

Hydrogen Embrittlement of a Cyclically Deformed High Strength Al Alloy

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High cycle fatigue experiments have been performed on a 7075 Al alloy, principally in the T6 temper in dry air, distilled water 0.5N NaCl and 0.5N Na₂SO₄ solutions as functions of cathodic charging and catalyst poisoning of the hydrogen evolution reaction. All aqueous solutions appreciably lowered fatigue resistance with Cl⁻ ion producing the greatest reduction in resistance and SO₄⁻ ion behaving essentially in the same manner as distilled water. Under cathodic charging conditions fatigue resistance is significantly reduced and both Cl⁻ and SO₄⁻ solutions produce similar fatigue lives. A catalyst poison (As) added to Cl⁻ solutions reduces fatigue resistance relative to neutral Cl⁻ solutions. Fractography of specimens fatigued in aqueous environments shows that a significant amount of cleavage and quasicleavage occurs, the extent of these features being apparently a function of hydrogen available to the alloy free surface and to the tips of growing cracks. On the basis of these observations, it is suggested that corrosion fatigue of 7075 alloy is essentially a hydrogen embrittlement phenomenon where the low diffusivity of hydrogen is counterbalanced by the fact that hydrogen need only be present in the alloy free surface for crack initiation and in the plastic zone of growing cracks for propagation.

ENVIRONMENTALLY accelerated fatigue crack initiation and growth have been the subject of a considerable amount of recent research.¹⁻⁹ Mechanisms for this phenomenon, particularly in chloride containing solutions, have included active dissolution of active slip bands and surface energy reduction at crack tips due to preferentially adsorbing environmental species.⁴⁻⁶ The possibility of a hydrogen embrittlement phenomenon was also suggested as one of several possibilities to explain reduced fatigue resistance of aluminum alloys exposed to water vapor.⁷

In previously reported work it was shown that corrosion fatigue crack initiation of 7075 Al alloys may be associated with hydrogen, generated by corrosion at non-metallic inclusions which intersect the alloy surface.⁸ Similarly, initial crack growth was associated with hydrogen generated in an acid environment in a growing crack which acts as a crevice. Additionally it was shown that these effects are due to hydrogen contained in the alloy lattice, in contrast to surface energy reduction at a crack tip, since fatigue resistance of precharged specimens could be improved by a post charging heat treatment which effectively "baked" the hydrogen out of the alloy.⁹ It was also shown that simultaneous cathodic charging of a cyclically stressed high purity analogue of the alloy (Al-5Zn-2.5 Mg) resulted in very low fatigue resistance with crack surfaces showing a cleavage type appearance. Greater reductions in fatigue resistance and large numbers of secondary cracks were observed for more negative cathodic potentials.⁹

The results of the present study are part of a continuing effort to assess and understand the effect of hydrogen on the fatigue resistance of high strength precipitation hardened aluminum alloys.

EXPERIMENTAL PROCEDURE

Axial fatigue experiments have been performed on cylindrical cross section (2.2 mm) specimens of a commercial 7075 alloy in the T6 heat-treatment in dry air, 0.5N NaCl, 0.5N Na₂SO₄ and in 0.5N NaCl solution with addition of 10ppm As. For some experiments specimens were cathodically charged to produce hydrogen. Additionally some experiments were performed on specimens in the T73 condition (which has been reported to show superior SCC resistance) in dry air and in 0.5N NaCl solutions. Fatigue loading was in the tension-tension mode with a constant applied mean stress of 172 MPa ($\approx \sigma_y/3$) under load control at 30 Hz. The environmental test apparatus has been previously described.⁸ Prior to testing, specimen surfaces were mechanically polished through 3 μ m diamond paste and subsequently electropolished.

Solutions were aerated and recirculated from an external reservoir during testing. Fracture surfaces and the specimen free surfaces for each case were examined by optical microscopy and SEM.

RESULTS

Fig. 1 shows the fatigue behavior of the alloy in air, distilled water, 0.5N Na₂SO₄ and 0.5N NaCl and indicates that, except at relatively low applied stresses, H₂O and Na₂SO₄ solutions show approximately the same fatigue behavior. Exposure to NaCl solution during cyclic stressing, on the other hand, results in very inferior fatigue resistance with the 10⁷ cycle fatigue life corresponding to an applied cyclic stress of only about 35 MPa. A static loading test in NaCl, at an applied stress of about 320 MPa ($a \sigma_{mean} + \sigma_{cyclic max}$ of this magnitude would result in $N_f = 3 \times 10^4$ cycles) showed no evidence of cracking for a period greater than 200 h.

