

On the propagation of stress-corrosion cracks in a magnesium-aluminum alloy

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Summary

A study has been made of the propagation of transgranular stress-corrosion cracks in thin-sheet specimens of a single-phase magnesium-7.6 wt.% aluminum alloy tested in an aqueous sodium chloride-potassium chromate solution. Metallographic studies established that cracking is discontinuous, the fracture surfaces exhibiting a series of parallel markings which represent successive positions of the crack front during discontinuous propagation. The rate of cracking is extremely high (0.35-2.5 mm/min) and for crack lengths less than 0.2-0.25 of the specimen width is proportional to the square of the stress-intensity parameter $P l^{1/2}$, where P is the applied load and l the crack length. The mechanism of stress-corrosion cracking in this system is discussed in terms of these observations, and it is suggested that failure occurs by the repeated formation and rupture of a brittle surface film at the tip of the advancing crack.

Introduction

Recent work has demonstrated that in certain systems failure by stress-corrosion cracking (SCC) involves the repeated formation and rupture of a brittle surface film [1, 2]. This 'brittle-film' model differs radically from other models based on film-rupture, e.g. that developed by Logan [3], in that stress-corrosion cracks are considered to propagate in bursts of mechanical rupture, initiated within the brittle film, rather than by dissolution. In addition, the brittle-film model postulates that the rate of SCC is determined by the rate of growth of the brittle film ahead of the crack tip.

The brittle-film model is considered to be operative in the failure of (i) alpha-phase copper alloys in tarnishing ammoniacal environments [1, 4], (ii) an alpha-phase titanium alloy in nitrogen tetroxide [5], and (iii) the non-metal silver chloride in certain complex-forming aqueous solutions [6]; the brittle films are oxides in the case of the metals (cuprous oxide and rutile, respectively) and a defect-hardened charge double layer in the non-metal. Fractographic studies have indicated that the stress-corrosion fracture surfaces in these systems are characterized by the presence of parallel markings [2], similar in appearance to those observed on fatigue fracture surfaces. These striations are perpendicular to the direction of cracking, and are considered to represent successive positions of the crack front during discontinuous propagation.

While the brittle-film model may not account for all cases of SCC, it is probable that it also operates in systems other than those mentioned above. The work of Fairman and West [7] strongly suggested that the transgranular failure of single-phase magnesium-aluminum alloys in aqueous sodium chloride-potassium chromate solutions is one such system, since it was reported that cracking was discontinuous and that the stress-corrosion fracture surfaces were striated. However, the latter conclusion was based on extremely limited fractographic evidence, for while parallel markings were shown to exist, no attempt was made to determine whether these markings were striations or simply slip traces. Indeed, recent work by Parkins [8] suggested that the latter is the case.

To clarify this situation, a detailed study has been made of the transgranular fracture surfaces of a stress-corroded magnesium-aluminum alloy. During these studies, data on crack-growth kinetics were obtained which are considered to be relevant to the mechanism of failure.

Experimental

The studies were carried out on a high-purity binary magnesium alloy containing 7.6 wt.% Al and <0.001 wt.% Fe, supplied by The Dow Chemical Company. Polycrystalline specimens of dimensions 10×2 cm were cut from 0.5 mm thick sheet with the long axis parallel to the rolling direction. They were solution treated for 1 hr at 350°C in an inert atmosphere and quenched into cold water, thus retaining single-phase δ [9]. This heat treatment produced a pronounced annealing texture, pole-figure determinations indicating that the basal planes were approximately parallel ($\pm 20^\circ$) to the plane of the sheet. The grain structure was uniform and equiaxed, the grain size being 0.07 mm. Before testing, specimens were etched with a 10% solution of formic acid in alcohol and then notched at one edge to a depth of about 1 mm, using a file.

Stress-corrosion testing was conducted at room temperature in an aqueous solution containing 40 g/l NaCl and 40 g/l K_2CrO_4 (pH = 9.0), the solution being held in a closed plexiglass cell attached to the central region of the gauge length. Specimens were stressed in an Instron testing machine to specific tensile loads. The cross-head was then stopped and the load allowed to relax to a constant value following some limited creep. The solution was then added to the cell. Following an incubation period, a single stress-corrosion crack initiated at the notch and propagated as a single crack to failure. The length of crack, l , measured from the tip of the notch, was determined as a function of time, using a travelling microscope ($\times 30$). Crack propagation was associated with a reduction in load and this was also recorded. Unless

otherwise stated, crack propagation proceeded under open-circuit conditions. A limited number of tests were carried out in which the potential of the specimen was controlled by means of a platinum gauze electrode and a Wenking Potentiostat.

