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THE FATIGUE BEHAVIOR OF HIGH STRENGTH
ALUMINUM ALLOYS UNDER CATHODIC CHARGING CONDITIONS

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THE FATIGUE BEHAVIOR OF HIGH STRENGTH ALUMINUM ALLOYS UNDER CATHODIC CHARGING CONDITIONS.

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RESUME: Chargement cathodique des alliages d'aluminium sous conditions de traction cyclique résulte en une forte réduction de la résistance au fatigue. Ces observations, couplées avec des essais de traction, suggèrent que l'hydrogène est associé avec des dislocations dans la région près de la fissure.

SUMMARY: Cathodic charging of cyclically stressed high aluminum alloys results in large decreases in fatigue resistance. These observations, coupled with tensile test experiments which show interrupted flow, suggest that hydrogen, interacting with dislocations effectively reduces plasticity in the region near the crack tip.

I. INTRODUCTION

High strength aluminum alloys, simultaneously exposed to corrosive solutions, in particular chloride containing aqueous solutions, show a marked degradation in fatigue resistance as evidenced both by lowered fatigue lives and accelerated fatigue crack propagation [1-6]. In general these effects have been attributed to either anodic dissolution or absorbed species [4,5]. Recent studies, however, have suggested that hydrogen, evolved by a corrosion reaction could be responsible for the degradation in fatigue resistance [7].

Additionally, it was shown that the hydrogen effect is at least partially reversible, since specimens which are solutionized and aged after a pre-corrosion treatment exhibited higher fatigue resistance than specimens which were tested immediately following the pre-corrosion treatment [8].

The present study represents a continuation of a program to characterize and understand the role of hydrogen on the fatigue behavior of aluminum alloys.

II. EXPERIMENTAL PROCEDURE

Axial fatigue experiments have been performed on a commercial 7075-Al alloy and its high purity analogue, Al-5.5Zn-2.5Mg-1.5Cu, in aerated, flowing distilled H₂O aqueous chloride and sulfate solutions as functions of pH, applied potential, catalyst poison (As as NaAsO₂). The majority of the experiments were performed on alloys heat treated to the peak yield stress condition (T6) although a few experiments were performed on alloys heat treated for stress corrosion cracking resistance (T73). The environmental test apparatus has been previously described [7]. Prior to testing, specimen surfaces were mechanically polished to 3 μm diamond paste and subsequently electropolished.

Conventional tensile tests of the high purity alloy were performed in laboratory air and in 1M H₂SO₄ + 0.2M NaAsO₂ under conditions of cathodic charging. In these experiments, the alloy was yielded to break the air formed oxide film, held at constant displacement for three hours and subsequently reloaded.

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III. RESULTS

Figure 1 shows the fatigue behavior of the alloy in air, distilled water, 0.5N Na_2SO_4 and 0.5N NaCl and shows that, except at relatively low applied stresses, H_2O and Na_2SO_4 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 10^7 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 $\sigma_{\text{mean}} + \sigma_{\text{cyclic max}}$ of this magnitude would result in $N_f = 3 \times 10^4$ cycles) showed no evidence of cracking for a period greater than 200 hours.

Figure 2 shows the S-N behavior for the alloy in a neutral solution and at pH 2 and 10.2 where the overall corrosion rates are approximately equal (about 100 mmd). The data of Fig. 2 show that there is not a direct correlation of fatigue behavior with overall corrosion rate, pH 2 solutions reducing the 10^7 cycle fatigue limit to a value of about 15 MPa. Additionally, there is a divergence of the data at higher applied stresses with the pH 10.2 solution showing longer lives than either the pH 6 solution or the pH 2 solution. At low applied cyclic stresses the pH 6 and pH 10.2 solutions produce approximately the same fatigue resistance while the pH 2 solution shows an almost constant percentage decrease in fatigue resistance when compared to the neutral solution. In an earlier paper, it was suggested that the reduction in fatigue resistance of high strength aluminum alloys was associated with hydrogen (which was produced by selective corrosion in the vicinity of non-metallic inclusions). The pH results also suggest a hydrogen interaction since pH 2 solutions result in lower fatigue resistance. In order to test this hypothesis, fatigue curves were generated for specimens which were maintained at a potential of -1300 mv versus the saturated calomel electrode (about 600 mv cathodic to the corrosion potential). The cathodic current density at this potential corresponded to $\approx 0.7 \text{ ma/cm}^2$ which could be expected to produce $\approx 10^{-2}$ molecules $\text{H}_2/\text{cm}^2\text{sec}$. (assuming that the measured current is only used to generate H_2). Figure 3 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 closer to the corrosion potential does not appreciably affect fatigue resistance, although charging at higher potentials (less hydrogen evolved) results in some cathodic protection, a maximum in protection being observed at -900 mv vs. the saturated calomel electrode. Anodic polarization results in a larger reduction in fatigue resistance (Fig. 4). 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. 5).

