

THE STRESS-CORROSION CRACKING OF AUSTENITIC STAINLESS STEELS IN AQUEOUS CHLORIDE SOLUTION*

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Abstract

The stress-corrosion cracking of 18-8 type steels in hot concentrated magnesium chloride solutions has been studied. There is an induction period, of which the processes are substantially unaffected by stress, followed by a period of rapid crack propagation — as shown by measurements of the electrode potential, the mechanical properties and the extension of direct-loaded wire specimens. The induction period is shortened by increase of applied stress and of temperature, and by cold-work on a fully softened material; it may be indefinitely lengthened by cathodic protection of the metal. Crack propagation is normally at rates of 1-4 mm./hr.; it is not greatly influenced by increase of applied stress, is somewhat accelerated by increase of temperature, and may be slowed down or stopped entirely by cathodic protection.

The results are explained by a theory of stress-assisted selective anodic dissolution for crack initiation and of stress — and yield-assisted anodic dissolution of the advancing edge of a crack for its propagation. Quantitative electrochemical measurements are in harmony with the general theory.

Some practical implications of the work are pointed out.

Introduction

ALTHOUGH many of the phenomena in the stress-corrosion cracking of austenitic stainless steels have gradually become established¹⁻⁷, little detailed investigation of its fundamental mechanism has hitherto been made. We have been engaged⁸⁻¹² in this field since 1951, and the present paper summarizes some of the work.

Experimental Technique

Thin wire metal specimens direct-loaded in tension were adopted, because (a) they

have a fairly uniform and simple stress pattern, (b) uniform corroding and electrochemical conditions can readily be provided, (c) any constant load can be applied, (d) temperature is easily controlled, (e) the onset and propagation of cracking is readily followed by electrochemical and mechanical means, and (f) replicate experiments are possible without undue expenditure of space and time.

0.02 in. diameter wire of the several usual compositions based on 18-8 chromium-nickel was used, usually in the as-received condition (fully softened, then reeled and unreeled, which introduces a small amount of cold-work — see later).

Hot concentrated aqueous magnesium chloride solutions (usually 42 wt. per cent $MgCl_2$) were adopted as corrosive media, because (a) much of the previous data has been obtained with them, (b) they will crack all usual grades of austenitic steel, (c) they are relatively simple electrolytic solutions for study, and (d) they are probably not unrepresentative of a number of industrial corrosive environments in which austenitic steels are used.

The apparatus is shown in Figs. 1(a) and (b). The direct-loaded wire is shielded at and above the water-line by dry nitrogen. Its extension can be followed by the dial gauge on the loading lever, and its fracture timed by a clock switched off by the lever when it falls. Its electrode potential can be measured with respect to the external silver/silver chloride half-cell, and current can, if required, be applied to it from the external platinum electrode. Manual control of rheostats in the heater circuit can maintain temperature

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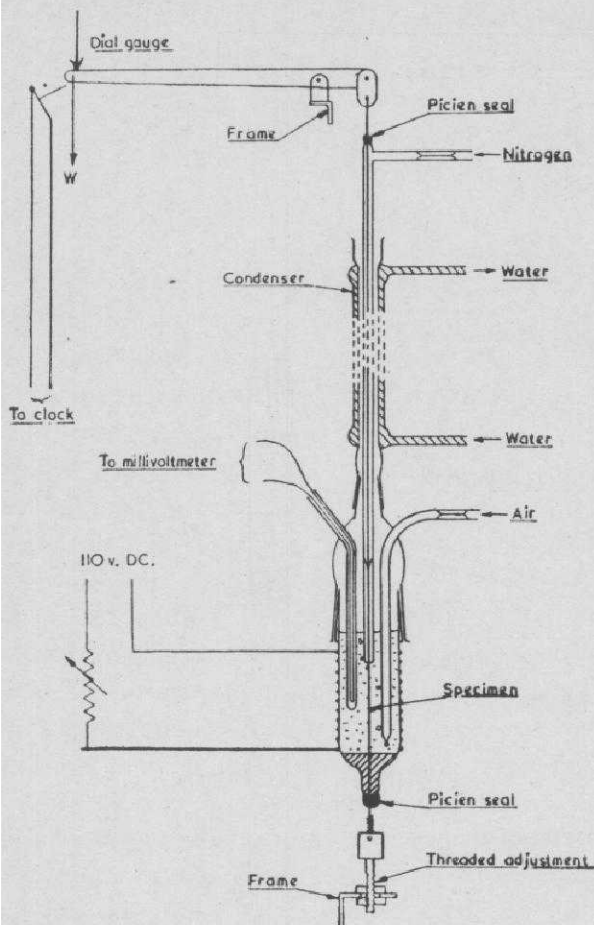


FIG. 1(a) — STRESS-CORROSION TESTING UNIT

to within $\pm 1^\circ\text{C}$., as measured by thermocouple. Five units such as those shown can be operated simultaneously for replicate experiments.