In an earlier paper,⁹ it was suggested that the reduction in fatigue resistance of high strength aluminum alloys was associated with hydrogen (which was pro-

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Manuscript submitted January 4, 1977.

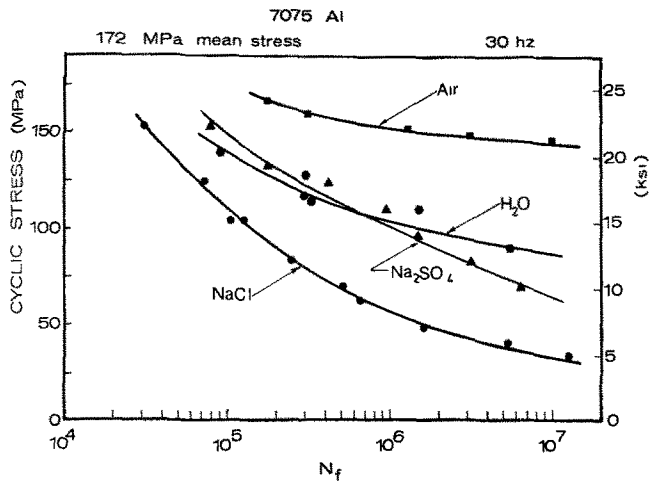


Fig. 1—Fatigue behavior of 7075-T6 aluminum alloy in air, distilled H₂O and aqueous solutions of 0.5N Na₂SO₄ and 0.5N NaCl.

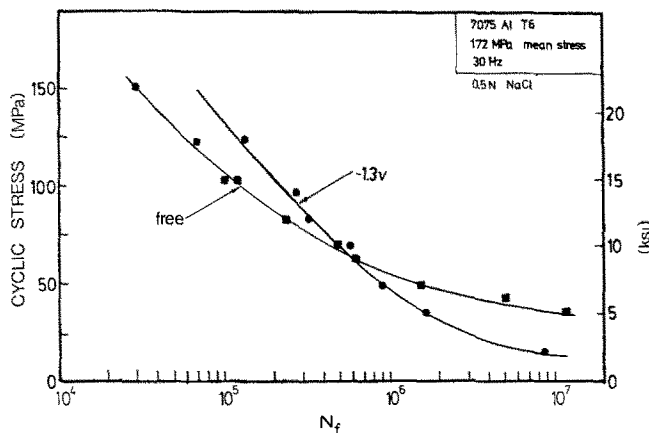


Fig. 2—Fatigue behavior of 7075-T6 Al in 0.5N NaCl under conditions of cathodic charging at $\phi_c = -1300$ mv vs. S.C.E.

duced by selective corrosion in the vicinity of non-metallic inclusions). In order to test this hypothesis, fatigue curves were generated for specimens which were maintained at a potential of about -1300 versus the saturated calomel electrode (S.C.E.) (about 600 mv cathodic to the corrosion potential). The cathodic current density at this potential corresponded to ≈ 0.7 ma/cm² which could be expected to produce $\approx 10^{15}$ molecules H₂/cm²-s. (assuming that the measured current is only used to generate H₂). Fig. 2 shows that, at high applied cyclic stresses cathodic charging results in an increase in fatigue resistance, while at lower applied stresses, cathodic charging results in decreased fatigue resistance with the 10^7 cycle fatigue limit reduced to a value of only ≈ 13 MPa. Charging at potentials more negative than -1300 mv S.C.E. does not appreciably affect fatigue resistance, although charging at more noble potentials (less hydrogen evolved) results in some cathodic protection, a maximum in protection being observed at -900 mv S.C.E. Anodic polarization results in a still larger reduction in fatigue resistance (Fig. 3). The addition of a hydrogen atom recombination poison (10 ppm As) to the sodium chloride solution also results in a small reduction in fatigue resistance (Fig. 4).

Cathodic charging of the alloy exposed to neutral 0.5N Na₂SO₄ results in a large reduction in fatigue resistance in a similar manner to cathodic charging in NaCl solution (Fig. 5). At stresses in the vicinity of the 10^7 cycle fatigue limit, cathodic charging in sulfate results in virtually the same fatigue resistance as is observed in chlorides. At higher stresses, however sulfate is less detrimental than chloride at -1300 mv S.C.E.

In addition to experiments on the 7075 alloy in the T6 condition, a limited number of experiments were conducted on specimens in the T73 condition, a heat-treatment which has been shown to be more resistant to stress corrosion cracking.¹⁰ Fig. 6 shows the results of these experiments with an expected slight decrease in fatigue resistance in dry air (YS and UTS are lower for T73 than they are for the T6 heat-treatment). In aerated 0.5N NaCl solution, however, there is no appreciable difference in fatigue resistance.

