THE
EFFECT OF TENSILE STRESS
ON THE
CORROSION OF
ALUMINIUM AND SOME
ALUMINIUM ALLOYS

A THESIS

PRESENTED

FOR THE DEGREE OF Ph.D.

OF

GLASGOW UNIVERSITY

by

ERIC LLOYD JONES, B.Sc., A.R.T.C., A.R.I.C.

OCTOBER, 1952.

THE ROYAL TECHNICAL COLLEGE, GLASGOW.
THE UNIVERSITY, EDINBURGH.

ACKNOWLEDGMENTS

The author expresses his thanks for the helpful advice and direction of Dr. W. M. Cumming, O.B.E., M.I.Chem.E., F.R.S.E., formerly Director of the School of Chemistry and Professor of Technical Chemistry, The Royal Technical College, Glasgow.

Grateful acknowledgment is made to Monsanto Chemicals Ltd. for a research scholarship held during the first year of this research.

Acknowledgment is also made to The British Aluminium Co. Ltd. for providing the aluminium alloys with their chemical analyses.

ABSTRACT

The effect of externally applied tensile stress on the rate of corrosion of Al in 0.1N HCl and 0.1N HCl containing 3% and 5% NaCl has been determined by measurement of the H_2 evolved. Elastic stress and overstrain up to 10% has little effect. 20% overstrain apparently reduces the rate of attack, but owing to the difficulty of assessing the true surface area of overstrained metal, the effect of this stress is difficult to ascertain. Similar tests conducted on Al-7% Mg alloy show that stress has no effect on the resistance of the annealed alloy, but increases the rate of attack of the strain-aged alloy, probably due to exposure of the anodic phase at the grain boundaries. Potential measurements on Al and Al-7% Mg alloy confirm these results.

The effect of stress on the corrosion of strain-aged Al-7% Mg in 3% NaCl has been determined by measurement of the O_2 absorbed and H_2 evolved. There is no characteristic difference between the rate of corrosion - time curves for the stressed and unstressed alloy.

A technique for investigating the stress-corrosion susceptibility of materials has been developed and experiments conducted on Al-7% Mg and Al-5% Mg alloys. From the curves of applied stress v. percentage of the loss of strength at failure which is due to stress-corrosion, a method is developed whereby the stress-corrosion susceptibility of materials may be expressed on a comparative basis.

The theory that stress concentrations at the base of cracks are responsible for mechanical failure is discussed and an alternative theory of the mechanical role of stress during stress-corrosion, based on eccentric loading, is put forward.

CONTENTS

PART 1

THEORETICAL CONSIDERATIONS AND LITERATURE SURVEY

PART 2

EXPERIMENTAL INVESTIGATION

SECTION A GENERAL CORROSION

I. MEASUREMENT OF CORROSION RATE IN ACID SOLUTIONS

II. MEASUREMENT OF POTENTIAL IN ACID SOLUTIONS

SECTION B THE INFLUENCE OF STRESS ON LOCALISED CORROSION OF ALUMINIUM-MAGNESIUM ALLOYS

I. MEASUREMENT OF OXYGEN ABSORBED AND HYDROGEN EVOLVED

INTRODUCTION

Metals are rarely found in the uncombined state; they are usually associated with oxygen, sulphur or chlorine. The reduction of the ore to the metal requires the expenditure of much energy and except for the noble metals there is a tendency for the reverse process of recombination with oxygen to take place with the liberation of the equivalent energy. The effect which is highly destructive and involves considerable economic loss is termed "corrosion".

There is little doubt that the destructive nature of corrosion was observed when the first metals were used thousands of years ago, but it was not until the late eighteenth and early nineteenth centuries that chemists gave serious thought to the phenomenon. Few theories of fundamental importance were propounded, although as early as 1819 it was suggested that corrosion was an electric effect. This theory, however, remained latent until the commencement of the present century when the modern electrochemical theory was introduced and the increasing evidence which followed in support thereof resulted in great advances in our knowledge of the theory underlying corrosion.

In the modern world, the metallic resources of the nation are of vital importance in domestic economy, world trade and defence. The advancements made in the metallurgical field and the increased use of metals and alloys have resulted in considerable intensification of corrosion research and the data now available have grown to enormous proportions. Nevertheless, the cost of corrosion damage is still prodigious and it can be appreciated that a knowledge of its principles is of primary importance to the Engineer, Metallurgist, Chemist and Chemical Engineer.

One of the major difficulties of corrosion research is the correlation of laboratory observation with behaviour under service conditions, where additional factors are likely to exist which may seriously affect the behaviour of a metal to a corrosive environment. One of the most important of these is the influence of mechanical stress, both internal stress set up during fabrication and applied stress operating in service, acting in conjunction with electrochemical forces. It is now well known that under certain conditions a metal or alloy with attractive mechanical and corrosion resisting properties, may fail when subjected to the simultaneous action of stress and corrosion, a phenomenon known as "stress-corrosion cracking".

The present investigation is a study of this field, particular attention being devoted to the properties of aluminium and its alloys used in the ship-building and aircraft industries where the need for light-weight structures has resulted in a large and increasing demand for such metals. Service failures of certain aluminium alloys have been reported, however, as due to stress-corrosion and this thesis deals with the effect of stress on the corrosion of this metal and some of its alloys.

The investigation was commenced with the object of determining the effect of stress on the general corrosion of aluminium in hydrochloric acid. Such corrosion is of an obviously exaggerated nature since aluminium would not be used in contact with hydrochloric acid in service, but it has the advantage that no protective films are formed on the metal during exposure to the corroding environment, thus any changes would be due to the effect of stress on the metal and not to rupture or to change in the nature of any protective film. Another advantage is that the strength of the acid may be adjusted to give convenient rates of attack, thus enabling useful observations to be made in a comparatively short period of time.

It was appreciated that although much work has been published on the effect of stress on the general corrosion of metals, the results are in some respects uncertain since several factors other than stress influence the corrosion, and unless a suitable experimental technique is employed the secondary factors may have a greater effect than that due to stress. Therefore, much of the present work was devoted to the development of suitable experimental methods. A rapid and accurate chemical method, viz., measurement of the hydrogen evolved, was devised and measurements of the effect of stress on the potential between aluminium and the corroding solution were made using a valve-voltmeter, thus enabling very small changes in potential to be detected. In both methods variation in corrosion rate due to factors other than stress were reduced as far as possible. The techniques developed for measurements on aluminium were then used to determine the effect of stress on the general corrosion of an alloy which exhibited stress-corrosion cracking in neutral sodium chloride solution.

The experimental work was then extended to study the effect of stress on the localised corrosion of certain aluminium alloys in solutions of sodium chloride, the service failures of aluminium alloys having occurred in an environment of sea water. Laboratory investigations on the stress-corrosion of these alloys, as described in the literature, have been largely of a qualitative nature and in many cases the effect of corrosion in the absence of stress has not been determined. Accordingly, in the present work, suitable techniques were developed using Al - 7%Mg alloy, which is known to be susceptible to stress-corrosion, to determine quantitatively the effect of corrosion alone and of stress and corrosion acting together.

A chemical method for determining the corrosion rate by measurement of the oxygen absorbed and the hydrogen evolved was investigated and a mechanical method, in which the loss in ultimate tensile strength of the alloy was used as the criterion of measurement, was satisfactorily developed. The latter method was further used for the study of other alloys of doubtful stress-corrosion characteristics.

PART 1

THEORETICAL CONSIDERATIONS
AND
LITERATURE SURVEY

INTRODUCTION

Corrosion damage by electrochemical action may be broadly divided into three groups. Firstly, uniform corrosion such as occurs when a base metal is immersed in acid solution. A large number of anodic and cathodic regions are set up on the surface, the metal passing into solution as ions at the anodes and combination of electrons with hydroxonium ions forming hydrogen at the cathodes. Secondly, pitting which occurs when a small anodic area is coupled with a relatively large cathodic area, usually in neutral solutions. The cathodic reaction is the combination of electrons with dissolved oxygen forming hydroxyl ions. For the same dissolution of metal, pitting results in greater damage than uniform corrosion since it can lead to premature perforation. Thirdly, intercrystalline corrosion which occurs when an anodic material is present along the grain boundaries of an alloy, usually the result of unfortunate heat-treatment.

It was recognised over 30 years ago that the presence of static stress may result in a greater deterioration of a material subjected to a corroding environment than when stress is absent. Season and corrosion-cracking of brass formed the subject of a discussion published in 1918 (1). Extensive research on this subject was made by many investigators and the results of Moore, Beckinsale and Mallinson (2) were of primary importance in the understanding of this phenomenon. Increasing interest in the effect of mechanical stress on the corrosion of many other metals and alloys was apparent during the 1920's and 1930's. A symposium on the stress-corrosion cracking of metals held in America in 1944 (3) indicated much of the important work done in this field, and the subject forms an important section of a symposium on internal stresses in metals and alloys held in this country in 1947 (4).

It would appear that the effect of stress on general corrosion is relatively small, but if a tensile stress is acting during corrosive conditions where the attack is concentrated on a limited number of grain boundaries, a highly dangerous type of attack may occur in which a rapid loss of strength results.

In the present section, a survey of the factors relevant to the effect of stress on corrosion is made. The theories of electrochemical corrosion are not discussed; detailed accounts being given in many well-known text-books and publications, notably Evans (5,6), Speller (7), Uhlig (8), Gatty and Spooner (9), Coates (10) and Vernon (11).

I. STRUCTURE, DEFORMATION, HEAT TREATMENT AND STRUCTURAL CORROSION OF METALS

Metal Structure

When a liquid metal is cooled to its freezing point, small nuclei form which act as seeds for crystal formation and during solidification these nuclei dissipate heat, this being greatest at the crystal corners. Radial arms are formed which send out secondary arms at right angles to them. This is repeated giving rise to dendritic formations. If the metal contains impurities, these are the last to solidify and accumulate in the interdendritic metal.

Pure metals often lack the necessary characteristics for certain applications and their properties may be modified by addition of an alloying element. Nearly all metals are mutually soluble in the liquid state and in the solid state most systems show some mutual solubility even though this may be over a limited range of composition. Solid solutions are homogeneous, but in the range of insolubility, the microstructure consists of one constituent dispersed in the other usually in a characteristic pattern.

If the proportion of eutectic is small compared with that of the solid solution, then since the former is the last to solidify, it will form as the interdendritic material and hence along the grain boundaries. As well as reducing the strength of the alloy, such formation may render the alloy susceptible to intercrystalline corrosion.

Deformation of Metals

Deformation of metals, effected by the application of stress, may be of two types, viz. elastic deformation and plastic deformation. In the former case the strain is removed when the stress is removed, and although the strain is of measurable dimension there is no apparent effect on a polished surface of the metal even under high magnification.

When a metal is stressed beyond the yield point, the strain persists after the applied stress has been removed and certain changes occur in the metal which have been examined by means of the microscope and by X-ray technology. A metal crystal consists of atoms arranged in a definite pattern and when stressed into the plastic region the atoms glide or slip along crystallographic planes. Initially only a few planes are affected, but as the stress increases more planes are deformed. With consequent disorganisation of the metal slipping becomes more difficult and the metal becomes harder, a process known as cold working when carried out at ordinary temperature. In a fine grained metal the work required for distortion is greater than that for a coarse grained metal, hence the former is generally stronger and harder than the latter.

An account of this subject is given by Carman (12).

Heat Treatment of Metals and Alloys

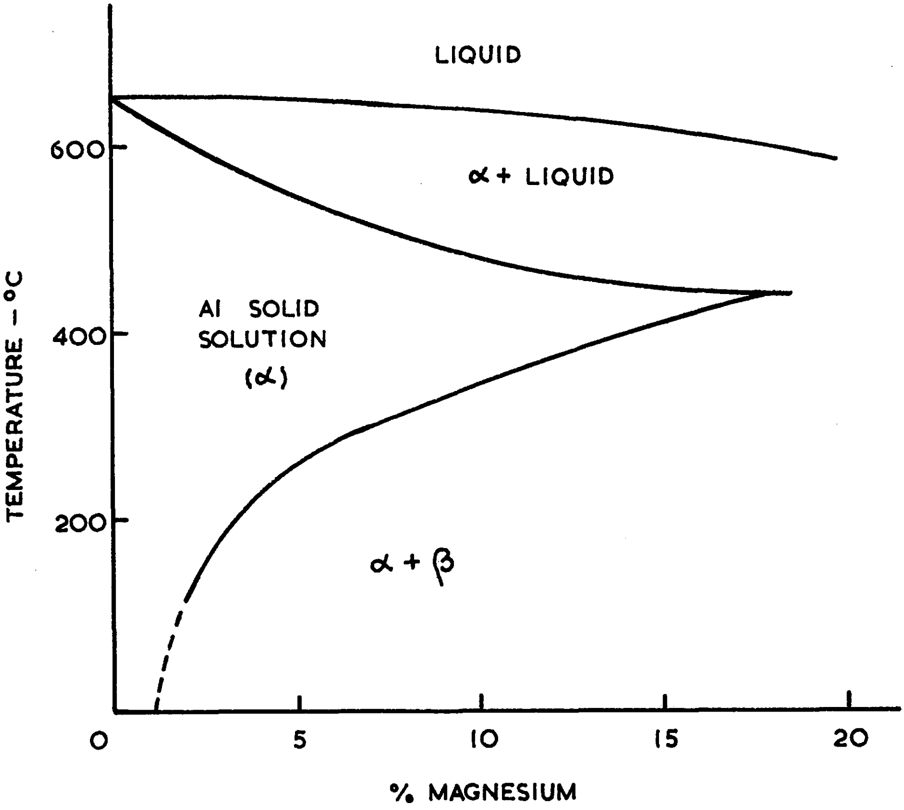
Annealing

Annealing a metal or alloy is effected by maintaining it at a temperature below the fusion point for a certain period of time, and then cooling. This results in certain changes in the texture of the metal. Annealing may be carried out for one or more of several reasons, but usually to relieve internal stresses caused by cold working or to refine grain structure. In the case of alloys, grain refinement brings about a greater degree of homogeneity, which is necessary in cases where segregation of a component at the grain boundaries may impair the properties of the alloy.

Quench-Ageing

A solid solution of two or more metals which normally deposits one of its constituents on cooling may often be retained in a supersaturated condition by quenching. The excess of dissolved substance may then separate in a fine state of dispersion when the alloy is maintained at atmospheric or moderately elevated temperature. This separation brings with it important changes in physical and mechanical properties, notably an increase in the hardness and a greater degree of resistance to corrosion. Age-hardening brought about in this manner is a characteristic of a large number of alloys.

In aluminium-copper alloys of the duralumin type, quenching from an elevated temperature produces a supersaturated metal of unstable structure, and on maintaining the metal at atmospheric or at somewhat elevated temperature to accelerate the process, separation of $CuAl_2$ of sub-microscopic dimensions from the solid solution results in an increase in hardness and general corrosion resistance. If, however, there is too long a delay in quenching the



PART OF THE EQUILIBRIUM DIAGRAM

ALUMINIUM – MAGNESIUM

(1a)

FIG. 1

alloy once cooling has commenced, precipitation of the $CuAl_2$ may occur along the grain boundaries rendering the alloy susceptible to intercrystalline attack.

Strain-Ageing

When certain alloys, which are in a relatively stable but supersaturated state at ordinary temperatures, are subjected to strain, the constituent held in solid solution may separate when straining is followed by ageing. This may be explained by the fact that diffusion occurs more rapidly in a deformed lattice. Strain-ageing will cause precipitation from the solid solution when the degree of supersaturation is so small that it will not occur after quenching; thus in aluminium-copper alloys precipitation of $CuAl_2$ from an alloy containing less than 2% Cu may be effected by strain-ageing but not by quench-ageing.

In the case of the aluminium-magnesium alloys, the solubility of magnesium in aluminium is approximately 1.5% at ordinary temperatures. Magnesium in excess of this amount will separate from the solid solution as the β-component, Al_3Mg_2. The condition of the precipitated β-phase is dependent upon the treatment of the alloy. Mockel (14) reports that in an aluminium alloy containing 7% Mg, ageing at 75°C. for prolonged periods causes the β-phase to separate along the grain boundaries as a continuous network. Annealing at 300°C. and above produces a "string of pearls" structure. Metcalfe (15) showed that aluminium alloy rivets containing 5% Mg are rendered susceptible to intercrystalline attack due to precipitation of the β-phase when subjected to tropical temperatures and that cold working the rivets before heating causes grain boundary precipitation of the β-phase to take place more readily. Perryman and Hadden (16) report that cold work before ageing aluminium-7% magnesium alloys has a profound effect on the mode of separation of the β-phase. The effect of the degree of cold work and time and temperature of ageing is discussed.

Structural Corrosion

It has been reported that the presence of boundary atoms which cannot orientate themselves simultaneously on two crystal lattices and therefore possess a higher potential energy than the atoms in a crystal, may result in preferential attack of the crystal boundaries of pure metals. It is doubtful, however, whether specific attack at the grain boundaries takes place unless a trace of impurity is present forming a phase which is anodic to the crystal grain (17). In the case of alloys in which a component or components separate at the grain boundaries, structural corrosion may occur due to the preferential attack of the more anodic phase or phases. Dix (18, 19) carried out measurements of potential difference between the grain boundary zones and grain bodies of large grain metal and verified that the presence of anodic regions at the grain boundaries was the cause of selective corrosion. However, the attack is seldom entirely preferential and occurs to some extent on all phases.

If, as in the case of the aluminium-magnesium alloys, the phase at the grain boundary is anodic to the solid solution, then this phase is preferentially attacked. If this phase forms a continuous network between the grains, considerable penetration may occur and it will cease only if the inner metal becomes inaccessible to the corroding medium due to film formation or if an accumulation of metallic salts shifts the potential in a cathodic direction. In the case of the precipitated component forming an agglomerated structure, there is a discontinuous path of preferential attack and regions of resistant material between regions of β -phase arrest penetration.

Retardation of the rate of quenching of aluminium-copper alloys after solution treatment results in $CuAl_2$ particles being precipitated at the grain boundaries. It was originally thought that this phase was cathodic to the grains and therefore would cause attack of the latter. Gayler (20) has shown that the Al-Cu solid solution is also a cathode, and in the view of Evans and Whitwham (21) is the main cathode, whilst the copper impoverished regions at the grain boundaries are the anodic regions and are attacked.

The grain boundaries are not always anodic to the grains and in a few cases the converse is true, the grains being preferentially attacked. In such an alloy, agglomeration of the constituent at the grain boundary is unlikely to retard the preferential attack.

II. SIMULTANEOUS ACTION OF STRESS AND CORROSION

Stress-Corrosion

Broadly the term stress-corrosion includes any combined effect of stress and corrosion on the behaviour of metals (22). The stresses may be of two main types, cyclic and static. The damaging effect of corrosion and cyclic stresses is known as corrosion fatigue, but this subject is outwith the scope of this summary.

The presence of static stresses may influence the rate of general corrosion or under certain conditions may result in cracking of the metal without general attack. In the latter case, the action is known as "stress-corrosion cracking".

There has been much confusion over the term "stress-corrosion" chiefly due to the rather wide interpretation by German investigators, and to avoid misunderstanding it has been specifically defined in this country as follows: "the term stress-corrosion implies a greater deterioration in the mechanical properties of the material through the simultaneous action of static stress and exposure to a corrosive environment than would occur by the separate, but additive action of these agencies" (23).

Influence of Stress in Acid Solutions

Whereas in stress-corrosion cracking, failure of a metal occurs without general attack, the presence of stress may influence the general corrosion which occurs in acid solutions. This subject is discussed by Evans (6), Speller (7), Uhlig (8) and Bryan (24) numerous references being cited. The investigations have been varied in nature and the results are confusing; increase, decrease and no change in the corrosion rate have been reported. It would appear that the effect is specific for both the metal and for the environment. However, in nearly all cases the effect has been small.

Several investigators have determined the difference in potential between stressed and unstressed specimens, but in general this amounts to only a few millivolts. Recent work by Evans and Simnad (25), while investigating the mechanism of corrosion fatigue of steel in acid solution, shows that although elastic deformation does not affect the chemical or electrochemical properties of the steel, deformation beyond the elastic limit alters these properties, making the iron behave like a more reactive metal.

In some cases the nature of the attack may be influenced by stress. Whiteley and Hallimond (26) report that when iron which has been strained is exposed to nitric acid, the relative proportions of the nitrogen compounds produced are different from those produced with unstrained iron.

Influence of Stress in Neutral Solutions

The rate of attack in neutral salt solutions is usually controlled by the availability of oxygen. If the cathodic reaction is such that the oxygen is used up at the same rate as it arrives at the metal surface, the sole governing factor is the rate of diffusion of oxygen to the metal, and changes wrought in the metal by stress have little or no influence on the rate of attack. This fact was verified by Friend (27) in investigations on the influence of stress on the corrosion of iron in sea water.

A metal immersed in a salt solution containing oxygen soon becomes coated with an oxide or hydroxide film which tends to stifle the attack. The presence of stress may damage such films causing an increase in the rate of attack and also ~~in~~ a variation in the distribution of the attack (28). Evans and

Simnad (29) studied the shift in potential with time of iron subjected to tensile and compressive stresses in neutral solution (vide also p. 102). They indicate that stressing within the elastic range affects the potential by altering the state of repair of the film covering the surface. They suggest that stresses within the plastic range depress the potential of the metal itself, irrespective of damage to the film

Stress-Corrosion Cracking

An important effect of stress on corrosion is that which results in the complete failure of the metal. Probably the best known example of stress-corrosion failure is the "season cracking" of brass. Failures have also been reported in other copper alloys (30), in aluminium alloys (3), in ordinary and stainless steels (31), in lead (32) and many other alloys.

Factors Involved in Stress-Corrosion Cracking

The intensive research devoted to the study of stress-corrosion cracking during the past few years has indicated that there are three principal factors involved: (a) stress, (b) environment, and

(c) the internal structure of the metal. The relative importance of each factor may vary according to the metal and they may interact, one accelerating the other.

(a) Stress. It is generally agreed that there must be a tensile stress acting on the surface of a metal, either internal or applied stress. Usually tensile stresses in the region of the yield strength are necessary, but failures have been reported at lower stresses.

(b) Environment. Stress-corrosion cracking has been observed in a large number of metal systems, but for each metal the failure appears to be associated with a specific environment. In each case it has been observed that the corrosive medium produces an effect between the extremes of general corrosion and passivity. The exact role of the corrosive medium after initiation of the attack is a subject of controversy and speculation.

(c) Internal Structure. The internal structure of a metal is of particular importance, stress-corrosion cracking being a development of structural corrosion. Mears, Brown and Dix (33) state that stress-corrosion cracking follows essentially the same mechanism as other types of intergranular corrosion in aqueous media.

Time. The time required for failure may vary from a few minutes to a matter of years. One of the difficulties of laboratory investigation is the correlation of accelerated tests with service failures in which the mechanisms may differ appreciably.

Theories of the Mechanism of Stress-Corrosion Cracking with Special Reference to Aluminium Alloys

There is more or less general agreement on the initial role of the corrosive environment, but as Dix (19) has pointed out, not only is it necessary for the corrosive medium to be such that it produces a localised type of attack, but in certain alloys, including those of aluminium, the structure of the alloy must be such that there exists a susceptibility to selective corrosion along continuous paths, as, for example, the grain boundaries. Investigation of the corrosive action of salt solutions on aluminium alloys in the absence of stress has shown that the susceptibility to corrosion is dependent upon the internal structure of the alloy (34-37).

When a metal susceptible to stress-corrosion is corroded under stress it is possible that the rate of corrosion is greater from the commencement than if corroded in the absence of stress. Just before failure, however, the rate of deterioration in mechanical properties increases rapidly (38-40). Champion (41,42) has explained these effects as being due in the first instance to high local stress at the base of pits, formed in the metal by corrosive action, rendering the anodic phases there even more anodic. This gives rise to the minor stress corrosion effect. The second stage or major stress corrosion effect arises when a pit has developed to such an extent that the stress concentration at its base exceeds the yield point of the metal. Local plastic deformation occurs, breaking the film which has hitherto retarded attack on the anodic phase at the grain boundary and rapid corrosion occurs. The yielding of the metal reduces the stress concentration at the base of the pit to below the yield point and corrosion proceeds until the stress concentration again exceeds the yield point and the process is repeated. The cross-sectional area of sound metal is successively reduced and hence the time interval between each process of yielding becomes progressively shorter until the metal fails. The process is therefore an accelerating one.

Keating (43) suggests that the function of stress in stress-corrosion cracking may be confined to the development of purely mechanical damage and that stress concentration regions which are developed by localised corrosion are initially opened out into fine cracks. He finds it difficult to visualise penetration of electrolyte to the base of a crack and especially renewal of active corrodent by diffusion at a rate which would keep pace with a propagating crack. However, Allen (44) points out that Keating's views cannot give a complete picture otherwise stress-corrosion cracking should be encountered whenever the corrosive conditions and nature of the metal are such that a pitting type of attack is produced.

A detailed theory of the mechanism of stress-corrosion in aluminium - 7% magnesium alloy was recently put forward by Gilbert and Hadden (45). It is postulated that stress concentration at the base of an advanced crevice causes mechanical fracture between β and the solid solution. Rapid corrosion of the newly exposed β surfaces then occurs with evolution of hydrogen, this process being retarded by film formation and reverting to attack by oxygen absorption. Subsequent mechanical disruption by the same process continues until the ultimate tensile stress of a residual metal is exceeded. It is suggested that a supply of active corrosive agent is maintained at the tip of the crack by capillary action immediately after extension of a crack.

Evidence of the discontinuous nature of the process is given by potential measurements on cracking specimens. Small and fairly frequent anodic kicks were observed during the period of active cracking. These observations were confirmed by the fact that small discontinuous movements of the loop specimen were observed during active cracking.

From experiments carried out on Al-7%Mg alloy, Edeleanu (46) concludes that stress exerts no influence during the first stages of the stress-corrosion process, but that corrosion plays a vital role during the final rapid cracking.

Non-Susceptibility to Stress-Corrosion Cracking.

The theories of stress-corrosion outlined above do not explain why many alloys susceptible to intercrystalline corrosion have not yet been shown to be susceptible to stress-corrosion cracking.

In the initial stages of attack, the degree to which stress may render the anodic phase of an alloy more anodic will probably vary according to the phases present and the conditions of these phases. In the case of the mechanical cracking of an alloy, Champion (42) has suggested that when the protective film at the deepest point of the attack is ruptured by plastic deformation the corrosion occurring before film repair is complete may be insufficient to take the local stress beyond the yield point again, in which case a rapid succession of film ruptures will not occur. Susceptibility to stress-corrosion will therefore depend on the film-forming characteristics and the deformability of the metal.

A second possibility is that stress-corrosion may follow an exponential law (47) and if the asymptotic portion of the curve is reached before the local stress has exceeded the yield point, then plastic deformation will not occur.

Evans (48) suggests that there may be two types of hold up to cracking along grain boundaries viz.

bridges of mechanically strong material and chemically resistant material. If these are not identical, the probability of permanent hold up will be negligible, but if they are identical then stress-corrosion will be less serious or possibly absent.

III. MEASUREMENT OF CORROSION

Tests which are designed to study the mechanism of corrosion are of wide variety. The actual method of estimating the amount of corrosion which has taken place may also be one of many, the particular test and method of measurement being designed as the most suitable for the purpose and circumstances of the test.

A table of the most important methods for determining the amount and influence of corrosion is given by Borgmann (49), various methods are also fully discussed by Evans (6). Many of the methods are highly specialised and mention will be made only of those methods applicable to the present problems.

In many corrosion tests it is sufficient to measure the corrosion after exposure of the specimens for a measured period of time. However, in the majority of cases it is necessary to determine the relation between corrosion rate and time of exposure. It is therefore an advantage to be able to make estimations of the amount of corrosion without disturbing the corrosion process, thus enabling a corrosion - time curve to be drawn for a single specimen. In many cases this is not possible but such curves may be obtained by corroding a large number of identical specimens under identical conditions and testing several samples at measured intervals of time.

Measurement of General Corrosion

The methods which may be employed in estimating the general corrosion of a metal such as occurs when a base metal is exposed to a non-oxidising acid are:

i. Loss in weight.
ii. Gain of metallic constituent by the solution.
iii. Volume of hydrogen evolved.

The first method entails disturbance of the metal specimen, the second requires disturbance of the corroding solution, the third enables measurements to be made without disturbing the specimen or the corroding solution.

Measurement of Corrosion in Neutral Solutions

In this type of attack gain or loss in weight of the metal does not give an accurate estimation of the attack and does not afford a continuous means of measurement. An accurate continuous method was developed by Bengough and his co-workers (50-52) in which the oxygen absorbed and the hydrogen evolved was measured; corrosion - time curves were obtained for a single specimen without disturbing the corrosion process. This method was further utilised by Champion (53) in investigations on the corrosion of high-purity aluminium in potassium chloride solutions.

Electrochemical Methods of Corrosion Testing

A direct method of estimating the corrosion is to measure the current flowing between the anodes and cathodes on a metal surface. If I is the current flowing, E the difference in potential between the electrodes and R the resistance of the electrolyte between them, then I may be determined by measuring E and R and applying Ohm's Law. However, this entails the separation of the anodes from the cathodes, a condition which can be made possible in special cases only. Details of this method are given by Evans (6).

The resultant of anodic and cathodic potentials existing on the surface of a metal may be obtained readily, but although the variation of potential with time may give valuable information regarding the corrosion process especially when protective films are formed, it does not give a quantitative measure of the attack except in isolated cases.

A quantitative determination is possible only by chemical estimation of either the anodic reaction viz. the quantity of metal taken into solution, or the cathodic reaction viz. the quantity of hydrogen evolved or oxygen absorbed.

Potential - Time Curves

Curves of the overall potential difference between a metal and an electrolyte have been widely used to indicate the tendency of a metal to corrode. A metal which becomes anodic with respect to the solution indicates a tendency to corrode, whilst a cathodic metal indicates passivity.

Potential - time curves may be misleading if a large area of metal is exposed to the corroding solution and the attack is of a localised nature. In such cases the area of metal exposed should be very small.

Measurement of Stress-Corrosion Cracking

Since the direct result of corroding a metal under stress is the reduction of its mechanical properties, it follows that the criterion of measurement most suitable is the loss in mechanical properties, notably elongation and ultimate tensile strength. This has the disadvantage of being a discontinuous method and a large number of specimens are required to obtain corrosion - time curves.

A number of investigators have recorded the decrease in yield strength, but Champion (54) points out that this effect may be small whilst the loss in ultimate tensile strength is appreciable.

PART 2

EXPERIMENTAL INVESTIGATION

INTRODUCTION

The main types of corrosion have been classified under the headings (24):

(a) General Corrosion
(b) Localised Corrosion
(c) Intercrystalline Corrosion

One type does not exclude the other and it is possible for the three types to occur simultaneously in the one piece of metal.

In general corrosion, almost uniform attack and general etching of the whole surface is brought about and is usually associated with strongly acid or alkaline conditions, it being seldom met with in the neutral range. In the case of aluminium, the oxide film on the metal is dissolved, exposing the metal. As such the full intrinsic properties of the metal will operate.

Localised corrosion is observed under conditions which bring about local breakdown of surface films and leaves large areas comparatively unaffected, whilst in intercrystalline corrosion the attack is concentrated at the grain boundaries of the metal due, e.g., to the precipitation of an anodic phase after strain-ageing.

Although stress-corrosion failures have been reported in several metals and many alloys, in most of the theories advanced to explain these failures stress is regarded as having a purely mechanical action or it is considered that the stress, in opening up cracks in the metal, ruptures protective films allowing access of the corroding medium to a hitherto protected surface. Little is known, however, about the effect of stress on the susceptibility of the metal itself to corrosion and the experimental work was commenced with the object of investigating this effect. This can be done only if there are no protective films formed on the metal during the corrosion process and therefore the first section of the experimental work was a study of the effect of stress on general corrosion in hydrochloric acid solutions. In order to avoid the complications involved in structural corrosion of an alloy, aluminium was used. The work was then extended to include aluminium - 7% magnesium alloy, which is known to be susceptible to stress-corrosion in sodium chloride solutions.

The investigation was further extended to study the stress-corrosion cracking of aluminium-magnesium alloys. Such failures have been reported as occurring in several of these alloys when they are strain-aged and subjected to an environment of sea-water, or in the laboratory to solutions of sodium chloride. The corrosive attack is intercrystalline and of a highly localised nature, differing from general corrosion in that the attack appears to be controlled by the formation of protective films. Experimental techniques were developed on an alloy known to exhibit stress-corrosion properties and then used for the investigation of alloys the properties of which have not previously been fully determined.

The experimental work is arranged under the following headings:

A. GENERAL CORROSION

  I. Corrosion rates,

    (a) aluminium in solutions of hydrochloric acid and hydrochloric acid containing sodium chloride,
    (b) aluminium - 7% magnesium alloy in hydrochloric acid containing sodium chloride.

  II. Potential measurements in acid solutions.

B. LOCALISED CORROSION

The effect of stress on the corrosion of strain-aged aluminium-magnesium alloys in sodium chloride solutions.

I. Measurement of oxygen absorbed and hydrogen evolved.

II. Measurement of the loss of mechanical properties.

PRELIMINARY CONSIDERATIONS

At the outset it was necessary to decide on the form of the metal specimens to be tested. Rolled sheet and wire are the only forms in which a metal can be obtained such that there is a high probability of reproducible samples. Most of the investigations on corrosion under stress have been carried out on specimens cut from rolled sheet. This, it appeared, had disadvantages in that it would necessitate comparatively large loads for stressing in tension in the region of the yield point, and that the corrosion would possibly involve edge effects. It was therefore decided to use specimens in the form of wire, Comparatively small loads would then be required for stressing 16 gauge wire, thus simplifying the apparatus, and edge effects would be non-existent.

Many methods have been utilised for stressing a metal specimen during stress-corrosion tests, but it was considered that the simplest means was by a tensile stress applied via a steelyard. The value of the stress would then be known accurately and the possibility of variations in the stress applied to other specimens stressed to the same value would be diminished.

SECTION A

GENERAL CORROSION

I. MEASUREMENT OF CORROSION RATE IN ACID SOLUTIONS

(a) CORROSION OF ALUMINIUM

Although it would have been desirable to use aluminium of the highest purity for this investigation, a supply was not readily available in the required form at the time and commercial purity metal was used.

The metal was received in the form of wire, 0.064 in. diameter, in coils. Chemical analysis carried out by the methods recommended by the British Aluminium Company (55) gave the composition as:-

Cu	...	0.02%
Si	...	0.15%
Fe	...	0.47%
Al	...	99.31% (not by difference)
Total	...	99.95%

Annealing

The metal was annealed by heating at 390°C. in an air oven for 3 hours.

Mechanical properties

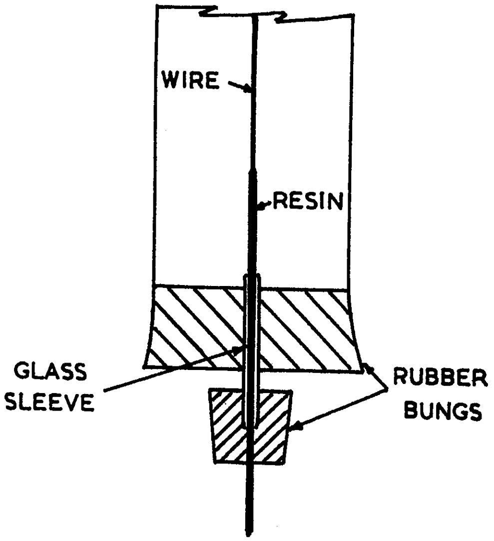
The stress-strain properties of the annealed metal were determined by direct loading on a length of 10 ft. The 0.1% proof stress was evaluated by the offset method.

0.1% proof stress = 2.43 tons/sq.in., equivalent to a direct load of 17.5 lbs.

Ultimate tensile strength = 4.46 tons/sq.in., equivalent to a direct load of 32 lbs.

Creep

For applied loads greater than about 80% of the 0.1% proof stress, the aluminium showed high creep properties and it was impracticable to apply a direct load of more than 14 lbs.



SEAL AT BASE OF CORROSION TUBE

FIG. 2

DEVELOPMENT OF TECHNIQUE FOR DETERMINING CORROSION RATES

An apparatus was constructed whereby the wire specimen was immersed in the corroding solution. A direct tensile stress was applied by means of a steelyard.

The apparatus consisted of a vertical corrosion tube, 3 ft. 6 in. in length, 1 in. internal diameter, in which the wire specimen was contained. This tube was jacketed and water from a constant temperature tank was circulated through the jacket, maintaining the corroding liquid at a constant temperature.

The wire specimen was clamped to a steelyard held above the corrosion tube and fixed to an adjustable clamp below the tube. A rubber bung was fitted at the lower end of the tube to retain the corroding liquid, the wire passing through it being sleeved by a narrow bore glass tube and sealed by a small rubber bung partly bored to fit over the glass sleeve and partly to allow the wire to pass through it as shown in Fig. 2. A length of 30 ins. of wire was exposed to the corroding medium, protection being given at the water line and at the base of the tube by coating with a polymethacrylic resin (I.C.I. Bedacryl, 144 T.L.). The method of sealing at the base of the tube permitted adjustment of the wire without rupturing the protective coating.

The apparatus was held in a framework constructed of "Ecofix" strip metal. Five corrosion units, all identical were set up.

The experimental determinations were commenced by corroding the metal in dilute hydrochloric acid. Several methods of estimating the rate of corrosion were apparent and these were investigated.

Analysis of the amount of aluminium taken into solution could be effected either by withdrawing the corroding liquid at definite intervals and analysing it for metal content or by withdrawing small samples and estimating the metal content by a micro-analytical method. It was thought that the latter method would disturb the corrosion process as little as possible and methods for effecting such an analysis were investigated.

Polarographic Analysis (56)

A Cambridge Polarograph was used for obtaining self recording current-voltage curves for the solution under investigation. The technique employed by Gull for the determination of aluminium in magnesium alloys was investigated (57), but it was found that the aluminium step in the current-voltage curve was so ill-defined that accurate analysis was not possible when the aluminium concentration was less than about 0.01%, whereas analysis of solution containing about 0.001% was required.

A recently developed method was investigated, which utilised the principle that ions such as bromate, in small concentrations, are catalytically reduced at the dropping mercury electrode in presence of a relatively large concentration of cations such as aluminium, but if the conditions are reversed so that the concentration of bromate is much larger than that of aluminium, the diffusion current obtained becomes proportional to the aluminium concentration (58). This method was found to be a considerable improvement over the direct method of analysis and a technique was developed whereby concentrations of 0.003% of aluminium could be analysed accurately. However, in order to carry out an estimation, it was necessary to withdraw comparatively large samples of the corroding solution and concentrate by evaporation, thereby defeating the original aim of taking small samples, and analysis of the larger samples could be carried out as rapidly by gravimetric analysis.

In much of the preliminary work for developing the experimental technique for corrosion in acid solutions, the polarographic analysis was employed and the more important of the results are given. A specimen analysis illustrates the method of analysis and calculation of the amount of corrosion.

The polarograph affords a rapid and accurate method of micro-analysis of a large number of samples, especially if estimation of more than one constituent is required. Since it is a useful tool in corrosion research, an account of the technique which was developed for the analysis of aluminium is given in full as an appendix to this thesis.

Specimen Analysis

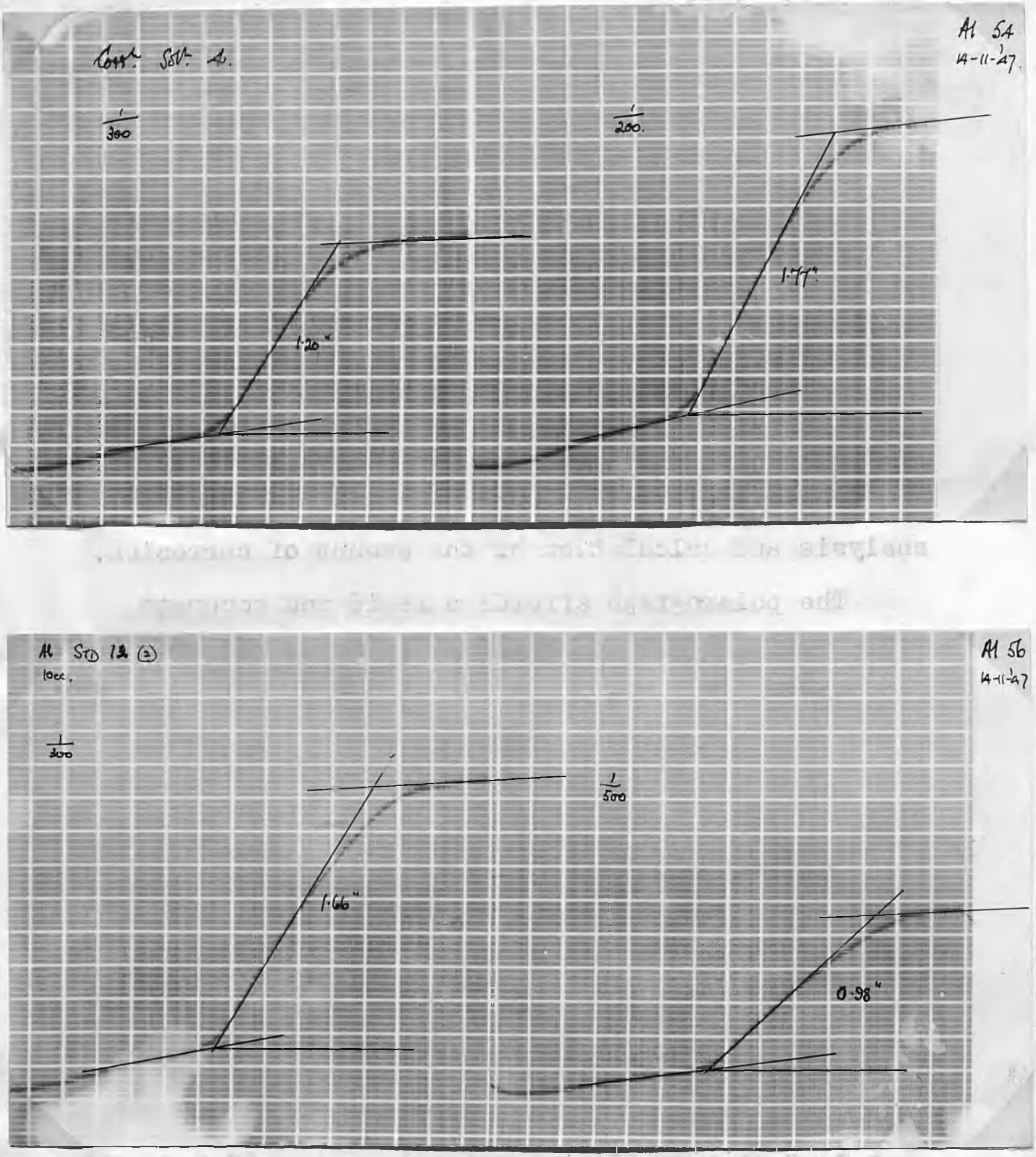
TABLE I

Annealed Al corroded in 0.1N HCl at 20°C.
Corrosion after 142 hours.

* Surface area of wire exposed	50.8 sq.cms.
Total volume of corroding solution	472 ml.

---

* Calculated from average diameter and length exposed



SPECIMEN POLAROGRAMS

FIG. 3

250 ml. of the corroding solution concentrated to 50 ml. 10 ml. of this, 5 ml. of bromate base solution and calculated volume of KCl solution made up to 25 ml. with distilled water. (see appendix).

Polarogram 54. - unknown solution

Sensitivity .. $\frac{1}{300}$
Ht. of step .. 1.20 in. Ht. at $\frac{1}{10}$ sens. .. 36.0 in.

Sensitivity .. $\frac{1}{200}$
Ht. of step .. 1.77 in. Ht. at $\frac{1}{10}$ sens. .. 35.4 in.

Average .. 35.7 in.

Polarogram 56. - Al standard soln. 0.005 gms./litre.
10 ml. std, 5 ml. base in 25 ml. total.

Sensitivity .. $\frac{1}{300}$
Ht. of step .. 1.66 in. Ht. at $\frac{1}{10}$ sens. .. 49.8 in.

Sensitivity .. $\frac{1}{500}$
Ht. of step .. 0.98 in. Ht. at $\frac{1}{10}$ sens. .. 49.0 in.

Average .. 49.4 in.

$$\text{Corrosion of wire in gms./sq. metre} = \frac{200 \cdot x \cdot z \cdot V}{y \cdot S}$$

where x = step height of unknown solution,
y = step height of standard at same sensitivity,
z = concentration of Al in standard solution before dilution, in gms./litre,
V = total volume of corroding solution used in corrosion test, in mls.,
S = surface area of wire exposed, in sq. cms.

$$\text{Corrosion of wire} = \frac{200 \cdot 35.7 \cdot 0.005 \cdot 472}{49.4 \cdot 50.8}$$

$$= 6.71 \text{ gms./sq. metre}$$

Experimental results

Experiments were carried out to determine the effect of the interval between renewal of the corroding solution, and also the effect of temperature, on the rate of attack. The effect of applied stresses less than the 0.1% proof stress was investigated.

TABLE II

Corrosion of annealed Al in 0.100 N HCl at 20°C. Solution completely withdrawn and fresh solution added at the intervals stated.

Corrosion expressed in gms. Al dissolved/sq.metre.

Interval (hours)	Average corrosion per 24 hours			
	a	b	c	d
24	1.34	1.32	1.36	1.31
24	1.28	1.16	1.36	1.42
24	1.42	1.28	1.32	1.35
96	1.21	1.15	1.11	1.18
96	1.15	1.15	1.10	1.16
330	1.00	0.96	0.96	0.99

The average corrosion rate per 24 hours when the corroding solution was renewed at 96 hour intervals was somewhat less than when renewed after 24 hours, and over 330 hours the average rate per 24 hours was considerably less. Estimation of the acidity of the corroding solution after various periods of immersion showed:-

Initial	..	0.100 N
24 hrs.	..	0.098 N
96 hrs.	..	0.095 N
330 hrs.	..	0.087 N.

Hence, reduction in the rate of attack was due, at least in part, to a reduction in the acid strength as the hydrogen ions of the acid were replaced by aluminium ions. Relatively small changes in the normality of the solution had an appreciable effect on the corrosion rate.

Samples withdrawn after 96 hours immersion required little evaporation to raise the concentration of aluminium to values which could be accurately analysed. It was therefore decided that in subsequent tests, this interval of corrosion would be adopted.

Effect of temperature

Experiments were conducted to determine the effect of temperature on the rate of corrosion. Wire specimens were corroded for 96 hours at the temperature stated. Fresh specimens were used for each test.

TABLE III

Aluminium. No applied stress.
Corroded in 0.1 N HCl.

Temp. (°C)	Corrosion in 96 hours (gms./sq.in./24 hrs.)			
20	1.21	1.32	1.30	1.36
25	1.80	1.85	1.71	1.91
30	2.58	2.54	2.62	2.75
35	3.48	3.61	3.65	3.51
40	4.50	4.82	4.65	4.89

The average increase in corrosion rate with each 5°C. increment of temperature rise was:

Increment	% Increase in corrosion rate
20° - 25°	40
25° - 30°	44
30° - 35°	36
35° - 40°	32

The temperature control of the corroding solution was ± ½°C., hence the variation in corrosion rate due to temperature fluctuation was about ± 4%.

Effect of stress

The effect of stress on the amount of corrosion after 96 hour intervals was determined. Fresh wire samples were used for each determination.

TABLE IV

Aluminium. Corroded in 0.1 N HCl at 20°C.

Applied stress (% of Proof stress)	Total corrosion (gms./sq. metre).			
ZERO	4.82	4.61	4.42	4.58
30	4.31	4.70	4.58	4.38
60	4.70	4.53	4.82	4.62
ZERO	4.61	4.40	AVERAGE:	4.57
30	4.29	4.37		4.44
60	4.65	4.70		4.67

Discussion

Although the polarograph was not used in the final technique for determining corrosion rates, results obtained were useful in establishing several details necessary for accurate reproducibility of results.

Small changes in acid strength had an appreciable effect on the rate of corrosion. The results given in Table II show that the average amount of corrosion per 24 hours during intervals of 96 hours and 330 hours were successively less than those during intervals of 24 hours due to a gradual reduction in acid strength during corrosion. The actual rates of corrosion after intervals of 96 hours and 330 hours would be even less, hence it was necessary that acid strength be made as nearly identical as possible in all tests.

Changes in the temperature of the corroding solution had a marked effect on the corrosion rate, but in this case, the accuracy of the determination was governed by the temperature control of the corroding solution which in turn was controlled by the circulation of water from a thermostatically controlled reservoir through jackets surrounding the corrosion tubes. By maintaining the corroding solution a few degrees above atmospheric temperature, the loss of heat from the solution to the surroundings would be reduced to a low value and the fluctuation in temperature would be reduced to a minimum.

Applied stress within the proof stress value appeared to have no effect on the amount of corrosion during an interval of 96 hours, the variation recorded in the average values of six tests (Table IV) being within the variation which could be caused by temperature fluctuation.

If samples of corroding solution were taken at more frequent intervals than about 96 hours, it was necessary to concentrate the solution for analysis. Since this entailed drawing off an appreciable volume of corroding liquid and therefore necessitated complete renewal of the solution to reproduce conditions of corrosion, other methods for estimating the corrosion rates were investigated.

Gravimetric Analysis using 8-hydroxy quinoline

The compound 8-hydroxy quinoline (oxine), $HO.C_9H_6N$, forms a compound with aluminium in which the metal replaces the hydrogen to give $Al(C_9H_6NO)_3$. The quantitative precipitation of aluminium oxinate is now recognised as being one of the most accurate methods for analysis of aluminium.

In an attempt to decrease the time of analysis, several other methods were investigated. Instead of drying the aluminium oxinate and weighing, the complex was dissolved in concentrated hydrochloric acid, the solution brominated and excess bromate estimated by titration. Although this proved to be time saving, the accuracy of the analysis was sacrificed.

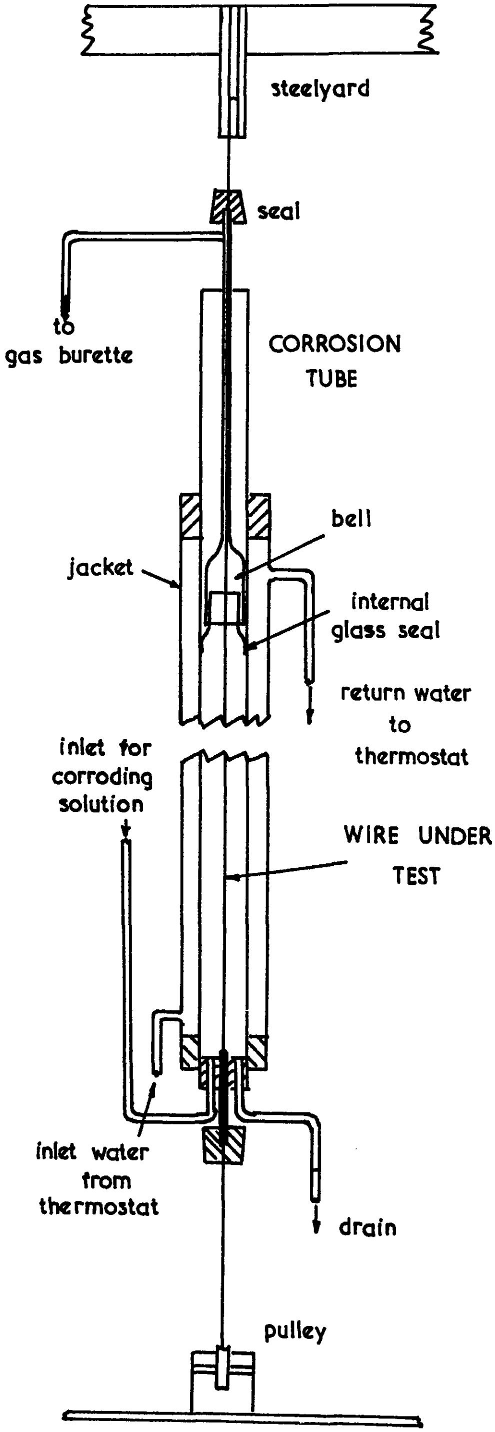
Colorometric analysis using aluminon reagent was attempted (59), but the accuracy was insufficient to make this an effective method.

