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Some Contributions to the Present Aspects of the Mechanism of Stress-Corrosion Embrittlement

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ABSTRUCT

In this paper, a brief summary on the present situation of a research programme directed towards obtaining a better understanding of the mechanism of stress-corrosion embrittlement, or cracking, in two systems, stainless-steel/magnesium-chloride and brass/ammoniacal solution, is presented and discussed, which comprises the following aspects of the problem; (1) cathodic reactant in $MgCl_2$ solution; (2) apparent activation-energy; (3) delayed time to fracture; (4) delayed-fracture curve; (5) effect of solute atoms; (6) protective current-density; (7) effect of cold work; (8) chloride-cracking of martensitic stainless steel; and (9) ammonia-cracking of brass.

INTRODUCTION

Stress-corrosion embrittlement, or cracking, is one of the most complicated problem in the field of corrosion science because it is incorporated by perplexing mechanical factors. Although, in response to this, much experimental and theoretical ingenuity has been applied in an attempt to answer the puzzling question of why inherently ductile metal, especially f.c.c. crystals, can behave in an apparently brittle fashion in certain specific, corrosive environments, a large number of unknown factors involved have made it difficult to suggest a plausible mechanism with any confidence. However, aside from the 'tarnish-rupture theory' suggested recently on brass in ammoniacal medium (1-3), in which case cracking, it was described (3), is only mechanical and confined to characteristic black-oxide layer, commonly termed tarnish, proceeding by repeated formation and rupture of this layer, considerations based on the fundamental studies concerning the mechanism may be classified into two major categories, the 'single-step mechanism' that postulates only a strain-accelerated anodic dissolution and the 'dual-step mechanism' that postulates a brittle-fracture step followed periodically by the strain-intensified corrosion.

Reviewing a diversity of the mechanisms so far proposed, it seems likely that there are some areas still remained unclear. It is

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therefore deemed of interest to provide a basis of discussion by presenting some significant facets of the problem obtained in the present stage of a research project in progress now aiming at getting some useful informations on the mechanism of stress-corrosion embrittlement. The investigations described here were conducted mainly on stainless steel in boiling-concentrated $MgCl_2$ solution and partly on brass in ammonia-containing media at room temperature, and all the results are summarized in brief without showing full details given of the experimental procedures and techniques.

BRIEF SUMMARY

1. Cathodic Reactant in $MgCl_2$ solution

Most tests on assessing for the susceptibility of stainless steel to stress-corrosion embrittlement have usually been performed by using a concentrated $MgCl_2$ solution boiling at 154 C, the 'Scheil solution'. In this case, a vital clue to the mechanism is whether the cathodic reactant being dissolved oxygen or hydrogen ion. Though Hoar and Hines (4-8) have inclined to taking dissolved oxygen for it, this point needs to be corroborated all the more since some allusion to hydrogen-uptake(9) has found increasing interest in spite of other argument against this view (10) in case of austenitic stainless steel in the Scheil solution, along with in other case of martensitic stainless steel in salt-containing environment (11-14). To give evidence of which reactant is predominant in boiling-concentrated $MgCl_2$ solution, some exploratory investigation was taken place, results of which are summarized as follows.

(1) Analysis of initial fraction from boiling $MgCl_2$ solution with different concentrations covering 10 to 60 per cent $MgCl_2$ revealed only HCl as the decomposition product.

(2) pH value of the Scheil solution was approximately zero when extrapolated from directly-measured pH values of weaker, lower temperrature and smaller concentration, solutions and, when estimated indirectly from the limiting-diffusion current-densities, 15.7 and 4.45 mA/ sq cm, observed on iron and chromium electrode respectively in the Scheil solution, it ranged between 0.65 and 1.85 on the assumption that hydrogen ion could diffuse with the velosities covering 0.005 to 0.025 mm/sec.

(3) Steady potentials of a platinized-platinum electrode in boiling $MgCl_2$ solutions, which were taken as indicating a measure of oxidizing power of the solutions, were nearly +150 mV in the Scheil solution and nearly 0 mV in 10 per cent $MgCl_2$ solution, becoming more noble with increasing concentration.

(4) Steady potential of a platinized-platinum electrode in 35 per cent $MgCl_2$ solution, which became gradually less noble from +635 mV at 20 C to +550 mV at 95 C, falled abruptly near the boiling point at which +100 mV was observed, suggesting a transition of the cathodic process from the reduction of dissolved oxygen to that of hydrogen ions.

(5) Most of exchange-current densities obtained by analizing data of cathodically polarized potentials on metals and alloys in the Scheil solution, determined potentiokinetically at a constant change in the potential, say, 10 mV/min, were, differed from that reported by Hoar and Hines (4), in the order of 10^{-6} amp/sq cm.

(6) Vaporfractometric analyses of gases resulting from corroding metals and alloys in the Scheil solution revealed that no others than hydrogen were liberated, as shown in Figure 1, in which each deceleration phase observed on the liberation-curves was taken as being derived from the activity product of hydroxy chloride formed.

Above evidences support the view that, in the Scheil and the like solutions, hydrogen must predominantly be reduced at the cathode.

2. Apparent Activation Energy

Apparent activation energy for embrittling process of Type 304 and Type 431 (17Cr-2Ni) stainless steels was estimated from the temperature-dependence of time to fracture in 35 per cent $MgCl_2$ solution, pH value of which had beforehand been adjusted to 3 at 22 C and boiling solution of which will subsequently be refered to as the 'acidified 35 per cent, $MgCl_2$, solution', with or without taking into account of a certain error arising probably from decrease in pH value with increasing temperature of the test solution, assuming, for convenience sake, two of the rate, in one, the reciprocal of the time to fracture and, in two, the embrittled area measured by a binocular microscope was divided by the time to fracture. After proving the Arrhenius plot to be linear, the activation energy was plotted against applied engineering stress, load divided by the initial cross-sectional area. Conclusive view obtained from this investigation is summarized as follows.

(1) Both considerations of selecting the rate and of adjusting the pH value brought on no remarkable merit for estimating the activation energy from the temperature-dependence of time to fracture in both cases of steels.

(2) The activation energy for martensitic Type 431, oil-quenched from 1060 C, was straightly and markedly correlated with applied stress, while austenitic Type 304 exhibited a moderate dependence on the applied stress and manifested a break at an applied stress corresponding nearly to 0.03 per cent proof yield strength of the steel, as an example shown in Figure 2, where no account was taken of the change in pH value, adopting the reciprocal rate.

(3) Estimating from above illustration, the activation energy, Q cal/g-mole, could be correlated with applied stress, σ kg/sq mm, as $Q = 12100 + 298\,\sigma$ and $Q = 15500 + 112\,\sigma$ respectively below and above

the yield-strength-level for Type 304, whereas $Q = 5500 + 448\,\sigma$ for Type 431 over the stress range applied.

A process of any kind may be analized kinetically as shown above and, in this case, plastic flow and therefore ductile fracture of large class of materials is also thermally activated and, it is postulated furthermore that activation of such process is aided by applied stress. For instance, when the applied stress causes yielding, it also does work and, therefore, this work is subtracted from the activation energy for the unstressed case because it is supplied by the mechanical means but by thermal energy and, for the reason, it should not be included in the expression for the temperature-dependence. True brittle fracture, on the other hand, may not be thermally activated, that is temperature-independence, from the nature of cleavage, but takes place at a speed that is probably that of propagation of an elastic disturbance.

Moreover, the activation energy of the Arrhenius equation is really the activation enthalpy which describes only the temperature-dependence of the rate and, hence, does not include entropy change, but, if a probable assumption that the entropy does not depend materially on the applied stress be allowed, the energy may be corresponded to the activation free-energy which determines the reaction rate usually in such the manner as the lower the energy the greater the rate results in under a given temperature , and the smaller the rate coefficient follows. This contradicts to the experimental data and, then the estimated activation-energy may include a specially valued function of applied stress. Thus, from consideration of the present results, a plausible relation between the energy and the stress may be expressed as follows,

$$DH^*(\sigma,T) = DH^*_o + V^*_x\sigma - V^*\sigma$$

where $DH^*(\sigma,T)$ is the activation enthalpy observed as a function of applied stress and absolute temperature, DH^*_o is that for corrosion process under stress-free condition, V^* is so-called the 'volume of activation' attributable to the mechanical work which, in case of stress-corrosion embrittlement, may naturally be associated mainly with a process caused by mechanical action after accomplishing the embrittling process and partly with other mechanical work as plastic constraint around the notches formed by corrosion, and V^*_x is an unknown 'volume of activation' that needs to be thermally activated without any connexion with plastic flow, which, it was infered, might be associated to such process as adsorption, absorption, diffusion, or change in composition etc., but the exact nature of it is beyond comprehension now.

The order of magnitude of the activation energy observed on the austenitic stainless steel coincided roughly with that estimated in similar case by Hoar and Hines (4,5), but the view that the value being equivalent to a considerable temperature coefficient for any corrosion and stress-corrosion-cracking process in the Scheil solution controlled wholly or partly by oxygen-reduction process in not necessarily correct because the energy has a positive dependence on applied stress. The greater dependence of the energy on applied stress and the smaller activation energy extrapolated to the unstressed case observed on martensitic Type 431 would imply some significant difference of the embrittling process from that of austenitic Type 304, but this is a sort of thing that has still to be investigated.

3. Nature of Delayed Time to Fracture

Delayed fracture has especially been appreciated as a salient features of hydrogen embrittlement but, physically speaking, other fractures of crystalline solid, aside here from amorphous solid, resulting from a certain specific combined action of stress and environment, liquid and gaseous but solid now, may be comprised in the category of delayed fracture, and, to say distinctly from an idea of time-function, delayed fracture and therefore delayed time are no more than a relative terms, so far as the two fundamental steps in fracturing process, the crack initiation composed of the nucleation of stable cracks, that are fiberous or ductile one, followed by the growth of them to an instable size and the crack propagation and, in most cases, a successive repetition of the two steps, be allowed.

That, in stress-corrosion embrittlement, time to fracture is made up of an induction period in which the cracks initiate plus a period of crack propagation has originally been mainly proposed by Hoar and Hines (5,6) in the investigation on austenitic stainless steels in the Scheil solution, in which they have drawn a distinction between the two periods at 5 to 30 minutes before the final fracture and described that propagation period occupies above-mentioned time and substantially all the cracking leading to extention of the test pieces and loss of the strength occur during this period and, furthermore, the rate covering 0.5 to 3.0 mm/hour was estimated basing upon this period too.

Later, Hines (7) modified above view of the propagation period by dividing it into two more periods, fine-crack propagation and open-crack propagation, but took a previous view that cracks can initiate fairly after the corrosion potential has passed over a potential-saddle or hump usually observed in this system with time elapsed. By other view of Barnartt and Rooyen (15) on similar case, it was supposed that very fine cracks do appear just after the corrosion potential has reached over the potential-saddle, where, it was suggested by Hoar and Hines, local breakdown of protective film, that is selective corrosion, bigins to occur.

In this context, origin of the delayed time, which, in this case, implied the induction period, was recently discussed by Uhlig and Sava (16), who draw attention to the investigations which prompted Hoar and Hines to attribute the induction period to the time necessary for the $MgCl_2$ solution to damage the oxide or passive films on the surface of the specimens, and to make the point that pre-exposure of the specimens to the test solution with or without applying stress or to air at high temperature, 200 or 400 C, constitutes a process of heat-treatment, and that metallurgical aging effects, as well as the film effects, have therefore also to be accounted for a mechanism explaining the changes observed in the cracking time. Uhlig and Sava followed up the exposure tests and concluded that the delayed time appears to be associated with the elevated temperature of the tests and with the time required by nitrogen and similar impurities to segregate at lattice-imperfection sites.

However, considerations of the present results cast some doubt on above views. The results are summarized as follows

(1) One evidence firstly pointed out is rather an accomplished fact which is inconsistent with the proposal of propagation period proposed by Hoar and Hines. That a rapid decrease in the corrosion potential, which is generally smooth in case of stainless steel but step-wise in case of brass, followed by an abrupt fall in the potential, which corresponds to the final fracture, can be observed only when any stress in excess of threshold is applied by dead-loading but by being bent, is indicative of that advancing of the embrittling process has no direct dependence on the change in the potential mentioned above, since by dead-loading the net stress must approximate eventually to infinite level while by being bent to zero.