SEM fractography of specimens exposed to dry air, free corrosion in NaCl and under cathodic charging conditions are shown in Fig. 7. As has been previously reported,⁸ in dry air the fracture surface consists of feathery river lines extending from a single initiation site at the alloy surface consistent with crystallographic (Stage I) cracking. In NaCl solution a featureless, thumbnail shaped area which is normal to the tensile axis is associated with the initiation site. As the crack grows out from this area, straight cleavage like markings develop which are unlike the feathery river lines observed in dry air in that they are straighter and more well defined. These markings are followed by the more traditional river line structure as the crack progresses, although the striations which are observed at longer crack lengths are of the "brittle" type observed by Forsyth² in contrast to "ductile" striations observed in air. The Na₂SO₄ solutions, the featureless region and the cleavage like area is smaller than that observed in air. In the Na₂SO₄ solutions, the featureless striations are observed near the overload failure region (Fig. 8(b)). Cathodically polarizing specimens to -1300 mv vs. S.C.E. in NaCl solutions also resulted in the production of a featureless plus cleavage zone and, additionally a significant amount of Stage II, or non-

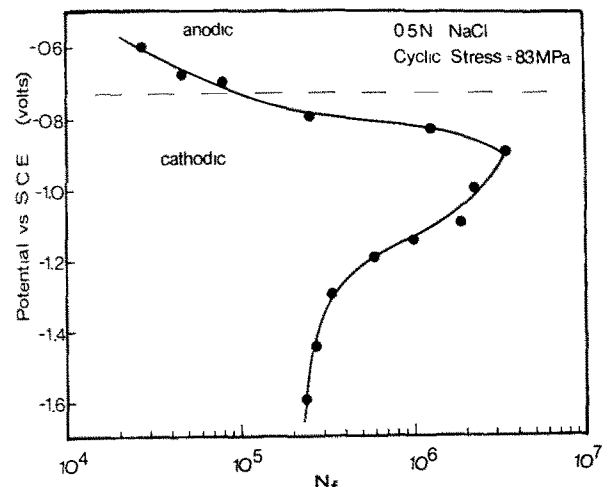


Fig. 3—Fatigue life of 7075-T6 Al in 0.5N NaCl under conditions of cathodic charging, $\sigma_{max} = 255$ MPa.

crystallographic crack propagation was observed in regions far from the crack initiation site (Fig. 9(a)). Polarization to -900 mv vs. S.C.E. also resulted in some grain boundary attack in regions removed from the initiation site (Fig. 9(b)). Additionally, for cathodic potentials less than -900 mv vs. S.C.E. in either NaCl or Na_2SO_4 , extensive secondary cracking and associated pitting was observed on alloy surfaces (Fig. 10(a)). Optical metallography of cross-sections of the free surfaces indicated that the pits were associated with the cracks rather than being responsible for their formation due to stress concentrations, since sharp cracks also intersected the free surface adjacent to cracks which were associated with pits. Presumably these cracks formed late in specimen life since they are not extensively pitted (Fig. 10(b) and (c)). Additionally, the blunted nature of the cracks on the specimen surface suggests that the cracks were broadened by a corrosion reaction.

DISCUSSION

The results of this study show that hydrogen, either produced by cathodic charging or by corrosion reactions, lowers the resistance of 7075 Al to cyclic deformation. Additionally, it has been shown that, under conditions of free corrosion, the anionic species is important to the fatigue process, Cl^- being considerably more damaging than SO_4^{2-} of the same ionic charge concentration. The application of cathodic currents in either Cl^- or SO_4^{2-} solution on the other hand results in a similar reduction in fatigue resistance, particularly at applied stresses in the vicinity of the 10^7 cycle fatigue limit. It has also been shown that a cathodic poison (As) reduces fatigue resistance in Cl^- solutions.

Correlation of the fatigue resistance results with electron fractography and optical metallography indicates that hydrogen induces a form of cyclic cleavage in high strength aluminum alloys which is characterized by crack initiation on a plane normal to the tensile axis. This zone, which is essentially featureless, transforms to a zone of quasi-cleavage with a considerably more brittle appearance than is observed when fatigue crack propagation occurs in laboratory air.