Gasometric Analysis

When a base metal is immersed in an acid solution, hydrogen is evolved, the volume of which is a measure of the weight of metal taken into solution. By frequent measurements of the volume of hydrogen liberated, the amount of corrosion may be ascertained without disturbing the specimen or the corroding solution. This method has the added advantage of being the most accurate means of analysis, a comparatively large volume of hydrogen being evolved for a small quantity of metal dissolved. 1 ml. of hydrogen is evolved for the dissolution of 0.00083 gms. of aluminium.

The method provided a difficulty in the means of sealing the wire specimen at the top of the corrosion tube, in order that the hydrogen evolved could be collected, such that the stresses were not arrested nor localised at the seal. It became evident that the only method by which this was possible was by making the seal independent of the corrosion tube. The method developed made use of a floating bell fitted inside the corrosion tube and sealed to the wire by means of a rubber bung.

The original design required certain modifications. An internal glass seal was constructed in the corrosion tube such that it contained the bell, ensuring that all the hydrogen liberated was collected. For the purpose of taking measurements, it was necessary to choose an arbitrary value of the gas space in the bell to which it could be adjusted prior to each measurement. The simplest means of effecting this was to adjust the levels of the liquid inside and outside the bell so that they corresponded. By submerging the bell such that this level occurred in the narrow stem above it, an accurate zero set was obtained.



UNIT OF APPARATUS FOR
CORRODING WIRE UNDER STRESS

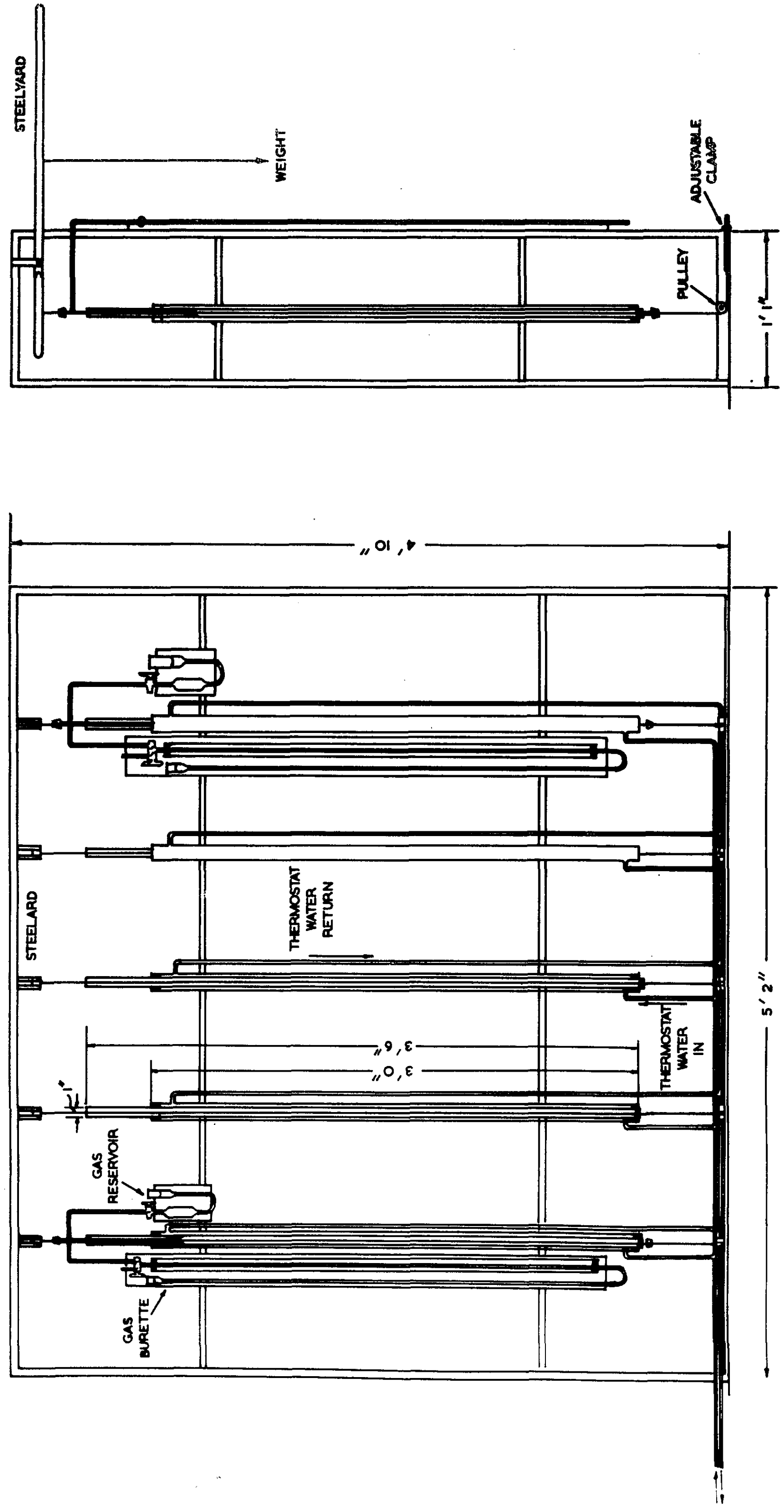
FIG. 4

The volume of gas was measured by means of a gas burette graduated in hundredths of a ml. The connections between the bell and burette were of capillary tubing in order that the dead space volume was as small as possible.

The volume of hydrogen collected overnight was frequently greater than the capacity of the bell. To accommodate the gas, a reservoir was constructed consisting of a bulb filled with water and fitted with a levelling tube. The reservoir was connected to the connecting tube between the bell and burette via a stopcock so that it could be disconnected when necessary.

A complete unit for measuring the volume of hydrogen is shown in Fig. 4, and the arrangement of the apparatus is shown in Fig. 5 (facing p.54).

Facing P. 54



ARRANGEMENT OF APPARATUS FOR CORRODING WIRE UNDER STRESS

FIG. 5

EXPERIMENTAL PROCEDURE

Pretreatment of the Wire

An oxide film is formed on aluminium when it is exposed to air, and when the metal is immersed in acid the film must be dissolved before attack on the metal can commence. Straumanis (60) found that the oxide skin is rapidly destroyed by concentrated hydrochloric acid, but with decreasing acid strength there is an increase in the "period of induction" which elapses before attack becomes vigorous and steady. With high purity aluminium, the period of induction is nearly 2 days when immersed in 2N hydrochloric acid. Maas (61) reports, however, that impurities shorten the induction period.

Preliminary tests were carried out in which the aluminium wire was pretreated by immersing in hydrochloric acid of various strengths. When the acid was sufficiently concentrated to dissolve the oxide film, the surface of the metal was etched and roughened, probably resulting in an appreciable increase in the surface area (vide also p. 65). A satisfactory technique was to immerse the wire in 0.2N hydrochloric acid for 24 hours, after which it was washed with the corroding solution used in the test, immersed in it for one hour and then fresh corrodent used for the test itself. Although it is probable that the oxide film was not completely destroyed by this procedure, there was no undue roughening of the metal surface and reproducible results were obtained during the subsequent experiments.

Details of Assembly

The length of wire exposed (30 ins., 76.2 cms.) was the same in all tests. It was arranged that the metal was protected at the surface of the liquid and was not exposed to gas when a depression in liquid level occurred due to accumulation of gas in the bell. When a specimen was stressed, final adjustment of the position of the wire was made by means of the adjustable clamp below the corrosion tube.

The corroding liquid was introduced into the corrosion tube via a tube entering the base of the latter (vide Fig. 4). Conditions were allowed to stabilise for half an hour before commencing observations.

A little water was introduced to the surface of the mercury in the gas burette to ensure that mercury vapour did not come into contact with the aluminium.

Method of taking Observations

The level of the water in the reservoir was adjusted to a graduation mark. At the time of measurement, the level of the liquid inside the bell was adjusted to the zero set by drawing gas into the burette. If the reservoir was in use, the level of the liquid in it was restored to the original set by drawing gas from it into the burette, and allowing it time to adjust itself to the temperature in the burette.

Tests Conducted

Experiments were carried out in order to determine the effect on the rate of corrosion of:-

i) External stresses below the proof stress.
ii) Internal stresses, caused by overstrain of the metal.
iii) External stresses applied to overstrained metal.

In (i) the stress was continuously applied, in (ii) the metal was overstrained to the extent indicated in the data obtained and corroded without external loading and in (iii) an external stress was continuously applied to the overstrained metal. In all cases, comparison was made with unstressed specimens.

The initial experiments were conducted with a solution of 0.1 N HCl. In order to link these tests with those conducted on the stress-corrosion of aluminium alloys, sodium chloride was added to the acid and a series of tests carried out with 0.1 N HCl containing 5% NaCl. It was decided afterwards to use 3% NaCl solutions in tests with alloys in order to conform with the work of other investigators and a series of tests using 0.1 N HCl containing 3% NaCl was carried out to give uniformity to the work discussed in this thesis.

In all cases the corroding solution was static and initially saturated with air. The solutions were renewed after 96 hours and observations continued for a second period of 96 hours.

Most of the tests were conducted at 25°C., but some were carried out at 30°C. since at one period the room temperature exceeded 25°C.

Presentation of Results

The data may be presented either as curves of the total corrosion v. time of exposure or of the rate of corrosion v. time of exposure. The latter appeared to afford a neater mode of expressing the results, especially for comparing the attack under different conditions of stress. This curve had the advantage that any inaccuracies incurred due to the collection of the comparatively large volumes of hydrogen evolved overnight were not recorded, and hourly measurements made at intervals during the day were sufficient to express the results.

The curves for each specimen were drawn as shown in Fig. 6. for the specimen set of observations given in Table V.

Specimen Observations

TABLE V

Corrosion rate of aluminium with time of immersion.

Aluminium Unstressed
Corroding solution : 0.1 N HCl + 3% NaCl.

Data recorded.

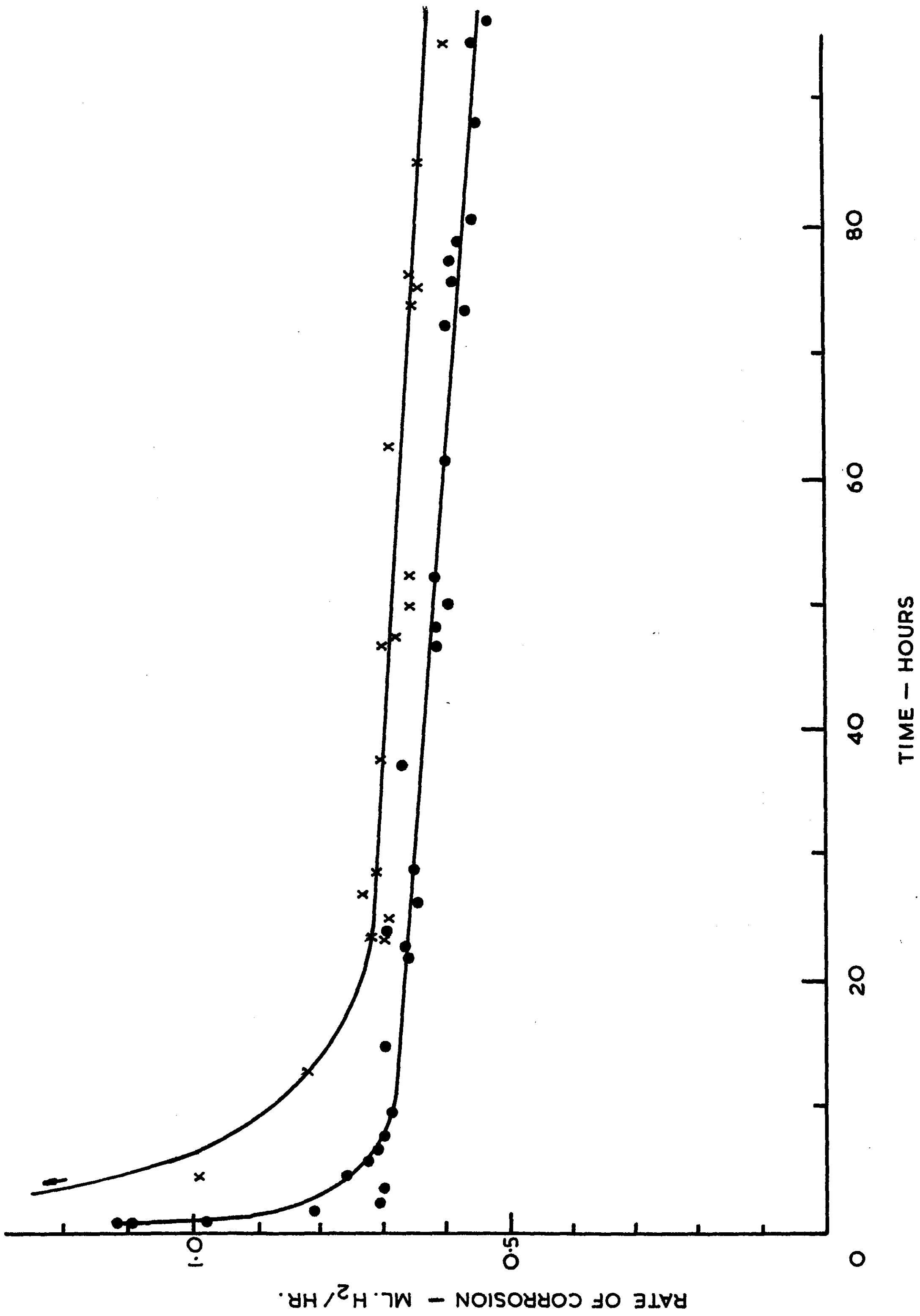
t : time since last volume reading, hours.
v : volume of hydrogen collected in interval, ml.
r : rate of corrosion during interval, ml. H_2/hour.
T : total time of immersion at which r is the average value, hours.

Interval time t	Volume H_2 v	Rate r	Total time T
0.25	0.27	1.08	0.13
0.25	0.28	1.12	0.38
0.75	0.72	0.96	0.88
0.75	0.60	0.80	1.63
1.00	0.69	0.69	2.50
1.00	0.68	0.68	3.50
1.00	0.75	0.75	4.50
1.00	0.72	0.72	5.50
1.00	0.70	0.70	6.50
1.00	0.69	0.69	7.50
13.00	9.01	0.69	14.50
1.00	0.65	0.65	21.50
1.00	0.65	0.65	22.50
1.00	0.68	0.68	23.50
4.00	2.53	0.63	26.00
1.00	0.63	0.63	28.50
17.00	11.18	0.66	37.00
1.00	0.61	0.61	46.50
1.00	0.60	0.60	47.50
3.00	1.75	0.58	49.50
2.00	1.21	0.61	52.00
18.00	10.77	0.60	62.00
1.00	0.60	0.60	71.50
2.00	1.14	0.57	73.00
2.00	1.17	0.59	75.00
1.00	0.59	0.59	76.50
1.50	0.91	0.61	77.75
3.00	1.73	0.58	80.00
12.00	6.70	0.56	87.50
1.00	0.56	0.56	94.00
1.30	0.82	0.54	95.25

Corroding solution renewed

Interval time t	Volume H_2 v	Rate r	Total time T
0.25	0.62	2.48	0.13
0.25	0.54	2.16	0.38
0.25	0.37	1.48	0.63
0.25	0.40	1.60	0.88
0.30	1.04	2.08	1.25
0.30	0.75	1.50	1.75
0.30	0.65	1.30	2.25
0.30	0.54	1.08	2.75

Continued



CORROSION OF UNSTRESSED ALUMINIUM IN 0·1N HCl + 3% NaCl AT 25°C.

FIG. 6

Interval time t	Volume H_2 v	Rate r	Total time T
1.00	1.21	1.21	3.30
1.00	0.98	0.98	4.30
16.00	13.00	0.81	13.00
2.00	1.41	0.71	23.00
1.00	0.72	0.72	23.50
2.00	1.37	0.69	25.00
2.00	1.46	0.73	27.00
1.00	0.71	0.71	28.50
16.30	11.52	0.70	37.25
1.00	0.71	0.71	46.25
1.50	1.01	0.68	47.25
3.00	1.98	0.66	49.50
2.00	1.31	0.66	52.00
19.00	13.15	0.69	62.50
2.00	1.32	0.66	73.50
1.00	0.64	0.64	74.50
2.00	1.32	0.66	76.00
16.00	10.41	0.65	85.00
3.00	1.84	0.61	94.50

General Observations

The rate of hydrogen evolution attained a maximum value within about an hour of adding the corroding solution. This rate diminished rapidly eventually reaching a steady rate. A subsequent reduction in the rate was due to a gradual increase in the pH of the solution as the hydrogen ions of the acid were gradually replaced by metal ions.

When the corroding solution was changed, the maximum rate primarily attained and the subsequent steady rate became successively greater with few exceptions. The time taken to attain a steady rate also increased with successive changes in the solution. Analysis of the gas evolved during the period of high rate proved it to be hydrogen.

These observations are shown in Figs. 7 - 9. Fig. 7 shows the increase in rates of attack when the corroding solution was renewed, Fig. 8 shows the increase in the maximum value of the initial attack when the solution was renewed and Fig. 9 shows that similar curves were obtained for stressed metal.

The curves are for corrosion in 0.1 N HCl + 5% NaCl. Similar results were obtained for the acid alone and with 3% NaCl.

NOTE

The different colours indicate different specimens and the numbers indicate renewal of the corroding solution.

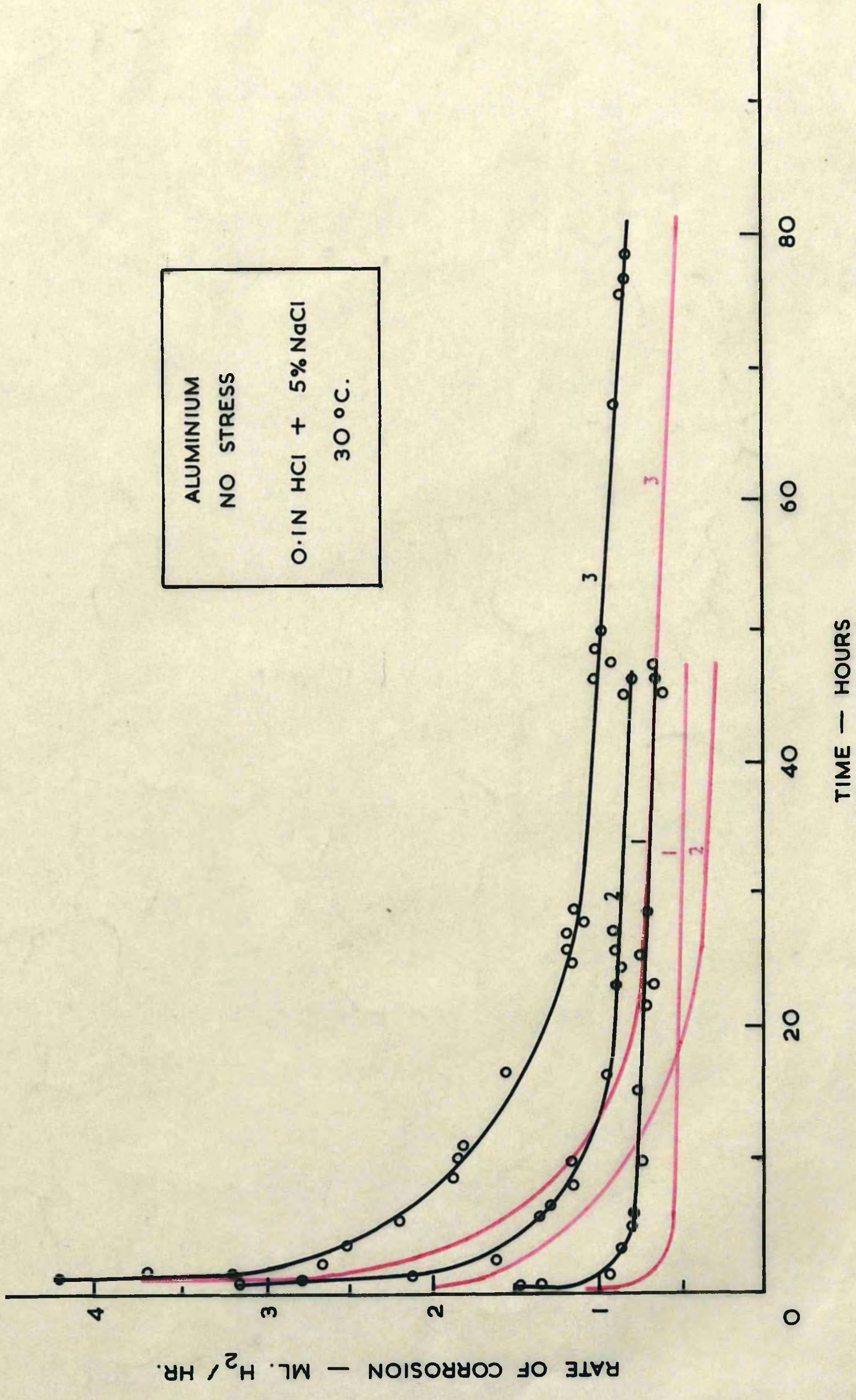

ALUMINIUM
NO STRESS
0·1N HCl + 5% NaCl
30 °C.
RATE OF CORROSION — ML. H2/ HR.
TIME — HOURS
0
20
40
60
80
1
2
3
4
1
2
3
1
2
3

FIG.7

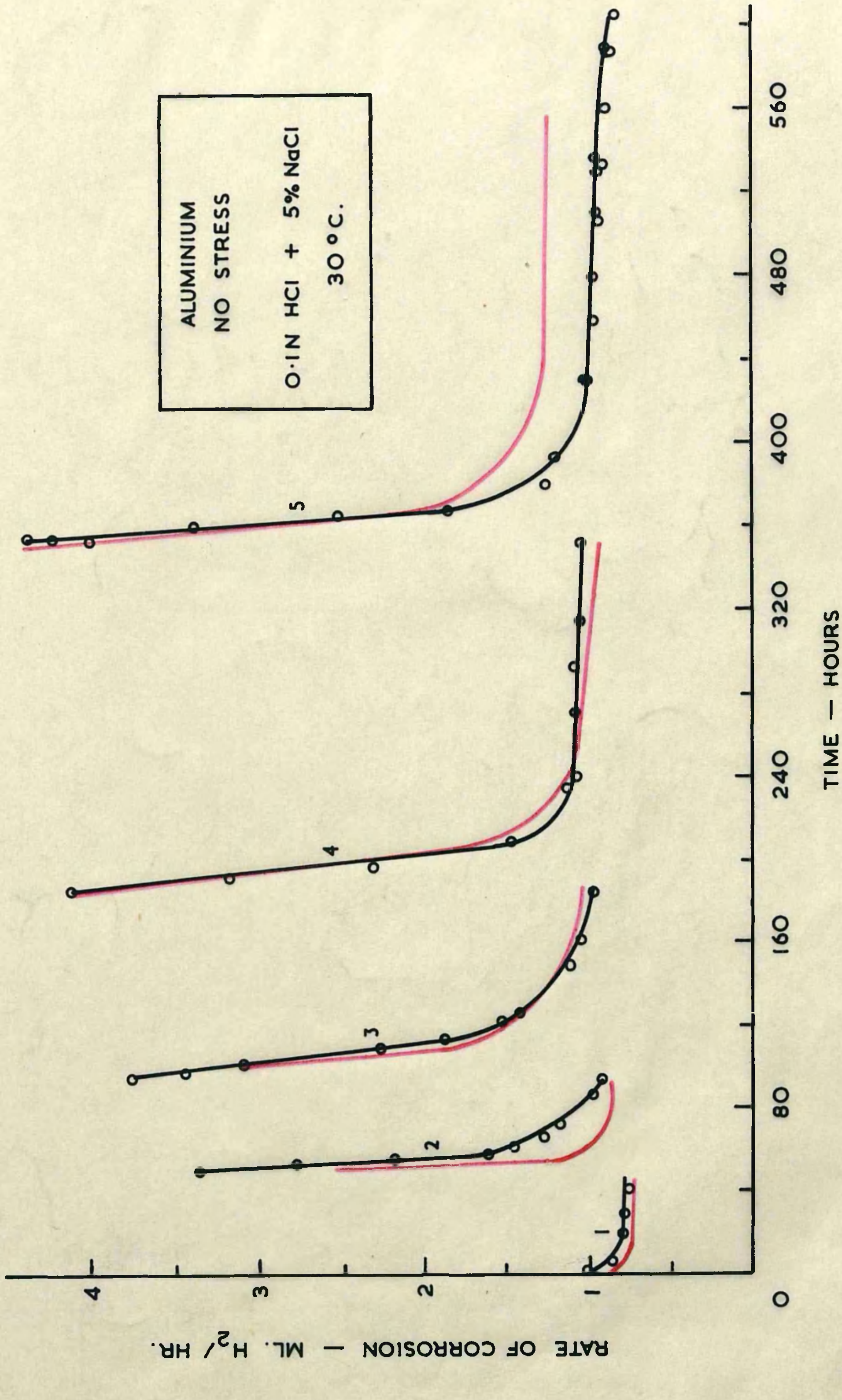

ALUMINIUM
NO STRESS
0·1N HCl + 5% NaCl
30°C.
RATE OF CORROSION — ML. H₂/HR.
TIME — HOURS
0
80
160
240
320
400
480
560
1
2
3
4
1
2
3
4
5

FIG. 8

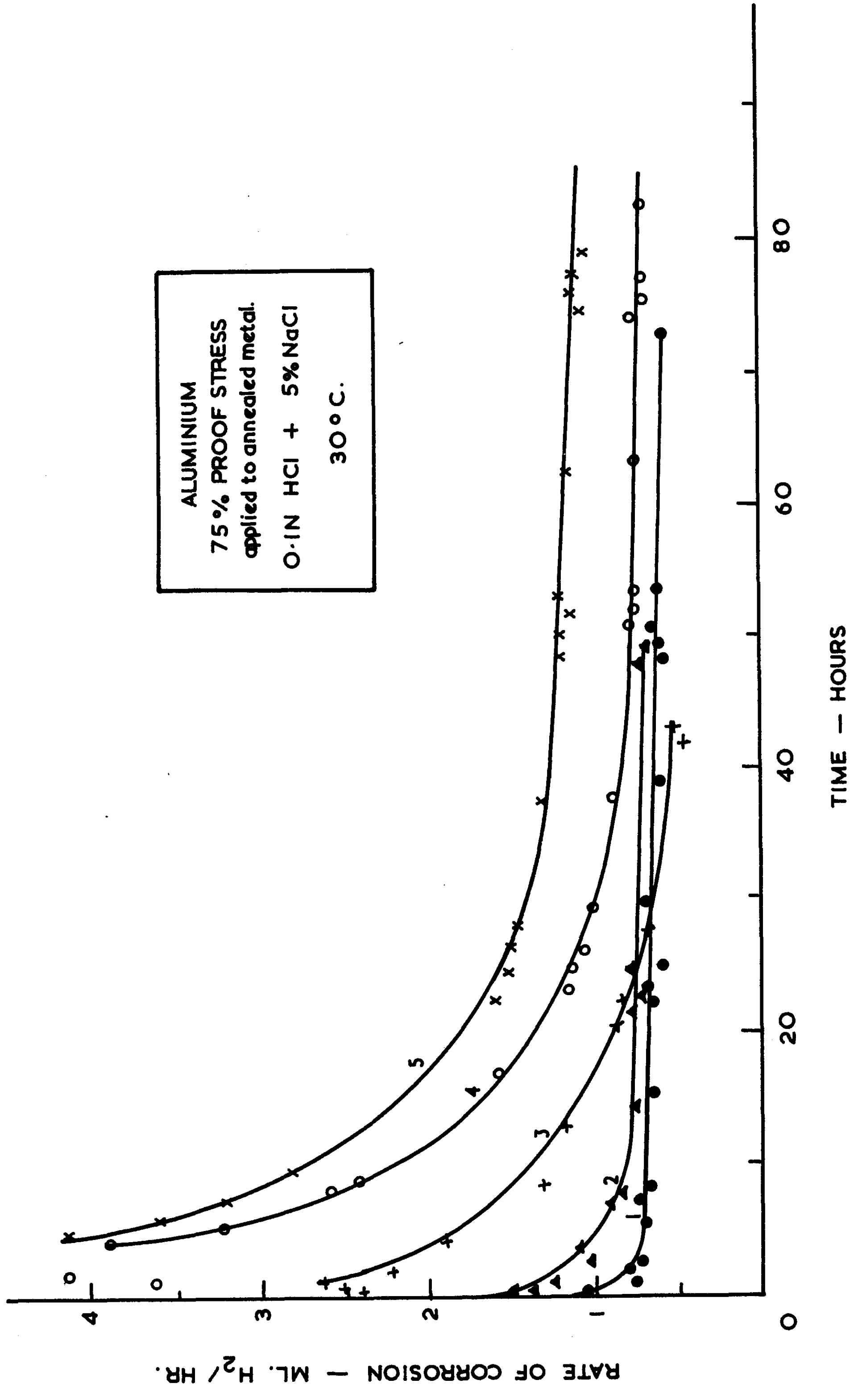

ALUMINIUM
75 % PROOF STRESS
applied to annealed metal.
O·IN HCl + 5% NaCl
30 °C.
RATE OF CORROSION — ML. H$_2$/ HR.
TIME — HOURS
0
20
40
60
80
1
2
3
4
1
2
3
4
5

FIG. 9

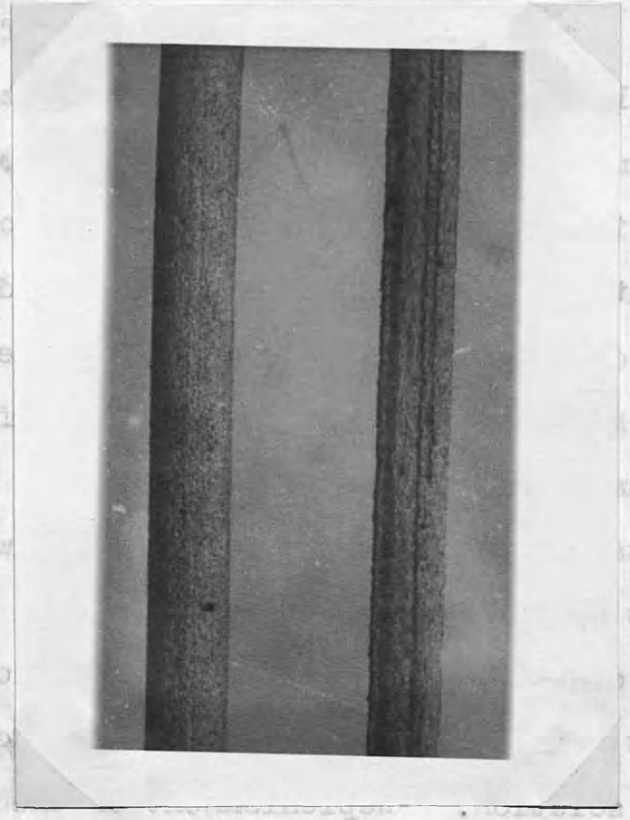
DISCUSSION

A possible explanation of the high initial rate of attack with subsequent decrease to an almost steady rate is that the system is initially in a state of non-equilibrium and thereafter tends to equilibrium.

Aluminium is initially immersed in a solution saturated with air, free from aluminium ions and containing a high concentration of uniformly distributed hydrogen ions. When attack commences, aluminium ions pass into solution at anodic points and the main cathodic reaction, which occurs at regions of low hydrogen overvoltage, is the combination of electrons with hydrogen ions with subsequent evolution of hydrogen gas. It has been shown by Whitman and Russel (62) that oxygen accelerates the attack of aluminium by 4% hydrochloric acid, whilst Bryan (63) has shown that oxygen appreciably increases the corrosion of aluminium by 0.1 N hydrochloric acid. Thus a second cathodic reaction is the combination of electrons with dissolved oxygen. The overall rate of attack is therefore greater than that due only to the discharge of hydrogen ions. As corrosion proceeds, the concentration of aluminium ions increases in the liquid immediately adjacent to the metal surface, eventually tending to a constant value as the ions diffuse into the main body of the solution at the same rate as they pass into the diffusion layer at the metal surface (vide Kemball (64)). The hydrogen ions originally in the liquid layers near the metal are discharged and hydrogen ions then diffuse from the bulk of the solution to the metal surface. Although it is unlikely that the rate of corrosion is dependent upon the rate of diffusion of hydrogen ions to the metal surface, as has been suggested in the case of magnesium (65), the characteristics of the solution in contact with the metal are different from what they were at the commencement of attack.

As the dissolved oxygen is used in the cathodic reaction, it must diffuse to the metal surface from the bulk of the solution. Replenishment of the oxygen in the bulk of the solution can occur only by passage of oxygen from the surface of the solution. The role of oxygen therefore diminishes, since the latter process can take place only by convection currents (vide also p.143) and may eventually become non-existent. Thus after a period, conditions tend to become steady with a constant rate of attack. Subsequent decrease in the rate of attack is due to a decrease in the hydrogen ion concentration of the solution.

Confirmation of the different conditions when the



INCREASE IN SURFACE AREA OF
ALUMINIUM WIRE DUE TO
CORROSION IN HCl

FIG. 10

corroding solution was introduced and after a period of time was obtained by running off the corroding solution after the steady conditions had been attained. The solution was mixed and saturated with air and returned. A fourfold increase in the rate of attack occurred, the rate returning to the original value after about four hours.

Explanation of the increase in the steady rate of attack after each change of corroding solution is that it was probably due to an increase in the surface area of the metal, as shown in Fig. 10. Destruction of an incompletely removed oxide film may also have contributed to an increase in the rate of attack. These reasons may also explain the marked increase in the maximum rate of hydrogen evolution in the initial stages which resulted when the corroding solution was renewed.

Factors Influencing Accuracy of Results.

Three factors may have an appreciable influence on the accuracy of the observations on the rate of corrosion as measured by the volume of hydrogen evolved.

First, hydrogen is slightly soluble in aqueous solution; about 6 ml. will dissolve in 470 ml. of the corroding solution. Hence the volume of gas collected is less than that formed in the cathodic reaction. However, dissolution of hydrogen is greatest in the early stages of the experiment and since the rate of hydrogen evolution was 0.4 - 0.5 ml. per hour in 0.1N hydrochloric acid, there should be little error in the measurement after about 20 hours. In the experiments, comparative values between stressed and unstressed metal were required rather than absolute corrosion rates, hence any error would tend to be eliminated.

Second, corrosion by dissolved oxygen was not measured. It was considered, however, that corrosion by this means rapidly diminished as the oxygen was removed and after about 20 hours would be relatively small. Any error would be of the same order in all tests and therefore the results under various conditions of stress would be comparable.

Third, a certain amount of uncontrolled stirring is caused by convection currents and by bubbles of hydrogen rising through the solution. It is probable that to obtain accurate values of the corrosion rate controlled stirring is necessary. This would ensure uniform concentration of ions and dissolved oxygen in the bulk of the solution and also control the size of gas bubbles leaving the metal surface; a factor which has been shown by Schnurmann (66) to affect the rate of dissolution. Again, however, any errors due to uncontrolled stirring would tend to be eliminated since comparative rates of attack were required.

THE INFLUENCE OF STRESS

The influence of stress on the corrosion rate of aluminium is shown in the curves which follow. To simplify comparison of results, the curves for each specimen were drawn as shown in Fig. 6 and then traced onto transparent paper, thus the results for several conditions of stress are visible simultaneously.

In order to avoid unnecessary complication, and to eliminate errors due to dissolution of hydrogen, the initial high rates of hydrogen evolution are omitted and steady state values only are shown. It was found that if all values for the rates of attack, as indicated in Fig. 6 (p. 59) were shown for all specimens, it was difficult to distinguish the curves drawn through these points due to the close proximity of the lines. To make comparison as clear as possible, a selection of values are shown for one specimen, the other curves being traced without including the plotted values.

Figs. 11 - 14 show the influence of stress for corrosion in 0.1 N HCl, Figs. 15 - 20 for corrosion in 0.1 N HCl + 5% NaCl and Figs. 21 - 26 for 0.1 N HCl + 3% NaCl.

The corrosion rate is expressed as the volume of hydrogen evolved per hour corrected to a pressure of 760 mm. Hg, since comparative rates are required. The absolute rate of attack may be obtained as gms. of aluminium dissolved per sq. cm. by multiplying the mls. of hydrogen by 0.0021.

NOTE

The different colours represent different specimens. Two curves per specimen were obtained, the corroding solution being renewed after 96 hours and the test carried on for a further 96 hours.

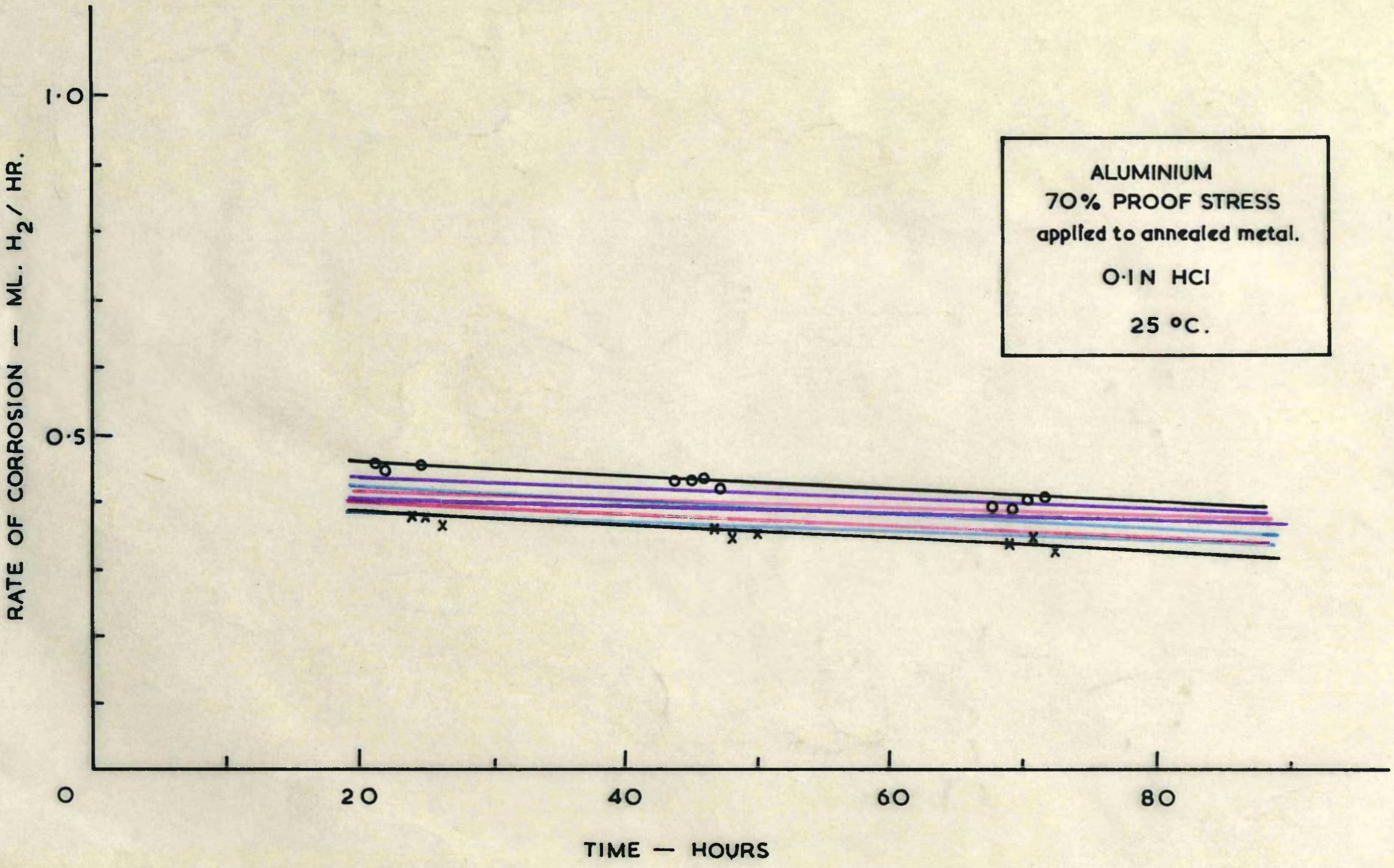

ALUMINIUM
70% PROOF STRESS
applied to annealed metal.
O·IN HCl
25 °C.
RATE OF CORROSION — ML. H_2/ HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS

FIG. 11

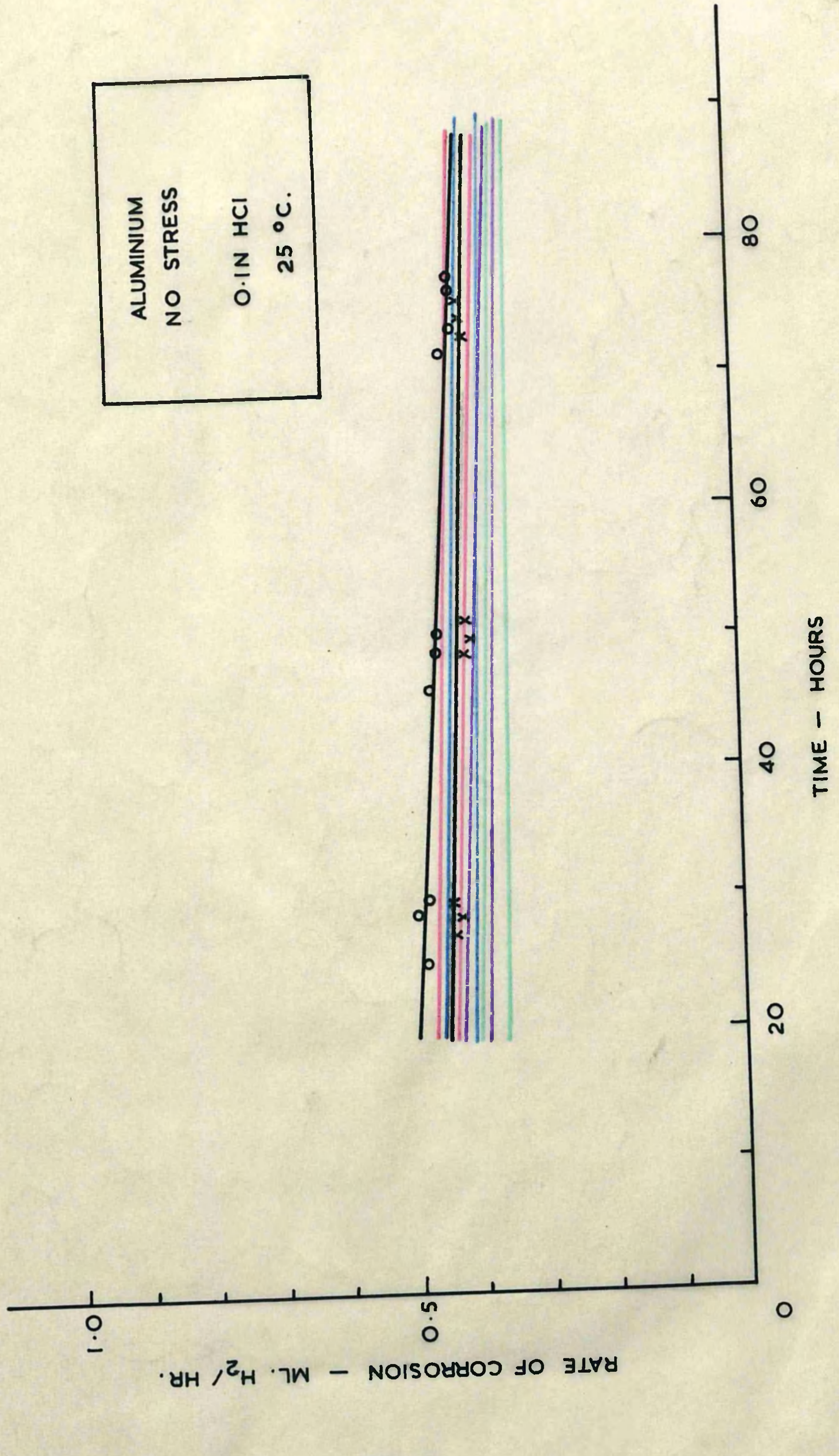

ALUMINIUM
NO STRESS
0·1N HCl
25 °C.
RATE OF CORROSION — ML. H_2/ HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS

FIG. 12

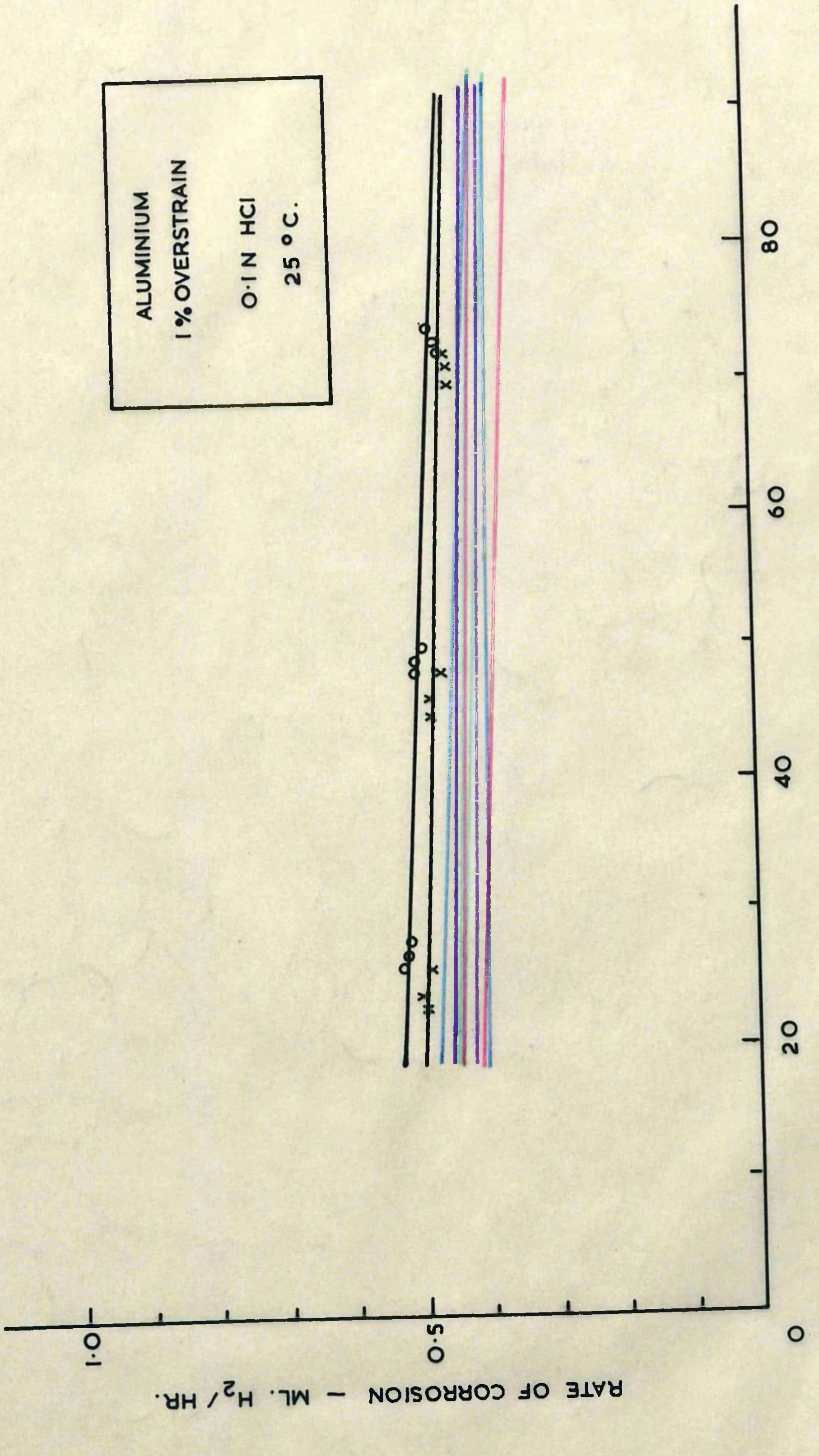

ALUMINIUM
1 % OVERSTRAIN
0·1 N HCl
25 °C.
RATE OF CORROSION — ML. H_2/ HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS

FIG. 13

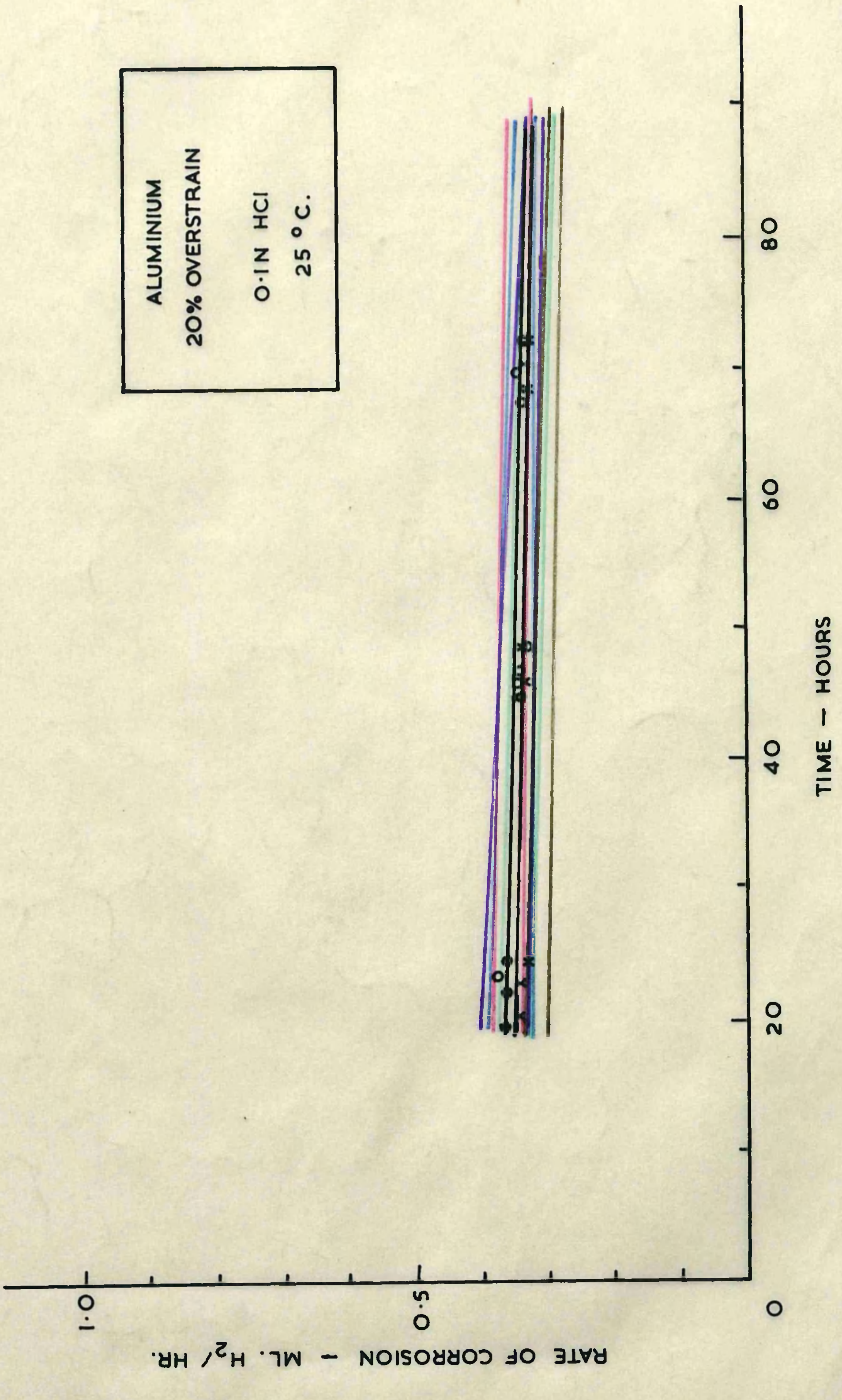

ALUMINIUM
20% OVERSTRAIN
0·1N HCl
25 °C.
RATE OF CORROSION — ML. H_2/ HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS

FIG. 14

Blank between pages 72 & 73

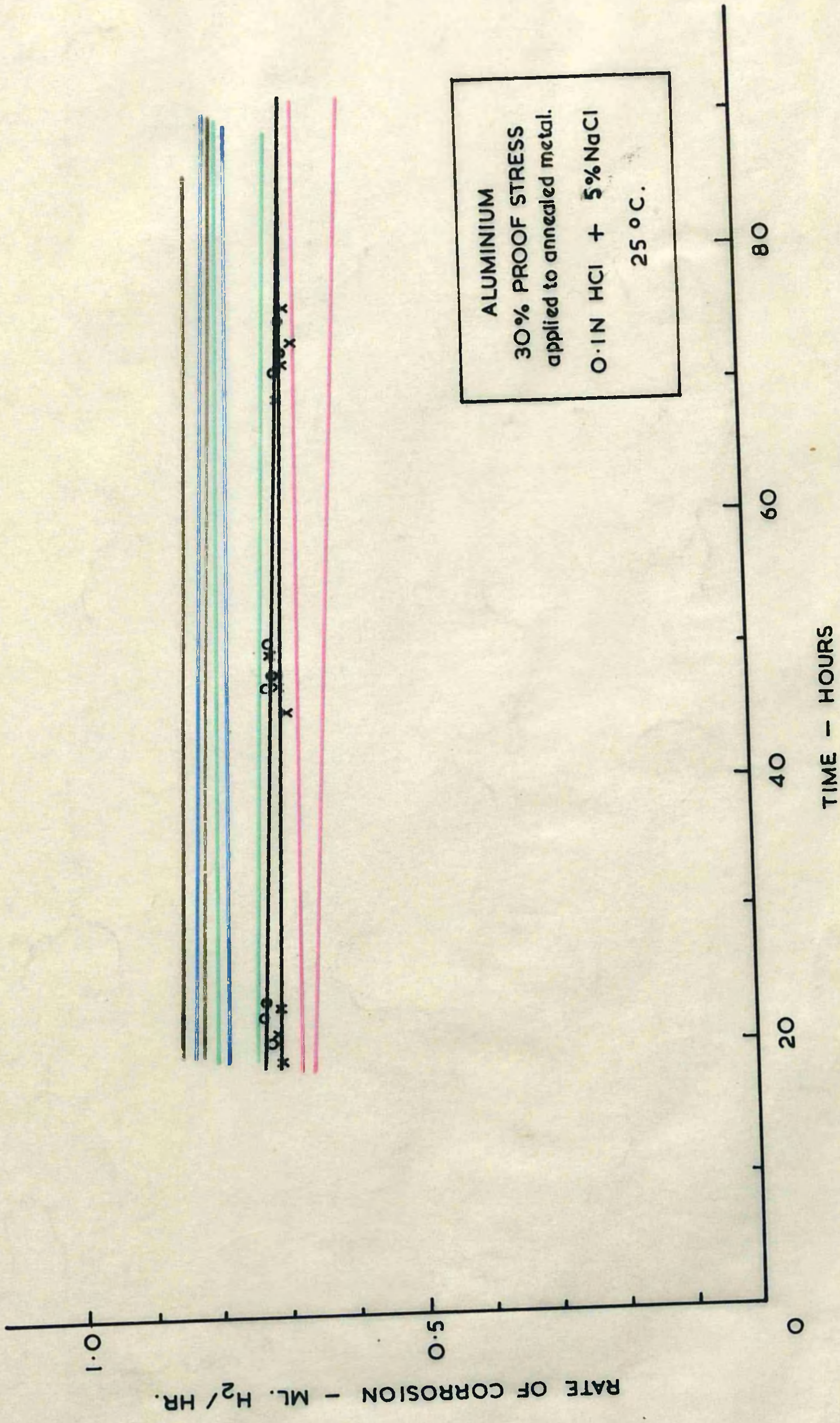

ALUMINIUM
30% PROOF STRESS
applied to annealed metal.
0·1N HCl + 5% NaCl
25 °C.
RATE OF CORROSION – ML. H$_2$/ HR.
1·0
0·5
0
20
40
60
80
TIME – HOURS

FIG. 15

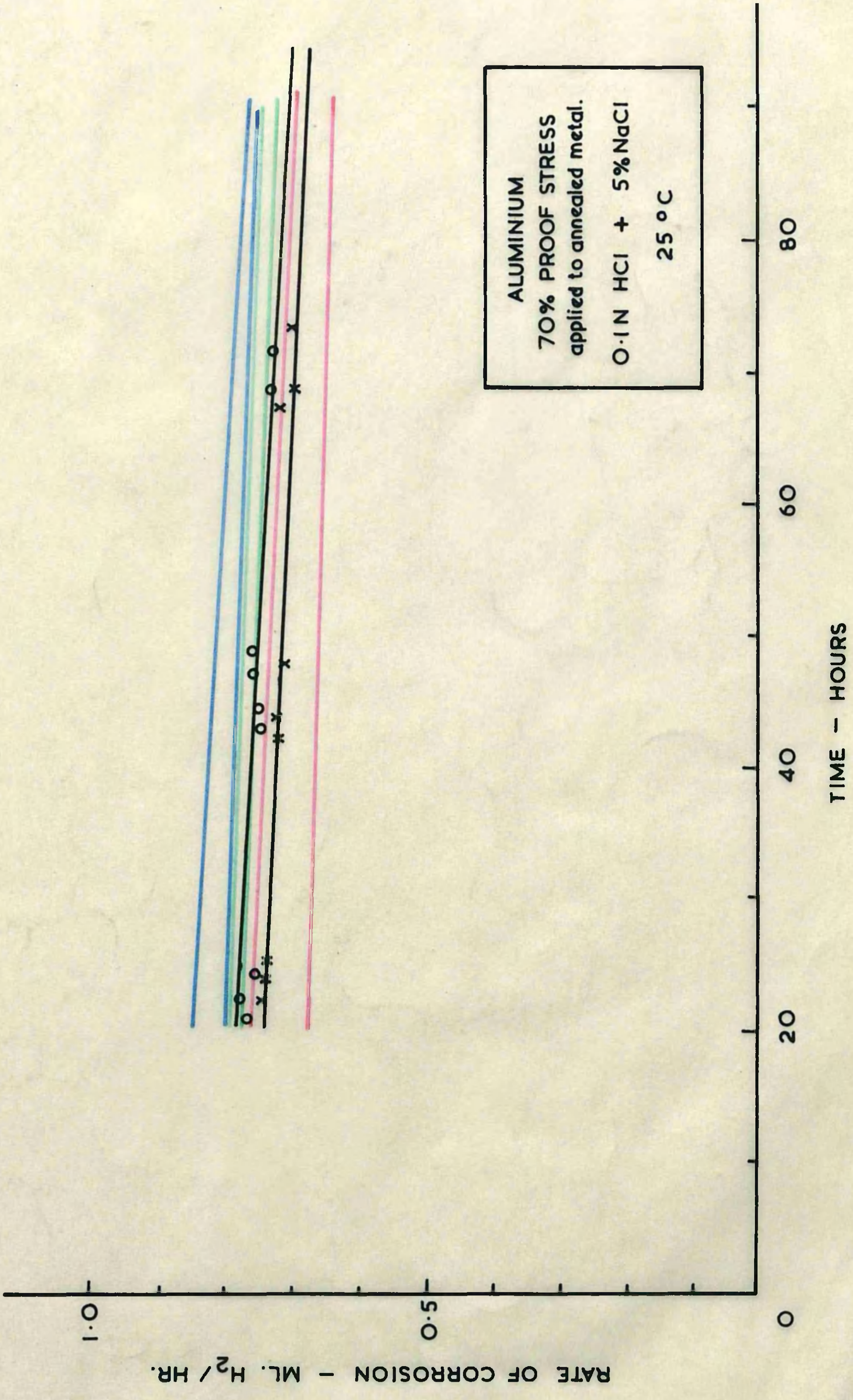

ALUMINIUM
70% PROOF STRESS
applied to annealed metal.
0·1N HCl + 5% NaCl
25 °C
RATE OF CORROSION — ML. H$_2$/ HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS

FIG. 16

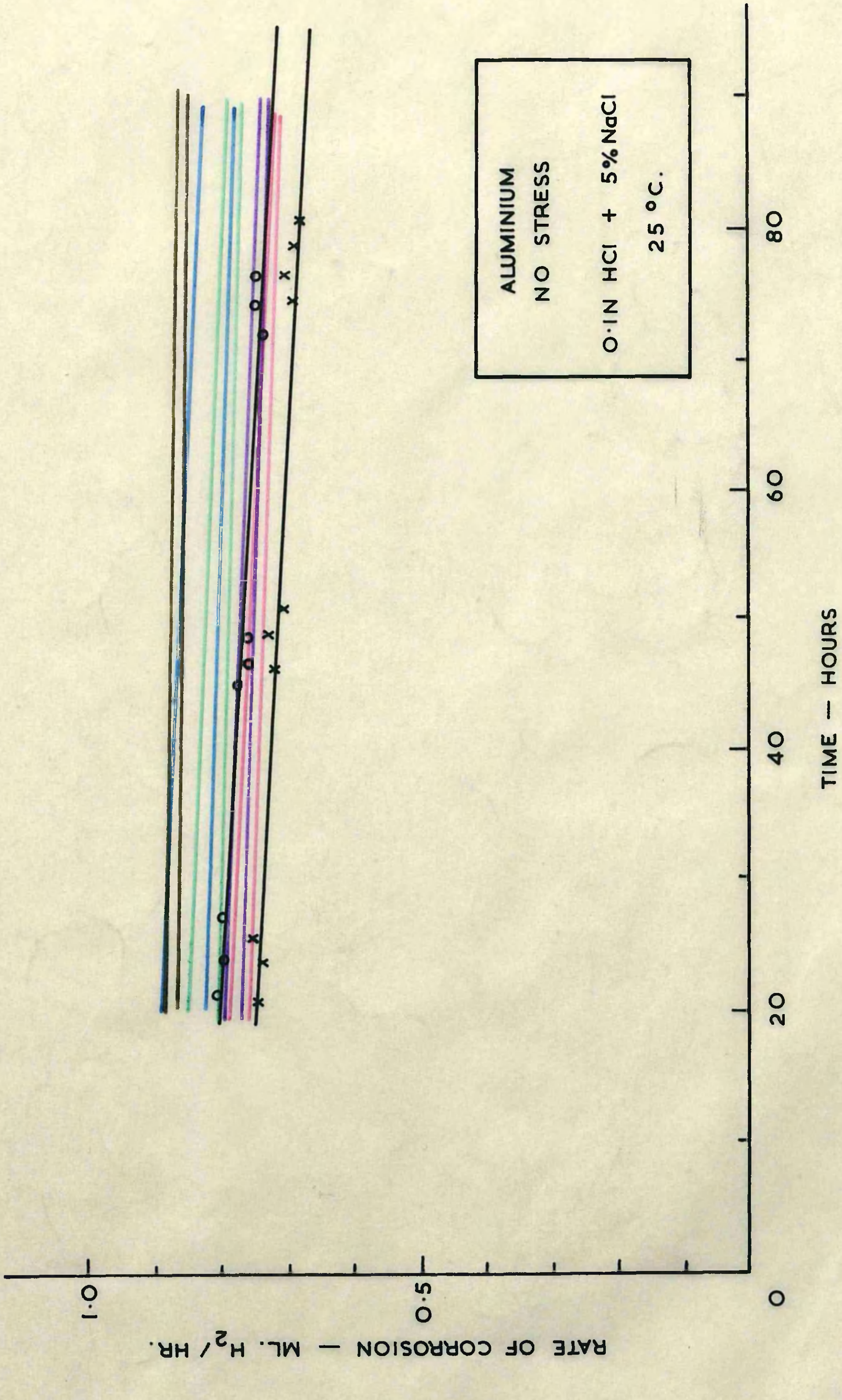

ALUMINIUM
NO STRESS
0·1N HCl + 5% NaCl
25 °C.
RATE OF CORROSION — ML. H_2/ HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS

FIG. 17

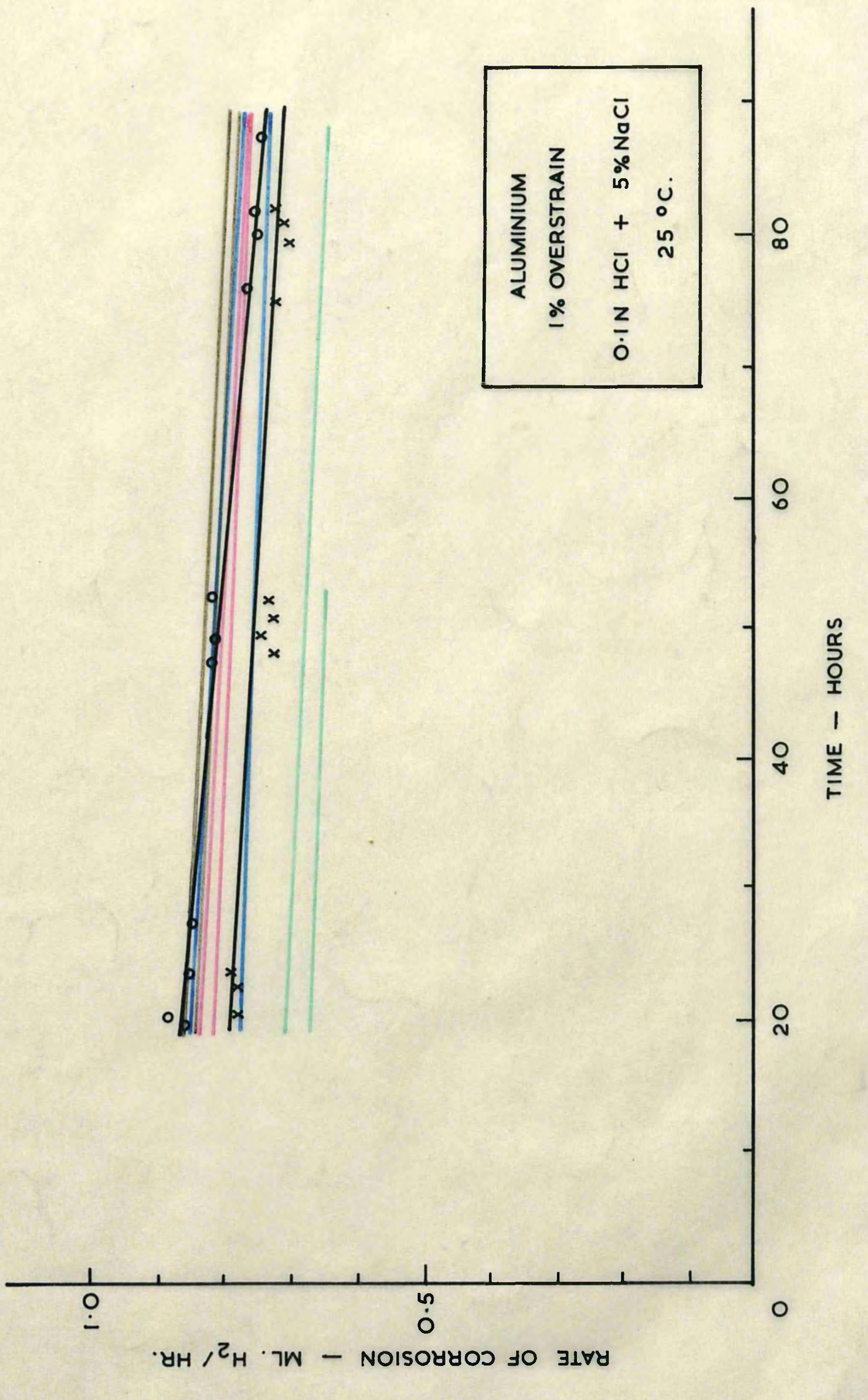

ALUMINIUM
1% OVERSTRAIN
O·1 N HCl + 5% NaCl
25 °C.
TIME — HOURS
0
20
40
60
80
RATE OF CORROSION — ML. H_2/ HR.
1·0
0·5

FIG. 18

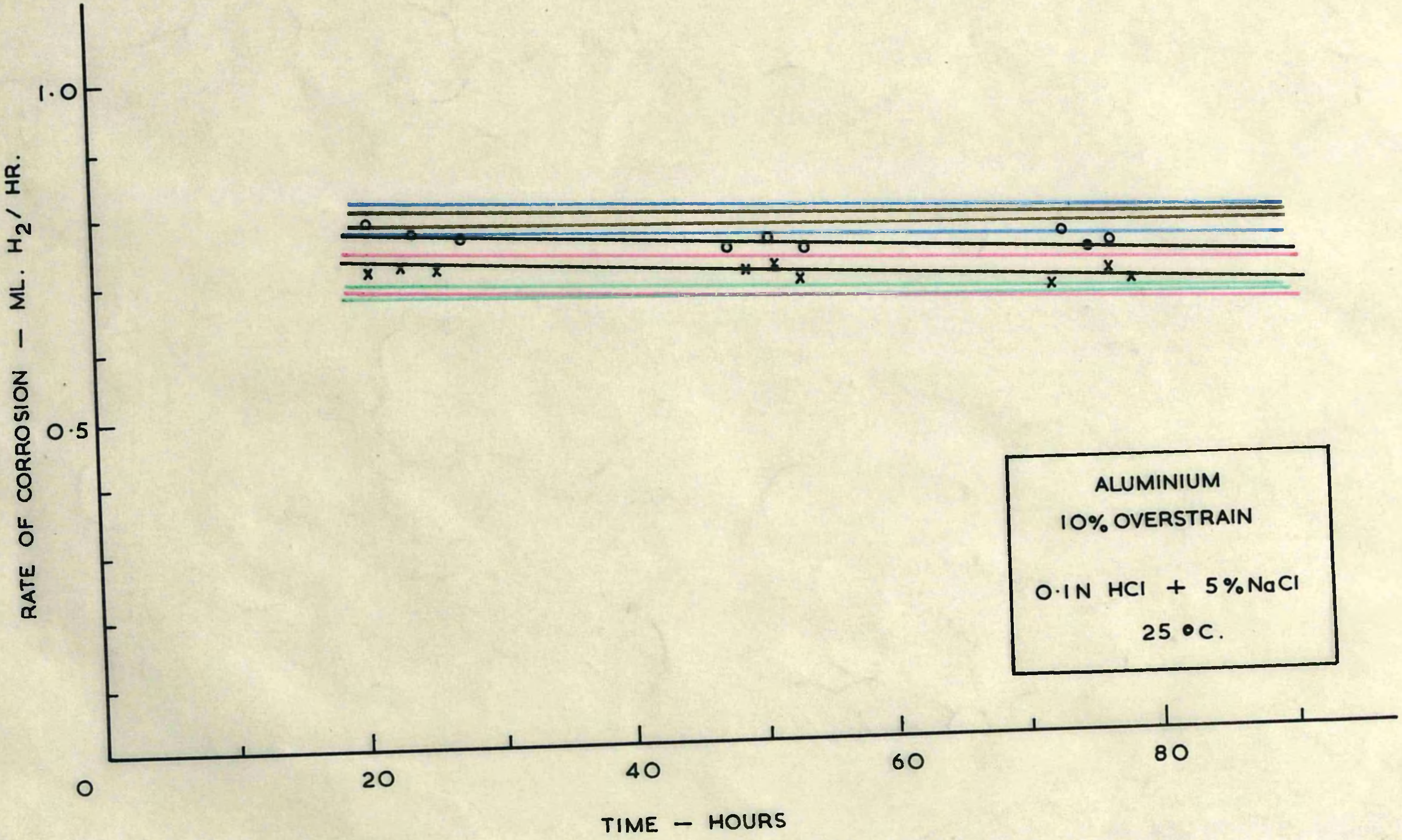

RATE OF CORROSION — ML. H_2/ HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS
ALUMINIUM
10% OVERSTRAIN
0·1N HCl + 5% NaCl
25 °C.

FIG. 19

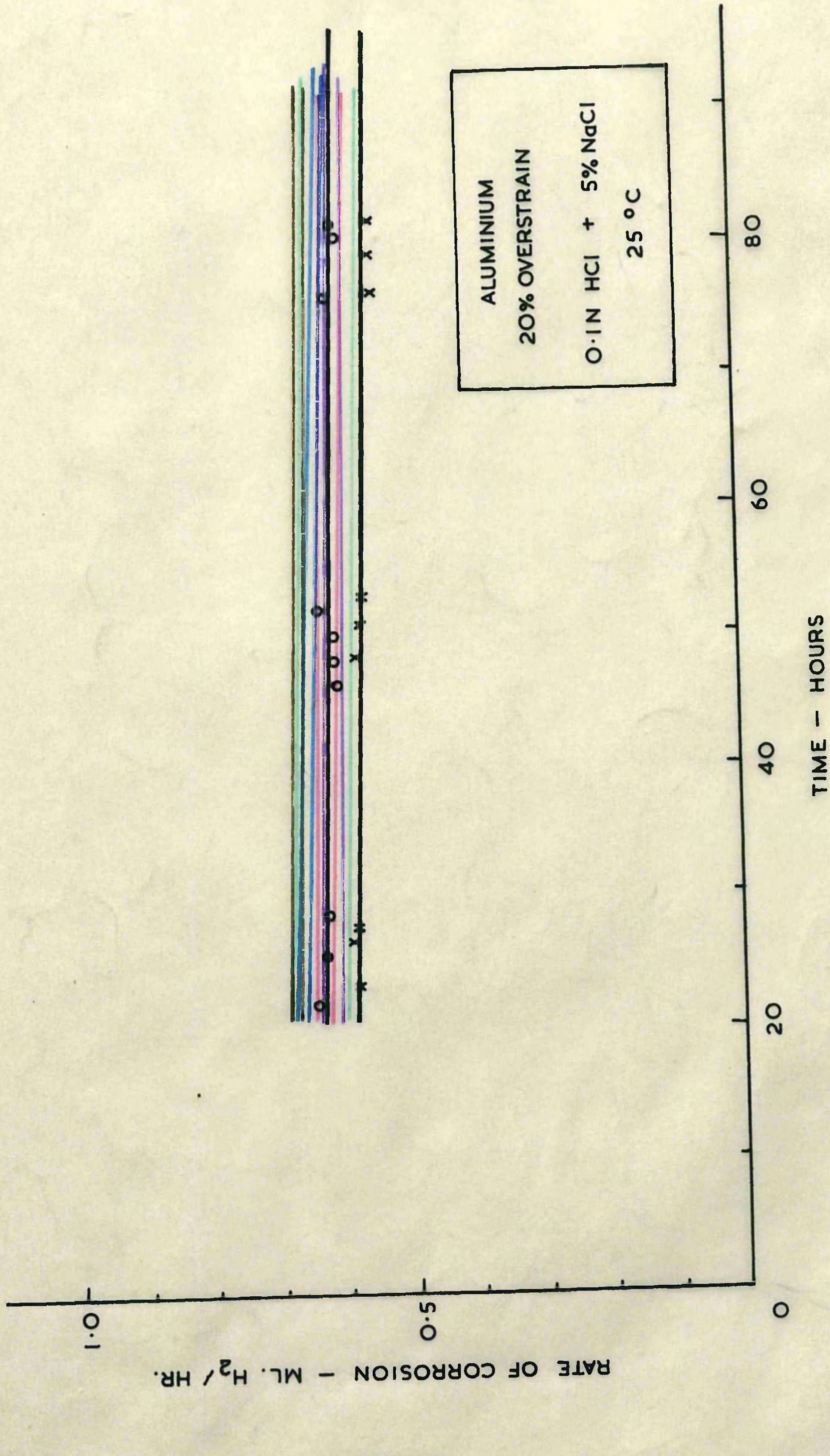

ALUMINIUM
20% OVERSTRAIN
0·1N HCl + 5% NaCl
25 °C
TIME — HOURS
0
20
40
60
80
RATE OF CORROSION — ML. H$_2$/ HR.
1·0
0·5

FIG. 20

Blank between pages 78 & 79

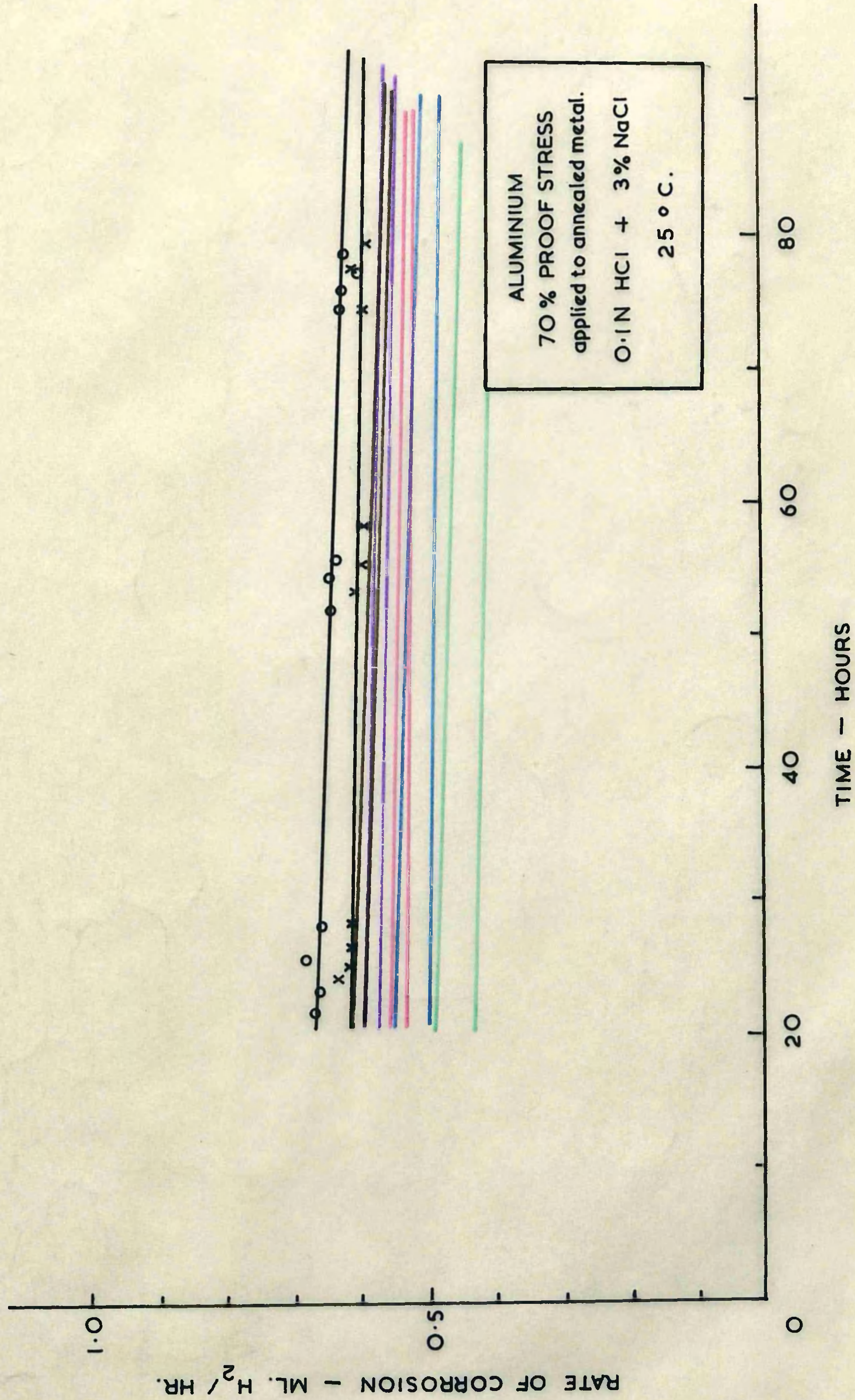

ALUMINIUM
70 % PROOF STRESS
applied to annealed metal.
0·1N HCl + 3% NaCl
25 °C.
TIME — HOURS
0
20
40
60
80
RATE OF CORROSION — ML. H_2/ HR.
1·0
0·5

FIG. 21

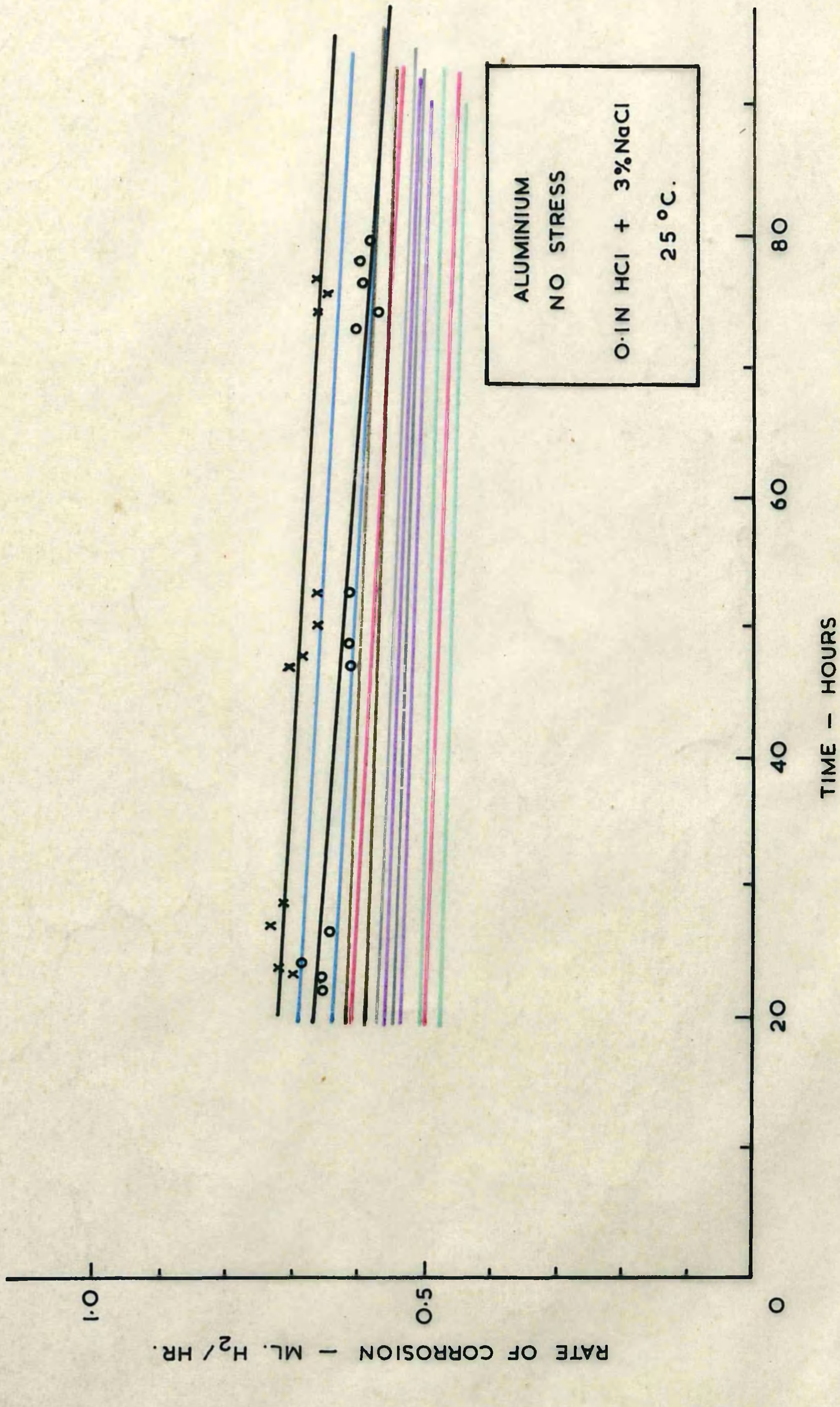

ALUMINIUM
NO STRESS
0·1N HCl + 3% NaCl
25 °C.
TIME — HOURS
0
20
40
60
80
RATE OF CORROSION — ML. H_2/ HR.
1·0
0.5

FIG. 22

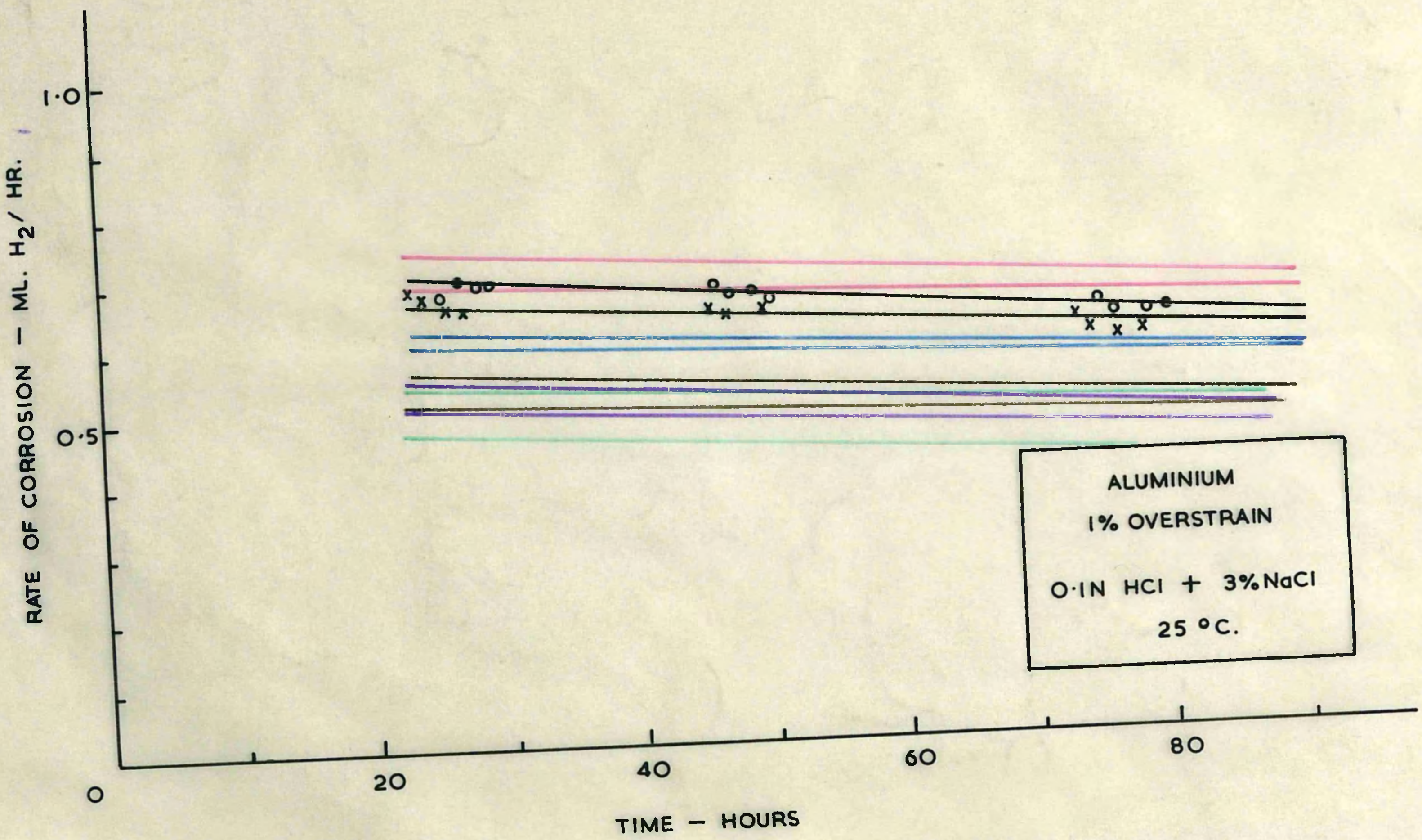

RATE OF CORROSION — ML. H_2/ HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS
ALUMINIUM
1% OVERSTRAIN
0·1N HCl + 3% NaCl
25 °C.

FIG. 23

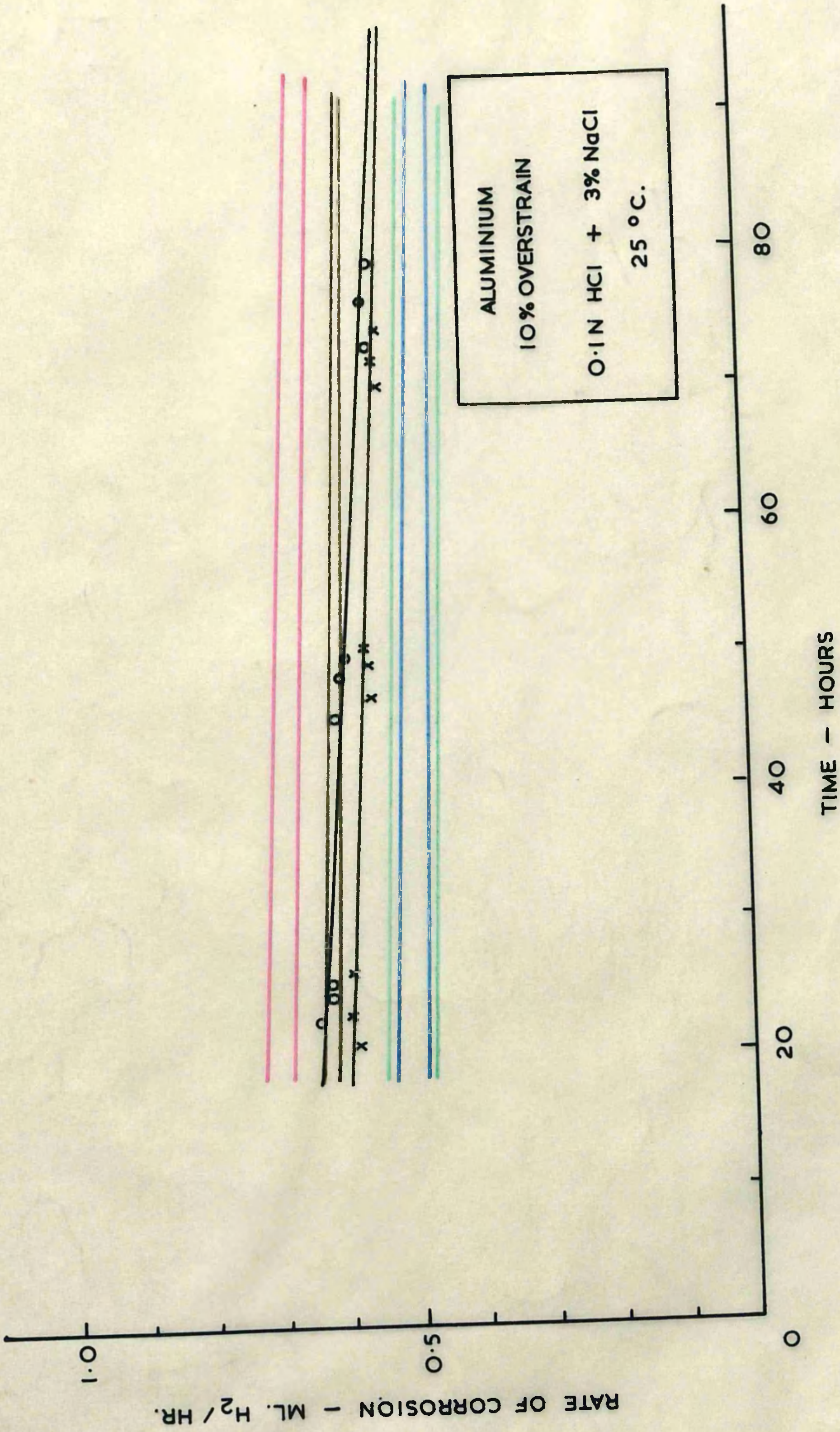

ALUMINIUM
10% OVERSTRAIN
O·1 N HCl + 3% NaCl
25 °C.
TIME – HOURS
0
20
40
60
80
0·5
1·0
RATE OF CORROSION – ML. H$_2$/ HR.

FIG. 24

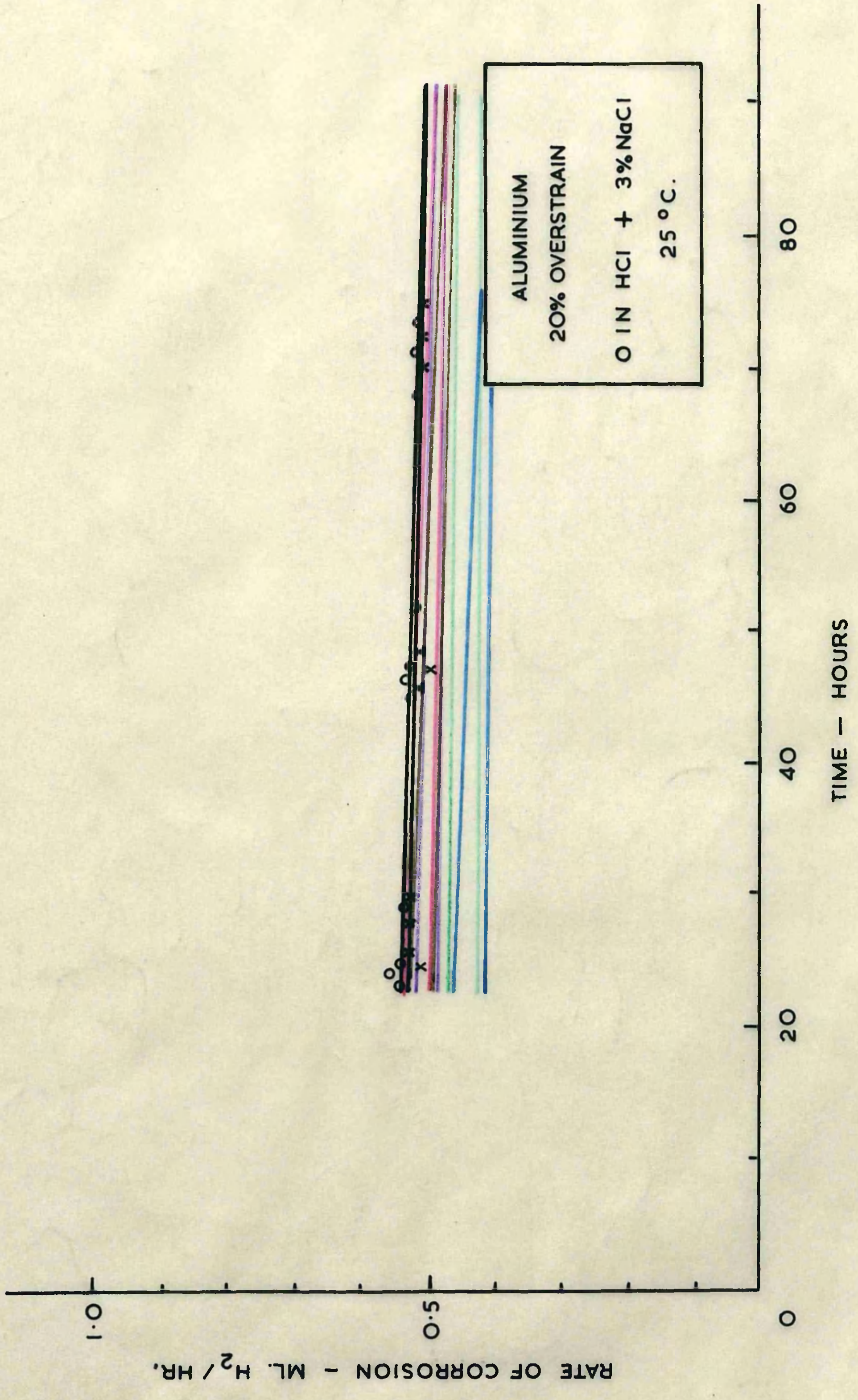

ALUMINIUM
20% OVERSTRAIN
O IN HCl + 3% NaCl
25 °C.
TIME — HOURS
0
20
40
60
80
0·5
1·0
RATE OF CORROSION — ML. H2 / HR.

FIG. 25

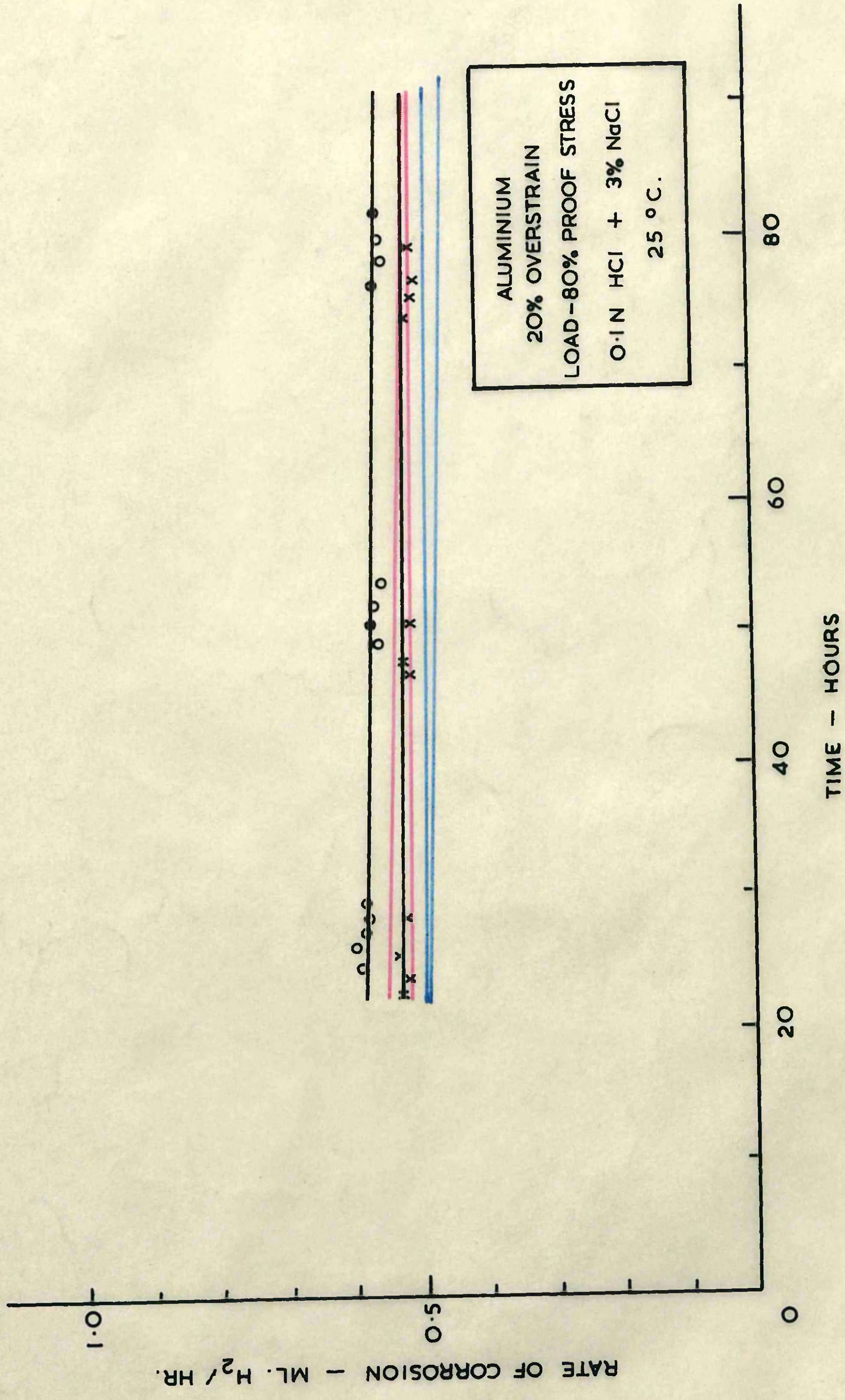

ALUMINIUM
20% OVERSTRAIN
LOAD-80% PROOF STRESS
0·1 N HCl + 3% NaCl
25 °C.
RATE OF CORROSION — ML. H$_2$/ HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS

FIG. 26

Blank between pages 84 & 85

ANNEALED 20% OVERSTRAIN
10% OVERSTRAIN

EFFECT OF OVERSTRAIN ON THE SURFACE OF ALUMINIUM

FIG. 27

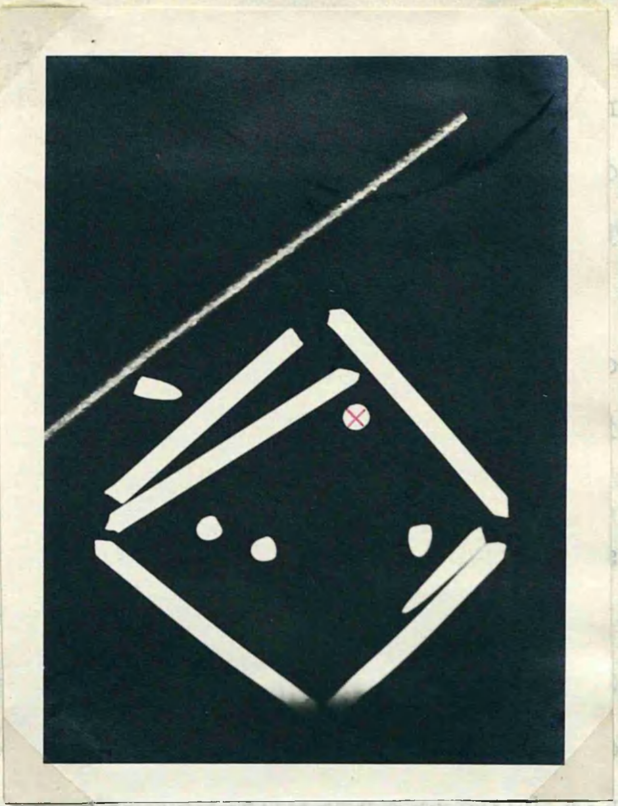
Discussion of Results

It may be concluded that the application of an external stress within the proof stress has no effect on the corrosion of aluminium in the corroding media used. These results are in agreement with those obtained by polarographic analysis and for the influence of stress on the potential of aluminium in these solutions, as described in the following subsection.

Internal stresses set up in the metal by overstraining have no apparent influence on the rate of attack up to 10% overstrain, but the rate of evolution of hydrogen from a length of metal overstrained 20% is less than that from the same length of unstrained metal. However, when a metal is overstrained, the cross-sectional area is reduced but the surface becomes roughened as shown in Fig. 27. It is, therefore difficult to determine accurately the true surface area. The average diameters of the metal measured by a micrometer were:-

Annealed	0.0640 in.
1% overstrain ...	0.0638 in.
10% overstrain ...	0.0605 in.
20% overstrain ...	0.0590 in.

An attempt was made to measure the true surface area of overstrained metal by mounting several



⊗ — Al mounted in plastic and polished to cross-section
Diameter — 0·070 in.

Unmounted wire shown above. Diameter — 0·059 in.

FIG. 28

specimens in plastic and polishing to expose the transverse cross-section. Manual polishing did not give a true cross-section, however, due to the soft nature of the metal the surface flattened into a flange as shown in Fig. 28.