(2) Figure 3 shows results of stress-corrosion-embrittling tests on Type 304 specimens suffering from a maximum fiber-stress of 28.2 kg/sq mm which was 4 kg/sq mm beyond the 0.03 per cent proof yield strength, by one-point bending in the Scheil solution. Curve A on the coordinates indicates a relationship between the corrosion potential and time elapsed for unstressed specimen and curve B that for stressed specimen which was accepted as a measure for selecting nine levels of potential maintained potentiostatically at constant as shown dotted lines with short distance, at which the specimen electrodes were exposed to the Scheil solution for 24 to 30 hours. Mode of the cracking after each run is given by legends illustrated, where CF is complete fracture with many other large cracks, MLC many large cracks, MMC many moderate cracks, MSC many small cracks, MFC many fine cracks and SP many crack-like pits that were very much shallow.

Even the test at potential -175 (hydrogen scale) which was

about 10 mV below the initial potential produced many fine cracks because of local-anodic current still remained to flow and, as a matter of course, over the potential range between the initial and the hump-potentials, where, according to Hoar and Hines, corresponds to time needed for film-reparing, all the potentials controlled were well enough to give rise to large to fine cracks. Above evidences are deemed to justify that stress-corrosion embrittlement can be induced so long as the local-anodic current persists to flow, without the potential to be carried above the potential-hump, which in some cases can be observed whereas in others can not according as varying both metallurgical and environmental factors. This also implies that the induction and propagation periods defined on the potential and time-to-fracture coordinates have little or no significance and, perhaps that whenever the applied stress being sufficient to cause yielding, the time required for initiating cracks of stainless steels in the $MgCl_2$ solution may be so much short that it can scarcely be recognized.

(3) The embrittled depth by stress-corrosion was measured microscopically on Type 304 specimens with no parallel and the minimum cross-section of 2 mm x 3 mm as a function of time after sectioning the center portion to the mid-thickness or to the mid-width after the specimens had been exposed to the acidified 35 per cent solution under applying a constant stress 35 kg/sq mm by dead-loading, results of which are shown in Figure 4, in which data presented indicate the average of long cracks measures at least in three runs.

Though advancing rate of the embrittlement from the side of the specimens was somewhat greater than that from the face because of more corrodable nature of the side and of residual stress remained after milling operation, influence of which being markedly pronounced in the early stage of measurement, the embrittled depth, d mm, was most pertinently correlated with time, t minute, as $d = 0.0002t^2$ for the side-advancing and $d = 0.00014t^2$ for the face-advancing, as given curves A and B respectively, if a very small penetration by uniform corrosion was allowed to neglect. Similar possivility that the curve could pass through the origin of the coordinates was suggested by Engell and Bäumel (17), whose data represented by points in their illustration can be arranged on a curve, $d = \text{constant} \times t^{1.8}$, with much confidence, which obtained on mild steel in boiling 55 per cent $Ca(NO)_2$ solution, where the steel manifested, contrary to stainless steel in this case, intergranular cracking. This possibility is deemed to warrant consideration that the cracking has to commence whenever yielding clean-surface of the specimens is brought into intimate contact with the $MgCl_2$ solution, provided the surface being suffered from some plastic deformation.

(4) Maintaining the corrosion potential of stainless steel, Type 304, in the acidified 35 per cent solution at a constant value by a potentiostat on the way of spontaneously rapid fall in the potential to less noble direction, that is also on the way of rapid increase in the extension of the specimens, which is also corresponded to a short period immediately before the final fracture, resulted in cessation of the cracking above a critical value of the potential or a critical value of the extension interupted, below or above of which the cracking leading to the final fractureing could never be prevented.

This is, of course, indicative of that stress-corrosion embrittlement can be advanced on up to a certain level of the potential fell to less noble direction just before the final fracture or that of extension just before it, but nevertheless, this can never reject any advance of the embrittlement done till that time, and, rather justifies that the final fracture had to be caused mainly by mechanical action.

(5) Figure 5 indicates change in corrosion potential with time observed on 60/40 brass in double-distilled water at room temperature, in which curve A was observed on unstressed specimen and curve B on stressed specimen at 30 kg/sq mm by dead-loading. In this system, any crack was recognized only after the corrosion potential had dropped abruptly at a point P but before it, when the stressed specimens were inspected microscopically and, after drop in the potential, small stepwise changes in both the potential and the extension were followed untill the final fracture occurred. The time required for crack initiation varied from about 3.5 to 4.5 hours, and specimens were covered with very much thin films, revealing very faint interference colour. It is apparent that, in some systems, the delayed time to initiate the cracking can exist and that temperature-effects causing some metallurgical change in susceptible alloys is not always necessary factor in causing the embrittlement.

Overall conclusion in this section is that the time required for crack initiation in stress-corrosion embrittlement may comprise a delay time necessary for susceptible and yielding clean surfaces being contacted with a certain functional media, which in some cases may be negligible and in others not negligible according to strength of corrosive media and to level of applied stress and, thereafter true advance of the cracking can start.

4. Features of Delayed Fracture-Curve

Usually, stress-corrosion-embrittlement tests have been performed to obtain a correlation of the susceptibility in terms of time to fracture with applied engineering stress below some level but above the yielding stress. In these case, data obtained are most adequately summarized in plots of applied stress versus logarithmic-time-to-fracture in case when the stress was applied directly by dead-loading, but of both logarithmic scales when applied indirectly by being bent and, furthermore, both plots usually show two straight lines with a intersection respectively and nearly parallel lines with the abscissa, which are commonly called as the threshold stress below which no fracture can practically be observed.

Aside from the latter case, characteristic shape of the former plots is given in Figure 6, which obtained on Type 304 in 35 per cent $MgCl_2$ solution with aforementioned pH value, say, 3 at 22 C, at different test temperatures, 80, 100 and 124.5 C (boiling point), respectively. Three starting points of the plots were corresponded to the ultimate tensile strength of the material at each test temperature and, in the region A instanced by the results for test temperature 100 C, dependence of the time to fracture was minor, in the region B it was conspicuous, in the region C it was considerable, and, in the region D it was nearly negligible. It is likely that in the region A fractures were under predominant control of pure-mechanical action while in the region D under pure-corrosive action, say, under uniform attack, between which the subject was embrittled by stress-corrosion. The intersections observed in this test programme and on other austenitic stainless steels including most Types of 300 series and Cr-Mn-Ni types were corresponded much more fitly with the 0.03 per cent proof-yield strength respectively than 0.1 or 0.2 per cent one reported elsewhere (5, 18), but other types of susceptible steels as 17-4PH, 17-7PH, Types 414 and 431 manifested more complicated behaviours according with heat-treatment applied and, in most cases of brass in ammoniacal solutions, the intersections were situated also at the proof-yield strength, below which, however, brass, 70/30 and 60/40, indicated suddenly very long life.

It may be suggested that the threshold stress so-called would be a superficial limit indicated in laboratory tests, since it is apparent that causing yielding of susceptible surfaces exposed to a certain specific media must provide necessary conditions for crack-initiation and, therefore, only stress just capable of causing the yielding of denuded surfaces may be a true limit, above which it may take time observable in some cases but not take in others, below which, however, it has to take time always in order to establish the conditions mentioned above, and, thus, it is infered that advance rate of stress-corrosion embrittlement may be proportional directly to net stress subtracted the proof stress from actually working stress, but this relation provides a baffling problem to be solved and, furthermore, if the dual mechanism be allowed to accept, it can never divide the advance rate into two rates of each step.

5. Effect of Solute Atom

Recently, particular attention has increasingly been arrested on nature of some constitutional defects induced by plastic deformation in solid solution, especially in f.c.c. crystals, such as stacking fault and local order in respectof causative factors leading to both restricted slip and preferential reactivity, which, it has been known, associate congenitally with the strengthening mechanism in solid solution. In this respect, consideration has been made mainly of the role of interstitials as carbon and nitrogen and partly of the role of substitutionals, but opinions on the influence of both type of solutes are not always congruent as discussed by many authorities (19-28). However, common opinions have inclined to allow the harmful effect of the interstitials and, in some cases, of substitutionals capable of increasing restricted slip. In the light of the present investigation, it is taken that there are still some rooms for discussion on the point concerning with the effect of solute atom, results of which are given below.

(1) Figure 7 shows stress versus time-to-fracture curves obtained in the acidified 35 per cent, $MgCl_2$, solution by dead-loading-method on three heats of vacuum-melt stainless steels with the following composition; EV1, carbon 0.015, nitrogen 0.038, molybdenum 2.38, nickel 14.63, chromium 17.09, per cent; EV2, carbon 0.007, nitrogen 0.008, nickel 9.36, chromium 17.55, per cent; EV3, carbon 0.029, nitrogen 0.040, nickel 10.56, chromium 18.89, per cent, and on three heats of air-melt stainless steels with accidentally raised nitrogen; 302N, carbon 0.12, nitrogen 0.15, nickel 8.25, chromium 18.18, per cent; 304N, carbon 0.06, nitrogen 0.15, nickel 8.69, chromium 18.64, per cent; 316N, carbon 0.019, nitrogen 0.13, molybdenum 2.89, nickel 11.94, chromium 17.71, per cent. The results indicated that with the exception of useful effect of nickel, no essential difference could not be observed among the steels.

Martensitic transformation in f.c.c. structures is diffusionless and not activated thermally as well accomplished, and may be taken place by atomic translation fundamentally driven by strain energy resulting from the presence of any solute atom according to the size effect and the trend to disordering f.c.c. structure and, on the other hand, there may be a natural sequence obeying to change in the interfacial energy in steps as austenite to α martensite and, therefore, there is no promise that 18-8 type stainless steels can undergo a transformation beyond h.c.p. structure by temperature-effect afforded by the boiling $MgCl_2$ solution. Both carbon and nitrogen in stainless steels have similar trend to stabilize austenite, but yet disparate properties in other points. Thus, if it touches on the effects on the susceptibility, much more searches into these points may need also to be done.

(2) It is rather a surprising fact that stainless steels including Fe-Ni, Fe-Cr-Ni and Fe-Cr-Mn-Ni classes, become susceptible to stress-corrosion embrittlement in the chloride media regardless of their crystalline structures becuase of the presence of an adequately small amount of nickel in them whereas become insusceptible because of an adequately large amount of it, and, moreover, to answer the question of why only nickel does so is very much more difficult than interest, since other substitutionals than nickel usually added to traditional stainless steels give no observable difference in their susceptibility, even though opinions on every particular effect have always not be agreeable along with diversified view concerning their influence on restricted slip (22, 25, 26, 29-32).

Aside from fault-consideration, it is firstly pointed out, in this context, that nickel, as well accomplished by Smialowska and Smialowski (33), indicates similar behaviour to palladium in the interaction between hydrogen, for instance, in the solubility of hydrogen and in the faculty of hydride-formation. Thus, nickel may stabilize hydrogen as atoms in the vicinity of metal/solution interface, provoding an expedient conditions for absorbing hydrogen into very much thin layers of susceptible surfaces. This view, however, does not necessarily concede a possibility of hydrogen embrittlement rate of which may be controlled by the anomalous diffusion.

Secondly, nickel in the $MgCl_2$ solution, as affirmed by the present investigation, corrodes hardly and accelerates other attendant elements as iron, chromium, manganese and copper, galvanically, while silicon, titanium, columbium and aluminum exhibits almost entirely no corrosion in the solution. Other salient finding was that corrosion of chromium, when coupled with iron, was accelerated unexpectedly by iron in such a manner as the extent of acceleration to become markedly increased with decreasing area of chromium specimen to that of iron. From consideration of the results, it being appeared that the restricted-slip region would be enriched in nickel as a result of the galvanic action, accelerating corrosion of chromium as well as of iron. Inferentially, chromium but nickel would segregate at the restricted-slip region. Thus, role of nickel relevant to the crack-initiation may, from corrosion viewpoint, be assigned to a significant influence on locally weakening action and on retaining hydrogen-atom by the presence of an adequate amounts, below or above of which, on the other hand, nickel may favour promoting of hydrogen discharge on overall surfaces of alloy, that is, increasing a tendency to uniform corrosion.

There is therefore some promise of improving the resistance of susceptible stainless steels by alloying film-reinforcing elements as molybdenum, silicon, and aluminum in some extent. The present studies on the susceptibility of Cr-Mn austenitic stainless steels including nickel verified this point, but the effects were small.

6. Protective-Current-Density

It is well-documented fact that stress-corrosion embrittlement can be protected by imposing cathodic current above a critical value, but this does not necessarily imply the embrittlement being cuased wholly by electrochemical action, because, even though the imposed current might prevent cracks to initiate, but nevertheless, there is no any reason of why the current might also prevent cracks to propagate in a brittle fashion. Furthermore, if it toughes on the critical-current-density, it must be described in connexion with applied stress-level. The work fell within this scope is summarized as follows.