Experimental Results I

Change of Electrode Potential and Mechanical Properties of Specimens with Time —

A rise of potential with time of a metal exposed to an electrolytic solution indicates repair of its protective oxide film, and a fall indicates film breakdown and the onset of corrosion. The present austenitic stainless steel wires, unstressed, in hot aqueous magnesium chloride solution, gave potential/time curves of the general form frequently found — Fig. 2 shows typical examples⁹. The initial fall is caused by the beginning of

anodic action at the base of the oxide film pores as solution penetrates; the slow rise by the partial plugging of the pores by anodically formed solid hydroxide^{13,14}; and the fall after the maximum by the partial breakdown of the film at the pores owing to the fall of pH within them (anodic acidity)^{13,15} and the consequent production of soluble anodic products that undermine rather than plug the film. The same steels stressed from the start of the experiment gave very similar curves, a few mV. more negative throughout, but showing also a rapid potential fall at the end of which fracture by stress-corrosion cracking occurred^{8,9}: the fractured specimens gave rapidly rising potentials indicating film repair on the now unstressed fracture surfaces (FIG. 3). When stress was applied after the start of an experiment, the rapid potential fall still occurred after about the same time as in a similar experiment in which the specimen was stressed throughout⁹.

The mechanical properties of specimens removed before fracture showed very little decline if the experiment had been interrupted before the start of the rapid potential fall, but rapid decline if the experiment had been allowed to continue into this stage; typical results are shown in Figs. 4(a) and (b)⁹. The extension of the specimen during an experiment was negligible — apart from that due to thermal expansion during the first few minutes when the apparatus was coming to temperature after filling — until the start of the rapid potential fall, when it became rapid, as typically shown in Fig. 5⁹.

These experiments show that cracking is initiated only after an induction period, during which the presence or absence of stress is unimportant. The induction period can be considerable, sometimes forming by far the major part of the time that the specimen is exposed to stress-corrosion conditions. However, in special experiments with the 42 wt. per cent aqueous magnesium chloride solution acidified with 0.02 vol. per cent of concentrated HCl, the induction period was