Calculation of the surface area on the assumption that no roughening occurred shows that on a length of 30 ins.:-

Annealed .... 6.03 in^2.
1% overstrain ... 6.01 in^2.
10% overstrain ... 5.70 in^2.
20% overstrain ... 5.56 in^2.

Allowing for this reduction, an observed rate of corrosion of 1 ml. hydrogen per hour equated to equal surface areas gives:-

1% overstrain ... 1.00 ml./hr.
10% overstrain ... 1.06 ml./hr.
20% overstrain ... 1.09 ml./hr.

If these corrections be applied to the curves for the corrosion of overstrained metal, then any variations due to stress will be very small. However, it is probable that roughening of the surface increased the surface area to some degree, but since data are not available, the rates of attack shown in the curves are not corrected, the values being the volume of hydrogen evolved per hour from a length of 30 ins.

The number of specimens tested for any particular condition is too small to permit statistical analysis, but a simple analysis may be made by taking the mean value of the rate of attack after 20 hours and after 80 hours immersion and evaluating the mean of this value for the two curves for each specimen. The results for various conditions of stress may then be compared.

TABLE VI

Example

A. Aluminium. No stress. (Fig. 22)
0.1 N HCl + 3% NaCl.

	ml. H_2/hour					
Specimen	1.	2.	3.	4.	5.	6.
1st. corrd. liqd.						
Rate after 20 hrs.	0.70	0.62	0.61	0.58	0.56	0.51
Rate after 80 hrs.	0.63	0.57	0.54	0.52	0.51	0.48
Mean value	0.67	0.60	0.57	0.55	0.54	0.50
2nd. corrd. liqd.						
Rate after 20 hrs.	0.65	0.59	0.50	0.55	0.54	0.48
Rate after 80 hrs.	0.58	0.54	0.45	0.51	0.50	0.44
Mean value	0.62	0.57	0.48	0.53	0.52	0.46
Mean of 1st. & 2nd.	0.65	0.59	0.53	0.54	0.51	0.48

Continued

B. Aluminium 20% overstrain (Fig. 25)
0.1 N HCl + 3% NaCl.

	ml. H_2/hour.				
Specimen	1.	2.	3.	4,	5.
<u>1st. corrd. liqd.</u>					
Rate after 20 hrs.	0.55	0.54	0.53	0.47	0.46
Rate after 80 hrs.	0.52	0.50	0.51	0.45	0.40
Mean value	0.54	0.52	0.52	0.46	0.43
<u>2nd. corrd. liqd.</u>					
Rate after 20 hrs.	0.54	0.50	0.53	0.43	0.41
Rate after 80 hrs.	0.52	0.47	0.48	0.41	0.39
Mean value	0.51	0.49	0.51	0.42	0.40
Mean of 1st & 2nd.	0.53	0.51	0.52	0.44	0.42

<u>Comparing A & B</u>

$a_1 = 0.65$	$b_1 = 0.53$
$a_2 = 0.59$	$b_2 = 0.51$
$a_3 = 0.53$	$b_3 = 0.52$
$a_4 = 0.54$	$b_4 = 0.44$
$a_5 = 0.51$	$b_5 = 0.42$
$a_6 = 0.48$	
$\Sigma a = 3.30$	$\Sigma b = 2.42$
$\bar{a} = 0.55$	$\bar{b} = 0.48$

Although the value of $\bar{b}$ is 0.07 less than $\bar{a}$, equivalent to a reduction of 13%, the deviation between

a_1 and $\bar{a}$ is 0.10 and the values of b_1 and b_3 are greater than a_5 and a_6 whilst b_2 is greater than a_6. Thus the reduction in the rate of attack caused by overstraining the metal 20% is less than the variation recorded in the corrosion of unstressed metal under identical conditions and several specimens of overstrained metal showed a higher rate of attack than specimens of unstressed metal which show the lowest rate of attack of the specimens tested.

Although a rigid analysis would require many more tests, it was considered that further experimental work on this subject was unnecessary, especially in view of the fact that factors other than stress showed an appreciable influence on the rate of attack.

During experiments in which analysis was carried out by means of the polarograph, it was shown that variation in the temperature had an appreciable effect on the rate of corrosion, Table III, p.47. A rise in temperature from 25°C. to 30°C. resulted in a 44% increase in the corrosion rate, equivalent to an average increase of nearly 9% per degree rise in temperature over this range. A fluctuation of ± ½°C. was possible in the temperature of the corroding solution, hence for a corrosion rate of 1 ml. of hydrogen evolved per hour, the error was ± 0.045 ml.

It has been shown by many investigators that the rate of attack of aluminium in hydrochloric acid is considerably influenced by the composition and purity of the metal. Straumanis (69) states that the presence of 0.01% copper produces appreciable increase in the rate of attack and 0.1% copper increased the rate 1600 fold. 0.1% iron increases the rate 160 fold. Moore and Liddiard (67) have shown that there is an enormous increase in the resistance as the metal approaches 100% purity:-

TABLE VII

% Aluminium	Loss in wt. (g./sq.dm.)	
	3.7% HCl	38% HCl (by wt.)
99.50	10 in 3 hrs.	10 in ½ hr.
99.90	-	3 in 15 hrs.
99.95	-	0.7 in 16 hrs.
99.99	0.044 in 52 hrs.	0.06 in 16 hrs.

Changes in the concentration of acid and of sodium chloride also have a marked influence on the corrosion rate. Clelland and Sly (68) obtained the following results for the variation of the rate of attack of 99.3% aluminium in hydrochloric acid containing various concentrations of sodium chloride:-

TABLE VIII

0.25 N HCl

% NaCl	Corrosion rate (mgms./sq.cm./day)
0	1.17
2	1.76
5	2.16
10	6.77
16	38.3
22.6	153.

It may therefore be concluded that whereas a high degree of overstrain may have a small effect on the rate of corrosion of aluminium in acid solutions, this is not significant when compared with the effect of slight changes in the corroding conditions and of the metal composition.

I. (b) CORROSION OF ALUMINIUM-MAGNESIUM ALLOYS

In Section B, the effect of stress on the structural corrosion of aluminium-magnesium alloys in sodium chloride solutions is described.

This section describes experiments conducted on one of the alloys, NW.7., to determine the effect of stress when corroded under conditions which result in general attack.

The properties of alloy NW.7. were:-

Composition:

Cu ... Nil
Mn ... 0.30%
Fe ... 0.20%
Si ... 0.17%
Mg ... 6.85%
Al ... Remainder.

Mechanical properties:

Annealed. 0.1% proof stress = 11.1 tons/sq.in. Equiv. to direct load 80 lbs.

Ultimate tensile strength = 20.8 tons/sq.in. Equiv. to direct load 149 lbs.

Overstrained 10%, aged 24 hours at 125°C.

0.1% proof stress = 16.0 tons/sq.in. Equiv. to direct load 106 lbs.

Ultimate tensile strength = 22.3 tons/sq.in.Equiv. to direct load 148 lbs.

Details of strain-ageing are given in Section B, p. 152.

Pretreatment of the Alloy Wires

Preliminary experiments were conducted in which the alloy wires were cleaned in the same manner as the aluminium wires, i.e. in 0.2N hydrochloric acid for 24 hours. (Vide P. 54). However, there were considerable variations in the rates of attack on different specimens which was considered to be due to appreciable attack on the alloy during the pretreatment. When no attempt was made to remove the oxide film and the wires were merely degreased in toluene, reasonably reproducible results were obtained. The strain-aged wires were sealed in a tube with argon during the ageing process in order that the oxide film on the strain-aged alloy should not differ from that on the annealed alloy.

The experiments conducted were similar to those carried out on aluminium. Shorter lengths of wire were exposed to the corroding solutions and corrosion tubes of a correspondingly shorter length were used.

Annealed Alloy.	A length of 12 in. (30.5 cm.) was exposed to the corroding solution.
Strain-aged Alloy.	A length of 6 in. (15.2 cm.) was exposed to the corroding solution.

The results are shown in Figs. 29 to 33.

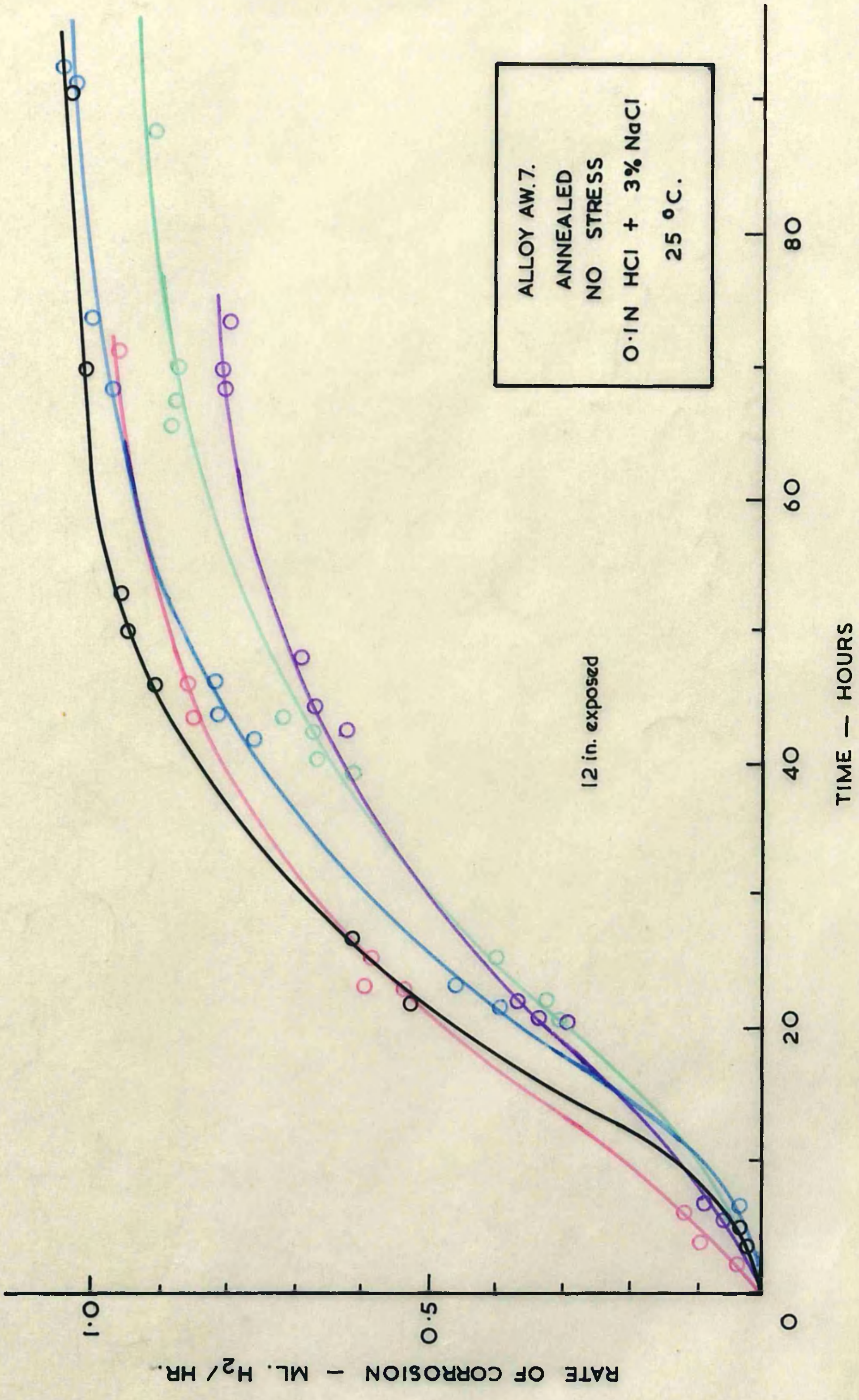

ALLOY AW.7.
ANNEALED
NO STRESS
O·1N HCl + 3% NaCl
25 °C.
12 in. exposed
RATE OF CORROSION — ML. H_2/ HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS

FIG. 29

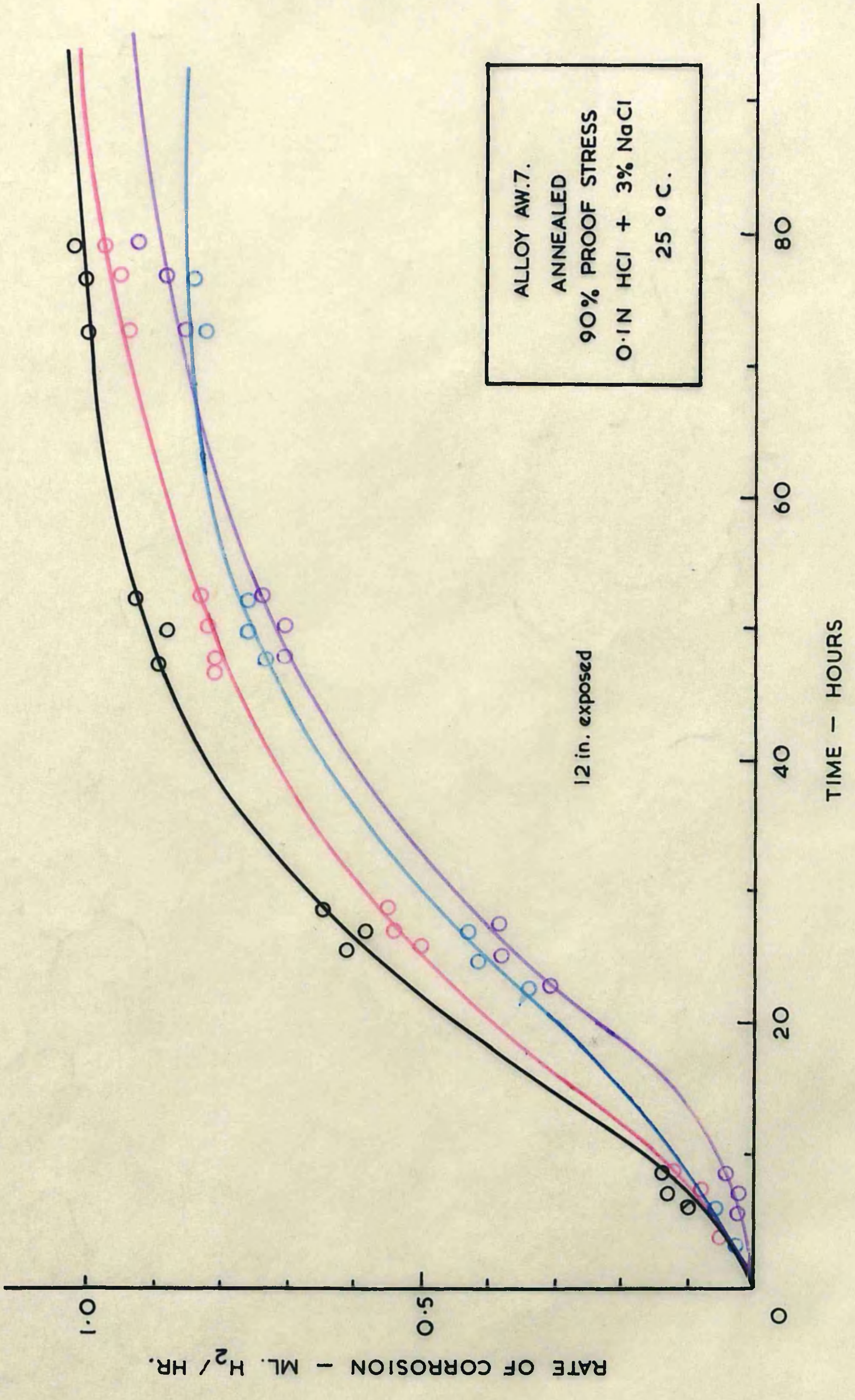

ALLOY AW.7.
ANNEALED
90% PROOF STRESS
0·1N HCl + 3% NaCl
25 °C.
12 in. exposed
RATE OF CORROSION – ML. H_2/ HR.
TIME – HOURS
0
20
40
60
80
0·5
1·0

FIG. 30

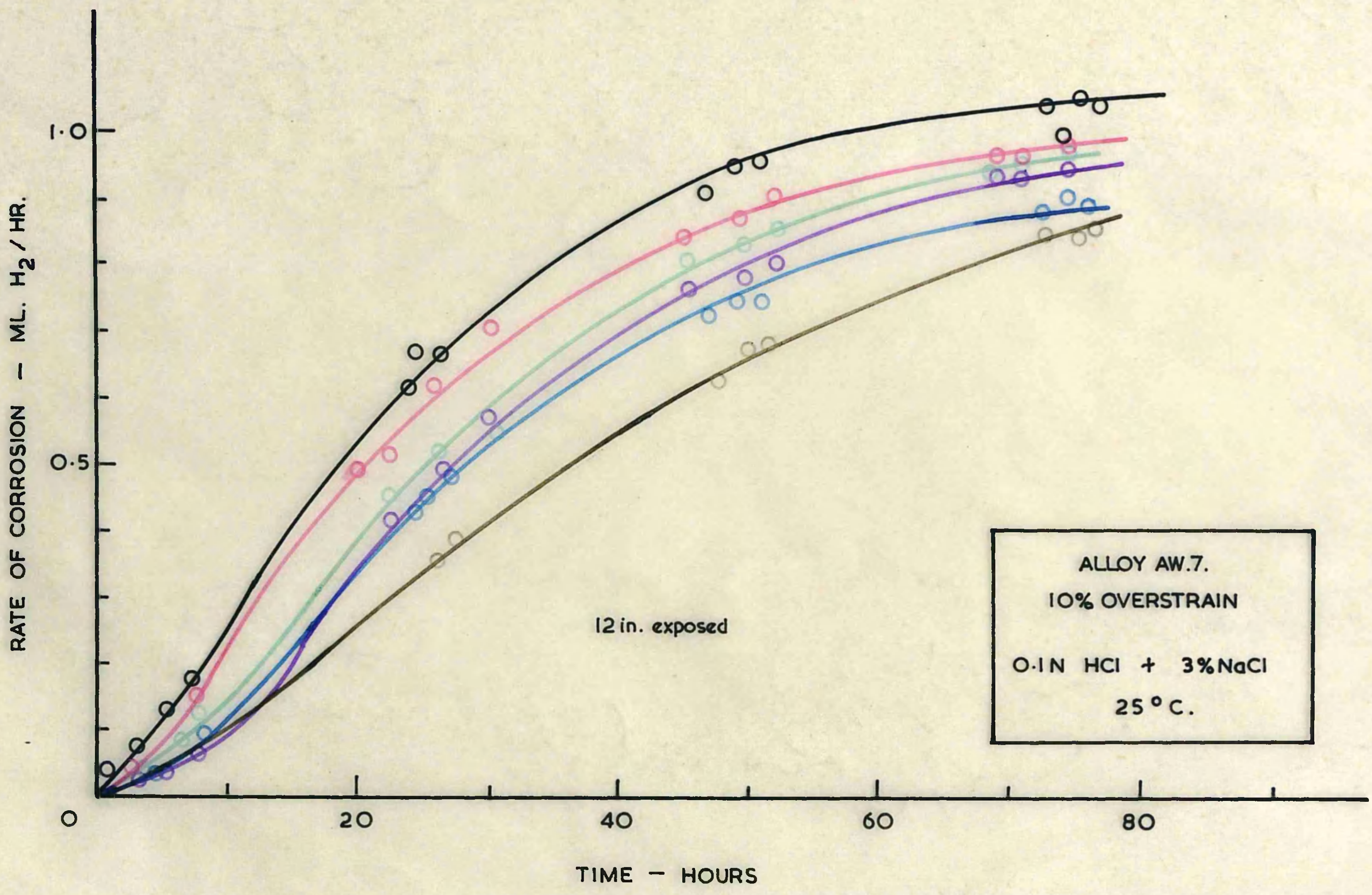

RATE OF CORROSION — ML. H_2 / HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS
12 in. exposed
ALLOY AW.7.
10% OVERSTRAIN
0·1N HCl + 3% NaCl
25 °C.

FIG. 31

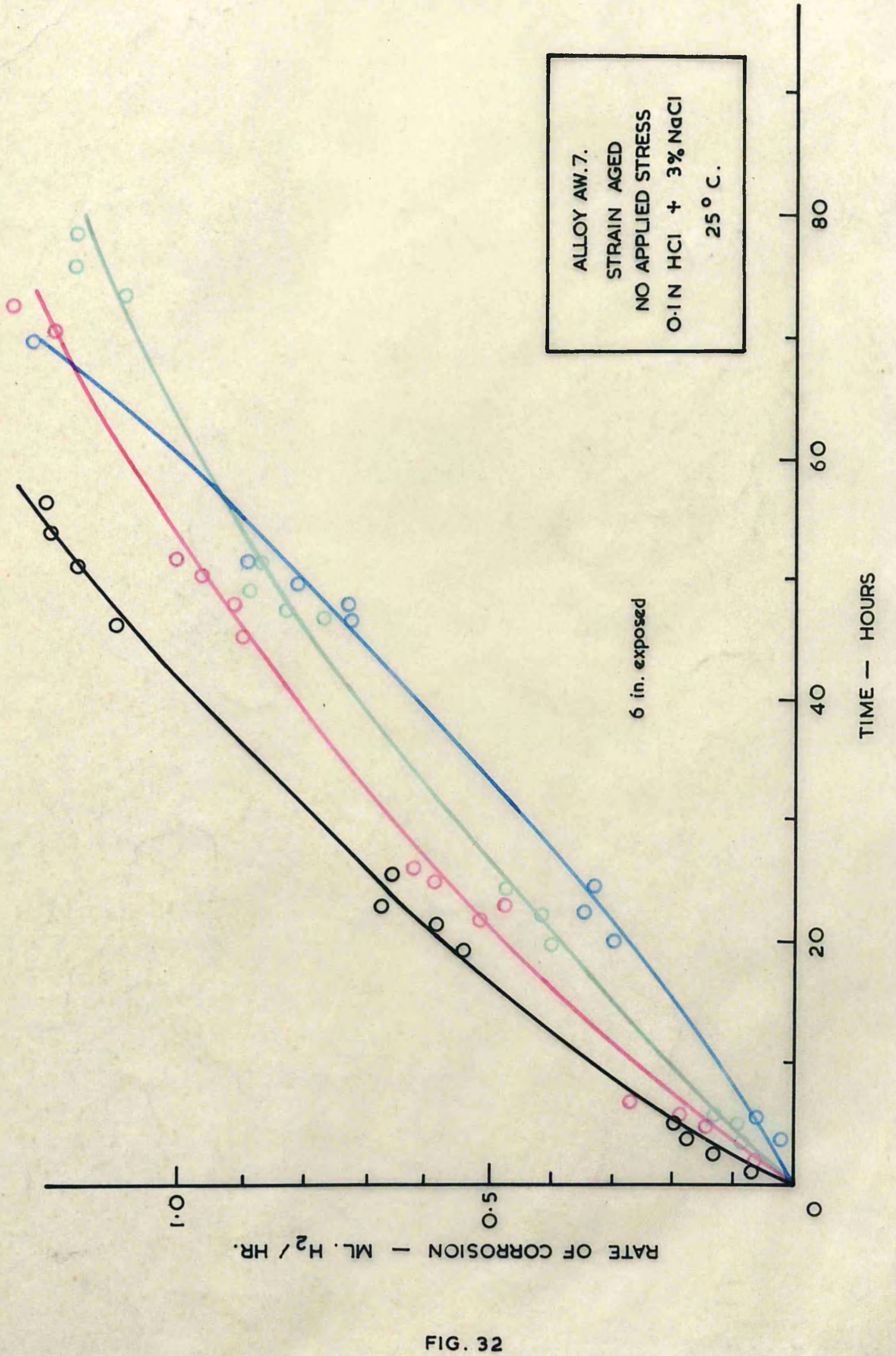

ALLOY AW.7.
STRAIN AGED
NO APPLIED STRESS
0·1 N HCl + 3% NaCl
25 °C.
6 in. exposed
0
20
40
60
80
TIME — HOURS
0·5
1·0
RATE OF CORROSION — ML. H$_2$ / HR.

FIG. 32

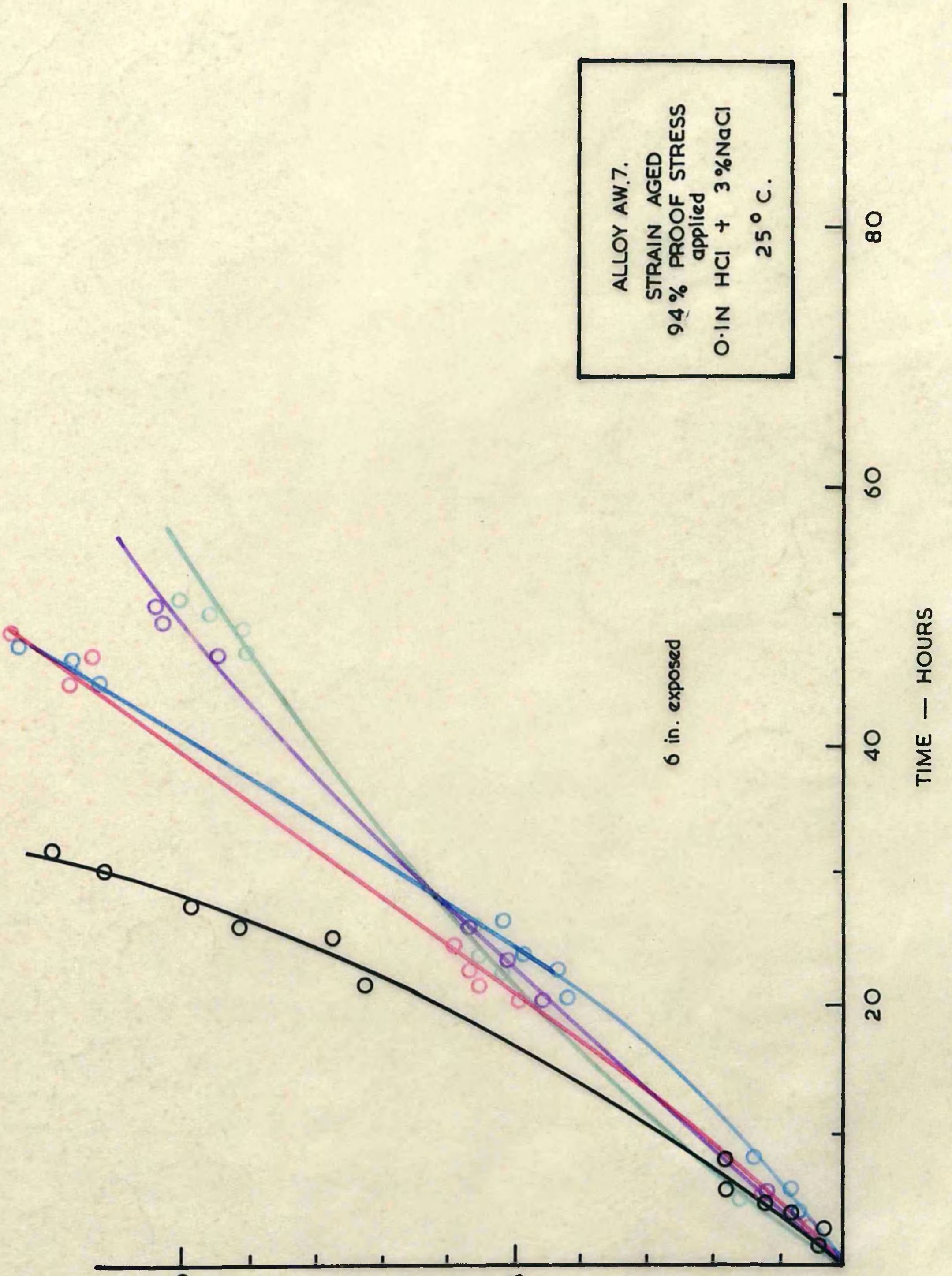

ALLOY AW.7.
STRAIN AGED
94% PROOF STRESS applied
0·1N HCl + 3%NaCl
25 °C.
6 in. exposed
RATE OF CORROSION — ML. H₂/HR.
1·0
0·5
0
20
40
60
80
TIME — HOURS

FIG. 33

Blank between pages 98 & 99

Discussion of Results

The rate of attack of annealed alloy NW.7. by saline hydrochloric acid was considerably greater than that of aluminium. The gradual increase in the rate of attack with time, followed by a subsequent falling off in the increase made comparison of results more difficult than in the case of aluminium.

The increase in the rate of attack was probably due to several reasons. Firstly, during an induction period, in which the oxide skin on the alloy surface was being dissolved, the attack gradually increased as this barrier to corrosion became less effective. Secondly, the surface area of the metal increased as the metal was dissolved, an effect which would not be so marked in the case of aluminium due to the smaller rate of attack. Thirdly, increase in the surface area due to corrosion increased the area of the β-phase uniformly distributed throughout the aluminium-magnesium solid solution, and of impurities with low hydrogen overpotential, which was exposed to the corroding solution. Fourthly, dissolution of hydrogen in the early stages of the attack.

The true rate of attack was difficult to ascertain since the pH of the solution increased as the hydrogen ions were displaced and the rate of attack decreased as the concentration of metal ions in solution increased. However, tests on the alloy in the same metallographic condition were conducted under identical conditions and comparison of results is therefore legitimate.

Examination of the curves for the rate of attack is sufficient to conclude that stress has little effect on the general corrosion of alloy NW.7 in the annealed state or when overstrained. As in the case of aluminium, secondary factors such as temperature and composition have a considerable influence on the rate of attack.

Strain-ageing, resulting in precipitation of the β -component at the grain boundaries, renders the alloy much more susceptible to corrosion in the absence of applied stress than the annealed alloy. This is to be expected since the corrosion is electrochemical in nature and the presence of a phase at the grain boundaries which differs in solution potential from the matrix solid solution results in intercrystalline corrosion. A further possibility is that overstraining, prior to ageing, ruptured the oxide film on the surface of the alloy

However, 10% overstrain had little effect on the corrosion rate of the annealed alloy (Fig. 31, p.96), thus it may be assumed that any effect due to film rupture was small compared with that due to the metallographic changes caused by strain-ageing. Application of stress appears to result in an increase in the rate of attack, but due to the degree of variation in the results and since greater variations in the rates of attack than those caused by stress were obtained when various methods of precleaning the metal were investigated, it was difficult to draw definite conclusions. However, increase in the rate of attack may be explained as being due to stress opening up the grain boundaries and exposing a larger area of the anodic phase to the corroding solution. This would be emphasised after some penetration along the grain boundaries had occurred since stress would tend to open out the narrow cracks formed by corrosion.

A.II. MEASUREMENT OF POTENTIAL IN ACID SOLUTIONS

GENERAL

The object of the experiments on potential measurements was to determine the effect of stress on the potential between a corroding metal and the solution in which it was immersed.

In acid solutions, no inhibitive film is formed on the metal and a steady potential should be attained in a short time. In neutral salt solutions containing dissolved oxygen, an oxide film is formed on the metal and the potential values are governed by repair or breakdown of the film.

The major difficulties in the study of potential under a given set of conditions are that no two specimens of a metal are exactly alike and even for a single specimen the potential drifts with time. Comparative measurements on different specimens may therefore be misleading. These difficulties were overcome by Evans and Simnad (29) by alternately stressing and unstressing iron wire in a fatigue testing machine and measuring the potential of stressed and unstressed metal at comparable instants.

Measurements on a single specimen are not possible on a metal which has been permanently deformed and the only apparent method of determining the effect of stress in the plastic range is by obtaining values for a large number of specimens.

EXPERIMENTAL

Measurement of Potential

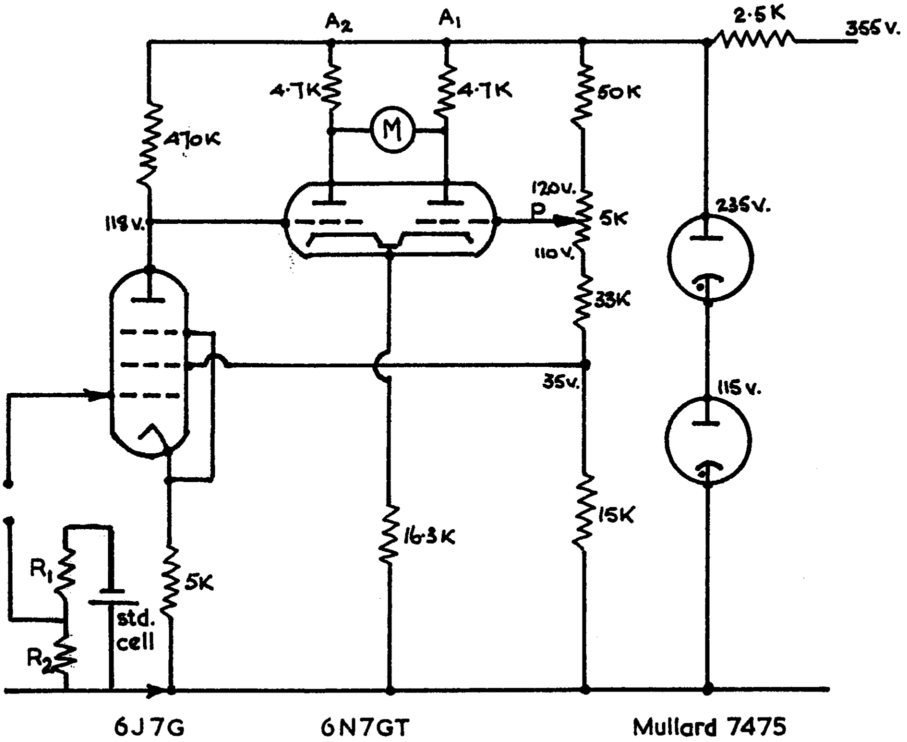
The potential of the metal in corroding solution was determined by measuring the E.M.F. of the corrosion cell coupled with a saturated calomel electrode by means of a valve voltmeter.

The Valve Voltmeter

In order to measure very small changes in potential and to indicate these changes on a scale rather than by adjusting resistances to bring galvanometer deflections to zero, a valve voltmeter was constructed.

An attempt was made to obtain a suitable circuit using a single pentode valve, but the sensitivity obtained was too small. A satisfactory circuit was eventually obtained by using a cathode follower, as shown in Fig. 34.

Facing P. 104



I_a	≑	·25 mA.	I_{a2}	3·3 mA.	I_{a1}	3·3 mA.
R_a		470K.	R_a	4·7K	R_a	4·7K.
E_a	≑	118 V.	E_{a2}	214 V.	E_{a1}	214 V.
R_K	≑	5K	R_K	16·3K.		
V_G	≑	−1·25V.	V_K	107 V.		

VALVE VOLTMETER CIRCUIT

FIG. 34

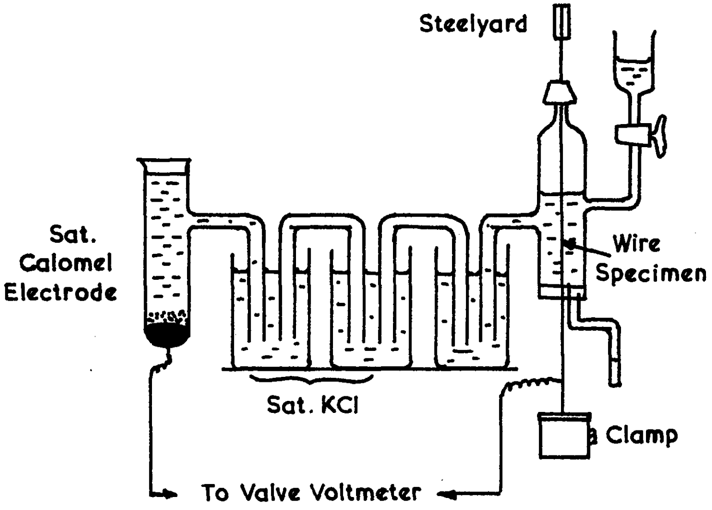
By adjustment of the stepped resistances R_1 and R_2, the reading on the scale (a millivoltmeter) could be set to any required value, small adjustments of this reading could be made by means of the potentiometer P_1. Changes in potential could then be observed directly from the meter, the values being converted into millivolts by means of a calibration curve.

Values of one-hundredth of a millivolt could be obtained at full sensitivity of the instrument, but fluctuations due to temperature changes and vibration did not warrant such sensitivity. By shunting the meter, a somewhat lower sensitivity was obtained which enabled values of one-tenth of a millivolt to be recorded.

Experimental

The metal under examination, in the form of wire, was contained in a glass vessel as shown in Fig. 35. The top end of the wire was attached to a steelyard, by means of which a tensile stress could be applied to the metal, the lower end was held in a clamp.

For measurements in acid solution, the metal was degreased in toluene vapour, polished by rubbing with a suspension of finely powdered calcium carbonate in toluene and washed in toluene to remove



APPARATUS FOR MEASURING THE POTENTIAL OF WIRE CORRODING UNDER STRESS

FIG. 35

the last traces of calcium carbonate. The metal was completely protected, excepting for a band 1 mm. wide by means of polymethacrylic resin. After addition of the corroding solution, a few minutes were allowed to permit a steady potential to be attained. The influence of stresses within the elastic limit was then determined by noting the potential when the metal was stress free, stressed and with stress removed.

Measurements were conducted on permanently deformed metal by simultaneously immersing specimens of unstressed metal and of overstrained metal in the corroding solution and the potentials measured against a calomel electrode and against themselves.

ALUMINIUM

Corroding solution : 0.1 N HCl + 3% NaCl.

Stresses within the elastic limit.

The potential of aluminium in acid solution oscillated considerably for periods ranging from one hour to several days. It was not possible to obtain accurate values since application of stress to a metal showing a steady potential caused the potential to oscillate through a range of 20-30 millivolts. Average values were recorded, however, but as may be seen a definite conclusion cannot be drawn, although it appears that the effect of stress is negligible.

TABLE IX

Potentials in millivolts on saturated calomel scale.

Time after addn. of acid. (mins.)	Stress free	Stressed (70% P.S.)	Stress free
5	-756	-756	-753
8	751	753	755
11	751	750	754
15	751	748	748
60	751	751	751
120	751	751	755
180	750	744	742
185	750	749	747
5	-767	-766	-766
15	765	765	765
120	760	761	761
240	767	767	766
1 day	767	766	762
5	-761	not readable	
20	758	758	755
60	756	755	not readable
3 days	748	748	749

Similar results were obtained for all other specimens of aluminium tested.

Stresses beyond the Elastic Limit

When a metal is overstrained, comparison of the potential for stressed and unstressed metal can be made only by comparing the values for a large number of specimens. The average potentials of 15 specimens of aluminium overstrained 1% and 10% and 20 specimens overstrained 20% were obtained and compared with the average value for the potential of unstressed metal, measurements being made under comparable conditions.

TABLE X

Corroding solution : 0.1 N HCl + 3% NaCl.

Potentials in millivolts on saturated calomel scale

UNSTRESSED

Specimen No.	Time of immersion (hours)		
	1	2	24
1	-751	-754	-755
2	760	760	759
3	756	755	757
4	761	763	760
5	755	756	756
6	751	753	752
7	751	750	753
8	759	756	755

Continued

Specimen No.	Time of immersion (hours)		
	1	2	24
9	-763	-761	-762
10	765	770	768
11	757	756	757
12	754	751	750
13	760	758	762
14	758	759	757
15	763	755	756
AVERAGE	-757.6	-757.1	-757.3

1% OVERSTRAIN

Specimen No.	Time of immersion (hours)		
	1	2	24
1	-759	-763	-762
2	763	763	764
3	756	755	755
4	751	751	750
5	748	755	754
6	755	754	755
7	759	760	760
8	763	761	760
9	761	759	756
10	768	760	755
11	753	754	754
12	752	753	752
13	759	758	759
14	758	755	754
15	759	760	755
AVERAGE	-757.6	-758.1	-756.3

10% OVERSTRAIN

Specimen No.	Time of immersion (hours)		
	1	2	24
1	-752	-756	-755
2	753	750	750
3	755	763	765
4	757	756	756

Continued

Specimen No.	Time of immersion (hours)		
	1	2	24
5	-761	-763	-765
6	758	758	759
7	753	750	751
8	763	764	762
9	759	748	748
10	755	757	755
11	761	760	760
12	763	764	762
13	751	751	751
14	749	753	755
15	752	751	753
AVERAGE	-756.1	-756.3	-756.5

20% OVERSTRAIN

Specimen No.	Time of immersion (hours)		
	1	2	24
1	-759	-757	-756
2	761	760	759
3	754	751	753
4	758	753	755
5	763	763	761
6	760	759	758
7	751	754	753
8	752	754	755
9	758	758	757
10	750	755	755
11	763	759	760
12	761	761	759
13	758	755	756
14	760	758	757
15	760	760	761
16	753	755	756
17	765	760	761
18	769	762	763
19	759	761	762
20	758	755	754
AVERAGE	-758.6	-757.5	-757.6

E.M.F. of cell between specimens.

The E.M.F. values of the cell between different specimens of stress-free metal and between stress-free and overstrained metal are tabulated below. Where oscillation of the potential made it impossible to make a reasonable estimation of the average value, a range of readings is given.

TABLE XI

Measurement after 60 minutes immersion

Unstressed metal

Cell between specimens No.	E.M.F. (millivolts)
1 & 2	-3
1 & 3	+1
1 & 4	0
1 & 5	+6 → -6
1 & 6	-6
1 & 7	+8
1 & 8	-12
1 & 9	+5
1 & 10	-4

Stressed specimens overstrained 10%

Cell between unstressed specimen No. & stressed specimen No.	E.M.F. (millivolts)
1 & 1	+10 → -10
1 & 2	+3
1 & 3	-5

Continued

Cell between unstressed specimen No. & stressed specimen No.	E.M.F. (millivolts)
1 & 4	+3
1 & 5	+3 → -8
1 & 6	0
1 & 7	+2
1 & 8	+10 → -18
1 & 9	-5
1 & 10	+12

Discussion

The oscillating values in the case of elastic stress applied to annealed metal makes it difficult to draw definite conclusions. However, when these results are considered in conjunction with those obtained by measurement of the corrosion rate, it may be stated that elastic stress has a negligible effect, as gauged by these methods on the corrosion of aluminium in acid solutions.

The average values of the potentials of overstrained metal compared with unstressed metal gave the following results:

	Time of immersion (hours)		
	1	2	24
Unstressed	-757.6	-757.1	-757.3
1% overstrain	757.6	758.1	756.3
10% overstrain	756.1	756.3	756.5
20% overstrain	758.6	757.5	757.6

After 1 hour immersion metal overstrained 10% showed a deviation of 1.5 mv. in the cathodic direction, whilst metal overstrained 20% showed a deviation of 1.0 mv. in the anodic direction compared with unstressed metal. After 24 hours immersion metal overstrained 10% showed a deviation of 0.8 mv. in the cathodic direction and metal overstrained 20% a deviation of 0.3 mv. in the anodic direction. These values are very small and comparison with the mean of the deviations of the results obtained for each condition of stress shows:

	Time of immersion (hours)		
	1	2	24
Unstressed	3.83	3.75	3.29
1% overstrain	4.08	3.21	3.10
10% overstrain	3.81	4.68	4.57
20% overstrain	3.52	3.43	2.61

Thus it may be concluded that the effect of stress in the plastic region is less than the variation in the potentials of specimens treated in a manner as nearly identical as possible.

The results for the potential between different samples of unstressed metal and between unstressed and overstrained metal emphasise these conclusions.

ALUMINIUM-MAGNESIUM ALLOY NW.7.

Corroding solution : 0.1 N HCl + 3% NaCl.

Stresses within the yield stress

The potential of the alloy in acid solution became steady in a short time, although this value drifted with prolonged periods of immersion.

Annealed metal

A steady potential was attained within 10 minutes after which the metal was stressed and the stress removed for various values of the stress.

In all cases stresses below 85% of the proof stress showed no effect on the potential. Stresses of greater magnitude showed a maximum deflection of 0.2 mv. in the anodic direction when stress was applied. On removing the stress the potential returned to the original value over periods varying from a few seconds to several minutes.

Strain-aged metal

Samples of the alloy overstrained 10% and aged for 24 hours at 125° C. were tested. Stresses in the region of the proof stress rendered the potential more anodic by a maximum value of 0.6 mv.

and in no case less than 0.2 mv. (20 samples tested). After application of stress the potential tended to drift a few millivolts but subsequent removal of the stress resulted in a sudden change of between 0.2 and 0.5 mv. in the cathodic direction followed by a slight drift. The final potential after removal of stress returned to the initial potential before stress was applied within 2 minutes.

Applied stresses below about 75% of the proof stress appeared to have no effect although in several cases a slow drift in either anodic or cathodic direction resulted, the potential eventually returning to the original value. A selection of results is given in Table XII.

TABLE XII

Potentials in millivolts on saturated calomel scale

Stress: 94% of 0.1% proof stress.

All readings 15 minutes after immersion of specimen.

Specimen No.	unstressed	stressed	unstressed
1	-797.8	-798.1	-798.0
2	785.1	785.6	785.2
3	776.8	777.2	777.0
4	764.7	765.3	765.2
5	798.0	798.2	797.8

Continued

Specimen No.	unstressed	stressed	unstressed
6	-770.4	-770.6	-770.3
7	758.2	758.5	758.4
8	761.2	761.8	761.2
9	791.6	791.8	791.7
10	799.0	799.4	799.4

Discussion

As in the case of aluminium, it may be concluded that any effect of stress is very small. However, a small deviation in the anodic direction was observed in all cases when a stress of 94% of the proof stress was applied to the strain-aged alloy.

In these experiments the effect of stress on the average potential of an electrode was measured. The corrosion of strain-aged alloy AW.7. was to a large extent preferential at the grain boundaries as well as general, the grains themselves suffering attack. Thus exposure of an increased area of anodic β-phase due to stress opening up cracks (vide p. 101) would not necessarily result in an appreciable change in the average potential in the anodic direction. In general, potential measurements provide little information on the rate of corrosion, but the experiments carried out were useful as confirmatory tests to those in which the rate of hydrogen evolution was measured.

SECTION B

THE INFLUENCE OF STRESS ON LOCALISED CORROSION OF ALUMINIUM-MAGNESIUM ALLOYS

It is known that aluminium-magnesium alloys containing more than 7% Mg are susceptible to stress-corrosion when their structure is such that they are susceptible to intercrystalline attack. This condition is not found in the annealed alloy but is induced by strain-ageing, which may be effected in service by the prolonged exposure in tropical climates of an alloy overstrained during fabrication.

Dix (18) discusses experiments on the stress-corrosion of these alloys and indicates that the probability of stress-corrosion failure is very high in alloys containing more than 7% Mg but decreases rapidly to zero probability for alloys containing less than 4.8% Mg. However, service failures in rivets containing 5% magnesium have been reported (15,69), but it is not known to what extent the 5% alloy is susceptible.

The purpose of the experimental work was to develop suitable techniques for stress-corrosion tests on an alloy known to exhibit stress-corrosion properties, viz. Al-7%Mg, and by conducting similar tests on an Al-5% Mg alloy to ascertain the stress-corrosion susceptibility of the latter alloy and by comparing the results for the two alloys to determine whether any light could be thrown on the mechanism of stress-corrosion.

Corrosion - time curves for alloys corroded with and without application of stress were investigated by utilising two different techniques:

i. The oxygen absorbed and hydrogen evolved.
ii. The loss in mechanical properties.

These are described in this section.

B.I. MEASUREMENT OF OXYGEN ABSORBED AND HYDROGEN EVOLVED

Measurements of the loss of strength due to corrosion do not indicate any changes which may occur in the mode of attack. It was therefore decided to investigate whether any changes do occur by measuring the oxygen absorbed and hydrogen evolved during the corrosion of strain-aged NW.7. with and without application of external stress. Details of strain-ageing are given in Section B.II, p.152

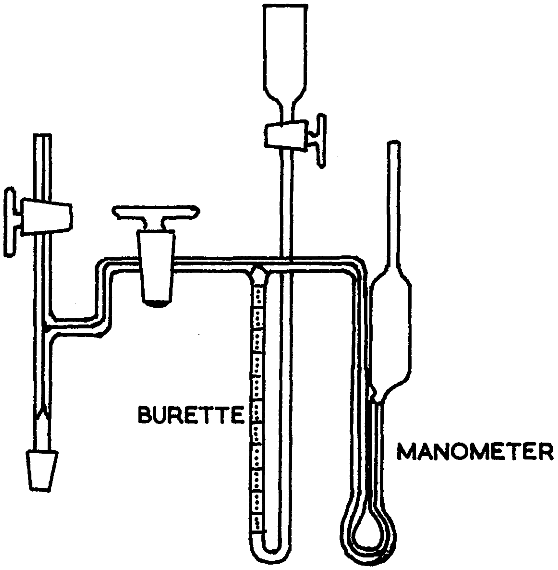
Development of Apparatus

The essential features of the corrosion apparatus used by Bengough and Champion (50-54) for the measurement of oxygen absorbed and hydrogen evolved were as follows:

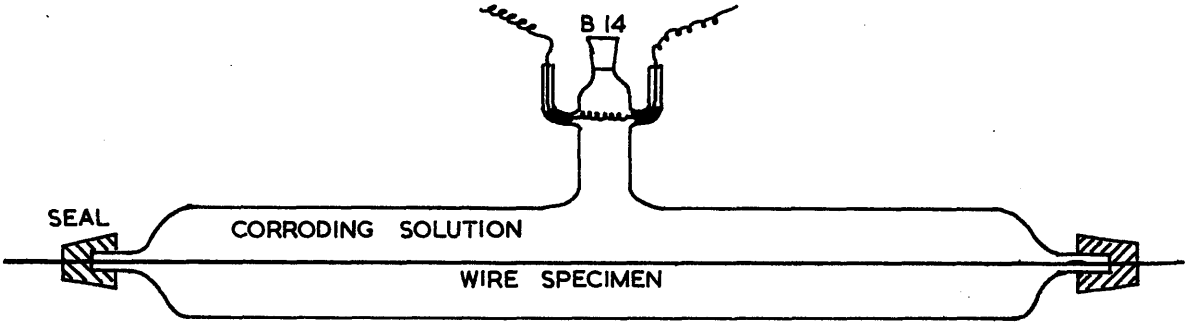
i. A corrosion vessel of specified dimensions in which the specimen was completely immersed in a pure saline solution saturated with air.

ii. A platinum spiral in the gas space of the corrosion vessel which could be heated to dull redness by passage of an electric current, to remove the hydrogen evolved during corrosion.

