STRESS CORROSION CRACKING IN LOW ALLOY STEELS

by

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INTRODUCTION

Stress corrosion cracking in its simplest terms is metal failure resulting, over a period of time from the conjoint action of stress and corrosion. In reality, the problem is more involved than this definition might suggest for the reason that the two operating factors, namely, stress and corrosion do not act in a simple additive way. Stress corrosion cracking is not a mere case of metal corrosion in the presence of stress. Although it is true that corrosive attack is part of the mechanism, the extent or severity of corrosion is not a guiding criterion for susceptibility to cracking. Many mildly corrosive environments have been recognised as strongly potent in causing this type of failure. A classical example was noted (1, 2) in an experimental alloy which was stressed and immersed in a mineral oil-Nujol-and which failed in 735 days. Failure was due, as later confirmed, to the small amount of moisture absorbed while the specimen was being machined in air prior to testing. Again, as Champion reports (3), aluminium alloys are much more suspectible to stress corrosion cracking in weak industrial acid environments than in strong acid solutions.

The complexity of the problem is further emphasized by the lack of any systematic classification of stress corrosive environments or a suitable explanation for the very different effects of closely related chemicals.

With regard to stress, common experience indicates that tension at the metal surface is essential if cracking is to occur. This may be produced by application of external tensile loads. It may also occur as residual stress, developed by assembly of improperly matching parts or by prior cold working or quenching without adequate stress relief. In practice, a far greater number of failures arise from internal rather than external stresses. This is probably related to the difficulty of estimating accurately the magnitude and direction of internal stresses which may, therefore, attain unexpectedly high values. On the other hand, stresses due to external loads are easily calculable and hence can be maintained within safe operating limits.

The earliest example of stress corrosion cracking dates back to 1886 (4) with mention by Robert Austen of a gold-silver-copper alloy failing in ferric chloride solution. Since then, many studies have been reported but no adequate theory is yet available to explain the phenomenon in its entirety, despite the lapse of nearly eighty years. One of the reasons for this is that effective remedies were easily hit upon by trial and error and were adopted in an empirical way to mitigate the problem in industry. For example, it was realized that cracking could be overcome by an adequate softening heat treatment or by a suitable compositional change in the material. Failure could also be prevented by superficial compressive stresses. The problem of stress corrosion cracking remained of active interest, therefore, only to the basic research worker. Recently, however, it has become evident that most commercial metals and alloys are prone to failure under suitable conditions. This realization, coupled with a partial understanding of the mechanism, has resulted in a tendency on the part of metallurgists to suspect stress corrosion in every dubious case of metal failure.

The very early problems in this field have been solved. The

"season cracking" of brass has been overcome by a proper annealing treatment and boiler failures resulting from "caustic embrittlement" have been reduced to a minimum by proper feed water treatment and the use of suitable steel. In spite of this, stress corrosion cracking continues to manifest itself. Rapid development of new alloys and the necessary reduction of safety factors in certain new applications are providing an ever-widening field for this phenomenon. It has become clear that the old trial and error methods are inadequate and expensive. A judicious approach would now seem to involve a concerted effort to understand the basic mechanism of the process so that the problem is averted from the start.

Several theories have been proposed from time to time of which the "electrochemical mechanisms" and the "partial electrochemical-mechanical mechanisms" enjoy the greatest popularity. Even these have their shortcomings and are by no means universal in application. This is evident from their inability to predict environments in which specific alloys will crack or, alternatively, to predict those alloys that will fail in a given environment. Such being the case, there is justification for another and closer look into the subject.

A critical review of the literature dealing with stress corrosion cracking and hydrogen embrittlement - the latter phenomenon representing the case of brittle failure due definitely to the action of hydrogen - reveals very interesting similarities between the two phenomena. The comparison is especially good in regard to the mode of failure, the nature of the fracture surfaces and the effects of variables such as "cold work", strength, hardness and composition of materials. This observation, coupled

with a lack of convincing differentation between the two modes of failure, has prompted the present investigation into the possible role of hydrogen in stress corrosion cracking.

LITERATURE SURVEY

The main factors in stress corrosion cracking are a) stress, b) corrosive environment, c) structure of the material and d) time. These factors interact and depending upon conditions, assume varying degrees of relative importance in different cases.

a) Stress

Stress may be defined as the intensity of force produced in a body either from within, due to unequal expansions or from the application of an external load. In so far as any given point within the body is concerned, the terms "external force" and "internal force" cannot be differentiated since, in both cases, the force is applied through the immediately adjacent material. However, the two terms serve the purpose of enabling a classification of stresses acting on a system.

Internal or residual stresses may be further sub-divided into two classes (5): macrostresses and microstresses. Macrostresses arise from heterogeneous plastic deformation and operate over areas comparable in size to dimensions of the material. Microstresses, on the other hand, act over domains of microscopic magnitude. They are generated by such factors as 1) grain boundary effect, 2) slip and 3) anisotropy.

Residual stresses are very important in relation to stress corrosion cracking because numerous failures result from their action. Considerable attention has been given to internal stresses, especially

in cold formed brass articles (6) and mild steel boiler plates (7,8). Difficulty of measuring the magnitude of internal stresses has focussed attention on practical remedial treatments consisting of common sense methods of keeping stress concentration at a low value. This is achieved by the avoidance of sharp changes in cross-section, the use of generous fillets and the proper alignment of mating parts. Heat treatment methods are, at best, a compromise between the desire to retain strength and hardness in the material and to provide the maximum stress relief.

Experimental work with known external loads has been done by Moore et al (9) on 70-30 brass in mercurous nitrate solution, by Parr and Straut (10) on boiler steel in caustic solutions and by Rawdon (11) on duralumin. There is general agreement with the view that time to failure increases with a decrease of tensile stress and that stress assumes significance only when it attains sufficient magnitude so as to cause at least some plastic deformation (12) in the material. This does not imply that the conventional elastic limit has to be reached. The boundary between elastic and plastic behaviour is not sharply defined (13); stress calculations based on applied load and gross cross-sectional area do not take into account stress concentrations which, in some instances, attain high enough values to produce localized plastic yielding.

According to Eckel (14), a decrease in the tendency to crack with a diminution of applied load suggests the existence of a "threshold" or "limiting" stress below which stress corrosion cracking does not occur. This claim has been substantiated by showing that graphs of applied stress against time to failure are asymptotic to the "time axis". Scheil (15)

for instance, reports a value of 10,000 psi for austenitic stainless steels in boiling magnesium chloride solution. Warren and Beckman (16), working on sulphide corrosion cracking of high strength, low alloy steels give threshold values as a function of hardness. Sufficient results, however, are not yet available to confirm the general existence of a threshold stress for all systems. Reproducibility of threshold values is poor (17), even for apparently identical test conditions and the consensus seems to be that threshold data should not be relied upon heavily in engineering design.

More important than the strains per se developed due to stress are the changes brought about in the rate and distribution of corrosion reactions. Tammann and Newbert (18) observed increased rates of corrosion for cold worked aluminium and magnesium alloys in hydrochloric acid over the annealed materials. Friend (19) noticed a similar effect in the case of iron in dilute sulphuric acid although he observed no marked difference in corrosion rate in sea water. These results were later confirmed by Skapski and Chyzewski (20).

Before attempting to explain these observations, it is important to study the effect of stress on the electrode potential of metals. Jacquet and Duet (21) observed that cold worked, high purity aluminium in neutral 3% sodium chloride solution was 40 to 50 mv more anodic (electronegative) than annealed metal, while Evans and Simnad (22) reported the potential of cold worked steel in dilute hydrochloric acid to be approximately 40 mv more anodic than annealed steel. Hoar and West (23) found a similar effect in strained 18-8 stainless steel wire.

One is tempted to ascribe the increased corrosion rate of cold worked metal to its greater anodic potential. However, it is difficult to explain on this basis the equal dissolution rates of annealed and cold worked iron in sea water, as observed by Friend, or of commercially pure nickel in hydrochloric acid, as shown by Copson (24).

For aluminum specimens, Thompson has shown that the potential variation caused by plastic straining gradually diminishes if the metal is left undisturbed for a period of time. This is explained on the basis that plastic deformation causes a rupture of the surface film, exposing fresh metal which is more anodic than the film. With lapse of time, the film is repaired and the potential approaches its original value. Logan (25) has studied this aspect of the subject in greater detail and has demonstrated large variations of potential - up to 0.76 volt in some cases - with breakdown of atmospherically formed surface film for aluminium and magnesium alloys and for brass and steel.

Uhlig (26) maintains that stressed metals corrode more rapidly than corresponding unstressed ones when the cathodic evolution of hydrogen is rate controlling. This is because plastic deformation produces compositional differences leading to the development of local cathodes where hydrogen evolution is facilitated. The manner in which compositional gradients arise during cold work depends upon the preferential segregation of foreign atoms to grain boundaries and other imperfections where dislocations tend to concentrate. By the same argument, when the oxygen depolarization reaction is rate controlling, the state of the metal does not affect its corrosion rate because then,

availability of oxygen at the metal surface is the governing factor.

b) Corrosive Environment

One of the characteristics of the phenomenon of stress corrosion cracking lies in the specificity of environments that produce failure of a given metal or alloy. Thus, boiling concentrated aqueous nitrates and alkalis produce failure of mild steel, while chlorides, sulphates and perchlorates are ineffective (27). Stainless steels, types 304 and 347, fail in oxygenated neutral sodium chloride solution at 74°C but remain uncracked when the pH is raised to 8.8 by sodium hydroxide addition (28). Again, 95% magnesium - 5% aluminium alloy cracks in aerated distilled water but does not in the absence of oxygen (29). Several similar examples could be cited to emphasize the diversity in behaviour of chemically similar corrodents or, alternatively, the wide range of susceptibility of similar metal systems in a single corrodent. A problem, however, arises when attempting a general explanation of all cases by means of any of the published stress corrosion theories. Numerous laboratory investigations have been conducted but these are restricted to media which produce failure in reasonably short periods. A list of environments for some of the sensitive metals is given in table I(30).

With regard to the nature of corrodents that produce cracking, only very broad generalizations can be made. Those most active in causing failure produce little general surface corrosion; the attack is highly localized and similar to "pitting corrosion" in unstressed specimens. The number and type of pits formed in the unstressed condition

TABLE I

Environments that cause stress corrosion cracking of some metals and alloys.

[After E.C. Roberts (30)].

