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Studies of the Stress-Corrosion Cracking of Low-Carbon Steels

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The mechanism of stress-corrosion cracking in low-carbon steels was investigated using notched specimens, stressed in tension to produce a slight amount of plastic deformation, and exposed in a boiling 20 percent aqueous solution of NH_4NO_3. Initiation and propagation of cracks were studied by removing specimens for metallographic examination after stated periods of exposure and by simultaneously recording extensions and electrochemical solution potentials. Cracks were initiated after about 20 minutes' exposure and complete failures occurred in 200 minutes or more. Both crack initiation and propagation were postulated to result from an electrochemical process in which the anodic areas were submicroscopic. Tensile fractures were initiated in the corroded specimens several times before complete failure occurred but were prevented from going to completion because of the energy involved in forming the surfaces of the cracks and the strain hardening and the strain aging of the steel at the tips of the cracks.

1. Introduction

Failures of riveted steel pressure vessels have frequently been attributed to stress-corrosion cracking, called in these instances "caustic embrittlement." The construction of pressure vessels by welding has prevented the leaks that were a factor in causing the cracking of riveted structures but has by no means eliminated stress-corrosion cracking of low-carbon steel vessels. The mechanism of the initiation and propagation of stress-corrosion cracking in low-carbon steels is not well understood. Several theories have been advanced to explain the mechanism; none are universally accepted. The data reported in this paper are used for the reexamination and refinement of some of the current theories of stress-corrosion cracking.

A brief review of conditions under which stress-corrosion cracking has been reported in low-carbon steels was given in an earlier paper [1].[1] Corrodents have included hydroxides, nitrates, cyanides, complex organics, and even humid weather conditions.[2]

In our earlier laboratory study of the stress-corrosion cracking of low-carbon steels [1] extensive exposure periods were required to produce failures in conventional (but subsize) tensile specimens in a boiling aqueous solution of NH_4NO_3. Failures of specimens in less than 300 hr were rare and some specimens were removed from the corrodent after 1,800 hr exposure with no evidence of the development of stress-corrosion cracks. Failures, when they occurred, were in regions of stress concentrations resulting from the combined action of stress and the general attack of the corrodent. A typical failed specimen is shown in figure 1.

Anodic polarization of specimens produced preferential grain boundary attack at a small number of boundaries, whether or not the specimens were subjected to externally applied stresses. In the stressed specimens the penetration of the corrodent along the grain boundaries as a result of the applied current (average current density, 0.06 ma/cm^2) eventually caused such stress concentrations that failures occurred in regions having fairly uniform cross-sectional areas. Again, however, the exposure periods to failure were more than 200 hr.

These data suggested that specimens designed to contain definite and reproducible regions of stress concentration, e.g., notches, would most probably fail after relatively short exposure periods. Accordingly, a notched specimen was designed that subsequently failed after a few hours' exposure under stress in the corrodent.

In earlier studies time lapse photographic records of the extension of a conventional specimen, that failed in 315 hr, showed that most of the strain indicative of the development of stress-corrosion cracks occurred during the last 3 hr of the life of the specimen. With a specimen that would fail in a few hours it was feasible to determine the incubation period to the initiation of cracking and to determine the extension-time and electrochemical solution potential-time relationships during the life of the specimen.

In the early work [1] with fine-grained materials the exposure periods to failure were much longer for a "ship plate steel" [3] having a high transition temperature from brittle to ductile fracture than for a similar steel having a lower transition temperature. Although the temperature of the corrodent was well above the higher transition temperature, it seemed desirable to compare these materials as notched specimens where the inherent brittleness of the steels, if present, would be expected to affect the results. Two steels, one silicon killed, the other

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Failure of steel hooks, designed to hold in place the concrete block facing on the Bureau of Engraving and Printing Annex, Washington, D.C., was attributed to stress-corrosion cracking [2].

[3] Plates had been removed from welded ships. A crack had run completely across one of these plates (high transition temperature from brittle to ductile fracture) while the crack had penetrated into and stopped in the second plate (low transition temperature from brittle to ductile fracture). For a report of the NBS work on "ship plate," see "Correlation of metallurgical properties and service performance of steel plates from fractured ships" by Morgan L. Williams, Welding J. Research Suppl., p. 445, (Oct. 1958).

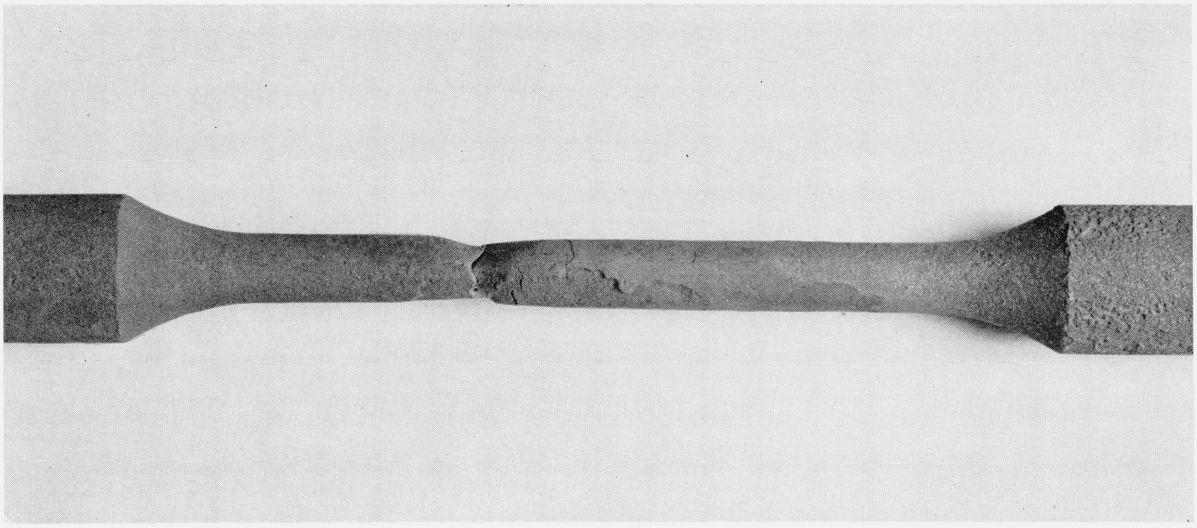

FIGURE 1. *Conventional stress-corrosion specimen that failed after 300 hr in the aqueous boiling* NH_4NO_3 *solution.*

Cracking was limited to reduced section containing regions of stress concentration.

aluminum killed, with about the same carbon content as the ship plate steels were also available. The susceptibility of these steels to stress-corrosion cracking was compared with the ship plate steels and data obtained used in an attempt to correlate mechanical properties, chemical composition, and susceptibility to stress-corrosion cracking.