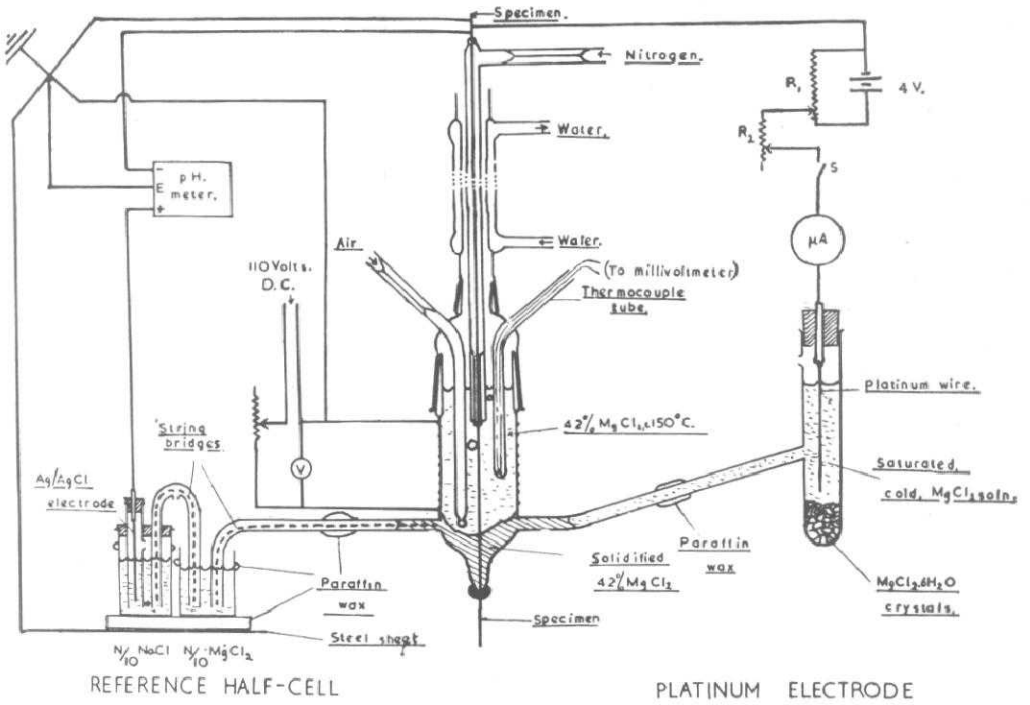


FIG. 1(b) — DETAILS OF CORROSION VESSEL, MODIFIED FOR ELECTROCHEMICAL MEASUREMENT

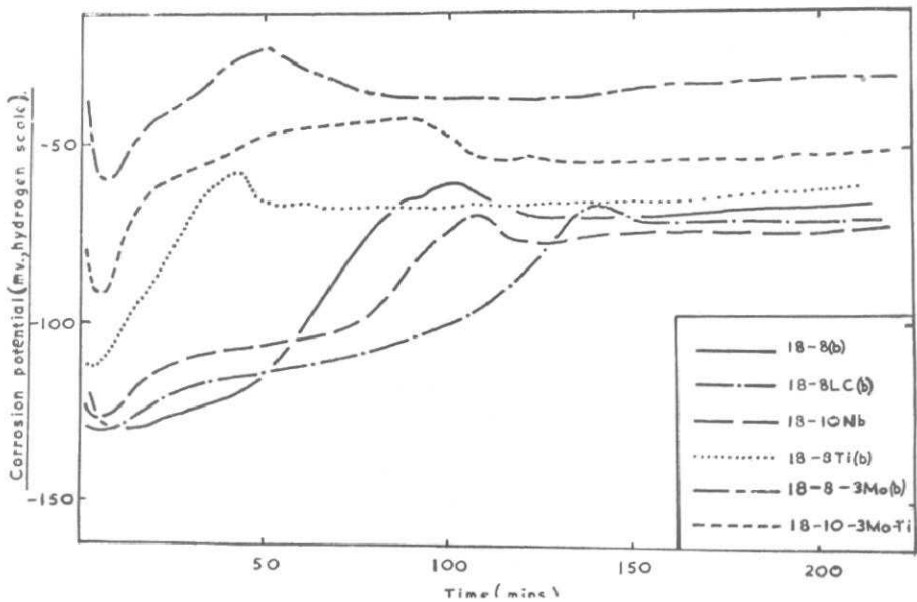


FIG. 2 — TYPICAL POTENTIAL/TIME CURVES FOR UNSTRESSED SPECIMENS 152°-154°C.

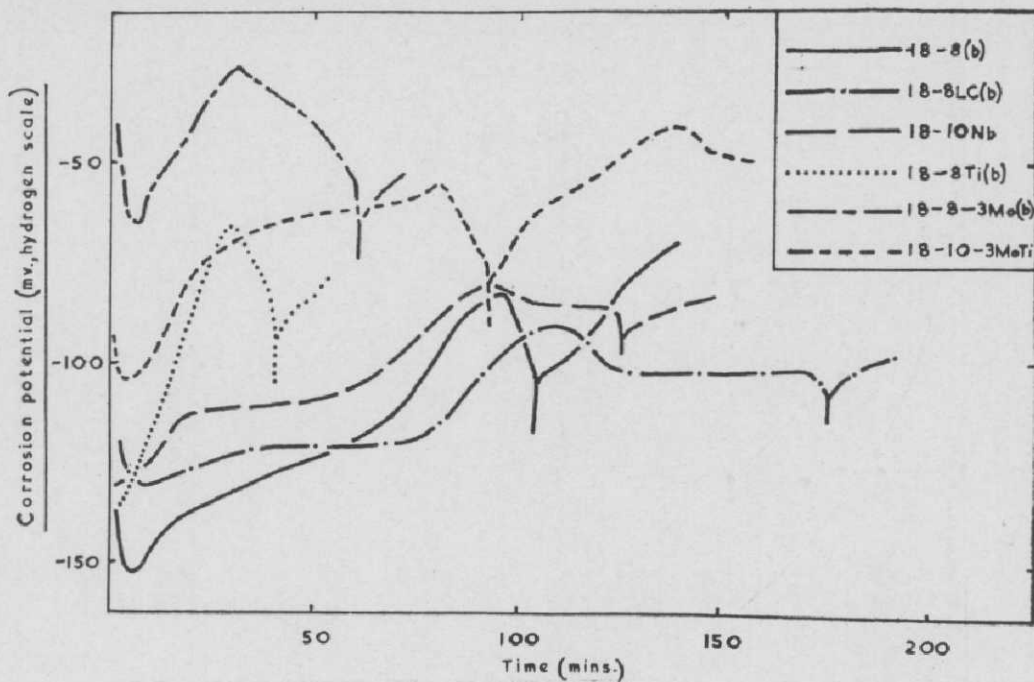


FIG. 3 — TYPICAL POTENTIAL/TIME CURVES FOR STRESSED SPECIMENS 151°-153°C.