No.	Material	Environment
1.	Copper alloys	Ammonia vapours and solutions; amines
2.	Aluminium alloys	Sodium chloride solutions including sea water, especially those containing hydrogen peroxide
3.	Gold alloys	Ferric chloride solutions; acetic acid solutions
4.	Incone1	Sodium hydroxide solutions
5.	Lead	Lead acetate solutions
6.	Magnesium alloys	Sodium chloride-potassium chromate solutions; saline atmospheres
7.	Monel metal	Fused sodium hydroxide; hydrogen fluoride; hydrofluosilicic acid
8.	Nickel	Fused caustic soda
9.	Plain carbon and low alloy steels	Sodium hydroxide solutions; sodium hydroxide- sodium silicate solutions; calcium, ammonium and sodium nitrate solutions; sulphuric acid- nitric acid solutions; hydrogen cyanide sol- utions; acidic hydrogen sulphide solution; sea water; molten sodium-lead alloy
10.	Stainless steel	Acid chloride solutions such as magnesium chloride and barium chloride; sodium chloride- hydrogen peroxide solution; sea water; sodium hydroxide - hydrogen sulphide solution.

offer an indication of the tendency of the material to crack under stress corrosion conditions. Tempering temperatures are important in this respect. For A.I.S.I. 403 stainless steel, Fontana (31) has shown that sharp pits develop in material tempered at 650°F and that acuity progressively decreases with increase of temperature up to 1100°F when round-based pits become evident. This is the basis of his explanation for the greater suspectibility of mildly tempered materials in comparison to those subjected to high tempering temperatures. Sharfstein and Brindley (28) report that sustenitic stainless steels fail in neutral sodium chloride solutions as dilute as 5 p.p.m. In basic solutions obtained by phosphate additions, fewer pits are produced and susceptibility to cracking decreases correspondingly.

Temperature and concentration of the corrosive solution may now be considered. On the basis of increased chemical reactivity, one might expect shorter times to failure at elevated temperatures. According to Roberts (30) this is not necessarily true, on several counts. Firstly, if the temperature is sufficiently high, internal stresses in the metal may be relieved with consequent reduction in the tendency towards cracking. Secondly, the nature of the corrosion product might be altered from a soluble type at room temperature to an insoluble, protective one at elevated temperature. If, however, the coating does not cover the metal completely, the situation may be rendered even worse because the small remaining areas of exposed metal become centres of intensified attack causing accentuated stress corrosion cracking.

Solution concentration is treated similarly (30). In some

cases, a dilute solution is more severe than a concentrated one simply because the material is passivated by the latter.

c) Nature of Material

It has been fairly well established that pure metals are immune to stress corrosion cracking. This statement needs clarification to indicate the degree of purity implied. In fact, there is no set limit and the amount of impurity sufficient to destroy immunity depends on the metal and the specific impurity under consideration. Thus, 99.999 + % copper (32, 33) is immune to aqueous ammonia atmospheres in which failure occurs with the presence of as little as 0.05% arsenic, 0.01% antimony or 0.004% phosphorus (34). Again, one atomic percent gold imparts susceptibility to pure silver which is otherwise immune in 2% ferric chloride solution (35).

In the case of alloys, impurities have a significant effect in some systems and not in others. For example, nitrogen and carbon contents are critical for stainless steels in boiling 42% magnesium chloride solution. In a test with 18-8 stainless steel (36) failure did not occur up to 300 hours when nitrogen and carbon percentages were held below 0.015, whereas 18-8 of commercial purity failed in 0.2 to 1.4 hours. Similar behaviour was observed for austenitic 20% Cr 20% Ni stainless steel; no failure occurred up to 250 hours when the nitrogen content was within 0.002% but cracking occurred in 59 hours for a similar alloy containing 0.115% nitrogen. As against these examples, Graf (35, 37) and others (38) point out, alloys of silver-gold (Ag - Au), copper-gold (Cu - Au) and aluminium-magnesium (Al - Mg) stress corrosion crack in ferric chloride solution, regardless of purity. Similar results were found for brass in ammonia atmospheres (39, 40).

No comprehensive explanation is available for these observations although preferential corrosive attack is believed to result from potential differences arising from segregation of foreign atoms to regions where the matrix atoms are in a state of greatest disarray. Because such regions contain a variety of defects, foreign atoms - both large and small accumulate there and hold the energy of the system to a minimum. Similarly, heat treatments that produce segregation or precipitation, develop compositional gradients and render initially resistant material susceptible to stress corrosion. For mild steels, prolonged heating just below the transformation temperature (700°C) causes migration of carbide to the grain boundaries and induces stress corrosion failure (41). In copper-aluminium alloys noted for age-hardening, precipitation of CuAl, particles along the grain boundaries (42) leaves the parent alloy in their immediate vicinity impoverished of copper. These denuded areas, according to Dix and Richardson (43) are anodic to both the unaffected parent matrix and the CuAl, particles and are thus susceptible to preferential attack. For aluminium-magnesium alloys aged below 212°C for a week, Beerwald et al (44) attribute stress corrosion to the precipitation of a β -phase of approximate composition Al₃Mg₂.

The importance of phase transformations is emphasized in an investigation (45) of steel employing an aqueous mixture of hydrogen sulphide and carbon dioxide as the corrosive environment. While no failure results when martensite constitutes less than 33% of the structure, the

same steel fails at a low stress - 25% of the yield strength - when it contains 75% martensite. With intermediate martensite content, failure occurs only at stresses in excess of 50% of the yield strength.

d) Time

The failure process resulting from stress corrosion is considered by different authors to consist of several stages.

1. An incubation period during which no cracks are formed but, presumably, local anode and cathode sites develop for subsequent preferential corrosion (14).

2. A crack propagation stage during which cracks appear in the material and propagate along paths generally perpendicular to the direction of the highest tensile stress (46).

3. A sudden failure when the remaining uncracked section is reduced to the extent that it can no longer bear the imposed load (47).

Some alloys do not fail when tested immediately after a heat treatment or a cold deformation but a lapse of six months to a year at room temperature renders them extremely prone to stress corrosion (1). Obviously, this is the result of internal changes due to "ageing". In these circumstances, time may be considered to play a dual role, namely, that of rendering the alloy susceptible to stress corrosion followed by its function in the actual failure process. Admittedly the two effects overlap in many instances.

In most cases, ageing times are curtailed by elevated tempe-

rature (1) and in laboratory investigations where times must be reasonably limited, this technique is often resorted to. Obviously, a great deal of caution must be exercised in these cases to ascertain that other relevant factors are not seriously affected.

Stress Corrosion Failure in Some Commercial Metals and Alloys.

a) Iron, Plain Carbon Steels and Low Alloy Steels

Stress corrosion cracking studies of iron and steel have been confined, more or less, to concentrated boiling calcium, sodium or ammonium nitrate solutions (48), boiling caustic soda, dilute nitric acid containing a small amount of manganese chloride and at a slightly elevated temperature, concentrated nitric acid (49), aqueous hydrogen cyanide (50) and hydrogen sulphide solutions (51). All of these corrodents are very effective in that failure occurs within a relatively short period of time and except for the last two mentioned, cracking is generally intergranular.

Early instances of failure in mild steels concerned "boiler embrittlement" in which cracks were frequently observed to originate from rivet holes (8). Failure occurred when the sodium hydroxide in alkaline feed waters attained a critical concentration in capillary spaces due to slow leakage and evaporation. In high pressure boilers, silicates (52) aggravate the attack while sodium nitrate or phosphates (53), waste sulphite liquor, tannins and lignins have the opposite effect. In modern welded boilers, embrittlement is much less likely if an adequate stress relief is provided after welding. U-bend specimens immersed in different concentrations of aqueous sodium hydroxide constitute popular laboratory practice for studying caustic embrittlement (54). The effects of chemicals present in service boilers are evaluated from the results of such laboratory test using controlled additions of these chemicals.

More recently, attention has been drawn to the large number of failures observed in the chemical industry and specifically to hydrogen sulphide cracking to which low alloy, high strength steels are particularly susceptible (55). While hydrogen sulphide is recognised to be the chief corrosive agent, the presence of water is also essential; no failures result in non-aqueous solutions (55). On the other hand, it appears from test results that oxygen or carbon dioxide have no significant influence. A small amount of acetic acid is an effective accelerator and test temperature assumes importance in borderline cases.

b) Stainless Steel

Among the three principal types of stainless steels, namely, austenitic, ferritic and martensitic, the first seems to be most susceptible to stress corrosion cracking (15, 56, 57). Many examples of this steel failing in practice have been reported (58, 59, 60) since the pioneer work of Dixon (61) in 1935. Slightly acid chloride solutions are very effective and a popular laboratory corrodent is boiling 42% magnesium chloride solution. Cracking is normally transgranular in this solution as well as in hydrogen sulphide and other sulphur containing compounds. However, if the steel is "sensitized" by heating to precipitate carbides along

the grain boundaries, intergranular failure results.

Ferritic and martensitic stainless steels are much more resistant; failure occurs only after longer exposures in the same solutions. Uhlig (62) has shown for ferritic 13% chromium steel that rapid cracking only occurs when conditions favour hydrogen discharge at the metal surface such as by cathodic polarization or by coupling the steel to a more anodic metal like aluminium. Surprisingly enough, cold drawn austenitic 18-8 wire does not crack under these conditions. It has been suggested that hydrogen is unable to diffuse easily enough into the austenitic structure to contribute to failure (56).

c) Copper Alloys

"Season cracking" of brass, so called because the fracture resembles cracked seasoned wood, has received continuous attention for almost three quarters of a century. Special interest was aroused during the first world war when numerous failures of brass cartridge cases were reported. Since then, brasses continue to maintain a prominent place in the field of stress corrosion and have been employed on numerous occasions for basic as well as applied research.

The important corrosive media are ammonia and its derivatives in the presence of carbon dioxide, water and oxygen. Other environments in which failure occurs include ferric sulphate (63) and mercurous nitrate solutions (64).

More often than not, cracking occurs intergranularly in aqueous

solution although small individual additions to the alloy of elements (39) like arsenic, tin, silicon, zirconium, phosphorus, manganese and silver induce simultaneous transgranular cracks. In some cases, hydrogen ion concentration in the corroding solution assumes importance. According to Mattson (65), 62% copper - 38% zinc alloy fails intergranularly in a neutral solution of ammonium sulphate and copper sulphate, but when the pH is raised above 7.8 or lowered below 5.7, transgranular cracks become evident.

Work by Tracy and Thompson (32) reveals that, starting with pure copper which is relatively immune to cracking, successive additions of zinc up to 15% produce a gradual increase in susceptibility to stress corrosion. Thereafter, there is a very rapid increase and brasses containing 20% zinc are highly susceptible. From this composition to 40% zinc, the alloys show only a small continuing trend in the same direction.

Impurity elements in the brasses have the reverse effect to that normally expected. According to Wilson et al (39), there is a decrease rather than an increase in cracking tendency when elements like silicon and phosphorus are added.

In comparison to the brasses, other copper alloys such as aluminium-bronze, cupro-nickel, tin-bronze and silicon-bronze season crack to a much lesser extent; only a few stray instances of failure have been reported to date.

d) Aluminium and Magnesium Alloys

The problem of stress corrosion cracking is very prevalent

amongst aluminium and magnesium alloys, some of which find important applications in the aviation industry.

