THE EFFECTS OF IMPURITIES IN CORROSIVE MEDIA CAUSING STRESS CORROSION CRACKING IN AISI 304 STAINLESS STEEL

by

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INTRODUCTION

Stress corrosion cracking has been defined as "damage resulting from a complex interplay of tensile stress, corrosion, and crack sensitive paths through an alloy"(1). Service failures frequently occur from residual stresses set up in structures during fabrication. These stresses may result from deep drawing of brass, work hardening of aluminum, the pressing of oversized bushings into aluminum alloy fittings, riveting or welding of steels, or even as a result of torques encountered in pipe line construction.

The term stress corrosion cracking should be limited to that type of corrosion in which no sensible damage results in the absence of tensile stresses. This distinction excludes stress accelerated corrosion in which corrosion is found to be intense even in the absence of applied stress, indicating that the mechanism is primarily electrochemical in nature and is simply accelerated by the application of stresses. The stress, if applied, plays no part other than to rupture the corrosion weakened grain boundaries.

Stress corrosion cracking may be either intergranular, as in aluminum alloys, alpha brass, and low alloy steels, or transgranular, as is common in magnesium alloys and austenitic stainless steels. Intergranular cracking, however, can occur in some austenitic stainless steels which have been sensitized. This attack apparently results from the precipitation of carbides along the grain boundaries of the alloy. Intergranular corrosion can be controlled in a particular application by the use of a suitable stabilized alloy or by proper heat treatment. Transgranular cracking, on the other hand, can not be easily controlled by alloy additions or heat treatments. Transgranular cracking is a characteristic failure of all of the common 18-8 stainless steels, including those containing carbide stabilizers, high nickel contents, or low carbon contents.

The media that cause stress corrosion cracking of susceptible alloys have been found by experience usually to contain the chloride ion, although it was later discovered that its presence was not altogether necessary for cracking to occur. The effect of various chloride salts on stress corrosion cracking of austenitic stainless steels has been studied by Edeleanu(2). He shows, in general, that it is the chloride ion itself that is the culprit, and the effect of the cation is only to produce a change in the relative time and temperature for cracking. Chemical media most apt to cause cracking are those containing chlorides at a pH slightly on the acid side of neutral. Hence, boiling concentrated magnesium chloride solutions constitute a severe environment and cracking occurs in a matter of a few hours. General corrosion in such media is only slight at most. In media for which general corrosion is pronounced, cracking may not occur at all.

The procedure for determining the susceptibility to stress corrosion cracking in the past has consisted of subjecting a stressed specimen to the corrosive medium for a given period of time. If cracking was observed, the results were expressed as "not cracked", in which case the alloy was termed "not susceptible", or as "slightly cracked", or "badly cracked", in which cases the material was termed susceptible. Another procedure was to subject the specimen to the corrosive medium until complete failure occured. A somewhat quantitative test was hence initiated, as the time to failure was a measure of the susceptibility of the material.

Even this somewhat quantitative measure of susceptibility to stress corrosion cracking seems to be inadequate because it does not differentiate the effects of each of the two processes contributing to eventual failure of the metal by cracking. It is desirable to distinguish between these two processes, crack nucleation and crack propagation, for any alloy because the degree of damage can be estimated at any time after exposure to a corrosive medium. The results obtained in this investigation are separated into the two processes, each process being described in terms of a characteristic constant of the process. This method establishes a quantitative measure of the general term "susceptibility".

Research was initiated by the Department of Metallurgical

Engineering at the Virginia Polytechnic Institute in order to gain the needed knowledge concerning the time for crack nucleation and the rate of crack propagation in austenitic stainless steels and to determine the effects of several factors that govern or have an effect on the crack nucleation time and the rate of crack propagation. In the course of these investigations, it was noted that different lots of technical grade magnesium chloride from the same supplier produced inconsistent results for the time of crack nucleation and the rate of crack propagation. These inconsistencies were attributed to the presence of varying amounts of impurities that are commonly found in technical grade magnesium chloride.

This thesis presents experimental work done to determine the quantitative effects of certain of these impurities upon the time to crack nucleation and the rate of crack propagation in AISI 304 stainless steel exposed to boiling 42% magnesium chloride solutions. For the purpose of this investigation, chemically pure magnesium chloride was employed with the impurity compounds being intentionally added in the amount of three weight per cent.

II

REVIEW OF LITERATURE

The earliest record of stress corrosion can be traced to Robert-Austen, who in 1886, reported the cracking of a gold-copper-silver alloy exposed to a ferric chloride solution. Since that time, many reports of failure by stress corrosion cracking have been recorded. With the increased use of stainless steels in recent years, much interest has been aroused, and the phenomenon has now become one of the most important metallurgical problems occuring in industry. The mechanism of stress corrosion is evidently complex, and many questions regarding the exact nature of the process remain unanswered.

Many laboratory experiments have been concerned with the problems of stress corrosion cracking for the purpose of attempting to propose feasible mechanisms. There have been numerous mechanisms proposed by a number of investigators, all of which have merit, yet each fails to provide a complete answer for certain observed effects.

It is generally agreed by investigators that the principal factors involved are stress, time, nature of the corrosive environment, temperature of the corrosive environment, and the internal structure of the alloy. Two other factors, about which agreement is not widespread, are plastic strain and the nature of protective films in mildly corrosive media(3).

The lowest stress at which stress corrosion cracking will occur in austenitic stainless steels in chloride solutions is apparently affected by the anion, temperature, and physical nature of the corrosive medium, which in turn control the chloride ion to oxygen ratio present at the cracking site(4). Some authors indicate that the minimum stresses required for cracking are of the order of the tensile yield strength(5,6), while other investigators indicate that stresses as low as 3000 to 10,000 pounds per square inch will produce cracking(7,8). Hoar and Hines(9) and Evans(10) have studied in detail the threshold stress for cracking. These authors indicate that in boiling magnesium chloride solutions, the threshold stress for austenitic stainless steel is approximately 20,000 pounds per square inch. Other authors indicate that no threshold stress is observed below which cracking will not occur.

For cracking to occur, surface or subsurface tensile stresses must be present; compressive stresses may be used as a method of alleviating the stress corrosion problem in many applications(5). In order to determine the effect of the rate of straining, 18-8 test specimens, stress relieved after shearing, were bent to a four inch span in times of 10 seconds, 5 minutes, and 10 minutes, then immediately tested in boiling magnesium chloride(11). No effect was observed. Additional specimens were bent at higher velocities by impact of falling weights held in a specially constructed jig; still no effect was observed.

Chemical media most apt to cause cracking are those containing chlorides at a pH slightly on the acid side of neutral(11). Edeleanu(2) has studied the effects of various chloride salts on stress corrosion cracking of austenitic stainless steels. It was determined that the chloride ion itself is responsible for cracking and the effect of the cation is to affect only the conditions of relative time and temperature for cracking. It is generally agreed that oxygen is necessary for chloride stress corrosion cracking of stainless steels when the corrosive media contain low concentrations of the chloride ion. The actual role of the chloride ion in stress corrosion cracking does not seem to be well understood. Numerous studies have shown its relationship to pit formation(8,12,13,14). It appeared to Hackmann and Stephens(15) that the chloride ion was absorbed on ferrous surfaces in preference to oxygen, and through the mechanism of continuous film repair and breakdown, forms local anodic areas which lead to pitting.