(1) Shapes of curve, plotted time to fracture on the ordinate aginst potentiostatically-controlled potential or galvanostatically-controlled-current-density on the abscissa, are classified roughly into three. Type 1 is expressed approximately by a hyperbolic relation, as examplified in Figure 8, which was obtained on Type 301 stressed directly in the acidified 35 per cent, $MgCl_2$, solution as a function of applied stress, 15, 25 and 35 kg/sq mm, under potentiostatic control,and similar relation was obtained under galvanostatic control, from which Figure 9 was derived, which shows relation between the critical current density, amp/sq cm, and applied stress, kg/sq mm, where line 1 was constructed with the measured data and line 2 with data arranged on a hyperbola. It is apparent that, in this case, logarithm of the density was proportional to the applied stress above the 0.03 per cent proof yield strength but constant below it. Similar relationship was found on 60/40 brass in 0.94M NH_3 + 0.02 g Cr^{6+} ions/liter-solution at room temperature.

(2) Examples of other shapes of curve are shown in Figure 10, which were obtained on 60/40 brass in the Mattsson solution (34), $CuSO_4$ 0.05M + $(NH_4)_2SO_4$ 0.48M solution with adjusted pH 7.25, under stress level of 20 (curve 1), 25 (curve 2) and 30 kg/sq mm (curve 3) respectively. As can be seen, curve 1 and curve 2 indicated nearly parting limits standing up vertically on the potential axis, which was ascribed to accelerated uniform corrosion imposed by anodic polarization, while curve 3 revealed an intermediate behaviour between types 1 and 3 mentioned above because of moderately general corrosion. In this case, effect of cathodic polarization on time to fracture was fairly mild compared to similar results obtained on Type 431 in the acidified 35 per cent solution shown in Figure 11, in which marked influence of cathodic current on the life, as well as moderate influence of anodic current, can be seen.

The fact that occurrence of stress-corrosion embrittlement can be prevented by imposing cathodic current is indicative of the rate being controlled by corrosion process even if the dual-step mechanism could be accepted, the fact that the protective current has a critical value is indicative of the embrittlement being stifled only when stress-corrosion being suppressed, the fact that the critical density depends on applied stress above the proof-yield strength but does not below it, where it become constant, is indicative of the cracking being initiated only by plastic-surface-deformation in the specific solution and, lastly, the fact that the susceptibility in terms of time to fracture decrease with increasing uniform corrosion is indicative of preferential reactivity being essential for initiating cracks, which must be of environmental as well as of metallurgical.

7. Effect of Cold Work

Setting the background against a model predicts that failure in stress-corrosion embrittlement eventually occurs by the linking-up of cracks that have nucleated on planes consistent with the dislocation arrangement at the barriers, Robertson and Tetelman (35) have drawn attention to a curve presented by Hines (36), for 18-8 stainless steel exposed to the Scheil solution after varying amounts of prior cold work, and explained an interesting feature that pre-strain is more important in producing maximum susceptibility, say, minimum time to fracture, for the alloy tested at a stress of 5 tons/sq in. than at 14 tons/sq in. and, also, given an explanation that at some intermediate degree of pre-strain, conditions should be such that the alloy will be most susceptible, and should expect a maximum in a curve of susceptibility versus amount of prior cold work, as evidenced by the Hines' curve. However, attention also must be drawn, if it touches on the effect of prior cold work on the susceptibility, to a fact that it, as a matter of course, depends closely on choosing manner of applying stress, as shown below.

(1) Figure 12, obtained on Type 301 in the acidified 35 per cent solution under dead-loading method, indicates relation between time to fracture and pre-strain applied as a function of applied stress, which was chosen by such a manner as it becomes constant level, 20 kg/sq mm that was below the 0.03 per cent proof yield strength of 25.2 kg/ sq mm, and 35 kg/sq mm above it, or by such a manner as it becomes various level as the applied stress to become constant proportion to the individual proof yield strength of pre-strained subjects, 0.8 x $\sigma_{0.06}$, 0.8 x $\sigma_{0.03}$ and 1.2 x $\sigma_{0.03}$ respectively.

The maximum susceptability given by Hines near 7 per cent pre-strain, method of which was not described by him, was observed only at applied stress 35 kg/sq mm in this case of pre-straining by a tensile testing machine near 5 per cent pre-strain, but did not at others and, furthermore, applied stress below the yield point, 20 kg/sq mm, very much increased the life with increasing pre-strain, while applied stress having individually constant ratio to each yield strength resulted in either small increase in the susceptibility in case of the stress being above respective yield strength, or a gradual increase in the susceptibility after passing a minimum susceptibility near 7 per cent pre-strain in case of below it.

(2) Figure 13, obtained on 70/30 brass in an ammoniacal solution with 0.94M NH_4 + 0.02g Cr^{6+} ions/liter + 100 ppm Cl^- at room temperature, indicated similar relation observed on Type 301. The mother material had a tensile strength 32.9 kg/sq mm, 0.1 per cent proof yield strength 8.7 kg /sq mm, and elongation 77 per cent, but, for convenience sake, yield strength determined from the initial breakpoint on the stress-strain diagram constructed by a resistivity-type strain gauge respectively after the specimens being pre-strined by tension, was adopted, as given σ_y in the illustration.

The results, somewhat differed from that of above steel, indicated a marked decrease in the susceptibility even at smaller stress-level than above, say 15 kg/sq mm, but general trend given at the levels of 20 and 25 kg/sq mm was resembled to that of above steel excepting no indication of minimum susceptibility near low pre-strain. Furthermore, both levels with constant ratio to the yield strength, 0.8 x σ_y and 1.0 x σ_y, resulted in a rapid decrease in the susceptibility.

From consideration of the present results, it being appeared that retention of ductility may be of essential, especially in case when applied stress being above the yield strength and, on one hand, conservation of elasticity also may be of significant in case when applied stress being below it.

8. Chloride-Cracking of Martensitic Stainless Steel

In connexion with stress-corrosion embrittlement of austenitic stainless steels in the $MgCl_2$ solution, a particular interest can not help taking in the embrittlement of non-austenitic stainless steels in the same solution, since similar embrittlement of non-austenitic stainless steels, as well as of high-strength low alloy steels, including Types 400 series, precipitation-hardenable and maraging steels in neutral salt solutions, in sea water, in marine and industrial atmospheres containing chloride has increasingly been getting more attention than interest in the mechanism. Consequently, a great deal of investigations have been carried out by many authorities in an attempt to answer the question of which cause, hydrogen or stress-corrosion, being ascribed to the embrittlement. Although the amount of hydrogen produced during corrosion in the neutral solutions containing chloride commonly used in delayed-fracture tests is extremely small, and only a proportion of that evolved would be absorbed by the corroding material, extremely small amounts of hydrogen have been shown to be capable of causing delayed fracture. Thus, although the embrittlement in neutral chloride solutions is generally held to be due to stress-corrosion, the possibility that it is due to hydrogen embrittlement, or at least contributed to by hydrogen,was deemed to be taken into consideration, especially in the embrittlement phenomina of non-austenitic, especially of martensitic, stainless steels exposed to such acid solution as boiling concentrated $MgCl_2$ solution.

Summary of the present investigation conducted in this context with the aim of elucidating the mechanism underlying the embrittlement of non-austenitic stainless steels is as follows.

(1) The susceptibility of semi-austenitic 17-7PH and martensitic 17-4PH precipitation-hardenable stainless steels exposed to the acidified 35 per cent, $MgCl_2$, solution was principally influenced by the amounts of martensite present, as the results of 17-4PH shown in Figure 14, in which prolonged life observed on specimen solution-treated at 1300 C may be ascribed to appearance of some copper-rich phase. In 17-7PH steel, maximum susceptibility was shown by the subject solution-treated, and higher resistance was achieved by the treatment of T1050, R955 and R880 (in expression of centigrade degree) than the treatment followed by precipitation, TH1050 and RH955 etc..

On one hand, the susceptibility of martensitic Types 414 (12Cr-2Ni) and 431 (17Cr-2Ni) showed roughly a trend that the more stable the martensite, the more susceptible became the alloy, for example, materials tempered at 550 to 750 C indicated far much lesser susceptibility than that of quenched material from 1060 C, and lower tempering resulted intermediate susceptibility between above.

It is pointed out here that notable difference between above two groups of steels resides in the nickel content with the exception of the chromium content, but it is not clear that this is ascribable to respective behaviour.

(2) Both changes in time to fracture and in impact strength of Types 414 and 431 stainless steels were well resembled each other with respect to change in tempering temperature when stress having a constant ratio to the individual tensile strength, 0.45 x σ_B, as shown the results of Type 431 in Figure 15. Roughly similar correspondence of time to fracture to impact strength was also observed on 17-4PH steel variously tempered after quenching from 1040 C.

(3) Figure 16 shows both corrosion potential and extension of Type 431, quenched from 1060 C, exposed to the acidified 35 per cent solution, plotted against time elapsed. Comparing this with Figure

17, obtained on Type 301 in the same solution, exhibited two distinct contrasts, in one, although corrosion potential of both types of steels abruptly dropped downwards to far less noble direction, say, to the potentials corresponding respectively to the fractured facet, in process of the final fracture, Type 301 showed a gradual decrease in the potential for a while before the fracture, but Type 431 indicated a sluggish increase in the potential followed by a just sudden drop in it and, in two, Type 431 fractured also just suddenly without being preceded by a gradual increase in the extension that is indicative of increasing number of cracks along with yawning them. Microscopical inspection proved that the steel specimens were broken through one fracture without accompanying many cracks, not as so in case of Type 301 or other austenitic stainless steels, but with a few hair cracks near the fracture.

Although some allusion to hydrogen theory for austenitic stainless steels must be taken into account, it may be still premature to accept it as it stands. Whiteman and Troiano (9) have concluded, after certifying hydrogen embrittlement of austenitic steels, that 'over the years, considerations have been given to association of stress-corrosion cracking with hydrogen in austenitic stainless steels, the strong arguments against such a causative relationship has generally resided in the following observations that a completely austenitic stainless steel is not subject to hydrogen embrittlement, and that cathodic protection provides a beneficial effect. However, the first of above, hydrogen embrittlement, is no longer a valid objection. Vaughan et al (11) have inclined to take a hydrogen view with respect to the formation of alloy hydride. Hoar (10), on the other hand, has flatly denied any contribution of hydrogen to the cracking of stressed austenitic stainless steels in the $MgCl_2$ solution.

The present results do not provide full basis of correlating the susceptibility of martensite in non-austenitic stainless steels with the kind of steels, but it is attractive to assume, from consideration of both the results indicated by the steels and other supporting evidences, that there would be a borderline phenomenon between hydrogen embrittlement and corrosion embrittlement, where hydrogen would be absorbed into surface layer of the metal but into the bulk matrix, by which the layer may be embrittled successively by loosing the atomic interaction of surface alloy, in which, however, such aspects against which the mechanism of hydrogen embrittlement being set as the rate may be controlled either by a process of the 'anomalous diffusion' (37, 38) or by a process of 'dissociation of hydrogen in voids' (39) will receive little or no attention.

9. Ammonia-Cracking of Brass

Ammonia-cracking of brass is an old problem but waiting for further investigations. Recently, Mattsson (34) has determined the most effective range of compositions of test solutions composed of ammonium- and copper sulphates for embrittling 70/30 brass by stress-corrosion under adjusting pH value by ammonia water. With stimulation by the Mattsson's studies, absolutely mechanical view of the tarnish-rupture mechanism has been proposed by Forty and Humble (1), which has been followed up further by McEvily and Bond (2) and by Pugh and Westwood (3). The last workers, however, have also allowed another mechanism to coexist, to which they alluded that 'for tarnish-free specimens, the mechanism is not fully understood, but it is suggested that failure involves preferential removal of zinc by reaction of cupric complex ions at the metal surface'. Mattsson's findings were also traced by Hoar and his colleagues (10) with the aim of correlating his results with potentials.

Lately. cracking of aluminum brass for use of condenser tubing by cooling water, especially by fresh water, has increasingly been closed up as a new fascinating episode. In this context, detailed reference by Shvartz and Kristal (4) to stress-corrosion cracking of ordinary brass in ammonia-free solutions, sea water, chromates. permanganates, carbonates, hydroxides, caustic etc., needs to be attached on by a renewed attention. Recently, Lynes (41), on the other hand, concluded that brass can be embrittled only by ammonia-containing solutions, and explained cracking mode affected by addition of chloride and nitrate.