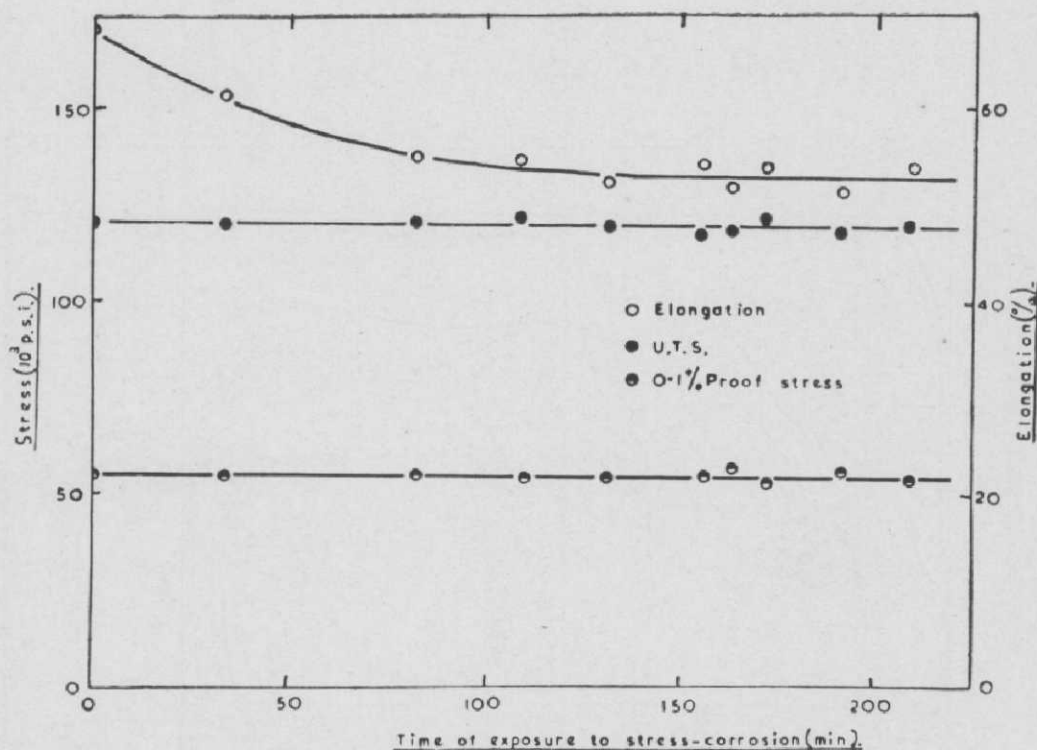


FIG. 4(a) — VARIATION OF MECHANICAL PROPERTIES WITH TIME OF EXPOSURE TO STRESS-CORROSION CONDITIONS. STEEL 18-8 STRESSED AT 48,000 LB./IN.², 153°C.; SPECIMENS REMOVED BEFORE THE START OF THE RAPID POTENTIAL FALL

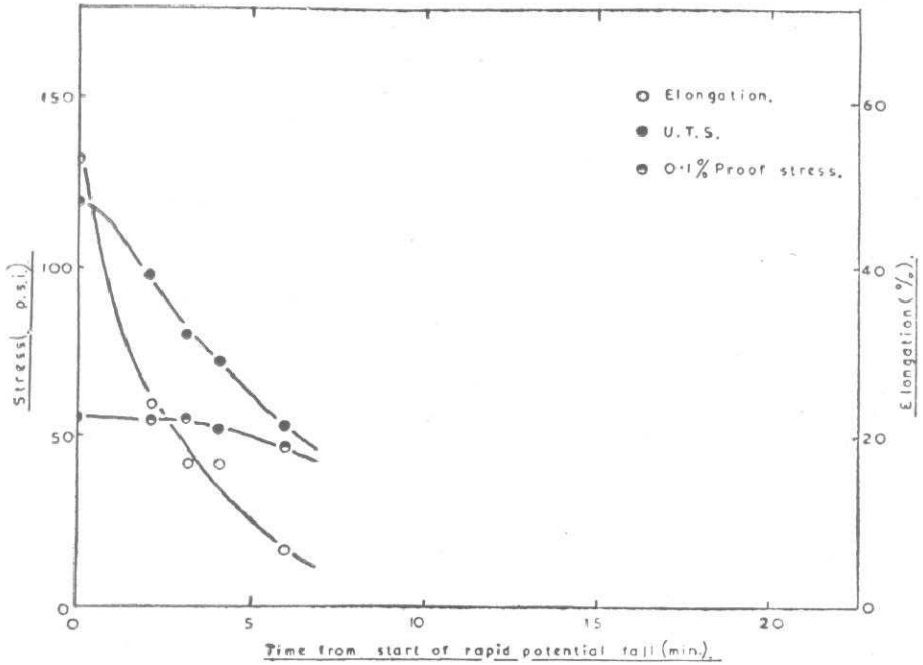


FIG. 4(b) — VARIATION OF MECHANICAL PROPERTIES WITH TIME OF EXPOSURE TO STRESS-CORROSION CONDITIONS. STEEL 18-8 STRESSED AT 48,000 LB./IN.², 153°C.; SPECIMENS REMOVED AFTER THE START OF THE RAPID POTENTIAL FALL

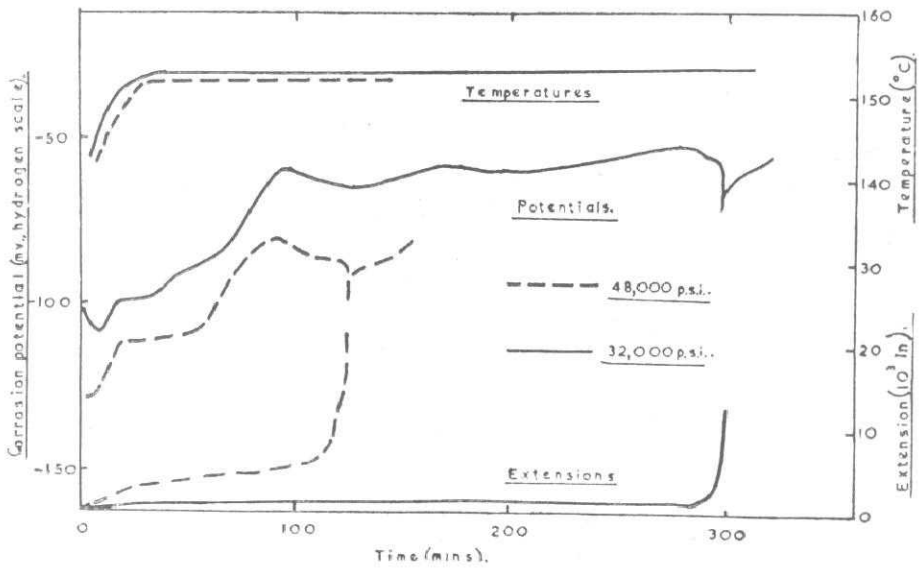


FIG. 5 — EXTENSION/TIME, POTENTIAL/TIME, AND TEMPERATURE/TIME CURVES. STEEL 18-10-Nb, STRESSED AT 48,000 AND 32,000 LB./IN.²

completely eliminated: under such conditions, the initial oxide film on the metal is rapidly removed, and the potential/time and extension/time relationships are typified by those of Fig. 6.

