SOME ELECTROCHEMICAL ASPECTS OF THE STRESS CORROSION OF Al-4.4 Zn ALLOY

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Abstract

Tests have been carried out to determine the stress corrosion susceptibility of Al-4.4 a/o Zn alloy in the aged condition. Flat, ribbon specimens were tested in aqueous solutions containing 3.5% NaCl at a constant stress of 5.76 Kg. mm^{-2} (32% of UTS). Polarization studies carried out on the stressed and unstressed specimens reveal that the tafel slopes have a much lower value in the stressed condition. The susceptibility to stress corrosion increases with the test temperature. An equation of the type $Z=K.\exp(-E/RT)$ with reciprocal life Z and test temperature T, is found to fit the data from which the value of the activation energy is found to be ca. 20 Kcal.mol^{-1}.

1. Introduction

The incidence of stress corrosion in aluminium-zinc alloys has been observed quite sometime back, but a satisfactory explanation of the involved mechanism is yet to be put forth. In the investigations that have been carried out, the electrochemical side of the aspect has suffered neglect compared with the metal physical side. Although the electrochemical factors may only be of secondary importance in the propagation of cracks, it is evident that they play a major role in their initiation[1]. Localized electrochemical dissolution may lead to pits and fissures causing stress concentrations and localized plastic deformation, leading either to failure or arrest of the crack by stress relief. Herenguel[2] suggests that intergranular cracking of the Al-Zn alloys occurs in vacuum also and asserts that the action of the corrodent is just to accelerate the mechanical cracking. Perryman and Blade[3] attribute the intergranular stress corrosion cracking of Al-Zn alloys to accelerated precipitation at the grain boundaries. These precipitate clusters are anodic with respect to the surrounding matrix. But if the precipitation proceeds to yield massive, discrete grain boundary particles, the susceptibility to stress corrosion is decreased.

The present investigation on the Al-4.4 a/o Zn alloy were carried out to obtain more information about the effects of temperature on the phenomenon and about its electrochemical aspects.

2 Experimental

2 (1) Materials

The alloy (Al-4.4 Zn) was prepared from commercial aluminium (Fe = 0.2%; Si = 0.25% Cu = 0.05%) and AnalaRgrade zinc (Fe = 0.002%; Pb = 0.002%; As = 0.0001%; oxidizable impurities = 0.0008%). Cylindrical ingots 180 mm long and 15 mm in dia were chill-cast, homogenized and chemically analysed[4]. The rods were then cold-rolled, with intermittent anneals, to 0.15 mm thickness. The strips were solutionized at 450°C for one week and quenched in iced water before they were allowed to age naturally at room temperature for two weeks. The stress corrosion and tensile specimens, identical in shape were then cut from these strips. The tensile properties of the alloy at a strain rate of 4×10^{-3} sec^{-1} on a gage length of 20 mm were; UTS = 18 Kg.mm^{-2}, YP = 13.5 Kg.mm^{-2} and elongation = 10%.

2 (2) Stress corrosion testing

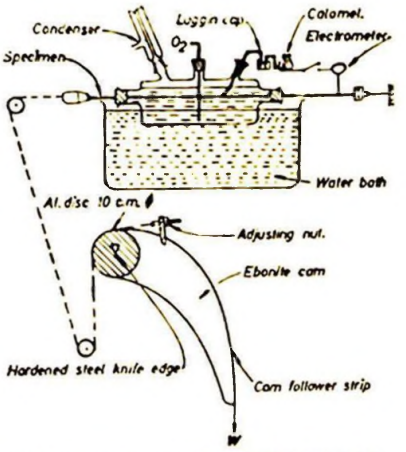


FIG:1 STRESS CORROSION CELL & TESTING ASSEMBLY

The stress corrosion testing assembly is shown in Fig. 1. This consists essentially of a pyrex glass cell through which the specimen is fixed horizontally, thus avoiding any water-line attack. The cell has four openings at the top. A condenser is fitted on to one of these to avoid concentration changes of the solution due to evaporation. The other three openings serve as inlets for a luggin capillary, for oxygen and either a thermometer, or, in polarization experiments, for introducing the cathode (of the same alloy). The cell is immersed in a temperature-controlled water bath, so that the test temperature can be controlled to $\pm 1^{\circ}C$.

All the specimens were tested at a stress level of 5.76 $Kg.mm^{-2}$, corresponding to 32% of the UTS. Since the Al–Zn alloys show no sharp yield point and plastic deformation occurs even at low stress levels, it was necessary to maintain the stress constant irrespective of the changes in cross section caused by plastic deformation. For this purpose a constant stress loading cam was designed following the principle used by Ward and Marriott[5]. This cam was made in two parts, the shorter arm made of an aluminium disc and the rest made of ebonite. When the cam profile had been machined in accordance with the calculated contour, it could maintain a constant stress (in the absence of chemical corrosion) on specimens of 20 mm gage length and had a leverage of 6.