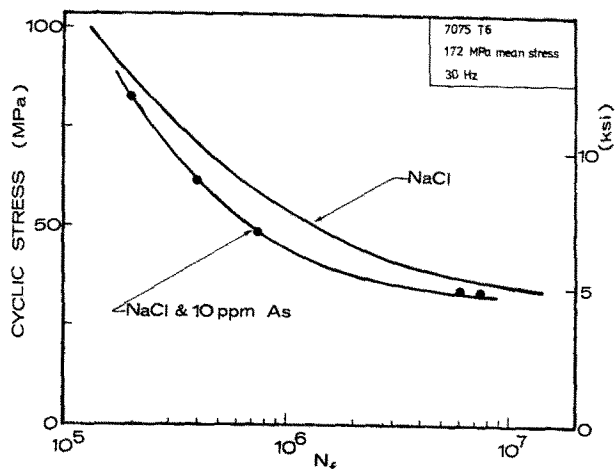


Fig. 4—Fatigue behavior of 7075-T6 Al in 0.5N NaCl + 10 ppm As.

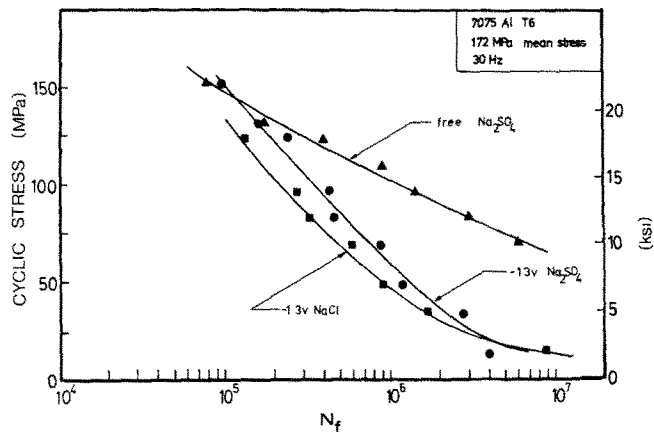


Fig. 5—Fatigue behavior of 7075-T6 Al in 0.5N Na_2SO_4 under conditions of cathodic charging at $\phi_c = -1300$ mv vs. S.C.E. compared to free corrosion in 0.5N Na_2SO_4 and under conditions of cathodic charging in 0.5N NaCl at $\phi_c = -1300$ mv vs. S.C.E.

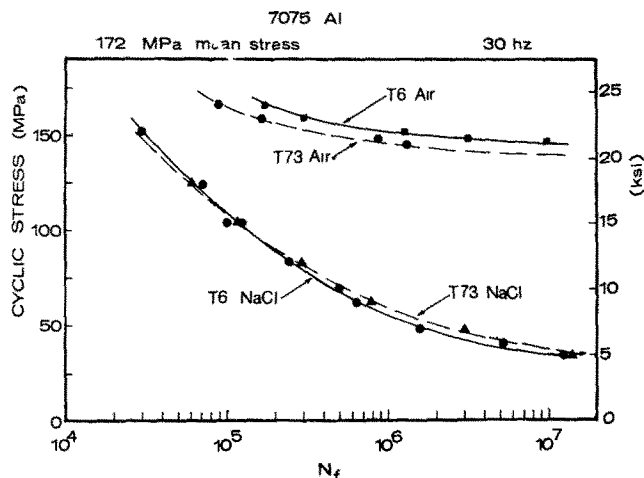
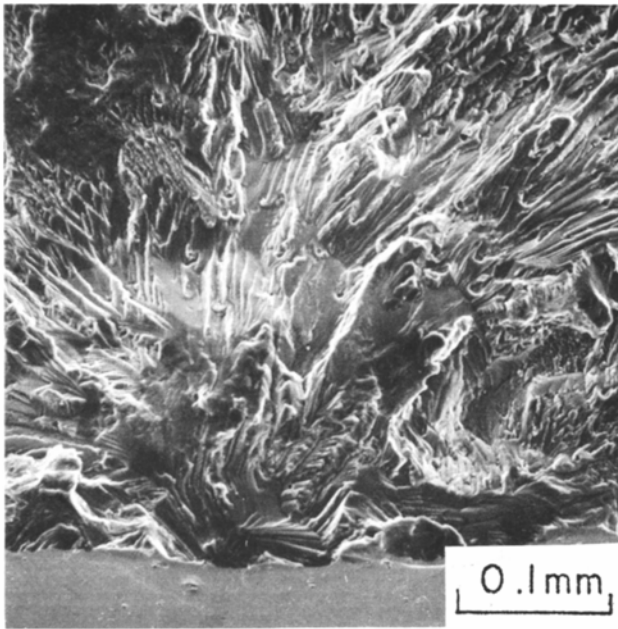


Fig. 6—Fatigue behavior of 7075-T73 Al in air and in 0.5N NaCl compared to behavior of 7075-T6 Al.