2. Materials and Methods

2.1. Materials

Four of the steels used in the previous work [1] were also used in the current investigation. Their chemical compositions, tensile properties, transition temperatures (if determined), hardnesses, and grain sizes are given in table 1. A and B were ship plate, C was the silicon-killed, and D the aluminum-killed steel.

2.2. Experimental Methods

The silicon- and aluminum-killed steels (C and D of table 1) were supplied as ½-in. diam rods. These steels were normalized before use by holding them for 1 hr at 1,700 °F and air cooling. Notched specimens, having the dimensions shown in figure 2, were machined from these normalized rods. The ship plate steels were ¾ and ⅝ in. thick, respectively, for the high transition and low transition steels. In order to avoid differences in notch geometry, coupons from these steels were machined to ½-in.-diam rods and the notches were then machined as indicated for the killed steels. Neither ship plate steel was heat treated in any manner at NBS.

In order to investigate the relative susceptibility of these various steels to stress-corrosion cracking, all specimens were insulated with plastic tape except over the notched areas, and placed in Pyrex cells

TABLE 1

A. Chemical composition of steels used in investigation

Lot	Carbon	Manganese	Phosphorus	Sulfur	Silicon	Aluminum	Chromium	Copper	Nickel
	%	%	%	%	%	%	%	%	%
A	0.20	0.41	0.01	0.029	0.03	0.070	0.02	0.05	0.02
B	.22	.44	.008	.025	.061	.016	.009	.015	.009
C	.19	.43	.008	.022	.17	<.01	ND	ND	ND
D	.19	.54	.008	.029	.018	.04	ND	ND	ND

B. Mechanical properties of steels used in investigation

Lot	Yield strength	Ultimate tensile strength	Reduction in area	Transition temperature	Hardness Rockwell B scale	Grain size ASTM No.
	psi	*psi*	%	°F.		
A	45,400	60,200	63	37	62	7.5
B	32,800	62,500	59	98	70½	6.0
C	49,700	66,800	66½	ND	72	8.0
D	46,200	63,200	68	ND	71	8.0

NOTE: ND—Not determined.

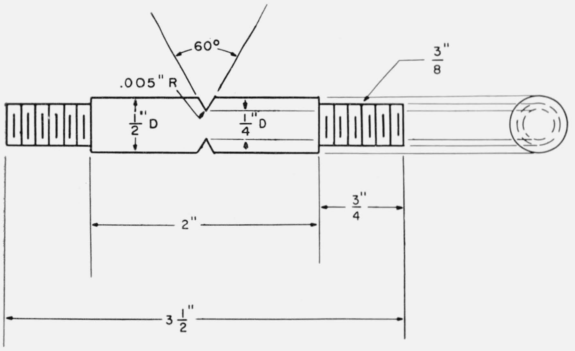

FIGURE 2. *Drawing of notched specimen used in the investigation.*

that were wrapped externally with resistance wire and heated electrically. The corrodent was a boiling aqueous 20 percent solution of NH_4NO_3. Loss of liquid was prevented by reflux condensers connected to the tops of the cells. The cell used in much of the work had a side arm that could be connected through a salt bridge to a calomel electrode. The electrochemical solution potential of the specimen (in terms of a calomel electrode of the saturated KCl type) was thus readily determined manually or recorded on one channel of an oscillograph.

Previous work in this laboratory [3] and studies of the data of other investigators have indicated that the order of procedure may be important in obtaining data, particularly those including periods to failure and electrochemical solution potentials. Most of the data to be reported were obtained using the following procedure. The corrodent was heated to boiling (103.5 °C) and the electrochemical solution potential of the specimen was noted. When the potential reached a value of -0.40 v, the specimen was stressed in tension by dead loading using a lever system. A few specimens, however, were stressed prior to adding the corrodent and bringing it to its boiling point.

In laboratory investigations, stress-corrosion cracking of low-carbon steels occurs only in specimens subjected to stresses high enough to produce some plastic extension. In order to determine the stresses to be used with the notched specimens, true stress-logarithmic strain curves [4] were obtained for two notched specimens from each lot of steel. The stresses selected for the various lots of steel were those that would produce approximately the same deviation (logarithmic strain of 0.01) in each case, from the modulus line in the room temperature true stress-logarithmic strain diagram. The logarithmic strain of one specimen removed from the corrodent after 10 min under stress, at temperature, was 0.033.

Most of the deformation of the specimen occurred on the initial loading. However, notched specimens continue to elongate but at a diminishing rate for a considerable period after the stress is applied. This elongation was followed by reading (or recording, using time-lapse photography) dial gages actuated by the motion of the ends of the loading levers. Inasmuch as the lever ratio was 25 to 1 and the dial gage could be read to 1×10^{-4} in., a change in length of the specimen-specimen support system of 4×10^{-6} in. could be observed.

In a few instances the elongation of the specimen[5] alone and in many instances the elongation of the specimen-specimen support system was recorded simultaneously with the electrochemical solution potential of the specimen.