It is also evident that the actual cracking process is quite rapid: the period of rapid potential fall, corresponding to crack propagation through some $\frac{2}{3}$ of the total cross-section of the 0.02 in. (0.05 cm.) diameter wire, was always in the range of 5-30 min., indicating a rate of crack propagation of some 1.4 mm./hr.

Influence of Variation of Applied Stress —

For all the steels studied, increase of applied stress, S , caused a decrease in the time to fracture, t_f . Typical results⁹ are shown in Fig. 7; all the $\log_{10} t_f/S$ plots can be similarly represented by two merging straight lines. This general form of the results may have been responsible for the earlier suggestions of a threshold value of applied stress below which stress-corrosion cracking cannot occur; but our results indicate that although the onset of cracking is indeed greatly delayed at applied stresses below that corres-

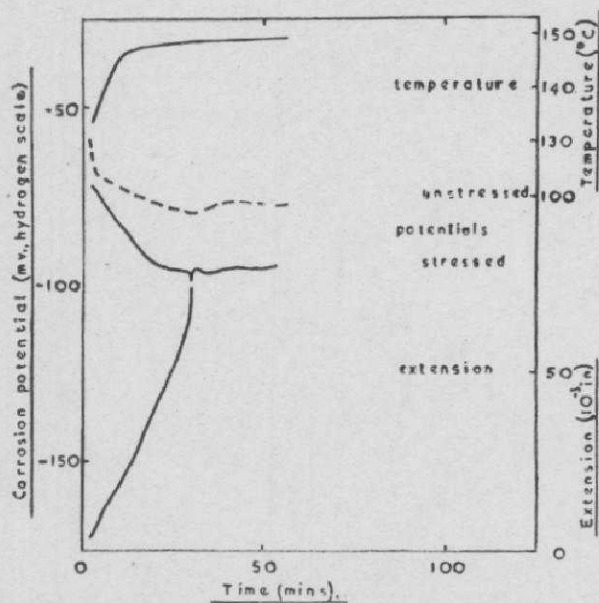


FIG. 6 — EXTENSION/TIME, POTENTIAL/TIME AND TEMPERATURE/TIME CURVES, IN 42 WT. PER CENT $MgCl_2$ AQ. CONTAINING 0.02 VOL. PER CENT CONC. HCl . STEEL 18-8, STRESSED AT 48,000 LB./IN.²

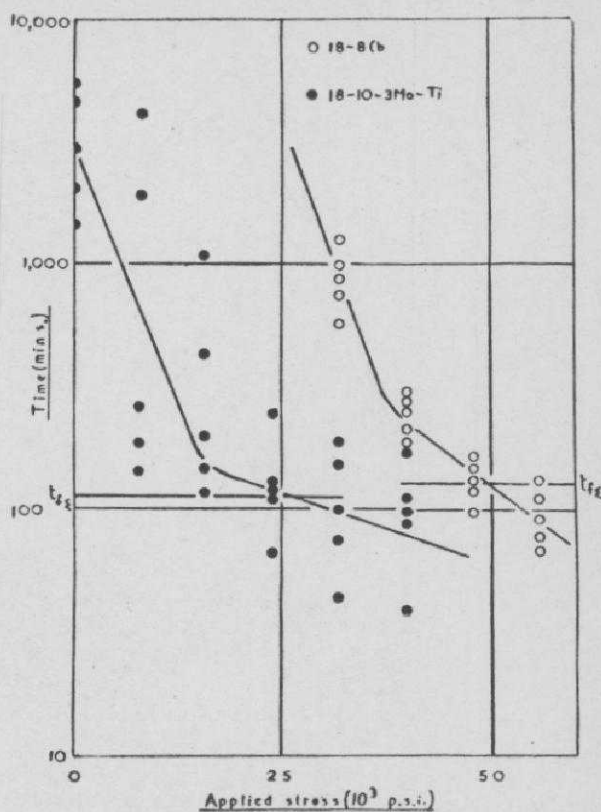


FIG. 7 — VARIATION OF TIME TO FRACTURE WITH APPLIED STRESS. STEELS 18-8, 153°C.; 18-10-3 Mo-Ti, 152°C. $t_f(\Sigma)$ IS DEFINED IN THE TEXT

ponding to the fairly sharp change of gradient of the $\log_{10} t_f/S$ curve, it is probably quite unsafe to conclude that it can never occur at stresses below a threshold value. Furthermore, the 'knee' of the $\log_{10} t_f/S$ curve for any one steel is altered by alterations of heat and mechanical treatment.

Potential/time curves such as those of Fig. 8⁹ show that the shortened time to fracture found with increased applied stress is almost entirely due to a shortened induction period: the rate of crack propagation is scarcely influenced by alteration of applied stress. The potential at any stage of the induction period is only slightly lowered by increase of applied stress. Thus, higher applied stresses initiate cracking after less preliminary corrosion damage.