Facing P. 120



MEASURING APPARATUS



CORROSION VESSEL

HORIZONTAL IMMERSION

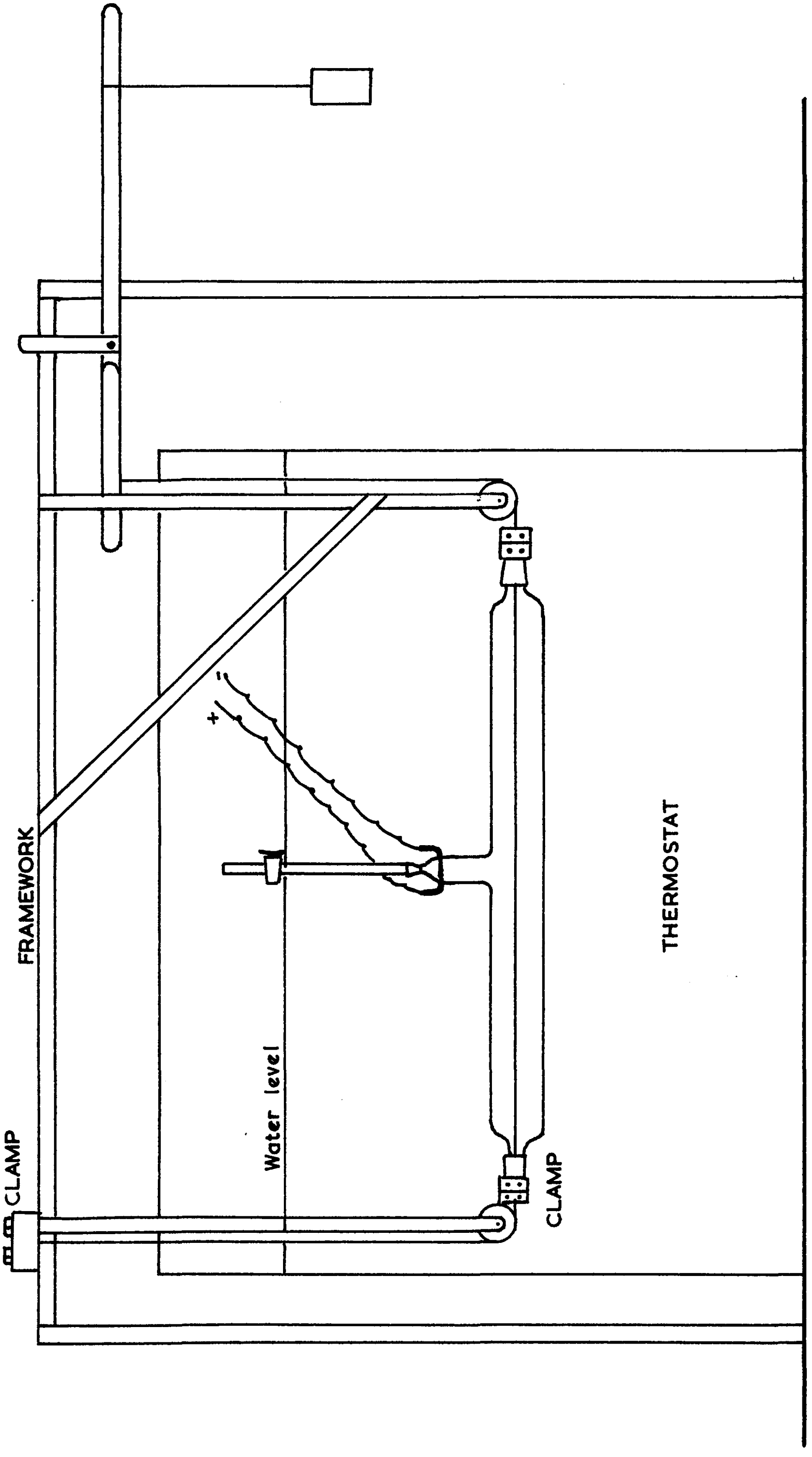
FIG. 36

iii. A gas burette and manometer connected to the corrosion vessel through a special stopcock, enabling the changes in volume of the gas in the corrosion vessel to be measured.

An additional feature required here was means for application of stress to the metal. It was decided to use direct loading by means of a steelyard as used in the other experiments described in this thesis and since the experiments of Bengough and Champion were conducted on a metal totally immersed in a horizontal position, it was decided to conduct experiments with the wire specimen immersed horizontally at constant depth.

A glass tube 11 in. in length and 1½ in. diameter was drawn out at the ends to a narrow tube ⅛ in. diameter, as shown in Fig. 36. A tube ¾ in. diameter and 1 in. in length was joined centrally and perpendicularly to the former tube, the open end of the latter being fitted with a B.14 "Quickfit" joint. A platinum spiral was sealed into the tube such that it could be heated by passage of current from a battery. A burette and manometer for determining changes in the volume of the gas was constructed as shown, such that they constituted

Facing P. 121



ASSEMBLY OF APPARATUS
HORIZONTAL IMMERSION

FIG: 37

a section which fitted into the corrosion vessel at the B.14 joint.

The wire specimen was passed through the horizontal tube and sealed into the vessel by means of two rubber bungs partly bored to fit over the ends of the tube and partly to fit over the wire. Two brass clamps were fitted at either end of the wire and joined to lengths of Monel wire which passed over two brass pulleys. One wire was clamped to the supporting framework, the other was attached to a steelyard by means of which the necessary stress was applied, as shown in Fig. 37. The whole apparatus was immersed in a tank comtaining water maintained at a constant temperature.

Experiments with Horizontal Immersion

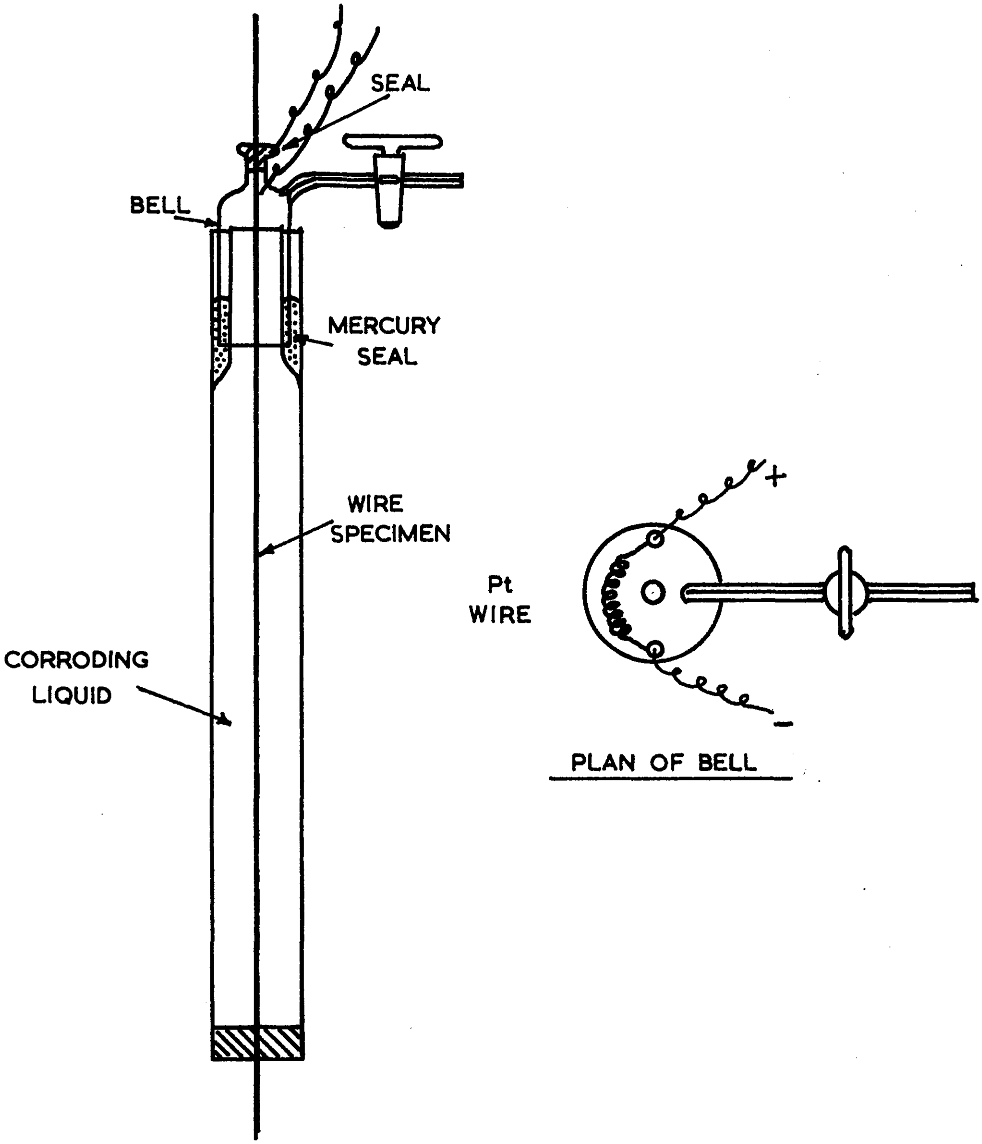
The experiments consisted of the measurement of the oxygen absorbed and hydrogen evolved whilst the metal was immersed in sodium chloride solution. The horizontal tube and part of the vertical tube were filled with corroding solution. Measurements of the gas volumes before and after burning the hydrogen were taken at daily intervals.

It became apparent that after a few days the corrosion of the wire was not uniform, the area immediately below the vertical tube suffering little attack compared with the extremities of the metal. The inference was that diffusion of oxygen to the metal surface was not uniform, the section below the gas space receiving a greater supply than the remainder of the metal rendering the extremities anodic to the central portion. In order to obviate this difficulty, the corrosion vessel was only partly filled with corroding solution, but the values of gas absorbed and evolved were erratic and reproducibility of results was poor. It was thought that the gas evolved from the extremities of the metal did not reach the platinum wire for burning, and the volume of gas space being comparatively large reduced the accuracy of the measurements.

Due to the fact that the apparatus was difficult to assemble for a test, and the difficulties outlined above, it was decided to construct an apparatus in which the metal was held in a vertical position under conditions of total immersion.

Apparatus for Vertical Immersion.

An attempt was made to rectify certain



CORROSION VESSEL
VERTICAL IMMERSION WITH INDEPENDENT BELL

FIG. 38

disadvantages apparent in the horizontal corrosion vessel. One of these was the method of sealing the wire into the corrosion vessel by means of rubber bungs. It was necessary, however, to effect the seal in such a manner that the wire could stretch when a load was applied and any elongation occurring during the corrosion could take place without loss in the applied stress. One method was to utilise the principle used in experiments on the general corrosion in acids, by sealing a bell to the wire and arranging a mercury seal between the bell and the corrosion vessel.

The apparatus constructed was as shown in Fig. 38. A glass tube 2 ins. in length and ⅞ in. diameter was sealed concentrically 2 ins. below one end of a tube 11 ins. in length and 1¼ ins. diameter. A glass bell 2 in. in length and 1 in. diameter was contained in the space between the seal and this in turn was sealed with mercury. The bell contained a platinum spiral which could be heated for burning the hydrogen and a capillary connection to a gas burette and manometer. A gas-tight seal between the wire and the top of the bell was made with polymethacrylic resin.

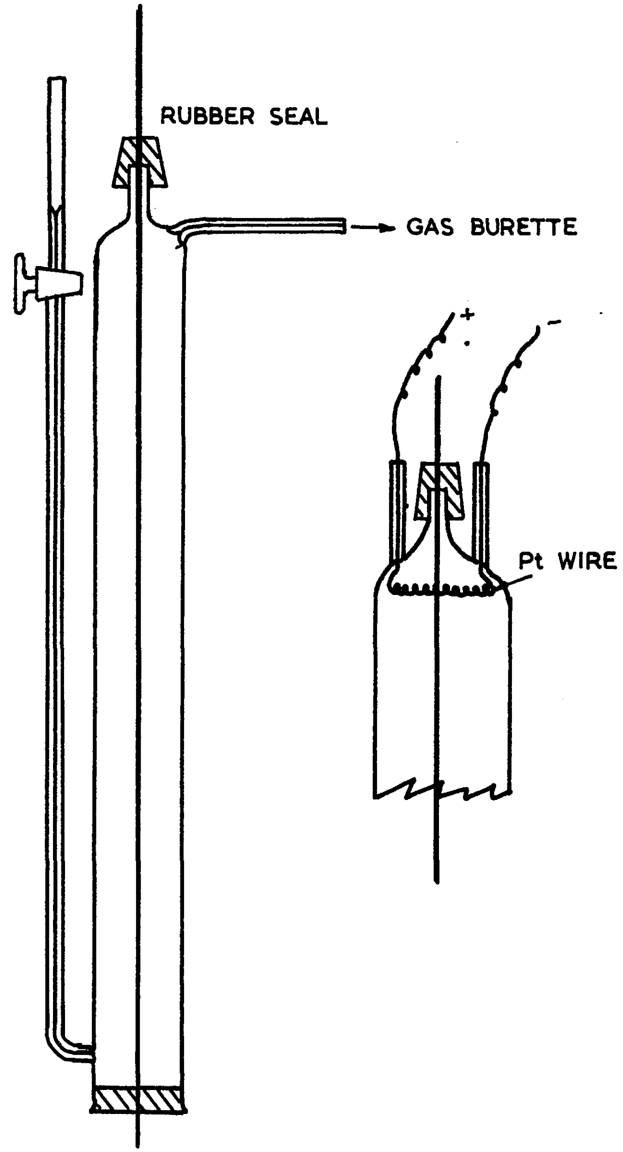
The corrosion vessel was filled with the corroding liquid leaving as small a gas space as convenient.

A blank test was conducted with the tube filled with corroding liquid, but no wire in the apparatus. The platinum wire was repeatedly heated to dull redness for about 15 seconds after which the gas was allowed to cool and any changes in the volume of the gas noted. It was observed that expansion of the gas as a result of heating the wire caused a depression in the level of the mercury in the inner side of the seal and on cooling a slight deviation of the mercury meniscus from its original position resulted in an error in the reading of the gas volume. Although the difference in volume was small, it constituted an appreciable error when compared with the volume changes being estimated during corrosion.

Modification of Apparatus.

A new design was constructed dispensing with the independent bell, the corrosion vessel being in one section and the wire sealed into the top of the vessel by means of a rubber bung. A difficulty was caused by expansion of the gas above the corroding solution when the platinum wire was heated. A side arm was constructed on the corrosion vessel, expansion of the gas then caused a depression in the liquid level in the corrosion tube which was compensated by the level rising in the side arm. Subsequent tests indicated that there was no error caused by changes in the liquid level as was the case with the mercury seal.

It was observed that the corrosion rate decreased rapidly after about 3 days and specimens of strain-aged NW.7. loaded to 91% of the proof stress did not fail within 25 days whilst in tests involving measurement of the loss of strength, failure occurred within 12 days when stress of this value was applied. It was thought that once the dissolved oxygen in the corroding liquid had been used, diffusion of a fresh supply from the surface was so slow that corrosion virtually ceased. By bubbling pure oxygen through the corroding liquid for 15 minutes, the corrosion rate increased and by repeating this procedure at 48 hour intervals, failure of NW.7. alloy occurred in less time than in the partial



MODIFIED CORROSION VESSEL FOR VERTICAL IMMERSION

FIG. 39

immersion tests described on p. 149.

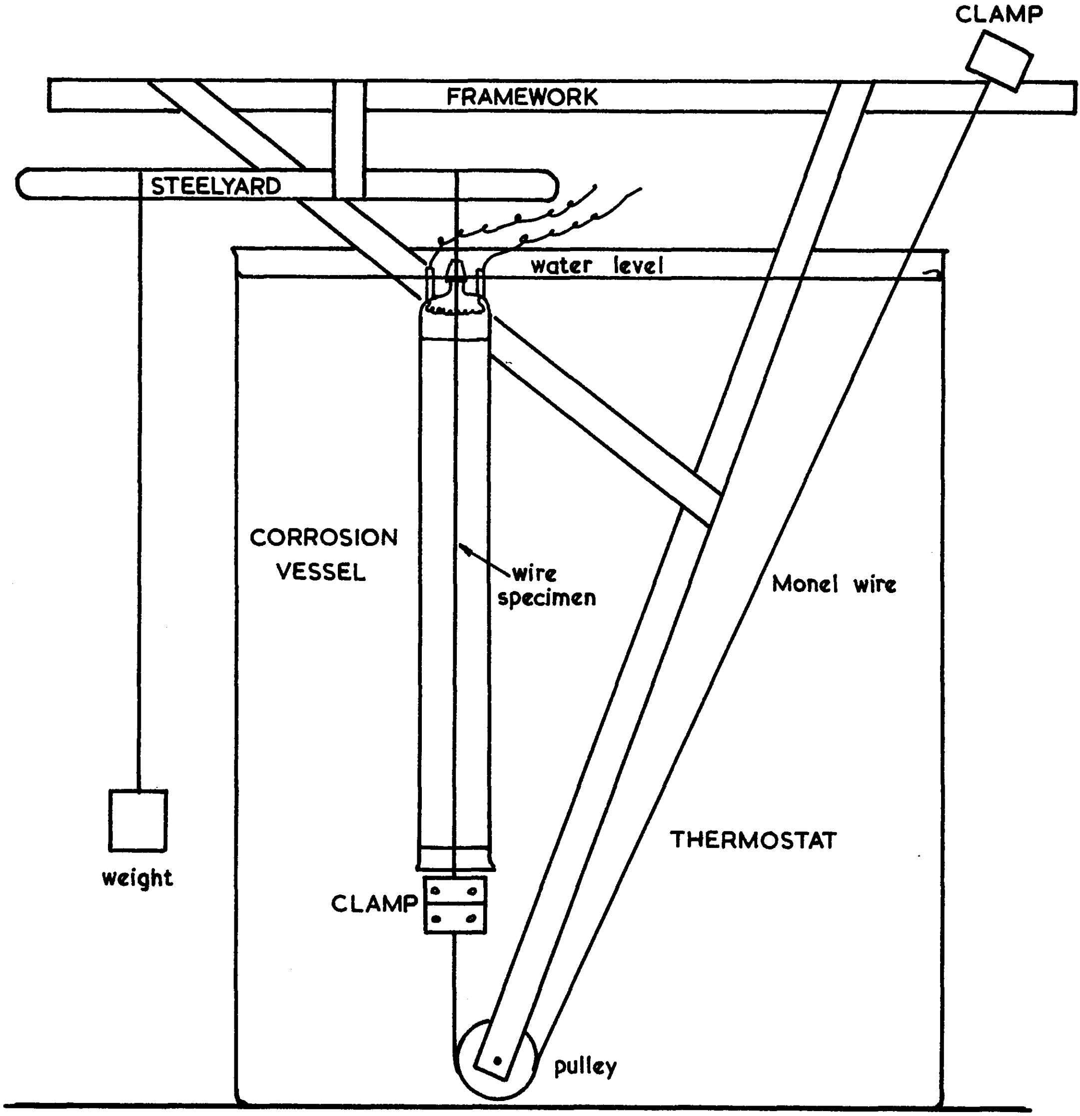
The oxygen was passed into the corrosion tube through the side arm, fitted with a tap, originally constructed to permit expansion of the gas. The manometer was enlarged to take the increased volume when the hydrogen was burned. The apparatus is shown in Fig. 39.

EXPERIMENTAL PROCEDURE.

Assembly of Apparatus

The alloy was cleaned by exposing to toluene vapour and the extremities of the wire specimens were coated with polymethacrylic resin so that protection was given at the water line for ½ in. below the surface and a length of 9 in. exposed to the corroding solution.

The specimen was fitted into the corrosion tube which was then filled with corroding liquid which had previously been saturated with oxygen at the temperature of the experiment. The gas burette and manometer were attached to the corrosion vessel via a short length of rubber tubing. The connection was arranged such that the glass ends of



ASSEMBLY OF APPARATUS FOR MEASURING HYDROGEN EVOLUTION AND OXYGEN ABSORPTION FOR STRESSED SPECIMEN

FIG. 40

the two sections, which were ground flat, were in contact, the rubber being bound with wire and coated with rubber cement to ensure that no volume changes were taken up by it. (Cf. Champion (53)). The whole apparatus was immersed in a thermostat tank, the wire attached to the steelyard and the required stress applied. The level of the water in the thermostat was adjusted so that the apparatus was completely submerged. The assembled apparatus is shown in Fig. 40.

Observations were commenced one hour after assembly in order to permit conditions to stabilise.

Blank tests showed that the apparatus was gas-tight and that after heating the platinum wire, the volume of gas returned to its original value, ± 0.002 ml., within 15 minutes.

The thermostat was controlled at 25°C. ± 0.1°. All readings were taken to within ± 0.01°C. as observed on a Beckman thermometer.

Observations

The observations which were made were:

i. Measurement of the volume at the initial time.
ii. Measurement of the volume at the end of interval.
iii. Measurement of volume after burning the hydrogen.

The volume of hydrogen was measured by heating the platinum wire to dull redness for periods of 15 seconds and permitting the gases to cool for 5 minutes after each heating. When there was a negligible change in consecutive readings the gas was allowed to attain temperature equilibrium for half an hour before the final reading was taken.

In the first series of tests the manometer was open to the atmosphere. Adjustments of volumes were made for changes in atmospheric pressure, the volume of the gas space being determined by raising the temperature of the thermostat a few degrees and noting the change in volume. In later experiments the manometer was sealed under a pressure of 760 mm. Hg. and in assembly of the apparatus the pressure of the gas above the corroding liquid was adjusted to correspond.

Experiments conducted

Experiments were carried out in order to determine the effect of stress on the corrosion of strain-aged NW.7. Observations were conducted on specimens with externally applied loads of 85%, 75% and 66% of the 0.1% proof stress and compared with those obtained for specimens to which no external stress was applied, when corroded in a solution of 3% sodium chloride with hydrochloric acid added to give the solutions a pH of 3. Oxygen was bubbled through at approximately 48 hour intervals.

Calculation of Results

A specimen calculation of the amount of corrosion and the observations obtained for a typical experiment are given. The results are presented as corrosion time curves, Figs. 41 to 47.

Specimen Calculation

Manometer open to atmosphere.

Let x be the volume of the gas space.

At 25.00°C. Vol. = x + 1.000 ml.
28.00°C. Vol. = x + 1.485 ml.

$\underline{x = 47.2 \text{ ml}}$.

Vol. at 10.00 a.m. 1st day	...	1.12 ml.
Atmos. pressure	......	759.1 mm.
Corrected vol.	......	0.9988x + 1.116 at 760 mm.
Vol. at 10.00 a.m. 2nd day	...	0.82 ml.
Atmos. pressure	......	760.1 mm.
Corrected vol.	......	1.0001x + 0.820 ml.

Hydrogen burned

Final firing at 10.30 a.m.

Vol. at 11.00 a.m. ... 0.68 ml.

∴ Contraction due to H_2 burning = 0.14 ml.

∴ VOLUME OF HYDROGEN EVOLVED = 0.093 ml.

Oxygen Absorbed

Vol. O_2 absorbed
10.00 a.m. 1st - 10.00 a.m. 2nd day
$= 0.30 - 0.0013x + H_2$ evolved
$= 0.24 + H_2$ evolved.

Hydrogen evolved
10.00 a.m. 1st - 10.00 a.m. 2nd day
= 0.093 ml.

Vol. of H_2 evolved per hour is very small and no correction is necessary.

∴ Vol. of oxygen absorbed = 0.24 + 0.093 ml.
= 0.333 ml.

Average absorption per hour = 0.014 ml.

∴ VOLUME OF OXYGEN ABSORBED

10.00 a.m. 1st - 11.00 a.m. 2nd day
= 0.333 + 0.014 ml.
= 0.347 ml.

These values may be converted into weights of aluminium dissolved:-

Corrosion due to hydrogen evolution

Anode: $Al = Al^{\cdot\cdot\cdot} + 3e^-$
Cathode: $3H_3O + 3e^- = 3H_2O + H_2$

Thus 1 ml. H_2 is evolved for dissolution of 26.97/22,410 gms. Al.
$= 8.03 \cdot 10^{-4}$ gms. Al.

Corrosion due to oxygen absorption

Anode: $4Al = 4Al^{\cdot\cdot\cdot} + 12e^-$
Cathode: $3O_2 + 6H_2O + 12e^- = 12OH^-$

Thus 1 ml. O_2 is absorbed for dissolution of $1.605 \cdot 10^{-3}$ gms. Al.

Presentation of Results

Since these tests were conducted on a wire immersed in a vertical position, the attack was probably unevenly distributed, eventually being concentrated near the water line. It was therefore considered that corrosion should be expressed as the total weight of aluminium dissolved rather than as the dissolution per unit of surface area exposed, the latter expression having little meaning unless uniform corrosion occurs on the whole of the surface exposed.

The observations and calculated results for one experiment are shown in Table XIII, and the experimental results are presented as corrosion-time curves and rate of corrosion - time curves in Figs. 41 - 47. In the corrosion - time curves, the amount of corrosion as measured by hydrogen evolution and by oxygen absorption is shown and a curve for the total corrosion included. In the rate of corrosion-time curves, the rates of attack as measured by hydrogen evolution and by oxygen absorption are shown.

TABLE XIII

Interval hours	Total interval	Vol. H_2 ml.	Total H_2 ml.	Int. H_2 per hr. – mgm.	Total H_2 mgm.	Vol. O_2 ml.	Total O_2 ml.	Int. O_2 per hr. – mgm.	Total O_2 mgm.	Total Corrn. mgm.
25·5	25·5	0·35	0·35	0·0110	0·281	0·23	0·23	0·0145	0·369	0·650
19·5	45·0	0·34	0·69	0·0282	0·554	0·46	0·69	0·0378	1·107	1·661
24·5	69·5	0·49	1·18	0·0161	0·948	0·45	1·14	0·0295	1·830	2·778
23·5	93·0	0·34	1·52	0·0116	1·221	0·35	1·49	0·0239	2·391	3·612
6·5	99·5	0·09	1·61	0·0111	1·293	0·09	1·58	0·0222	2·536	3·829
90·0	189·5	0·67	2·28	0·0060	1·831	0·90	2·48	0·0161	3·980	5·811
24·7	214·2	0·24	2·52	0·0078	2·022	0·26	2·74	0·0169	4·400	6·422
46·8	261·0	0·26	2·78	0·0045	2·235	0·32	3·06	0·0110	4·920	7·155
25·2	286·2	0·14	2·92	0·0044	2·340	0·14	3·20	0·0088	5·130	7·470
48·0	334·2	0·14	3·06	0·0023	2·457	0·29	3·49	0·0097	5·511	7·968

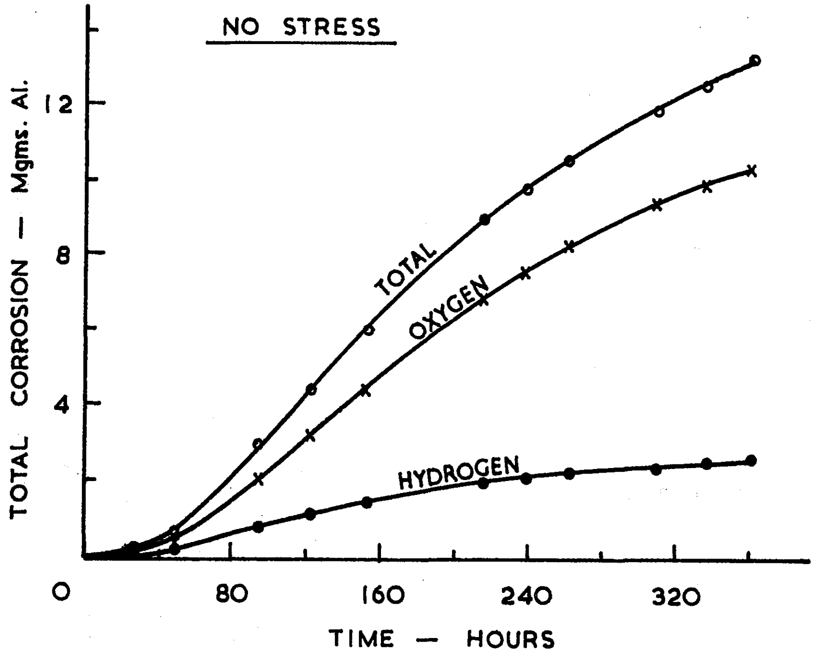
SPECIMEN OF OBSERVATIONS

ALLOY MW.7. CORRODED IN 3% NaCl CONTAINING HCl, pH 3.

66% of 0·1% proof stress APPLIED LOAD

FIGS. 41 - 47

Curves for the total corrosion-time and rate of corrosion-time for alloy NW.7, wires, 0.061 in. diameter, strain aged, immersed vertically in 3% NaCl solution containing HCl, pH 3.


NO STRESS
TOTAL CORROSION — Mgms. Al.
12
8
4
TOTAL
OXYGEN
HYDROGEN
0
80
160
240
320
TIME — HOURS

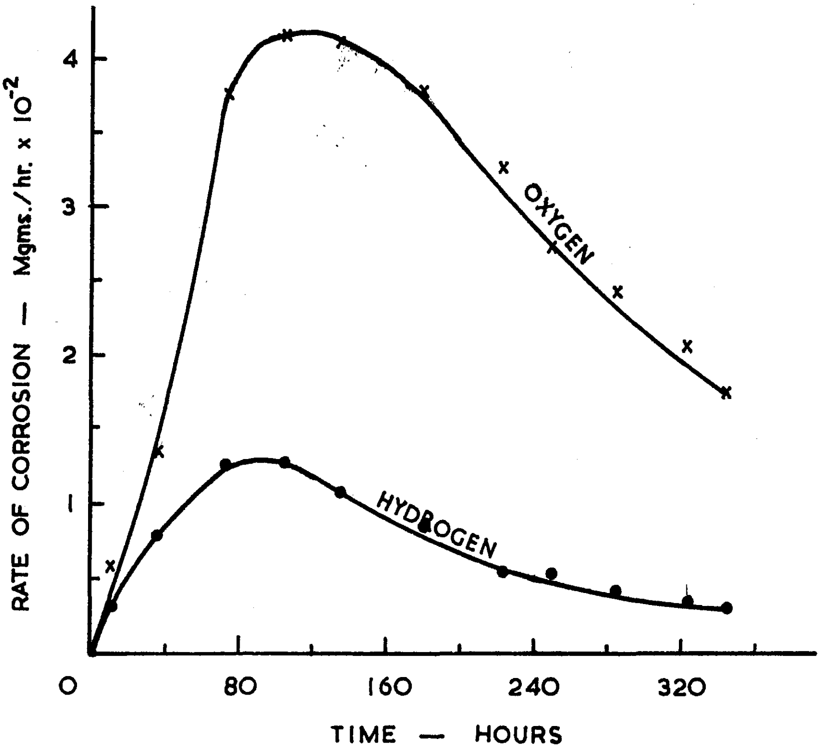

RATE OF CORROSION — Mgms./hr. x 10^{-2}
4
3
2
1
OXYGEN
HYDROGEN
0
80
160
240
320
TIME — HOURS

FIG. 41

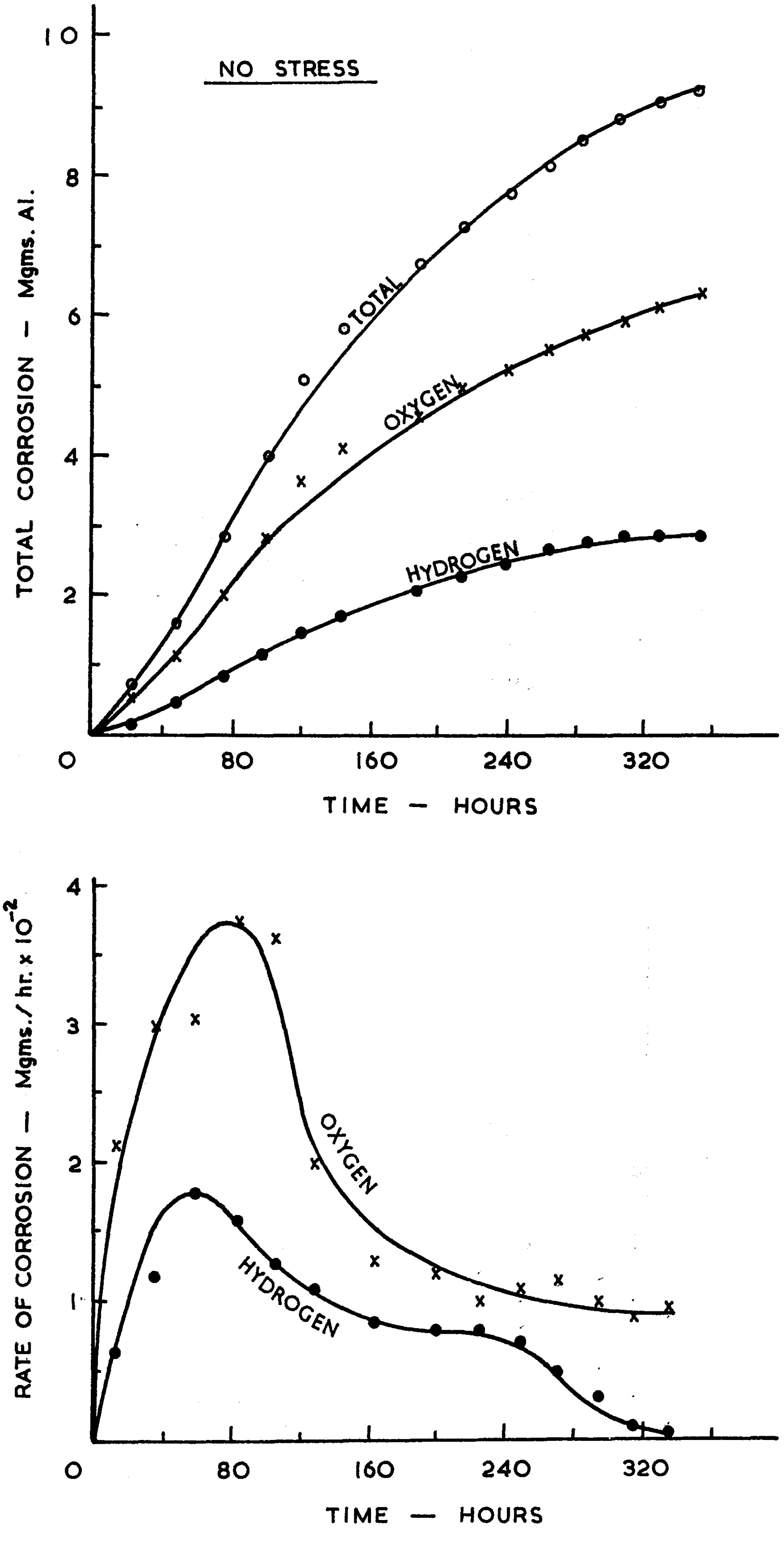
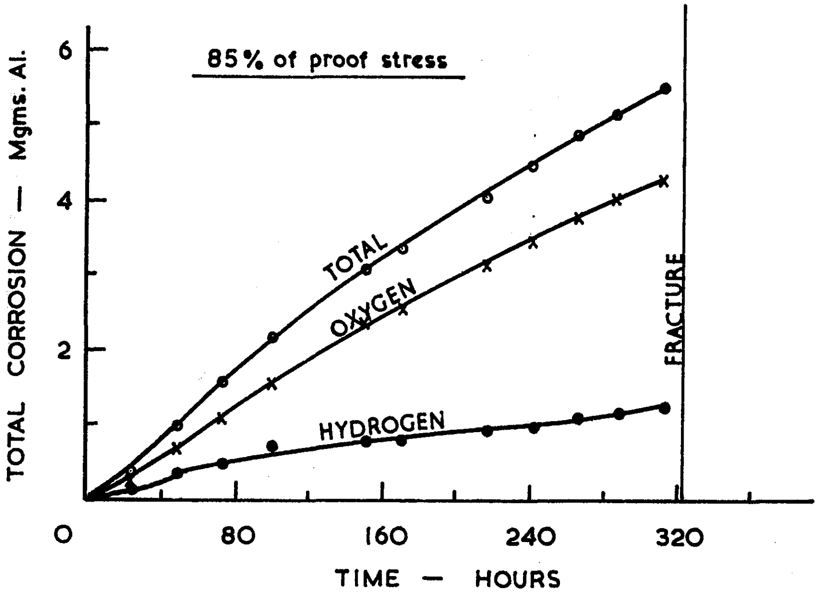

NO STRESS
TOTAL CORROSION — Mgms. Al.
10
8
6
4
2
TOTAL
OXYGEN
HYDROGEN
0
80
160
240
320
TIME — HOURS
RATE OF CORROSION — Mgms./hr. x 10^{-2}
4
3
2
1
OXYGEN
HYDROGEN
0
80
160
240
320
TIME — HOURS

FIG. 42


85% of proof stress
TOTAL CORROSION — Mgms. Al.
6
4
2
0
80
160
240
320
TIME — HOURS
TOTAL
OXYGEN
HYDROGEN
FRACTURE

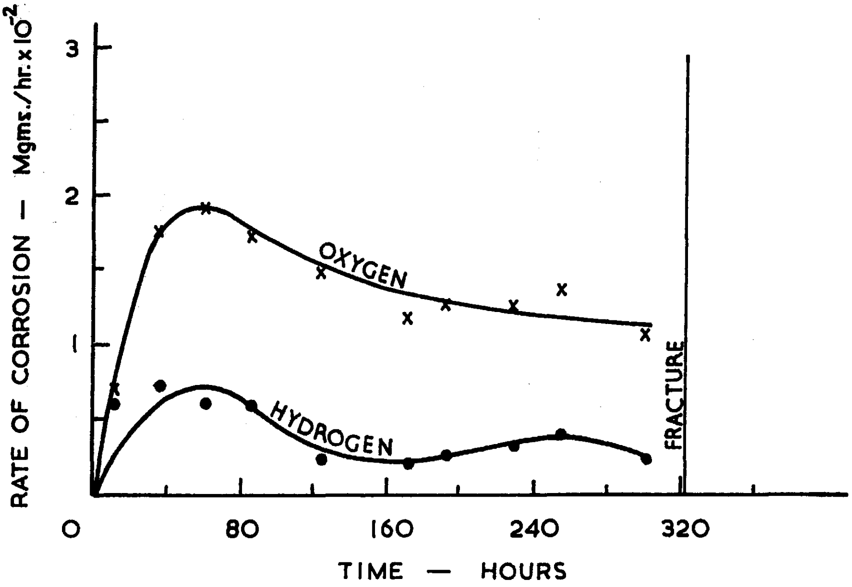
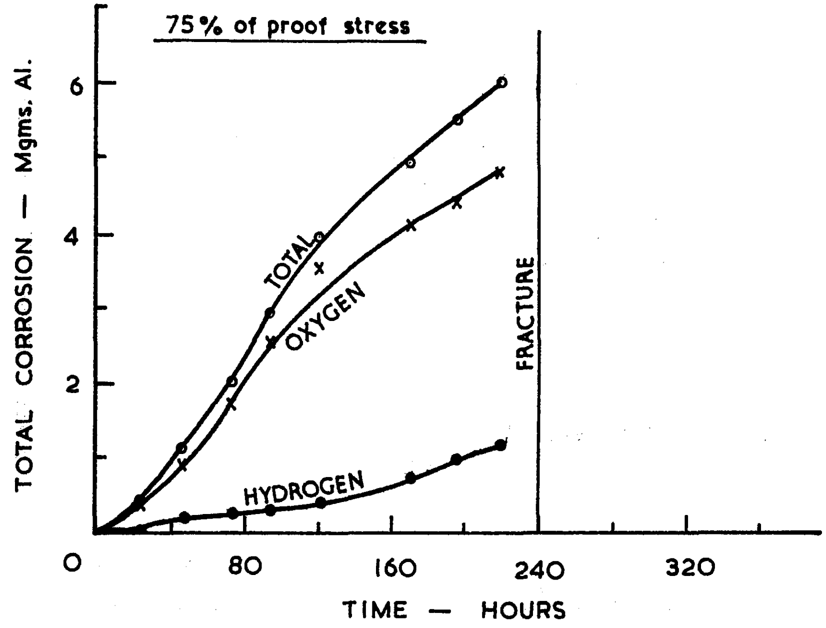

RATE OF CORROSION — Mgms./hr. x 10^{-2}
3
2
1
0
80
160
240
320
TIME — HOURS
OXYGEN
HYDROGEN
FRACTURE

FIG. 43


75% of proof stress
TOTAL CORROSION — Mgms. Al.
6
4
2
0
80
160
240
320
TIME — HOURS
TOTAL
OXYGEN
HYDROGEN
FRACTURE

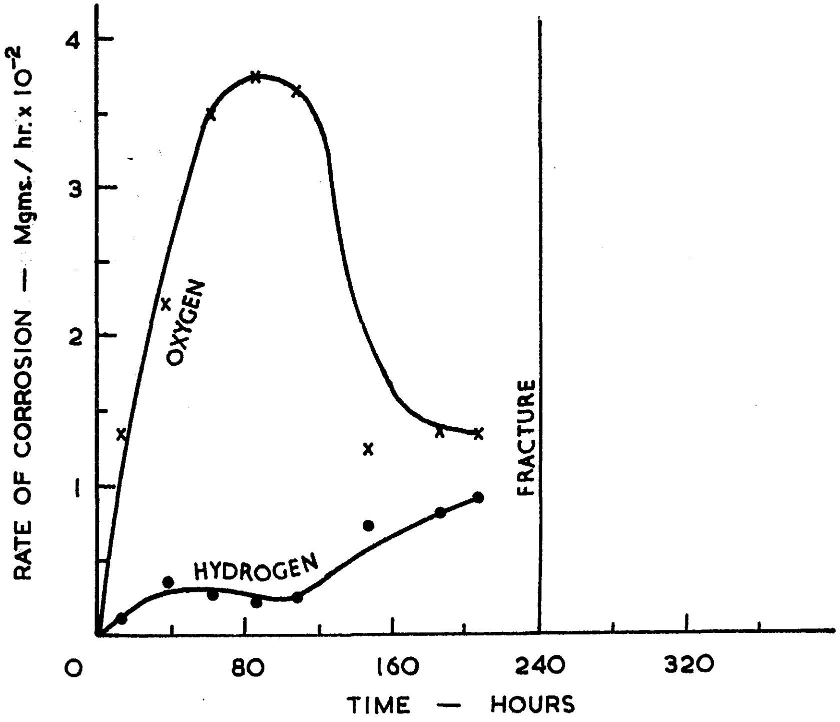
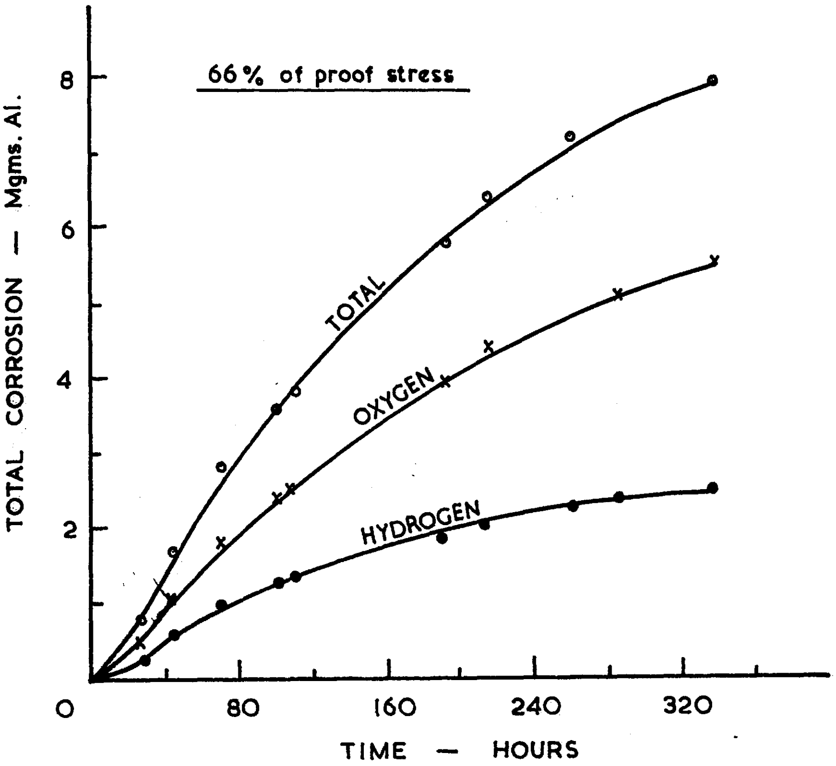

RATE OF CORROSION — Mgms./ hr. x 10^{-2}
4
3
2
1
0
80
160
240
320
TIME — HOURS
OXYGEN
HYDROGEN
FRACTURE

FIG. 44


66 % of proof stress
TOTAL
OXYGEN
HYDROGEN
TOTAL CORROSION — Mgms. Al.
8
6
4
2
0
80
160
240
320
TIME — HOURS

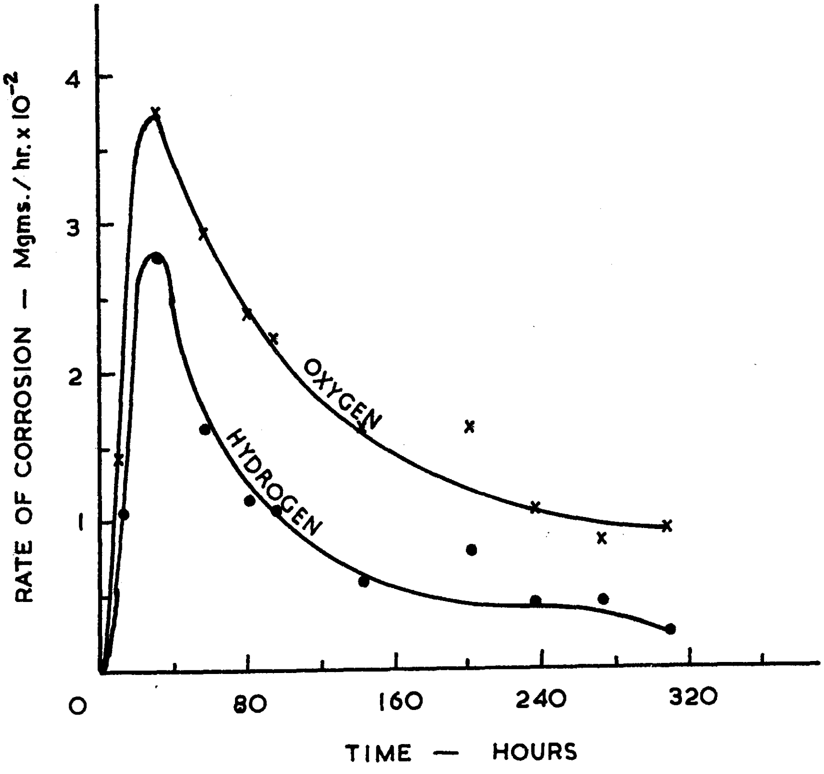

OXYGEN
HYDROGEN
RATE OF CORROSION — Mgms./hr. x 10^{-2}
4
3
2
1
0
80
160
240
320
TIME — HOURS

FIG. 45

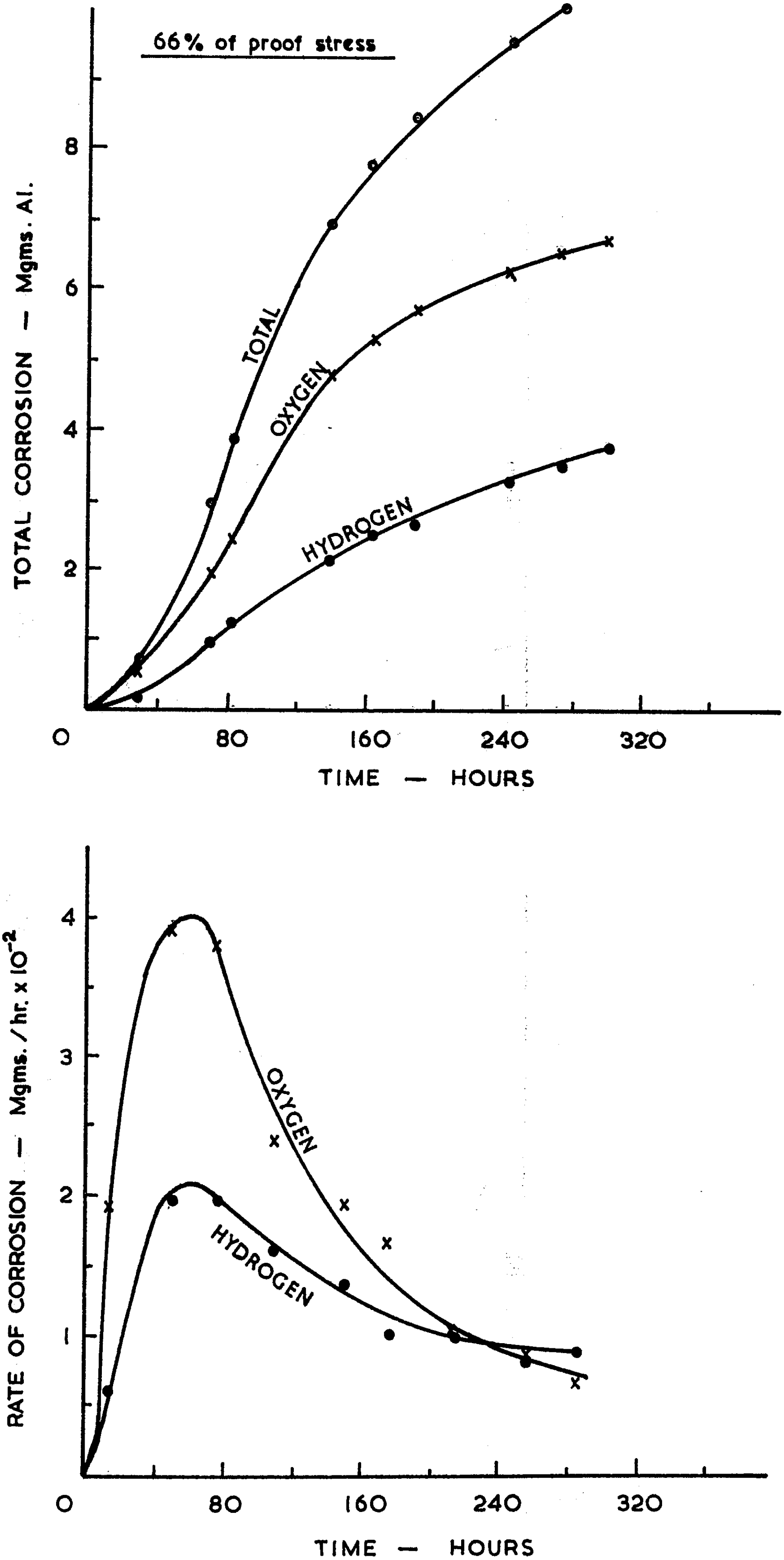

66% of proof stress
TOTAL CORROSION — Mgms. Al.
8
6
4
2
TOTAL
OXYGEN
HYDROGEN
0
80
160
240
320
TIME — HOURS
RATE OF CORROSION — Mgms. / hr. x 10^{-2}
4
3
2
1
OXYGEN
HYDROGEN
0
80
160
240
320
TIME — HOURS

FIG. 46

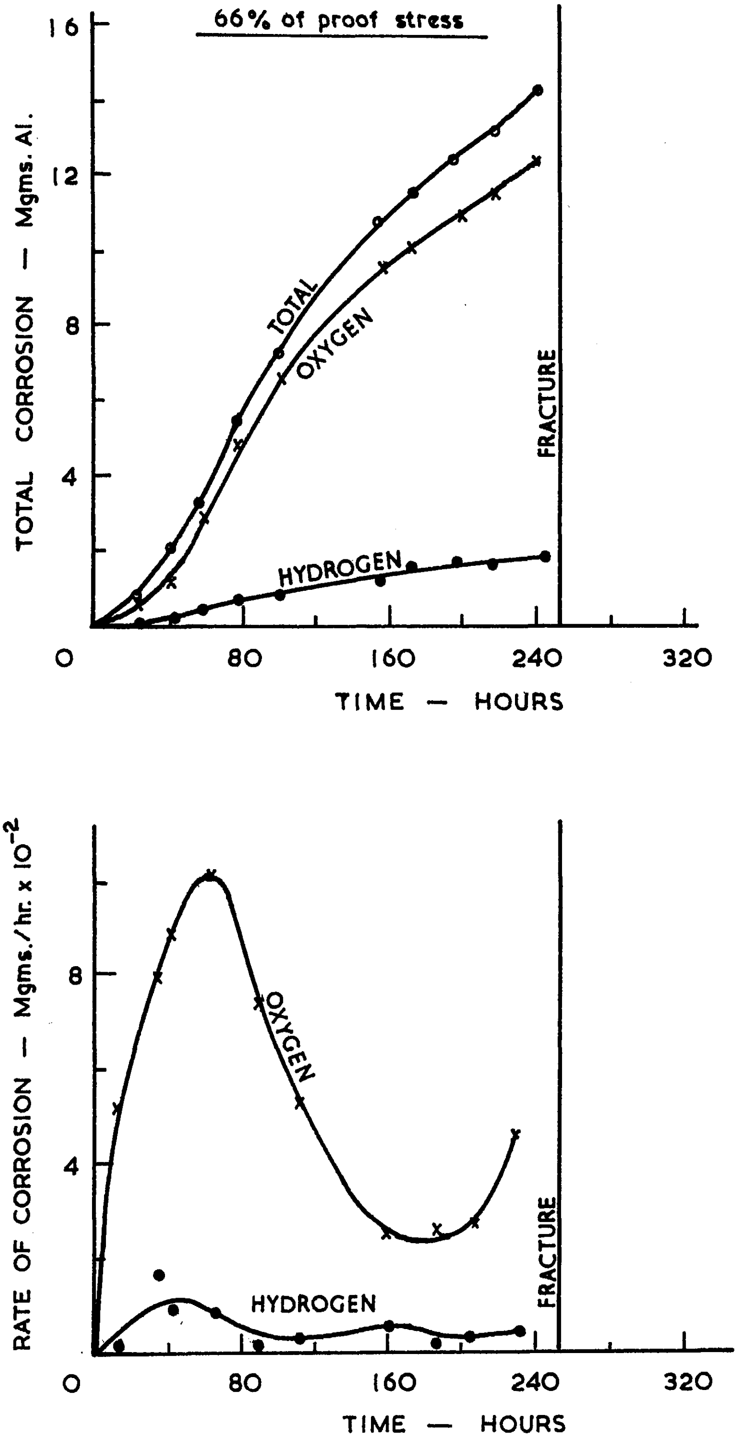

66% of proof stress
TOTAL CORROSION — Mgms. Al.
16
12
8
4
0
80
160
240
320
TIME — HOURS
TOTAL
OXYGEN
HYDROGEN
FRACTURE
RATE OF CORROSION — Mgms./hr. x 10⁻²
8
4
0
80
160
240
320
TIME — HOURS
OXYGEN
HYDROGEN
FRACTURE

FIG.47

DISCUSSION OF RESULTS

The curves for the rate of attack as measured by oxygen absorption are similar in all experiments, the attack rapidly rising to a maximum and then falling at a decreasing rate. There is considerable variation in the time taken to reach the maximum rate and the values for this rate differ appreciably even in experiments conducted under identical conditions. There is apparently no distinction between the nature of the curves for stressed and stress-free alloy.