For the aluminium base alloys, cracking is predominantly intergranular and occurs with great rapidity even in relatively mild environments.

Considerable importance is placed on the electrochemical nature of stress corrosion in the failure of these alloys. Preferential attack at grain boundaries in suitable environments is attributed to precipitation of an anodic phase in these areas. The seriousness of the potential difference depends on the electrochemical nature of the precipitating phase with respect to the matrix and on the relative amounts of precipitation in the boundaries and the interiors (42). Minor alloying elements are considered to play an important role in this respect.

That a real potential difference is developed and that anodic dissolution of the grain boundaries does result is vividly demonstrated for aluminium - 4% copper alloy in the work of Mears et al (34). They compared the potential of a specimen in which the grains were insulated with a suitable varnish with that of another in which the grain boundaries were similarly coated. On the basis of such electrochemical relationships, the ability of certain alloying elements to cause stress corrosion cracking was explained. Metals like copper, zinc and magnesium which have a higher solubility limit in aluminium at elevated temperature and which, on ageing, form precipitating constituents at grain boundaries or planes of slip, render aluminium susceptible to stress corrosion failure. For example, aluminium alloys containing more than 6% magnesium, 12% zinc or 4% copper

fail easily after a suitable ageing treatment. On the other hand, aluminiummanganese alloys are relatively immune because the manganese solubility is low and the aluminium-manganese phase exhibits approximately the same potential as pure aluminium.

With magnesium - base alloys, the problem of stress corrosion cracking assumes importance when the alloying elements are aluminium and/or zinc. While pure magnesium and magnesium - manganese alloys are relatively immune (66), susceptibility increases rapidly with aluminium content (67). This is rather unfortunate because the same metal is capable of rendering high mechanical strength to magnesium and is, therefore, an important constituent in the light alloy series that find wide application, especially in the aircraft industry.

As in austenitic stainless steels, and in contrast to aluminium - base alloys, cracking in magnesium alloys is predominantly transgranular and apparently independent of the alloy structure (68).

Only residual stresses resulting from heat treatment or improper assembly of parts have been reported to cause failure; in no case has an applied load under service conditions, been known to cause cracking (69). This suggests that plastic deformation may be a very important factor, and has led several authorities to advocate a low temperature, stress relieving treatment as a means of alleviating the problem. Whether, in fact, the beneficial effects of the thermal treatment result from the stress relief, is open to question.

Chloride solutions containing chromates or bi-chromates of

alkali metals are popular environments in laboratory investigations because they produce little general surface corrosion while causing rapid stress corrosion cracking. However, according to Perryman and Brook (70), these corrodents do not reflect practical conditions and give results that are not as valid for practical interpretation as those obtained using milder corrodents such as distilled water or very dilute sodium chloride solutions.

Theories and Mechanisms of Stress Corrosion

Cracking

The phenomenon of stress corrosion cracking is well known though not well understood. In the past, work in this field has been devoted mainly to a search for immediate solutions to practical problems rather than a better understanding of what was happening. Possible mechanisms have been proposed from time to time but none of these is completely satisfactory.

Jones (48) was among the early investigators to make a systematic study of the phenomenon. He confirmed the conclusions of Andrew (7) and Merica (8) that failure occurred due to rapid solution of "amorphous material" at the grain boundaries by the environment (56). Opposite to this view were other theories that ignored the corrosion aspect entirely. They emphasized the importance of stress to the extent of stating that the sum of the internal and external stresses were alone sufficient to cause failure. Subsequent realization that stress corrosion cracking occurs only when both stress and corrosion were operative, invalidated these earlier ideas and confined further speculation to theories that took into consideration the combined action of both factors.

a) Electrochemical Theories

Dix was among the first to propose an electrochemical theory for stress corrosion (1). Stated in simple terms, crack propagation was considered to result from selective dissolution of more or less continuous regions of the material exhibiting a less noble potential than areas comprising the major part of the structure. The action of stress was to extend the preferential dissolution by pulling the metal apart along these continuous paths and permitting the corrodent to come in contact with fresh anodic surface.

The existence of potential variations along a metal surface has been demonstrated experimentally. Aluminium - 4% copper alloy, exposed to an electrolyte of sodium chloride - hydrogen peroxide solution exhibits an open circuit potential on the $\frac{N}{10}$ calomel scale of -0.748 v at the grains and -0.792 v at the grain boundaries. Large grained annealed brass (68) develops a potential difference of about 0.072 v between grains and boundaries in aqueous ammonium solutions. An important question is, how are these potential differences created. Observations by Hoar and West (23) that strained metal lattices undergo dissolution with greater ease than unstrained lattices lead one to suggest preferential dissolution of grain boundaries on the same basis, since these areas also represent a high energy state (71). The work of Lacombe (72) using aluminium in 10 % hydrochloric acid indicates that boundaries between grains of widely differing orientation suffer much greater attack than those where differences are small. Similar results were obtained for copper alloys by Robertson (73).

From the stress corrosion point of view, it is important to ascertain whether the greater energy release during strained metal dissolution is alone sufficient to account for the rate at which crack propagation occurs. Uhlig (26) is of the negative opinion and has shown thermodynamically that the change in chemical potential of a metal from the annealed to the cold worked state is far too small to account for the observed increase in corrosion rate. Rather, a compositional gradient produced by localized plastic deformation or preferential precipitation during ageing is claimed to be responsible. Kellar (74) provides experimental support for this by his work on duralumin alloys which being initially resistant, are rendered susceptible to intergranular cracking by the same heat treatment that causes precipitation of discrete particles along the grain boundaries. Again, Fink and Smith (75) have made the observation that susceptible aluminium copper alloys show marked precipitation at the grain boundaries. In all these cases, three distinct zones are developed. These are:

- 1. The major part of the grain that remains unaffected,
- 2. The grain boundary where precipitation occurs,
- The adjoining region which undergoes a compositional change.

The nature of the corresive attack depends upon the relative potentials of the three zones. The situation is conducive to rapid preferential corrosion when (2) is anodic to (1) and (3) or when (3) is anodic to (1) and (2) because, in either case, a condition of small anode and large cathode exists. In other words, stress corrosion cracking is anticipated when either grain boundary precipitates or the adjoining regions become anodic to the main part of the structure.

While experimental results on aluminium alloys seem to conform to this observation, there is considerable doubt, specially in other metal systems, whether preferential precipitation is the only cause of selective attack. At least for mild steels, Waber and McDonald (76) believe it is and name iron nitride as the precipitating constituent. They have developed the empirical formula:

$$F_{N,F_{*}} = (2 N \% + P \% - A1 \% - 0.1 C \%) \times 10^{3}$$

which is claimed to give the "free nitrogen factor" and consequently a measure of susceptibility to stress corrosion cracking. Parkins (41), however, questions the validity of the relationship on the grounds that deductions apparent from the equation do not hold true. For example, cracking susceptibility does not bear a simple relationship to chemical composition and aluminium, added to eliminate the "free nitrogen" fails to impart immunity.

Dix' theory, in general, suffers from several limitations. Firstly, it assumes the pre-existence of a network of anodic material along the grain boundaries and is therefore unable to account for transgranular corrosion cracking or for failures in relatively homogeneous alloys such as stainless steel and brass. The role of stress is also poorly defined. The existence of threshold stress (at least for some metal systems) makes it appear highly unlikely that tensile forces

merely serve to open up fissures in the material and facilitate corrosion.

To overcome these shortcomings, Waber (77) postulated the "strain accelerated decomposition theory" in which the major function of stress was to initiate precipitation by decomposition of a meta stable phase and thus produce electrochemical contrast. According to the theory, cracking is possible only if the following requirements are fulfilled (56):

1. A phase transition occurs on elevation of temperature.

2. The phase change reaction rate is slow enough that on cooling, the high temperature phase continues to exist at room temperature.

3. The meta-stable phase decomposes isothermally under stress.

4. A fraction of the tensile strength of the material is sufficient to produce decomposition of the matrix.

5. At least one of the products of decomposition - if there are two - is anodic to the matrix.

 Corrosion products formed are permeable enough so as not to hamper entry of corrodent into cracks.

This approach suitably explains some facets of the stress corrosion phenomenon which Dix' theory is unable to account for. A serious objection, however, is that for spontaneous transformation, there must be a decrease of Gibb's free energy and the reaction products be cathodic to the reactant (56). This poses the problem of explaining the formation of an anodic product as required for the stress corrosion

mechanism. Waber, in attempting an explanation, provides separate answers for two classes of strain accelerated transformations. For the case in which one transformation product is obtained, the spontaneous reaction gives a final cathodic product in accordance with the laws of thermodynamics but is considered to proceed through a transient stage which is anodic. Thus, martensite is considered to be the transient product in the transformation of austenite. When two new phases are formed, e.g., during precipitation along grain boundaries where precipitate and adjacent denuded region represent stable products, the average product potential is cathodic but one of the phases may be anodic to the parent matrix.

A prominent feature of this theory consists of ascribing to tensile stress the role of initiating the decomposition reaction. It is also attractive from several other viewpoints but still fails to qualify for universal application. It has been pointed out (78, 79), for example, that austenite is an unlikely source for yielding anodic material and further, that 18-8 steels do fail at temperatures above which martensite transformations can occur. Finally, stable austenitic alloys which do not undergo transformation when plastically deformed are sometimes prone to stress corrosion failure.

Another function of tensile stress is visualized (80) as the breaking of protective, passivating film on the metal. Proposed sites include the base of corrosion pits, where stress concentration is high and local tearing of the metal occurs, and grain boundaries where the film is considered to be relatively weak. In either case, a

cell is developed between covered and film-free surfaces and the latter, being anodic, dissolve. If film repair can occur fast enough, corrosion stops; otherwise freshly exposed anodic surface continues to corrode. According to this viewpoint, susceptibility to stress corrosion depends upon film repair and deformability characteristics of the material as well as the passivating nature of the corrosive solution.

In summary, the electrochemical theories discussed visualize stress corrosion cracking as resulting from the combined action of stress and corrosive environment. Crack sensitive paths either pre-exist in the metal due to compositional variations or are developed in situ by 1) decomposition of a meta-stable phase, 2) rupture of protective films or 3) lowering of potential due to localized plastic deformation. In any case, a condition for preferential corrosion is achieved. However, stress corrosion cracking rates cannot be accounted for by a simple anodic dissolution process as implied by the electrochemical theories (81, 82). This has led to several other proposals, discussions of which follow.

b) Electrochemical - Mechanical Mechanisms

The electrochemical-mechanical mechanism postulated by Keating (83) is similar to electrochemical theories only in regard to the process of crack initiation. The latter theories propose continuous dissolution of anodic areas with failure ultimately resulting therefrom; the role of stress lies in developing or maintaining such anodic sites. Supporters of the electrochemical-mechanical mechanisms hold the view that crack propagation occurs by purely mechanical means, arrested

periodically by obstacles in the crack path which serve to lower the stress concentration; these must be removed by chemical dissolution to permit further crack extension. Such obstructions take the form of non-metallic inclusions, lattice discontinuities and unfavourably oriented grain boundaries. Pending arrival of the corrodent at the crack tip, corrosion may occur along the sides to account for the branching nature of cracks observed in several cases.

