water chemistry in their da/dN-vs-ΔK data.

In discussing the effects of bulk-solution chemistry on corrosion-fatigue crack growth, consideration must be given to the possibility of a modified local-solution chemistry at the crack tip. The local acidification of crack-tip solutions in SCC is well recognized, even for bulk solutions which are distinctly alkaline [9]. Barsom [10] has made similar measurements of local crack-tip acidity in corrosion-fatigue crack-growth tests of high-strength 12Ni-5Cr-3Mo maraging steel. However, Hartt et al. [11] have hypothesized that the repeated opening and closing of a crack in fatigue should produce a mixing of bulk- and local-solution chemistry not found in SCC tests under static loading. From this hypothesis, it would seem possible that bulk-solution chemistry could be of greater importance in fatigue testing than in SCC testing. To date, the limited observations cited here suggest more similarities than differences among bulk-solution-chemistry effects in SCC and corrosion-fatigue crack-growth-test results.

CONCLUSIONS

Although natural seawater, ASTM substitute ocean water, and aqueous 3.5% NaCl are often used interchangeably for corrosion-fatigue crack-growth-rate testing, they can produce differing results. Crack-growth-rate values can vary by as much as a factor of three among these three bulk-solution chemistries. In high-strength steels, natural seawater can be significantly more aggressive than either laboratory substitute. As a laboratory substitute for natural seawater, ASTM substitute ocean water does not appear to offer any significant advantage over aqueous 3.5% NaCl in crack-growth-rate tests. However, neither ASTM substitute ocean water nor 3.5%-NaCl solution fully duplicates the effects of natural seawater in in laboratory tests.

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