The rate of attack does not appear to show marked changes when oxygen is introduced at 48 hour intervals, but the periods between measurements of oxygen absorption were possibly too long to show any effect. However, when oxygen is not introduced, the rate of absorption of oxygen attains a maximum in periods similar to those shown when oxygen is introduced, and then falls almost to zero.

The attack as measured by hydrogen evolution shows considerable variation for specimens corroded under the same conditions of stress. In several cases the shape of the hydrogen curve is similar to that of the oxygen curve in that a maximum rate is attained within about 80 hours, followed by a gradual decrease in the rate of attack. This is evident in the case of one of the unstressed specimens, Fig. 41, but for the other unstressed specimen, Fig. 42, the rate of hydrogen evolution shows a second decrease after about 240 hours immersion, becoming almost zero after 320 hours. A similar tendency is shown by stressed alloy, Fig. 45. In other experiments the hydrogen evolution is very irregular, showing several maxima and minima during the period of measurement, and in one case, Fig. 44, the rate shows a marked increase after about 120 hours, there being no previous maximum.

In general, the rate of corrosion as measured by oxygen absorption is always greater than that measured by hydrogen evolution, but in one test, 46 Fig. 4~~7~~, the rate due to hydrogen evolution becomes greater than that due to oxygen absorption after about 270 hours.

Possible Mechanism of Attack on the Alloy Wire

Initially, the corroding solution was saturated with oxygen and therefore in equilibrium with the oxygen in the gas space above the solution. Corrosion by oxygen absorption, in which cathodic regions were distributed at random over the surface of the wire, would result in exhaustion of the oxygen in the bulk of the solution, upsetting the equilibrium between the oxygen in the solution and in the gas space. Replenishment of the oxygen could occur only by diffusion from the gas space and by passage of oxygen from the surface of the solution by convection currents. It has been shown by Bengough and his co-workers (70,71) that the rate of attack on horizontal discs of zinc and of mild steel, fully immersed in static solutions of potassium chloride, falls off rapidly with the depth of immersion. Below a depth of about 1.5 cm. the rate of attack is almost constant at a fraction of that when very close to the surface. The constant rate which occurred below a critical depth was accounted for by replenishment of oxygen by convection currents, which are almost independent of depth.

After exhaustion of the oxygen in the bulk of the solution, the cathodic region would be concentrated at the water line, where oxygen could be replenished by diffusion. Thus attack would change from "primary distribution" to "secondary distribution" (cf. Evans (72)). During the primary attack, precipitation of aluminium hydroxide would occur when anodic and cathodic products came into contact. Some of this would form a protective film on the alloy surface, the attack on the wire being retarded, whilst some would fall to the bottom of the corrosion vessel.

A visible film of corrosion product was first observed on the lower regions of the exposed wire. The film subsequently covered the whole surface. Examination of the wire after completion of a test indicated that corrosion was most severe near the uppermost end of the exposed surface, this being verified by the fact that when a stressed specimen failed, it invariably did so at a section within one inch of the top of the exposed metal.

It would appear that the corrosion of the alloy took place in two repeating phases. One when oxygen was distributed uniformly throughout the solution, the other when the oxygen in the bulk of the solution was exhausted, or at least the concentration diminished. Bubbling oxygen through the solution at intervals would replenish the oxygen supply in the bulk of the solution, re-establishing equilibrium with the oxygen in the gas space. The attack would thus revert to that of the original phase, then pass into the second phase until oxygen was again bubbled through the solution.

It is doubtful whether the volume of oxygen absorbed from the gas space had a direct relationship with the quantity used in the corrosion. It has been recognised by several investigators that the rate of absorption of oxygen from the gas space is not necessarily equal to the rate of consumption of oxygen by the metal at the same moment. This will not, however, vitiate the accuracy when the corrosion velocity is constant or only slowly changing. (Evans (73), Bengough et alia (52). Vide also discussion by Evans and Bengough (74)). In the present case, it is probable that the corrosion velocity was changing and discrepancies between oxygen absorption as measured and the true quantity of oxygen used may partly account for the variation in the results.

Evolution of Hydrogen

Hydrogen evolution was due to cathodic reactions involving combination of hydrogen ions from the solution with electrons from the metal, with formation of hydrogen gas.

Since hydrogen ions were uniformly distributed through the corroding solution and were at no time supplied from an external source, the corrosion rate as measured by hydrogen evolution was a measure of the rate of attack due to hydrogen ion reaction at cathodic regions, although there might be an error due to dissolution of hydrogen in the corroding solution (cf. p. 65). Champion (53) in experiments on completely immersed aluminium, found that the hydrogen evolution was proportional to the total corrosion, but further experimental work would be necessary to establish this in the case of the alloy wire.

B.II. MEASUREMENT OF THE LOSS IN MECHANICAL PROPERTIES

Published work indicates that many techniques have been employed in the study of stress-corrosion. The methods of exposing the specimen to the corrosive environment include total immersion, partial immersion, salt spray and intermittent immersion. The application of external stress has been effected by direct loading, loading via levers, eccentric loading and by indirect methods. In most cases the specimens have been in the form of strips cut from rolled sheet (3, 75, 76). In the present investigation, specimens in the form of wire were used, for the reasons expressed on p. 38.

The destructive effect of stress-corrosion has been recorded as the loss of ultimate tensile strength of elongation and of yield strength (or 0.1% proof stress). Champion (54) has produced results showing the relation between the loss of 0.1% proof stress and the loss of ultimate tensile strength for several aluminium alloys. It is shown that in some cases a marked loss of tensile strength can occur before the proof stress is affected. Elongation measurements have been used to check the results obtained by tensile strength measurements, but in the present case the scatter of results obtained for the elongation of uncorroded wires was considered to be too large to render this method of assessment reliable. The criterion of corrosion measurement adopted was therefore limited to determination of the ultimate tensile strength.

Development of Technique.

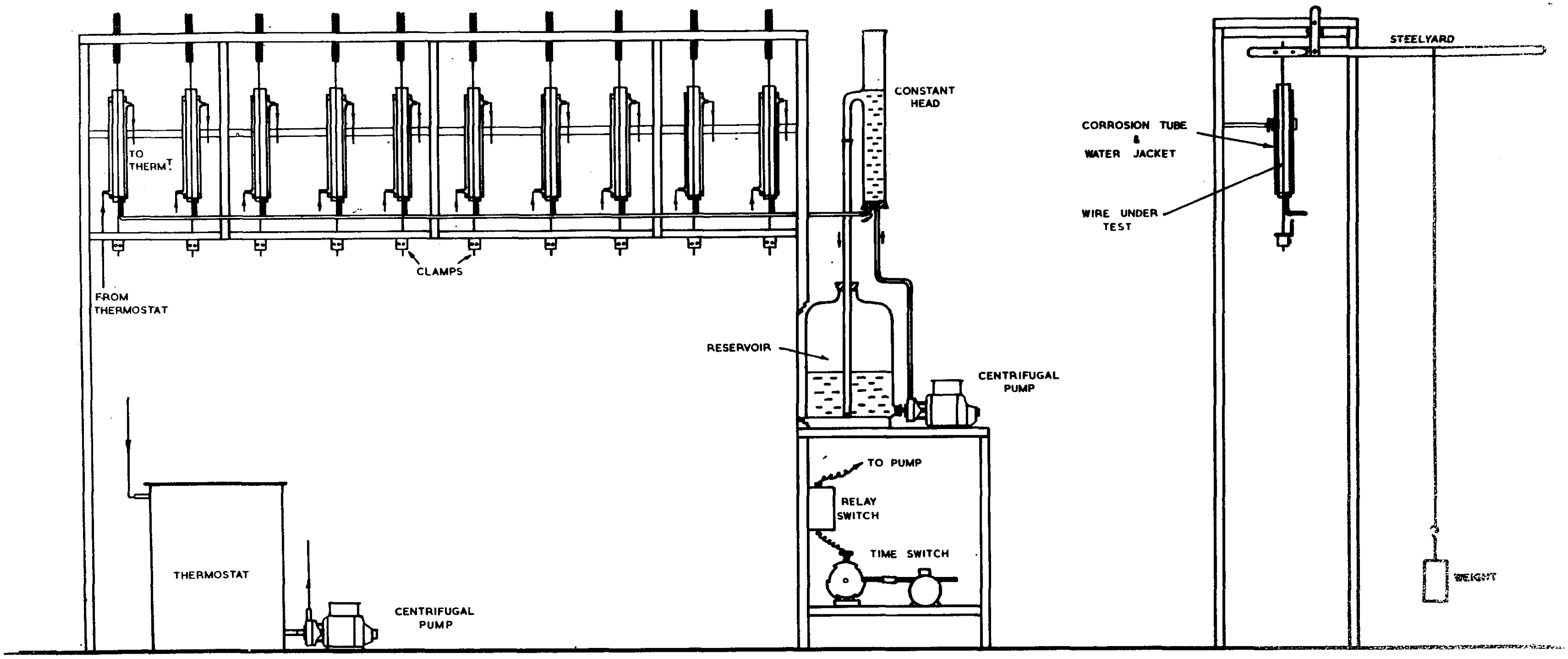
Stressing in tension by means of a steelyard proved to be a satisfactory method for applying stress in the experiments on general corrosion. This method was therefore adopted in the present tests.

The simplest means of exposing the alloy wire to the corroding solution was by total immersion in static solution. In preliminary experiments the corroding solution used was 3% sodium chloride, and in order to accelerate the attack hydrochloric acid to give a pH of 3 was added. However, although stresses in the region of the proof stress, when applied to strain-aged Al-7% Mg alloy, caused failure within 12 hours, the time-to-failure ranged from 8-32 days with stresses of 85% of the proof stress. With smaller stresses specimens were unbroken after 6 weeks.

In order to accelerate the attack, experiments were carried out in which the specimens were partially immersed. However, with stresses less than 60% of the proof stress, the time-to-failure was on an average longer than 6 weeks and reproducibility of results was poor. During earlier experiments involving measurement of oxygen absorbed and hydrogen evolved it was observed that little attack took place unless the dissolved oxygen in the solution was regularly replenished. In this event cracking occurred in less time than in the partial immersion tests described above. This indicated that dissolved oxygen played an important role in stress-corrosion and as later shown by Gilbert and Hadden (45) its presence is necessary for occurrence of stress-corrosion. These considerations led to the development of a technique whereby the corrosion process took place in an ample supply of oxygen by subjecting the specimens to intermittent immersion in the corroding solution.

Intermittent Immersion in the Corroding Solution.

Experiments utilising intermittent immersion, which have been described in the literature, in



ARRANGEMENT OF APPARATUS FOR CORRODING WIRES UNDER TENSILE STRESS BY INTERMITTENT IMMERSION

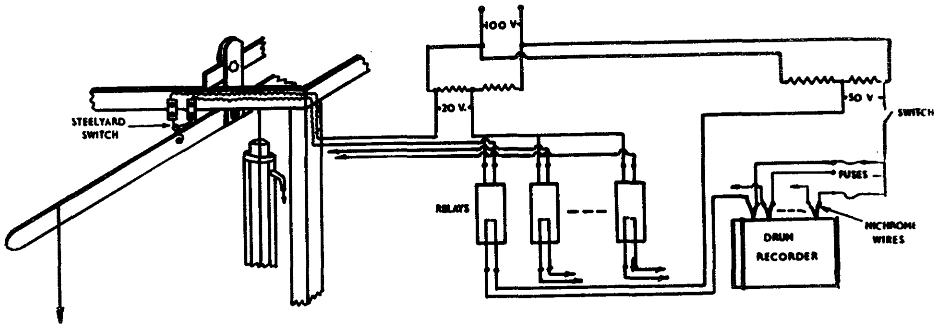
FIG. 48

general entail raising and lowering the specimens into and out of the corroding solution at set intervals. In the present case this was not a practicable preposition, so the procedure was reversed, the corroding vessels being filled with and emptied of the corroding solution at set intervals whilst the alloy specimens remained in position. The apparatus finally developed is shown in Fig. 48.

The corroding solution was fed to ten vertical corrosion tubes, each 11 in. in length by 1 in. diameter, from a reservoir via a manifold. A centrifugal pump, operated from a motor driven time switch, passed the solution from the reservoir to a vertical tube with constant head bypass return to the reservoir. The solution passed into the manifold from the base of this tube and flowed into the corrosion tubes under gravity. The height of the bypass governed the maximum height of the liquid in the corrosion tubes.

The corrosion tubes were jacketed with water circulating from a constant temperature tank maintained at 25°C. By suitable lagging, the corroding solution was maintained at 25°C. ±½°.

A cycle in which the corrosive solution pump was



APPARATUS FOR DETERMINING BREAKING TIMES OF TEST WIRES

FIG.49

in operation for two minutes and off for two minutes was found to be satisfactory since under these conditions the wire specimens were not permitted to dry out during the interval when the corrosion tubes were empty even when the atmospheric humidity was low. This, it was considered, eliminated the effect of variable air humidity shown to be of consequence by Perryman and Hadden (77).

Time-to-failure recorder.

In many experiments, the time-to-failure of a specimen corroding under stress was required. An automatic recorder was constructed as shown in Fig. 49. An electrical circuit was arranged so that when a specimen fractured the steelyard arm dropped and broke the circuit to a relay. This action completed a secondary circuit which heated a 32 gauge nichrome wire, in the form of a 'V' which was fixed above a clockwork-driven revolving drum so that it burned a small hole in a chart wrapped around the drum. A 36 gauge nichrome wire in series with the heavier gauge wire fused and broke the circuit after sufficient time had elapsed for the latter wire to mark the chart. Each specimen was linked with a separate circuit so that the time-to-failure of individual specimens was recorded. The chart was graduated and the time of fracture could be estimated to within 5 minutes.

Materials Employed.

The alloys tested were received in 500 ft. coils of 16 S.W.G. wire, in the commercially annealed condition, Chemical analyses are given in Table XIV.

TABLE XIV

Analysis of Aluminium - Magnesium Alloys

Alloy	Mg %	Mn %	Fe %	Si %	Cu %
NW.7	6.85	0.30	0.20	0.17	Nil
NW.6	4.80	0.28	0.20	0.15	Trace

(Kindly supplied by the British Aluminium Co. Ltd.).

Specimens of a suitable length (14 in.) were cut from the coil and immersed in 20% nitric acid for 2 minutes followed by a thorough wash under running water for 5 minutes. The wires were then wiped with wet cotton wool, washed again under running water, finally agitated in toluene to remove the water and dried with filter paper. The specimens were then overstrained 10% and aged in an air oven at 125°C. for 24 hours, this treatment causing precipitation of the anodic β-phase at the grain boundaries (16). In preliminary experiments the cleaned wires were sealed in a tube filled with argon for the ageing process in order to minimise oxide film formation. Comparative tests, however, indicated that the results were unaffected by this procedure.

The average mechanical properties of the strain-aged alloys as determined on a gauge length of 10 in. are given in Table XV.

TABLE XV

Mechanical Properties of Strain-Aged Alloy Wires.

Average diameter of strain-aged wire = 0.0613 in.

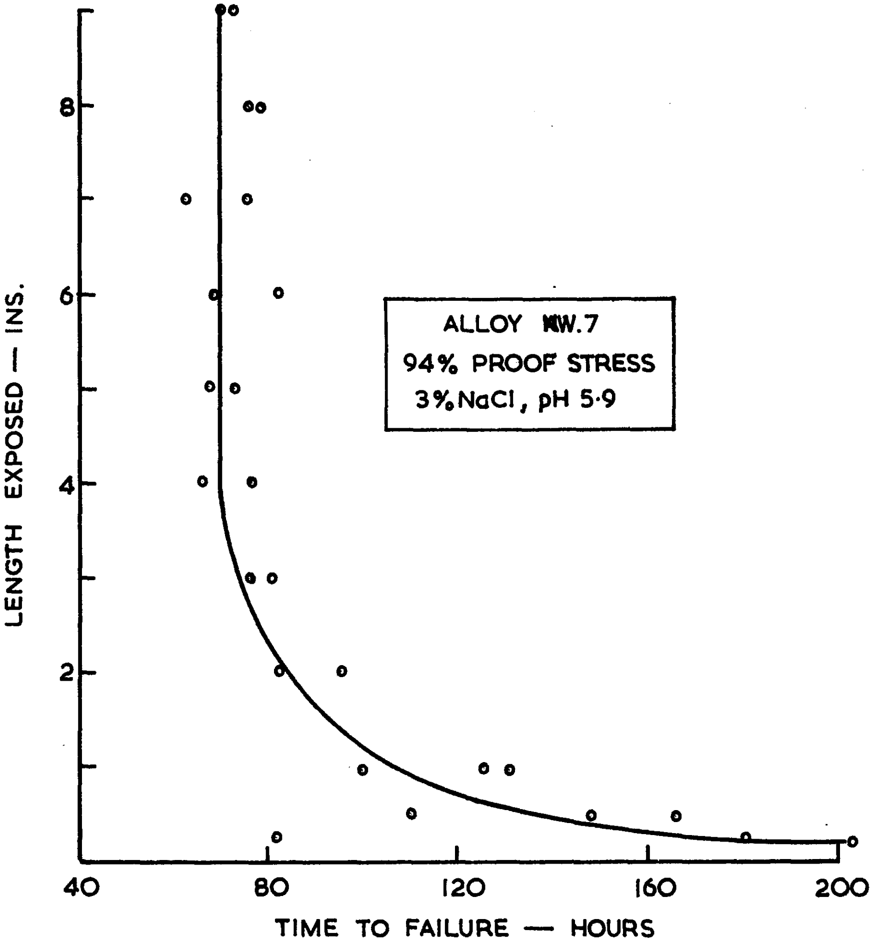
	NW.7		NW.6	
	Direct load, lbs.	tons/sq. in.	Direct load, lbs.	Tons/sq. in.
0.1% proof stress	106	16.0	81	11.3
U.T.S.	148	22.3	124	17.3

Corroding Solution

Preliminary tests were conducted using (a) 3% sodium chloride and (b) 3% sodium chloride containing hydrochloric acid to give a pH of 3. In both cases, changes in the pH of the solution during the corrosion process were observed. Thus in order to maintain conditions as identical as possible for all tests and to prevent the solution from changing its pH during a test, it was buffered at pH of 6 by addition of the requisite quantity of acetic acid - sodium acetate. The choice of buffer was limited in that it was necessary that there be no ions present which would precipitate an insoluble aluminium salt and hence inhibit the attack. The value of 6 for the pH was as near neutral as possible using this buffer.

Determination of Suitable Length of Exposure.

In order to ascertain a suitable length of wire to be exposed to the corroding medium during stress-corrosion experiments the time-to-failure of the Al-7% Mg. alloy under a stress of 68% of the U.T.S. (94% of the 0.1% proof stress) was determined for various lengths of wire exposed. The specimens were protected, except for the lengths indicated, by coating with polymethacrylic resin (I.C.I. Bedacryl, 144 T.L.). The results are shown in Table XVI and expressed graphically in Fig. 50.



EFFECT OF LENGTH OF WIRE EXPOSED ON THE TIME TO FAILURE

FIG. 50

TABLE XVI

Effect of Exposed Area on Time-to-failure of Al-7% Mg Alloy.
Applied stress = 68% U.T.S.

Length exposed, in.	Time-to-failure, mins.
¼	82, 180, 210
½	110, 148, 265
1	100, 125, 130
2	82, 95
3	76, 80
4	65, 75
5	67, 72
6	68, 81
7	62, 75
8	76, 77
9	70, 72

Increasing the length exposed above 4 in. had little effect on the time-to-failure and a length of 7 in. was chosen as being convenient. Protection was given for about 2 in. below the maximum liquid level and 1 in. above the base of the corrosion tube.

It is of interest to compare these results with those obtained by Perryman and Hadden (78) on the effect of exposed area on the stress-corrosion of Al-7% Mg alloy. They also show that the life of a specimen becomes greater and the scatter of results increases as the exposed area decreases. They suggest that a likely explanation is that there exists on the surface a certain distribution of points at which the susceptibility to stress-corrosion is greater than elsewhere. The probability of such points occurring in the exposed area decreases as the exposed area decreases and thus the stress-corrosion life would increase as the exposed area is decreased. If, however, one of the susceptible points existed in the smallest exposed area, the specimen would fail as quickly as the most susceptible specimen with the largest exposed area. This view is somewhat confirmed by the results shown in Table XVI. The scatter of results increases with decreasing length of exposure, but one specimen with an exposed length of ¼ in. failed in a time comparable with that of specimens with a much larger exposed length. It would appear, however, that the points of susceptibility are graded, there being relatively few points of maximum susceptibility, a larger number of points of a smaller susceptibility, a still larger number of points of yet smaller susceptibility and so on. Attack on all these points would eventually lead to failure if this does not first occur at a more susceptible point.

Corrosion of Stress-Free Alloys.

In order to ascertain the stress-corrosion susceptibility of the alloys, it was necessary to compare the loss of strength when corroded without application of external stress and when stress was applied to the corroding alloys, the corroding environment in both events being identical.

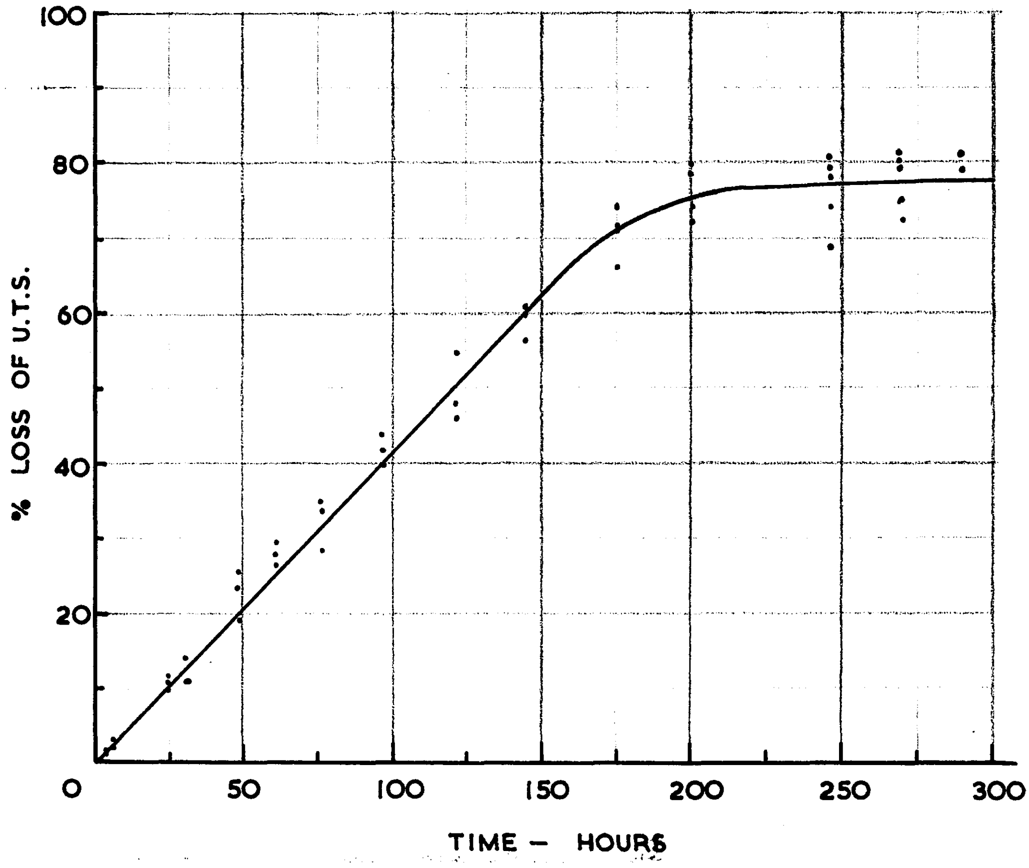
The susceptibility to corrosion in the stress-free state was determined by fitting the wire specimens in the corrosion testing apparatus, but without application of stress. Specimens were removed after various intervals of time and the ultimate tensile strength determined. The results for the Al-7% Mg alloy are shown in Table XVII and for the Al-5% Mg alloy in Table XVIII (P.162). The data are shown graphically in Figs. 51 & 54, P.158 & 162 respectively.

TABLE XVII

Loss of strength of stress-free Al-7% Mg alloy after various times of exposure.

Time of Exposure hours	Breaking Load lbs.	Mean Breaking Load, lbs.	Mean % Loss of Strength
0	148, 148, 148	148	0
4	146, 145	146	2
6	144, 143	144	3

Continued



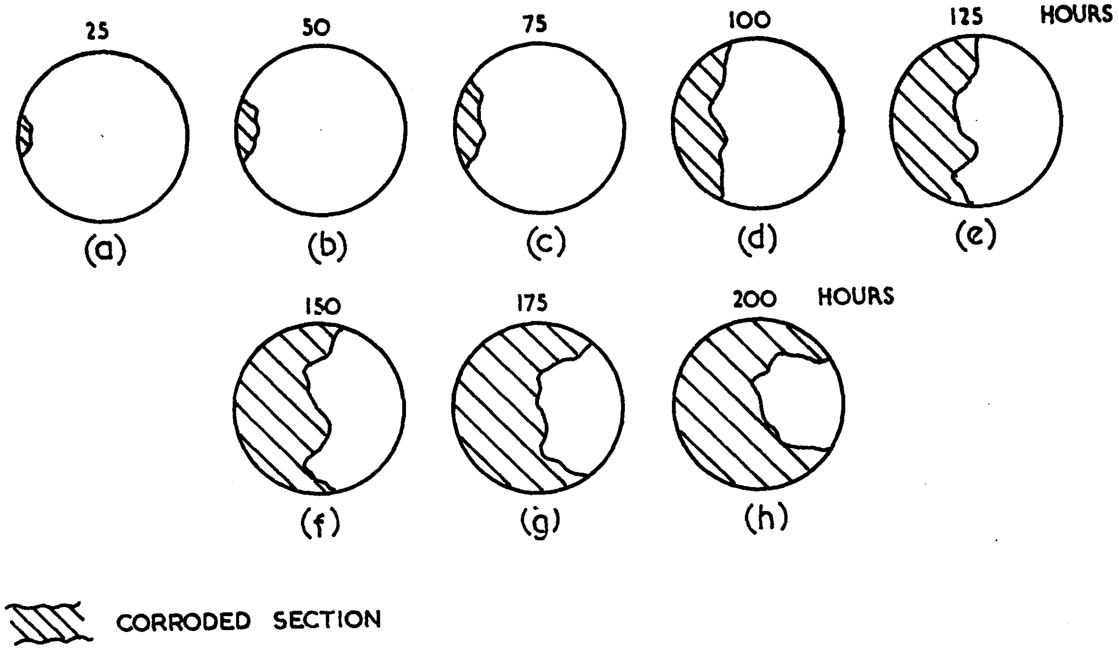
CORROSION OF STRAIN AGED Al-7% Mg ALLOY
NO APPLIED STRESS

FIG. 51

Time of Exposure hours	Breaking Load lbs.	Mean Breaking Load, lbs.	Mean % Loss of Strength
24	133, 131	132	11
31	132, 132, 127	130	12
48	120, 113, 110	114	23
60	109, 107, 104	107	28
76	106, 98, 96	100	32
96	89, 86, 83	86	42
122	80, 77, 66	74	50
144	64, 60, 58	61	59
175	50, 42, 38	43	71
200	41, 38, 31, 30	37	76
247	47, 45, 38, 33, 31, 28	37	76
270	41, 35, 31, 30, 28	33	77
290	31, 29	30	80

The rate of loss of strength of the Al-7% Mg alloy was constant during the first 180 hours or so, after which it decreased rapidly and tended to zero after about 210 hours.

An oxide-hydroxide film became visible after 2-3 hours. The film became progressively more difficult to remove as the time of exposure increased and after about 24 hours it appeared to consist of two layers. A layer next to the alloy surface could be removed only by comparatively severe abrasion or by dissolution in acid: on top of this was a loose, fluffy film which was soft and easily removed by gentle wiping. Observations were made on the inner film by mounting the alloy in plastic and



CROSS-SECTION OF Al-7%Mg ALLOY WITH INCREASING TIME OF EXPOSURE

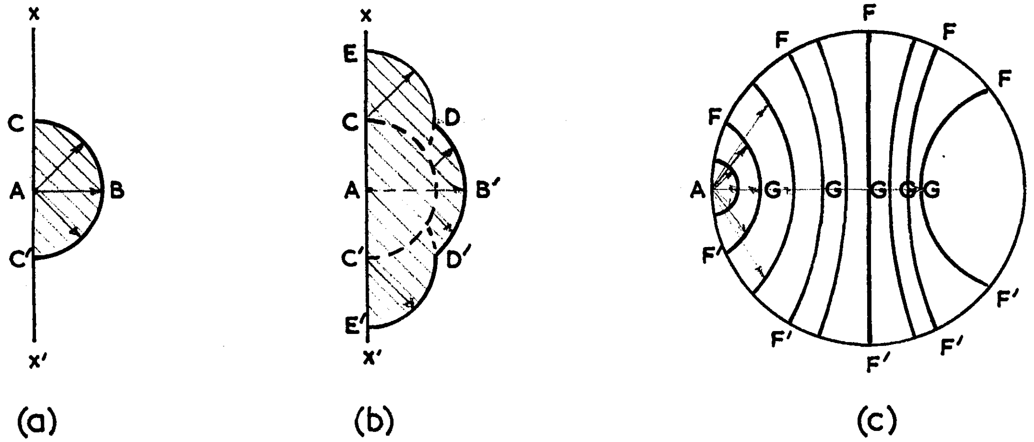
FIG. 52

polishing until a longitudinal cross-section was obtained. This method possibly damaged the film and measurements of the film thickness gave indefinite results. An indication of the nature of the film was given, however, by noting the time required for its dissolution in concentrated nitric acid. It was concluded that the inner film became more resistant with time of exposure up to about 150 hours exposure, after which the results were indefinite.

Observations on the Corrosion of Al-7% Mg Alloy Wire.

Examination of the fracture of specimens broken in the tensile testing machine showed that, in general, the corroded section increased in size as shown in Fig. 52. In the cross-sectional plane of the wire, penetration by intercrystalline attack proceeded as a segment of increasing area. The penetration reached the centre of the section as an approximate semicircle and thereafter tended to envelop an uncorroded portion. When the asýmptotic part of the corrosion-time curve (Fig. 51) had been reached, the fracture was, in general, as indicated in Fig. 52(h).

A possible explanation of the manner in which corrosion proceeded is that the rate of corrosion is proportional to the penetration. Consider a small



(a & b) xx' shows small section of circumference of wire. (b) Front is EDB'D'E'. AE>AB'

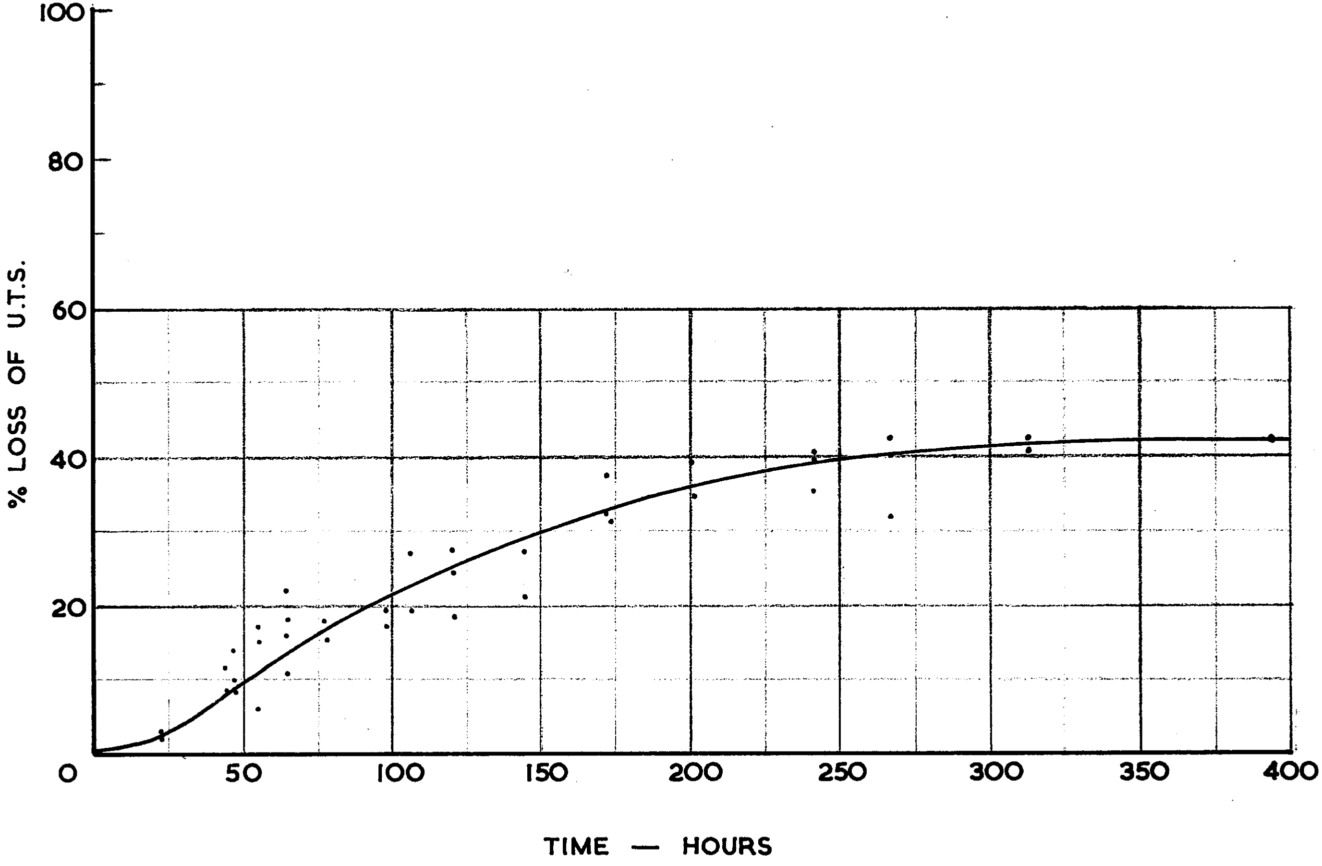
(c) FGF' shows ideal corrosion fronts as corrosion proceeds across section of wire.

FIG. 53

part of the circumference of the cross-section of the wire, Fig. 53(a). Let the corrosion commence at point A. Intercrystalline penetration will proceed in all directions and a corrosion 'front' CBC' will be formed. Initially the area CBC' will be very small and the points C and C' form new points on the surface of the wire from which attack proceeds. Thus new corrosion fronts CDE and C'D'E' are formed. During the interval in which the latter fronts have formed, however, the original front CBC' will have extended, B advancing to B', as shown in Fig. 53(b). This process continues and by addition of the differential fronts, e.g. ED, DB'D', D'E', penetration proceeds as shown in Fig. 53(c). The corrosion front in this case is FGF'.

The intercrystalline material constitutes a relatively small volume of the alloy. As this is attacked by the corroding solution, narrow channels are formed along the grain boundaries. These are filled with the corroding solution linking the bulk of the solution, outside the wire, with the solution engaged in active corrosion at the tip of a channel. The volume of liquid in the channels is relatively small, thus the corroding solution at the tip of a channel is rapidly depleted of its active constituents, viz. dissolved oxygen and chloride ions. Replenishment of active corrodent at the point of attack will be effected by diffusion from the solution outside the surface of the wire, thus it is probable that the rate of replenishment and hence the rate of attack is proportional to the depth of penetration. (Vide also Keatings' remarks on the function of the corrosive medium during stress-corrosion (79)). According to this reasoning, the rate of corrosion will be greatest in the direction AF, AF' (Fig. 53(c)), since the depth of penetration is least, and the rate of corrosion will be least in the direction of greatest penetration, i.e. AG.

As the attack proceeds, a protective film of hydrated alumina is formed on the surface of the wire. The film is a barrier to diffusion of active constituents from the bulk of the corroding solution to that inside the wire, the stifling action increasing as the film increases in thickness. Thus, as the corrosion front moves forward across the section of the wire, the rate of penetration in all directions decreases. The relative effect on the rates of attack in the directions AF and AG (along the



CORROSION OF STRAIN-AGED Al-5% Mg ALLOY
NO APPLIED STRESS

FIG. 54

circumferences and towards the centre of the wire) will depend on the effect of depth of penetration on the rate of attack. It is probable, however, that the shape of the corrosion front changes as it moves forward, as indicated in Fig. 53(d), and may finally tend to that shown in Fig. 52(h), in which the remaining uncorroded section is circular in shape.

Corrosion of Stress-free Al-5% Mg Alloy

The data for the corrosion of stress-free Al-5% Mg Alloy are shown in Table XVIII and graphically in Fig. 54 (OPPOSITE).

TABLE XVIII

Loss of strength of stress-free Al-5% Mg alloy after various times of exposure.

Time of Exposure, hours	Breaking Load, lbs.	Mean Breaking Load, lbs	Mean % Loss of Strength
0	124, 124, 124	124	0
22	121, 120	120	3
42	114, 109	112	10
46	114, 111, 107	111	11
54	116, 110, 105, 103	109	12
64	110, 104, 102, 97	103	17
78	105, 102	104	17
98	103, 101	102	18
106	101, 91	96	23
120	102, 94, 91	96	23
144	98, 90	94	24

Continued

Time of Exposure, hours	Breaking Load, lbs	Mean Breaking Load, lbs	Mean % Loss of Strength
172	84, 78	81	35
200	82, 75	79	36
240	80, 76, 74	77	38
266	85, 75, 72	77	38
312	74, 74, 72	73	41
390	72, 72	72	42
504	70, 66	68	45

The rate of attack on the Al-5% Mg alloy increased somewhat during the first 24 hours and subsequently it gradually decreased, eventually tending to zero. The film formed on the wire appeared to consist of two layers but the outer film was more gelatinous and its volume considerably greater than the outer film formed on the Al-7% Mg alloy.

Conclusions which may be drawn from observations on the corrosion of the stress-free alloys are that film formation plays an important role in retarding the rate of attack. In the case of the Al-7% Mg alloy, the film does not appear to offer an appreciable resistance to the attack until an ideal maximum penetration is attained. Eventually, however, the film offers a high resistance to the attack. The film formed on the Al-5% Mg alloy appears to have given more effective protection, the rate of attack being markedly retarded from the commencement, and only a limited penetration is finally attained.

The nature of the path of easy corrosion along the grain boundaries has a considerable effect on the rate of attack. Microscopic examination of etched specimens indicated that there is a continuous network of material which suffered selective attack along the grain boundaries of both alloys.

Application of Stress to Corroding Alloys.

The effect of tensile stress on the Al-7% Mg alloy was determined by applying stresses below the 0.1% proof stress, removing specimens after various times of exposure and determining the residual strength. Control tests, carried out on specimens completely covered with protective resin, showed that stress alone, when applied for the periods of the stress-corrosion tests, had no effect on the ultimate tensile strength. The loss of strength due to stress-corrosion was then taken as the difference between the loss of strength of a stressed specimen and the average loss of strength of an unstressed specimen after the same period of exposure (vide P. 180). The latter value was taken from the corrosion-time curve, Fig. 51, P. 158.

The loss of strength due to stress-corrosion under various stresses, for increasing time of exposure is given in Table XIX and shown graphically in Fig. 55, P. 166'.

TABLE XIX

Effect of Stress and Time of Exposure on the Stress-corrosion of Al-7% Mg alloy.

Time of Exposure Hours	Mean % Loss of U.T.S. Stressed.	Mean % Loss of U.T.S. Unstressed.	Mean % Loss U.T.S. due to Stress-Corrosion.
A. APPLIED STRESS = 68% U.T.S.: 94% Proof Stress.			
0.5	0 (3)*	0	0
0.75	0.5 (1)	0	0.5
1.00	0.5 (2)	0	0.5
1.08	0.5 (1)	0	0.5
1.17	1.0 (2)	0	1.0
1.28	3.0 (2)	0	3.0
1.42	6.0 (1)	0	6.0
SPECIMENS FAILED IN : 0.7, 1.08, 1.17, 1.22, 1.25, 1.25 1.33, 1.50 hours.			
LOSS OF U.T.S. DUE TO STRESS-CORROSION AT FAILURE = 32%			
B. APPLIED STRESS = 54% U.T.S. : 75% Proof Stress.			
1.0	1.5 (2)*	0	1.5
2.0	4.0 (2)	0	4.0
3.0	7.5 (2)	0.5	7.0
4.0	15 (3)	1.5	14
4.5	16 (2)	1.5	15
5.0	28 (3)	2.0	26
5.3	17 (2)	2.0	15
6.0	31 (2)	3.0	28
SPECIMENS FAILED IN : 4.5, 4.7, 5.3, 6.5, 7.7 hours			
LOSS OF U.T.S. DUE TO STRESS-CORROSION AT FAILURE = 44%.			

Continued

Time of Exposure Hours	Mean % Loss of U.T.S. Stressed.	Mean % Loss of U.T.S. Unstressed.	Mean % Loss U.T.S. due to Stress-Corrosion.
C. APPLIED STRESS = 41% U.T.S.: 57% Proof Stress.			
2.5	4 (2)*	0	4
4.0	12 (3)	1	11
5.0	22 (3)	2	20
5.8	24 (2)	2	22
6.1	30 (2)	3	27
6.5	30 (1)	3	27
7.0	32 (2)	4	28
8.3	34 (1)	4	30
SPECIMENS FAILED IN : 6.3, 6.7, 6.9, 7.3, 7.6 hours			
LOSS OF U.T.S. DUE TO STRESS-CORROSION AT FAILURE = 56%.			
D. APPLIED STRESS = 34% U.T.S.: 47% Proof Stress.			
2.5	1.5 (1)*	0	1.5
4.0	4.5 (2)	1	4.5
5.0	6.5 (2)	2	4.5
6.0	13 (2)	3	10
8.2	26 (2)	4	22
8.8	22 (1)	4	18
9.0	33 (3)	5	28
9.5	33 (2)	5	28
9.7	28 (2)	5	23
10.3	41 (1)	6	35
11.0	38 (1)	6	32
SPECIMENS FAILED IN : 8.5, 8.8, 9.1, 9.7, 9.8, 10.4 hours			
LOSS OF U.T.S. DUE TO STRESS-CORROSION AT FAILURE = 62%			
E. APPLIED STRESS = 20% U.T.S.: 28% Proof Stress			
6.0	4 (1)*	3	1
19.5	18 (2)	8	10
22.0	18 (2)	9	9
24.0	25 (2)	10	15

Continued

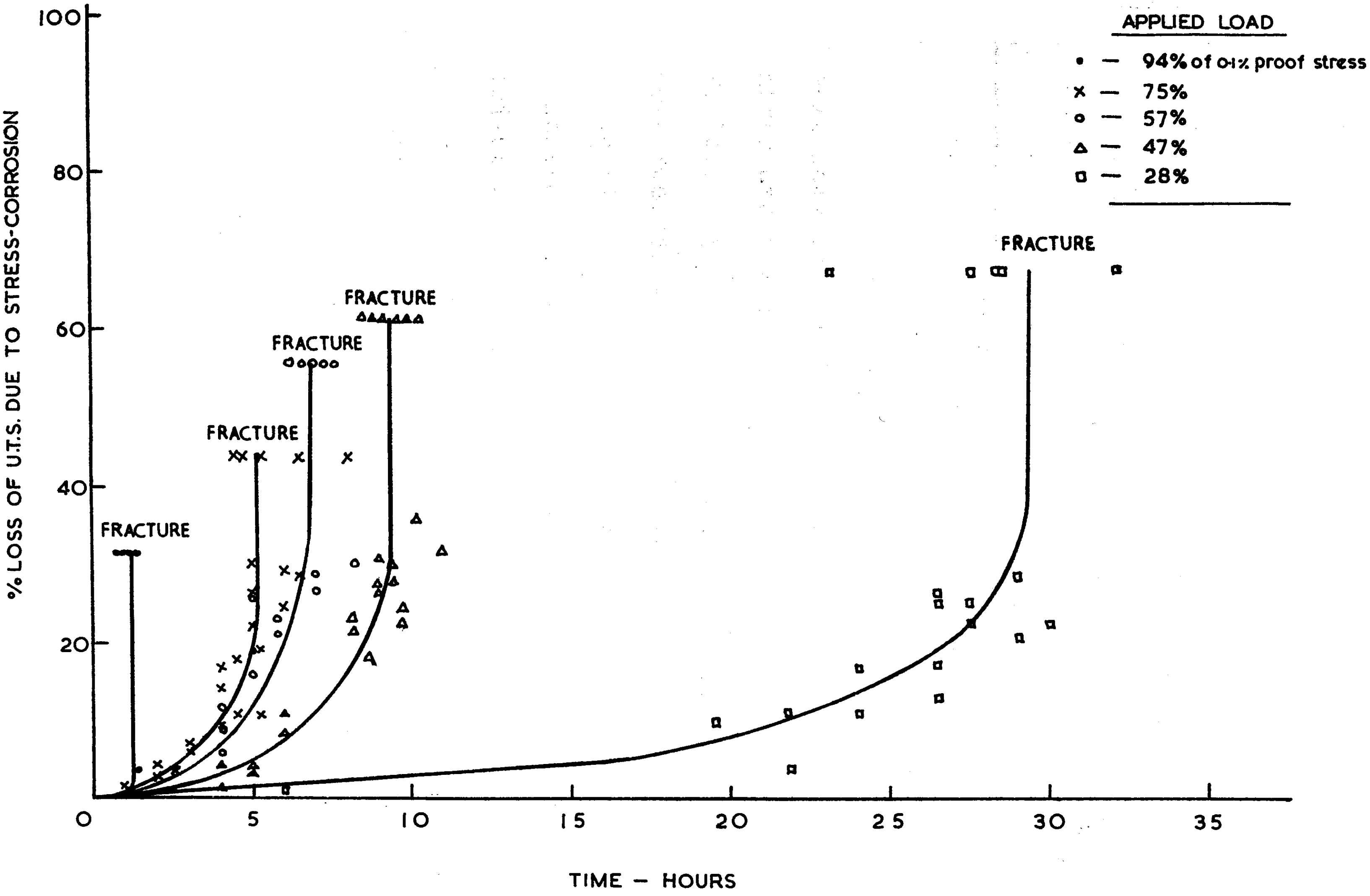

APPLIED LOAD
• — 94% of 0·1% proof stress
× — 75%
o — 57%
△ — 47%
◻ — 28%
FRACTURE
FRACTURE
FRACTURE
FRACTURE
FRACTURE
% LOSS OF U.T.S. DUE TO STRESS-CORROSION
0
20
40
60
80
100
5
10
15
20
25
30
35
TIME — HOURS

FIG. 55

Time of Exposure Hours	Mean % Loss of U.T.S. Stressed.	Mean % Loss of U.T.S. Unstressed.	Mean % Loss U.T.S. due to Stress-Corrosion.
26.5	32 (4)*	11	21
27.5	36 (2)	12	24
29.0	37 (2)	13	24
30.0	36 (1)	14	22

SPECIMENS FAILED IN : 23, 28, 28, 29, 32 hours.

LOSS OF U.T.S. DUE TO STRESS-CORROSION AT FAILURE = 68%

* Number of specimens tested.

Under each condition of stress, several specimens were removed and their residual strength determined after other specimens stressed to the same value had failed. It is therefore probable that some specimens were removed within a very short time of failure, indicating that most of the loss of strength due to stress-corrosion occurred in a short period just before failure.

Similar tests were carried out on the Al-5% Mg alloy, the results being given in Table XX, P.168.

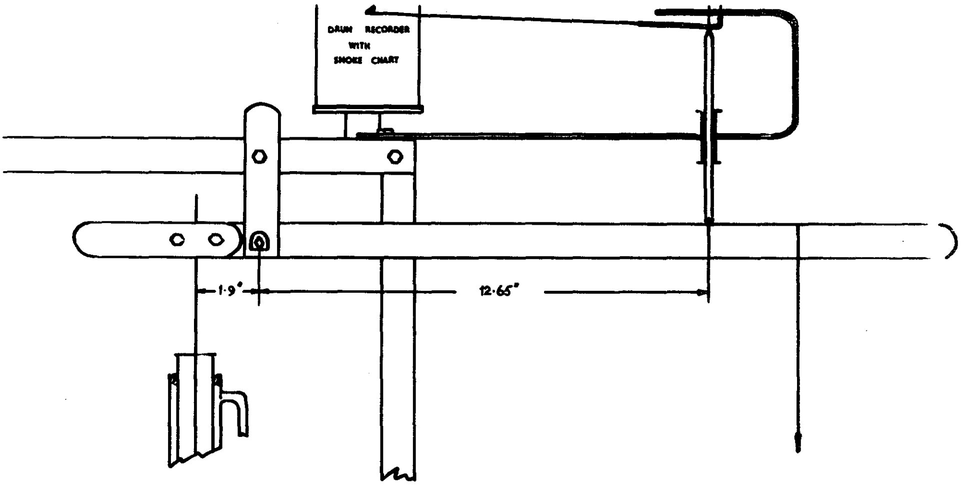
TABLE XX

Effect of Stress and Time of Exposure on the Stress-Corrosion of Al-5% Mg alloy.