Additions of acid to the corrosive medium in tests by Uhlig and Lincoln(11) decreased the cracking time to a minimum of about one-half the normal time, whereas additions of alkali increased the time only slightly. These results proved that shorter times for cracking in used test solutions did not result, as was previously thought, from a decrease in acidity caused by the reaction of metal with magnesium chloride. Instead, the effect was undoubtedly caused by ferric chloride accumulation(2) through corrosion of specimens.

The decrease in cracking time by additions of acid were thought to have been associated with films on the metallic surfaces, but it also may have been instrumental in increasing the electrical conductivity of the magnesium chloride solution through additional hydrogen ions. The acid also increased the operating electromotive force of the metal electrode-hydrogen electrode cells, presumably responsible for crack propagation, to the extent of 4.2 millivolts for each unit pH change. Ferritic salts, on the same basis, were found to decrease cracking time because they are active depolarizers serving to accelerate the cathode reaction(11).

The internal structure of the metal has a definite relationship to its susceptibility to stress corrosion cracking. Uhlig(1) has stated that pure metals are immune to stress corrosion cracking regardless of the stress applied. It was determined that pure copper, stressed in an atmosphere of ammonia, will not crack, but when alloyed with 0.1% or more of phospherous, antimony, arsenic, or silicon, becomes susceptible and cracking occurs. This is an indication that either an electrochemical process or lattice distortion is responsible for cracking.

Austenitic stainless steels offer a high resistance to general corrosion due to its property of passivity, and there has been a theory proposed by Heger(16) to explain this property. This theory, generally accepted by other investigators, involves the formation of protective oxide films over the surface of the alloy. It is thought that the film is an oxide of chromium, but its nature has not been definitely established. If it were possible to maintain a continuous, unbroken, protective oxide film over the entire surface of the alloy, stress corrosion cracking, according to Leu and Helle(17), could be prevented. Environments containing the chloride ion, however, have been found to be detrimental to these protective films, resulting in breaks or discontinuities in the film which expose unprotected metal surfaces to the action of the corrosive medium.

Leu and Helle(17) postulated that corrosive attack resulting in stress corrosion cracking occurs only at these areas where the film has been broken. A brittle film which may be fully protective will, upon deformation, show many breaks and discontinuities. A ductile film, however, may yield with the metal under deformation and remain protective. The physical properties of the protective film therefore affect the role of the films in the stress corrosion mechanism of stainless steels.

A cyclic mechanism in which slow electrochemical propagation alternates with a short but rapid mechanical fracture was proposed by Keating(18). The strongest support for this mechanism was a motion picture study of crack propagation along the surface of a susceptible alloy, which revealed short and rapid steps of propagation on the surface. This, according to Barnartt and Van Rooyen(19), is not sufficient evidence, because it is possible for a crack to grow smoothly in three dimensions but break through the surface in bursts, particularly if surface films impede parting.

The mechanical fracture step, in a theory proposed by Keating(18), is initiated when corrosion produces a stress concentrating notch which is located at an appropriate lattice site or boundary. A different cause was assumed by Nielson(20), who, from electron microscopy investigations of corrosion products deposited in cracks, concluded that solid corrosion products can exert a wedging action and produce periodic fracture by mechanical means. Pickering, Beck, and Fontana(21) have conducted tests to determine the magnitude of this wedging action. It was determined that three conditions are necessary for stress corrosion cracking to occur: (1)an insoluble corrosion product must be found, (2)the corrosion product must be larger in volume than the metal from which it forms, (3)the corrosion product must form in a restricted region, as in a crack.

The application of stress to a crack sensitive alloy does not affect the anodic and cathodic reaction rates within the period of crack initiation. During this period, metal dissolution would develop cracking sites, either by uncovering unprotected metal or by creating stress raising pits, or both. If crack propagation is entirely electrochemical in nature, the surface of the metal at cracking sites must, by stress induced changes in structure, have a reversible potential appreciably more active than the surrounding metal. Unusually high metal dissolution rates will be exhibited by sites at a given potential. Therefore, during the propagation of cracks the overall anodic polarization curve will be shifted toward higher currents and the corrosion potential will decrease, as was observed by Barnartt and van Rooyen(19).

Crack propagation is relatively slow in stainless steels compared to brittle failure; this and the observation that a growing crack can be stopped by cathodic protection have led to the concept of a purely electrochemical mechanism by Hoar and Hines(9). It was proposed that stress corrosion cracking of 18-8 type chromium-nickel steels takes place in three stages, which was demonstrated by following the electrode potentials and the mechanical properties of steel specimens during the stress corrosion process. There was observed an induction period of corrosion damage, not greatly influenced by the presence of applied stress or by its value, followed by a stage of initiation of cracks at points on the bared metal surface, then the propagation of these cracks in a direction roughly perpendicular to the greatest resolved tensile stress.

The induction period is proposed to include a period of oxide film repair and may also include a period of film breakdown and pitting corrosion. In 42% magnesium chloride solutions boiling at 154 degrees C., the induction period was found to be of the order of 20 to 200 minutes for softened 18-8 steels stressed to 40,000 pounds per square inch. The induction was shortened slightly by the application of higher stresses, and lengthened greatly at lowest applied stresses. It was found to be considerably shortened by an increase in temperature over the range from 135 degrees C. to 155 degrees C. It may be shortened to only a few seconds by acidification of the corrosive medium with 0.2% hydroflouric acid, which removes the initial oxide film. The induction period was indefinitely lengthened by the application of cathodic protection.

It has been popular among investigators to describe the initiation of a crack to the presence of a corrosion pit that acts as a stress raiser, such that the stress at the base of the pit exceeds the fracture stress of the material. Results obtained by Hoar and Hines(9) appear to support this view, but other considerations do not. Leu and Helle(17) have found that not all aqueous chloride solutions give rise to stress corrosion to the same extent. Stainless steels were found to be resistant to general corrosion in magnesium chloride, calcium chloride, and zinc chloride, but in the presence of a tensile stress, stress corrosion cracking led to rapid failure. In solutions where pitting was normally observed, (sodium chloride, potassium chloride, and ammonium chloride) the phenomenon of cracking was observed only after very long times. In solutions causing very heavy general corrosion, (chromium chloride, ferric chloride, and mercuric chloride) no stress corrosion cracks were observed even after very long times. It is known, furthermore, that the addition of oxidizing compounds to chloride solutions promote this type of attack. Passivating films thus are of utmost importance in the stress corrosion problem.

A generalized theory of the mechanism was proposed by Logan(22) that involved the rupture of the protective film. Corrosion was postulated to occur by an electrochemical mechanism along localized paths that were anodic to the surrounding metal. Stress concentrations would be built up at the bases of these locally corroded areas, the deeper the attack and the smaller the radius of curvature at the base of the crack, the greater would be the stress concentration. Such a condition would tend to pull the metal apart at more or less continuous paths. At sufficient concentrations of stress, the metal might start to tear apart by mechanical action. The tearing action would expose fresh metal, unprotected by films, to the action of the corrosive environment. It is seen from this statement that Mears, Dix, and Brown(23) postulate a mechanism in which protective films on metal surfaces are ruptured. Keating(18) suggested that each advancing section of the crack in time encounters an obstacle, either a non-metallic inclusion, a lattice discontinuity, or an unfavorably oriented grain boundary. In each case the result may be reduction of the stress concentration to a level at which stress corrosion cracks will stop. Such a process could be used to explain the branching of stress corrosion cracks, sudden changes in direction at grain boundaries, etc.