The idea of discontinuous propagation resulting from rapid mechanical cracking alternating with slow electrochemical dissolution has obtained support from a number of ingenious experiments. Gilbert and Hadden (84) have noted, during intergranular cracking of aluminium - 7 % magnesium alloy in an oxygenated sodium chloride solution, sudden deflections in a beam of light reflected by a mirror attached to U-bend specimens. Sporadic behaviour was observed by van Rooyen (85) in the form of sudden jumps in electrochemical potential, together with simultaneous acoustic signals during the cracking of aluminium - 4 % copper alloy in sodium chloride - sodium bicarbonate solution. Microscopic examinations of single and polycrystalline & -brasses stress corroded in ammonia (86, 87) and motion picture studies of austenitic stainless steels in aqueous sodium chloride (88) revealed evidence of similar periodic effects.

In spite of this evidence, a word of caution is offered regarding the interpretation of microscopic and motion picture data. Discontinuous progression of a crack in two dimensions does not imply similar propagation in the bulk material (89). Also, there are cases such a

as the cracking of 18-8 stainless steel in boiling 42 % magnesium chloride solution (81, 85) and that of furnace cooled magnesium - 6 % aluminium -1 % zinc alloy in sodium chloride - potassium chromate solution, in which a cyclic cracking process is not definitely established.

The possibility that corrosion products fill cracks and exert a wedging action, thereby contributing to tensile stresses in the system, is a novel and interesting approach to the problem. Conditions under which effective wedging action can occur are well defined and automatically restrict such an effect to particular systems. These conditions are (93):

1. That the corrosion product is insoluble in the corrodent,

2. That it occupies a larger volume than the metal consumed in its production,

3. That it forms in the crack and remains there.

Nielsen (90) has demonstrated for stainless steel in magnesium chloride solution that corrosion products can exert sufficient pressure to extend stress corrosion cracks. The direction of propagation is quite random, at least on a macroscopic scale, implying (93) that wedging action occurs immediately behind the advancing tip as shown in figure 1A and not further back as shown in figure 1B. Further, the thickness of corrosion products measuring only a few hundred angstroms, limits the radius of curvature of the crack root to the order of lattice dimensions. Such a narrow advancing front has been confirmed independently by Gulbransen and Copan (91). Numerous results to date substantiate Nielsen's wedge theory but more work will be necessary to establish general validity.

FIGURE 1

Schematic drawings of crack showing location of corrosion product. [After Pickering, Beck and Fontana (93)]



Another model for electrochemical-mechanical failure is presented by Forty(92). He states that an embrittled zone of material is required for crack initiation but that propagation can occur through relatively ductile regions. The role of the corrosive environment is restricted to the initiation step only. Implicit in this theory is the assumption that cracking is possible only when crack propagation is faster than dislocation movement so that local yielding at the advancing crack front does not occur.

Support for Forty's restricted slip theory is provided by experiments on purified 16 % chromium - 20 % nickel stainless steel (94). This alloy was immune to stress corrosion cracking under the test conditions employed but became susceptible when 1.5 % molybdenum was added (95). Thinfoil transmission studies on deformed specimens of both alloys indicated easy cross-slip in the former and restricted slip in the latter.

In reviewing electrochemical-mechanical mechanisms, one observes that all assume the factors of stress and corrosive environment to act sequentially. Although this offers a satisfactory explanation for discontinuous crack extensions, it fails to explain the specificity of metalsolution pairs. According to Romanov (96) there are difficulties associated with the effect of cathodic polarization. Again, if the mode of stress corrosion cracking is essentially non-ductile, body centered cubic metals should fail along cleavage planes and face centered cubic systems along slip planes (56). This is in contradiction to the large number of intergranular failures that take place below the equicohesive temperature.

Some improvement accrues if conditions prevalent during crack initiation are assumed to persist during the propagation stage. The
proposition has been made (97, 98, 99) that, since only a mono-layer of adsorbate is sufficient to reduce appreciably, forces between adjacent adsorbent metal atoms (100), certain ion species in the corroding solution diffuse into the crack, are absorbed at the tip and thus favour metal separation. On this basis, a modified Keating's model would be possible in which mechanical separation along a path of low surface energy alternates with anodic dissolution.

c. Hydrogen Embrittlement

Brittle fracture, known to result from the action of hydrogen is classified under the heading "hydrogen embrittlement". It has not been definitely established whether the difference between this phenomenon and stress corrosion cracking is of a basic nature or not. Here again, the mechanism of embrittlement is not known with certainty because none of the theories proposed to date is completely satisfactory. These theories, generally grouped under the names of their proponents, will be reviewed in some detail because of obvious possible connections with stress corrosion cracking.

Zapffe's planar pressure theory (101), based on Smith's theory of solution (102) states that interstitial atomic hydrogen, initially present in the metal lattice, diffuses to "voids" or "cavities", recombines into molecular form and thereby builds up hydrostatic pressure to the critical value at which the metal lattice seperates.

The effects of strain rate and temperature are explained in

the following manner. When the metal undergoes plastic deformation by the action of a tensile stress, lattice voids increase in size and fresh hydrogen from adjacent regions diffuses into them to maintain the embrittling pressure level. If the strain rate is too high or the temperature too low, the supply of hydrogen is not rapid enough and failure is not brittle. The planar pressure theory also accounts for certain other aspects of the phenomenon. For example, in hydrogenated steel samples, the appearance of blisters, flakes and "hairline" cracks may be explained in terms of disruptive hydrogen pressures.

There are, however, several points on which the validity of the theory may be questioned. Some of these are:

1. Zapffe's theory predicts a continuous increase in embrittlement with test temperature. Actually, for a given hydrogenation procedure, steels exhibit a decrease and then an increase in ductility as the test temperature is progressively elevated (103, 104, 105).

2. For low hydrogen concentrations at which the critical hydrogen pressure is not developed, embrittlement should be absent. Experiments show a continuous curve of ductility against hydrogen content.

3. A high hydrogen pressure existing in voids should give rise to internal stresses which, in turn, should be revealed by internal friction tests. In actuality, no such results are obtained (106, 107).

Following Zapffe's work, Petch (108) proposed a theory based on "Griffith's model" for brittle fracture (109). According to

this model, crack nuclei exist in a material in a state of equilibrium under the opposing influences of the strain energy of the lattice on the one hand and the surface energy of Griffith cracks on the other. Application of an external force of critical magnitude upsets this equilibrium by producing a net energy gain due to crack enlargement, and initiates catastrophic crack propagation. Thus, any change lowering the crack surface energy is reflected in the decreased critical stress requirement for cracking. Petch suggests that this lowering of surface energy is effected by hydrogen adsorbed on the surface of microcracks and attributes the migration of hydrogen from the lattice, to relief of strain energy.

Petch's theory, like. Zapffe' claims that embrittlement is diffusion controlled and suffers the same inability to explain the temperature - embrittlement relationship described previously.

Kazinczy (110) expanded Petch's theory by pointing out that adiabatic expansion of hydrogen during crack propagation would add to the total energy liberated, therefore lower the critical stress for fracture. Simultaneously, hydrogen continues to diffuse into the expanding void to maintain crack growth.

Bastien's theory (111) of embrittlement is a more sophisticated form of Zapffe's theory. It is based on the concept that protons of hydrogen congregate at dislocations and form a "Cottrell atmosphere" (112). Under the influence of stress, these dislocations move through the lattice dragging the hydrogen "atmosphere" along. When they encounter

an obstruction such as a grain boundary, a pile-up occurs with temporary oversaturation of hydrogen and attendant build-up of high pressure. The mechanism requires that hydrogen diffusion is at least as fast as dislocation movement. At high strain rates or low temperatures, this condition is not fulfilled and embrittlement is effectively eliminated.

Another theory of embrittlement developed in 1950 by Troiano et al (105) offers a new and revolutionary approach to the problem. Whereas Zapffe, Petch, Kazinczy and Bastien have considered the damaging effect of hydrogen contained in internal voids in the metal, Troiano et al attribute the blame to a critical concentration of hydrogen in the lattice. The presence of hydrogen in the voids influences embrittlement only indirectly "by regulating the hydrogen content in the lattice adjacent to the void" (113). The mechanism is related to the distribution of stress Just beyond the tip of the in a notched system under tensile load. notch (crack) a point of maximum triaxial stress occurs and, under the stress gradient, hydrogen diffuses in this direction. When a critical concentration is reached a crack is formed which now serves as a new notch tip. The process continues, and when sufficient hydrogen has diffused to the new region of maximum triaxiality, a new crack forms. Thus, the process is represented as a series of discontinuous crack extensions with final fracture. A variation in temperature effects hydrogen mobility and consequently its ability to diffuse to regions of triaxiality.

Troiano et al (105) investigated the ageing characteristics of plastically strained S.A.E. 4340 steel. Hydrogenated specimens were pre-strained at $-321^{\circ}F$ (where hydrogen diffusion is curtailed), aged at

higher temperatures and then tested under constant embrittling strain rates. A typical ageing time - ductility curve is shown in figure 2. The behaviour is inexplicable by the earlier theories of hydrogen embrittlement but Troiano explains the changes in the following manner:

<u>Stage 1.</u> During the initial period of ageing, hydrogen diffuses from the lattice to the voids in an effort to regain equilibrium which was disturbed by enlargement of voids during the low temperature straining. This causes a depletion of hydrogen in the lattice neighbouring the voids, including the triaxiality regions and therefore a decrease of embrittlement.

<u>Stage 2.</u> As the level of hydrogen in the voids rises, so it does in the surrounding lattice, including the triaxiality point, and embrittlement increases.

<u>Stage 3.</u> The increase in ductility during this stage, in which ageing times are of the order of several hundred hours, is attributed simply to the reduction of gross hydrogen content of the specimen by loss to the surrounding atmosphere.

Finally, Troiano's sustained load test (114, 115, 116) on notched and hydrogenated specimens stressed to fractions of their yield strength, give results of failure occurring after a finite lapse of time, similar to delayed failure phenomenon in stress corrosion cracking. The importance of Troiano's theory lies in its ability to explain several aspects of hydrogen embrittlement and perhaps, to offer a unifying concept between hydrogen embrittlement and stress corrosion cracking.

Ageing time vs. reduction of area percent for S.A.E. 4340 steel, aged at $150^{\circ}F$ and tested at a slow strain rate at room temperature. [After Troiano et al (105)].



Ageing Time, Hours

EXPERIMENTAL

The available methods of stress corrosion testing may be broadly divided into two major categories according to the mammer in which stresses are induced in the specimen. In the constant deflection method, specimens are constrained to a curvature of such radius to produce the required stress in the outermost fibres. The constraint is achieved by jigs and holders of suitable design and capacity. In the constant load method, the specimen is supported in a suitable apparatus and subjected to an externally applied dead weight.