Cathodic charging of the alloy exposed to neutral 0.5N Na_2SO_4 results in a large reduction in fatigue resistance in a similar manner to cathodic charging in NaCl solution (Fig. 6). 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, sulfates are slightly less aggressive than chlorides.

In addition to experiments on the T6 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. 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.

Fatigue results for the high purity analogue alloy show essentially the same trends as are observed in the commercial alloy except that, at a potential of -1300 mv vs. SCE fatigue resistance is approximately the same as under conditions of free corrosion with polarization to -1750 mv vs. SCE resulting in a significant further reduction in fatigue resistance (Fig. 7). (Cathodic current density (i_c) at -1300 mv

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vs. SCE is = 0.08 mA/cm^2 and at -175 mv vs. SCE is = 1 mA/cm^2 . These values may be compared with $i_c = 0.7 \text{ mA/cm}^2$ at -1300 mv vs. SCE for the commercial alloy.) Load vs. time curves for the hydrogen charged high purity analogue in the T6 condition are shown in Fig. 9 and indicate a significant amount of stress relaxation. Subsequent reloading resulted in brittle failure at a load lower than the yield point. Fracture analysis of this specimen indicated that the failure was totally intergranular. In order to assess the role of hydrogen on failure of this alloy, tensile tests were performed on specimens in the as-received condition (hot rolled at 460°C and aged at room temperature). Figure 10 shows load/time data in air and shows a stress relaxation phenomenon and a significant lower yield point followed by some serration of the stress-strain curve prior to failure. The result of a tensile test experiment for the hydrogen charged alloy is shown in Fig. 11. A stress relaxation phenomenon is observed after initial yielding; however, the extent of stress relaxation is less pronounced and, contrary to the case for air where stress relaxation does not reach steady state in a 24 hour period, stress relaxation under charging conditions reaches steady state after only a few minutes. Upon reloading, significant serration of the load amplitude curve occurs. This experiment was stopped for a 30 minute period after the repeated load fluctuation period ceased, and allowed to stress relax. As in the initial loading situation, stress relaxation rapidly reached steady state. On restarting the experiment extensive load fluctuations were observed which diminished with further straining until failure occurred, again in an intergranular mode.

IV. DISCUSSION

The results of this study show that hydrogen, either produced by cathodic charging or by corrosion reactions, lowers the fatigue resistance of 7075 Al and its high purity analogue. 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 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 and that acid solutions are more damaging than basic solution of the same aggressiveness (as measured by overall corrosion rate).

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. Since Cl^- is known to attack the protective film formed on Al alloys in neutral environments, it is likely that, at high stresses the film damage allows better access of the hydrogen to the alloy and accordingly lowers the crack initiation time. At low stresses, crack initiation time and initial crack propagation rates are slow so that there is ample time for the hydrogen to diffuse into the surface of the alloy and to the tip of a small growing crack without necessitating film damage by Cl^- . This hypothesis is further supported by the observation that cathodic charging at high stresses in the SO_4^{2-} solution does not affect fatigue resistance (relative to free corrosion in SO_4^{2-}), probably because the crack propagation rate is sufficiently large to prevent an equivalent H_2 concentration in the vicinity of a growing crack tip. In chloride solutions, on the other hand, there is a slight improvement of fatigue resistance at high stresses and a reduction at lower stresses. Since it is believed that, while free corrosion is occurring, hydrogen is evolved in the vicinity of preferentially corroded pits and in a growing crack [10], the increased resistance at high stresses may be due to a reduction in H_2 in a growing crack due to some anodic polarization of the crevice created by the growing crack. 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.