Investigations by Logan(22) produced data indicating that when stresses are high enough to promote plastic deformation, the oxide film will be ruptured and the exposed metal will be electronegative with respect to the filmed metal. These film free areas are very small compared to the filmed metal area. If these filmed areas are connected to the film-free areas by a conducting liquid, a short circuited cell will be set up, the circuit being completed through the alloy itself. The current density on these small anodic areas will be very high, so corrosion will proceed rapidly until a reduction of stress allows the protective film to reform. Corrosion will become more general until the stress concentration at the particular path under consideration again becomes sufficient to rupture the protective film. If the stresses are readjusted, the film may again be broken and stress corrosion cracking will proceed discontinuously until failure. If the film were not alternately repaired and ruptured, cracking would be expected to proceed continuously.

Apparently, there has been no reason given to suppose that when initial corrosion damage is more extensive, the stress raising effect is necessarily more pronounced. Exactly the opposite effect is actually experienced; when pits formed by corrosion extend, they extend sideways rather than in depth. The pits must extend in depth in order to produce a pronounced stress raising effect. Cracking was found to start most quickly and most generally under the special conditions of low pH where the oxide film was quickly removed. Hoar and Hines(6) state that "the probability of crack initiation depends on the amount of bare metal surface exposed to the electrolyte by the initial corrosion reactions". However, a "stress raising" pit may possibly form, advance on a very narrow front, continually accelerate its own progress by an increase in stress at its advancing apex, causing very rapid failure.

It is likely that certain features of metal surfaces from atomic considerations are the sites of crack initiation. These possible sites may be vacancies, grain or sub-grain boundaries, ends of dislocations on the surface of the metal, or strained parts of the metallic lattice. At these points, anodic dissolution of the metal is especially rapid, and the removal of the protective film assists mechanical deformation. The exact nature of the points on the bare metal surface that are sites of crack initiation is still not clear; however, it is certain that they are of varying effectiveness. The lower applied stress necessary for crack initiation when the induction period is longer is readily explained by the assumption that as corrosion reactions proceed, points of increasing effectiveness are exposed and the effectiveness is increased by hydrogen absorption(24).

Cracks were found to propagate at the rate of 0.5 to 3.0 millimeters per hour(22); this rate is somewhat increased by small increases in temperature, but is almost independent of the applied stress over a wide range. Other investigators have observed comparable rates of crack propagation, which are much too slow for a purely mechanical parting process, yet much too rapid for a purely electrochemical mechanism. It has been suggested by Keating(18) and Evans(10) that cracking is an alternate mechanism of rapid mechanical and slow electrochemical steps.

This suggestion has merit in that the stress at the advancing tip of a crack plays an essential part in the cracking process; if the stress is removed, even after cracking has progressed some distance, the progress of the crack will be stopped. The discontinuous nature of the cracking process has been supported by Eckel(25) on the basis of calculations which show an infinite initial rate of crack propagation. Electrochemical action plays an equally important role because it has been shown by Mears, Brown, and Dix(23) that stress corrosion cracking could be prevented by cathodic protection. If external currents were applied to the specimens such that the specimens were the cathodes, the cathodic areas on the surface of the metal were polarized by means of the externally applied current to the open circuit potential of the anode points on the specimen. Consequently, no current would flow from the anodic to the cathodic areas which had been polarized. If the mechanism of stress corrosion cracking were purely electrochemical, then corrosion, and stress corrosion, would be prevented by the applications of the cathodic current. Mears, Brown, and Dix(23) indicated that all metals anodic to stainless steel by 0.10 volt or more would prevent stress corrosion cracking. If the metals coupled to the stainless steel were less than 0.10 volt anodic, the time required for failure was greater than if the specimen remained unprotected. If metals definitely cathodic to the stainless steel were coupled to the specimens, the rate of stress corrosion failure was greatly accelerated.

The evidence presented to this point indicates a joint mechanical-electrochemical mechanism of crack propagation, rather than an alternate one. Uhlig(26) pointed out that the thermodynamic reactivity of anodic metal can be only very slightly affected by stress or strain energy. It is certain, however, that the rate of anodic dissolution can be considerably increased by the presence of stress and strain, as was shown by Evans(10). The stress may act to disrupt an otherwise passivating oxide film on the anodic areas of the metal.

Hoar and Hines(9) have postulated a mechanism of crack propagation in which film growth proceeds on the fractured sides of the crack. At the advancing tip of the crack, the stress applied puts the metal atoms in an especially favorable state for easy anodic reaction. If the reaction forms soluble products, these are mechanically disrupted and prevented from forming a protective film. As the crack proceeds, more corrosive electrolyte is sucked in continuously to maintain the process. Thus, the mechanism is one of joint actions of stress and electrochemical action, rather than alternate actions. The crack, by this mechanism, would propagate continuously.

This joint mechanical-electrochemical mechanism for crack propagation derives features from many previous models, notably, the "general theory" of Mears, Brown, and Dix(23), the "alternate mechanism" of Keating(18), the "film rupture theory" of Logan(22), and the "film breakdown theory" of Leu and Helle(17).

In industrial practice, the stopping of already present stress corrosion cracks is of little value. Rather, the cracks must be prevented from initiating or at least greatly delayed. The onset of cracking can be delayed by a reduction of applied stress or a relief of internal stress, but these steps will by no means prevent crack initiation. In addition, these steps would be difficult, at least, to employ industrially because values of residual stress and strain in structures are difficult to estimate; moreover, this would require an estimate of the degree of strain hardening which inevitably occurs during fabrication. For stainless steels, little significance is shown of varying the composition except in altering the mechanical properties, which in turn may affect the plastic strain; specific heat treatments which will eliminate or delay crack initiation are unlikely to be determined. On the other hand, means of reducing the corrosion damage, particularly cathodic protection, offer some promise in the alleviation of the stress corrosion cracking problem.

III

EXPERIMENTAL PROCEDURE

A. Selection of Material

All specimens used in this investigation were AISI type 304 stainless steel, supplied by the United States Steel Corporation. The steel was received in sheets of 0.0625 inch thickness, having the following heat analysis:

Chromium——18.70%
Nickel————9.40%
Manganese——1.59%
Silicon————0.56%
Molybdenum——0.36%

Copper————0.18%
Carbon————0.050%
Phospherous——0.030%
Sulfur————0.025%
Iron—————Balance

This particular alloy was chosen for this investigation because it is susceptible to stress corrosion cracking, and cracking occurs in a relatively short time when exposed to boiling concentrated magnesium chloride solutions. Previous investigations that had revealed considerable scatter in results with different batches of magnesium chloride also employed this grade of austenitic stainless steel.

B. Preparation of Specimens

All specimens used in this investigation were sheared from the same sheet in order to eliminate changes in crack nucleation time and crack propagation rate caused by composition changes.

The sheet stock was sheared into strips 5.0 inches in length and 0.625 inches in width. The strips were then milled with a rotary cutter in order to obtain a final width of 0.50 inch. A hole 0.172 inch in diameter was then drilled 0.50 inch from each end of the specimen. Immediately before exposure to the corrosive medium, each specimen was formed around a one inch diameter brass mandrel in such a way that the inside diameter of the curved part of the specimen conformed to the mandrel, forming the standard "u-bend" specimen. A stainless steel screw inserted through the holes maintained the stress in the curved portion of the specimen by holding the ends together at a distance of one inch. Each specimen was then rinsed in benzene and in distilled water, then dried.

