

# Stress-Corrosion Cracking of the AZ31B Magnesium Alloy

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Both the incubation period prior to stress-corrosion cracking and its initiation in the AZ31B magnesium alloy were studied using electrochemical solution potential-time and extension-time oscillographic curves obtained simultaneously. From these data it is postulated that the crystals most favorably oriented for slip were deformed, on initial stressing of the specimen, to such an extent that they were resistant to further extension and the protective films on their surfaces, destroyed in the early deformation, were repaired. Subsequent extension occurred as the result of stresses concentrated in relatively more resistant crystals with strain rates as high as 1 percent/sec at limited sites rupturing the protective surface film. This exposed metal was anodic to very much larger areas on which the film had been repaired and cracks developed by electrochemical processes.

Stress-corrosion cracks were initiated on planes that made large angles with the basal crystallographic plane of the magnesium alloy and in crystals of a polycrystalline aggregate that were unfavorably oriented for basal slip.

## 1. Introduction

The stress-corrosion cracking of magnesium-base alloys has been the subject of several studies at NBS. A study of the relative susceptibility of the various wrought magnesium alloys then available was made during World War II and the results were subsequently published [1].<sup>1</sup> A service failure that led to the initiation of that study proved to be an isolated case. Stress-corrosion cracking of magnesium alloys in service has not been a problem. However, magnesium alloys lend themselves particularly well to general studies of stress-corrosion cracking in that complete failures, for example, of the FS-1 alloy, can be obtained in the laboratory in less than 5 min. Studies since the war years have been made with the objective of increasing our understanding of the mechanism of stress-corrosion cracking.

A paper published in 1958 [2] gave the results of an investigation initiated to answer certain questions that had been raised but never answered during the war work. In that investigation [2] it was shown that if the specimen was strained in the corrodent at a rate in excess of  $500 \times 10^{-6}$ /min, measured 1 min after the stress<sup>2</sup> was applied, failure could be expected in less than 5 min. On the other hand if the strain rate was less than  $500 \times 10^{-6}$ /min the specimen would most probably not fail even in 1000 min. Further, it was found on examining many specimens that there was no evidence of cracking for the first 40 sec after the stress was applied even though failures occurred in 2½ min. A short hypothesis was presented to explain this incubation period. In the

present paper, experiments designed to verify some of the ramifications of that hypothesis are described and the hypothesis is expanded. The crystallographic planes on which stress-corrosion cracks originated were also determined.

## 2. Experimental Procedure

Specimens for this investigation were prepared from sheet and extruded AZ31B magnesium alloy stock. The chemical compositions of these materials were well within the tolerances of ASTM Specification B-90-58 for this alloy.<sup>3</sup>

Sheet tensile specimens, having a ½-in. reduced section, were machined from ⅙- and ⅛-in. thick sheet material originally obtained for the earlier work [1]. Most of the specimens used in the present investigation were in the annealed condition although a few were from "hard-rolled" sheet.

A very few notched specimens were machined from ½-in. diam extruded rod. The specimens contained a 90° notch ⅛ in. deep. The diameter at the root of the notch was 0.250 in. and the root radius 0.005 in.

Specimens used in determining the crystallographic planes on which the stress-corrosion cracks originated were also machined from the extruded rod. The reduced sections of these specimens were about 2 in. long with a square cross section ¼ in. on a side. They were similar in design to the low carbon steel specimens used by the author in another investigation [3]. After machining, the specimens were annealed for 30 min at 400 °C, cooled to room temperature, strained 0.3 to 0.5 percent, and subsequently heated slowly to 520 °C. The resulting specimen was multigrained, with individual grains

<sup>1</sup> Italicized figures in brackets indicate the literature references at the end of this paper.

<sup>2</sup> A stress in excess of 95.5 percent of the yield strength of the annealed material was required to produce stress-corrosion cracking of this alloy in the corrodent used.