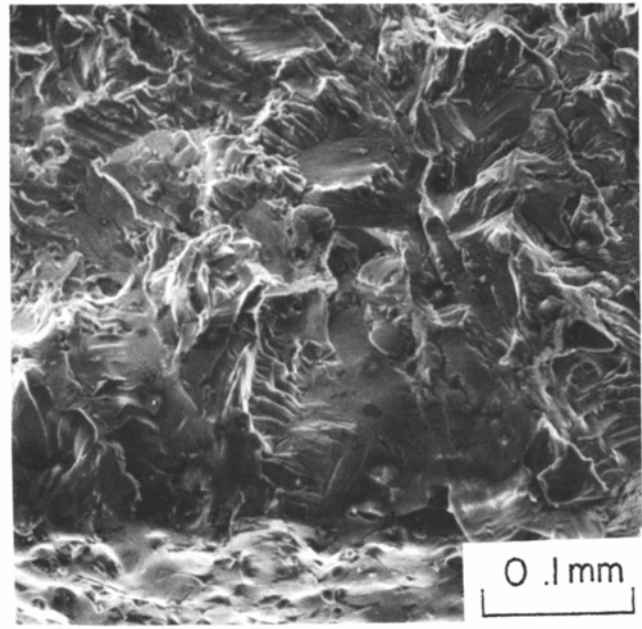
This region transforms to the feathery river line appearance similar to that of cracks propagated in air as the crack grows.

The featureless and quasi-cleavage zones are observed under all conditions of environmental fatigue, including under conditions of a small applied anodic potential.

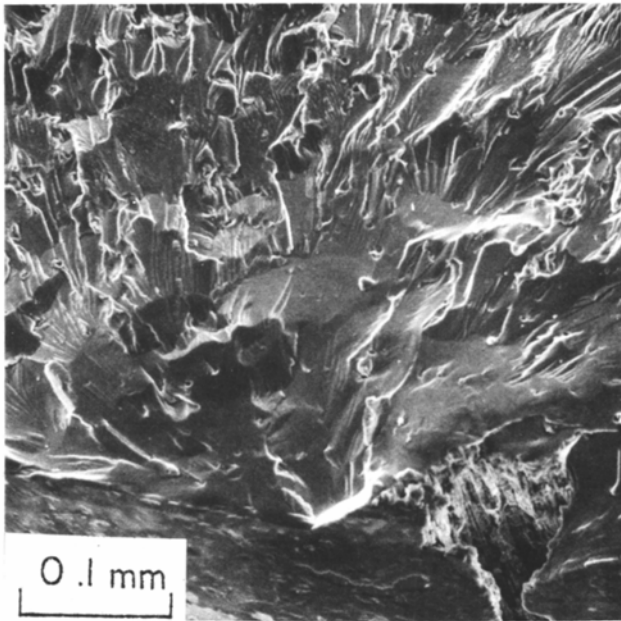
It is interesting to note that, in sulfate, externally generated hydrogen (in contrast to H_2 generated from an intrinsic corrosion reaction) results in almost the same fatigue resistance as is observed in Cl^- solutions. At relatively high stress levels, cathodic charging in the sulfate solution shows a slightly superior fatigue resistance while at stresses near the 10^7 cycle fatigue limit fatigue resistance is virtually identical. At low fatigue stresses crack initiation and early propagation represent a large percentage of the fatigue life and under these conditions hydrogen has ample time to diffuse to highly stressed regions and facilitate the fatigue process. In chloride solutions, on the other hand, there is a slight improvement of fatigue resistance at high stresses and a reduction at lower stresses. The improvement realized at high stresses may be



(a)



(c)



(b)

Fig. 7—Fracture surfaces of 7075-T6 Al in *a*) air, *b*) freely corroding 0.5N NaCl solution and *c*) 0.5N NaCl solution under conditions of cathodic charging at $\phi_c = -1300$ mv vs. S.C.E., $N_f \approx 10^6$.

related to a reduced hydrogen concentration in the vicinity of a rapidly growing crack. As Pickering¹¹ has pointed out, there is anodic polarization of the crevice created by the growing crack which could significantly reduce the amount of hydrogen produced by the corrosion reaction. At low stresses, crack initiation and early propagation are the limiting rate factors and the excess hydrogen produced by cathodic polarization serves to shorten the time required for these processes.