C. Description of Apparatus

All specimens used in this investigation were exposed to the corrosive environment by means of a flask equipped with a reflux condenser. The reflux condenser permitted convenient boiling of the corrosive medium at atmospheric pressure with no sensible change in the boiling temperature or composition of the solution throughout the duration of each test. A laboratory hot plate was used as the source of heat.

D. Corrosive Environment

Of the many known corrosive media that will cause stress corrosion cracking of austenitic stainless steels, magnesium chloride solutions were chosen because they produce cracking in a reasonably short time and do not produce appreciable surface corrosion or pitting. These solutions also remain stable throughout the duration of the tests.

Previous investigations involving stress corrosion cracking of type 304 stainless steel utilized aqueous solutions of technical grade magnesium chloride. Considerable difference in crack nucleation times and crack propagation rates were experienced when solutions of different lots of technical grade magnesium chloride were employed.

Uhlig and White(24) have reported that a difference in cracking time was experienced when a given alloy was exposed to different batches of chemically pure magnesium chloride. Uhlig and Lincoln(11) reported that batches of analytical grade magnesium chloride from different suppliers performed differently.

In order to investigate the effects of impurities commonly found in technical grade magnesium chloride, chemically pure magnesium chloride having the following chemical analysis was used in this investigation with impurity compounds intentionally added in the amount of three weight per cent.

Fe————————0.00005%

Mn————————0.00001%

Insoluble Matter—0.004%

NO_3———————Trace

PO_4———————0.0001%

SO_4———————0.0002%

Ca————————0.010%

K—————————0.005%

Na————————0.005%

Sr————————0.005%

Five hundred grams of chemically pure $MgCl_2 \cdot 6H_2O$ crystals were melted and dissolved in the water of crystallization. Demineralized and distilled water was added through the reflux condenser to lower the boiling point of the solution to 154°C. By controlling the boiling point of the solution at atmospheric pressure, the composition of the solution was controlled. At standard atmospheric pressure, a 42 per cent by weight solution boils at 154°C. After the temperature reached equilibrium, the specimens were submerged in the solution for a predetermined length of time.

The analysis of several lots of technical grade magnesium chloride revealed that the anions present in the greatest quantities were the sulfates, nitrates, and phosphates. The calcium cation was found in all lots examined to be present in an amount far exceeding all other cations. In order to introduce these impurities to the magnesium chloride solutions, the compounds magnesium sulfate, magnesium nitrate, and calcium chloride were added in the amount of three weight per cent to the boiling $MgCl_2$ solution. The boiling point was readjusted to 154°C. after each addition.

IV

RESULTS

Data were accumulated to determine the effect on stress corrosion cracking of several impurities commonly found in technical grade magnesium chloride. The crack depth measurements are tabulated in Tables I through IV and are represented graphically in Figures 1 through 4. In these figures, it will be noted that a straight line relationship exists between the maximum crack depth and the logarithm of the exposure time. These straight lines have been expressed in terms of empirical equations containing two constants, one of which is the time required for cracks to nucleate; the other is a function of the rate at which the nucleated cracks propagate. The best fitting lines of Figures 1 through 4 were determined by the method of least squares.

Figure 5 is a photomicrograph of the AISI 304 stainless steel, as received, before bending, and represents the general structure representative of the material used in these tests. Figure 6 is a photomicrograph of a portion of the material after exposure to the boiling magnesium chloride solution. The stress corrosion crack can be seen to follow a transgranular path, revert to an intergranular path for a short distance, then return to a transgranular path. Although all cracks did not traverse an intergranular path, many did, indicating that stress corrosion cracks in this grade stainless steel can be either intergranular or transgranular.

From Figures 1 through 4, it can be seen that there exists some scatter in the data. There are several factors to which this scatter may be attributed, the two most important being the non-uniformity of bending and the inherent differences in surface and internal structures between individual specimens. The forming of the U-bend specimen necessitates considerable plastic deformation, which far exceeds the yield strength of the alloy. The exterior surface of the specimen is held in a tensile stress, while the interior surface is held in compression. The stress distribution of this shape specimen is complex, however, it is known that the stress is tensile on one face, is zero near the center of the specimen, and becomes more compressive throughout the remainder. As the stress corrosion cracks propagate, they impart a stress relieving action, which constantly changes the already complex stress distribution in the specimen. Because of this complexity, there is no way the stress existing in a specimen can be measured quantitatively.

Other factors that would have an effect on the reproducibility of results are the accuracy of temperature control, the degree of work hardening, the nature and thickness of surface films present, and the presence or absence of inclusions in the material. Some of these variables could be avoided if it were not necessary to use a fresh quantity of magnesium chloride solution and a new specimen for each test. A continuation of the cracking process would not be expected for measured specimens re-immersed in the same corrosive medium because the cracking process will have been interrupted.

Data presented show the susceptibility of AISI 304 to stress corrosion cracking in boiling 42% magnesium chloride solutions, and show the effects of some commonly found impurities on the time to crack nucleation and the rate of crack propogation.

V

DISCUSSION OF RESULTS

It is evident from Figures 1 through 4 and the data presented in this thesis that the compounds intentionally added to boiling 42% magnesium chloride solutions have an appreciable effect on the time to nucleation and the rate of propagation of stress corrosion cracks in AISI 304 stainless steel.

The maximum crack depths are certainly a reliable measure of the susceptibility to stress corrosion cracking, and are also the most important, for these cracks of maximum depth are certain to be those to cause failure, The time to nucleation of the deepest crack is represented by the extrapolation of the maximum crack depth curve to the time abscissa.

The cracks of maximum depth may not necessarily be the very first to nucleate, although they are among the first. Their rates of propagation, however, are faster, a necessary condition for maximum depth at any time after nucleation. The propagation rates will be faster if the cracks follow high energy paths through the specimen, called "crack sensitive paths"(23).

The cracks of greatest interest are those causing the earliest failure. Often these cracks are referred to as "runaway cracks" because their propagation causes stress relief at the roots of other cracks and consequently they cease to grow. The runaway crack then continues to propagate until failure of the alloy occurs.

It can be seen in Table V that the time required for nucleation of cracks in 42% certified grade magnesium chloride is considerably longer than that experienced in previous investigations using the technical grade. This difference is undoubtedly caused by the absence or very low concentrations of certain impurity ions in the certified grade that are commonly found in the technical grade. The analyses of several batches of certified grade magnesium chloride showed the impurity anions in the greatest quantities to be the nitrates, sulfates, and phosphates; the cation in the greatest amount was found to be calcium. The effect of the phosphate radical was not investigated because the solubility limit of magnesium phosphate is very low, hence, its concentration would not be comparable with that of other compounds. The compounds used in this investigation were magnesium nitrate, calcium chloride, and magnesium sulfate.