<sup>3</sup> The nominal composition of the AZ31B alloy is Al 3.0 percent, Zn 1.0 percent, Mn 0.20 min, with maximum values for Si, Cu, Fe, Ni, and Ca of 0.10 percent, 0.05 percent, 0.005 percent, 0.005 percent, and 0.04 percent respectively.

sufficiently large that their crystal orientations could be determined by the conventional back reflection X-ray technique.

The sheet specimens were insulated from the corrodent, except for a 2 in. gage length, by means of plastic tape. All of the notched specimens were also insulated with tape except over the notched areas. One set of the notched specimens was exposed to the corrodent with the entire notched area exposed. In the other set the notch was covered with lacquer and after the lacquer had dried it was cut through with a razor blade to expose the metal at the root of the notch.

All specimens were contained in glass cells of the type described earlier [1]. The corrodent was the conventional NaCl,  $K_2CrO_4$  solution (35 g NaCl and 20 g  $K_2CrO_4$ /liter) at approximately 30 °C. The specimens were stressed in tension by dead loading with a lever system. In all cases care was exercised to avoid impact in applying the stress. If the specimen strain was to be followed, the lever was supported by a hydraulic jack until the load, etc., were adjusted. The jack was then released, applying the stress at a rapid rate.

The strain or extension of the specimen was followed by measuring the movement of the end of the loading lever (lever ratio 25 to 1). This was done by reading a dial gage (smallest division 1/10,000 in.) or by recording the unbalance of a bridge circuit, one arm of which contained wire strain gages actuated by the motion of the end of the lever. In a few instances wire strain gages cemented onto the specimen itself (but insulated from the solution) were incorporated in the bridge circuit.

The electrochemical solution potentials of the sheet and notched specimens were determined against a calomel electrode of the saturated KCl type. Connection between the electrode and the corrodent was made by means of a salt bridge. The electrochemical solution potential and the extension of the specimen (as determined by the unbalance of the bridge circuit) were recorded simultaneously on a two-channel oscillograph.

No extensions nor electrochemical solution potentials were determined for the large-grained specimens on which the crystallographic orientation of the plane of fracture was determined. The stress was removed from some of these specimens after cracks had developed but before the final fracture had occurred. If fracture was complete, no attempt was made to determine the plane on which this fracture occurred, but analyses were made to determine the planes of origin of other cracks that formed but had not led to complete failure.

Visual observations showed that cracks generally originated at a corner of the specimen where adjacent surfaces met. Hence, the crystallographic planes on which the cracks originated were determined from the angles that the cracks made on the adjacent faces with the corners of the specimen [4].

The orientation of the tension axis of the specimen with respect to the crystallographic axes was determined for the grains containing cracks and also for a number of grains free from cracks.

### 3. Results and Discussion

#### 3.1. Extension Time and Electrochemical Solution Potential Curves

The idealized curves shown in figure 1 were based on a study of simultaneous oscillographic records of the strain and accompanying changes in electrochemical solution potentials for a number of specimens. The extension increased very rapidly upon initial loading of the specimen. It continued to increase but at a diminishing rate for 40 to 50 sec. The rate then increased again, with the development of stress-corrosion cracks, to final failure of the specimen after about 150 sec exposure. The electrochemical solution potential changed about 90 mv in the anodic direction on the initial loading of the specimen. This was attributed to the rupturing of the protective film on the surface. The further marked change of potential in the anodic direction with the exposure of bare metal, on the failure of the specimen, substantiated this idea. The total change in potential from the unstressed condition amounted to approximately 200 mv, a value that is in good agreement with previously published data [5]. It should be noted that once failure had occurred and the metal was no longer being strained the potential changed very abruptly, probably within 1 sec, to a value only about 20 mv more active than that of the specimen in the original condition. The extremely rapid rate of change in potential after the fracture of the specimen indicated that a protective film was being formed on the surface of what had been bare metal.