The present results concerning ammonia-cracking of brass are summarized below with intimate reference to above situations.

(1) All ammonium salt solutions prepared with distilled water and with all ammonium salts customarily came to hand from market fractured 60/40 brass specimens, stressed at 30 kg/sq mm after annealing at 550 C for 1 hour, within the test duration for 7 days or somewhat above at room temperature, but each effective range of the concentration for producing the fracture was varied from salt to salt, as examples shown in Figure 18 and Figure 19.

Figure 18 shows the results plotted the susceptibility, time to fracture, against organic salts added, borate (curve 1), oxalate (curve 2), arsenate (curve 3) and ferric citrate (curve 4), and Figure 19 shows similar results on inorganic salts, chloride (curve 1), nitrate (curve 2), sulphate (curve 3) and carbonate (curve 4) respectively. It was revealed that most ammonium salts, organic and inorganic, have, with some exceptions, an effective range of concentration respectively for causing the cracking, in more concentrated range, the susceptibility becomes immune, while in far less concentrated range, the susceptibility becomes nearly constant, which, as mentioned next, also equivalent to that in single distilled water.

(2) A perplexing fact brought to light was that the distilled water used above tests was originally contaminated with extraneous ammonia near 0.05 to 0.07 ppm, which were determined by the direct Nesslerization method and, furthermore, it could not be reduced further not only by additional distillation but also by deionization treatment. Thus, the abscissae in above illustrations do not indicate true ammonia content regarding the salts added. Another fact of miracle found was that 60/40 brass, along with 70/30 brass under the same conditions as 60/40 brass, were embrittled by both immersions in distilled water and in deionized water. For instance, 60/40 brass stressed at 30 kg/sq mm was fractured, in the average at least five tests, at 1834 minutes in single-distilled water, 4576 minutes in double-distilled water, which was specially treated in order to reduce ammonia content to 0.03 ppm thrugh alkalification followed by neutralization during the distillation, and 9100 minutes in deionized water, which contained 0.05 ppm ammonia, but in tap water it does not indicate any sign of the cracking within the same duration of 7 days.

(3) Further perplexing fact revealed by a limited number of tests was that the cracking of 60/40 brass was produced not only by an ammonium salt solution but also by another salt solution containing the same anions as the former salt but ammonia, in such a manner as both trend in the susceptibility with respect to the amount added being aproximately similar, as an example to the point shown in Figure 20 obtained in ammonium- and sodium picrate solutions respectively.

(4) Most ammonium salt solutions having a qualified range of the maximum susceptibility respectively exhibited pH values near 5, say, ranged from about 4.5 to 5.5, where is also the most stable region of cuprous oxide from thermodynamics point of view. This is not agreeable with the most effective range of pH given by Mattsson because of difference between both ammoniacal solutions used.

(5) Species of anions also, in some cases, has a significant influence on the susceptibility of brass, for instance, embrittling strength of 0.1 ppm ammonium oxalate solution and 0.1 per cent ammonium molybdate solution, that is time to fracture within test duration for 7 days under applied stress at 30 kg/sq mm, was stifled by adding with sodium chloride of 1 ppm and 150 ppm respectively to the solutions.

Similarly, dissolved gas behaves, also in some cases, in unexpected fasion, for instance, the cracking of 60/40 brass in distilled water was alleviated so as not to cuase fracturing by slow aeration, and time to fracture of the brass in aerated 0.05 ppm ammonium oxalate solution was little differed from that in non-aerated case, but the fracture was rather stifled by dissolving carbon dioxide into the solution so as the pH value to become 5 after pre-boiling the solution in order to scavenge pre-exist gas.

(6) Minimum concentration of aqueus ammonia, prepared with tap water in the laboratory, required for fracturing 60/40 specimens stressed at 30 kg/sq mm by dead-loading within 7 days was about 0.044 M NH_3. The intensity for fracturing the specimens increased acceleratingly with the concentration up to 1.88M, but more concentrated solutions brought on a little increase in the intensity. Raising oxidizing power of the solutions by adding oxidizing agents resulted in at first an acceleration phase of the susceptibility followed by a deceleration phase of it, for instant, the maximum susceptibility was, when chromate ions were added, observed near 0.02 to 0.05 Cr^{6+} ions/liter irrespective of the concentration of ammonia used.

(7) Figure 21 shows effects of amounts of two oxidizing agents, cupric ammonium complex ions and chromate ions expressed by cupric ions and hexavalent chromium ions respectively, on corrosion rate of unstressed 60/40 brass specimens, finished with 240 grit emery paper, exposed to 0.94 M NH_3 aqueous ammonia containing the ions for 5 days at room temperature. The oxidizing ions were added either cupric salts as chloride, ammonium sulphate, nitrate, sulphate, basic carbonate and acetate, or by chromate salts as cupric, sodium and ammonium.

Change in the corrosion rate with divalent copper ions differed inversely from that with hexavalent chromium ions, but respective group of change was almost entirely similar to each other irrespective of species of conjugated ions in the salts used. Copper ions exceeding 0.01 g/l increased the rate acceleratingly with adding the ions until maximum rates were reached at 10 g/l excepting a case when the ions were added with cupric carbonate, where the maximum rate was indicated at 1 g/l, thereafter all the rates decreased again markedly. The corrosion rates were decreased gradually, on the other hand, by adding chromium ions until about 3 g/ l, but very much remarkably exceeding the addition.

After the runs, continuous tarnishes, which were much thiner than that observed in Mattsson solution, were inspected on surface of the specimens exposed to the solutions added with copper ions by nitrate, cupric sulphate and acetate at 15 g/l respectively, and by basic carbonate at 5 g/l, which produced the most adherent and compact tarnish. The additions that produced above stable tarnishes were also corresponded to the maximum solubilities of the salts used. In cases of cupric ammonium sulphate and chloride, brownish mud-like deposits were formed on the specimen surfaces at 15 g/l, which were superficially similar to that observed by additions of nitrate and sulphate at 10 g/l. On the other hand, addition of chromium ions produced no tarnish, but increasingly formed very much thin films with no inteference colour, which were similar to that generally were observable in fresh water. It is pointed out here that the maximum corrosion did not corresponded to the most stable tarnishes.

It is thought that the films or tarnishes on brass were formed by an electrochemical process of exchanging ions, that is, precipitation of copper from cupric complex ions and dissolution of zinc to zinc complex ions, with the aid of some oxidizing agents, because they can not be formed either in case when any oxidizing agent was scavenged from aqueous ammonia or in case of cupric complex ions being removed from the solution. On one hand, other oxidizing agents than cupric ions will not take place such exchange process because of the inability to forming ammonium complex ions. The oxidation/reduction potential of chromate/chromic couple is far higher than that of cupric/cuprous ammonium complex couple and, therefore, chromate ions can not remove galvanically zinc from brass lattice and metallic copper as well as metallic zinc may be oxidized readily effectively by the ions.

As a rule, corrosion behaviour of brass caused by addition of cupric complex ions is similized by unstable passivity and that by addition of chromate ions meta-stable passivity, with respect to the oxidizing power of the solutions, because anodic polarization is equivalent to increase in addition of oxidizing agents, both fundamentally are corresponded to increase in the partial pressure of dissolved oxygen, that may be attributed to both air and water molecules.

(8) Figure 22 shows effect of copper contents, which was added to 0.94M NH$_3$ water with the same salts as used in the corrosion stusies, on time to fracture of 60/40 brass specimens stressed at 30 kg/sq mm, and Figure 23 shows similar relationship to above obtained by adding chromate ions.

Both divalent copper and hexavalent chromium ions afforded respectively, with some exceptions, two same trends of time-life with respect to the amounts of each ions added. In case of copper ions, maximum suscepibility was achieved by adding copper ions near 10 g/l or a little below where the maximum corrosion had been observed in preceding corrosion studies and, in this case of stressed specimens, the most stable tarnishes began to form there, with the exception of additions with chloride and amminium sulphate. Copper ions above 10 g/l increased the time-life again because of the tarnishes being injured at highly stressed center-portion of the specimens. Furthermore, shear fractures caused mechanically were observed in case of additions of chloride and ammonium sulphate as a result of enhanced corrosion. Addition of basic carbonate produced all the more readily most stable tarnishes and provided most expedient conditions for the cracking because of the least solubility and, perhaps, of conjugated anions, barbonate and hydroxyle ions. In case of chromate ions, maximum susceptibility was situated near 0.05 g/l, below which the susceptibility was reduced remarkably with decreasing amount of chromium ions, as

similar trend to this exhibited in case of copper ions, above which the susceptibility was alleviated again, but inclined gradually towards some constant levels. In no case was shear-type fracture observed because corrosion resistance of the brass became more than ever increased with increasing addition of chromate ions.

It is interesting to remark that the results obtained by adding copper dichromate to the aqeous ammonia revealed that the effect of cupric ammonium complex ions was almost entirely swamped by the effect of chromate ions. It is attractive to think that only oxidizing power of the ions is a determinant factor in causing the fracture. That maximum susceptibility was near 0.05 g/l, where the corrosion of brass was hardly influenced by the presence of chromate ions, might be explained only by allowing an assumption that filming process on surface of the specimens being the most faviourable conditions for initiating cracks, but full reasons for it remains unclear.

(9) Generally speaking, extension behaviour of brass in ammoniacal solutions was in contrast with that of stainless steel in the MgCl$_2$ solutions. For instance, Figure 24 illustrates characteristic step-wise extension, which was recorded on 60/40 brass specimens stressed at 30 kg/sq mm in 0.94M NH$_3$ + 0.02 g Cr^{6+} ions/liter solution at room temperature under potentiostatic control, -40 mV and -170 mV. After some incubation periods, the specimens extended suddenly and, thereafter followed the step-wise extensions successively at some time intervals. The step-wise increase in the extension is taken as being indicative of step-wise exposure of fracture newly cleated suddenly by yawning of the cracks and, consequently by proceeding of stress-corrosion embrittlement.

(10) Copper corroded moderately with the rate of 1.10 g/sq m.hr in the Mattsson solution, but zinc corroded vigorously with the rate of 39.5 g/sq m.hr, while both aluminum and nickel indicated no weight loss. Corrosion rates 60/40-and 70/30 brass, Albrac (an aluminum brass for condenser tubing produced by Sumitomo Light Metals Co., Ltd.), Admiralty brass and Naval brass were 1.96, 1.67, 0.45, 1.55 and 1.87 g/sq m.hr, whereas that of 90/10-and 80/20 cupro-nickel were 4.00 and 0.13 g/sq m.hr, respectively. Reason of why the specimen of 90/10 cupro-nickel was attacked so severe remains unclear. A pronounced, or deep, brown tarnishes, that were continuous, compact and relatively thick, were observed on surfaces of alloys excepting Albrac and 80/20 cupro-nickel. Corrosion-embrittling tests at an engineering stress-level of 25 kg/sq mm in the Mattsson solution fractured four zinc-containing brass, but no case was any cracking observed on Albrac and both cupro-nickels within 7 days. In case of brass, as a class, visual films, or tarnishes, with blackish brown colour generally were intimately connected with the susceptibility in the Mattsson solution, as well as in most ammonium salt solutions, but neveretheless, many exceptions were also realized. It being appeared that tarnish itself

is not a harbinger for predicting occurrence of stress-corrosion embrittlement only by reason of the tarnishes or films being visible.

(11) Corrosion potential of copper in the Mattsson solution was near +290 mV against hydrogen throughout the measuring duration, while the potential of 60/40 brass was +150 mV at the incipience, that is after immersion for 2 minutes, but the steady potential after 24 hours or above became +270 mV, and that of 70/30 brass and of 90/10 cupro-nickel were +280 mV and +250 mV respectively, which were corresponded to apparent potentials of tarnishes formed on respective electrode-material but to real corrosion potentials. On one hand, the steady potentials of aluminum and nickel were +120 mV and +400 mV respectively, but both metals exhibited passivity in the solution, indicating each steady current-density of 10^{-6} and 3×10^{-7} amp/sq cm.

The tarnish on 60/40 brass in the Mattsson solution was formed at a constant potential of +200 mV controlled by potentiostat but at +100 mV, nevertheless, in both cases were fractures observed in spite of specimens being exposed to the same solution.