The knee in the $\log_{10} t_f/S$ curves always occurs at stresses a little lower than the stress Σ required to make the total time of

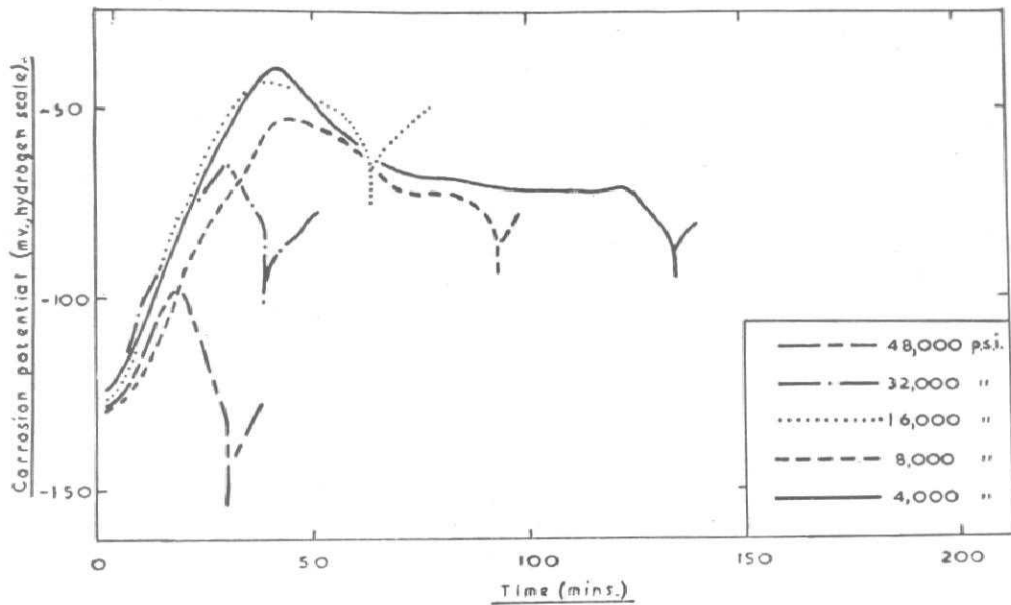


FIG. 8—TYPICAL POTENTIAL/TIME CURVES FOR VARIOUS APPLIED STRESSES. STEEL 18-8-Ti, 151°-154°C.

fracture ($t_f(\Sigma)$) equal to the time of film repair before general film breakdown for an unstressed specimen plus the average time of crack propagation. Thus the two parts of the $\log_{10} t_f/S$ curves correspond approximately to cracking initiated before and after general film breakdown⁹.

Influence of Temperature—Variation of temperature between 125° and 154°C. causes a very considerable change in the time to fracture of 18-8 type steels in 42 wt. per cent aqueous magnesium chloride solution: Fig. 9 shows results for a plain 18-8 steel⁹. The variation is mainly in the induction period, although there is also a definite variation in the rate of crack propagation. Approximate values for the apparent activation energy of the processes of the induction period and of crack propagation can be calculated as respectively 40 and 10 K.cal./g. mol.

Influence of Composition of Steel—Experiments with all the usual grades of 18-8 type steels, tested as received, have given qualitatively similar results. The quantitative differences appear to depend only indirectly on composition in so far as

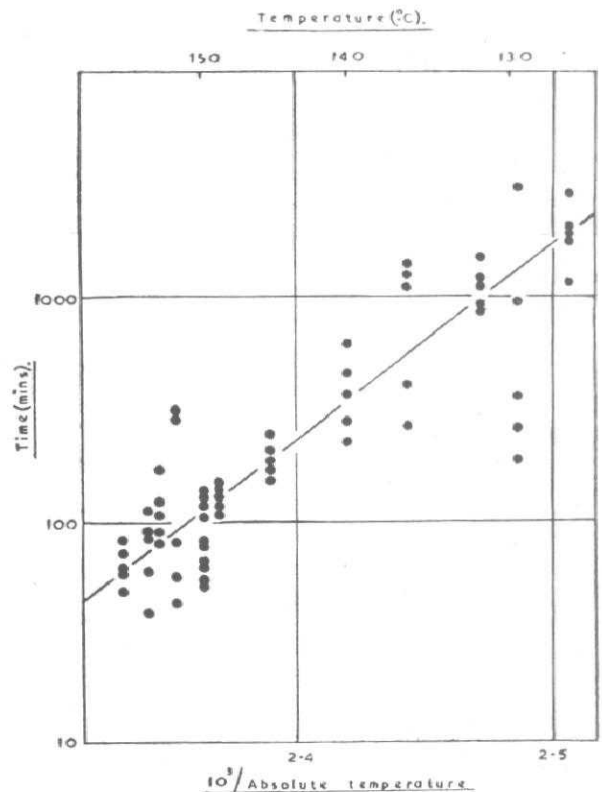


FIG. 9—VARIATION OF TIME TO FRACTURE WITH TEMPERATURE. STEEL 18-8, STRESSED AT 48,000 LB./IN.²

this influences the initial state and repair-breakdown behaviour of the oxide film and the susceptibility of the steel to cold-work, discussed below.

*Fully Softened, Pre-strained and Refrigerated Materials*¹⁰ — In the experiments so far discussed, with as-received wires, certain compositions (notably 18-8-3 Mo, and one 18-8-Ti steel) fractured in quite short times at very low applied stresses. It seemed likely that either the residual stress, or the strain or both, produced by reeling and unreeling of the fully softened wire were sufficient to produce this result in compositions especially susceptible to cold-work. Consequently, selected lengths of several wires were straightened, very carefully annealed in argon, quenched, pickled, aged in air and then tested as truly representative of the fully softened condition. Other similar fully softened specimens were pre-strained in tension, others were surface-strained by mechanical polishing, and yet others were refrigerated in liquid oxygen at -184°C .