The yield strength of the annealed alloy can be increased about 50 percent by cold work. From the extension curve, figure 1, it is to be expected that the alloy is being cold worked. It is postulated that

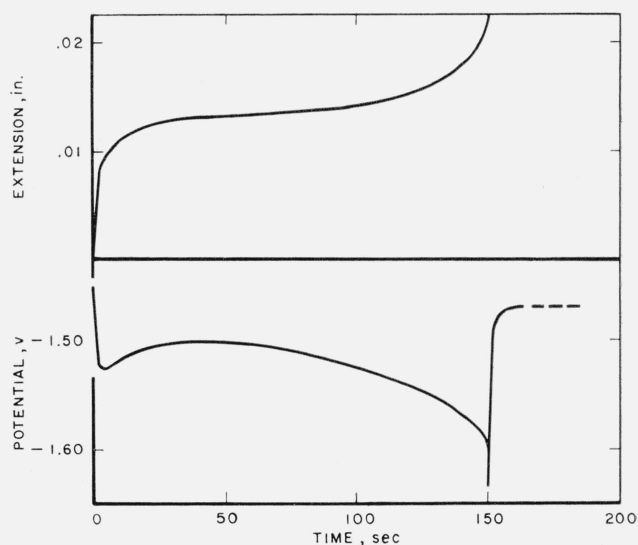


FIGURE 1. Idealized extension-time and potential-time curves for the AZ31 alloy specimen that failed in about 150 sec.

with the application of stress, those grains most favorably oriented with respect to the stress pattern were deformed by basal slip, kinking, etc., and were hardened to the point where further deformation occurred only very slowly. Specifically, dislocations moved through the material until they were blocked at barriers such as grain boundaries, subgrain boundaries, inclusions, etc. Stress concentrations were built up as a result of this dislocation pileup and slip then occurred in some of these grains that had previously resisted deformation. This process would be repeated as stresses concentrated in successively more resistant grains and produced deformation. The delayed strain in these relatively resistant grains thus accounted for the slow increase in extension after the initial deformation. While the deformation of individual grains was postulated to be a discontinuous process, the average effect over many grains was recorded as a continuous process.

The increase in the potential (in the active direction) on the initial loading of the specimen is postulated, as was indicated above, to be due to the rupturing of the protective film on those grains that were most readily plastically deformed.

The data obtained at the final fracture of the specimen would indicate that as a given grain was work hardened to the point where it became resistant to further strain, i.e., where the strain rate was low, the protective film was repaired on its surface. As the ratio of grains being strained at a rate sufficient to rupture the film decreases with respect to those on which the film had been repaired, the potential would change in the noble direction. This would account for the change in potential, after the initial extension of the specimen. If the average extension rate of the specimen, determined 40 or 60 sec after the stress was applied, was below some critical value, the potential would continue to change in the noble direction until it approached the value obtained prior to stressing the specimen.

If the average strain rate exceeds this critical value, stress concentrations at a few sites will deform the specimen surface at a sufficient rate to prevent the film from reforming. If these sites are localized for a sufficient time, cracks will be initiated by an electrochemical process. As was indicated earlier, the bare metal is at least 200 mv anodic to the film-covered surface in the corrodent used. If a relatively large area is film-free, attack will be of the pitting type. If the film-free area is very small and is surrounded by a large film-covered area, the condition of a small anode and large cathode will exist; this is an ideal condition for rapid corrosion of the anode. Such corrosion on a small area will form a sharp pit or trench that will further concentrate the stresses, preventing the film from reforming at its apex, and will lead to the initiation of stress-corrosion cracks.

Once cracking is initiated, the continuous exposure of bare metal at the tips of the cracks will change the potential of the specimen in the anodic direction. A very marked change occurred, as was pointed out earlier, with the exposure of a considerable surface of bare metal at the failure of the specimen.