3. Results and Discussion

3.1. Comparison of the Relative Susceptibility of Four Lots of Steel to Stress-Corrosion Cracking

Four specimens of each of the four lots of steel whose compositions are given in table 1 were exposed under stress in the boiling NH_4NO_3 solution until failure occurred. As was indicated earlier, while the applied stresses were different for each lot of material they were determined from true stress-logarithmic strain curves to give approximately equal plastic strains. The average exposure periods to failure and the standard deviations are given in table 2.

TABLE 2. *Exposure periods to failure for the lots of steel exposed, subjected to approximately the same strain, in a boiling* NH_4NO_3 *solution*

Lot	Average exposure period to failure	standard deviation
	min.	*min.*
A	240	85
B	422	101
C	255	2, 2
D	204	17, 6

Specimens from the ship plate steel (lot B), with the highest transition temperature, were the most resistant to stress-corrosion cracking of any of the steels studied. The fact that this steel had brittle characteristics below 98 °F (37 °C) apparently had no effect on its properties in the NH_4NO_3 solution at 103.5 °C.

There were slight differences in the chemistry of the four steels. The carbon content of all was approximately 0.20 percent and according to Parkins [5] they should be resistant to stress-corrosion cracking. He reported that the resistance of steels to stress-corrosion cracking in a $Ca(NO_3)_2+NH_4NO_3$ solution increased with increased carbon content up to 0.18 percent and that steels containing more of carbon were relatively resistant to stress-corrosion cracking.

The principal differences in the composition of the four steels are in their silicon and aluminum content. The silicon contents of A and D are relatively low; B, however, has a silicon content between that of A and C. The aluminum contents of A and D are higher than that of either B or C. Whether the difference in the resistances of these

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[4] True stress is defined as $\frac{\text{load}}{\text{area}_t}$, and logarithmic strain as $\ln \frac{\text{area}_0}{\text{area}_t}$. Area_0 is the original cross-sectional area at the root of the notch and area_t is the area at any time *t*.

[5] In this case a specimen 9 to 10 in. long was used.

steels is due to the differences in silicon and aluminum contents or other factors cannot be determined from these data.

A fractured surface, characteristic of that found on specimens from lots B, C, and D, is shown in figure 3. In all of these specimens, the area of fracture due to stress-corrosion cracking was clearly delineated from that produced in the final tensile failure of the specimen. The fractured surface from a typical specimen of lot A steel is shown in figure 4. With careful study the area of fracture due to stress-corrosion cracking could be determined. The unusual appearance of the fractured surfaces of these specimens was due to shearing of the specimen, in the final tensile fracture, along planes approximately parallel to the tension axis. A longitudinal section of the specimen, including the fractured surface, is shown in figure 5. The steel contained an unusual amount of stringers of nonmetallic inclusions and the shearing action occurred along these stringers.

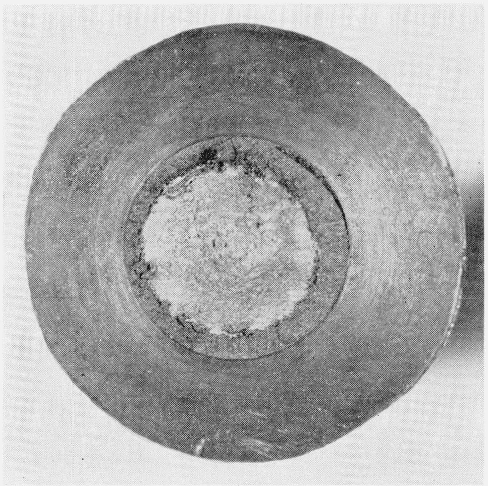

FIGURE 3. *Fractured surface of specimen characteristic of that found on specimens from lots B, C and D.* × 4½.

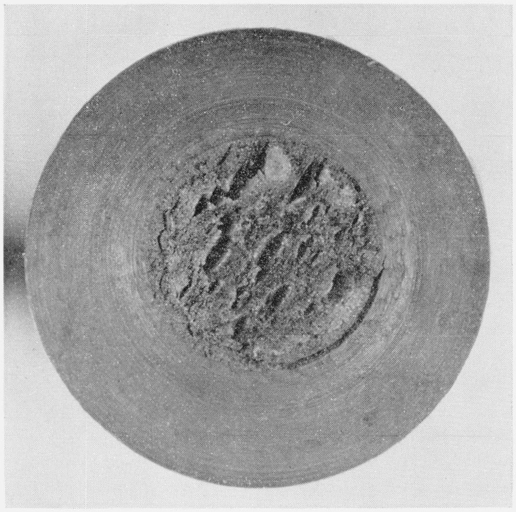

FIGURE 4. *Surface of fractured specimen of lot A steel.*
Note difference in appearance from fractures from lots B, C and D.

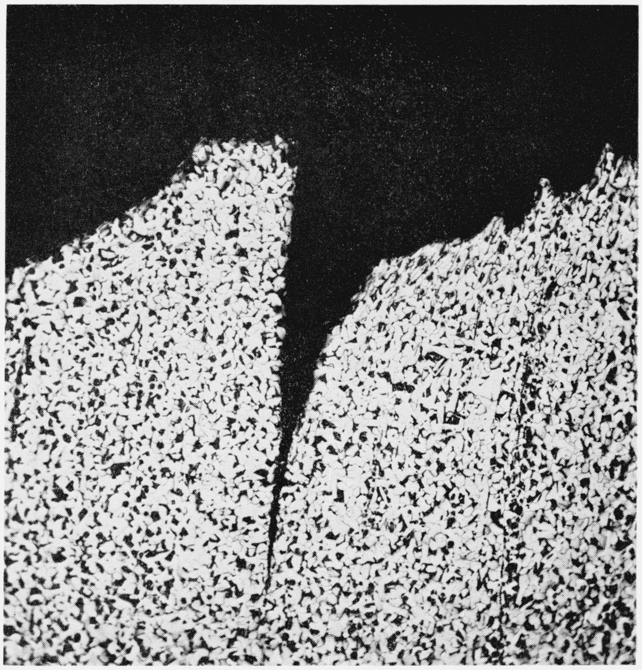

FIGURE 5. *Longitudinal section through fracture in specimen shown in figure 4.*
Void in the center of the figure resulted from shearing action at failure. Appearance of failed surface at the left of the void indicated that a stress-corrosion crack probably penetrated to that point. Distortion of grains to the right of the void occurred during tensile fracture. Etched 1 percent nital. × 50.