Stress-corrosion fracture surfaces were examined using the optical microscope, the electron microscope (carbon replicas), and the scanning electron microscope.

Metallographic studies

Examination of the surface of the gauge length in the vicinity of the stress-corrosion crack confirmed that failure was transgranular. Slip traces and deformation twins were evident in the grains in this region, Fig. 1; a *single* set of slip markings existed within each grain. The orientation of selected grains was determined by means of the Laue back reflection method, and one-surface trace analysis indicated that glide occurred on the basal plane. This conclusion is in agreement with recent findings by Clark [10] on the deformation of solution-treated specimens of a binary alloy containing 9 wt.% aluminum, and is consistent with earlier work [11]. The orientation of the twins was not determined but, from the literature [10, 11], it is probable that they occur on $\{10\bar{1}2\}$ planes.

It has been suggested that transgranular SCC in magnesium-base alloys occurs on the basal plane [12]. No attempt was made to determine the orientation of the fracture surface in the present studies, but it is clearly not basal, since the fracture surface was approximately perpendicular to the tensile axis while, because of the texture, the basal planes were parallel ($\pm 20^\circ$) to this direction. Other workers [13-15] have also reported that failure is not confined to the basal plane in these alloys.

Fractographic studies

Examination of the stress-corrosion fracture surfaces using the optical and scanning electron microscopes indicated that a single set of coarse parallel markings existed within each grain, Fig. 2. The direction of these markings varied from grain to grain, but in all cases they were approximately parallel to the direction of crack propagation*. Measurements taken from a large number of grains established that the maximum deviation from parallelism was $\pm 20^\circ$. It is evident from a consideration of the annealing texture and from the metallographic observations that these coarse markings represent the traces of basal glide planes. These

* The propagation of a single edge crack in thin sheet permits the direction of cracking to be accurately defined; it is parallel to the intersection of the fracture surface and the surface of the sheet, e.g. edges *AB* and *CD* in Fig. 2.

markings, which appear to be identical to those shown in the micrographs of Fairman and West [7], do not have the characteristics of striations – they are not continuous from grain to grain, and they are not approximately perpendicular to the direction of cracking.

Electron-microscope studies revealed that each grain exhibited a second series of parallel markings, considerably finer than the basal-slip traces, and which were approximately perpendicular to the macroscopic direction of cracking, Fig. 3 (a). The average spacing between the fine markings was $0.1-0.8\mu$, and did not vary significantly with position on the fracture surface, i.e. the spacing was not dependent on the crack length. It can be seen that neighbouring markings in some instances merge together, forming 'triple points', Fig. 3 (a), and in this respect they resemble cleavage markings. However, it should be emphasized that the markings in the present case are *perpendicular* to the cracking direction, whereas cleavage markings would be *parallel*.

The absence of secondary slip (i.e. slip on systems other than the basal plane) on the surface of the gauge length within grains adjacent to the fracture surface, e.g. Fig. 1, would appear to rule out the possibility that the fine markings correspond to slip steps. This conclusion is supported by observations on specimens which were cold rolled (25% reduction in thickness) before testing. It was considered that slip during crack propagation would be suppressed by the 'cold work', and it was found that the basal-slip traces were in fact virtually eliminated from the fracture surfaces in such specimens. Significantly, the fine markings persisted, Fig. 3 (b). The density of twins in grains adjacent to the fracture surface (~ 2 per grain) is not sufficient to account for the fine markings. By a process of elimination, then, it is concluded that the markings represent striations, that is, they correspond to the successive positions of the crack front during discontinuous crack propagation. The presence of the 'triple points' indicates that the crack front does not advance uniformly in all instances, segments advancing ahead of, or remaining behind, the main crack front. Similar configurations have been observed in the striations on the fracture surfaces of embrittled silver chloride [2].

Kinetics of crack growth

The variation of crack length, l , and load, P , with time is illustrated for several tests in Fig. 4. The decrease in load appears continuous in Fig. 4 (b), but relatively large load drops are evident on a finer scale. Fig. 4 (c). The total number of these load drops is small relative to the total number of striations, so that they do not correspond to successive stages of propagation of the stress-corrosion crack. It is possible that such load drops are associated with stages of ductile failure. For

example, it may be argued that the stress-corrosion fracture surface is not flat, but that cracking occurs on a series of closely-spaced parallel planes and that ductile tearing is necessary to link the stress-corrosion cracks. Although the recorder trace displayed a slight 'ripple', there was no conclusive evidence for small load discontinuities which could be correlated with discrete stages of stress-corrosion cracking, and this is presumably due to the limited sensitivity of the test method.