Experiments¹⁰ showed that truly fully softened 18-8-3 Mo and 18-8-Ti steels, stressed for the first time (after softening) at 154°C ., do not fracture in the short times at low applied stresses found with the as-received wires. Room-temperature pre-straining (either bulk or surface), or refrigeration, of fully softened material in general shortened the time to fracture, again almost entirely by shortening the induction period. The quasi-martensite formed by such treatments appears to be one important factor in crack *initiation*, but to have little or no effect on crack propagation.

The effects produced by pre-straining or refrigeration on different 18-8 type compositions are quantitatively very different. Quite small amounts of cold-work produced large effects — rapid onset of very dense stress-corrosion cracking — on duplex steels and on those that are the more readily hardened by quasi-martensite formation. Plain 18-8 steel, however, gave results much less affected by cold-work.

Qualitative Mechanism of Stress-corrosion Cracking

The experiments indicate clearly that there are two stages in the overall phenomenon of fracture of 18-8 type steels by stress-corrosion cracking:

(i) The induction period, during which electrochemical reactions leading to corrosion, but substantially no mechanical damage, occur, and at the end of which cracks are initiated.

(ii) The propagation of the cracks.

It is convenient to consider these separately.

The Induction Period and Crack Initiation — The processes of the induction period are evidently entirely electrochemical, very similar to those found under conditions leading to local corrosion on tin¹³, iron¹⁴ and aluminium¹⁵ and scarcely influenced by any applied stress. During film repair, very slight corrosion at the base of the pores in the film must occur to provide the film-repairing material: during film breakdown (if this stage is reached) much more extensive corrosion damage sets in.

It has often been suggested that preliminary corrosion damage can form pits that act as stress-raisers and consequently initiate cracking at applied loads giving stresses apparently well below the fracture stress. While this may well be true of stress-corrosion cracking associated with intergranular corrosion, where the 'pits' can be deep and sharp, it must be rejected for the present case. The visible pits formed, as observed microscopically on sections of wires exposed with low applied stresses for long induction periods, are saucer-shaped rather than sharp, and tend to become flatter as corrosion proceeds. Moreover, cracking is initiated at once, without an induction period, when the original oxide film is quickly removed as in the acidified solution, and here there is no preliminary pitting at all. Crack initiation appears, in fact, to depend on the mere exposure of *bare* metal to the solution: the more

bare metal exposed, the greater the probability of crack initiation and the smaller the necessary applied stress.

The bare metal surface must contain a distribution of small regions of disarrayed metal, such as grain boundaries, sub-grain boundaries, the surface ends of dislocations, and strained regions produced by local quenching stresses, during cold-work, or by actual phase change. Disarrayed regions may be expected to be approximately randomly distributed in space, and the degree of disarray will also be randomly distributed. When metal is dissolving anodically, the disarrayed regions will dissolve somewhat more easily than the more orderly parts: and if stress is present perpendicular to the direction of anodic dissolution, it seems likely that it will facilitate the dissolution of disarrayed regions more than the orderly parts of the surface. Thus galvanic action between cathodic zones on the surface — oxide film or orderly metal — and a small, stressed disarrayed region may produce a *sharp*, perhaps sub-microscopic, pit following the disarrayed region in depth. Such a process of crack initiation would clearly be favoured by increase of the area of bare metal exposed (more disarrayed regions and thus greater probability of a sufficiently intense one), by increase of applied stress (sites of less intense disarray now activated), and by any treatment such as cold-work or refrigeration that is known to produce one or another kind of disarray — thus well fitting the experimental facts.

Crack Propagation — When a sharp, stress-raising sub-micro pit has been initiated by the mechanism suggested above, its advancing edge will be in a condition of high stress and this may well produce yielding. We think that metal in such a state is in a still more favourable state for preferential anodic dissolution and that the crack propagates by the continuous anodic dissolution of its advancing edge at a high current density. A rate of crack propagation of 2 mm./hr. would

require a current density of 1440 mA./cm.² at the advancing edge and, if the edge is 1000 Å wide, a current of some 3×10^{-1} μA. per crack. These magnitudes are not unreasonable. Ferrous materials can be anodically dissolved at current densities equivalent to penetration rates of over 1 cm./hr.¹⁶ provided that the accumulation of compact corrosion products is prevented — here, by the continuing strain at the advancing edge and by the 'yawning' of the crack. Also, the total current required from the oxide-film cathode to propagate the observed number of cracks can be estimated as some 40 μA./cm.²: and we find experimentally that a lowering of potential of the order of that found during crack propagation, 50 mV., is produced on an unstressed specimen by the application of an external cathodic current density of some 20-80 μA./cm.².

We have discussed this mechanism of crack initiation and propagation in more detail elsewhere⁹.