The main difference between the two methods lies in the direction of change in the magnitude of stress during cracking. In the first case, a stress relief occurs as cracks nucleate and propagate (14). In the second case, specimens experience an increase of stress as progressively smaller cross-sectional areas have to withstand the same load.

Much can be said in favour of both methods. The inherent simplicity and convenience of handling loading frames and jigs in the first method is unquestionable, while the ease and accuracy with which initial tensile stresses can be evaluated are among the favourable features of the second. The choice, however, is determined predominantly by the purpose of the investigation. In the present case, the important features of the apparatus consisted of its ability to detect hydrogen embrittlement and its adaptibility to stress corrosion testing.

Figure 3 is a diagram of the apparatus designed (details

Dead weight tension apparatus for sustained load

tests



available in Appendix I) to withstand loads corresponding to a maximum of 3000 lb on the test specimen. "A" was a horizontal beam supported by two vertical columns "B" through a pivot pin. The tensile test specimen "C" was held by the base of the frame at the lower end and attached to the short arm of the horizontal beam at the upper. A universal joint ensured unaxial loading. Dead weight, in the form of lead pellets contained in a bucket "D" suspended from either of two hooks "E" or "E₂" served to load the specimen to the required stress level. Time to failure was measured by an electric clock suitably arranged to stop automatically with fracture.

For calibration of the load system, a "proving ring" of the type extensively employed in soil mechanics was used. The ring itself was calibrated using standard dead weights and a standard load frame manufactured by the Photo-elastic Polarizing Instrument Company, Irvington-on-Hudson, New York. A suitable jig was prepared to transform the tensile load into a compressive load on the proving ring and dial gauge readings were plotted against dead weights to evaluate the beam ratios. Details of the calibration are given in Appendix II.

Specimen

The selection of the material, its heat treatment and hydrogenation procedures corresponded closely with those of Troiano et al except for minor modifications, where necessary to fulfil requirements peculiar to the present work. The steel was purchased from Bowsteel Distributors (Canada) Ltd. in the form of annealed 1/4" diameter rod of aircraft quality S.A.E. 4340. The analysis was 0.425 % C; 0.78 % Mn; 0.008 % P; 0.013 % S; 0.29 % Si; 1.70 % Ni; 0.78 % Cr and 0.25 % Mo. The microstructure of a random sample is shown in figure 4. Finely spherodized cementite is seen in a matrix of ferrite. Specimens prepared from this stock were 20" in length, threaded at both ends for a length of 3". A notch of root radius 0.001" and minimum diameter 0.10" was machined 7-1/2" from one end as shown in figure 5.

Heat Treatment

This material is susceptible to delayed failure only at 200,000 psi (117) and the development of a suitable heat treatment was hindered by the following considerations:

1. The slow dissolution rates of chromium, molybdenum and silicon carbides in austenite (118).

 A high susceptibility to bowing and cracking during quenching.

3. The possibilities of decarburization.

The procedure finally adopted was as follows:

1. Specimens were thoroughly cleaned in varsol and suspended by a jig for 20 minutes in a Vapo-carb furnace maintained at a temperature of $1550^{\circ}F$ and containing a neutral hydrocarbon atmosphere. The average furnace temperature in the notch area of the specimens, as measured independently by a potentiometer and chromel-alume1 thermocouple, was $1603^{\circ}F$.

Microstructure of S.A.E. 4340 steel, as recived. Etchant

2 % nital (x 750)



Dimensional details of test specimen



2. At the end of the austenitizing treatment, specimens and jig were duenched vertically, in oil.

3. Specimens were cleaned of quenching oil with varsol, dried and subjected to a tempering treatment taking 40 minutes in a Hayes Certain Curtain furnace set at $700^{\circ}F$, corresponding to a temperature of $640^{\circ}F$ at the specimen notch.

4. Specimens were quenched in water and allowed to dry in air at room temperature.

Randomly selected samples were tested to destruction in a Hounsfield tensometer and all samples were tested for Rockwell C hardness as a check on the heat treatment.

Hydrogenation

The hydrogenation bath shown in figure 6 consisted of a painted wooden trough "A" containing four parallel strands of thin platinum wire stretched between two lucite plates "B" to serve as anode in an electrolyte of 4 % sulphuric acid. The specimen "C" as cathode, was placed approximately equi-distant from the platinum wires. The complete electrical circuit, represented in figure 7, consisted of appropriate meters, resistances and a bank of Nicad batteries adequate to meet current and voltage requirements. The voltmeter was used to ensure proper maintenance of the batteries.

Hydrogen_delayed failure_tests

Only those specimens that acquired the proper hardness on

The hydrogenation bath



Circuit diagram for hydrogenation

- V Voltmeter (0. to 15 v)
- M Ammeter (0 to 1α D.C.)
- R Rheostat (0 to 27_harma, 4 lpha)
- S Switch
- B Nicad Batteries
- A Anode
- C Cathode



heat treatment were used for subsequent tests. Hydrogenation was accomplished by cathodic charging for a period of 15 minutes at a current density of 0.02 amps. per sq.in. Electrical connection to the external circuit was made through a copper wire tightened between two nuts at one end. Threaded areas were insulated from the electrolyte with paraffin wax. After charging, specimens were rinsed in water, then in alcohol and located in the dead weight tension apparatus. Ten minutes, allocated to ageing, were found sufficient for rinsing, drying and locating the specimen in its proper position. After failure, the notch diameter was determined using a vertical cathetometer of least count 0.001 cm. Fracture was essentially brittle and this measurement permitted an accurate calculation of the imposed stress during the test.

Stress Corrosion Tests

Modification of the apparatus for stress corrosion tests was accomplished as follows. The bottom of a 2-1/2 litre chemical reagent bottle was removed with a diamond saw. With the bottle inverted, a test specimen was passed through a 5/16'' hole in the cap. A liquid seal was obtained by washers, rubber tubing and two nuts, as shown in figure 8.

To check the system for leaks, extended tests were conducted with ordinary tap water. During these preliminary runs, each lasting approximately a week, failure occurred at the notch in one specimen. This aroused much interest and further tests were made to determine whether or not the failure was a manifestation of stress corrosion cracking.

Inverted bottle containing stress corrodent

- A test specimen
- B stress corrodent
- C inverted reagent bottle
- D cover
- E liquid seal
- F part of tension apparatus



In one set of experiments, five specimens were loaded in tap water to various fractions of their yield strengths and times to failure were recorded. In a second series, specimens were immersed, unstressed in tap water for approximately twice the average failure time obtained in the first series. After removal from the liquid, they were dried and subjected to the same loads.

A third set of experiments repeated the first series but distilled water was used in place of tap water.

The deviation from an original plan to use common stress corrosion solutions is justified on the grounds that water is an important environment in many applications of S.A.E. 4340. Results from water tests are, therefore, likely to provide a better correlation with service conditions.

RESULTS AND DISCUSSION

Table II gives readings of tensile tests on non-hydrogenated samples. Five specimens, representing approximately 20 % of the total number were randomly chosen and tested to obtain an average value of the strength acquired by heat treatment. A typical stress-strain curve, shown in figure 9, indicates the characteristically high yield strength with respect to the U.T.S. of hardened S.A.E. 4340 steel. In computation of loads for subsequent hydrogen and stress corrosion test, the yield strength was taken as 90 % of the ultimate tensile strength.

Results of tests on hydrogenated samples are presented in Table III. In addition to delayed failure, several other interesting features were noted.

1. Failure occurred over a wide range of applied stress below the yield strength of the material.

2. Times to failure did not bear a strong relation to the magnitude of applied stress.

3. There was considerable scatter in results.

4. Macroscopic examination of typical fractures using a low power binocular microscope, revealed two distinct portions of the fractured surface. A flat but rough central portion, which was perpendicular to the direction of loading, possessed a "granular" appearance characteristic of cleavage fracture. This was surrounded by a

TABLE II

Ultimate Tensile Strengths and Hardness Readings of Typical heat treated test specimens.

Test No.	A ver age hardness	Breaking load	Cross-sectional area	U.T.S. k.s.i.	
	Rc	$1b \times 10^3$	sq.in. \times 10 ⁻³		
1	45	3.226	7.70	418.0 ^a	
2	46	. ⊜ .3⊊808 °	9.33	409.5	
3	47	2.621	6.65	394.1	
4	45	2.845	7.54	377.3	
5	46	2,912	7.54	386.2	

a Ignored for computation of average U.T.S. because the value seems much higher than nominal.

Average <u>U.T.S. = 391.8</u> k.s.i.

A stress-strain curve for tempered S.A.E. 4340 steel



TABLE III

Results of Hydrogen Delayed Failure Tests

Test No.	Average hardness R	Testing condition	Dead weight ₃ 1b x 10	Cross- sectional area	Stress	Time to failure hr.min.		S tress % average	Stress % yield	
	C			$sq.in.x 10^{-3}$	k.s.i.	S	ec.		U.T.S.	
1	47	Ha	2,803	8,49	330.2	Inst	antane	eous	84.1	93.6
2	48	H	2.803	8,99	311.8		17		79.6	88-4
3.	47	H	2,803	9.50	295.1	15	51	10	75.3	83.6
4 ^b	47	H	2.803	-		10	45	51	-	-
5	47	H	2.803	10.75	260.7	0	27	30	66.6	74.0
6	45	Н	1.954	7.85	249.0	Ō	10	30	63.5	70.6
7	46	H	1.872	8,99	208.2	0	30	29	53.1	59.0
8	46	H	1.872	8,99	208.2	22	45	45	53.1	59.0
9	46	H	1.603	8.17	196.2	0	4	20	50.1	55.6
10	48	Н	1.603	8,66	185.1	1	9	0	47.2	52.4
11	42	Н	1,603	9.16	175.0	3	55	30	44.6	49.6
12	42	Н	1.872	11.31	166.4	0	0	45	42.4	47.1
13	48	Н	1,603	9,85	162.7	1	20	45	41.4	46.1
14 ^C	41	Н	→ -	-	-	-		_	_	-
15	48	н.	1,603	11.12	144.1	. 0	25	56	36.8	40,9
16	48	NHa	1,603	-	-	No	failu	re in	35-50 ^e	
						10	0 hou	rs		
17	47	NH	1.603	-	-	No	failu	re in	35 - 50 [€]	
						10	0 hou	rs		

a) H - hydrogenated specimen

b) Fracture occurred at the lower threads instead of the notch

c) Not used on account of low hardness reading

d) NH - not hydrogenated

e) In the absence of failure, estimated area used to calculate stress.

ភ្ល

ring, not strongly concentric, which also exhibited a crystalline structure and occurred in a different plane, as shown in figures 10 and 11.