### 3.2. Strain-Rate Associated With Initiation of Cracks

The extension of many specimens was followed by readings, at stated intervals, of the dial gage in contact with the end of the lever system. This method was highly sensitive and although it was not possible to measure the extension of the specimen during the first 10 to 20 sec of exposure, data was obtained subsequently from which extension rate—time curves could be drawn. Three such curves are shown in figure 2. Breaks in curves A and B resulted from the development of stress-corrosion cracks in those specimens. No cracks developed in specimen C which extended at a slower rate than either A or B. Cracks began to develop in specimens extending at the approximate rate shown for B after about 40 sec exposure in the corrodent [2]. If the strain at sites where cracks will develop is postulated to account for the difference in the strain rates of specimens B and C after 40 sec, if certain assumptions are made as to the width of the regions in which cracks will develop, and if the number of cracks that develop per inch of specimen length is determined, an estimate can be made of the strain rate at these crack sites. It was found that approximately 25 crack sites develop for each inch of gage length. Assume that the strain is confined to a region 1000 times the "a" parameter of the magnesium lattice; then the average strain rate in the areas where cracks were being initiated can be calculated to have been approximately  $1 \times 10^{-2}/\text{sec}$  (1%/sec). This value seems reasonable within one order of magnitude. It is comparable with the value of 5 percent/sec reported by Hoar and West [6] as the strain rate necessary to prevent polarization that would have stifled development of cracks in austenitic stainless steel specimens.

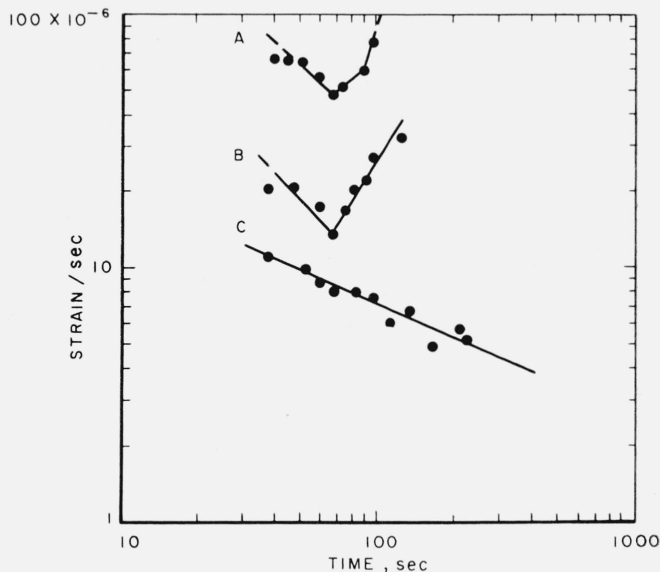


FIGURE 2. Relations between time and strain rate for specimens stressed above and below the critical strain rate at which stress-corrosion cracks develop.

Breaks in curves A and B indicate the development of stress-corrosion cracks. No cracks developed in the specimen from which curve C was obtained.

### 3.3. Effect of Ratio of Cathode to Anode Areas on Incubation Period

Several notched specimens were exposed to the corrodent at a stress of approximately 46,000 lb/in.<sup>2</sup>; this stress<sup>4</sup> could produce failures by stress-corrosion cracking in 60 sec or less. As was indicated above, all of the metal in the notched areas of some of these specimens was exposed to the corrodent while only the metal at the root of the notch was exposed in other specimens.

All specimens failed at the stress level used. However, the incubation period (exposure period before there were indications that cracks were initiated) was about six times as long for specimens that were completely insulated except at the root of the notch, as for those specimens where the whole notched area was exposed to the corrodent.

The stresses concentrated at the roots of the notches of these latter specimens limited all strains of any appreciable magnitude to those regions. The protective film will be ruptured only at the root of the notch. The sides of the notch (when exposed to the corrodent) will be film-covered, cathodic to the root of the notch, and very much larger than the anodic (film-free) area at the root of the notch. Thus there exists the condition of a very small anode and large cathode that is ideal for rapid corrosion by electrochemical processes.

In specimens on which only the roots of the notches are exposed to the corrodent there will be some small areas where the strain rate is higher than others, that is, on which the protective film will be ruptured. Conversely, there will be some areas where there will be more opportunity for the film to repair than on others. The resulting anodic and cathodic areas may be nearly the same size and while electrochemical corrosion may occur and cracking eventually develop, the rate will be much slower than if a large cathode-small anode relationship exists.