Comparison of Figures 1 through 4 reveals that the addition of these compounds causes an acceleration of stress corrosion cracking. It can be seen in Figure 2 that the magnesium nitrate addition causes a shorter time to crack nucleation, as do the calcium chloride and magnesium sulfate additions. It was stated by Phillips and Singley(27) that nitrates appear to be satisfactory inhibitors for chloride stress corrosion in boiler applications. These tests, however, employed type 347 stainless steel and a corrosive medium of alkaline-phosphate boiler water containing either 50 or 500 parts per million of chloride. The same inhibiting effect may not be experienced in the utilization of other corrosive media or other grades of stainless steels. It is feasible that the accelerating effect observed in this investigation is attributed either to the donation of oxygen ions through the breakdown of the nitrate radicals into nitrite, or a decrease in the pH of the corrosive medium.

The calcium chloride addition was expected to reduce the time to nucleation, as was experienced; the results are shown in Figure 3. This effect is very likely a result of the increased chloride content, but may possibly be a result of a change in pH caused by the calcium cation.

The magnesium sulfate addition to the magnesium chloride solution produced an accelerated stress corrosion attack on the stainless steel. Although the sulfate radical is fairly stable, some oxygen ions may have been donated through the breakdown of the sulfate radical into a sulfite radical. It is entirely possible that the addition of these compounds lowers the pH of the corrosive medium, causing a more readily removed oxide film, an increased operating electromotive force of the metal electrode-hydrogen electrode cells, in addition to increasing the conductivity of the electrolyte. An increase in the conductivity of the electrolyte would create an increased rate of propagation of nucleated cracks. The time for crack nucleation included the period required for the specimens to reach thermal equilibrium after immersion in the corrosive media. This time was practically the same for all solutions used, so any effect on the time to nucleation would be small.

It was not determined in this investigation if the addition of these compounds resulted in an overall change in pH of the corrosive media. The compounds used were selected on the basis that they introduced no new ions to the corrosive media other than those under investigation. However, it is possible that the pH was lowered or raised, which would respectively decrease or increase the time to crack nucleation.

The data presented in this thesis tend to confirm the postulate of Higgins(28) that a linear relationship exists between the maximum crack depth and the logarithm of the exposure time. This linear relationship can be expressed empirically by the equation:

$$\text{Log } t = {}^{D}/_{M} + \text{Log } C \qquad (1)$$

where t is the time of exposure, D is the depth of the deepest crack, and C and M are constants expressing the time to crack nucleation and a function of the rate of crack propagation, respectively. The constant C can be evaluated by extrapolation to the time abscissa of the maximum crack depth versus log exposure time curve.

For the linear relationship, Solanky(29) stated that the empirical equation:

$$\text{Log } t = a + bD \qquad (2)$$

produces more accurate results. When the maximum crack depth D is plotted against the logarithm of the exposure time t, the constant a represents the time to crack nucleation, as does the constant C in equation 1. The constant b is physically the slope of the curve, and corresponds to the constant M in equation 1.

Rearrangement of equation 2 yields:

$$D = \frac{\log t - a}{b} \qquad (3)$$

Differentiation of this equation with respect to time produces an expression for the rate of crack propagation:

$$\frac{dD}{dt} = \frac{0.4343}{bt} \qquad (4)$$

A similar expression can be obtained from differentiation of equation 1 to yield:

$$\frac{dD}{dt} = 0.4343 \frac{M}{t} \qquad (5)$$

It can be seen from equations (4) and (5) that the rate of crack propagation decreases as the exposure time t increases. Many investigators attribute this solely to the relief of stress as cracks propagate.

The question arises as to whether this decrease in crack propagation rate is actually produced from a decrease in mechanical action only, a decrease in electrochemical action only, or from a simultaneous decrease in each. In order to determine this, it must first be determined exactly what phenomenon fixes the rate of propagation. If a continuous process of crack propagation is assumed, then the rate of crack propagation must be determined by some combined effect of electrochemical and mechanical phenomena. On the other hand, if a discontinuous process of crack propagation is assumed, the crack propagation rate may be determined by several factors. If cracking in a discontinuous process is assumed to occur by the mechanical "bursting" of small embrittled areas, the propagation rate may depend upon the size of these embrittled areas, the number of embrittled areas, or the frequency of the mechanical "bursts" from one brittle area to the next. Also, the rate of formation of the embrittled areas may be the rate controlling factor.

The results tabulated in Table V of this thesis indicate that the rate of crack propagation is decreased by the addition of certain impurity compounds. This is an indication that a change in composition of the corrosive medium is responsible for a change in the rate of crack propagation, which could result only in a decrease in the rate of electrochemical attack or in a decrease in the rate at which embrittlement occurs. It seems unlikely that the addition of other ions could result in embrittled areas of smaller dimensions or a change in the number of these areas. However, it does seem possible for these ions to affect the rate of fracture, or the frequency of "bursts", by a change in electrochemical activity either through an increase in the conductivity of the corrosive medium or through a decrease in its pH.

Data tabulated in Table V indicate that the constant M, a function of the rate of crack propagation, varies widely for the same alloy exposed to corrosive media of slightly different compositions. It can be seen that the propagation rate is considerably lower in tests where technical grade magnesium chloride solutions were used as the corrosive media. This can be attributed to the differences in composition only, as the technical grade magnesium chloride contains a higher level of impurities than does the certified grade used in this investigation.

VI

SUMMARY AND CONCLUSIONS

Experiments have been performed to determine the effects of several impurity ions in boiling magnesium chloride solutions upon the time to crack nucleation and the rate of crack propagation in AISI 304 stainless steel. From the experiments performed utilizing standard U-bend specimens, the following conclusions may be drawn:

1. The straight line relationship between maximum crack depth and logarithm of exposure time, as postulated by Higgins(28), was found to be applicable to specimens exposed to certified grade magnesium chloride solutions as well as those solutions to which had been added impurity compounds.

2. Cracking can be either intergranular or transgranular, indicating that cracks follow "crack sensitive paths" through the alloy.

3. The addition of magnesium nitrate to a magnesium chloride solution decreases the time to crack nucleation but also decreases the rate of crack propagation.

4. The addition of calcium chloride to a magnesium chlo-

ride solution decreases the time to crack nucleation but also decreases the rate of crack propagation.

5. The addition of magnesium sulfate to a magnesium chloride solution decreases the time to crack nucleation, but also decreases the rate of crack propagation.

6. The rate of crack progagation decreases with increasing exposure time. The exact mechanism of stress corrosion cracking must be determined before this phenomenon can be explained completely.

7. It is necessary to control the composition of the corrosive medium, particularly with regard to impurity content, in order to expect reproducable results.

8. The continuation of experimentation is necessary in order to determine the effect of the impurity additions on the pH of the corrosive media.