3.2. Initiation of Stress-Corrosion Cracks in a Notched Specimen

The use of notched specimens has made possible the study of the initiation and propagation of stress-corrosion cracks in low-carbon steel exposed in the ammonium nitrate solution.

The room temperature (25 °C) electrochemical solution potential of a typical steel from this group ($\sim 0.20\%$ carbon) was -0.6 to -0.7 v with respect to a calomel electrode of the saturated KCl type. As the corrodent and specimen were heated to the boiling point the electrochemical solution potential became more noble. The change was generally rather slow until the solution began to boil at about 103.5 °C. With continued boiling, the potential drifted slowly in the positive direction and could reach -0.30 v after several hours exposure in the boiling corrodent. The change in potential from -0.6 to -0.380 v on heating the corrodent from 25 to 103.5 °C indicated that a protective film (or polarized condition) had formed on the exposed surface of the specimen.

Stressing of a specimen that was at the boiling temperature of the corrodent and had an electrochemical solution potential of -0.38 v or less changed this potential almost instantly as much as 70 mv in the active direction. A typical oscillographic trace for this change is shown in figure 6. The stress applied to the specimen was calculated to be sufficiently large to produce plastic deformation at the root of the notch. Thus, the change in potential was due to the rupturing of the protective film (or

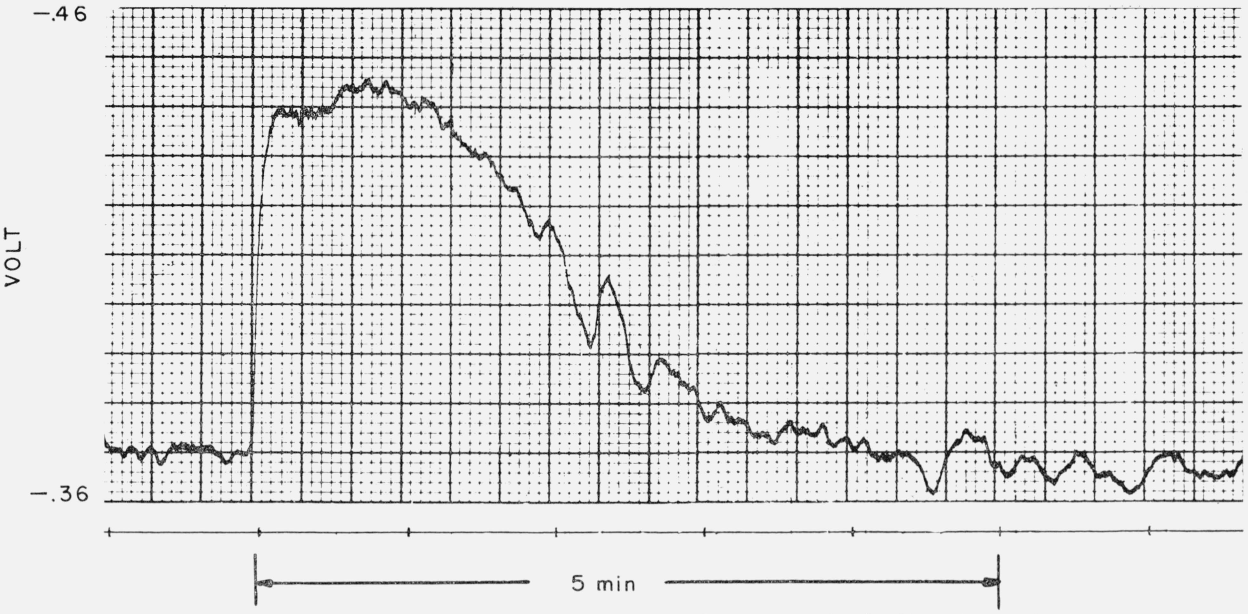

FIGURE 6. *Oscillographic record of change in potential accompanying loading of a specimen.*
Markings on lower scale indicate successive minutes. Irregularities in potential curve at equilibrium positions are caused by boiling of the solution.

disruption of the polarized condition) at the root of the notch.

Some minutes were required for the specimen potential to change from the maximum value (see fig. 6) to its value prior to the application of the stress. Extension measurements made directly on the specimen have indicated that it continued to extend, but at a diminishing rate, after the initial extension accompanying the stressing of the specimen.[6]

The measured potential of the stressed specimen depends on the relative rates of film rupture and repair. Measurements of the rate of change in potential of a specimen, taken immediately following its complete failure, indicated that 10 min or more may be required for the freshly exposed metal to be polarized to the prefractured condition of the surface. This is not unexpected considering the relatively slow rate [7] at which the potential of the specimen changes during the heating period. Hence, the data indicate that the rate of film repair rather than the continued extension of the specimen was the primary factor that delayed the return of the specimen potential to the prestressed value. The electrochemical solution potential continued to change slowly in the noble direction, as was indicated above, after the prestressed potential had been reached.

There was no abrupt change in the extension rate of the specimen, such as was found for stainless steel [6], indicating the initiation of stress-corrosion cracking.[8] Specimens were removed from the corroding medium after various exposure periods, sectioned longitudinally, and examined metallographically for evidence of stress-corrosion cracks. In this manner, it was determined that cracks may start to develop within 20 min after the specimen was stressed. Figure 7 shows a stress-corrosion crack in a notched specimen removed after 30 min exposure under stress. Examinations of newly initiated stress-corrosion cracks have usually revealed corrosion products on the surface of the metal at the mouths of the cracks in these specimens. Cracks followed intercrystalline paths (see fig. 8) and usually developed in pairs in a notched specimen as is shown in figures 8, 9, 10, and 11. Hetenyi and Liu [7] have shown that the maximum shearing stress is not at the root of the notch but is displaced about ½ the root radius from that point. This may explain the location of the stress-corrosion cracks in figures 8, 9, 10, and 11. Kies, Smith, and Irwin [8] have postulated that the direction of the maximum tensile stress near the root of the notch is not parallel to the tension axis but makes an angle of about 60 degrees with it. This may explain the direction taken by the cracks.