These observations conform generally with Troiano's delayed failure studies and indicate that the apparatus and procedures used will reveal hydrogen failure.

Results of tests in tap water and distilled water are summarized in Table IV. A scatter in times to failure is again apparent and the average time is in the order of a week as against a few hours for the hydrogen tests. A fracture surface obtained in tap water is shown in figure 12. Again, fracture was essentially brittle and consisted of two distinct areas, although a peripheral ring was markedly absent. An upper elliptically shaped portion of the fracture surface, extending from the edge to almost the centre, is distinguished by its darker appearance.

The last three tests in Table IV, namely 9), 10) and 11), refer to corrosion tests in which specimens were immersed unstressed in tap water for 744 hours, removed, dried and subjected to tensile loads approximating 75 % of the yield strength. No failure was observed in any of the three specimens in spite of the fact that duration of immersion represented approximately twice the time to failure under comparable loads in stress corrosion tests. This clearly indicates that failure in tap water of stressed specimens is not due to the action of corrosion alone.

The behaviour of hydrogenated specimens subjected to sustained loads below the yield point is well recognised by virtue of extensive

Photograph Showing a Typical Failure Surface of a Hydrogenated

Specimen.

Load 52.4 % yield (x 20)



Photograph Showing a Typical Delayed Failure Surface of a Hydrogenated Specimen. Load 46.1 % yield (x 20)



TABLE IV

Summary of Corrosion and Stress Corrosion Tests

Test	Average hardness	Testing condi-	Dead weight	Cross- sectional	Stress	Time to failure	Stress % average U.T.S.	St r ess % yield
No.	R c	tion	1b ₁₀ 3 ^x	area sq.in.x10 ³	k.s.i.	hr.min.sec.		
_		[`] a						
1	45	T.W	2.310	7.85	294.2	49 32 -	75.0	83.4
2	47	T.W.	1.954	6.64	293.9	377 25 -	75.0	83.4
3	45	T.W.	1.954	7.12	274.4	242 21 -	70.0	77.8
4	44	T.W.	1.954	7.85	249.0	36 13 -	63.5	70.6
5	46	T.W.	1.603	-	-	No failure in	7 5 e	1
		_				960 hours		
6	46	D.W. ^b	1.954	6,65	293.9	0 5 0	75.0	83.4
7 ^C	47	D.W.	1.954	_	-	0 36 0	-	-
8	45	D.W.	1.954	-	-	No failure in		
-						384 hours		
9	46	c ^d	1,954	-	-	No failure	75 ^e	
10	47	C	1.954	-	-	No failure	75 e	
11	47	C	1.954	-	-	No failure	75 ^e	

a) T.W. - tap water

b) D.W. - distilled water

c) Fracture occurred at the lower threads instead of the notch

d) C - corrosion test

e) In the abgence of failure, estimated area used to calculate stress
Photograph of delayed failure in tap water under a load of 83.4 %, yield (x 20)



work devoted to the subject (105, 114, 119, 120). Thus, deleyed failure is explained on the basis of the time required for diffusion of a critical amount of hydrogen to the triaxiality point; the scatter of results is attributed to a number of variables which are difficult to control and evaluate. Such critical variables comprise residual stresses and impurity elements in the metal and electrolyte. In the present work, a similar pattern of results was observed in stress corrosion tests as evident from Table IV: delayed failure, brittle fracture and the characteristic scatter of results.

These and other similarities have been reported in the literature, e.g.

1. The display of threshold stress (30, 48, 119, 120)

2. Electron microscopic comparison of fractured surfaces (121)

3. The dependence of susceptibility on hardness (16, 122), strength (26, 119), grain size (97), extent of cold work (41, 123, 124) and purity (26) of the material.

Further, one finds many instances of so called stress corrosion cracking in which the failure mechanism is associated with the presence of hydrogen (125, 126). For example, conditions which favour hydrogen discharge on the surface of cold worked metals appreciably reduce stress corrosion cracking times. This has been verified for hydrogen generated in the following ways (62):

1. by coupling specimens to a more anodic metal,

- 2. by cathodic polarization and
- 3. by pickling.

One is more or less forced to regard interpretations which preclude the action of hydrogen in stress corrosion failure with the greatest degree of caution, even when experimental results indicate that it does not exert a significant influence on the cracking mechanism. The setting up of experimental conditions in which the presence of hydrogen is definitely eliminated is very difficult, especially for steel in aqueous solution. The relative size of hydrogen as it occurs in metal lattices is small in comparison to the interstitial spaces (127). This affords great ease with which hydrogen can diffuse through the metal. Multiplicity of sources from which hydrogen can be picked up is another important criterion. The steel making process itself is a major source. Pickling, electroplating and corrosion are other sources from which hydrogen can be derived.

In attempting to differentiate between stress corrosion and hydrogen embrittlement, many workers have based their conclusions upon the behaviour of metals with respect to the effect of impressed anodic and cathodic potentials. Thus, if cathodic polarization decreased time to failure, the mechanism was considered to be hydrogen embrittlement, an increase in time to failure indicated stress corrosion cracking. These conclusions are not altogether justified (26) because they presuppose the effect of impressed potential to be limited to the fracture process alone. It is true that cathodic polarization causes the generation of hydrogen but the important point is, how much of this hydrogen evolves harmlessly as gas and how much enters the metal lattice. Cathodic polarization might simultaneously bring about other changes, for example the formation of an intervening film impervious to hydrogen

penetration. This would increase time to failure even though the mechanism is hydrogen embrittlement. By the same token, an impressed anodic voltage can cause dissolution of elements like arsenic, sulphur and phosphorus from commercial metals in which they are usually present. These impurities, even in minute quantities, are effective catalysts for hydrogen intake by the metal and can thus produce effects contrary to what one might anticipate from anodic polarization itself.

Results of the present investigation are inconclusive. The reduction of fracture strength of hydrogenated samples is attributed to the deleterious action of that part of the hydrogen which enters the metal and accumulates to critical concentrations. In figures 10 and 11, the ring is believed to represent the area over which fracture occurred in slow, discontinuous steps, initiated by hydrogen. The central portion failed at a high velocity, due to mechanical overload.

Tap water failures are similar to hydrogen failures in many respects and may well be from the same cause. The hydrogen requirements may be met from local cell action during corrosion. It is true that only a small quantity of hydrogen would be generated under the test conditions but then, only a minute quantity distributed in a particular way is required to produce failure (120). The absence of a concentric ring for specimens fractured in tap water is not surprising. For hydrogen induced cracks to develop uniformly around a periphery by local cell action is most unlikely. Hydrogen enters the metal predominantly at a few active sites and its action is distributed accordingly. The darker area of the fractured surface in figure 12 is believed to represent such

an affected region (128), while the remaining surface failed mechanically.

The cathodic evolution of hydrogen can be represented as follows (129):

$$2e + 2H^{+} \longrightarrow 2H \longrightarrow (1)$$

$$2H \longrightarrow H_{2} \longrightarrow (2)$$
or
$$H + H^{+} e \longrightarrow H_{2} \longrightarrow (3)$$

Phosphorus, arsenic, antimony, sulphur, selenium and tellurium are known to inhibit hydrogen re-combination (equations "2" and "3") (130) and their presence serves, therefore, to create active sites where hydrogen enters the metal.

The much longer times to failure of tap water test specimens is explained on the basis of hydrogen supply. In hydrogenated specimens, the required concentration was achieved prior to the failure test which therefore involved only the time necessary for diffusion. In stress corrosion specimens, failure time included the hydrogenation step which, under the mild test conditions was very slow.

SUMMARY

The primary object of the present investigation was to obtain a better understanding of the problem of stress corrosion cracking. Previous work on the subject was reviewed, during the course of which, certain interesting similarities were observed with hydrogen embrittlement. The possibility of similar failure mechanisms was examined.

Experimental conditions were set up to afford a comparison between failure modes of notched, hydrogenated S.A.E. 4340 steel specimens subjected to sustained loads, and non-hydrogenated specimens, similarly loaded in tap and distilled water.

Delayed failure was demonstrated in both cases at fractions of the yield strength ranging from 40 to 85 %. Three other similarities were noted:

- 1. Brittle fracture,
- 2. Sporadic nature of results,
- 3. Fractured surface comprising two distinct areas.

The possible role of hydrogen in stress corrosion was con-

An explanation for the much longer failure times of specimens stressed in water as compared to the hydrogenated specimens tested in air was given.

SUGGESTIONS FOR FURTHER WORK

The present work has indicated that numerous problems exist even in a qualitative study of stress corrosion cracking. Many of the variables are difficult to control and evaluate. Experimental results are significantly influenced by concentricity of loading, heat treatment, surface finish and composition of the material, impurity elements, applied current and potential during hydrogenation, temperature and ageing time. In an attempt to overcome some of these for a better evaluation of stress corrosion, the following suggestions are offered:

1. The use of a more sophisticated tension apparatus designed to permit more accurate alignment.

2. Arrangements for studying the effects of temperature, pH and impurity elements in the stress corrodent.

3. Provision to follow crack propagation by electrical resistance measurements.

4. The use of high purity distilled water as a stress corrodent.

5. The employment of sheet specimens.

APPENDIX 1

Design of Dead Weight Tension Apparatus

It was decided to use notched specimens of minimum crosssectional area 0.01 sq.in., heat treated to an ultimate strength of 230,000 psi. The design of the tension apparatus was therefore, based on the ability of its various components to withstand loads corresponding to 230,000 x 0.01 = $2300 \approx 3000$ lb. on the test specimen. A line diagram of the apparatus is given below:



a) Universal Jeint





The design of the universal joint was envisaged as in figure on p. 66. Material used was hot rolled, medium carbon steel of yield strength 42,000 psi (131).

Cross-sectional area at section "AA" = $(1/2 \times 1)2 = 1$ sq.in. Using a safety factor of 2 and a stress concentration factor of 3 Safe load carrying capacity = $\frac{42,000 \times 1}{2 \times 3} = 7000$ lb > 3000 lb Safe load carrying capacity of section "BB" = $\frac{42,000 \times 5 \times 2}{2 \times 3 \times 8} = 8750$ lb > 3000 lb

Hence design is satisfactory.

b) Short Pin Supported by Universal Joint and Carrying Test Specimen

A stress concentration effect occurs due to the presence of the circular hole. From reference (132)

$$\frac{r}{d} = \frac{\widetilde{Om}}{\widetilde{\sigma}} = \frac{\text{maximum stress}}{\text{average stress}}$$

where r = radius of the hole





d = diameter of the pin minus that of the hole.

Therefore

$$\frac{r}{d} = \frac{\frac{1}{8}}{1 - \frac{1}{4}} = 0.167$$

From reference (132), stress concentration factor $K = 2.35 \approx 3$.

Maximum bending moment occurs at the centre and $=\frac{\mathbf{p}}{2} \times \frac{3}{4} = \frac{3\mathbf{p}}{8}$

where **P** = magnitude of impressed load.