DISCUSSION AND CONCLUSION

Although much experimental and theoretical ingenuity must be applied in attempt to argue persuasively on the mechanism of stress-corrosion embrittlement and to uncover the fundamental factors underlying the mechanism, consideration of the experimental data and of other theoretical background set against other similar environmental embrittlements as hydrogen embrittlement, liquid metal embrittlement, environmental stress-cracking of polymers and the like, lead to the following discussion and conclusion.

According to a currently accepted concept, any crystalline solid having a brittle strength near its yield strength could be fractured almost without absorbing energy for plastic deformation, namely in a brittle fashion. In case of metal, a particular emphasis has been placed on a presupposition that a critical event leading to brittle fracture would be a localized inhomogeneous plastic deformation because of a realization that even in most brittle appearing fractures have generally been preceded by some plastic surface-work, which is the largest energy has to be supplied by strain energy.

The first consideration is, in order to carry the argument forwards, placed on mechanical factors influencing on the behaviour of brittle fracture. Temperature-dependent brittle fracture can not be observed on f.c.c. metal, as a class, because of its temperature-independence on the strengthening mechanism by solute atoms. Furthermore, other main causes for inducing brittle fracture, raising strain-rate and increasing triaxiality of applied stress, also are not so beneficial for embrittling f.c.c. metal as in case of b.c.c. metal.

If so-called the stress-corrosion cracking involves a kind of brittle-fracture process, it is needed to be elucidate that why a certain specific aqueous environments could restrain apparently the plasticity of cencerned metal, especially of f.c.c. crystals, even such conditions to which the metal being subjected as high temperature, negligibly small strain-rate and scarece triaxiality present.

The second consideration is placed on environmental factors that associate dissolution process with mechanical behaviour of metal. It admits of no discussion that clean, or truely bared, surface of metal can not be found in ambient atomospheres. Recent studies by Schwabe (42) revealed that the incipient step in dissolution process of metal must be an exchange-adsorption between oxygen or water molecules on metal and cations in solution. There may be some types of effect affected by some types of dissolution process, but two of which may be of significance. Mild dissolution of clean surface would weaken the mechanical properties by continuously removing surface barriers to dislocation egress but surface sources of dislocations. Severe dissolution, on the contrary, would strengthen the mechanical properties by continuously eliminating any cause of crack initiation present at the surface, as generally documented by the phenomena of Joffe effect (43). There may be more types of effect afforded by dissolution, that intervene between above two. It might be most interest to argue, in this context of the solvent effect, that if the stress-corrosion cracking is nothing but an anodic dissolution assisted by applying stress, it might be necessary to prove some answers to a question of why the strain-accelerated anodic dissolution, showing faster rate of which than the rate of crack initiation can be free from any fracturing.

The third consideration is placed on environmental factors affecting on the deformability of surface metal. It is well-established fact that films on metal surface disturbe active movement of dislocations and, therefore, strengthen the mechanical properties of it, which has been known as Roscoe effect (44). This is a positive effect byfilming action. On the other hand, a negative effect afforded by defilming action may be termed Andrade-Randall effect (45), by which onset of surface-plastic flow can be fully facilitated and, as an overall effect, mechanical properties, contrary to above, can be weaken. More significant contribution of corrosive media to fracturing process is adsorption effect, by which effective surface-energy may, in most cases, be reduced to such a level as brittle fracture of ductile metal can start. Adsorption-dependent embrittlement, might, in case of hydrogen, concede some absorption at surface but matrix, where hydrogen embrittlement being possible to occur.

The forth consideration is placed on plastic constraint at apex of notch formed by single stress-corrosion, which results from triaxiality. It is very significant to point out here that coefficient of plastic constraint would rationally approach to the ratio of longitudinal/transverse-modulus of a concerned metal or of two concerned metals in case when one being constrained by one more. Thus, the more plastic the metal being constrained, the greater the coefficient might be afforded by other metal being not constrained. In this regard, films or tarnishes on wall of notches might become very significant with respect to defilmed sites at apex of them if they are formed adherently on the wall.

Many opinions have mostly agreed with in respect that occurrence of stress-corrosion embrittlement postulates essentially for some establishment of preferential reactivity between alloys and environments, since pure metal can never be embrittled by stress-corrosion and restricted slip alone is not a unique prerequisite for making alloys susceptible to the embrittlement.

Necessary conditions for establishing the preferential reactivity may, in brief statement, be provided by some precipitations in hetrogeneous alloys or by segregations in some homogeneous alloys either at grain boundaries or at grain matrices in both cases. In this context, even though the restricted-slip consideration is very much 'bulk things', it may be remembered that it does not indicate all the chances of stress-corrosion embrittlement.

Sufficient conditions for establishing the preferential reactivity will be met by some environmental factors, but to delineate this is so perplexing that it might be only suggested that the role of corrosive environments may be twofold, in one a certain specific species will adsorb on surface of alloys in order to breakdown protective films very much locally, and in one more some other species will adsorb on fracturing surface in order to lower the surface energy.

On the basis of the preceding arguement and consideration, a possible model of mechanism of stress-corrosion embrittlement is presented as follows.

(1) Stress-Corrosion Process

It is suggested that only role of stress-corrosion, that means in this paper only strain-accelerated anodic dissolution, is to produce acute notches enough to provide conditions for crack initiation as a result of the preferential reactivity.

(2) Crack-Initiation Process

Cracks may be nucleated and then grown to instable sizes by means of plastic constraint at apex of the acute notches aiding exceedingly by both filming action on the sides of notches and defilming action at

the apex. In this model, the tarnish-rupture theory. that is purely mechanical view only with respect to the tarnish, must be argued against, because that films either being visible or not, or being observable or not, is not a matter of concern here.

(3) Crack-Propagation Process

Cracks may propagate after an energy criterion for crack-propagation has been established by reducing effective surface-energy by adsorption. That what adsorbate could be useful in respective case is a further problem to be clarified, but, if it may be supposed, hydrogen atoms may be in case of stainless steel and hydroxyl ions may be in case of brass and, therefore, other specific species such as chloride ions in case of stainless steel and ammonium ions, not ammonia gas, in case of brass may be faviourable for providing an expedient conditions for breaking some protective films. In this context, attention must be placed on a prerequisite that the adsorption needs to be completed preceding surface-plastic work, that is before relieving from strain energy, which comprises an elastic-after-effect. Furthermore, in some case of stainless steel, a possibility that hydrogen acts as an embrittling factor by means of loosing interatomic force by being absorbed into skin-surface of it without affording any diffusion-effect as observed in case of true hydrogen embrittlement.

(4) Overall Process

The processes 1 to 3 will be repeated periodically, and the overall process determine advancing rate of the stress-corrosion embrittlement.

Above model accepts the dual-step mechanism in the outline, but differs from it in particulars, describing role of stress-corrosion in providing acute notches, of films in enhancing triaxiality and then in initiating cracks, and of adsorption in propagating cracks with consideration of elastic-after-effect. Also, restricted-slip consideration, as well as corrosion consideration, may be enphasized.

Lastly, one important view must be added here, that,if completely pure water can cause embrittlement by stress-corrosion, saliently characteristic features in stress-corrosion embrittlement will disappear, may be true. Consequently, the terms of chloride-free solution and ammonia-free solution are taken as being literally relative one.

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REFERENCE

1. A.J.Forty and P.Humble; Phil. Mag., 8(1963)247
2. A.J.Jr.McEvily and A.P.Bond; J. Electrochem. Soc., 112(1965)131
3. E.N.Pugh and A.R.C.Westwood; 2nd Technical Rep. to A.R.C.(D), Aug., 1965
4. T.P.Hoar and J.G.Hines; C.I.T.C.E., 8(1958)273
5. T.P.Hoar and J.G.Hines; J. Iron Steel Inst., 182(1956)124
6. J.G.Hines and T.P.Hoar; J. Iron Steel Inst., 184(1956)166
7. J.G.Hines; Corrosion Science, 1(1961)2
8. J.G.Hines; Corrosion Science, 1(1961)53
9. M.B.Whiteman and A.R.Troiano; Corrosion, 21(1965)53
10. T.P.Hoar; Corrosion, 19(1963)331t
11. D.A.Vaughan et al; Corrosion 19(1963)315t
12. H.J.Bhatt and E.H.Phelps; Corrosion, 17(1961)430t
13. J.F.Bates and A.W.Loginow; Corrosion, 20(1964)189t
14. J.E.Truman et al; J. Iron Steel Inst., 202(1964)745
15. S.Barnartt and D.van Rooyen; J. Electrochem. Soc., 108(1961)222
16. H.H.Uhlig and J.L.Sava; Corrosion Science, 5(1965)291
17. H.J.Engell and A.Bäumel; Arch. Eisenhüttw., 23(1962)
18. H.P.Hawkes et al; Corrosion, 19(1963)247t
19. E.E.Denhard; Corrosion, 16(1960)357t
20. F.S.Lang; Corrosion, 18(1962)378t
21. J.G.Hines and E.R.W.Jones; Corrosion Science, 1(1960)88
22. H.H.Uhlig and R.A.White; Trans. A.S.M., 52(1960)830
23. P.R.Swann; Corrosion, 19(1963)102t
24. D.L.Douglass et al; Corrosion, 20(1964)15t
25. S.Barnartt et al; Corrosion Science, 3(1963)9
26. R.Stickler and S.Barnartt; J. Electrochem. Soc., 109(1962)343
27. P.R.Swann and H.W.Pickering; Corrosion, 19(1963)369t
28. K.C.Thomas et al; Corrosion Science, 5(1965)71
29. J.Bourrat and J.Hochmann; Acier Speciaux, Monographies Techniqes, 1964, No. 9, 8pp
30. D.Dulieu and J.Nutting; The Nickel Bulletin, 37(1964)145
31. G.Riedrich and H.Kohl; Berg-und Hüttenmännische Monatschefte, 81(1963)1
32. D.T.Llewellyn and J.D.Murray; The Nickel Bulletin, 37(1964)146
33. Z.Szklarska-Smialowska and M.Smialowski; J. Electrochem. Soc., 110(1963)444
34. E.Mattsson; Electrochim. Acta., 3(1961)279
35. W.D.Robertson and A.S.Tetelman; 'Strengthening Mechanism in Solids', A.S.M., 1962, p217
36. J.G.Hines; 'Physical Metallurgy of Stress Corrosion Fracture', Interscience Publishers, New York, 1959, p116

37. R.C.Frank et al; J. applied Physics, 29(1958)392
38. R.C.Frank; 'Internal Stress and Fatigue in Metals', Elesivier Publishing Co., 1959, p411
39. K.Farrell and A.G.Quarrell; J. Iron Steel Inst., 202(1964)1002
40. G.L.Shvartz and M.M.Kristal; 'Corrosion of Chemical Apparatus', translated from Russian, Consultants Bureau, Inc., 1959, p160
41. W.Lynes; Corrosion, 21(1965)125
42. K.Schwabe; Werkstoffe u. Korrosion, 15(1964)71
43. A.F.Joffe; 'Physics of Crystals', McGraw-Hill, 1929
44. R.Roscoe; Nature, 133(1934)912
45. E.R.da C.Andrade and R.F.Y.Randall; Nature, 162(1948)890

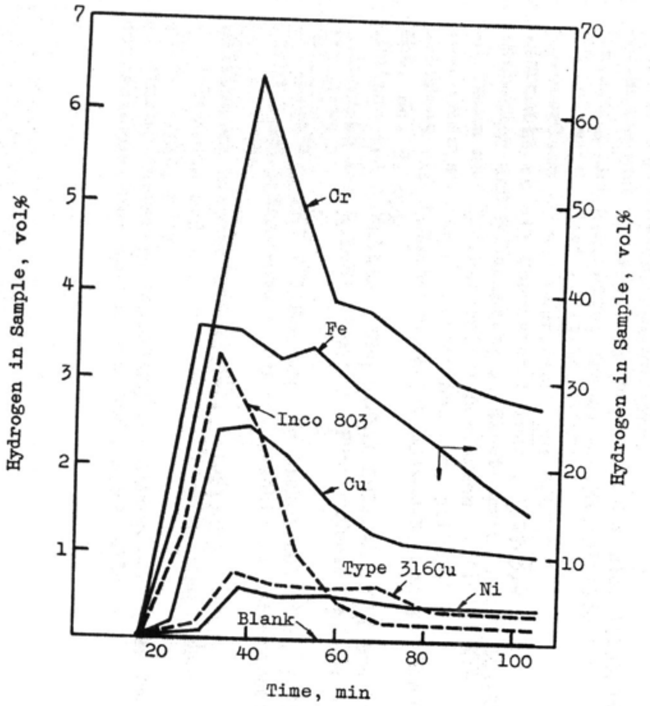

Figure 1.- Amount of hydrogen liberated by corroding metal in the 'Scheil solution', determined intermittently by vaporfractmetric analyses. In no case was other than hydrogen detected after removal of water.