All the tests were carried out under constant immersion in oxygen saturated 3½% NaCl solutions. The specimen was first cleaned with washing soda and then degreased with benzene. After cleaning again with a 20% $AlCl_3$ solution, distilled water and alcohol, the specimen was stoppered off with two coats of nitrocellulose lacquer exposing only an area of 100 mm^2 to the action of the corrodent. After loading the specimen to 5.76 Kg. mm^{-2}, the corrodent, preheated to the required temperature, was poured into the cell.

2 (3) Polarization studies

The anodic polarization experiments were conducted under potentiostatic conditions using the classical potentiostat[6]. The potentials of the specimens were measured against a saturated calomel electrode, using an electrometer capable of reading to 5mV. The anodic currents were measured with the help of a microammeter. The polarization experiments were started after the specimens had attained steady state potentials in the solutions.

3 Results and Discussion

The temporal variation of the corrosion potential showed two general trends. Typical curves are depicted in Fig. 2. The

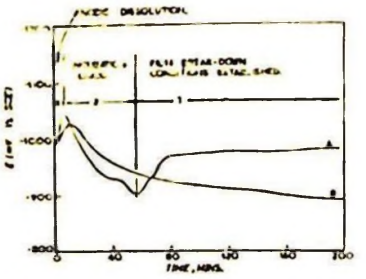


FIG. 2. VARIATION OF CORROSION POTENTIAL(SCE) WITH TIME A-SUSCEPTIBLE CONDITION, B-RESISTANT CONDITION

susceptible condition (load = 32% UTS and temperature = 60°C) is indicated by the curve A, the resistant condition (load = 8% UTS and temperature = 24°C) by the curve B. In both of these, there is an initial anodic potential peak, followed by a steep fall towards the cathodic side. The mechanism suggested by Hoar and and Hines[7] seems to explain this behaviour. The initial anodic dissolution of the metal caused by the penetration of the solution into the pores and cracks is responsible for the potential increase observed immediately after the corrodent comes into contact with the metal surface. The protective film, which slowly forms, shifts the potential towards the nobler end. Whereas in the resistant condition the potential is stabilized at this stage, it again increases towards the anodic side in the susceptible condition. This increase is due to the initiation of a stress corrosion crack. The 'incubation period' observed before a crack appears is necessary for the film-breakdown condition to be established, and Barnartt et al.[8], in agreement with this, state that an appreciable period of general corrosion is usually unnecessary before the first crack appears. This general corrosion is essential to raise the concentration of the metal complexes in the environment[9], so that the interaction between the metal surface and rhe complexes in the solution provides the necessary deficit energy required for breaking the metal--metal bond.

The anodic potentiostatic polarization curves are given in Figs. 3 to 6. A sharp upward trend in the potential in the case

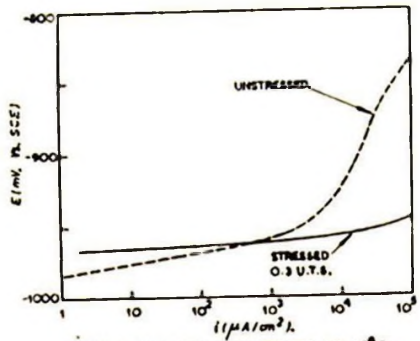


FIG.3. POLARIZATION CURVES AT 45°C.

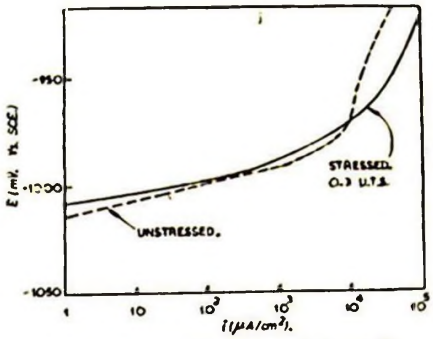


FIG.4. POLARIZATION CURVES AT 60°C.

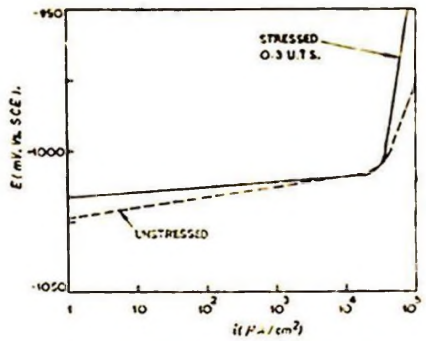


FIG.5. POLARIZATION CURVES AT 70°C.