The results obtained by stressing a specimen in the corrodent prior to heating it were different in some respects than those reported above. For example, applying the stress to specimens at room temperature did not produce any appreciable change in the electrochemical solution potential. The potential of the stressed specimen, however, became more positive with increasing temperature as was noted above for the unstressed specimen heated in the corrodent. Specimens remained in the solution at temperature for 60 min after rapid boiling had begun and during this period there were no changes in potential, in the active direction, indicative of film rupture. Specimens were then removed

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[6] The stress was applied by releasing a hydraulic jack supporting the end of the lever with the load in place. Hence, the stress was applied rapidly but without impact.

[7] This slow rate of film repair contrasts sharply with the very rapid film repair found in the AZ31 magnesium alloy [3]. In this latter case film repair takes place in less than 1 sec.

[8] Changes in the extension rate for stainless steels were noted using conventional tensile specimens with the extension resulting from the formation of many cracks. Normally on a section through the root of the notch only two cracks were found.

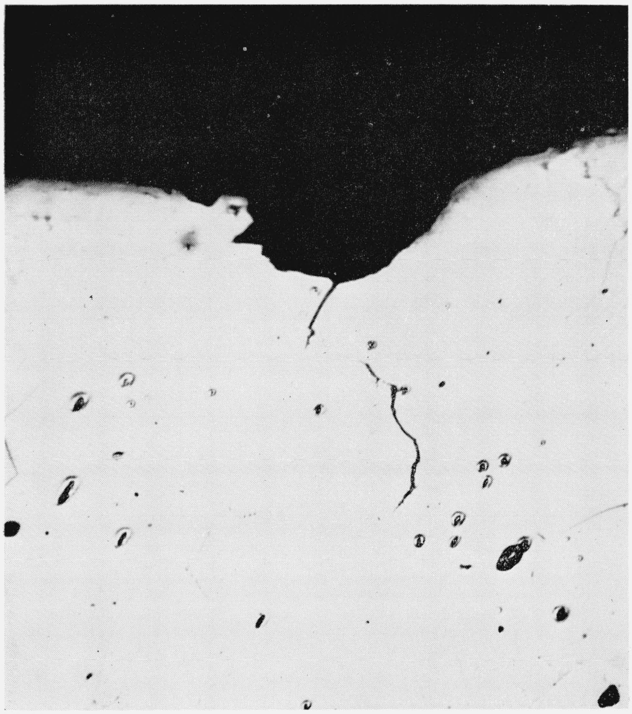

FIGURE 7. *Stress-corrosion crack developing in specimen exposed under stress for 30 min in the boiling 20 percent* NH_4NO_3 *solution.*

Root of the notch to the left. Unetched. × 500.

FIGURE 8. *Intercrystalline stress-corrosion cracks developing in a C specimen after 1 hr exposure in the corroding medium.*

Unetched. × 250.

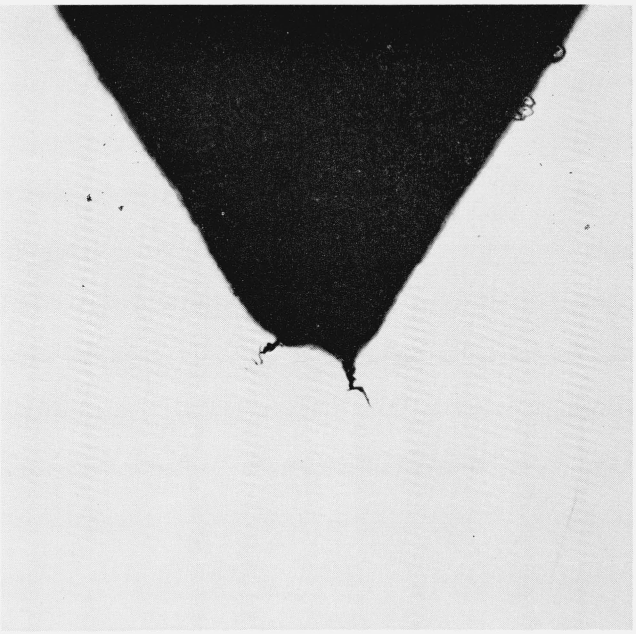

FIGURE 9. *Stress-corrosion cracks that had developed in a D specimen exposed under stress for 60 min without any evidence of sudden extension.*

Unetched. × 100.

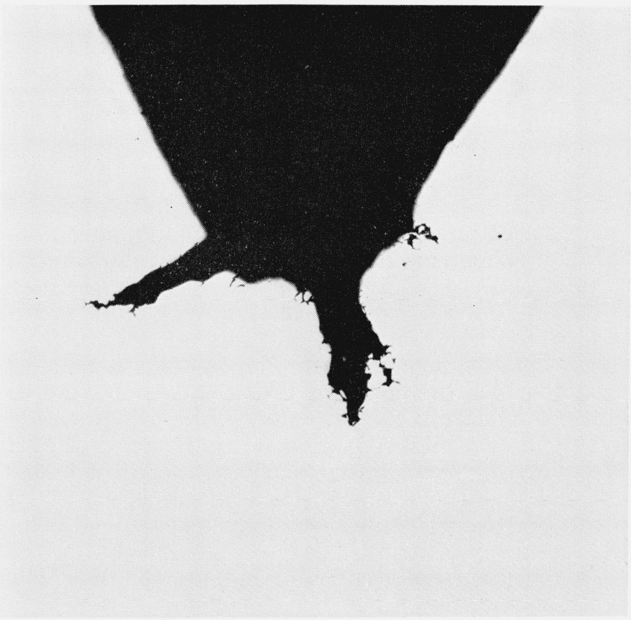

FIGURE 10. *Stress-corrosion cracks that developed in a D specimen with sudden extension occurring during the last minute of exposure.*

Compare the extent of crack in this specimen with figure 9. Unetched. × 100.

and sectioned longitudinally to determine the extent of stress-corrosion cracking. The depth of penetration of the cracks was not appreciably different from that found in specimens of the same lot of steel (C) that had also been stressed for a period of 60 min but after the solution had come to a boil.