Experimental Results II

Cathodic Protection.—Mears, Brown and Dix⁵ observed qualitatively that the stress-corrosion cracking of 18-8 type steels can be prevented by mild cathodic protection, and Edeleanu¹⁷ has recently demonstrated a similar phenomenon for aluminium alloys. In a series of experiments to be detailed elsewhere¹², we have obtained the following results:

(a) Crack initiation, ordinarily found on an 18-8 specimen stressed to 48,000 lb./in.² in boiling 42 wt. per cent aqueous magnesium chloride at 154° after some 2 hr., was delayed for some 50 hr. by the continuous application of a constant cathodic current-density of *c.* 30 μA./cm.² and for more than 250 hr. (probably indefinitely) by current densities > 50 μA./cm.². During the passage of current, a dark film formed on the surface of the metal, and after its formation smaller current densities (e.g. 15 μA./cm.²) were sufficient

to maintain protection. This film doubtless contains magnesium hydroxide, and its additional protection is similar to that afforded by the 'calcareous' films deposited on mild steel cathodically protected in seawater.

(b) Crack propagation, ordinarily occurring under the above conditions at some 2 mm./hr. and leading to fracture of the wire specimen in a few minutes, was *stopped immediately* and *indefinitely* by the continuous application of a cathodic current density of $> c. 170 \mu\text{A./cm.}^2$. Smaller current densities slowed down the rate of crack propagation and if $> c. 80 \mu\text{A./cm.}^2$ eventually arrested it altogether. On the other hand, small applied anodic current densities increased the rate of crack propagation.

These results afford very strong evidence for an electrochemical mechanism of the processes of the induction period and of crack propagation itself, and are quantitatively consistent with the detailed mechanism proposed above.

Practical Considerations

Several points of interest in the practical use of 18-8 type steels are suggested by the present work.

(1) There is evidently no true threshold applied stress that can be specified for a particular steel, above which stress-corrosion cracking may occur and below which it will *never* occur. Even the apparent threshold stress below which stress-corrosion cracking will occur *only after a very long period* is markedly influenced by the heat and mechanical treatment of a steel, some steels being much more influenced than others. Since in fabricated structures it is quite impossible to ensure that all the metal is in the fully softened state, or indeed in any specified state throughout, and furthermore since it is impossible to estimate residual stresses except in a highly qualitative way, any attempt to define even apparent threshold stresses can only lead to confusion.

(2) The prevention of the stress-corrosion cracking of 18-8 type steels in hot concentrated magnesium chloride solutions and similar brines by the adoption of particular alloy compositions is clearly impossible with all the usual grades, and seems unlikely to be achieved even by the adoption of more expensive higher-alloyed grades.

(3) The amelioration of this stress-corrosion cracking by modification of the environment is also an unpromising field. Anodic inhibitors are not practicable in concentrated chloride solutions; cathodic inhibitors are ineffective in reducing the already quite small overall corrosion rates; and the exclusion of oxygen to a degree rendering the cathodic process so slow as to delay the onset of cracking to an acceptable extent is scarcely possible in practice.

(4) Cathodic protection is by far the most promising method of ameliorating or indeed eliminating the present kind of stress-corrosion cracking. This method is often, properly, rejected for the protection of the interior of steam-raising or chemical plant, because the corrosion may be widespread and in narrow places, while the conductivity of the corrosive environment may be low. But in 18-8 type steel plant carrying corrosive concentrated solutions, the points most liable to stress-corrosion cracking may often be well known from experience, and are usually in quite limited areas where applied stress, residual stress and unfavourably treated metal combine to make conditions worst: thus *local* cathodic protection, with good 'throw' into quite narrow places owing to the high conductivity of the liquor, seems by no means impossible.

Acknowledgements

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References

1. HODGE, J. C. & MILLER, J. L., *Trans. Amer. Soc. Met.*, **28** (1940), 25.
2. ROCHA, H. J., *Stahl und Eisen*, **62** (1942), 1091.
3. SCHEIL, M. A., Symposium on Stress-Corrosion Cracking of Metals, Amer. Soc. Test. Mat. & Amer. Inst. Min. Met. Eng., 1945, 395.
4. FRANKS, R., BINDER, W. O. & BROWN, C. H., Symposium on Stress-Corrosion Cracking of Metals, Amer. Soc. Test. Mat. & Amer. Inst. Min. Met. Eng., 1945, 411.
5. MEARS, R. B., BROWN, R. H. & DIX, E. H., JR., Symposium on Stress-Corrosion Cracking of Metals, Amer. Soc. Test. Mat. & Amer. Inst. Min. Met. Eng., 1945, 323.
6. DAVIS, F. W., *Trans. Amer. Soc. Met.*, **42** (1950), 1233.
7. EDELEANU, C., *J. Iron & Steel Inst.*, **173** (1953), 140.
8. HOAR, T. P. & HINES, J. G., *J. Iron & Steel Inst.*, **177** (1954), 248.
9. HOAR, T. P. & HINES, J. G., *J. Iron & Steel Inst.*, (1956) (in the press).
10. HINES, J. G. & HOAR, T. P., *J. Iron & Steel Inst.* (in course of publication).
11. HINES, J. G. & HOAR, T. P., *J. App. Chem.* (in course of publication).
12. HINES, J. G. & HOAR, T. P., *J. Iron & Steel Inst.* (1956) (in preparation).
13. HOAR, T. P., *Trans. Faraday Soc.*, **33** (1937), 1152.
14. HOAR, T. P., *Trans. Faraday Soc.*, **45** (1949), 683.
15. EDELEANU, C. & EVANS, U. R., *Trans. Faraday Soc.*, **47** (1951), 346.
16. HOAR, T. P. & AGAR, J. N. (unpublished work) (1939).
17. EDELEANU, C., *J. Inst. Met.*, **80** (1951), 187.