Safe stress for the material used was estimated at 30,000 psi from its average Rockwell hardness value.

Hence load carrying capacity =
$$\frac{3.1416 \times 30,000}{36} \approx 2,600$$
 lt

This is less than the allowable value of 3000 lb. The material was therefore heat treated as follows: Austenitized for 30 minutes at 1700° F and quenched in oil. The stress level increased to 54,000 psi and the load carrying capacity now became

$$\frac{3.1416 \times 54,000}{36} \approx 3,000 \text{ lb}$$

hence satisfactory.

c) Pin Connecting Universal Joint to Horizontal Beam



Bending moment at section "C" = $2R = 2 \times \frac{P}{2} = P$.

Therefore, $\mathcal{O}_{c} = \frac{32P}{\pi d^{3}} = 24.2 P$

Bending moment at section "B" = $\frac{P}{2} \times \frac{3}{8} = \frac{3P}{16}$

Therefore $\sigma_{b} = \frac{3P}{16} \times \frac{32(2^{3})}{\pi} = 15.5 P$

Hence, maximum bending moment occurs at the centre.

Safe load carrying capacity = $\frac{30,000}{24.2}$ = 1,240 lb

The material was required to be heat treated. Austenitized for 30 minutes at 1700° F and water quenched.

Safe load carrying capacity = $\frac{115,000}{24.2}$ > 3,000 lb hence satisfactory.

Maximum bending moment = $\frac{3000}{2} \times 4 - \frac{3000}{2} \times 2 = 3,000$ in.1b. Allowing a maximum stress of 54,000 psi for austenitized and oil quenched mild steel

$$54,000 = \frac{3000 \times 32}{d^3}$$
 or $d = 1.21''$

Hence the central portion of the pin is required to be 1.21" diameter.

e) Bearing Plates for Fulcrum Pin Support

Diameter of pin at support = $\frac{1''}{2}$ Thickness of plate intended to be used = $\frac{1''}{4}$ Bearing pressure due to load = $\frac{1}{2} \times 3000 \times 4 \times 2 = 12,000$ psi which is below the allowable limit, hence satisfactory. APPENDIX II

Calibration of Dead Weight Apparatus

Uniaxial load beam of photoelastic apparatus, manufactured by Photoelastic Polarizing Instrument Company, Irvington-on-Hudson, N.Y.

> F = fulcrum L = point of support of proving ring E = point of support of standard dead weights Beam ratio = $\frac{31.0}{3.75}$ = 8.26 : 1.



TABLE V.

Proving Ring Dial Gauge Readings Corresponding to Applied

Standard Dead	Weights.	(Standard	Beam	Rat io	8.26:1;	fig-

<u>ure 13</u>)

Magnitude of	Corresponding dial	gauge readings	(x10 ⁻³ in.)
standard dead weights (1b.)	Initial	Final	Difference
1	240.0	241.0	1.0
2	240.0	243.5	3.5
4	239,5	248.0	8.5
6	239,5	25 2. 0	12.5
8	239,5	257.0	17.5
10	239.0	260.5	21.5
12	239.0	266.0	27.0
14	239.0	271.0	32.0
16	239.0	277.5	38.5
20	239.0	285.5	46.5
24	238.5	296.5	58.0
28	238.5	305.0	66.5
32	238.5	315.0	76.5
36	238.0	325.0	87.0
40	238.0	335.0	97.0

Plot of Standard Dead Weights Against Corresponding Dial Gauge Readings Using Standard Load Frame of Photoelastic Apparatus.



Details of Arrangement to Transform Tensile Load to Compressive Load in Dead Weight Tension Apparatus

A = beam
B = universal joint
C = vertical supporting columns
D = proving ring
E = compression jig
F = base



TABLE VI

Dial Gauge Readings Corresponding to Dead Loads

Suspended from Point "E"1 in figure 3.

Test	Dead wts.	Corresponding	dial gauge read:	ings (x 10 ⁻³ in)
10.	(15.)	Initial	Final	Difference
1	5	210.5	224.0	13.5
2	10	211.0	238.0	27.0
3	15	211.0	253.0	42.0
4	20	211.0	267.0	56.0
5	25	211.5	281.5	70.0
6	30	212.0	296.0	84.0
7	35	212.0	310.5	98.5

Plot of Readings Presented in Table VI



TABLE VII

Dial Gauge Readings Corresponding to Dead Loads Suspended

from Point "E2" in figure 3

Test No.	Dead wts. from "E."	Corresponding	dial gauge readin	ngs (x 10 ⁻³ in)
	(1b) ⁻²	Initial	Final	Difference
5				
1	5	219.5	239.5	20.0
2	10	219.5	261.0	41.5
3	15	220.0	282.0	62.0
4	20	220.5	303.5	83.0
5	25	221.0	326.5	105.5
6	30	221.5	348.0	126.5
7	35	222.0	368.5	146.5

Plot of Readings Presented in Table VII



TABLE VIII

Date for Determining Self Weight of

the Beam

Test No.	No-load r Incr.	eadings Decr.	Beam weight Incr.	readings Decr.	Average
1	276	276	332	334	57.0
2	394	394	449	451	56.0
3	438	438	492	492	54.0
4	529	525	579	580	55.0
5	581	580	636	637	56.0
6	625	626	682	683	57.0
7	675	675	730	731	56.0

Calculation of beam ratios

Slope of line in figure 16. $k_1 = 2.826$ Slope of line in figure 14. k = 2.431

Beam ratio (load at E_1) = $\frac{k_1}{k}$ x standard beam ratio

$$= \frac{2.826}{2.431} \times 8.26 = 9.615 : 1$$

Similarly, slope of line in figure 17 $k_2 = 4.265$ Beam ratio (load at E_2) = $\frac{k_2}{k}$ x standard beam ratio = $\frac{4.265}{2.431}$ x 8.26 = $\frac{14.500 : 1}{2}$

Calculation of Self Weight of the Beam Acting at the Point of Loading of Test Specimens

From table VIII, beam weight less weight of compression jig corresponds to a dial gauge reading of 56 x 10^{-3} in.

Load corresponding to this reading was obtained from each of the graphs in figures 14, 16, 17 and the average value calculated. Thus,

> from fig.14, 23.4 B.R. = 8.26 Load = 23.4 x 8.26 = 193.45, from fig.16, 20.0 B.R. = 9.615 Load = 20.0 x 9.615 = 192.30, from fig.17, 13.4, B.R. = 14.50 Load = 13.4 x 14.50 = 194.30 Average = 193.35

Dead weight of compression jig = 4.25 lb Therefore, effective self beam weight = <u>189.10</u> lb

BIBLIOGRAPHY

1.	Dix, E.H., Trans. A.I.M.E., Vol.137, (1940), p.11.
2.	Somers, F.P. and Craighead, C.M., Unpublished work. Aluminium Research Laboratories.
3.	Champion, F.A., Metallurgica, Vol.53, Feb. (1956).
4.	Roberts-Austen, W.C., Proc. Roy. Inst., Vol.11 (1884-86), p.395.
5.	Orowan, E., "Symposium on Internal Stresses in Metals and Alloys", Inst. of Metals, London, (1948), p.47.
6.	Crampton, D.K., Trans. A.I.M.E., Vol.89, (1930), p.233.
7.	Andrew, J.H., Trans. Faraday Soc., Vol.9 (1913), p.316.
8.	Merica, P.D., Metallurgical and Chemical Eng., Vol.16, (1917), p.496.
9.	Moore, H., Beckinsale, S., and Mallinson, C.E., J. Inst. of Metals, Vol.25, (1921), p.35.
10.	Parr, S.W. and Straub, F.G., Bull. 155, Eng. Expt. Sta., U. of Illinois.
11.	Rawdon, H.S., Proc. A.S.T.M., Vol.29, pt. 11 (1929), p.314.
12.	Priest, D.K., "A Study of Stress Corrosion, Motion Picture Film", The Pfaudler Co.
13.	Uhlig, H.H., "Corrosion Handbook", N.Y., John Wiley and Sons, 1948.
14.	Eckel, J.F., Corrosion, Vol.18, July (1962), p.270 t.
15.	Scheil, M.A., "Symposium on Stress Corrosion Cracking of Metals", Phil., Pa. A.S.T.M A.I.M.E., (1944), p.395.
16.	Warren, D. and Beckman, G.W., Corrosion, Vol.13, Oct.(1957), p.631 t.
17.	Suss, H., Corrosion, Vol.17, No.2, (1961), p.61 t.
18.	Tammann, G. and Newbert, F., Zeitsch. Anorg. Chem., 207, (1932),

p.87.

19.	Friend, J.N., Jour. Iron and Steel Inst., Vol. CXVII, No.1. (1928), p.639.
20.	Skapski, A. and Chyzewski, E., Metaux et Corrosion, 13, (1938), p.21.
21.	Druet, Y. and Jacquet, P.A., Metaux et Corrosion, 22, (1947), p.139.
22.	Evans, U.R. and Simnad, M.T., Proc. Roy. Soc. (London), Vol.188, Ser.A, (1947), p.372.
23.	Hoar, T.P. and West, J.M., Nature, Vol.181, JanMar.(1958), p.835.
24.	Uhlig, H.H., "Corrosion Handbook", N.Y., John Wiley and Sons, 1948, p.577.
25.	Harwood, J.J., "Symposium on Corrosion Fundamentals", A. de S. Brasunas and E.E. Stanbury, ed. 1956.
26.	Uhlig, H.H., "Physical Metallurgy of Stress Corrosion Fracture", T.N. Rhodin, ed, N.Y., Intersc. Publishers, 1959, p.1.
27.	Engell, H.J. and Baumel, A., Ibid, p.341.
28.	Scharfstein, L.R. and Brindley, W.F., Corrosion, Vol.14, Dec. (1958), p.588 t.
29.	Perrymann, E.C.W., Jour. Inst. of Metals, Vol. LXXVIII, (1950-51), p.621.
30.	Roberts, E.C., The Trend, Jan.(1962), p.8.
31.	Fontana, M.G., W.A.D.C. Report, T.R. 56, Aug.(1956), p.242.
32.	Thompson, D.H. and Tracy, A.W., Trans. A.I.M.E., Vol.185,(1949), p.100.
33.	Brown, R.H., Mears, R.B., and Dix, E.H., "Symposium on Stress Corrosion Cracking of Metals", A.S.M., A.I.M.E., (1945), p.67.
34.	Ibid, p.323.