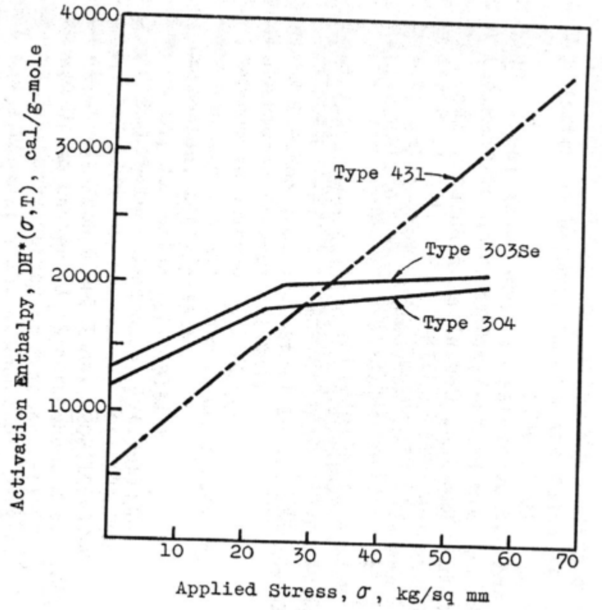

Figure 2.- Relationship between apparent activation-energy obtained from temperature coefficient of the reciprocal of time to fracture of martensitic Type 431 and austenitic Types 303Se and 304 stainless steels and applied stress by dead-loading. Stressed specimens were exposed in the 'acidified 35% $MgCl_2$ solution.

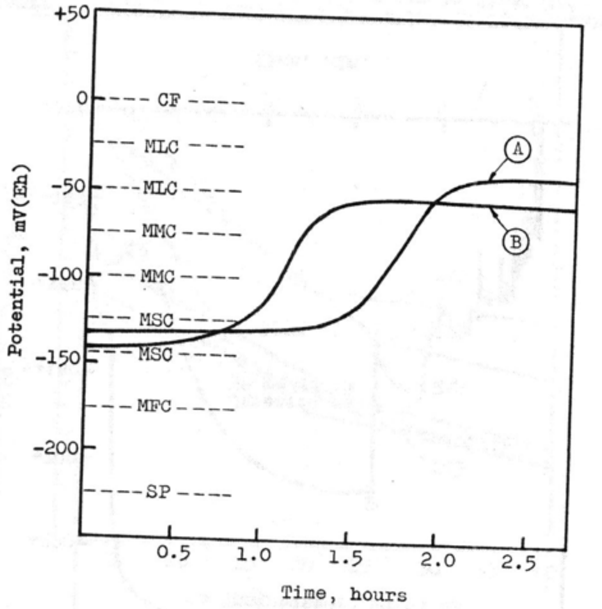

Figure 3.- Potential versus time curves for unstressed Type 304 stainless steel (curve A) and for stressed at 28.2 kg/sq mm by one-point bending, and results of embrittling tests of the stressed specimens by stress-corrosion at constant potential-levels indicated by the dotted lines, in the 'Scheil solution'. Abbrevations indicate mode of failure.

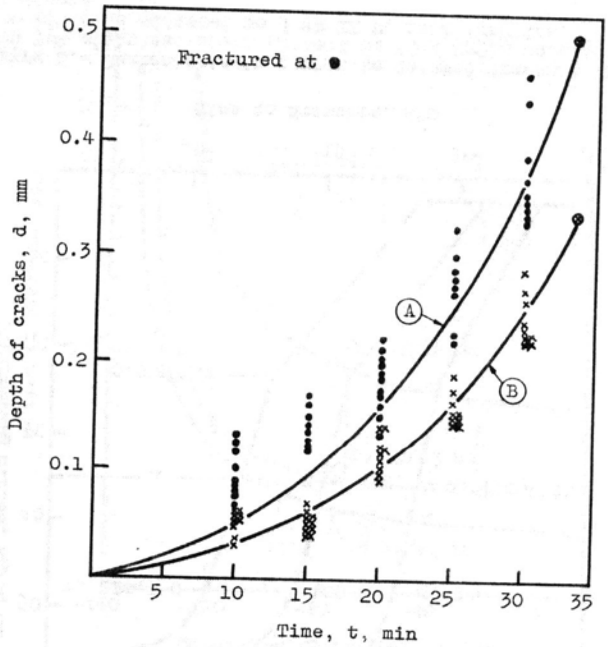

Figure 4.- Relationship between depth of cracks and time elapsed, obtained on Type 304 stainless steel specimens stressed at 35 kg/sq mm by dead-loading in the 'acidified 35% $MgCl_2$ solution'. Curve A exhibits side-advancing, $d = 0.0002t^2$, and curve B plane-advancing, $d = 0.00014t^2$.

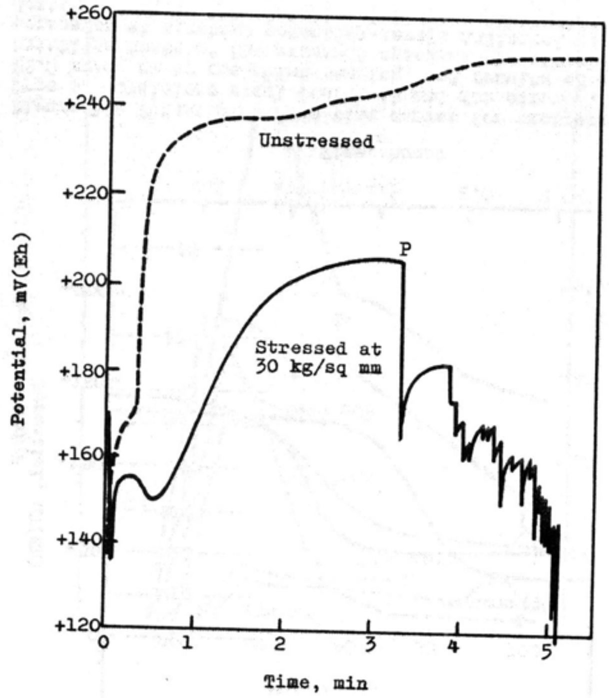

Figure 5.- Change in corrosion potential of 60/40 brass stressed at 30 kg/sq mm by dead-loading in distilled water at room temperature in comparing with unstressed one. Note step-wise fluctuation in the potential change.

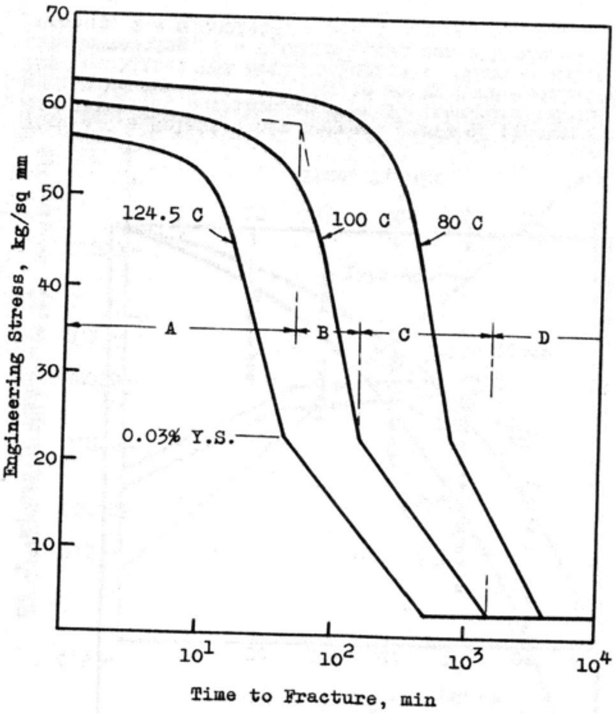

Figure 6.- Characteristic curves in delayed fracture of Type 304 stainless steel exposed to 35 % $MgCl_2$ solution, with pH value adjusted to 3 at 22 C, as a function of test-temperature.

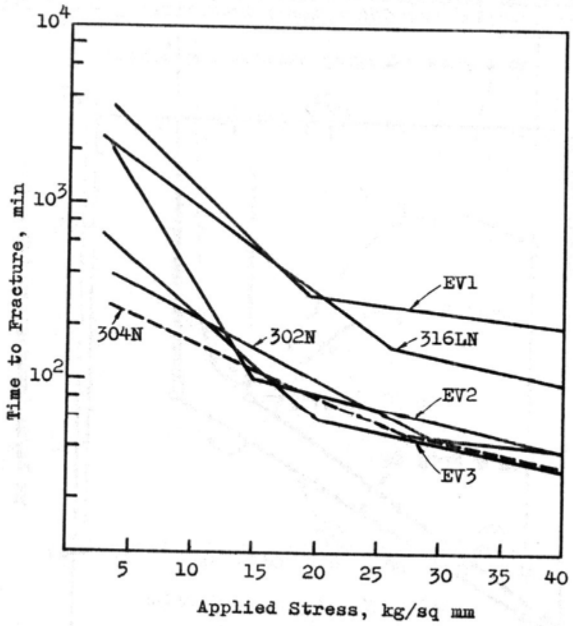

Figure 7.- Relationship between applied engineering-stress and time to fracture of three heats of vacuum-refined and three heats of air-melt high nitrogen-type stainless steels in the 'acidified 35% $MgCl_2$ solution'. EV1, EV2 and EV3 are vacuum-melt 18-8 type Steels.

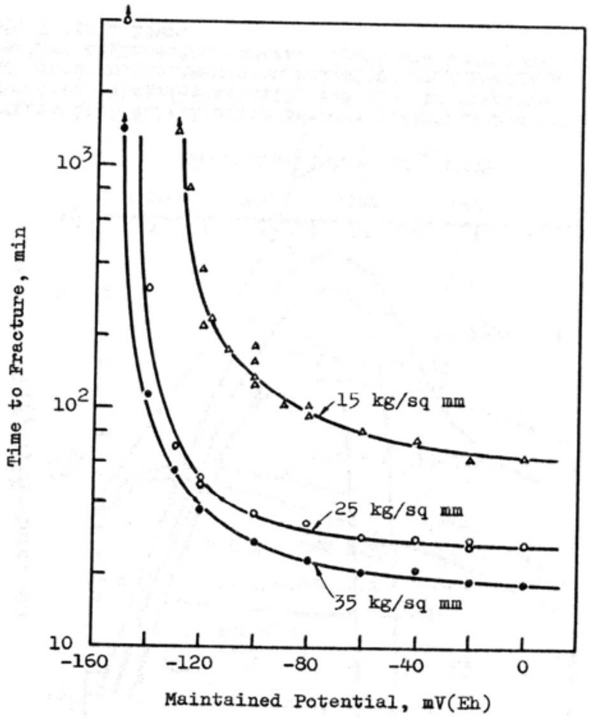

Figure 8.- Effect of potential held potentiostatically at constant on time to fracture of Type 301 in the 'acidified 35% $MgCl_2$ solution' as a function of applied engineering stress by dead-loading. Specimens were quenched from 1060 C into oil.

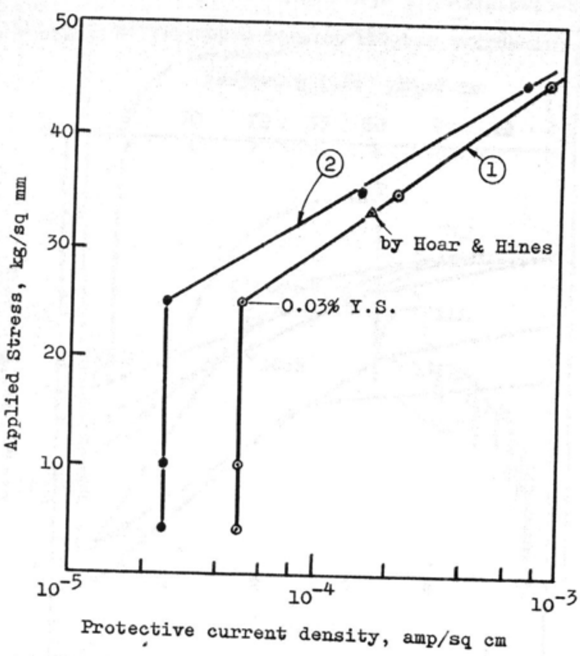

Figure 9.- Relationship between applied engineering stress and cathodic current density for protecting embrittlement of Type 301 stainless steel by stress corrosion in the 'acidified 35% $MgCl_2$ solution'. Line 1 indicates measured data, and line 2 data from a hyperbolic relation assumed between maintained current density and time to fracture as a function of applied stress.