For thin sheet, the stress-intensity parameter for relatively short cracks is $P l^{1/2}$ [16]. In Fig. 5, the rates of cracking, obtained by taking the slopes of the curves in Fig. 4 (a), are plotted against the square of the stress-intensity parameter. It can be seen that for $l < 0.2-0.25$ sheet width, the relationship is linear, so that

$$\frac{dl}{dt} = k P^2 l \quad (1)$$

where k is a constant.

Several tests were carried out in which the potential of the specimen was controlled potentiostatically. It was found that cathodic polarization prevented crack initiation and halted propagating cracks. Application of anodic potentials on the other hand, accelerated the rate of cracking.

Discussion

The present observations have established that the transgranular stress-corrosion fracture surfaces in a magnesium-aluminum alloy tested in an aqueous sodium chloride-potassium chromate solution are striated, thus supporting the report by Fairman and West [7] that crack propagation is discontinuous. The high rates of cracking ($0.35-2.5$ mm/min, Fig. 5) also support the contention that cracking involves a stage of mechanical fracture since they do not appear to be consistent with the alternative possibility that cracking proceeds purely by electrochemical dissolution. If cracking involved only dissolution, then, from Faraday's Law, the rate of cracking (cm/sec) would be related to the current density (CD) at the crack tip by

$$\frac{dl}{dt} \approx \frac{A}{nF\rho} \cdot CD \quad (2)$$

where A is the atomic weight of magnesium* (24.3), n is the charge on the magnesium ion in solution (2), F is Faraday's constant ($96,500$ coulombs/g-equivalent), and ρ is the density of magnesium (1.74 g/cm³). Using (2), the observed rates of cracking are found to correspond to current

*The presence of aluminum is not taken into account for the purpose of this calculation.

densities of 8.05-57.5 amps/cm². In other systems, where the rates of SCC are typically ~0.07 mm/hr, current densities of ~2 amp/cm² would be required, and this value has been considered prohibitively large [17]. Thus the present values would appear to be totally unrealistic, and it is concluded, therefore, that crack propagation in this system involves repeated cycles of a slow corrosion stage followed by a stage of mechanical rupture.

Fairman and West [7] suggested that the corrosion stage involves dissolution at the crack tip, leading to an increasing stress concentration, so that cleavage eventually occurs. It was proposed that the crack becomes arrested after limited propagation and that further corrosion is then necessary for its re-initiation. Such a model may be criticized for several reasons. For example, it does not explain why stress concentrations at the tip of a stationary crack lead to cleavage rather than to plastic deformation; nor why the resulting cleavage crack stops, since crack propagation is associated with an increasing stress intensity. It is considered that the observed stress-corrosion behavior can be better explained by the brittle-film model, the slow stage corresponding to the formation of a brittle film and the fast stage to rupture of the film, the crack blunting out when it enters the ductile substrate. This view is supported by the fact that for relatively short cracks the rate of cracking is proportional to the square of the stress-intensity parameter, equation (1), since this relationship was also observed in the brass/ammonia system [1].

The nature of the brittle film in the magnesium alloy has not been established. The possibility that the surface layers are embrittled by the presence of cathodically generated hydrogen can be ruled out because cracking is halted by cathodic polarization and accelerated by the application of anodic potentials. By analogy with the brass/ammonia and alpha-titanium/nitrogen tetroxide systems (see above), it might be expected that the brittle film is an oxide. The stress-corrosion fracture surfaces showed no visible oxide film. However, high-resolution electron diffraction studies of the fracture surfaces indicated the presence of lines whose spacings corresponded to MgO. Such lines were not present in patterns taken from fracture surfaces of specimens fractured in air. An alternative possibility is that the brittle film corresponds to a 'spongy' or porous surface layer formed by the selective dissolution of magnesium or aluminum. The presence of such a mechanically weak layer was suggested by Forty [18] in the brass/ammonia system before the brittle film was identified as cuprous oxide. A similar gold-rich film is formed during the SCC of copper-gold alloys in aqueous ferric chloride [19]. It is evident that further work is necessary to identify the film in the present system.

It is unlikely that the observed inter-striation spacing, 0.1-0.8μ, corresponds to the thickness of the brittle film at rupture since this would require exceptionally high rates of film growth. More probably, the crack propagates for a finite distance into the substrate. The latter distance is presumably determined by such factors as dislocation mobility and the availability of slip systems, and therefore it is interesting to note that the inter-striation spacing is ~0.1μ for the ductile alpha-brass tested in aqueous ammonia [1], and ~4μ for the notch-sensitive silver chloride tested in an aqueous chloride solution [2].