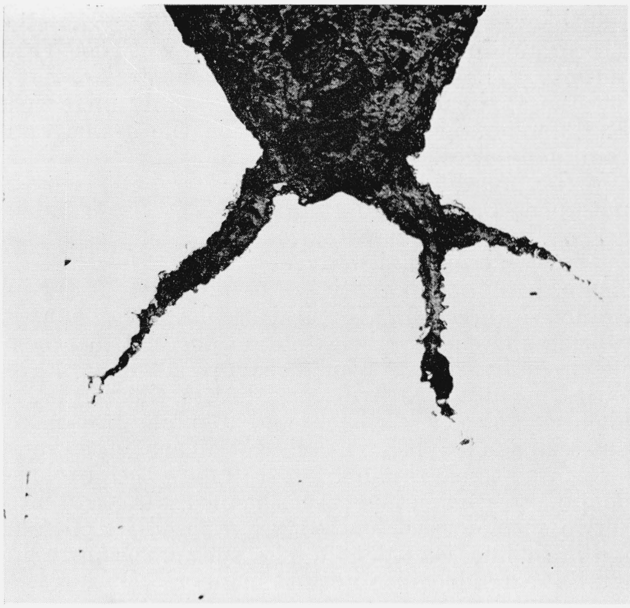

FIGURE 11. *Cracks that developed in specimen from lot D steel after 2 hr exposure in the corrodent.*
Unetched. × 90.

Most investigators in the field agree that stress-corrosion cracking is initiated by an electrochemical process. The fact that no cracks developed in a specimen to which cathodic protection was applied during the entire exposure period under stress substantiates this idea for low carbon steels.

If a continuous anodic region exists at the grain boundaries, and if this region is attacked in the corrodent in the absence of stress, there is no problem in explaining the initiation of intercrystalline stress-corrosion cracking. Material at grain boundaries may be in a higher energy state (and hence more active) than that on the exposed faces of crystals. There was no evidence in this investigation, however, that the grain boundaries were sufficiently energetic, in the absence of stress, to provide a continuous anodic path for either the initiation or propagation of stress-corrosion cracks. Hence, the appearance of active anodic areas where certain grain boundaries contact the surface of the metal must be associated with the application of the stress. Two explanations of this mechanism have been proposed.

The first of these postulates that the polarized condition on the surface film developed during the heating of the corrodent protects the specimen from corrosion generally as long as it is intact. Applying stress to the specimen immersed in the boiling corrodent destroys the polarized condition (or ruptures the film) in the highly stressed region at the root of the notch. Electrochemical solution potential measurements obtained at the final failure of specimens indicated that this exposed surface may actually be 0.20 to 0.25 anodic to the material on the sides of the notch. Thus, an ideal condition exists for corrosion by an electrochemical process with all of the required elements present: a relatively small anode, a large cathode, and an electrolyte.

The data, however, indicate that cracks do not begin to develop until the film rupture associated with the initial loading has been repaired. While several minutes were usually required for the repair of the protective film (or polarized condition) at the root of the notch metallographic data given above indicate that approximately 20 min of exposure was required for the initiation of cracking. Furthermore, stress-corrosion cracking was approximately as extensive in those specimens stressed in a cold solution, which never showed an appreciable change in potential that could be attributed to film rupture, as in specimens showing a change in potential of 0.07 v on initial stressing. If rupturing of the protective film on the surface of the specimen is responsible for the initiation of stress-corrosion cracking the active areas must be small compared to those exposed on the initial loading of the specimen, in fact, probably little wider than grain or crystal boundaries.[9] These active areas must also result from the extension of the specimen after the initial loading. Transducer data obtained in one experiment indicated that 20 min after the initial extension the specimen was continuing to extend at the rate of 1 to 2 $\times$ 10^{-6} cm/sec. Theory, metallographic evidence, and the data listed above, all indicate that this extension occurred in a region of the steel less than one root radius in length, i.e., less than 10^{-2} cm and hence with the strain rate greater than 10^{-4}/sec. If the extension was limited to the width of the stress-corrosion cracks, the strain rate could by as large as 10^{-2}/sec. A conservative estimate would be 10^{-3}/sec and the strain would be expected to be confined largely to those regions at the tips of the cracks. The strain rate calculated above is postulated to be high enough to produce an anodic region at or on a submicroscopic area adjacent to a grain boundary by rupturing the protective film [9], destroying the polarized condition [10], or inducing a condition favorable for anodic dissolution [11]. Such anodic areas would have so small an effect on the average recorded electrochemical solution potential of the specimen as to be masked by the background (see fig. 6) but could be highly effective in the initiation of stress-corrosion cracks by an electrochemical process.

A second possibility that must be considered for the initiation of stress-corrosion cracking is a strain-induced precipitate at the grain boundaries. Waber and McDonald [12] suggested that an Fe_4N precipitate is the responsible anodic material at the grain boundaries. More recently, in explaining the mechanism of propagation of stress-corrosion cracks in stainless steel. Uhlig and White [13] had postulated the formation of a precipitate cathodic to the matrix, with the immediately adjacent material anodic to both the precipitate and the matrix, i.e., an "impoverished region." Such a theory might also apply to low-carbon steel.