Time of Exposure Hours	Mean % Loss of U.T.S. Stressed	Mean % Loss of U.T.S. Unstressed.	Mean % Loss U.T.S. Due to Stress-Corrosion.
A. APPLIED STRESS = 61% U.T.S.: 91% Proof Stress.			
4	1 (2)*	0	1
5	0 (2)	0	0
8	1 (2)	0	1
12	1 (2)	1	0
SPECIMENS FAILED IN : 4, 11, 14, 17, 21 hours.			
LOSS OF U.T.S. DUE TO STRESS-CORROSION AT FAILURE = 38%			
B. APPLIED STRESS = 48% U.T.S.: 73% Proof Stress.			
24	5 (3)*	3	2
32	8.5 (3)	7	1.5
42	11 (3)	9	2
47	14 (3)	10	4
SPECIMENS FAILED IN : 24, 25, 36, 40, 68 hours.			
LOSS OF U.T.S. DUE TO STRESS-CORROSION AT FAILURE = 45%			

*Number of Specimens Tested.

These results, although not so conclusive as those obtained on the Al-7% Mg alloy due to the greater scatter of the times-to-failure of the Al-5% Mg alloy, confirm the inference that most of the loss



APPARATUS FOR MEASURING ELONGATION OF WIRE DURING STRESS – CORROSION

FIG. 56

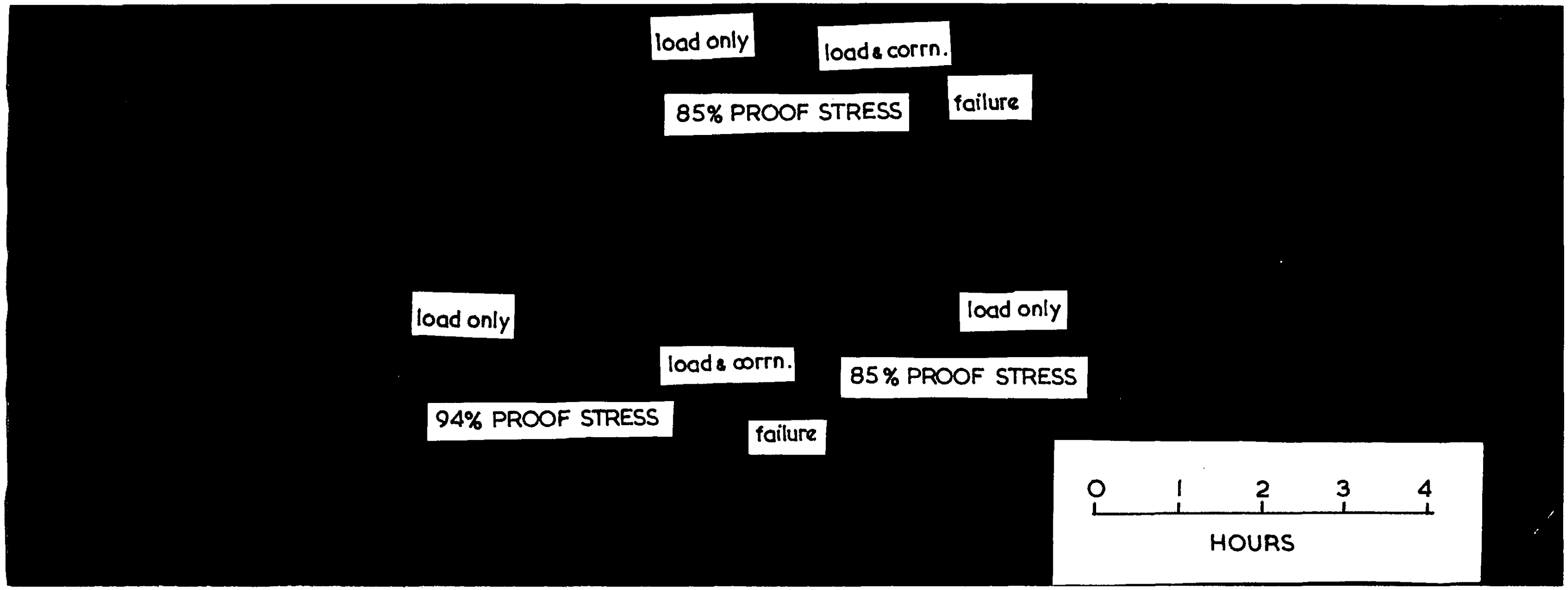
of strength due to stress-corrosion occurred in a short period just before failure.

In order to obtain more information regarding the final period of failure, the elongation of the wires during stress-corrosion was studied, as described below.

Mechanical Disruption during Stress-Corrosion.

It has been suggested that stress-corrosion cracking is discontinuous in nature, as discussed on P. 23. Gilbert and Hadden (45) obtained evidence of this by magnifying the movement of the side of a stressed loop, used in their stress-corrosion tests, and observed that when the specimen was immersed in 6% sodium chloride solution, a crack appeared after about an hour and a series of small jumps occurred in the movement of the loop. At least 20 such movements were observed in the subsequent 2 hours; cracking was complete in about 5 hours. Edeleanu (46) observed that cracks on a stressed specimen became visible only a few minutes before actual failure. It was also observed that there was an increase in the rate of evolution of hydrogen bubbles a few minutes before failure indicating an increase in the corrosion rate in the cracks during the final stages.

It would appear that in the present experiments,



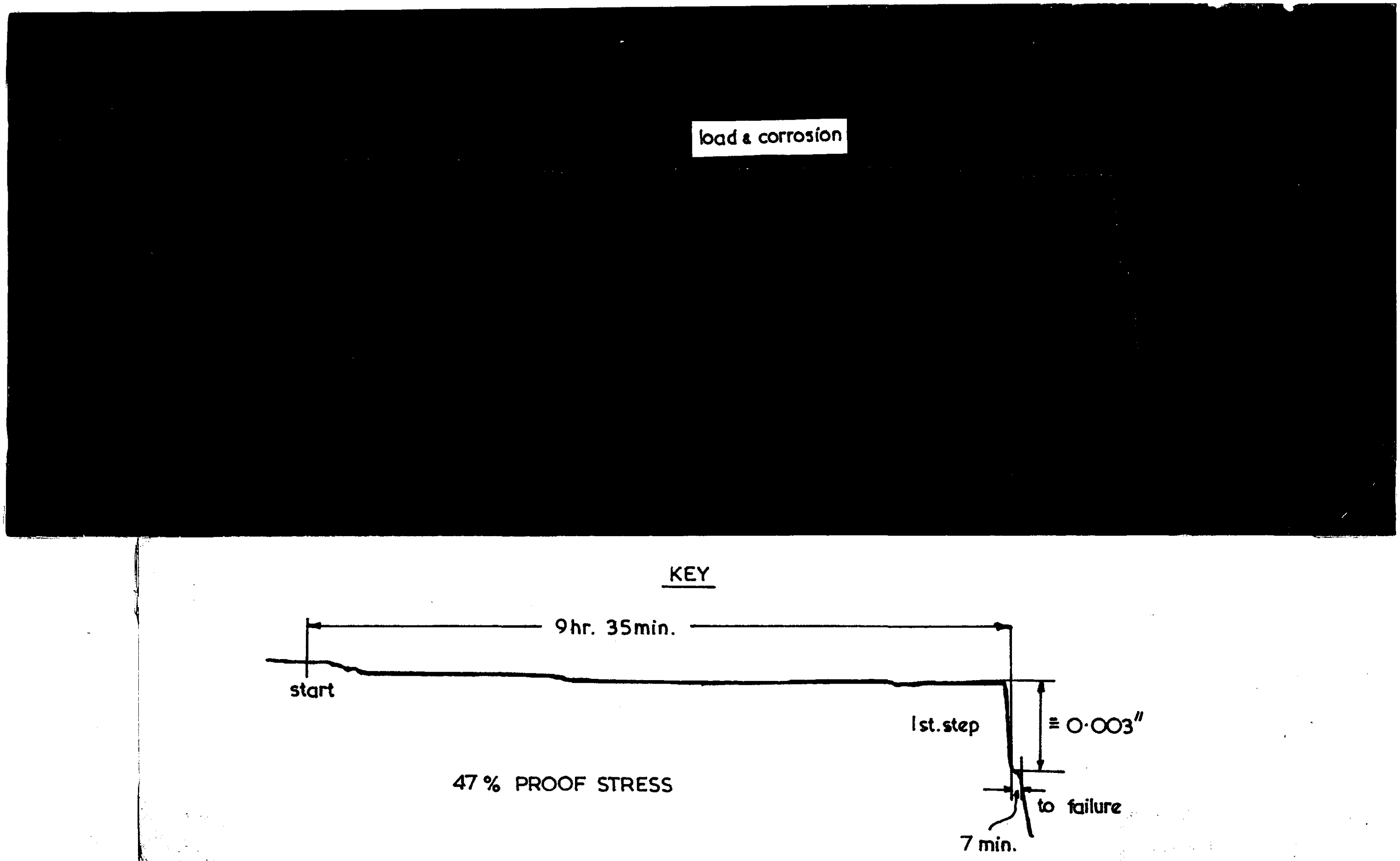
EXAMPLES OF WIRE ELONGATION DUE TO STRESS AND SIMULTANEOUS ACTION OF STRESS AND CORROSION

FIG. 57

the period of failure was limited to a very short interval and in order to obtain more information on this the extension of the Al-7% Mg alloy during stress-corrosion tests was measured by arranging a lever system of magnification as shown in Fig. 56, facing P.169. Any extension was magnified 200 times and recorded on a smoked chart which was wrapped around a clock-work-driven revolving drum.

Tests were conducted in which a specimen was stressed and the extension recorded for a period before immersion in the corroding solution. The recording was then continued during a normal stress-corrosion test.

When stresses in the region of the proof stress were applied, high creep rates were apparent and it was difficult to distinguish between extensions due to creep and those due to stress-corrosion. It was evident, however, that the final failure of the alloy took place in one stage. In all tests with applied stresses of 94% of the proof stress, no change was observed in the nature of the extension curve until 30-40 seconds before fracture when a continuous extension of the wire took place until the specimen fractured. Specimens removed before an



EXTENSION OF WIRE DURING STRESS-CORROSION

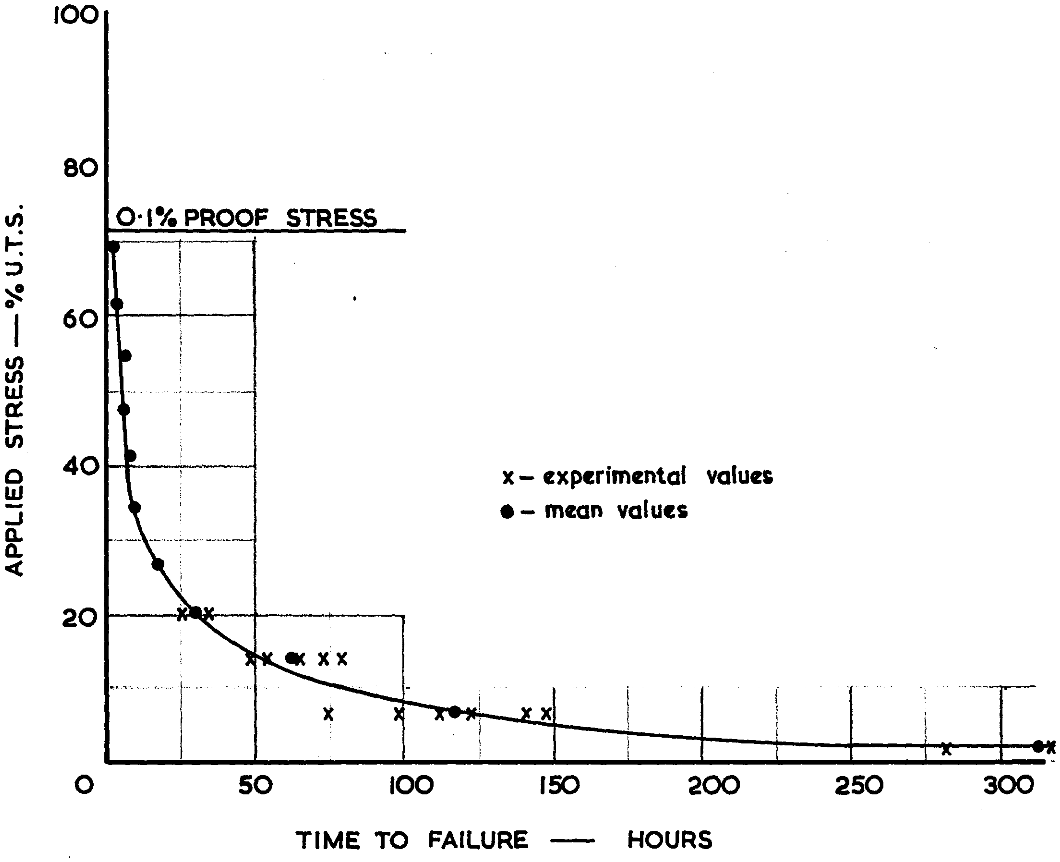
FIG. 58

extension was observed showed only a small loss of strength, but when the stress was removed immediately the final extension became apparent, the breaking strength in all cases was equal to the original applied stress. Therefore the period of final failure, during which nearly all the loss of strength due to stress-corrosion occurred, would appear to be not longer than 30-40 seconds. Typical curves are shown in Fig. 57.

The characteristic creep curves were distinguished for smaller applied stresses, but the final period of failure was longer. In several cases a limited extension occurred, followed by a short interval before a final extension which continued until failure. For example, when a stress of 47% of the proof stress was applied the failure appeared to take place in two stages with an interval of several minutes between each movement, as shown in Fig. 58.

Measurement of the Time-to-failure.

It is apparent from the previous section that assessment of stress-corrosion susceptibility by determination of the residual strength of unfractured specimens can be misleading. The effect of stress on corrosion susceptibility was therefore ascertained



EFFECT OF STRESS ON THE CORROSION OF
STRAIN AGED Al-7%Mg ALLOY

FIG. 59

by recording the time-to-failure of specimens under various applied stresses. The results for the Al-7% Mg alloy are shown in Table XXI and for the Al-5% Mg alloy in Table XXII (P.173).

TABLE XXI

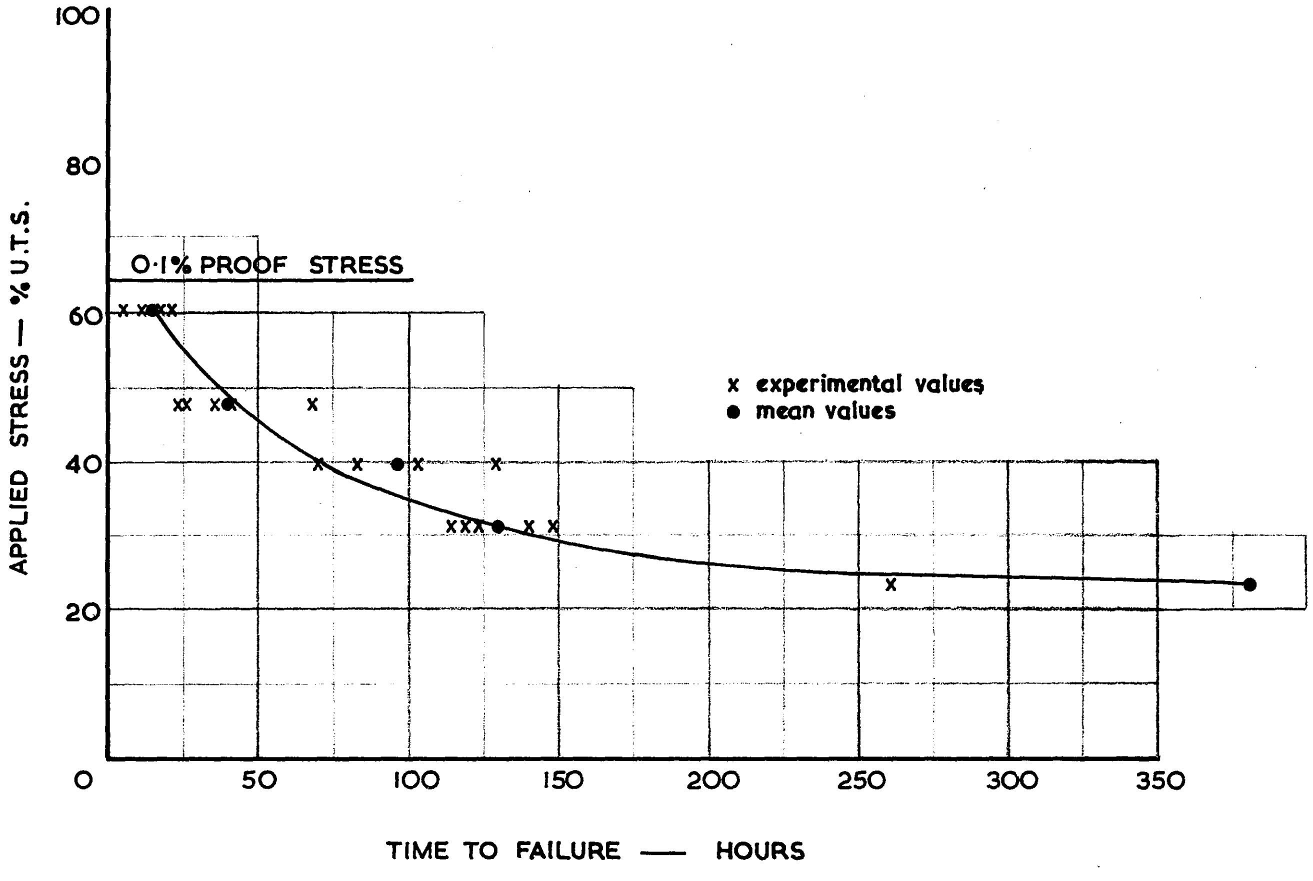
Effect of Stress on the Time-to-failure of Al-7% Mg alloy.

Stress, % U.T.S.	Time-to-failure hours	Mean Time-to-failure hours.	Standard[+] Deviation	Mean % Loss* U.T.S. due to Stress-corrosion.
0.1% Proof Stress = 72% U.T.S.				
68	0.70, 1.08, 1.17, 1.22, 1.25, 1.25, 1.50.	1.2	0.2	32
61	2.25, 2.33, 2.50, 2.75, 2.92.	2.6	0.3	39
54	4.50, 4.67, 5.33, 6.50, 7.67.	5.7	1.3	44
47	3.17, 4.83, 6.17, 6.58, 7.25.	5.6	1.6	51
41	6.25, 6.67, 6.92, 7.33, 7.58.	7.0	0.5	56
34	8.5, 8.8, 9.1, 9.7, 9.8, 10.4.	9.4	0.7	62
27	15.5, 15.8, 16.5, 17.9, 18.3.	16.8	1.3	66
20	23, 28, 28, 29, 32,	28	3	68
14	48, 51, 55, 61, 67, 73, 79.	62	12	62
7	72, 95, 111, 122, 123, 139, 146.	116	25	45
2	280, 301, 319, 350. (5 specimens unbroken after 360 hours)	>312	-	(17)

[+] Standard deviation $= \sqrt{\frac{\Sigma\delta^2}{\phi}}$, δ = (actual value) - (average value)

ϕ = degrees of freedom

*Figures in this column were obtained by subtracting the applied stress from the % residual strength of unstressed specimens for the mean time-to-failure of stressed specimens.



EFFECT OF STRESS ON THE CORROSION OF STRAIN-AGED Al-5% Mg ALLOY

FIG. 60

The results shown in Table XXI indicate that strain-aged Al-7% Mg alloy is susceptible to stress-corrosion cracking with applied stresses as low as 2% of the U.T.S. The time-to-failure increases with decreasing stress except for the range 54%-47% of the U.T.S., when the difference in the time-to-failure is not significant. The loss of strength due to stress-corrosion increases from 32% for an applied stress of 68% of the U.T.S. to 68% for an applied stress of 20% of the U.T.S. Thereafter it decreases rapidly with decreasing applied stress.

TABLE XXII

Effect of stress on the Time-to-failure of Al-5% Mg alloy.

Stress % U.T.S.	Time-to-failure hours.	Mean Time-to-failure hours.	Standard* Deviation	Mean % Loss* U.T.S. due to Stress-corrosion
0.1% Proof Stress = 65% U.T.S.				
61	4, 11, 14, 17, 21,	13	7	38
48	24, 25, 36, 40, 68	39	15	45
40	70, 83, 104, 129	97	26	45
32	115,120,123,141,149	130	15	41
24	262,408,477 (2 specimens unbroken after 540 hours)	>382		(34)
20	(4 specimens unbroken after 560 hours)			
16	No specimens broken after 672 hours, 5 tested.			

* See foot note to Table XXI, P. 172.

It is established that strain-aged Al-5% Mg alloy is susceptible to stress-corrosion, but failure occurs only with applied stresses greater than about 24% of the U.T.S. (37% of the proof stress). The time-to-failure increases with decreasing stress, but the loss of strength due to stress-corrosion is almost constant down to applied stresses of 32% of the U.T.S. Thereafter it decreases somewhat with decreasing applied stress.

Effect of Applied Stresses smaller than the Threshold Stress.

The effect of applied stresses which did not cause failure of the Al-5% Mg alloy was determined by subjecting the alloy to a stress of 16% of the U.T.S., removing specimens at intervals and determining their residual strength. Comparison with the loss of strength of stressed and unstressed specimens is shown in Table XXIII.

TABLE XXIII

Effect of Stress of the Tensile Strength of Corroding Al-5% Mg alloy. Applied stress = 16% U.T.S.

Time of Exposure, hours	Mean % Loss of U.T.S.	
	Without stress	With stress.
96	18	22 (3)*
242	38	43 (2)
350	41	41 (2)
505	46	46 (2)
600	48	50 (2)

* Figure in brackets indicates number of specimens tested.

Whereas stress may have had some effect in the earlier stages, the effect was at least not increased with the time of exposure as occurred when a specimen was subjected to a stress which caused failure (Table XX, P. 168).

Role of Stress and Corrosion.

Certain conclusions may be drawn regarding the role of stress and corrosion in stress-corrosion.

In the early stages, corrosion was almost entirely responsible for the loss of strength incurred. This has also been shown by Edeleanu (46) who demonstrated that there was little difference in the life of a specimen when stress was applied from the commencement of attack or when applied after the specimen had been corroded without stress for a considerable proportion of the total time-to-failure.

When corroded without stress, the rate of penetration along the grain boundaries was gradually retarded by the formation of a protective film, but when stress was applied, there was an increase in the loss of strength which became greater with increasing applied stress. Thus the maximum observed loss of strength due to stress-corrosion before the final period of rapid failure was, in the case of

Al-7% Mg alloy, 24% after 29 hours exposure for an applied stress of 20% of the U.T.S. and approximately constant at about 30% for stresses of 34%, 41% and 54% of the U.T.S. even though the times of exposure were 11, 8 and 6 hours respectively (Table XIX, P.165).

The cross-sectional area of sound metal is reduced by corrosion, thus the applied stress increases and the wire stretches. Elongation may also occur by creep. Thus the protective film on the wire may be weakened or ruptured with consequent increase in the rate of corrosion. Supporting evidence is given by the fact that the contribution of stress before final failure was considerably less in the case of the Al-5% Mg alloy than for the Al-7% Mg alloy (Table XX. P.168), the protective film on the former being thicker and more gelatinous than on the latter and therefore less prone to rupture by stress.

During the final stage of failure Edeleanu (46) observed that there was an increase in the corrosion rate. The effect of stress during this stage has been discussed by several investigators (vide P. 24) and it is considered that stress-concentrations exceeding the yield strength are built up at the base of cracks resulting in local yielding and film rupture followed by further penetration. However, in the light of present observations an alternative theory for the role of stress is discussed in a separate section (P.198).

METHODS FOR EXPRESSING THE EFFECT OF STRESS ON THE CORROSION OF MATERIALS SUSCEPTIBLE TO STRESS-CORROSION

Most of the published work on stress-corrosion is of a qualitative nature, investigations having been directed to the determination of whether a metal or alloy is susceptible to stress-corrosion in various media, and to the study of the effect of composition and heat-treatment on stress-corrosion susceptibility. Much of the quantitative work which has been published is of little value because the corrosion susceptibility of the material in the stress-free condition has not been determined.

The stress-corrosion experiments conducted on the aluminium-magnesium alloys in buffered sodium chloride solution, described in this thesis, were designed so that the loss of ultimate tensile-strength due to corrosion acting alone and due to stress and corrosion acting simultaneously were determined. In the present section, methods are suggested whereby the effect of stress on the corrosion of materials susceptible to stress-corrosion is expressed on a comparative basis, the corrosion of the stress-free material being taken into account. The methods are illustrated by using the data obtained on the alloys investigated in the present work.

Presentation of Stress-Corrosion Data

Stress-corrosion implies a greater deterioration in the mechanical properties of the material through the simultaneous action of static stress and exposure to a corrosive environment than would occur by the separate, but additive, action of these agencies (vide P.18). Thus, if:

S_s = % loss of U.T.S. when corroded under static stress,
S_u = % loss of U.T.S. when corroded without stress for the same period of exposure,
S_1 = % loss of U.T.S. when stressed to the same extent and for the same period, but not exposed to the corrosive environment,

evidence of stress-corrosion is provided if S_s is greater than $(S_u + S_1)$. A function f_s may be defined as the increase in the loss of tensile strength due to the application of stress during corrosion, i.e.

$$f_s = S_s - (S_u + S_1) \quad \ldots \quad \ldots \quad \ldots \text{Eqn. 1}$$

f_s is thus the % loss of U.T.S. due to stress-corrosion. (Vide also Perryman & Hadden (16)).

It has been shown by Liddiard (38), Perryman &

Hadden (40), Edeleanu (46) and also in this thesis (P.167) that the effect of stress is most marked in the last stages of the life of a specimen. During the time prior to the period when stress exerts this marked effect, the application of stress may have a relatively small effect (vide Table XIX, P. 165). Hence, as Perryman & Hadden point out, in order to gain a true assessment of stress-corrosion susceptibility, it is necessary to expose some specimens to failure.

A true assessment of stress-corrosion susceptibility may be obtained if the loss of strength due to stress-corrosion is taken as the effect of the application of stress during corrosion at the time of failure. Thus, if:

S_s^c = % loss of U.T.S. at failure when corroded under stress,
S_u^c = % loss of U.T.S. of unstressed specimen exposed to the time-to-failure of the stressed specimen,
S_1^c = % loss of U.T.S. of a specimen stressed to the same extent and for the time-to-failure, but not exposed to the corrosive environment,

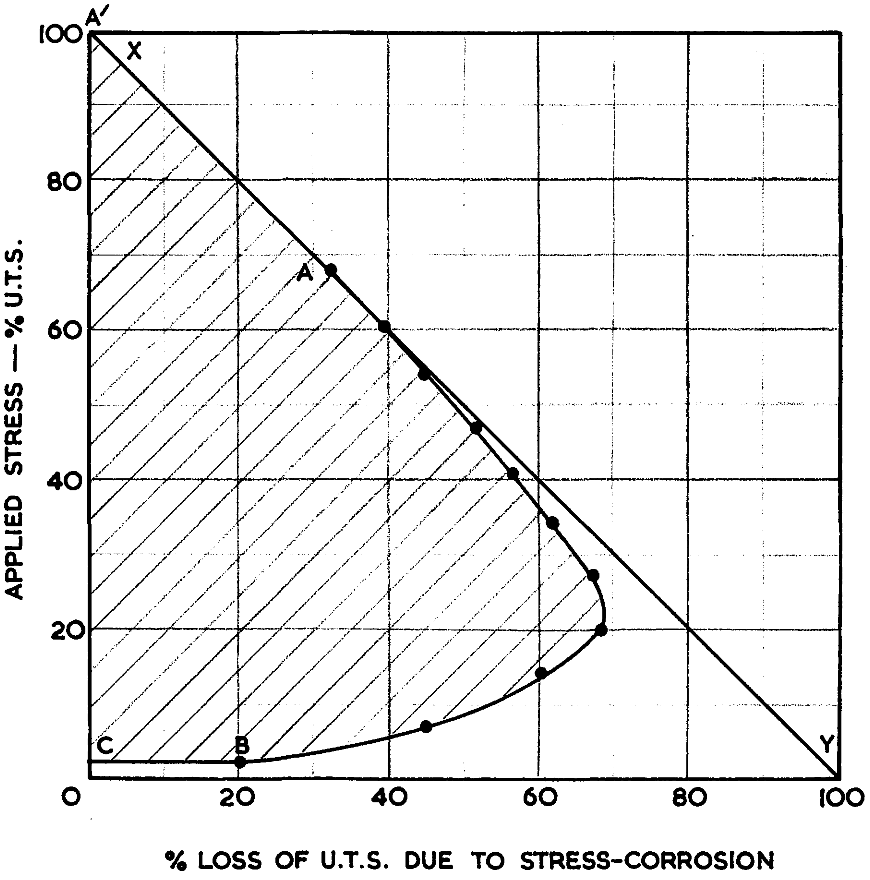
$$f_s^c = S_s^c - (S_u^c + S_1^c) \qquad \dots \qquad \dots \qquad \dots \text{ Eqn. 2}$$

where f_s^c is the % loss of U.T.S. due to stress-corrosion at failure.

For example, an applied stress of 41% of the

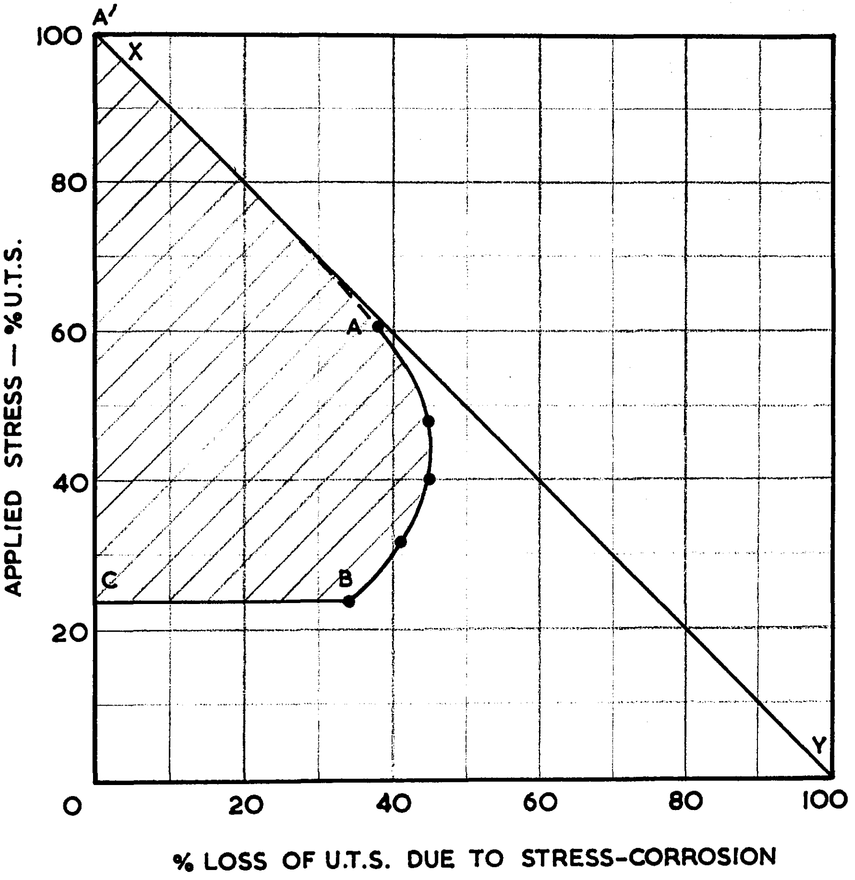
U.T.S. (57% of the proof stress) resulted in failure of Al-7% Mg alloy in an average time of 7 hours (Fig. 59, P.172). The loss of strength at failure (S_s^c) was thus (100 - 41), i.e. 59% of the U.T.S. After 7 hours, the average loss of strength when corroded without stress (S_u^c) was 3% of the U.T.S. (Fig. 51, P. 158). Application of stress to the uncorroded alloy had no effect. Thus, the loss of strength at failure which was due to stress-corrosion (f_s^c), as defined above, was (59 - 3) i.e. 56% of the U.T.S.

A curve may be drawn showing the loss of strength at failure which was due to stress-corrosion for various applied stresses by plotting f_s^c against the applied stress. Such curves for Al-7% Mg and Al-5% Mg alloys are A.B. in Figs. 61 & 62 respectively. The times-to-failure under various applied stresses and the loss of strength when corroded without stress for the time-to-failure were taken from the respective curves for the corrosion v. time and applied stress v. time-to-failure, Figs. 59 & 51, P. 172 & 158 for the Al-7% Mg alloy and Figs. 60 & 54, P. 173 & 162 for the Al-5% Mg alloy. (Vide also Tables XXIV & XXV, P. 187).



EFFECT OF STRESS ON THE CORROSION OF STRAIN AGED Al–7% Mg ALLOY

FIG.61



EFFECT OF STRESS ON THE CORROSION OF
STRAIN-AGED Al-5% Mg ALLOY

FIG. 62

Limit of Stress-Corrosion Susceptibility

Ideally, a material with the maximum susceptibility to stress-corrosion fails when stressed during exposure to a corrosive environment, but suffers no loss of strength when subjected to the separate action of stress and corrosion, i.e. the loss of strength at failure is entirely due to stress-corrosion. Thus,

$$\text{Max. } f_s^c = \frac{\text{U.T.S. - stress applied}}{\text{U.T.S.}} \times 100 \quad \ldots \quad \ldots \text{Eqn. 3}$$

$$\text{or Max. } f_s^c = 100 - P \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \text{Eqn. 4}$$

Where P is the stress applied expressed as a % of the U.T.S.

A line X.Y. may be drawn in Figs. 61 & 62 satisfying Eqn. 4. This represents the maximum % loss of strength due to stress-corrosion which is theoretically possible under any applied stress. If a material has no stress-corrosion susceptibility, f_s^c is zero for all applied stresses. Hence the curve A.B., showing the experimental results, must lie within the area bounded by O.X.Y. The stress-corrosion susceptibility of a material subjected to any applied stress may then be assessed by comparison of the actual loss of strength due to stress-corrosion, as given by A.B., and the maximum value, as given by X.Y.

Comparison of Stress-Corrosion Susceptibility

The stress corresponding to point B (Figs. 61 & 62, P.182) is the lowest which was observed to cause failure of the alloys by stress-corrosion, and in the case of the Al-5% Mg alloy, stresses smaller than that corresponding to B (Fig. 62) had little effect on the residual strength of the alloy (vide Table XXIII, P.174). Hence, the stress corresponding to B is approximately equal to the threshold stress, i.e. the maximum stress which the alloy will sustain without failure by stress-corrosion (43). The position of A.B. for various materials may vary from the applied stress axis to X.Y., thus the area between A'.B., where A' is the value of A extrapolated to an applied stress equal to the U.T.S., and the applied stress axis is a measure of the effect of stress on the corrosion of the material. This is the shaded area A' .B.C. for the alloys examined (Figs. 61 & 62). The "area of stress-corrosion" for a material with the theoretical maximum stress-corrosion susceptibility is O.X.Y., whilst for a material with no stress-corrosion susceptibility the area is zero. The area of stress-corrosion obtained from the experimental data may therefore be expressed as a percentage of the maximum area, and it is suggested that the susceptibility of materials to stress-corrosion may thus be expressed on a comparative basis. An alloy with the theoretical maximum stress-corrosion susceptibility will have a value of 100%, and if there is no tendency to stress-corrosion the value is0%.

The results for the two alloys examined were:-

Stress-corrosion susceptibility of Al-7% Mg alloy = 79%
Approximate threshold stress = 2% of the U.T.S.

Stress-corrosion susceptibility of Al-5% Mg alloy = 45%
Approximate threshold stress = 24% of the U.T.S.

Alternative Method for Presenting Stress-Corrosion Data

The method for presenting stress-corrosion data as discussed above and illustrated in Figs. 61 & 62, is possibly the simplest. It has the disadvantage, however, that assessment of the effect of stress necessitates comparison of two values of the loss of strength due to stress-corrosion viz. the experimental and the theoretical maximum value, both of which vary with the applied stress. This disadvantage may be overcome by fixing one of these values so that it is independent of the applied stress.

Define a function of the stress-corrosion at failure, g_s^c, as the ratio of the % loss of strength due to stress-corrosion to the ideal maximum % loss of strength due to stress-corrosion for the same applied stress, expressed as a percentage. Thus,

$$g_s^c = \frac{f_s^c}{\text{Max. } f_s^c} \times 100 \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \text{Eqn. 5}$$

$$\text{or} \quad g_s^c = \frac{S_s^c - (S_u^c + S_1^c)}{S_s^c} \times 100 \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \text{Eqn. 6}$$

(Nomenclature as previously, P.180).

Thus g_s^c is the % of the loss of strength at failure which is due to stress-corrosion.

The maximum value of g_s^c which is theoretically possible occurs when the loss of strength is entirely due to stress-corrosion,

i.e. $(S_u^c + S_1^c) = 0$. Thus,

$$\text{Max. } g_s^c = 100 \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \text{Eqn. 7}$$

which is independent of the applied stress. When there is no stress-corrosion susceptibility,

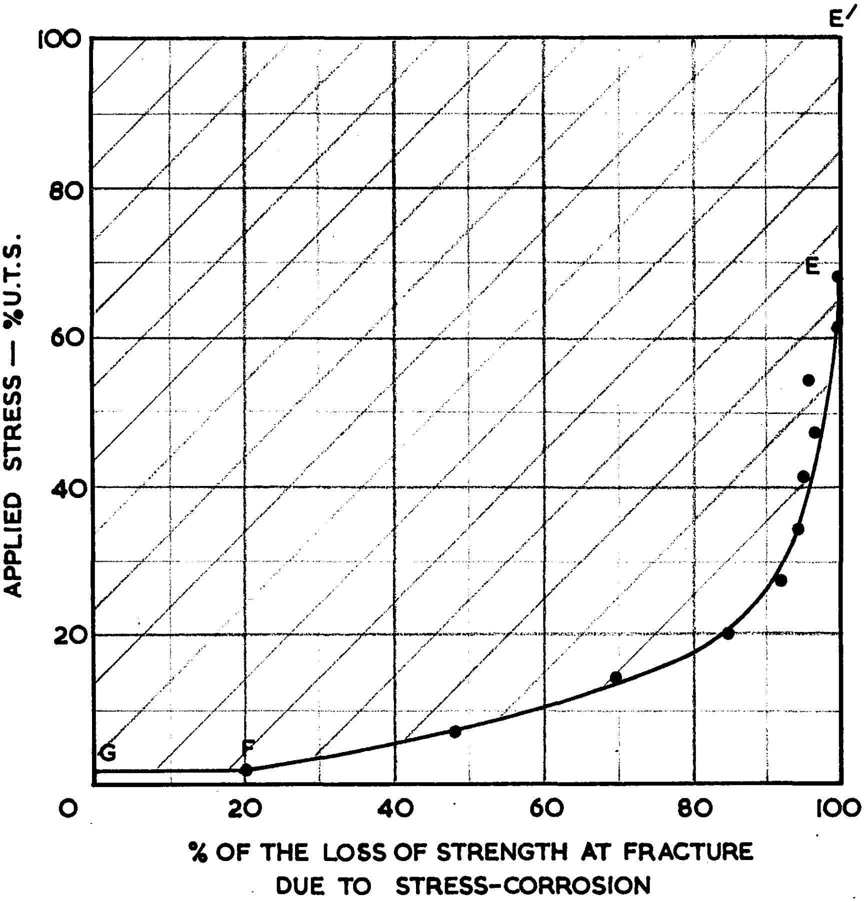
$(S_u^c + S_l^c)$ is equal to S_s^c, thus g_s^c is zero for all applied stresses.

The effect of stress on corrosion may be illustrated by plotting the % of the loss of strength at failure which is due to stress-corrosion (g_s^c) against the stress applied. Curves E.F. are obtained for Al-7% Mg and Al-5% Mg alloys in Figs. 63 & 64 respectively. Data for plotting these curves are given in Tables XXIV & XXV, below.

TABLE XXIV

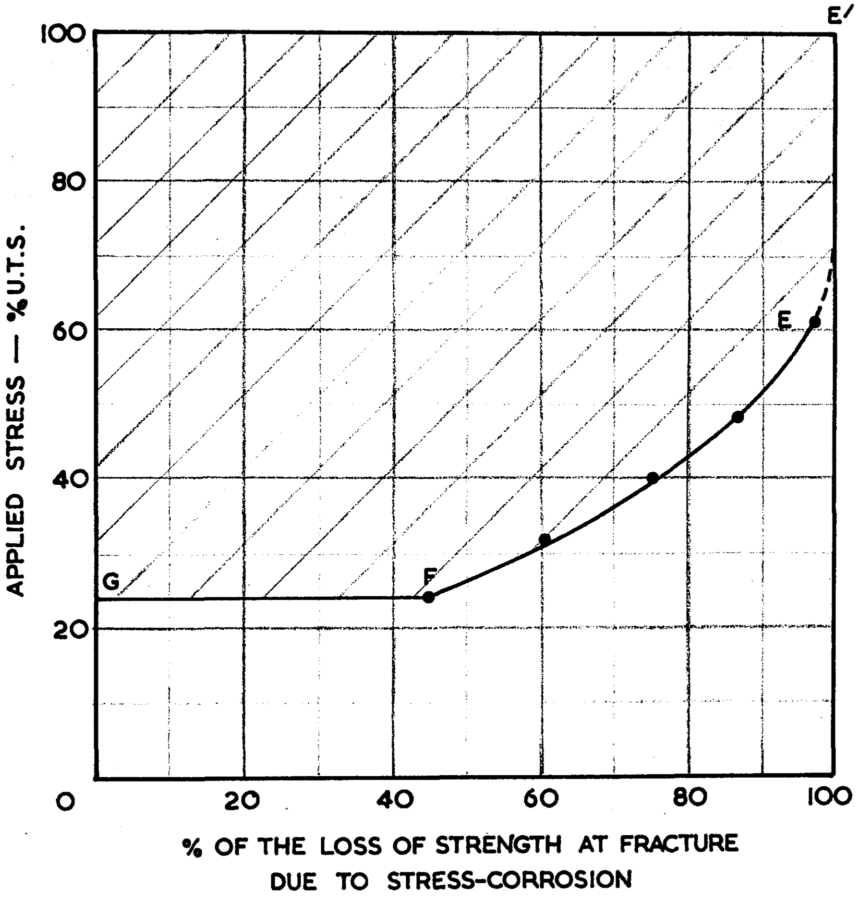
Stress-Corrosion Data for Al-7% Mg alloy.

Applied Stress, % U.T.S.	Mean Time-to-failure, hours. (Fig.59,P.172)	Loss due Corrn. only, % U.T.S. (Fig.51,P.158)	% Loss U.T.S. due Stress-Corrosion f_s^c	% of loss U.T.S. due Stress-Corrosion g_s^c
68	1.2	0	32	100
61	2.6	0	39	100
54	5.7	2	44	96
47	5.6	2	51	96
41	7.0	3	56	95
34	9.4	4	62	94
27	16.8	7	67	92
20	28	12	68	85
14	62	26	60	70
7	116	48	45	48
2	312	78	20	20



EFFECT OF STRESS ON THE CORROSION OF STRAIN AGED Al–7% Mg ALLOY

FIG. 63



EFFECT OF STRESS ON THE CORROSION OF STRAIN-AGED Al-5% Mg ALLOY

FIG. 64

TABLE XXV

Stress-Corrosion Data for Al-5% Mg Alloy

Applied Stress, % U.T.S.	Mean Time-to-failure, hours: (Fig.60,P.173)	Loss due Corrn. only, % U.T.S. (Fig.54,P.162)	% Loss U.T.S. due Stress-Corrosion f_s	% of Loss U.T.S. due Stress-Corrosion g_s
61	13	1	38	98
48	39	7	45	87
40	68	15	45	75
32	130	27	41	60
24	382	42	(34)	(45)

By a reasoning similar to that discussed on P.184, expression of the area bounded by E'.F.G., where E' is the value of E extrapolated to the U.T.S., as a percentage of the maximum area, i.e. that bounded by the axes, together with the threshold stress, appears to give a useful summary of the stress-corrosion susceptibility of a material.

The results for the two alloys examined were:

Stress-corrosion susceptibility of Al-7% Mg Alloy = 85%
Approximate threshold stress = 2% of the U.T.S.

Stress-corrosion susceptibility of Al-5% Mg alloy = 67%
Approximate threshold stress = 24% of the U.T.S.

DISCUSSION ON THE MECHANICAL ASPECTS OF STRESS-CORROSION

Stress Concentration at the Base of Cracks

Many of the theories of stress-corrosion which have been put forward are based on the assumption that a local stress concentration is built up at the base of a narrow crevice formed by corrosion, the initial production of such a crevice being due to some kind of selective attack, usually along the grain boundaries. These views have been discussed in the literature survey of this thesis (P.24).

If, in a tension member, a fine crack is of such dimensions that the stress concentration at its base exceeds the yield strength, a small region at the base of the crack will yield and the radius of curvature at the base of the crack increases so that the stress concentration is reduced to below the yield strength (80). If such a member is slowly loaded to fracture, the breaking stress of the original sound area of metal is at least not less than that of an unnotched specimen. Thus, although the theoretical stress concentration at the base of a crack may be many times the yield strength, relief is given by local yielding and the ultimate breaking stress is not appreciably affected.

It may be visualised that if in a specimen stressed in tension, a crack is formed perpendicular to the direction of the stress by corrosive action, yielding of a small region at its base will occur soon after the stress concentration has exceeded the yield strength and the stress will be relieved by an increase in the radius of curvature. Further corrosion may subsequently reduce the radius of curvature so that the yield strength is again exceeded and the process continues until the applied tensile stress is greater than the ultimate strength of the residual sound metal. The time required between each yielding decreases since the applied stress increases with decreasing area of sound metal. However, unless the corrosive action which reduces the radius of curvature between successive processes of yielding is very rapid, the rate of decrease in strength of the metal will not increase appreciably until the applied stress exceeds the yield strength of the residual sound metal. Yielding of the whole section will then occur. Subsequent propagation of the crack will then occur with rapid acceleration, although complications may arise due, e.g., to work hardening of the metal, and to the fact that no two specimens will behave in exactly the same manner. Values for the oxidation of aluminium as observed by Steinheil and quoted by Champion (53) show that a film is formed on the oxide-free metal with extreme rapidity, subsequent building up of the film following an exponential law. A film 0.0104 microns thick was formed in 1.3 minutes whilst after 30 days the thickness was 0.0410 microns. Therefore, if it be considered that rapid corrosion occurs at the base of a crack after yielding and relief of stress concentration due to exposure of the metal by film rupture, it would appear that this is to a very limited extent due to the rapid film repair.

Calculation of stress concentration at base of cracks.

The stress concentration factor has been evaluated by Inglis (80) for an elliptical hole 2a x 2b in a plate subjected to a uniform tensile stress f as:

$$f_A = f\left\{1 + 2\sqrt{\frac{a}{\rho}}\right\} \qquad \text{——— Eqn. 1}$$

where f_A = the tensile stress at the base of the hole,
a = half the major axis of the ellipse and therefore the depth of the hole,
ρ = the radius of curvature at the end of the major axis of the ellipse, i.e. at the base of the hole.

It is considered that a fine crack is an ellipse with a very high ratio of a : b, and Keating (43) has applied the above equation to show the extent to which stress concentration varies with the dimensions of a crack as shown in Fig. 64(a).

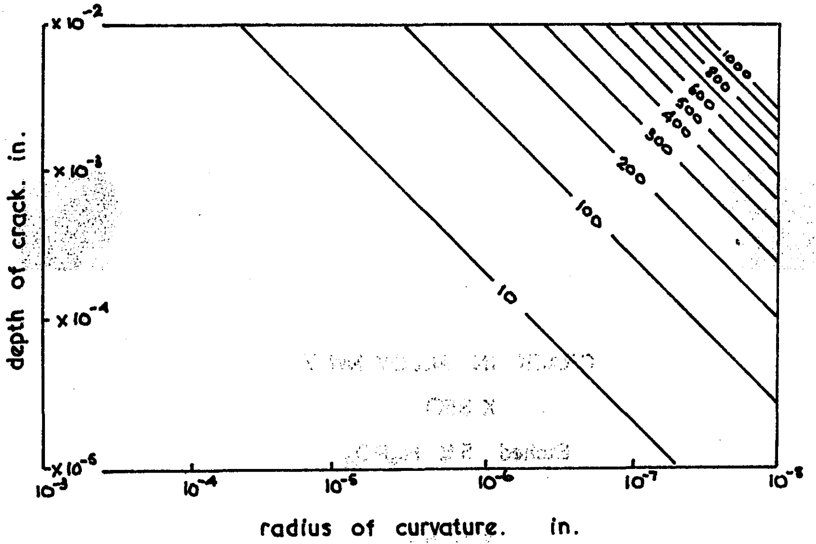
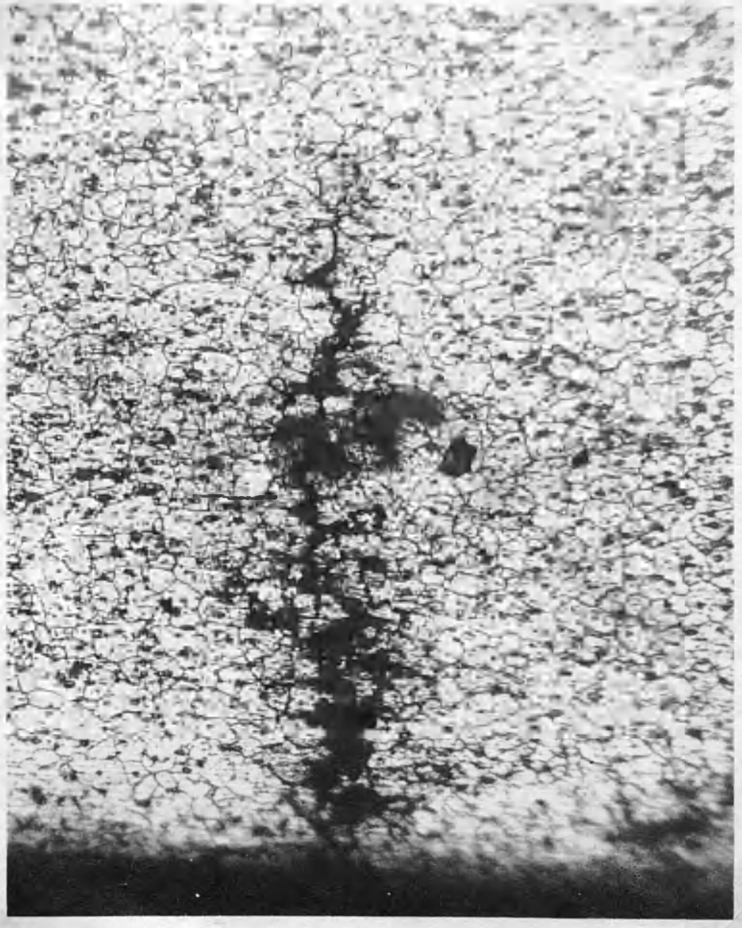


FIG. 64(a)



CRACK IN ALLOY NW.7

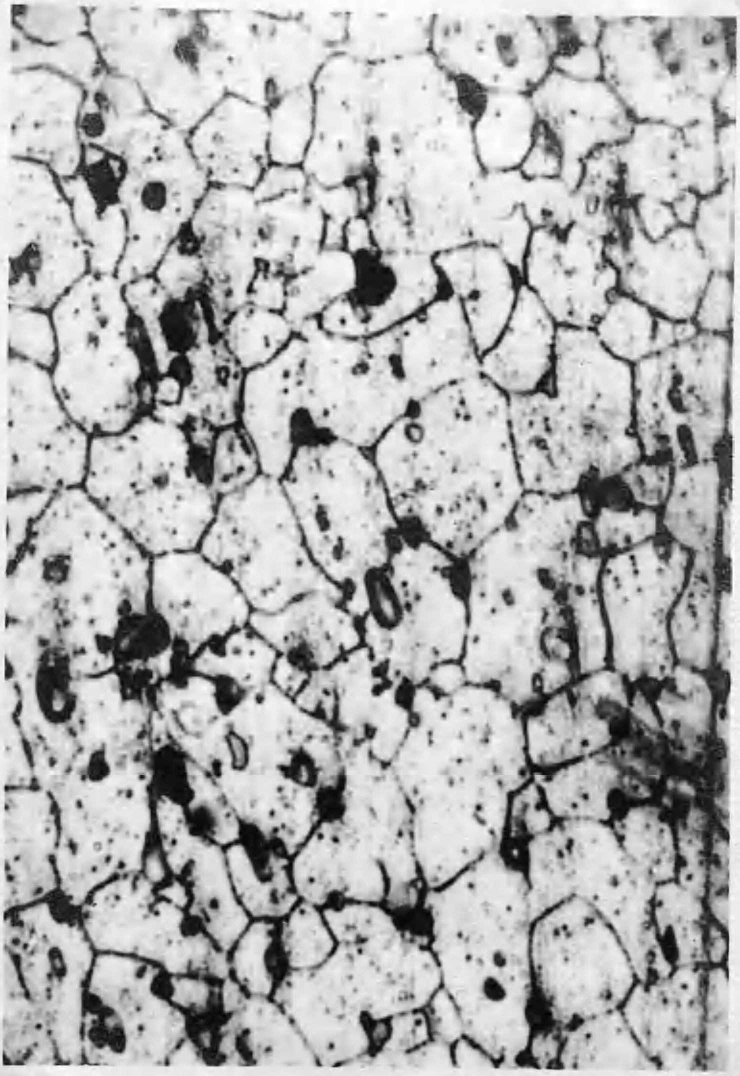
X 350

Etched 5% H_3PO_4

FIG. 65

Very small changes in the depth and radius of curvature at the base of a crack may result in very large changes in the stress concentration factor.