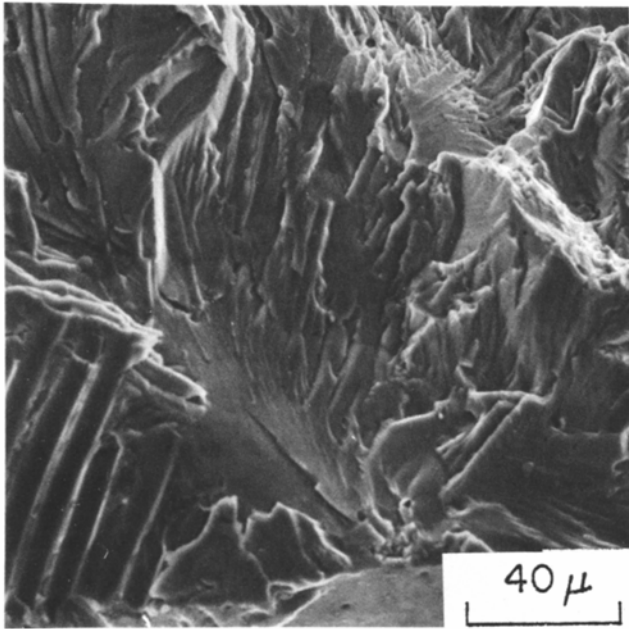
The results obtained for the effect of applied poten-

tial on fatigue life is quite similar to those presented by Endo *et al.*¹² Despite differences in chloride concentration and alloy chemistry, Endo found that initial cathodic polarization ($-0.9V \rightarrow -1.3V$) S.C.E. suppressed electrochemical corrosion which delayed crack initiation and propagation and resulted in increased fatigue lives. Further cathodic polarization resulted in enhanced crack initiation and a decrease in fatigue life which Endo attributed to embrittlement due to excess hydrogen ions. Endo found changes in the fracture morphology associated with applied cathodic potentials. On a macroscopic level, initial crack extension changed from a shear mode to a tensile mode as the potential was shifted in the negative direction. The microscopic striation morphology shifted from brittle striations at the corrosion potential to ductile striations at the potential of maximum protection. Further polarization resulted in the reappearance of brittle striations.

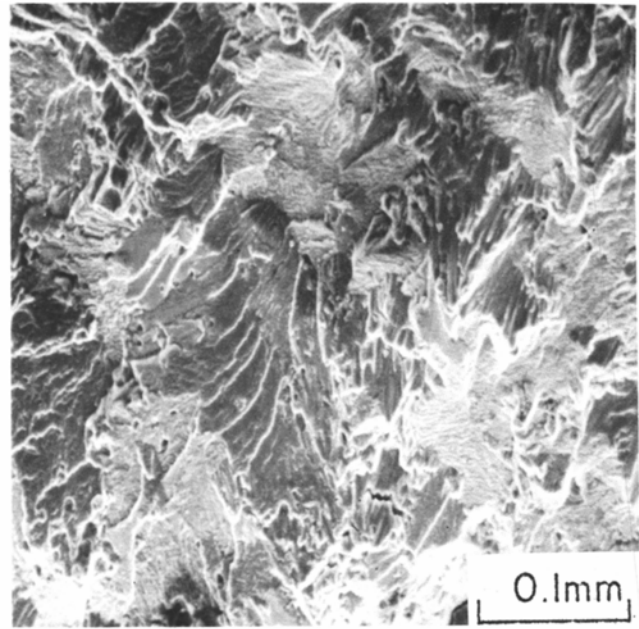
It is interesting, although probably not surprising, to note that the T73 heat treatment does not improve corrosion fatigue resistance in a chloride environment. Since the T73 heat treatment was developed to provide intergranular SCC resistance by altering grain boundary area structures, while the corrosion fatigue process is transgranular, no beneficial effect should be expected.

The fractography results support the view that a form of hydrogen embrittlement is responsible for the reduction in fatigue resistance observed in this study since the featureless and cleavage like zones could result from local embrittlement of the alloy.

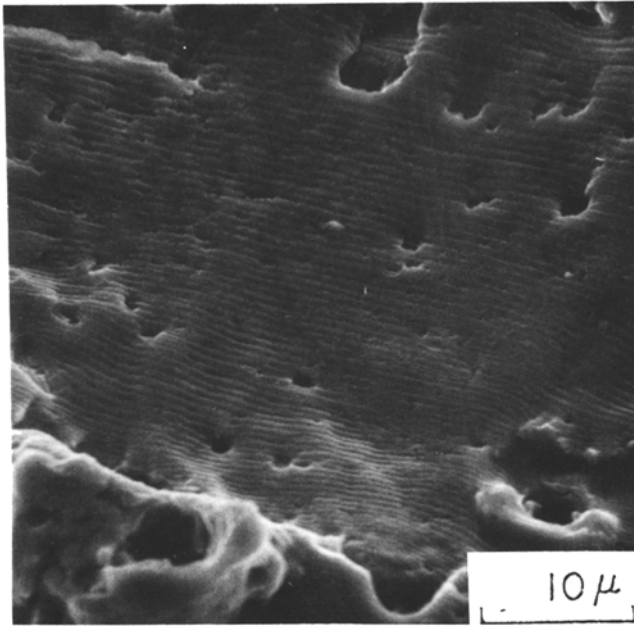
It has been suggested that aluminum alloys should not be expected to be susceptible to hydrogen embrittlement because of the low diffusivity of hydrogen in aluminum. However, the effect of hydrogen on fatigue behavior of aluminum alloys does not depend strongly on bulk diffusivity of hydrogen but only requires that hydrogen be present in the vicinity of the growing crack, *i.e.*, in the plastic zone. In this region fresh