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[9] Initial loading ruptures an area at the root of the notch that is relatively large, probably containing both crystal boundaries and crystal interiors. Intercrystalline corrosion can take place, however, only if the exposed crystal faces are cathodic to the material at or adjacent to the crystal boundaries.

3.3. Propagation of Stress-Corrosion Cracks

Two general mechanisms have been proposed for the propagation of stress-corrosion cracks. These are designated the electrochemical and the electrochemical-mechanical theories. The propagation of stress-corrosion cracking in the electrochemical theory is postulated as resulting from an electrochemical process in which the advancing tip of the crack is the anode and the sides of the crack the cathode. This provides a small anode-large cathode condition, ideal for rapid corrosion, but nevertheless, may require current densities of the order of several amperes/cm^2 [3, 10] at the tip of the crack.

In the electrochemical-mechanical theory, cracks are postulated to both start and penetrate into the metal by an electrochemical process until sufficiently high-stress concentrations have been built up for them to propagate as a mechanical fractures. Keating [14] suggested that such cracks would travel until they were stopped by an inclusion, unfavorably oriented grain boundary, or other obstacle. More recently the cracks started by electrochemical processes have been considered "Griffith cracks," and further cracking has been treated as "brittle fracture." [15] According to this theory the decrease in elastic strain energy of the specimen (due to the reduction in cross section of the supporting metal) must be greater than the energy associated with forming the surfaces of the new cracks plus the energy used in the plastic deformation of the metal at the apex of the crack, that is

$$\gamma_E > \gamma_S + \gamma_P$$

where γ is the energy and the subscripts indicate elastic, surface, and plastic energies respectively.

Perryman [16] has suggested that "it is possible that the spread of cracks along boundaries is assisted by the reduction in surface energy associated with the wetting of the crack . . . ." This idea has been developed further by Coleman, Weinstein, and Rostoker [17]. They state, however, that at some stage an electrochemical reaction enters into the process.

In the present investigation stress-corrosion cracks have penetrated as deeply as 1 to 1.5×10^{-2} cm in 1 hr under stress in the boiling corrosive medium. If cracking occurred only after the first 20 min of exposure the subsequent penetration rate was approximately 5×10^{-6} cm/sec. If the crack tip is assumed to be continuously anodic to the crack sides (as a result of one of the mechanisms discussed earlier) and if it is further assumed that the resulting electrochemical dissolution process is 100 percent efficient, a current density of about 0.15 amp/cm^2 would be sufficient to produce crack penetration at the rate indicated above. Such a current density is considered entirely reasonable.

Engell and Baumel [18] have determined the electrochemical solution potentials of grain boundaries and grain interiors of "coarse-grained samples of mild steel." From their curves one can estimate that, with the steel in the unstressed condition, the grain boundaries were approximately 75 mv anodic to the grain interiors in a boiling 55 percent $Ca(NO_3)_2$ solution. These authors state, without explanation, that the application of stress appreciably increased the difference in potential between the grains and grain boundaries.

In the present work if the exposure periods were continued beyond 60 min there were sudden marked increases in extension [10] of the specimens that were accompanied by changes in the electrochemical solution potential of as much as 70 mv in the active direction. Typical oscillographic curves showing the changes in extension and potential are shown in figure 12. Such changes have been recorded as many as five times before the specimen failed completely. Engell and Baumel [18] have reported similar behavior in specimens of a very low-carbon steel. Figures 9 and 10 show the development of stress-corrosion cracks at the roots of notches of two specimens of lot D steel exposed for 60 min in the boiling corrodent. The specimen shown in figure 9 extended in a normal manner. During the last minute of exposure of the specimen shown in figure 10, a sudden extension and change in potential occurred, as described above. The photomicrographs and the oscillographic data indicate that there was a sudden tearing of the metal at the tip of the stress-corrosion crack. This produced a sharp increase in elongation and exposed unpolarized or film-free metal to the corrodent with a resulting change in potential in the negative direction. A considerable amount of energy is required to form the new surfaces. Furthermore, the energy required to produce the plastic deformation most probably increases rapidly with the crack propagation because of the resulting strain hardening and strain aging of the material. Hence, the decrease in elastic strain energy as the result of fracture is very quickly balanced by the sum of energies associated with the formation of the new surfaces and the energy of plastic deformation at the tip of the crack and rapid cracking stops.

Tensile tests on notched specimens of lot C steel made in boiling water indicated that this steel was subject to strain aging at 100 °C. Geil [19] reported that a 0.02 percent carbon ingot iron, similar in composition to that used by Engell and Baumel was also subject to strain aging in boiling water.

The final failure of any material resulting from stress-corrosion cracking is by tensile fracture of material whose supporting section has been reduced by the development and propagation of stress-corrosion cracks, see figure 3. The sudden extension of the stress-corrosion cracks, just discussed, may be considered as the initiation of the final tensile fractures of the specimens. These fractures are prevented from going to completion by the strain hardening and the strain aging of the metal ahead of the tips of the cracks. Rapid crack propagation then ceases until cracks developing further by the relatively slow electrochemical process again produce stress concentrations and a condition of tensile overload.

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[10] One D specimen extended abruptly during the 60th min, see figure 10.