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It is interesting, although probably not surprising, to note that the T73 heat treatment does not improve corrosion fatigue resistance in Cl^- resistance. 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.

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 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 [11,12]. 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 [10]. 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, 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. This suggestion is supported by the tensile test experiments which showed serrated stress-strain behavior, more rapid stress relaxation and a reduction in stress relaxation at constant strain amplitude. Thus, hydrogen associated with dislocations prevents the collapse of stressed dislocations when the strain is held constant. Additionally, the serrated yielding indicates a strong dislocation-solute (presumably hydrogen) interaction. It is thus suggested that mobile dislocations sweep hydrogen into the plastic zone ahead of a growing crack where it tends to embrittle the alloy in a still unspecified manner. Conversely, hydrogen associated with dislocations appears to impede their motion, thus effectively reducing the plasticity of the crack tip region. The brittle intergranular failure of the high purity alloy in the T6 condition, while not a major portion of this study, lends strong support to the suggestion that stress corrosion cracking of these high strength Al alloys may be due to hydrogen embrittlement [13].

V. 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 H_2O . Both solutions lower fatigue resistance when compared to laboratory air. Neutral chloride solutions are considerably more aggressive under free corrosion conditions.
2. Corrosion fatigue behavior of 7075 Al is not directly coupled to general corrosion rate, acid solutions reducing fatigue resistance more than basic solutions of the same corrosivity.
3. Cathodic charging of 7075 Al or of a high purity analogue alloy results in a dramatic reduction in fatigue resistance in either sulfate or chloride solutions.
4. There is no inherent advantage to the T73 temper for resistance to corrosion fatigue for smooth surfaced specimens.
5. Tensile experiments support a hydrogen dislocation interaction model which tends to retard the motion of dislocations.

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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.

VI. ACKNOWLEDGEMENTS

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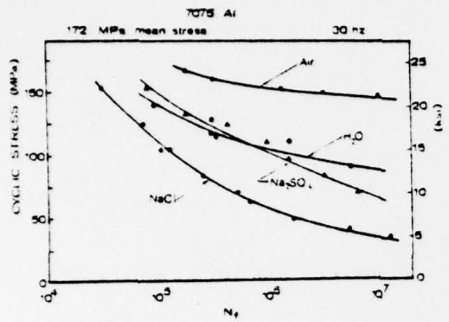


Fig. 1. Fatigue behavior of 7075-T6 Al in an H_2O , $0.5M$ NaCl and $0.5M$ Na_2SO_4 .

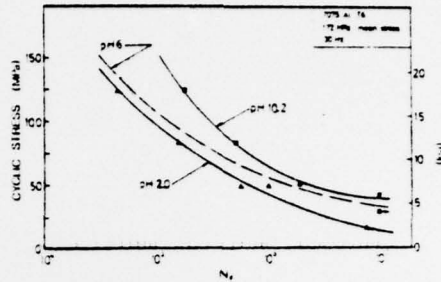


Fig. 2. Fatigue behavior of 7075-T6 Al in $0.5M$ NaCl, pH 2, 6 and 10.2.

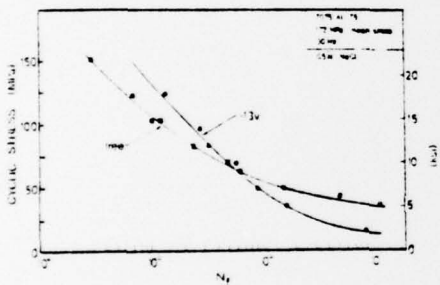


Fig. 3. Effect of cathodic polarization on the fatigue behavior of 7075-T6 Al as $r(r)$ in $0.5M$ NaCl.