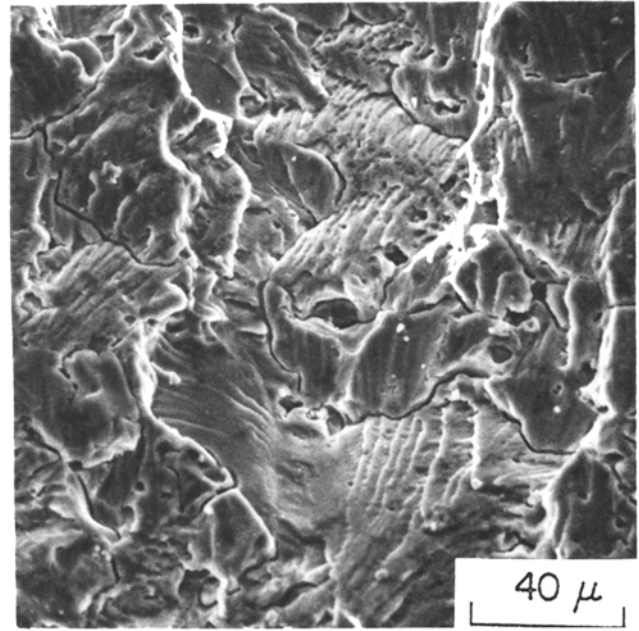
(a)



(a)



(b)



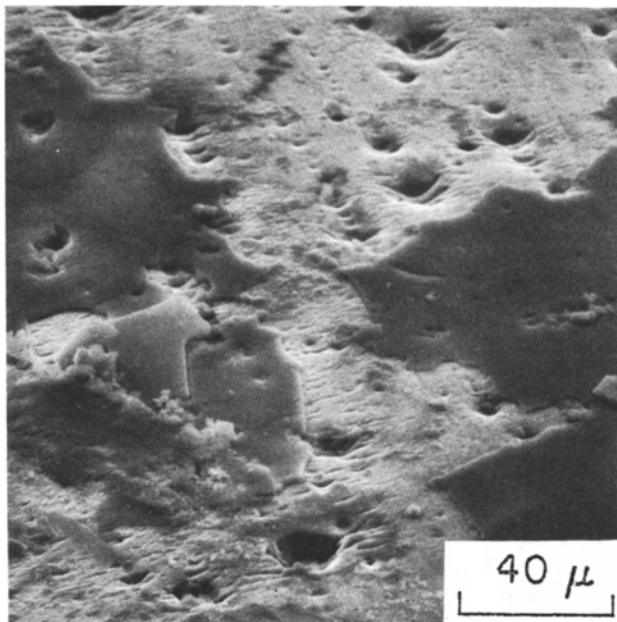
(b)

Fig. 8—Fracture surface of 7075-T6 Al in 0.5N Na_2SO_4 solution, $N_f = 5 \times 10^5$. a) Note that featureless region and cleavage-like area is smaller than that observed for fatigue in chloride solutions. b) Striations observed are of the ductile variety.

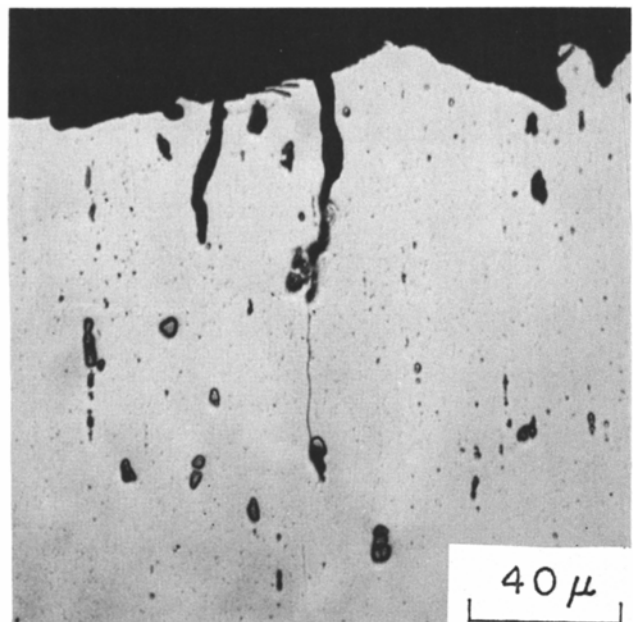
Fig. 9—Fracture surface of 7075-T6 Al in 0.5N NaCl under conditions of cathodic charging a) $\phi_C = -1300$ mv vs. S.C.E. showing Stage II cracking and b) $\phi_C = -900$ mv vs. S.C.E. showing intergranular corrosion.