The evidence [7, 8] indicated that once cracks have penetrated into the metal, the sides of the cracks become the cathodic areas; whether or not the sides of the notches are insulated is then of little further importance.

### 3.4. Crystallographic Data on Crystals Containing, and Free From, Stress-Corrosion Cracks

The poles of the planes on which stress-corrosion cracks were initiated are shown in a single stereographic triangle in figure 3. In every case these planes make large angles with the basal plane. If the same condition exists in this alloy as has been reported for relatively pure magnesium [9], namely, that the basal planes of the crystals in an extrusion are approximately parallel to the direction of extrusion, then the fact that the poles of the stress-corrosion cracks make high angles with the pole of the basal plane is to be expected.

With the exception of C-2, C-8, and possibly C-11, the planes of fracture do not lie close to any low-index crystallographic planes. These results agree in a general way with those obtained by Meller and Metzger [10] on single crystals of an AZ61 alloy and do not agree with those reported by Priest [7] for the same alloy.

It is well recognized that the planes of stress-corrosion cracks are generally approximately normal to the stress axis. The data obtained in this investigation further confirm that observation. The resolved tensile stress normal to the plane of the stress-corrosion crack is proportional to the cosine of the angle between the tension axis and the normal to the plane of the stress-corrosion crack. These angles for the various stress-corrosion cracks are given in column 2 of table 1. The corresponding cosines are listed in column 3. The component of the stress normal to the stress-corrosion crack is in no case smaller than 0.934 times the tensile stress.

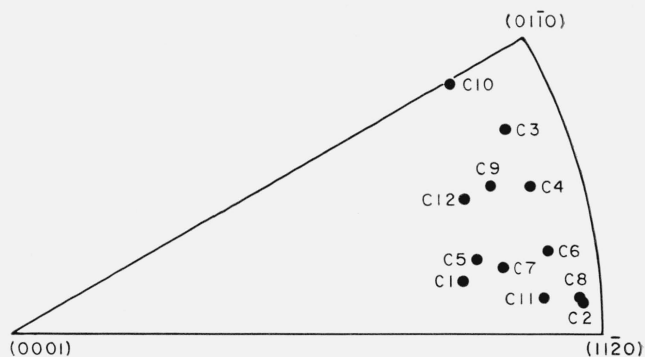


FIGURE 3. Poles of planes on which stress-corrosion cracks were initiated.

TABLE 1. Components of stress normal to the plane of stress-corrosion cracks, and probability of slip at a constant stress,  $f(\phi, \lambda)$ , for crystals (C) containing and crystals (N) free from stress-corrosion cracks.

$f(\phi, \lambda) = \sin \phi \cos \lambda$ , where  $\phi$  and  $\lambda$  are angles between the stress axis and the slip plane and slip direction, respectively.

Crystal	Angle between tension axis and normal to stress-corrosion crack	Component of the tensile stress normal to stress-corrosion crack	Probability of slip at constant stress
	deg		$\sin \phi \cos \lambda$
C 1	12	0.978	0.000
C 2	2	.999	.008
C 3	21	.934	.028
C 4	18	.951	.031
C 5	10	.985	.043
C 6	9½	.986	.071
C 7	16	.961	.071
C 8	4½	.997	.071
C 9	7½	.991	.074
C 10	10	.985	.078
C 11	16½	.959	.079
C 12	15	.966	.114
N 1			.023
N 2			.091
N 3			.149
N 4			.150
N 5			.162
N 6			.201
N 7			.342
N 8			.365
N 9			.405
N 10			.472

<sup>4</sup> Stresses of this magnitude will produce a true strain of approximately 0.03; this included a deviation from the modulus line of about 0.015.