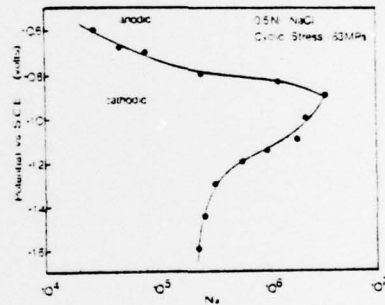


Fig. 4. Effect of polarization on the fatigue behavior of 7075-T6 Al at constant stress in $0.5M$ NaCl.

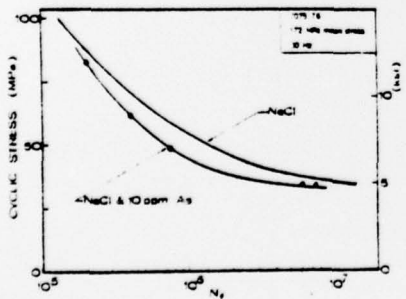


Fig. 5. Effect of As additions to $0.5M$ NaCl on the fatigue behavior of 7075-T6Al.

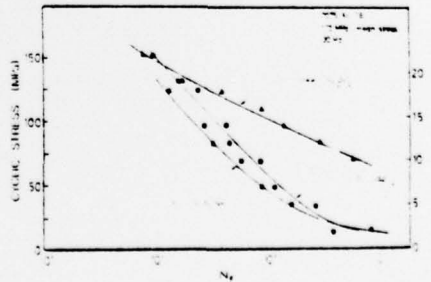


Fig. 6. Effect of cathodic polarization of 7075-T6 Al in $0.5M$ Na_2SO_4 .

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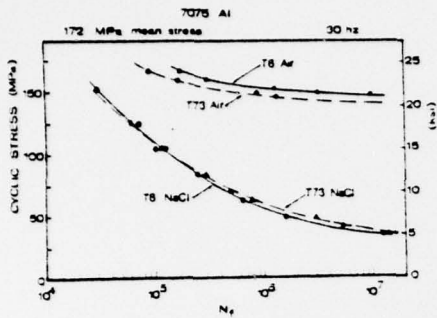


Fig. 7. Fatigue behavior of 7075-T73 Al in air and 0.5N NaCl.

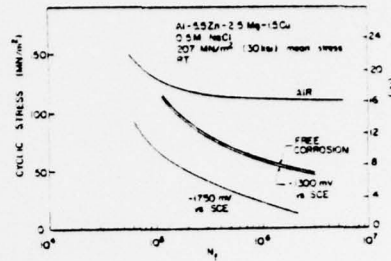


Fig. 8. Effect of free corrosion and cathodic polarization on the fatigue behavior of Al-5.5Zn-2.5Mg-1.5Cu in 0.5N NaCl.

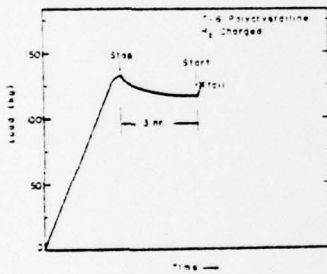


Fig. 9. Tensile behavior of Al-5.5Zn-2.5Mg-1.5Cu in the T-6 heat treatment for interrupted strain conditions in 1N H₂SO₄, H₂ charged.

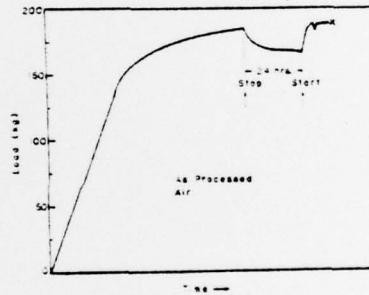


Fig. 10. Tensile behavior of Al-5.5Zn-2.5Mg-1.5Cu, as-processed, for interrupted strain conditions in air.

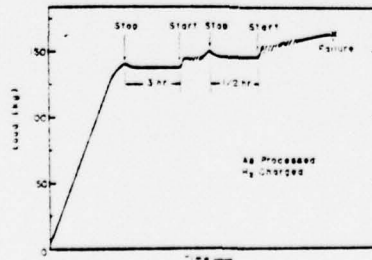


Fig. 11. Tensile behavior of Al-5.5Zn-2.5Mg-1.5Cu, as-processed, for interrupted strain conditions in 1N H₂SO₄, H₂ charged.

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