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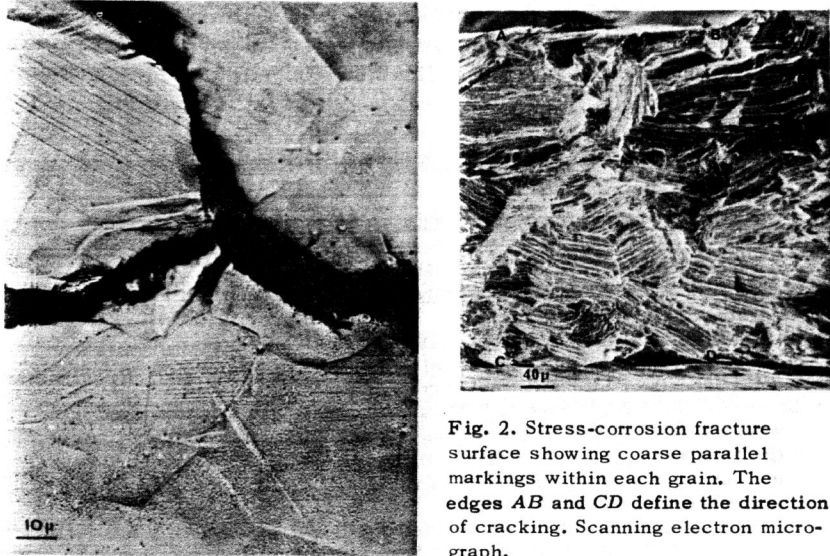


Fig. 2. Stress-corrosion fracture surface showing coarse parallel markings within each grain. The edges AB and CD define the direction of cracking. Scanning electron micrograph.

Fig. 1. Surface of gauge length in vicinity of a transgranular stress-corrosion crack, showing slip bands and deformation twins. Optical micrograph.

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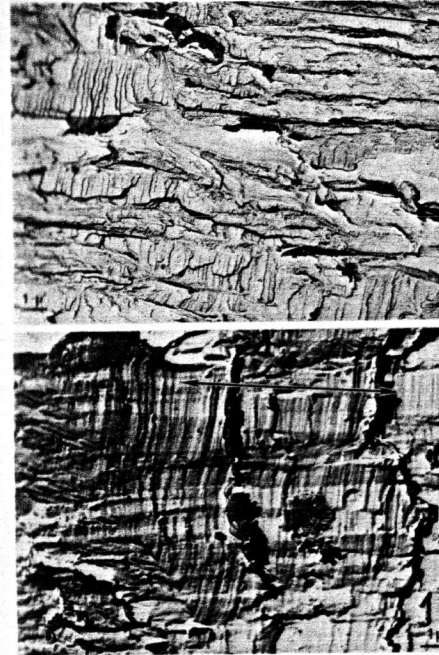


Fig. 3. Replicas of stress-corrosion fracture surfaces of (a) solutions treated and (b) cold rolled specimens, illustrating striations. The arrows indicate the direction of cracking. Electron micrographs.

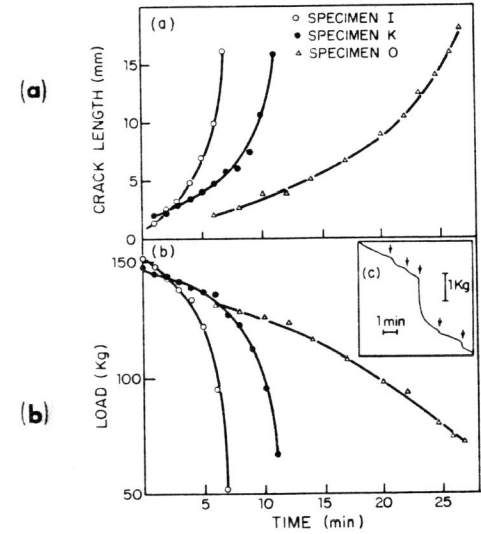


Fig. 4. Data illustrating the variation of (a) crack length and (b) Instron load with time during the propagation of stress-corrosion cracks. (c) represents a portion of a typical recorder trace, illustrating the relatively large load drops (arrowed).

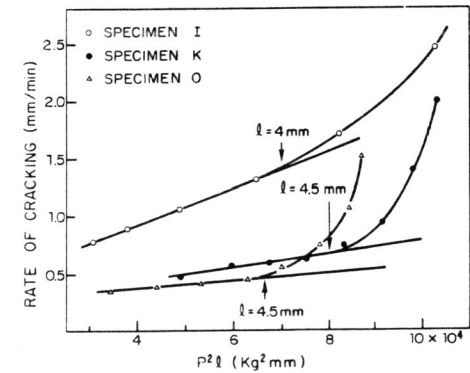


Fig. 5. The relationship between the rates of stress-corrosion cracking and the square of the intensity parameter, $P^2 l^2$.