VII

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VIII

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TABLE I

Stress Corrosion Cracking of AISI 304 Stainless Steel Exposed to Boiling 42% Certified Grade Magnesium Chloride

Specimen No.	Time of Exposure (Minutes)	Maximum Crack Depth (Microns)
M1	135	1448
M2	100	1182
M3	60	683
M4	30	367
M5	45	485
M6	60	527
M7	60	712
M8	45	474

TABLE II

Stress Corrosion Cracking of AISI 304 Stainless Steel Exposed to Boiling 42% Certified Grade Magnesium Chloride to which has been added 3% Magnesium Nitrate

Specimen No.	Time of Exposure (Minutes)	Maximum Crack Depth (Microns)
M9	60	796
M10	75	989
M11	75	1060
M12	30	480
M13	45	703
M14	45	640
M15	30	410
M16	30	378
M17	40	570
M18	25	260
M19	20	120

TABLE III

Stress Corrosion Cracking of AISI 304 Stainless Steel Exposed to Boiling 42% Certified Grade Magnesium Chloride to which has been added 3% Calcium Chloride

Specimen No.	Time of Exposure (Minutes)	Maximum Crack Depth (Microns)
M20	20	306
M21	30	845
M22	37	1020
M23	37	960
M24	60	1325
M25	75	1260
M26	45	1120

TABLE IV

Stress Corrosion Cracking of AISI 304 Stainless Steel Exposed to Boiling 42% Certified Grade Magnesium Chloride to which has been added 3% Magnesium Sulfate

Specimen No.	Time of Exposure (Minutes)	Maximum Crack Depth (Microns)
M27	30	438
M28	45	1020
M29	60	928
M30	75	1040
M31	100	1155
M32	135	1389

TABLE V

Evaluation of Constants C and M

Corrosive Environment	M $(\frac{\text{microns}}{\text{log time}})$	C (minutes)
42% $MgCl_2$	1780	23.33
42% $MgCl_2$ + 3% $Mg(NO_3)_2$	1640	17.43
42% $MgCl_2$ + 3% $CaCl_2$	1577	9.67
42% $MgCl_2$ + 3% $MgSO_4$	1261	10.72
42% Technical Grade $MgCl_2$; Previous Investigation, Higgins,(28) Thesis, VPI, 1959	962	5.4
42% Technical Grade $MgCl_2$; Previous Investigation, Anderson,(30) Thesis, VPI, 1960	873	3.4
42% Technical Grade $MgCl_2$; Present Investigation, Greene,(31) Thesis, VPI, 1962	738	2.3