metal is constantly being exposed to the environment. Additionally, dislocations associated with the plastic zone may act as high diffusivity paths for hydrogen, thus locally increasing the hydrogen concentration.^{13,14} At rapid crack propagation rates the crack would be expected to grow more rapidly than a “critical” (as yet undefined) concentration of hydrogen can be developed in the vicinity of the crack tip, and the fracture

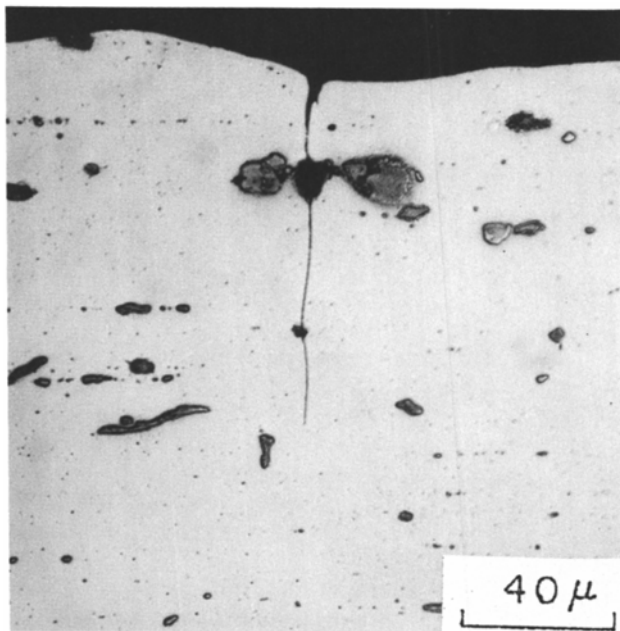
surface appearance will resemble that observed in air. An additional factor is that it has been shown that cathodic charging of a surface containing a crack or crevice can result in anodic polarization of the metal or alloy in the defect.¹¹ Thus less hydrogen would be available for embrittlement as the crack becomes longer. This suggestion may explain the constant life for decreasing potentials below some critical value,



(a)



(c)



(b)

Fig. 10—*a*) Secondary cracking and pitting of 7075-T6 Al alloy in 0.5*N* NaCl under conditions of cathodic charging at $\phi_c = -1300$ mv vs. S.C.E. *b*) and *c*) optical micrographs of a cross-section of 7075-T6 alloy showing secondary cracking and pits associated with secondary cracks under cathodic charging conditions.

since the production of hydrogen at the surface would not greatly affect conditions in the crack at long distances from the free surface.

The specific mechanism of embrittlement is still not completely understood, although it may be associated with a reduction in plasticity at the crack tip by a Cottrell atmosphere phenomenon. For example,

recent tensile tests conducted on a high purity analogue of the 7075 alloy showed serrated yielding of cathodically polarized specimens, suggesting a dislocation-solute interaction.¹⁵ This observation, of a hydrogen dislocation interaction, also supports the hypothesis that dislocations in the plastic zone ahead of a growing crack may act as high diffusivity paths for hydrogen.

SUMMARY AND CONCLUSIONS

1. Neutral sulphate solutions under free corrosion conditions affect corrosion fatigue of 7075 Al alloys to approximately the same degree as distilled H₂O. Both solutions lower fatigue resistance when compared to laboratory air. Neutral chloride solutions are considerably more aggressive under free corrosion conditions.

2. Cathodic charging of 7075 Al results in a dramatic reduction in fatigue resistance in either sulfate or chloride solutions. This observation, coupled with fractographic evidence of cyclic cleavage, indicates that a form of hydrogen embrittlement is responsible for corrosion fatigue of this alloy.

3. There is no inherent advantage to the T73 temper for resistance to corrosion fatigue in smooth surface specimens. The results of this investigation suggest that dissolved hydrogen need only interact with the surface at nascent cracks and in the plastic zone of growing cracks, which accounts for the embrittlement effect in cyclic deformation experiments which is not observed in smooth surfaced, static deformation experiments.

ACKNOWLEDGMENTS

The authors would like to acknowledge the support of the U.S. Office of Naval Research under contract # N00014-75-C-0466.

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