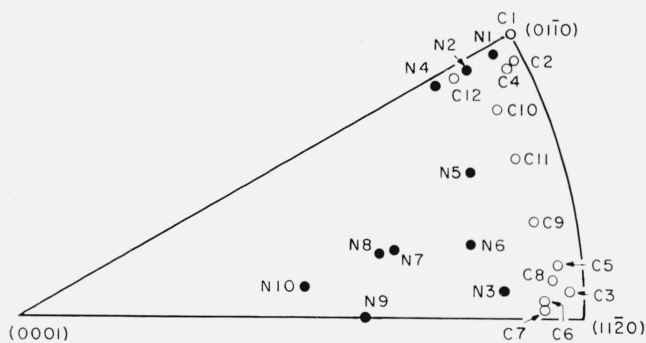


FIGURE 4. Tension axes for crystals "C" in which cracking occurred and for crystals "N" in which no cracks were found.

The ease with which slip will occur in a given crystal is dependent, in part at least, on the magnitude of the product  $\sin \phi \cos \lambda$ , where  $\phi$  is the angle between the stress axis and the slip plane and  $\lambda$  is the angle between the stress axis and the slip direction. The slip plane is (0001) and the slip direction is  $[11\bar{2}0]$  for polycrystalline magnesium [9] and it is to be expected that they are the same for the AZ31 alloy. The values of  $\sin \phi \cos \lambda$  have been calculated for each of the 12 crystals in which cracks were analyzed and for 10 crystals, from some of the same specimens, in which no cracks were found. These data are given in column 4 of table 1. The tension axis, with respect to each crystal, is plotted in a single stereographic triangle, in figure 4.

Data in table 1 and figure 4 indicate that crystals in which cracking occurred were generally less favorably oriented for slip than those crystals analyzed in which no cracks were found. It is recognized that in polycrystalline specimens the neighboring crystals may be the determining factor in whether or not slip occurs in a particular crystal. However, the fact that the stress-corrosion cracks occurred in the crystals least favorably oriented for slip is in agreement with the mechanism postulated earlier for the initiation of stress-corrosion cracking in the magnesium alloy.

#### 4. Summary

1. Idealized curves were prepared showing the simultaneous changes in extension and electrochemical solution potential for AZ31B magnesium alloy specimens that were exposed under constant tensile load in an aqueous solution of NaCl and  $K_2CrO_4$  until failures by stress-corrosion cracking occurred.

2. Initiation of stress-corrosion cracking, after an incubation period, is postulated to occur in grains that were deformed as the result of stress-concentrations built up by the initial deformation and the hardening of those grains that were favorably oriented for initial plastic extension.

3. Making several assumptions, the strain rate (in microscopic sections) associated with, and most probably required for, the initiation of stress-corrosion cracking was calculated to be of the order of 1 percent/sec.

4. The incubation period (period prior to initiation of cracking) was much longer for specimens on which the passive (film covered) and active (film free) areas were approximately the same than for those on which the passive area was many times larger than the active area.

5. Stress-corrosion cracks made large angles with the basal crystallographic plane in large-grained specimens but were not generally associated, at their initiation, with any low-index crystallographic plane.

6. Stress-corrosion cracks were generally approximately normal to the stress axis and occurred in grains unfavorably oriented for slip.

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#### 5. References

- [1] H. L. Logan and H. Hessing, J. Research NBS **44**, 233 (1950) RP2074.
- [2] H. L. Logan, J. Research NBS **61**, 503 (1958) RP2919.
- [3] H. L. Logan, Physical metallurgy of stress corrosion fracture, Edited by Thor Rhodin, p. 298 (Interscience publishers, New York, N.Y., 1959).
- [4] C. S. Barrett, Structure of metals, p. 40 (McGraw-Hill Book Co., New York, N.Y., 1952).
- [5] H. L. Logan, J. Research NBS **48**, 99 (1952) RP2291.
- [6] T. P. Hoar and J. M. West, Nature **181**, 835 (1958).
- [7] D. K. Priest, F. H. Beck, and M. G. Fontana, Trans. ASM **47**, 473 (1955).
- [8] R. D. Williams, Motion picture film of stress-corrosion cracking of magnesium alloy produced by Aluminum Company of America Research Laboratories.
- [9] F. E. Hauser, C. D. Starr, L. Tietz, and J. E. Dorn, Trans. ASM **47**, 102 (1955).
- [10] F. Meller and M. Metzger, US NACA Tech. Note (1957) No. 4019.

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