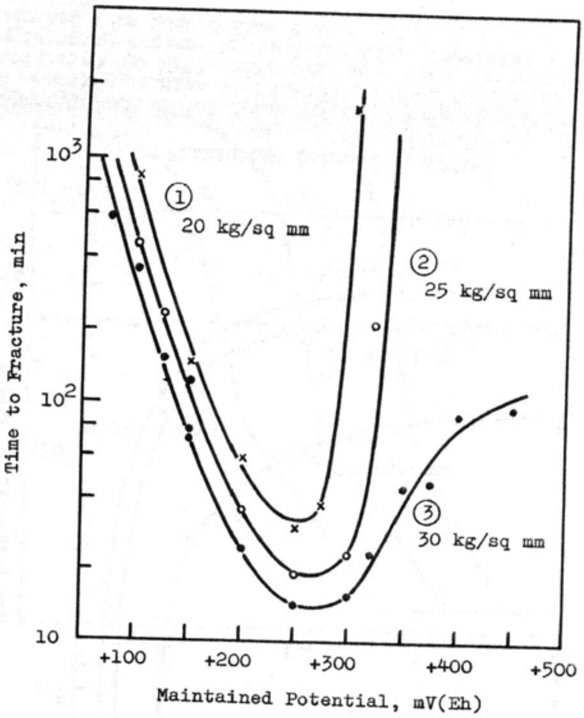

Figure 10.- Relationship between potential kept at constant potentiostatically and time to fracture of 60/40 brass in the 'Mattsson solution' as a function of applied engineering stress. Specimens were annealed at 550 C for 1 hour.

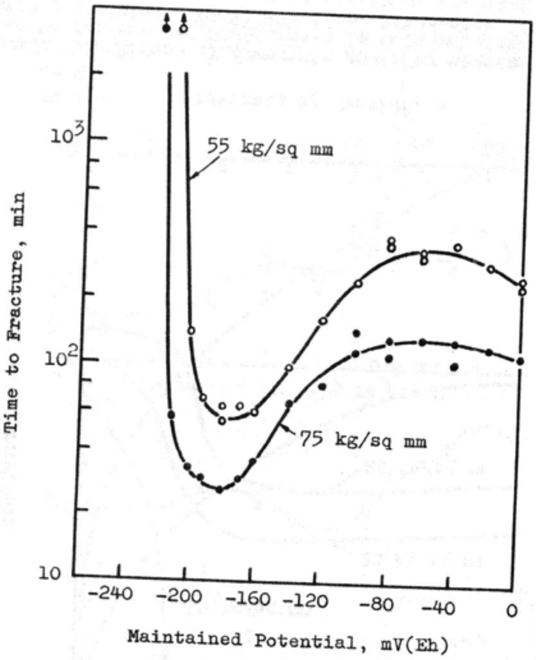

Figure 11.- Relationship between time to fracture of Type 431 quenched from 1060 C and potential maintained potentiostatically at constant in the 'acidified 35% $MgCl_2$ solution as a function of applied engineering stress by dead-loading.

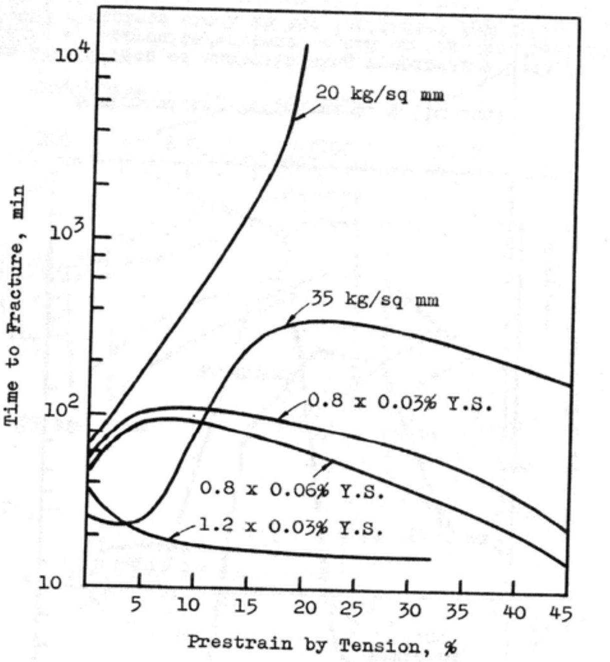

Figure 12.- Effect of prestrain given by tension on time to fracture of Type 301 stainless steel in the 'acidified 35% $MgCl_2$ solution', as a function of choosing manner of applying engineering stress. Y.S. indicates proof yield strength.

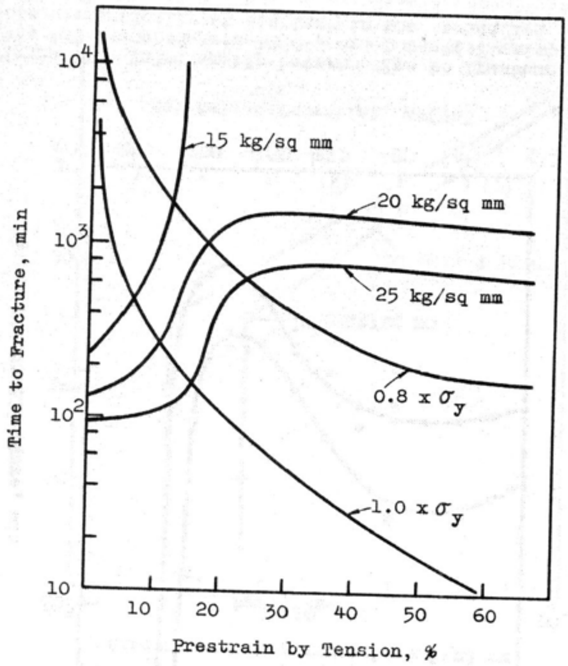

Figure 13.- Effect of prestrain given by tension on time to fracture of 70/30 brass in 0.94 mole ammonia water containing 0.02 g Cr^{6+} ions/ liter plus 100 ppm Cl^- as a function of choosing manner of applying engineering stress.

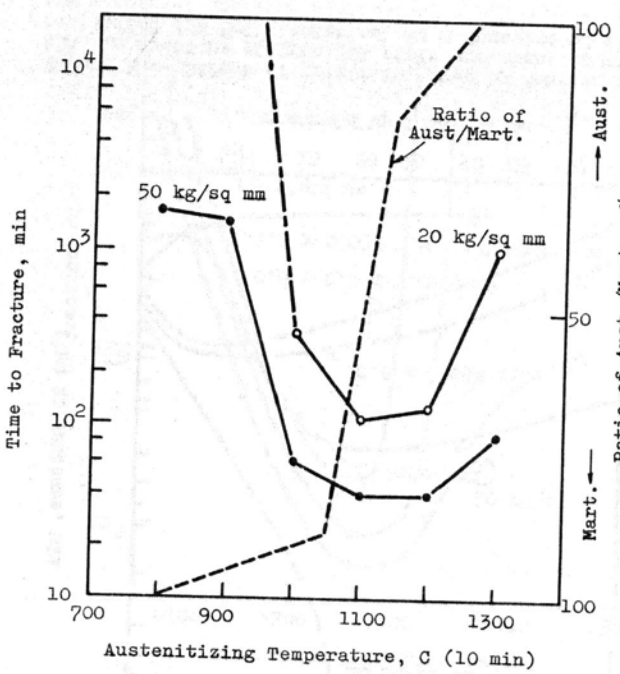

Figure 14.- Effect of austenitizing temperature both on the ratio of austenite/martensite and on time to fracture of 17-4PH stainless steel in the 'acidified 35% $MgCl_2$ solution' at two stress levels, 20 and 50 kg/sq mm.

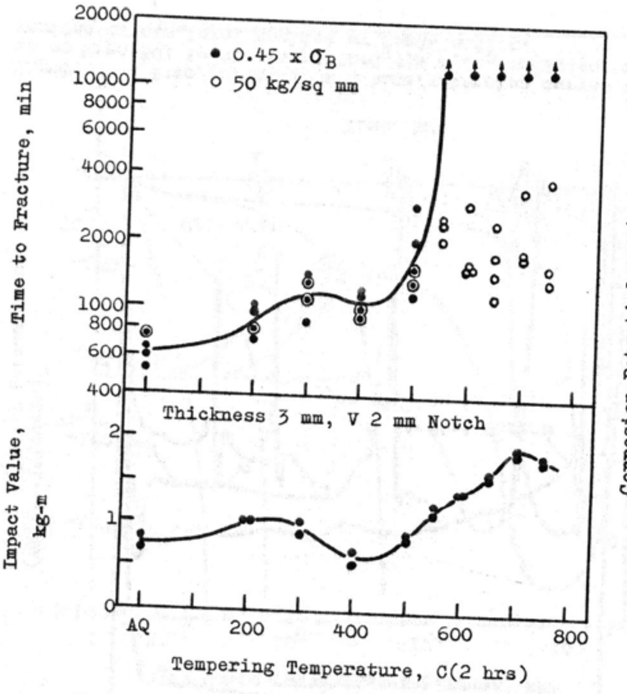

Figure 15.- Changes in time to fracture of Type 431 in the 'acidified 35% $MgCl_2$ solution' and in the Charpy impact-value both with tempering temperature after the specimens being quenched from 1060 C into oil.

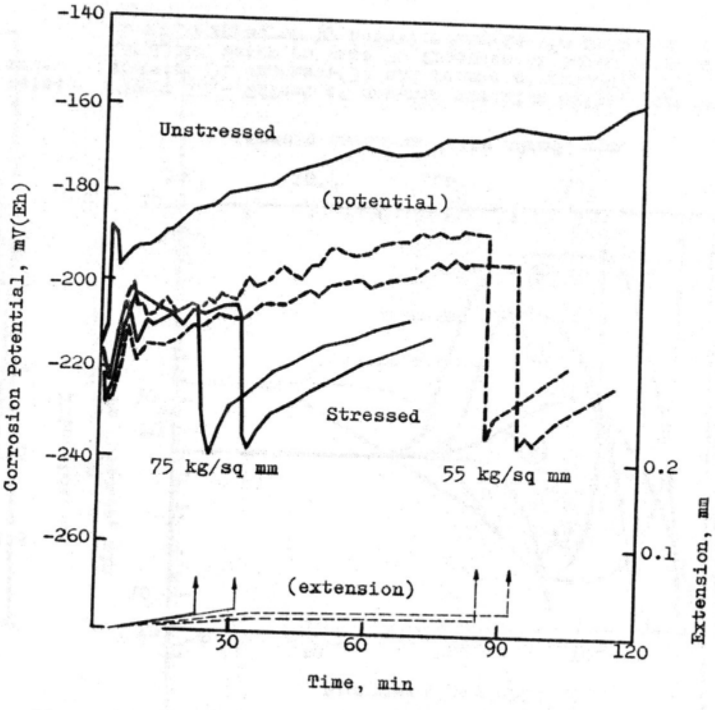

Figure 16.- Changes in corrosion potential and in extension of Type 431 stressed at 55 and 75 kg/sq mm respectively in the 'acidified 35% $MgCl_2$ solution'. Fractures ocurred at upright extensions.

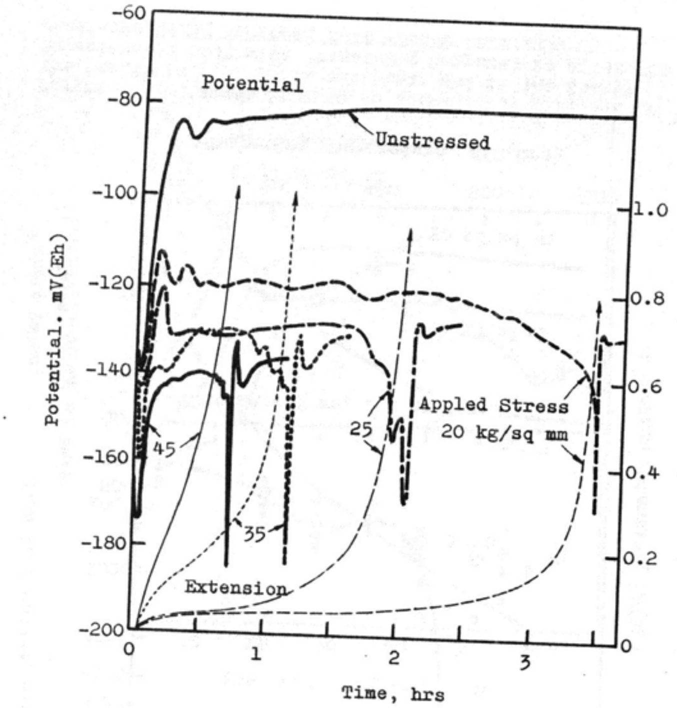

Figure 17.- Time/potential and time/extension curves obtained on Type 301 in the 'acidified 35% $MgCl_2$ solution' under various stress level applied by dead-loading.