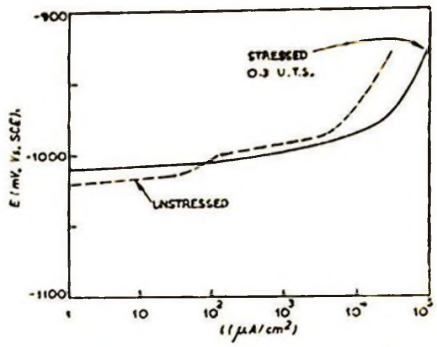


FIG.6. POLARIZATION CURVES AT 70°C.

of both the stressed and the unstressed specimens at high current densities is due to the setting in of concentration polarization. The straining of the specimen has little, if any, effect on this concentration polarization, which is chiefly controlled by the stirring conditions of the solutions. The activation polarization, on the other hand, is controlled to a large extent by the strain in the metal. As demonstrated by Hoar and West [9], the yielding metal is anodic to a static one and thus dissolution is easier when the metal is being strained. From the polarization curves, it can be seen that the stressed specimens show a smaller tafel slope (1/30 to 1/200) compared with the unstressed ones (1/5 to 1/15). Bombara[11] has reported that the conditions of steel most susceptible to stress corrosion cracking occupy the transition regions between corrosion and passivity. These transition regions correspond to a very low value of the tafel slope on the polarization curves. The present work bears out these observations.

The influence of temperature on the activation polarization is negligible in the unstressed state. In the case of the stressed specimens, the tafel slope rises sharply from about 1/200 at 45°C to about 1/35 at 60°C and from then on, there is little change. This would mean that the passive film formed on the surface becomes more compact beyond 60°C, due to chemical transformations. This observations confirms the findings of Radovici and Kovacs[12] on Al–Mg alloys.

When the polarizing current was cut off, the potential of the specimen shot up to –1260 mV (SCE). On scratching the specimen under solution, the same value was obtained. The film re-formed in 15 minutes. These results are in agreement with those of Perryman and Blade[3] and of Akimov and Clark [8].

The dependence of stress corrosion on temperature was further investigated and an activation plot for the stress corrosion process, between logarithm of reciprocal life time and inverse of test temperature, is given in Fig. 7. The result is a straight line obeying the relation :

$$\ln Z = 28 - \frac{10{,}000}{T}$$

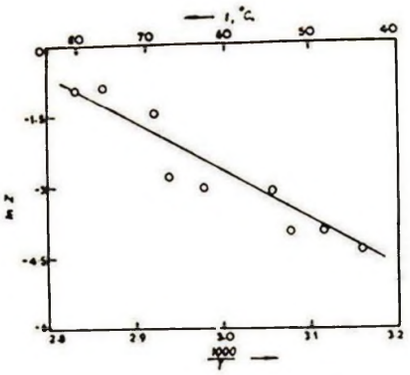


FIG.7. PLOT OF Ln Z AGAINST 1000/T.

for reciprocal life time (Z in hr^{-1}) in terms of the test temperature (T in °K). Comparing this equation with the empirical equation obtained by Gruhl[14]

$$Z = K.\exp\ (c\sigma) .\exp\ (-E/RT)$$

where, Z = Reciprocal life time, hr^{-1}, K, c=constants, R = gas constant, σ = applied stress, $Kg.mm^{-2}$ and T = temperature, °K., the value of activation energy for the stress corrosion process is obtained to be 20 Kcal mol^{-1} or 0.88 eV $atom^{-1}$. Gruhl[14] has correlated the migration of vacancies to the temporal course of stress corrosion of the Al-Zn-Mg3 alloy. But in the present case the value of activation energy obtained is very high compared with that for the migration of vacancies in Al–4.4Zn (ca. 0.4 eV $atom^{-1}$). Indeed, since some amount of plastic deformation is inevitably present when the alloys are stressed to about a third of the UTS, an analogy with cold worked material may not be out of the place, and the value of the activation energy might be expected to be lower. Since a very high value for the activation energy (for the stress corrosion process) is obtained, some process other than vacancy migration might control stress corrosion of the Al–Zn Alloy.

4 Conclusions

The Al-4.4% Zn alloy is susceptible to stress corrosion in chloride solutions. The susceptibility increases with increasing temperature. The potentiostatic polarization studies indicate that stress has a marked influence on the tafel slope. From the high value obtained for the activation energy for the stress corrosion process, it can be said that vacancy migration might not, by itself, be the controlling factor.

Acknowledgements

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