- 84
- 35. Graf, L., Z. Metallkunde, 38, (1947), p.193.
- Uhlig, H.H., White, A., and Lincoln, J., Acta Metallurgica, 5, (1957), p.473.
- 37. Graf, L., "Stress Corrosion Cracking and Embrittlement", W.D. Robertson, ed., N.Y., John Wiley and Sons, 1956, p.48.
- 38. Bakish, R. and Robertson, W., Acta Metallurgica, Vol.4, (1956), p.342.
- 39. Wilson, T.C., et al., "Symposium on Stress Corrosion Cracking of Metals", A.S.T.M. - A.I.M.E., (1944), p.173.
- 40. Edmunds, G., Ibid, p.67.
- 41. Parkins, R.N., J. Iron and Steel Inst., Vol.172, Part III (1952), p.149.
- 42. Fink, W.L. and Smith, D.W., Trans. A.I.M.E., Vol.122, (1936), p.284.
- 43. Dix, E.H. and Richardson, H.H., Trans. A.I.M.E., Vol.73, p.560.
- 44. Beerwald, A. and Grober, H., Aluminium, 22, (1948), p.502.
- 45. Baldby, M.F. and Bowdon, R.C., Corrosion, Vol.11, Oct. (1955).
- 46. Morris, A., Discussion of the paper by D.K. Crampton, Trans. A.I.M.E., Vol.89, (1930), p.248.
- 47. Tipper, C.F., "The Brittle Fracture Story", Cambridge University Press, 1962, p.38.
- 48. Jones, J.A., Trans. Far. Soc., Vol.17, (1921), p.102.
- Houdremont, E., Bennek, H., and Wentrip, H., Stahl u. Eisen,
 60, (1940), p.757.
- 50. Buchholtz, H. and Púsch, R., Stahl u. Eisen, 62, (1942), p.21.
- 51. Gifkins, R.C. and Rees, W.P., Metal Treatment 15, No.5, (1948), p.109.
- 52. Schroeder, W.C. and Beck, A.A., U.S. Bureau of Mines, Bull.443, (1941).

53.

(1943), p.343.
54. Berk, A.A. and Waldeck, W.F., Chem. and Eng., Vol.57, No.6, (1950), p.235.
55. Fraiser, J.P. and Treseder, R.S., Corrosion, Vol.8, No.10, (1952), p.342.
56. Harwood, J.J., Corrosion, Vol.6, No.8, (1950), p.249, and Vol.6,

Purcell, T.E. and Whirl, S.F., Trans. Electrochem.Soc., Vol.83,

- 57. Hodge, J.C. and Miller, J.L., Trans. A.S.M., Vol.28, (1940), p.25.
- 58. Davis, F.W., Trans. A.S.M., Vol.42, (1950), p.1233.

No.9, p.290.

- 59. Collins, J.A., Corrosion, Vol.11, Jan. (1955), p. 11 t.
- 60. Nathorst, H., Welding Research Council, Bull., Ser. No.6, (1950).
- Dixon, E.S., "Petroleum Refineries. The Book of Stainless Steels", 2nd Ed., E.E. Thum, A.S.M., 1935.
- 62. Uhlig, H.H., Metal Progress, Vol.57, April (1950), p.486.
- 63. Robertson, W.D., J. of Metals, 3, (1951), p. 1190.
- Dix, E.H., "Symposium on Stress Corrosion Cracking of Metals",
 A.S.T.M. A.I.M.E., (1944), p.1.
- 65. Mattson, E., Electrochem. Acta, Vol.3, (1961), p.279.
- 66. Stroup, P.T., Sager, G.F., and West, J.B., Trans. A.S.M., Vol.35, (1945).
- 67. Heidenreich, R.D., Gerould, G.H., and McNulty, R.E., Trans. A.I.M.E., Vol.166, (1946), p.15.
- 68. Mears, R.B., Brown, R.H., and Dix, E.H., "Symposium on Stress Corrosion Cracking of Metals", A.S.T.M., A.I.M.E., (1944), p.323.
- 69. Loose, W.S. and Barbian, H.A., "Symposium on Stress Corrosion Cracking of Metals", A.S.T.M. - A.I.M.E., (1944), p.273.

Perryman, E.C.W. and Brook, G.B., Jour. Inst. of Metals,

- Vol.LXXIX, (1951), p.19.
 71. Chalmers, B., "Progress in Metal Physics", Pergamon Press, 1961, Vol.1, p.157-162.
 72. Lacombe, P. and Beauyard, L., Comptes Rendus, Tombe 218, (1944), p.878.
- 73. Robertson, W.D., J. of Metals, Vol.2, May (1950), p.790.
- 74. Waber, L.J., and Somers, F.P., Unpublished work. Aluminium Research Laboratories.
- 75. Fink, W.L. and Smith, D.W., Trans. A.I.M.E., Vol.128, (1938), p.223.
- 76. Waber, J.T. and McDonald, H.J., "Stress Corrosion Cracking of Mild Steel", Pittsburg, Corrosion Publishing Co., 1947.
- 77. Waber, J. T., Trans. A.S.M., (1949).

70.

- 78. Edeleanu, C., Jour. Iron and Steel Inst., Vol.173, No.1. (1953), p.140.
- 79. Heger, J.J. and Dulis, E.J., Further correspondence on the paper by C. Edeleanu, Jour. Iron and Steel Inst., Vol.175, No.111, (1953), p.390.
- 80. Logan, H.L., Jour. of Research, N.B.S., Vol.48, (1952), p.99.
- Hoar, T.P. and Hines, J.G., Jour. Iron and Steel Inst., No.11, (1954), p.248.
- 82. Logan, H.L., Jour. of Research, N.B.S., Vol.61, (1958), p.503.
- Keating, F.H., "Symposium on Internal Stresses in Metals and Alloys", Inst. of Metals, London, Vol.311, (1948).
- Gilbert, P.T., and Hadden, S.E., Jour. of Metals, Vol.LXXVII, (1950), p.237.
- 85. van Rooyen, D., Corrosion, Vol.16, No.9, (1960), p.421 t.
- 86. Edeleanu, C. and Forty, A.J., Philosophical Mag., Vol.5, (1960), p.1029.

87. Edeleanu, C., "Physical Metallurgy of Stress Corrosion Fracture", T.N. Rhodin, ed., N.Y., Intersc. Publishers, 1959, p.79. 88. Kirk, W.W., Beck, F.H., and Fontana, M.G., Ibid, p.227. 89. Hines, J.A. and Hugill, R.W., Ibid, p.193. 90. Nielsen, N.A., Ibid, p.121. 91. Gulbransen, E.A. and Copan, T.P., Ibid, p.155. 92. Forty, A.J., Ibid, p.99. 93. Pickering, H.W., Beck, F.H., and Fontana, M.G., Corrosion, Vol.18, No.6, (1962), p.230 t. 94. Barnartt, S. and van Rooyen, D., Jour. Electrochem. Soc., Vol. 108, (1961), p.222. 95. Stickler, R. and Barnartt, S., Jour. Electrochem. Soc., Vol.109, (1962), p.343. 96. Romanov, V.V., "Stress Corrosion of Metals", Translated from Russian. Published for the National Sciences Foundation, Washington, D.C. 97. Coleman, E.G., Weinstein, D., and Rostoker, W., Acta Metallurgica, Vol.9, (1961), p.491. 98. Uhlig, H.H., "Corrosion and Corrosion Control", N.Y., John Wiley and Sons, 1962, p.114. 99. Williams, W. Lee, Corrosion, Vol. 17, No.7, (1961), p.92. 100. Langmuir, I., Jour. Am. Chem. Soc., Vol. 38, Pt.2, (1916), p.2221. 101. Zapffe, C., Trans. A.S.M., Vol.39, (1947), p.193. 102. Smith, D.P., "Hydrogen in Metals", U. of Chicago Press, 1948. 103. Bastien, P. and Azou, P., Trans. A.S.M., (1951), p.535. 104. Brown, J.T. and Baldwin, W.M., Trans. A.I.M.E., (1954), p.298. 105. Morlett, J.G., Johnson, H.H., and Troiano, A.R., Jour. Iron

and Steel Inst., May (1958), p.37.
106.	Bastien, P. and Azou, P., Comptes Rendus, Tombe 231, (1950), p.147.
107.	Bastien, P. and Azou, P., Rev. Met., 54, (1957), p.94.
108.	Petch, N.J. and Stables, P., Nature, Vol.169, (1952), p.842.
109.	Griffiths, A.A., Phil. Trans., Vol. A221, (1920), p.163.
110.	de Kazinczy, F., Jour. Iron and Steel Inst., Vol.177, No.11, (1954), p.185.
111.	Bastien, P.G., "Physical Metallurgy of Stress Corrosion Fracture", T.N. Rhodin, ed., N.Y., Interscience Publisher, 1959, p.311.
112.	Cottrell, A.H., "Dislocations and Plastic Flow in Crystals", Oxford, 1953.
113.	Blanchard, P.A., et al., W.A.D.C., T.R. 59-172, April (1959).
114.	Johnson, H.H., Morlett, J.G. and Troiano, A.R., Trans. A.I.M.E., Vol.212, (1958), p.528.
115.	Daniels, R.D., Quigg. R.J., and Troiano, A.R., Trans. A.S.M., Vol.51 (1959), p.843.
116.	Troiano, A.R., Corrosion, Vol.15, (1959), p.207 ‡.
117.	Klier, E.P., Muvdi, B.B., and \$achs, G., Trans. A.I.M.E., Vol. 209, (1957), p.106.
118.	Bain, E.C. and Paxton, H.W., "Alloying Elements in Steel", 2nd ed., A.S.M., 1961, p.89.
119.	Troiano, A.R., "The Role of Hydrogen and Other Interstitials in the Mechanical Behaviour of Metals", Reprint, 1959.
120.	Frohmberg, R.P., Barnett, W.J., and Troiano, A.R., Trans. A.S.M., Vol.47, (1955), p.892.
121.	Davis, R.A., Corrosion, Vol.19, No.2, (1963), p.45 t.
122.	Tetelman, A.S. and Robertson, W.D., Trans. A.I.M.E., Vol.224, (1962), p.775.

123 ,	Grant, N.J. and Lundsford, J.L., Iron Age, Vol.175, No.22, (1955), p.92.
124.	Seabrook, J., Grant, N., and Carney, D., Jour. Inst. of Metals, Trans. A. I.M.E., Vol.188, p.1317.
125	Geller, W., and Ho-Sun, Tak, Archiv, fuer Eisenhuttenwesen, 21, (1950), p.423
126	Schuetz, A.E. and Robertson, W.D., Corrosion, July (1957), p.437 t.
127.	Bastien, P.G., "Physical Metallurgy of Stress Corrosion Fracture", T.N. Rhodin, ed., N.Y., Intersch Publishers, 1959, p.311.
128.	Shank, M.E. et al., Metal Progress, Vol.76, Dec. (1959).
129,	Evans, U.R., "Stress Corrosion Cracking and Embrittlement", W.D. Robertson, ed., N.Y., John Wiley and Sons, 1956, p.158.
130	Smialowski, M., "Hydrogen in Steel", Addison Wesley Publishing Co. Inc. 1962.
131.	"Metals Handbook", Vol.1, 1961, p.180.
132	Timoshenko, S., "Strength of Materials", Pt.I, p.92, Pt.II, p.319.