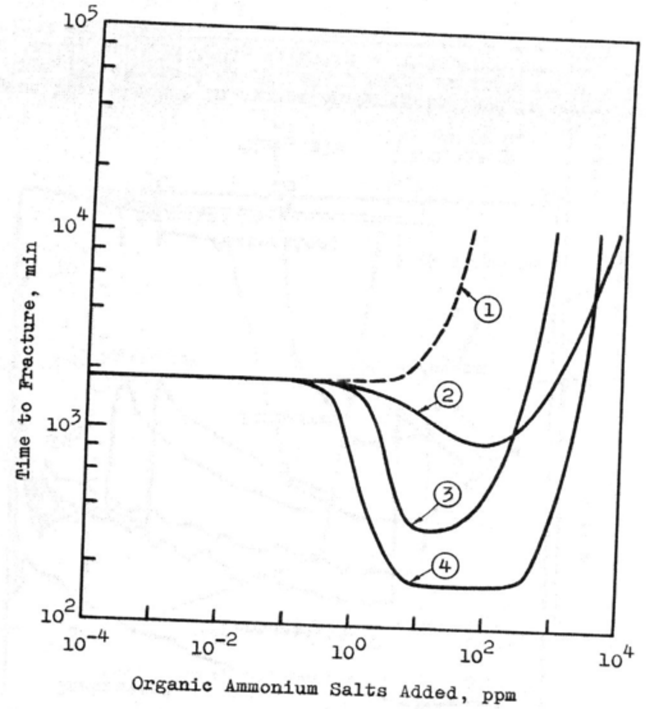

Figure 18.- Effect of organic ammonium salts, borate(1), oxalate(2), arsenate(3) and ferric citrate(4), added to distilled water on time to fracture of 60/40 brass stressed at 30 kg/sq mm by dead-loading in the solutions at room temperature.

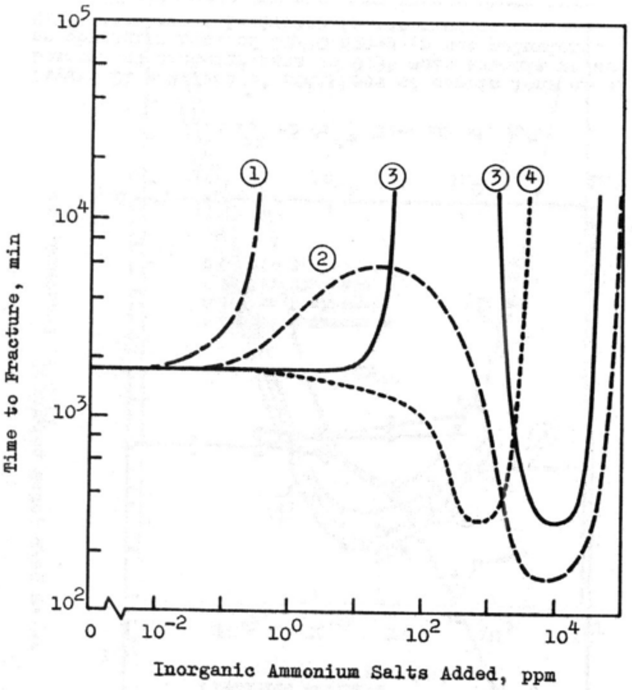

Figure 19.- Effect of inorganic ammonium salts, chloride(1), nitrate(2), sulphate(3) and carbonate(4), added to distilled water on time to fracture of 60/40 brass stressed at 30 kg/sq mm by dead-loading in the solutions at room temperature.

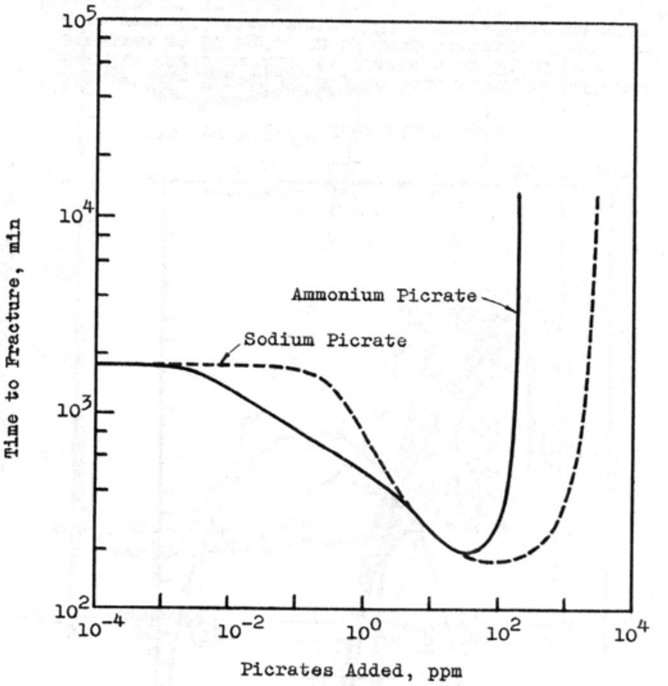

Figure 20.- Relationship between concentration of ammonium- and sodium picrates added to distilled water and time to fracture of 60/40 brass stresed at 30 kg/sq mm by dead-loading in the solutions, indicating effect of species of cations.

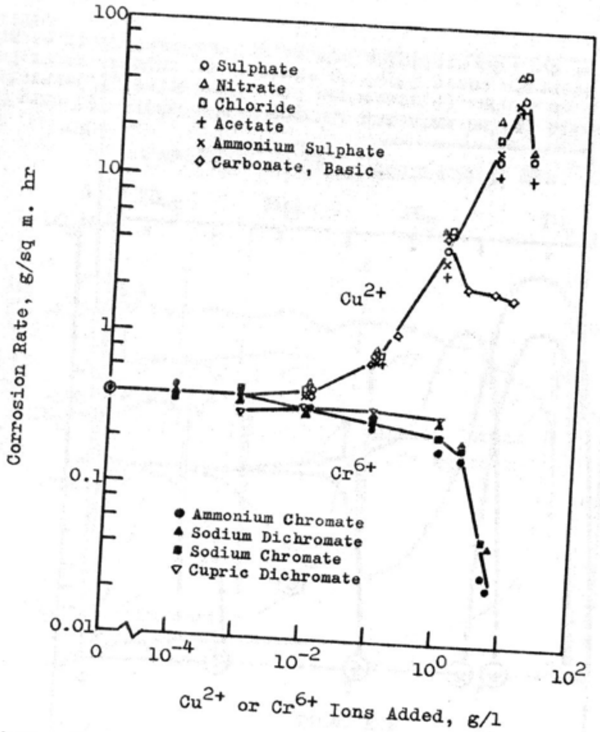

Figure 21.- Effect of additions of cupric ions or of hexavalent chromium ions to 0.94 mole ammonia water on corrosion rate of 60/40 brass in the solutions. Salts used are illustrated in the figure.

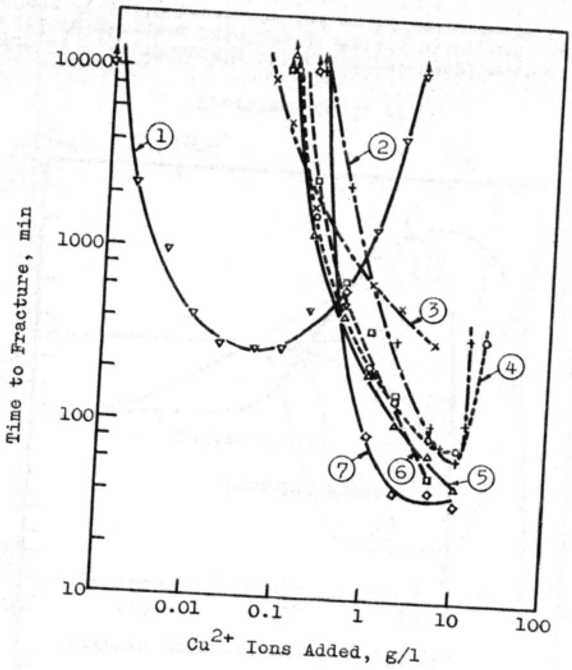

Figure 22.- Effect of cupric ions added to 0.94 mole ammonia water on time to fracture of 60/40 brass stressed at 30 kg/sq mm by dead-loading. Cupric salts used were (1) dichromate, (2) acetate, (3) ammonium sulphate, (4) sulphate, (5) nitrate, (6) chloride and (7) carbonate, basic.

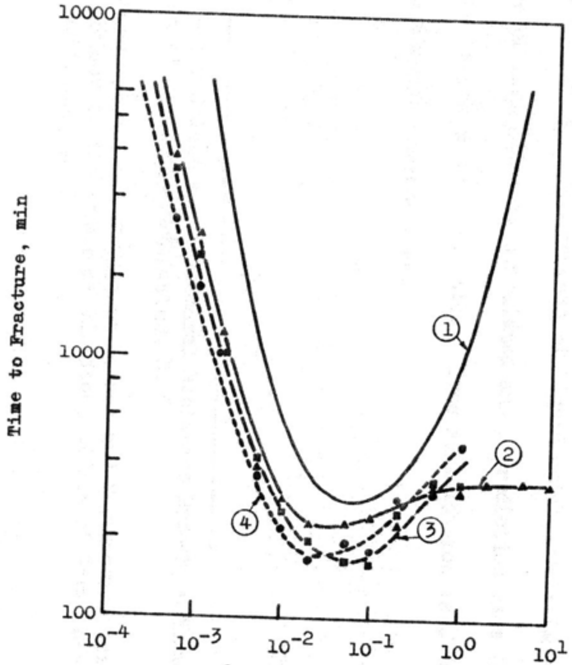

Figure 23.- Effect of hexavalent chromium ions added to 0.94 mole ammonia water on time to fracture of 60/40 brass stressed at 30 kg/sq mm by dead-loading in the solutions at room temperature. Hexavalent ions were added with (1) cupric dichromate, (2) sodium chromate, (3) sodium dichromate and (4) ammonium chromate.

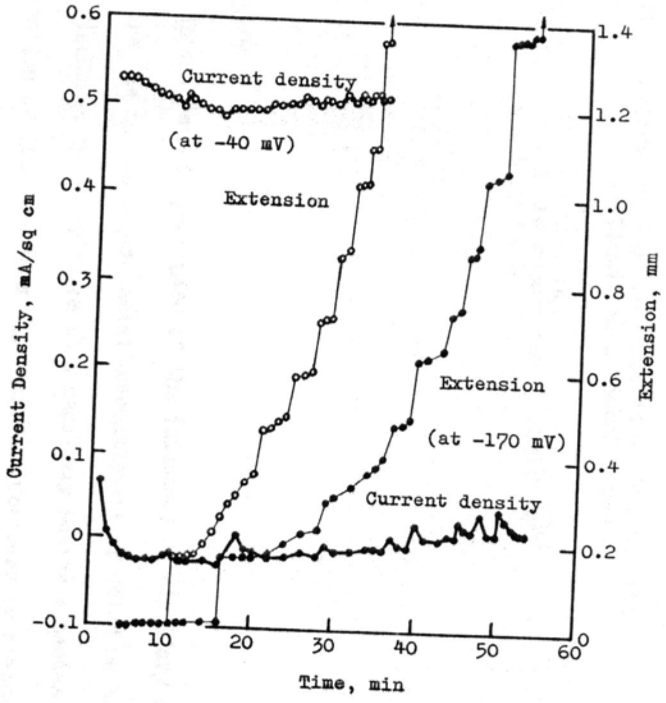

Figure 24.- Changes in current density and in extension of 60/40 brass stressed at 30 kg/sq mm in aqueous ammonia containing 0.94 mole NH_3 and 0.02 g Cr^{6+} ions/liter under potentiostatic control at -40 and -170 mV. Stress was applied by dead-loading.