Fig. 65 shows a photomicrograph of a crack in a specimen of NW.7 which failed when subjected to a load of 85% of the proof stress at another section of the metal. Thus the crack shown is a subsidiary one in which the stress concentration apparently did not exceed the yield strength of the metal, or if it did so this crack did not propagate to the extent offailure. Since the crack follows the grain boundaries of the alloy, the radius of curvature at the base is not more than half the width of the grain boundary. This value may be estimated from Fig. 66 which shows the grain boundaries magnified 1500 times and is about 4.10^{-6} in., the depth of the crack being about 10^{-2} in. Hence, when the specimen is subjected to load the stress concentration at the tip, as calculated from Equation 1, was apparently more than 100 times the applied stress. Keating suggests that the tip of a crack is the minute opening between planes of atoms, in which case the stress concentration would be considerably higher than that calculated.



STRAIN AGED MW.7

X 1500

FIG.66

Such a high stress concentration would be expected to result in immediate tearing of the specimen.

Gilbert and Hadden (45) enlarging the views of Keating as a result of their experimental work, put forward the following reasons to explain why local mechanical fractures occurring during stress-corrosion, once started, should stop after making limited progress:

(a) The formation of subsidiary crevices in the vicinity of the main crevice would reduce the stress concentration.

(b) The stress concentration may be reduced owing to an increase in the radius of curvature at the tip of the crevice; this could occur for a number of reasons, e.g. encountering an obstacle such as an inclusion.

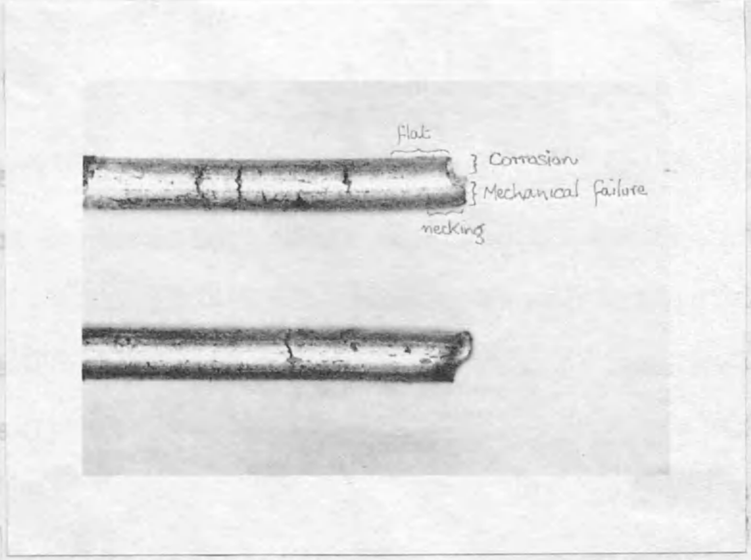
(c) The fracture might stop when an unsuitably orientated grain boundary was reached, because only a component of the stress at the tip of the crevice is acting to cause fracture along a grain boundary not perpendicular to the stress direction.

(d) If the stress concentration necessary to cause fracture along a grain boundary containing β is less than that necessary to cause fracture along a boundary not containing β, it is possible that fracture may be stopped when a gap in the β at the grain boundaries is encountered.

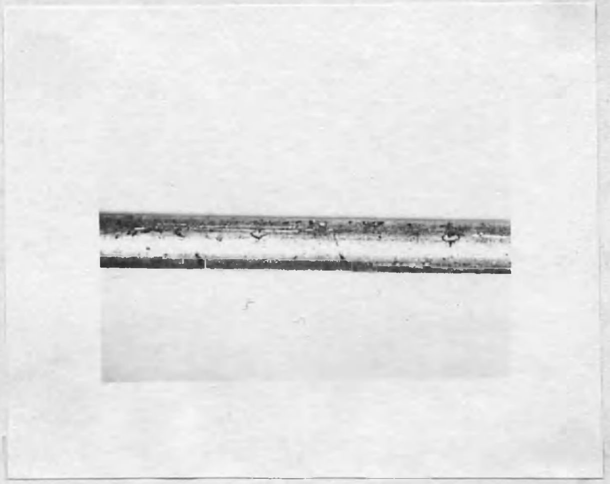
The above views may be divided into two classes: in (a), (b) and (c) the value of the stress concentration is reduced by some means and in (d) the stress concentration remains constant but the strength of the material along the grain boundary varies. It is difficult to appreciate that in the former class, reduction of stress from 100 times the applied stress to a value which does not exceed the yield strength occurs or that in the latter class, the difference in strength between grain boundaries containing β and those not containing β is 100 fold. A possible explanation is that the equation for the stress concentration at the base of an elliptical hole is applicable only within limits of the ratio of the major axis to the minor axis, for as the ratio of a : b increases, f_A tends to infinity. It is more probable that f_A tends to some maximum value as a : b increases and therefore the equation for the stress concentration at the base of an elliptical hole is modified to:

$$f_A = f \left\{ 1 + \left[2\sqrt{\frac{a}{\rho}} \cdot \quad G \cdot \frac{a}{b} \right] \right\} \qquad \text{Eqn. 2}$$

where $G \cdot \frac{a}{b}$ is some function of the ratio of a : b. The stress concentration at the base of a crevice may therefore be very much less than that indicated in Fig. 64(a), in which case the reasons for limited mechanical fractures can be more readily understood.



TYPICAL STRESS-CORROSION FAILURES, Al-7% Mg ALLOY
Subsidiary cracks visible on wire



UNSTRESSED WIRE EXPOSED FOR SAME PERIOD

FIGS. 67 & 68

ALTERNATIVE THEORY OF THE MECHANICAL ROLE OF STRESS

Experimental observations

During the experimental work on the Al-7% Mg alloy, it was observed that when a specimen failed, part of the section at the crack showed destruction purely by mechanical damage whilst the remainder showed destruction by corrosive action. The section which failed mechanically was irregular and slight necking of the wire was evident whereas the corroded section was almost flat with no necking of the wire. Figs. 67 & 68 show two typical stress-corrosion failures. Confirmation of the two types of failure were obtained by microscopic examination of the section at which failure occurred. Mechanical failure was evident by elongation of the grains, corrosive failure by intercrystalline attack.

In most cases the section which had failed by corrosive action and combined corrosive action and stress was a circular segment, the base forming an approximate chord of the circular cross-section of the metal. Furthermore, several fairly large cracks were formed at other points along the surface of the wire which was exposed to the corroding medium, the magnitude of these cracks, in general, decreased with distance from the point of fracture although a large number of very small cracks were visible along the whole length of the specimen. Exposure of the section of the larger cracks showed that they were in various stages of development from a small pit to a segment of the cross-section. These proved difficult to photograph as opening up the cracks deformed the adjacent metal to such an extent that the whole cross-section could not be brought into focus. A sketch of the observations is given below in Fig. 69:

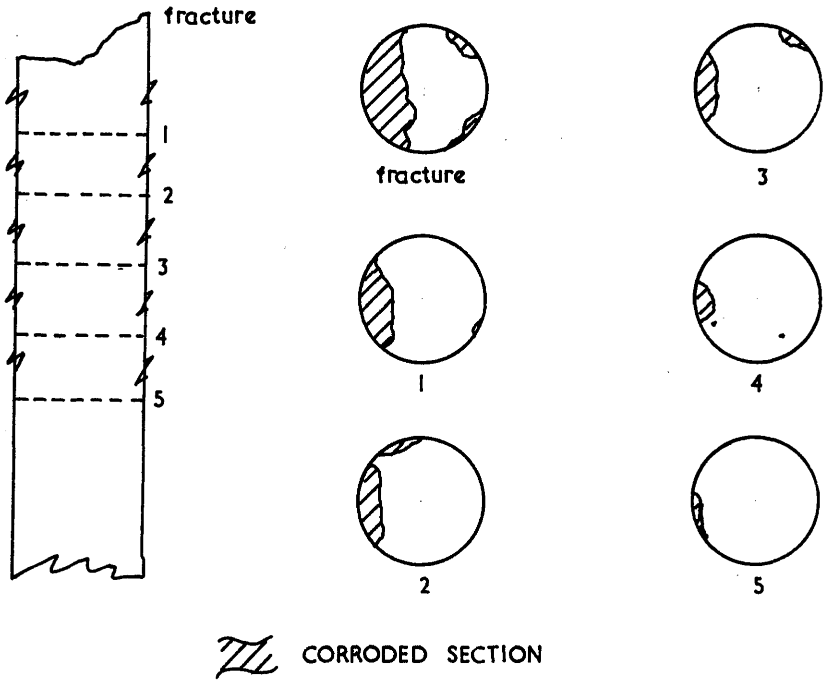
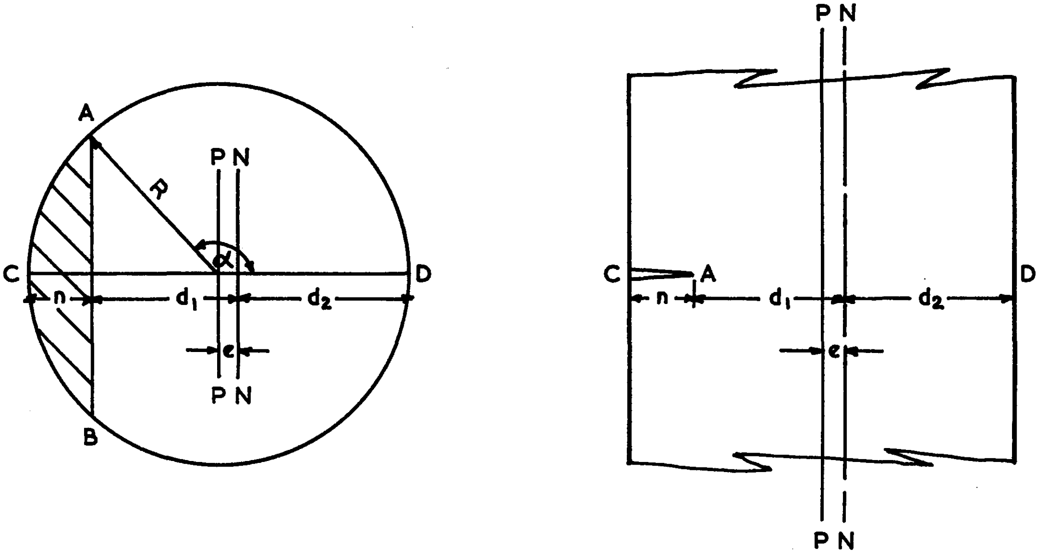


FIG. 69



Bending stress along AB $= \frac{My}{I}$

M = bending moment about principal axis,
y = distance AB from principal axis,
I = moment of inertia of cross section ADB

BENDING STRESS ALONG BASE OF STRESS-CORROSION CRACK

FIG. 70

The similarity between the development of these cracks and the development of the corroded section of unstressed metal will be apparent.

Theoretical considerations

If it be assumed that the increase in stress at the base of a crack is due to eccentric loading of the specimen, the centre of stress being displaced from the central axis of the wire, an analysis of the stresses involved may be made.

Referring to Fig. 70 opposite, the centre of stress of a tensile load of p lbs. applied to the wire is the central axis PP. If a crack, depth n, is developed such that it forms the segment ABC, the centre of stress will now be along NN and the metal along AB will be subjected to a bending stress ${}^{AB}f_b$ tending to open the crack, such that

$$ {}^{AB}f_b = \left[\frac{My}{I}\right] = \frac{p.e.d_1}{I} $$

The tensile stress ${}^{AB}f_t$ acting on AB is $\frac{p}{A}$, where A is the area of the segment ADB, hence the total stress ${}^{AB}f_{b+t}$ is given by:

$$ {}^{AB}f_{b+t} = p\left[\frac{ed_1}{I} + \frac{1}{A}\right] $$

For a circular segment it can be readily shown that:

$$\text{Area} = \tfrac{1}{2}R^2(2\alpha - \sin 2\alpha)$$

The centroid position: $NN \rightarrow AB = d_1$

$$= R\left[\frac{4\sin^3\alpha}{6\alpha - 3\sin 2\alpha} - \cos\alpha\right]$$

$$: NN \rightarrow D = d_2$$

$$= R\left[1 - \frac{4\sin^3\alpha}{6\alpha - 3\sin 2\alpha}\right]$$

The moment of inertia I_{NN}

$$= R^4\left[\tfrac{1}{8}(2\alpha - \sin 2\alpha)\left(1 + \frac{2\sin^3\alpha\cos\alpha}{\alpha - \sin\alpha\cos\alpha}\right) - \frac{8}{9}\,\frac{\sin^6\alpha}{2\alpha - \sin 2\alpha}\right]$$

Consider a crack 0.01 in. in depth in a wire 0.06 in. diameter:

$$\text{Area of sound metal} = \frac{(0.03)^2}{2}\left[4.6 + 0.9939\right]$$

$$\underline{= 0.002517 \text{ in}^2.}$$

$$d_1 = 0.03\left[\frac{4(0.7453)^3}{13.8 + 3(0.9939)} + 0.6667\right]$$

$$\underline{= 0.023 \text{ in.}}$$

$$\underline{d_2 = 0.027 \text{ in.}}$$

$$I_{NN} = (0.03)^4\left[\tfrac{1}{8}(4.6 + 0.9939)\left(1 + \frac{-2(0.7453)^3(0.6667)}{(2.3 + (0.7453)(0.6667))}\right) - \frac{8}{9}\,\frac{(0.7453)^6}{4.6 + 0.9939}\right]$$

$$\underline{I_{NN} = 4.316 \,.\, 10^{-7} \text{ in}^4.}$$

Hence:

$$f_{b+t} = p\,.\,\frac{(0.003)(0.023)}{4.316 \,.\, 10^{-7}} + \frac{p}{0.002517}$$

ALLOY NW.7.

STRESS AT THE BASE OF SEGMENTAL CRACKS
DUE TO ECCENTRIC LOADING.

Wire diameter taken as 0·0600 ins.

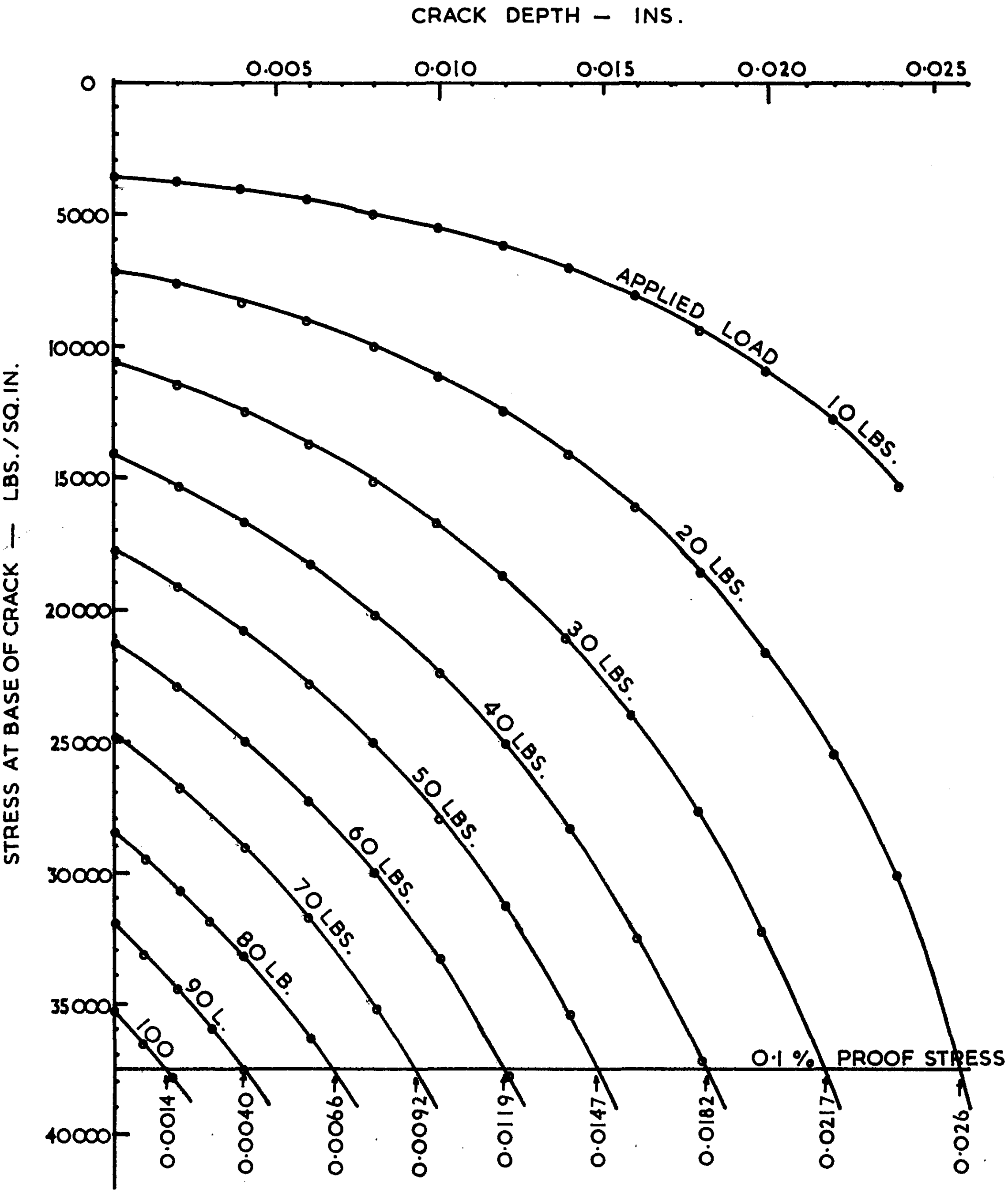


FIG. 71

$$= 457.3\ p\ \text{lbs./in}^2.$$

Values of f_{b+t} may be calculated for cracks 0.02 and 0.03 in. deep and curves drawn for the variation of A, d_1, d_2 and I with depth of crack. Values of f_{b+t} may then be obtained for any intermediate depth of crack.

TABLE XXVI

f_{b+t} in lbs./in^2.
n in inches.

p =	100 lbs.		90 lbs.	80 lbs.
n	$AB_{f_{b+t}}$	$D_{f_{b+t}}$	$AB_{f_{b+t}}$	$AB_{f_{b+t}}$
0.001	35,380	35,380	31,840	28,300
0.002	36,700	34,800	33,030	29,360
0.003	38,300	33,900	34,470	30,640
0.004	39,900	33,000	35,910	31,920
0.005	41,800	31,700	37,620	33,440
0.006			39,060	34,720
0.007				36,320
0.008				38,160
0.009				40,080
0.010				

The values for lower loads may be tabulated in a similar manner, and shown graphically as in Fig. 71.

Application of the eccentric loading theory

For a load of p lbs., corrosion will proceed until a crack has developed such that the combined stress at the base exceeds the yield strength. The bending stress tends to open the crack and deformation of β at the base of the crack will proceed. Such deformation will result in slip occurring in β until the stress exceeds the inter-atomic forces in this component and tearing will result which may occur without deformation of the surrounding grains. The tear may be temporarily arrested due to an unsuitably orientated grain boundary or to intermetallic inclusions when further corrosive action will be necessary to pass the obstacle, when overcome the combined stress at the base of the crack will be greater than that which resulted in the original tear, hence further obstacles will be less effective in arresting the process. With high initial loads on the specimen, little arrest of the process would be expected and for lower loads only obstacles present after yielding had just commenced would be expected to arrest the cracking for any period of time. This is confirmed by the observations on the extension of the wire during stress-corrosion when loads in region of the proof stress resulted in sudden failure while the failure which occurred with lower loads appeared to take place in two steps.

Analysis of the curves in Fig. 71 show that the direct load required for yielding to occur at the base of a crack are as shown below:

TABLE XXVII

Load % proof stress	Depth of crack at yield (ins.)	Direct load reqd. for yielding (lbs.)
94	0.0014	145
85	0.0040	140
75	0.0066	137
66	0.0092	133
57	0.0119	127
47	0.0147	119
38	0.0182	110
28	0.022	100
19	0.026	89

The minimum strength of specimens of NW.7 just before fracture were (Table XIX, p.165):

Load (% of proof stress)	Strength (lbs.)
94	142
75	100
57	98
47	87
28	87

The strength for loads of 94% of the proof stress and 28% are of the order of the direct load required for fracture although for intermediate loads the values deviate considerably, however the depth of crack required for fracture to occur may be somewhat greater than that for yielding to commence, and the strengths just before fracture as recorded above are the minimum values observed, which may be exceptionally low, in which case the calculated values and experimental values will be closer than those shown.

Fracture of notches

The experiments of Gilbert and Hadden (45) showed that when artificial notches were made in a tensile test piece, parts of the fracture were intercrystalline and no deformation of the crystals was apparent, whilst the fractures of unnotched specimens were wholly transcrystalline with gross deformation of the crystals. However, in experiments where a gradually increasing stress was applied, intercrystalline cracks began to appear in the surface at about 3% overstrain, and at about 11% overstrain transcrystalline cracks also appeared. It would therefore appear that the nature of the crack depemds on the rate of loading. The tearing action at the base of a notch caused by stress-corrosion would be very slow to begin with and as the area of sound metal decreased, the overall stress on the section would increase with increasing rapidity until it exceeded the ultimate strength of the residual metal and sudden mechanical fracture would result, this being a transcrystalline fracture.

Criticisms of failure by eccentric loading.

An objection to the theory of failure by eccentric loading is that a tension member with a semi-circular notch does not fail at a lower load than that calculated for the strength of the residual cross-section. Assuming an increased stress at the base of the semicircular notch, if this exceeded the yield strength then in a ductile specimen the stress would distribute itself over a small area at the base of the notch. If, however, there were a selective path at the base e.g., the β phase, then the stress distribution would be localised on this phase and tearing might occur if the distribution could not reduce the stress to below the yield stress. Tearing would increase the local stress and the process would accelerate across the section of the metal. If there were no selective path, deformation would not be localised to an extremely small area and would therefore reduce the combined stress due to bending and tension to below the yield stress and tearing would not occur. Such distribution of stress would occur until the yield strength of the residual section was passed and hence fracture would occur with the applied stress which would fracture an unnotched specimen.

Conclusion

In conclusion, a considerable amount of work has recently been done on stress distribution around notches, much of it involving complex mathematical analyses. One of the chief difficulties appears to be the correlation of the results obtained by photo-elastic measurements on transparent material e.g., perspex, nitro-cellulose etc., and those obtained on metals which have entirely different structures. The subject is considerably complicated by the fact that no two metal~~s~~ specimens are exactly alike and may therefore behave in a different manner when subjected to standard tests.

It is possible that stress concentration due to fine cracks and the effect of eccentric loading both play a part in the stress-corrosion failures encountered in the work of this thesis and there will probably be much speculation on the effect of mechanical stress before a theory is universally accepted.

APPENDIX

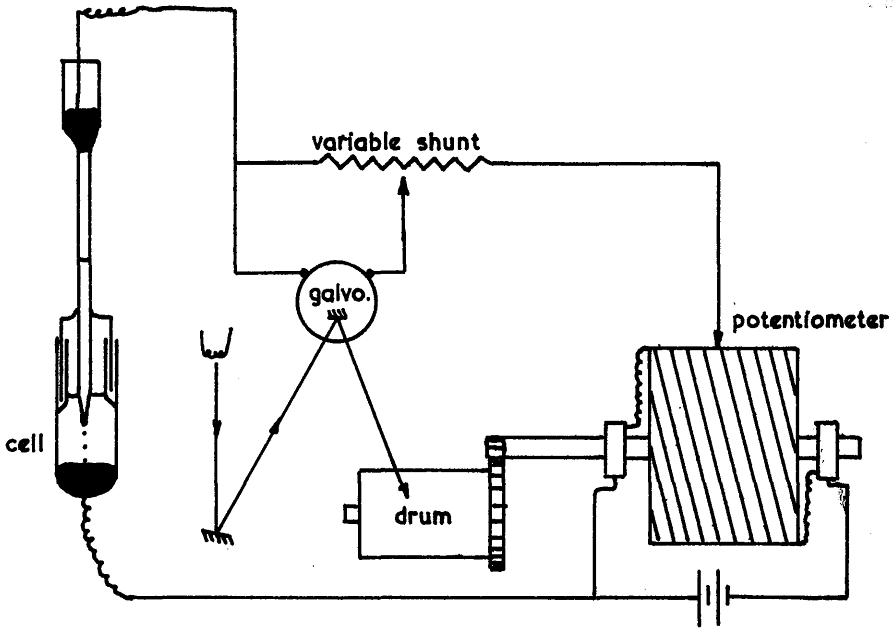
POLAROGRAPHIC ANALYSIS

OF ALUMINIUM

POLAROGRAPHIC PRINCIPLES

The polarograph, in a simple form, consists of an electrolytic cell in which an aqueous solution of the material to be examined is contained, the anode of which is a pool of mercury and the cathode of which is mercury dropping from a glass capillary. A gradually increasing E.M.F. is applied to the cell by means of a rotating potentiometer which is geared directly to a recording drum. A strip of photographic paper is wrapped around the drum and the current passing through the cell is recorded by means of a spot of light reflected from the mirror of a galvanometer onto the photographic paper. The galvanometer is connected in series with the cell by way of a variable shunt which is used to alter the sensitivity of the galvanometer as required. The record obtained, termed a polarogram, is a current-voltage curve.

In practice, the electrical resistance of the electrolyte in the cell is made negligible by the addition of a salt with a cation having a high deposition potential, e.g. lithium chloride. The anode is of a large area and unpolarisable in comparison with the dropping cathode, hence the



THE POLAROGRAPH (DIAGRAMMATIC)

FIG. [illegible]72

electrical resistance of the whole cell is determined solely by the processes occurring at the cathodic mercury-water interface. As the E.M.F. of the cell is gradually increased from zero, the current passed by the cathode remains negligible until the deposition potential of one of the cations present in the electrolyte is reached. At this point a sudden but limited increase in current occurs and concentration polarisation sets in. The cathodic mercury-water interface becomes denuded of cations having that decomposition voltage and further electrolysis is limited by the rate at which fresh ions can diffuse to the interface from the bulk of the solution. No further increase in current occurs with increasing applied voltage until the next deposition potential is reached. In this manner a current-voltage curve consisting of a number of steps is obtained, the voltage at which a step occurs gives a qualitative indication of the cation responsible and the height of the step is directly proportional to its concentration.

The polarograph as originally designed by Heyrovsky and Shikita (81) is shown diagrammatically in Fig. 72.

POLAROGRAPHIC ANALYSIS OF ALUMINIUM

Direct Method

During the experiments on the corrosion of aluminium by hydrochloric acid, the polarograph was used for estimating the amount of aluminium taken into solution. The determination presented some difficulty by reason of the comparatively low pH (4.1) at which hydrolysis of aluminium salts to insoluble aluminium hydroxide occurs. Exact polarographic determinations cannot be made in solutions of lower pH than 3.5 since the general slope of the flat portions of the curve becomes too steep, due to increase in hydrogen deposition with increasing voltage, to allow accurate measurements to be made. These difficulties were overcome by Gull (57) who used the polarograph for the analysis of aluminium in magnesium alloys. After dissolution of the alloy in hydrochloric acid, most of the excess acid was neutralised with potassium hydroxide, with vigorous shaking to avoid local precipitation of aluminium hydroxide. Neutralisation to the change point of bromophenol blue indicator at pH 3.8 was completed by careful addition of 0.1 N KOH and the solution left for 3-4 hours to ensure complete dissolution of any traces of colloidal aluminium hydroxide.

The above method was investigated by preparing solutions containing a known quantity of aluminium in 0.1 N HCl, to simulate the corroding solutions for analysis, and the following technique was used. 10 drops of bromophenol blue were added to 20 ml. of a standard solution and the free acid carefully neutralised with potassium hydroxide solution. Sufficient of a concentrated solution of magnesium chloride was then added to make the final concentration in the solution as polarographed equivalent to 0.125 N, this reproducing the conditions used by Gull. The solution was diluted, the neutral point redetermined and finally made up to 25 ml. with water. Prior to analysis the solution was de-oxygenated by passing hydrogen through it for 30 minutes.

Experiments indicated that whereas concentrations of aluminium in the solution to be analysed (i.e. before dilution) which were greater than 0.01% gave well-defined current-voltage curves, for lower concentrations the height of the step was difficult to measure and below about 0.005% aluminium the step was so ill-defined that it was not possible to estimate the height with any degree of accuracy. Since in the corroding solutions to be analysed the aluminium concentrations were of the order of 0.001% modifications of the above technique were investigated.

The effect of salts with a cation having a high deposition potential other than magnesium chloride was examined. 0.05 N barium chloride gave better defined curves for aluminium concentrations in region of 0.01% but the curves for lower concentrations were no better than those obtained with magnesium chloride. 0.1 N lithium chloride had much the same effect as magnesium chloride.

Indirect Method using Bromate Solution

It became apparent that the method of analysis described above was unsuitable for aluminium concentrations below about 0.01% and an indirect method of analysis recently developed by the Cambridge Instrument Co. (58) was investigated.

It is well known that nitrate ion in small concentration is catalytically reduced at the dropping mercury electrode in the presence of a relatively large concentration of cations such as aluminium. The present method of analysis is dependent upon the fact that if the conditions are changed so that the concentration of nitrate is much larger than that of aluminium, the diffusion current obtained becomes nearly proportional to the aluminium concentration. Other oxidising agents such as bromate and iodate behave in a similar manner. The Cambridge Instrument Co. investigated the behaviour of aluminium in the presence of a large excess of nitrate, bromate or iodate and concluded that the method was superior to the direct measurement of aluminium since in the latter the step occurs at a high potential and does not give a well-defined diffusion current and also the hydrogen ion concentration of the solution must be very carefully regulated. In the new method hydrogen ion concentration was much less critical, a better diffusion current was obtained and interference by other substances was considerably less. Of the three solutions bromate was the most satisfactory.

The base solution suggested was a solution containing:

0.20 N $KBrO_3$
0.2 N KCl
0.002 N HCl

and the technique recommended was to add a known volume of the aluminium solution to 5 ml. of the base solution, followed by a few drops of bromophenol blue indicator and after neutralisation firstly with 0.1 N KOH and finally with 0.01 N KOH, to make up to 10 ml. with distilled water.

The record gives two steps, at E½, -0.35 v. and E½, -0.78 v. against a saturated calomel electrode. The second step is used for aluminium measurement, the first being due to hydrogen ions.

Experimental Investigation

Experiments were carried out to determine the scope of the bromate method.

Effect of acidity

The effect of variation in the pH of the solution in the region of the change point of bromophenol blue indicator was investigated.

TABLE XXVIII

Solution as polarographed:

10 ml. of base solution, 10 ml. of an Al standard solution, made up to 25 ml. after addition of KOH:

(a) until yellow colour just retained,
(b) to green change point,
(c) until blue colour just formed.

Step heights equated to $\frac{1}{10}$ sensitivity.

(a) 9.74 in., (b) 9.66 in., (c) 9.68 in.

Thus slight variation in the pH of the solution in the region of the change point of bromophenol blue has no effect.

Effect of KCl concentration in solution as polarographed

Preliminary experiments indicated that the bromate method was unsuitable for the analysis of aluminium in concentrations of less than about 0.003% in the solution to be analysed (i.e. before dilution with base solution). In order to carry out analyses on the aluminium content of the corroding solutions, it was necessary to concentrate by evaporation. The concentration of potassium chloride in the solution as polarographed therefore varied with the degree of evaporation. The effect of vafious concentrations of potassium chloride in the supporting electrolyte was investigated.

TABLE XXIX

Base solutions containing (a) 0.2 N KCl, (b) 1.0 N KCl, (c) 2.0 N KCl prepared. 10 ml. Al standard solution in 0.1 N HCl added to 10 ml. base solution, neutralised and made up to 25 ml. The quantity of KCl in solutions as polarographed therefore (a) 0.21 g., (b) 0.77 g., (c) 1.47 g.

Concn. in soln. as polarographed		Av. step height equat. $\frac{1}{10}$ sens.
KCl	Al	
0.21 g. 0.77 1.47	0.0019%	4.30 in. 6.50 6.80
0.21 g. 0.77 1.47	0.0039%	8.10 in. 9.25 9.55
0.21 g. 0.77 1.47	0.0065%	14.4 in. 16.0 15.8
0.21 g. 0.77 1.47	unknown	11.6 in. 10.5 12.0

The change in KCl content from 0.21 g. to 0.77 g. had an appreciable effect on the step height. Change from 0.77 to 1.47 had a relatively small effect.

It was therefore decided to standardise the concentration of potassium chloride in the solution as polarographed. After five fold evaporation of the corroding solution, subsequent neutralisation resulted in the formation of approximately 0.35 g. of KCl in 10 ml. This quantity was chosen as a convenient standard.

Final technique

A sample of the corroding solution was evaporated to a known extent and 10 ml. of the concentrated solution was added to 10 ml. of a base solution containing 0.2 N $KBrO_3$ only. A calculated quantity of standard KCl solution was added to make the final quantity of KCl in the solution as polarographed equal to 0.35 g. and the mixture neutralised to the change point of bromophenol blue firstly with 1 N KOH and finally 0.01 N KOH, shaking vigorously to dissolve the aluminium hydroxide. After making up to 25 ml. the solution was left for at least 3 hours to ensure complete dissolution of the aluminium hydroxide.

Prior to analysis, the solution was deoxygenated by bubbling hydrogen through for 15 minutes.

Accuracy of results

A series of analyses conducted by the polarograph were checked by gravimetric estimation of the aluminium using 8-hydroxyquinoline.

TABLE XXX

	Concn. Al in g./litre				
Polarograph	0.395	0.358	0.310	0.362	0.398
Oxine	0.409	0.362	0.313	0.346	0.382

The maximum deviation between the estimations carried out on the polargraph and gravimetrically was approximately 4%, and since the deviations were in either direction, the usefulness of the polarograph is demonstrated.

SUMMARY

AND

CONCLUSIONS

SUMMARY

It is well known that stress applied to a corroding metal or alloy may influence the rate of attack and in some cases may cause premature failure. The role of stress may be to alter the intrinsic properties of a metal, i.e. render it more reactive or otherwise, and to alter the nature of protective films by stretching or rupturing them. Certain alloys which are susceptible to intercrystalline corrosion may suffer severe loss of strength when comparatively small stresses are applied, even though the actual amount of metal corroded is relatively small.

In the present investigation, the effect of tensile stress on Al corroding in acid solutions where no protective films are formed, has been investigated to determine whether stress influences the reactivity of the metal. The effect of stress on Al-7% Mg alloy in the annealed state and strain-aged, to render it susceptible to intercrystalline corrosion, has also been investigated in acid solution.

A technique for investigating the stress-

corrosion susceptibility of aluminium alloys has been developed and the effect of stress on the corrosion of strain-aged Al-7% Mg and Al-5% Mg alloys in neutral 3% sodium chloride solution has been determined.

In all the experiments the stress was applied via a steelyard and the specimens were in the form of 16 gauge wire. A high probability of obtaining reproducible samples was thus obtained. Only comparatively small loads were required for applying high stresses, thus simplifying the apparatus, and "edge" effects which may be apparent when specimens are in sheet form were eliminated. The experiments were conducted at constant temperature. A summary of the experimental work is given below.

The effect of (a) external stress below the proof stress and (b) internal stress caused by overstrain on the corrosion of Al was determined by measuring the rate of attack in 0.1N HCl, 0.1N HCl containing 5% NaCl and 0.1N HCl containing 3% NaCl.

Methods for determining the rate of corrosion were investigated. The aluminium taken into solution was determined by the polarographic method, but the method was not sensitive enough and necessitated a five-fold concentration of the solution before analysis could be carried out. Under these conditions this method was rapid and accurate, especially when a large number of analyses were required and a detailed account is given in the appendix. Gravimetric analysis using 8-hydroxy-quinoline was effective, but as in the case of the polarograph, necessitated disturbance of the corrosive environment. Colorimetric analysis using aluminom reagent was not sufficiently accurate. The method finally adopted was measurement of hydrogen evolved. Measurements were taken without disturbance of the corroding metal or of the solution. Certain inaccuracies may have been introduced due to (a) dissolution of hydrogen, (b) non-measurement of corrosion by dissolved oxygen and (c) uncontrolled stirring. Since comparative rates of attack were required, however, the effect of these inaccuracies was reduced and further minimised by presenting the data as rate of hydrogen evolution - time curves, omitting the results for the first 20 hours.

The effect of tensile stress on the rate of corrosion of Al-7% Mg alloy in 0.1N HCl containing 3% $NaCl$ was determined by measuring the rate of hydrogen evolution. The effect on corrosion of elastic stress on the strain-aged alloy was determined.

The effect of tensile stress on the potential between Al and 0.1N HCl containing 3% NaCl was investigated. Measurements in the elastic range of stress were conducted on single specimens, eliminating difficulties of variation of specimens. Measurements of the potential against a calomel electrode and against other specimens were made on permanently deformed metal by simultaneously immersing specimens of unstressed and overstrained metal in the corroding solution.

Measurements were made of the potential between annealed and strain-aged Al-7% Mg alloy and 0.1N HCl containing 3% NaCl.

The effect of stress on the corrosion of Al-7% Mg alloy under conditions where a protective film of corrosion products is formed was investigated by measuring the volume of oxygen absorbed and hydrogen evolved when the wire specimen was vertically immersed in a 3% NaCl solution containing HCl, pH 3. Measurements were conducted by observing the changes in volume of the gas above the corroding solution, the hydrogen evolved being removed at a heated platinum wire.

A technique for determining the effect of stress on corrosion in neutral salt solution was developed. The specimens were subjected to intermittent immersion and the rate of corrosion assessed by determining the loss of ultimate tensile strength.

Experiments were conducted on strain-aged Al-7% Mg and Al-5% Mg alloys. The specimens were exposed to 3% NaCl solution buffered at pH 6 by NaAc - HAc for a cycle of 2 minutes immersion and 2 minutes out of contact with the solution. The cycle was arranged so that the specimens did not dry out during the interval when they were out of contact with the solution. The extent of corrosion with increasing time of exposure was determined for stressed and unstressed specimens, and the time to failure of stressed specimens determined using an automatic recorder.

Measurements of the elongation of stressed specimens with time were made by recording the extension, magnified 200 times by means of a system of levers, on a smoked chart.

Methods have been developed whereby the stress-corrosion susceptibility of materials may be expressed on a comparative basis.

(i) by plotting the percentage loss of strength due to stress-corrosion against the applied stress,

(ii) by plotting the percentage of the loss of strength at failure due to stress-corrosion against the applied stress.

The conception that stress concentrations at the base of fine cracks, caused by corrosion, are responsible for local yielding and subsequent extension of the crack, ultimately resulting in failure, is discussed. An alternative theory of the mechanical role of stress is advanced, based on the concept that the presence of a combined bending and tensile stress at the base of a crack due to eccentric loading is greater than the applied tensile stress. This causes extension of the crack and ultimately leads to failure.

CONCLUSIONS

1. Application of tensile stress within the proof stress has no effect on the rate of corrosion of Al in dilute acid solutions.

2. Internal stresses set up by overstrain have no effect on Al up to 10% overstrain.

3. The rate of H_2 evolution from a length of Al overstrained 20% is less than that from the same length of unstrained metal.

4. Variations in conditions other than stress have a greater effect on the rate of corrosion of Al than stress alone.

5. Elastic stress and 10% overstrain have no effect on the rate of corrosion of annealed Al-7% Mg alloy in dilute acid solution.

6. The rate of corrosion of stress-free strain-aged Al-7% Mg alloy is considerably greater than that of the annealed alloy.

7. Application of elastic stress to the strain-aged Al-7% Mg alloy results in a small increase in

the rate of attack.

8. Potential measurements confirm that elastic stress has no effect on the corrosion rate of Al in dilute acid solution.

9. The effect of plastic stress on the potential of Al is small, and less than the variation in the potentials of specimens given identical treatment.

10. The effect of stress on the potential of annealed Al-7% Mg alloy in dilute acid solution is negligible.

11. A stress of 94% of the proof stress causes a small deviation in the anodic direction of the strain-aged Al-7% Mg alloy.

12. The curves for the rate of attack of Al-7% Mg alloy by 3% NaCl solution, pH 3, as measured by oxygen absorption are similar irrespective of the applied stress.

13. The attack as measured by hydrogen evolution shows considerable variation for specimens corroded under the same stress.

14. It is confirmed that Al-7% Mg alloy is susceptible to stress-corrosion.

15. The time-to-failure of Al-7% Mg alloy increases with decreasing applied stress, ranging from 1 hour for stresses of 68% of the U.T.S. to longer than 300 hours for stresses of 2% of the U.T.S.

16. The loss of strength due to stress-corrosion of Al-7% Mg alloy increases from 32% of the U.T.S. for an applied stress of 68% of the U.T.S. to 68% for an applied stress of 20% of the U.T.S. Thereafter it decreases rapidly with decreasing applied stress.

17. The threshold stress of Al-7% Mg alloy is about 2% of the U.T.S.

18. It is established that Al-5% Mg alloy is susceptible to stress-corrosion.

19. The time-to-failure of Al-5% Mg alloy increases with decreasing applied stress, ranging from about 13 hours for stresses of 61% of the U.T.S. to 380 hours for stresses of 24% of the U.T.S.

20. The loss of strength due to stress-corrosion of

Al-5% Mg alloy is almost constant at about 40% of the U.T.S. for stresses from 61% to 32% of the U.T.S. Thereafter it decreases somewhat with decreasing applied stress.

21. The threshold stress of Al-5% Mg alloy is about 24% of the U.T.S.

22. The effect of stresses smaller than the threshold stress applied to Al-5% Mg alloy is relatively small and any effect does not increase with time of exposure after the early stages of attack.

23. The loss of strength of the alloys is most marked in the last stages of the life of the alloy. All the loss of strength of the Al-7% Mg alloy stressed to 68% of the U.T.S. occurs within 1 minute of failure. With smaller stresses the loss is most marked within minutes of failure.

24. The stress-corrosion susceptibility of the alloys examined as assessed by the methods described is:

Method (i) Al-7% Mg alloy = 79%
Al-5% Mg alloy = 45%

Method (ii) Al-7% Mg alloy = 85%
Al-5% Mg alloy = 67%.

REFERENCES

1. Proceedings, A.S.T.M. 1918, 18, Part 2.

2. Moore, H., Beckinsale, S. & Mallinson, C.E.
J. Inst. Metals 1921, 25, 35.

3. A.S.T.M. - A.I.M.E.,
"Symposium on Stress Corrosion Cracking of Metals" 1944.

4. Inst. Metals
"Symposium on Internal Stresses in Metals and Alloys" 1948.

5. Evans, U.R.,
"An Introduction to Metallic Corrosion"
London, E.J. Arnold & Co. 1948.

6. Evans, U.R.,
"Metallic Corrosion, Passivity and Protection"
2nd Edn. London, E.J. Arnold & Co. 1946.

7. Speller, F.N.,
"Corrosion, Causes and Prevention"
2nd Edn. New York, McGraw-Hill 1945.

8. Uhlig, H.H., (Editor)
"Corrosion Handbook"
New York, John Wiley & Sons. 1948.

9. Gatty, O. & Spooner, E.
"The Electrode Potential Behaviour of Metals in Aqueous Solutions"
Oxford University Press. 1938.

10. Coates, G.E., Chem. & Ind. 1944, 63, 306.

11. Vernon, W.J.H., J.Roy.Soc.Arts. 1949, 97, 578.

12. Carman, P.C.,
"Chemical Constitution and Properties of Engineering Materials"
London, E.J.Arnold & Co. 1949.

13. Raynor, G.V., Inst. Metals Ann. Equilib. Diag. No. 5, 1945.

14. Mockel, E., Aluminium 1937, 19, 433.

15. Metcalfe, C.J., J.Inst.Metals 1946, 72, 487.

16. Perryman, E.C.W. & Hadden, S.E., ibid 1950, 77, 207.

17. Evans, U.R., "Metallic Corrosion, Passivity and Protection" P.425.

18. Dix, E.H. Jr., "Symposium on Stress Corrosion Cracking of Metals" P.325.

19. Dix, E.H. Jr., Trans.Amer.Inst.Min.Met.Eng. 1940, 137, 11

20. Gayler, M.L.V., J.Inst.Metals 1946, 72, 243.

21. Evans, U.R., "Symposium on Internal Stresses in Metals and Alloys" P.302.

22. Copson, H.R., "Corrosion Handbook" Loc.cit. P.569.

23. Sutton, H., Liddiard, E.A.G., Chalmers, B. & Champion, F.A. Monthly J. Inst. Metals 1945, (Aug), XXII.

24. Bryan, J.M., "Aluminium and Aluminium Alloys in the Food Industry" London, H.M. Stationery Office. 1948.

25. Simnad, M.T. & Evans, U.R. J. Iron Steel Inst. 1947, 156, 531.

26. Whiteley, J.H. & Hallimond, A.F., Carnegie Schol. Mem. 1918, 9, 1
1925, 14, 163.

27. Friend, J.A.N. J. Iron Steel Inst. 1928, 117, 639.

28. Evans, U.R. J. Chem. Soc. 1929, P.92.

29. Evans, U.R. & Simnad, M.T.
Proc. Roy. Soc. 1947A, 188, 372.

30. Sahs, G., Iron Age 1940, 146, 21.

31. "Corrosion Handbook" Loc.Cit. PP. 137, 174, 571.

32. Rawdon, H.S., Ind. Eng. Chem. 1927, 19, 613.

33. Mears, R.B., Brown, R.H., & Dix, E.H. Jr.,
"Symposium on Stress Corrosion Cracking of Metals" P. 323.

34. Sidery, A.J., Lewis, K.G. & Sutton, H.,
J. Inst. Metals 1932, 48, 165.

35. Bollenrath, F. & Grober, H.,
Aluminium 1937, 19, 349.

36. Bungardt, W. & Schaitberger, G.,
Metallwirtschaft 1941, 20, 719

37. Bungardt, W. & Bedarff, H.,
ibid 1942, 21, 31.

38. Liddiard, E.A.G.,
"Symposium on Stress Corrosion Cracking of Metals" P.373.

39. Perryman, E.C.W.,
"Symposium on Internal Stresses in Metals and Alloys" P.474.

40. Perryman, E.C.W. & Hadden, S.E.
J. Inst. Metals 1950, 77, 225.

41. Champion, F.A.,
"Symposium on Internal Stresses in Metals and Alloys" P.468.

42. Champion, F.A.,
Metal Ind. 1947, 71, 422.

43. Keating, F.H.,
"Symposium on Internal Stresses in Metals and Alloys" P.311.

44. Allen, N.P., ibid P.463.

45. Gilbert, P.T. & Hadden, S.E.,
J. Inst. Metals 1950, 77, 237.

46. Edeleanu, C. ibid 1951, 80, 187.

47. Champion, F.A., Private Comm. 3 Sept. 1948.

48. Evans, U.R., J. Inst. Met. 1950, 77, 635.

49. Borgmann, C.W.,
"Corrosion Handbook" Loc.Cit. P.953.

50. Bengough, G.D., Stuart, J.M. & Lee, A.R.,
Proc. Roy. Soc. 1927(A), 116, 425.

51. Idem ibid 1928(A), 121, 88.

52. Idem ibid 1930(A), 127, 42.

53. Champion, F.A.,
Trans. Faraday Soc. 1945, 41, 593.

54. Champion, F.A.,
"Symposium on Stress Corrosion Cracking of Metals" P.367.

55. "Chemical Analysis of Aluminium and its Alloys"
London, The British Aluminium Co. Ltd., 1938.

56. Kolthoff, I.M., Lingane, J.T. & Heyrovsky, J.,
Chem. Rev. 1939, 24, 1

57. Gull, J., J.S.C.I. 1937, 56, 177T.

58. Cambridge Instrument Co., Private Com. 8 Sept. 1947.

59. Hammett, L.P. & Sottery, C.T.,
J. Amer. Chem. Soc. 1925, 47, 142.

60. Straumanis, M.,
Korrosion u. Metallschutz 1938, 14, 1.

61. Maass, E., ibid 1927, 3, 25.

62. Whitman, W.B., & Russell, R.P.
Ind. Eng. Chem. 1925, 17, 348.

63. Bryan, J.M.,
Rep. Food Invest. Bd., London, 1936, P.196.

64. Kemball, G.E., J. Chem. Physics 1940, 8, 199.

65. Coates, G.E., J. Inst. Metals 1945, 71, 457.

66. Schurmann, R. J.S.C.I. 1939, 58, 174.

67. Moore, H. & Liddiard, E.A.G.
ibid 1935, 54, 786.

68. Clelland, D.W., Sly, R.A.
B.Sc. Theses (Glasgow) 1948.

69. George, C.W. & Chalmers, B.,
"Symposium on Stress Corrosion Cracking of Metals" P.348.

70. Bengough, G.D., Lee, A.R. & Wormwell, F.
Proc. Roy. Soc. 1931(A), 131, 494.

71. Bengough, G.D. Chem. & Ind. 1933, 52, 195 & 228.

72. Evans, U.R.,
"Metallic Corrosion, Passivity and Protection" P.271

73. Evans, U.R. ibid P.755

74. J. Iron Steel Inst. 1935, 131, 265,

75. Madden, B.C.,
"Symposium on Stress Corrosion Cracking of Metals" P.233.

76. Sager, G.F., Brown, R.H. & Mears, R.B.
ibid P.255.

77. Perryman, E.C.W. & Hadden, S.E.
J.Inst. Metals 1950, 77, 219.

78. Idem. ibid 1950, 77, 220.

79. Keating, F.H.
"Symposium on Internal Stresses in Metals and Alloys" P.327.

80. Inglis, C.E.,
Trans. Inst. Nav. Archit. 1913, 55(2), 219.

81. Heyrovsky, J. & Shikata, M.,
Rec. Trav. Chim. 1925, 44, 496.