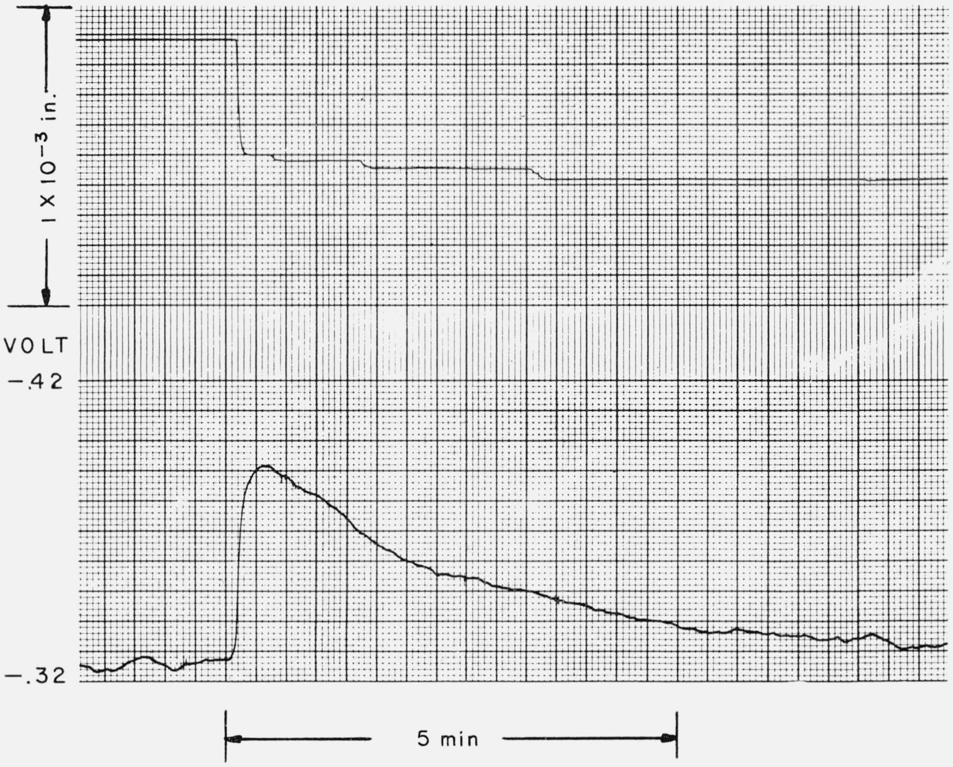

FIGURE 12. *Oscillographic charts showing increases in elongation of specimen (upper curve) and accompanying change in potential (lower curve)*

3.4. Cathodic Protection of Low-Carbon Steels

The application of cathodic protection can prevent stress-corrosion cracks from starting in low-carbon steels exposed under conditions described in the earlier sections of this paper. Cathodic protection can generally stop further propagation of cracks even if they have progressed a considerable distance into the steel, and one or two rapid crack extensions, such as those described in the preceding section, have occurred.

Cathodic protection is effective in that it polarizes the whole specimen (including the tips of the cracks) to the potential of the film-free metal. Hence, there are neither anodes nor cathodes but a uniform potential on the surface of the specimen.

Cathodic protection stops the electrochemical reaction that accelerates the rate of extension of the specimen. In this investigation, however, it did not stop the extension at once. This is to be expected. The tips of stress-corrosion cracks are extremely sharp notches that produce very high stress concentrations in the metal. Hence, the specimen will extend until the metal at the tips of the cracks is sufficiently strengthened by strain aging or cold work to resist further plastic deformation. This will have the effect of shifting the stress pattern and reducing the stress concentration. Thus, the net effect of stopping the electrochemical reaction would be a continued extension of the specimen but at a steadily diminishing rate. This has been found to occur after the application of cathodic protection, not only in low carbon steel but also in stainless steel and in the AZ31 magnesium alloy.

Some specimens containing very severe stress-corrosion cracks, before cathodic protection was applied, would probably fail eventually in spite of cathodic protection as has happened with one stainless steel specimen. The important point is that the final failure, that could be expected in seconds or minutes, may be delayed for minutes, hours, or possibly days, by cathodic protection.

The fact that the rate of extension is slowed by cathodic protection is a very strong argument for the importance of electrochemical processes in the propagation of stress-corrosion cracking. Once stress-corrosion cracks have been initiated, sharp notches, effective as regions of stress concentration, are present whether or not cathodic protection is applied. The essential difference is that with cathodic protection the electrochemical solution potential of the specimen is the same over the entire surface and if further crack development occurs it must be entirely mechanical and generally very slow. In the absence of cathodic protection there are differences in potential at different areas on the surface of the specimen and crack propagation is rapid. The logical assumption is that electrochemical attack, occurring at anodic regions at the tips of the cracks, accelerates the cracking process by the continued development of regions of high stress concentration.

4. Summary

1. The mechanism of stress-corrosion cracking and the relative susceptibility to cracking of four low-carbon steels (carbon content 0.20%) have been studied using notched specimens and boiling 20 percent NH_4NO_3 as the corrodent.

2. Stress-corrosion cracking failures of these steels, stressed to produce a small amount of plastic extension at the roots of the notches, occurred in 4 to 8 hr compared to several hundred hours for unnotched specimens.

3. At a temperature well above the transition temperature (for either steel) a steel with a high transition temperature from ductile to brittle fracture, in the Charpy V notch test, was more resistant to stress-corrosion cracking than a steel with a much lower transition temperature. There was no correlation between the resistance of the four steels to stress-corrosion cracking and their chemistry.

4. Cracks at the root of the notch were most probably initiated after major damage to polarization or the protective film (that resulted from initial stressing) had been repaired. Cracks generally develop in pairs on opposite sides of the root of the notch and in the areas where the shear stresses are postulated to be the greatest.

5. Crack initiation is at grain boundaries and is postulated to be by an electrochemical reaction with submicroscopic anodes formed as the result of plastic extension at the strain rate of the order of magnitude of 0.001/sec.

6. In its early stages crack propagation is intercrystalline. It is postulated to be an electrochemical process requiring a current density of about 0.15 amp/cm^2 at the tip of the crack. The anode at the tip of the crack may result from plastic extension at a strain rate of the order of magnitude of 0.001/sec or from a stress-induced cathodic precipitate at the grain boundary.

7. Tensile fracture, resulting from overload, was initiated as many as five times before it went to completion. Earlier failures were prevented by the strain hardening and strain aging of the metal ahead of the tips of the stress-corrosion cracks.

8. Cathodic protection can prevent the initiation of stress-corrosion cracking in these steels and can stop or delay propagation of cracks in material already severely damaged. This fact is considered to be a very strong argument for an electrochemical mechanism for the initiation and propagation of stress-corrosion cracks.

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