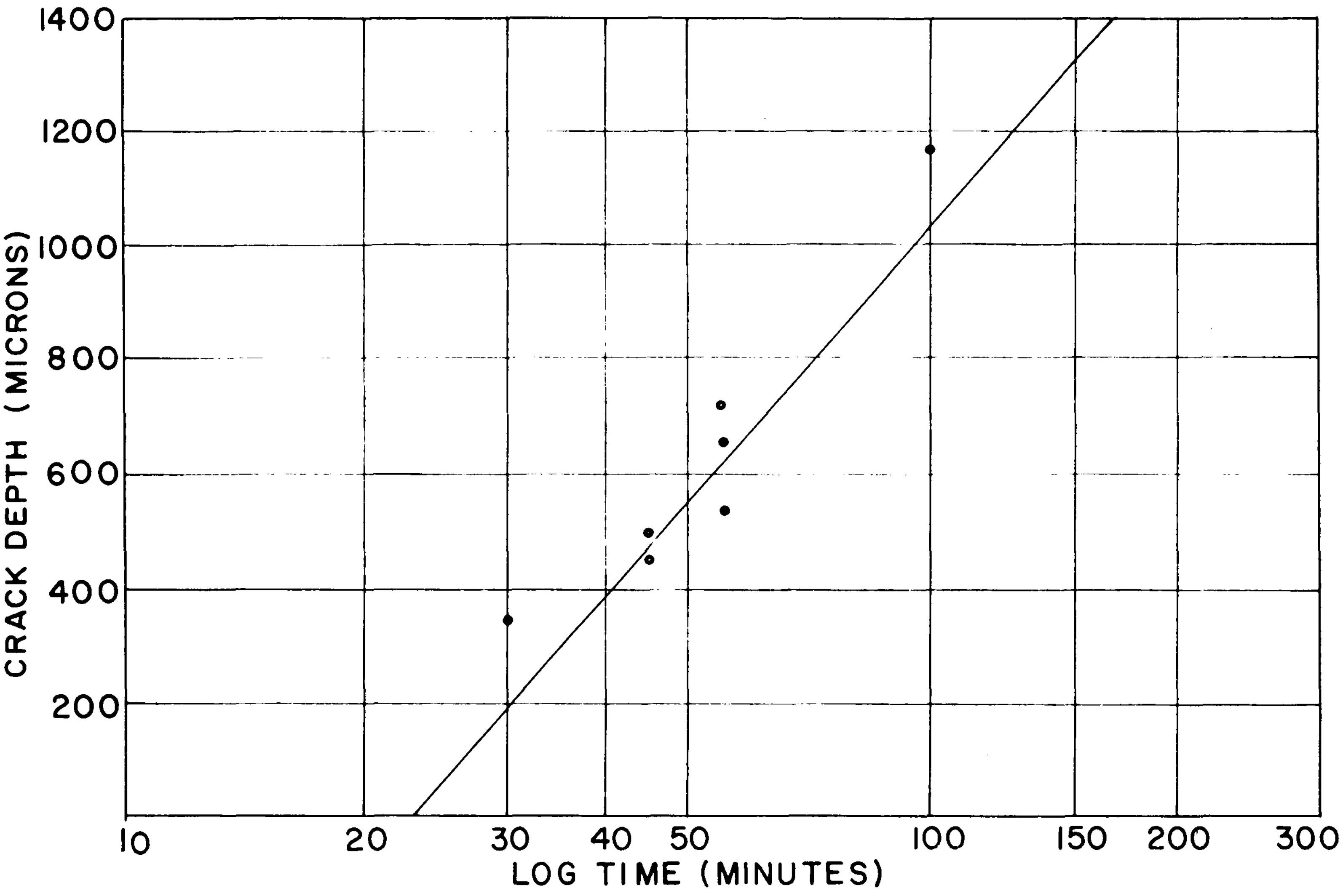

FIGURE 1. CRACK NUCLEATION AND GROWTH IN AISI 304 EXPOSED TO BOILING 42% $M_G Cl_2$

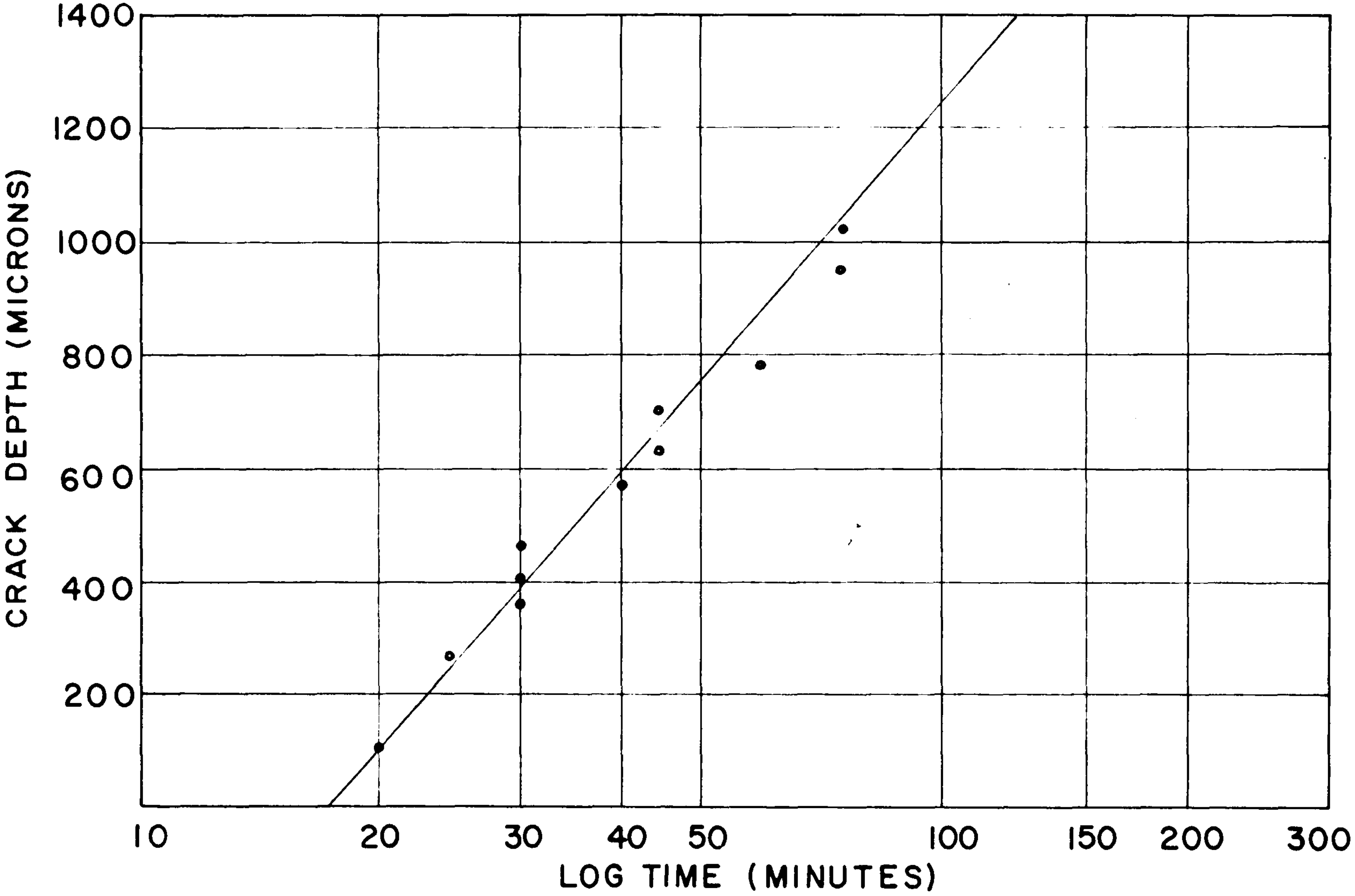

FIGURE 2. CRACK NUCLEATION AND GROWTH IN AISI 304 EXPOSED TO BOILING 42% $MgCl_2$ WITH 3% $Mg(NO_3)_2$

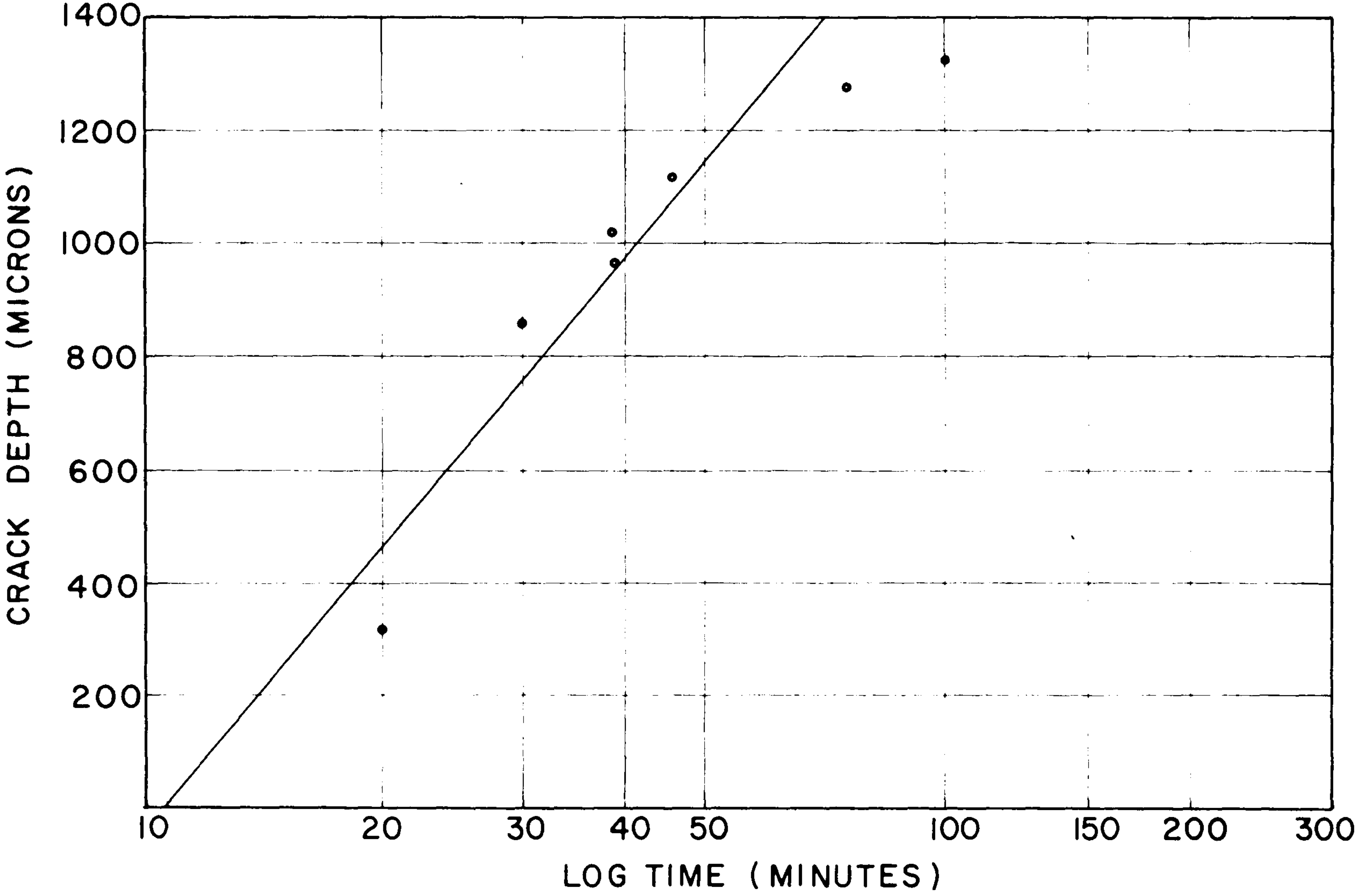

FIGURE 3. CRACK NUCLEATION AND GROWTH IN AISI 304 EXPOSED TO BOILING 42% $MgCl_2$ WITH 3% $CaCl_2$

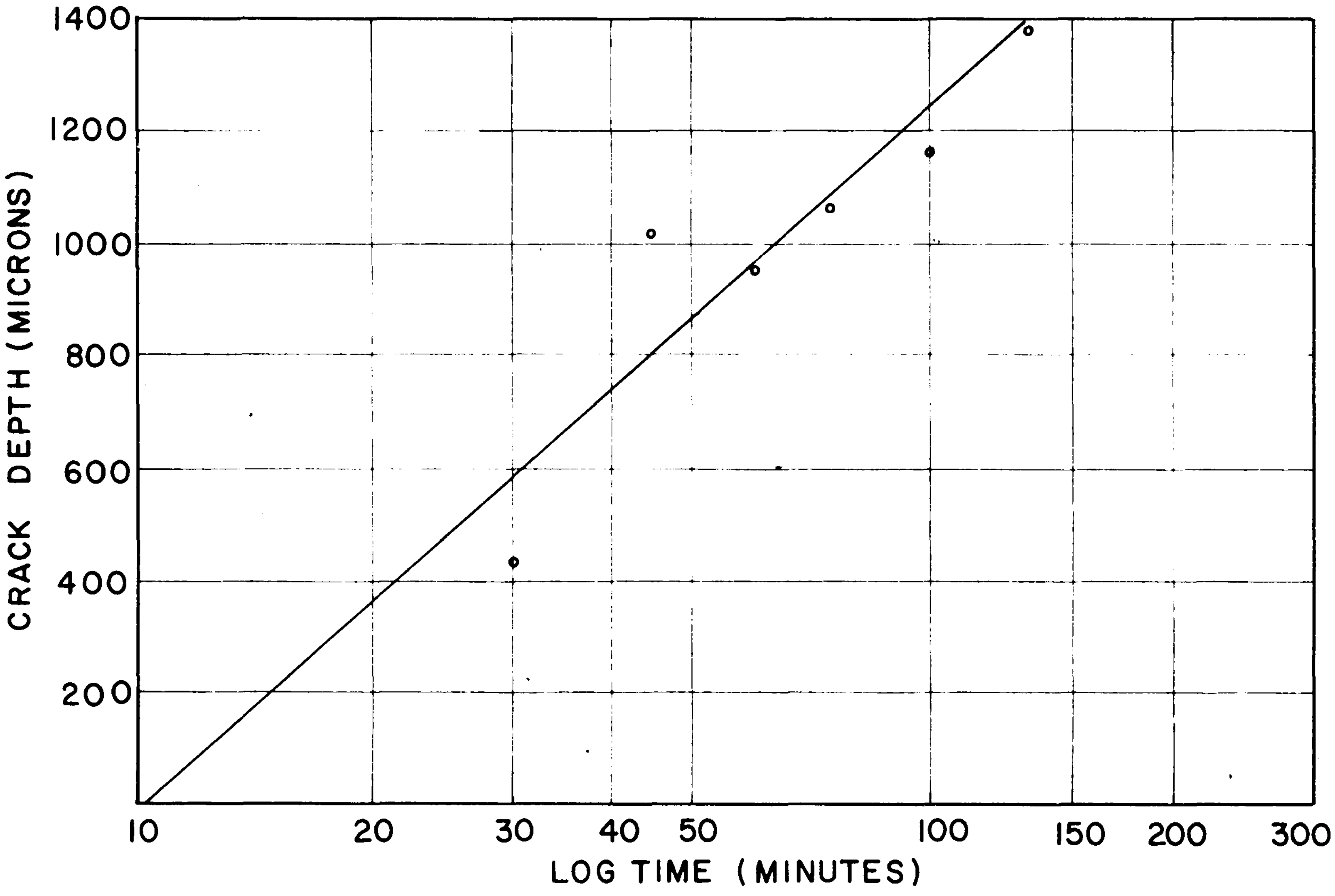

FIGURE 4. CRACK NUCLEATION AND GROWTH IN AISI 304 EXPOSED TO BOILING 42% $MgCl_2$ WITH 3% $MgSO_4$

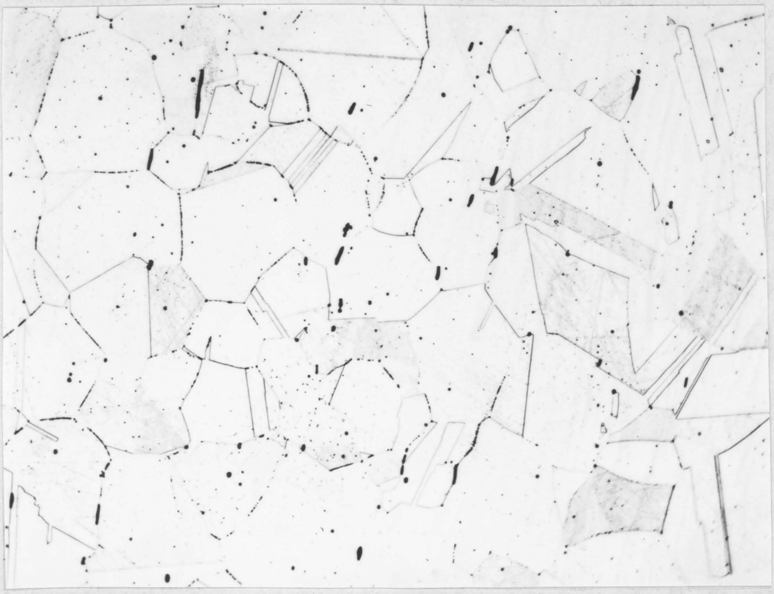

Figure 5. AISI 304 Stainless Steel
As-Received: Etched in
Chromic Acid. 500X

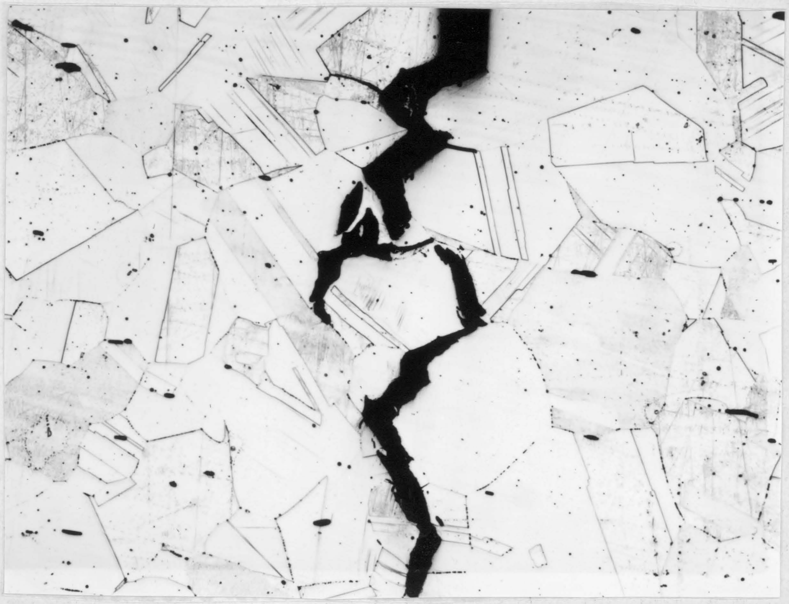

Figure 6. Transgranular Stress Corrosion Crack Characteristic of AISI 304 Exposed to Boiling Magnesium Chloride: Etched in Chromic Acid. 500X

ABSTRACT

The influence of impurities in magnesium chloride upon the rate of attack of stress corrosion cracking in AISI 304 stainless steel has been investigated. Previous investigations in this laboratory indicated that different batches of technical grade magnesium chloride produced poor reproduceability of results. These inconsistencies were attributed to the presence of varying amounts of impurities which are commonly found in technical grade magnesium chloride.

In this investigation, certified grade magnesium chloride was used with impurities intentionally added in order to determine how each affected the constants M and C in the following equation, which relates the maximum crack depth D, to the time of exposure to the corrosive medium, t:

$$\log t = {}^{D}/_{M} + \log C$$

The constant C represents the time of exposure to the corrosive media to nucleate cracking, and M is a function of the rate at which cracks propagate.

It was determined that the impurity ions most commonly found in magnesium chloride were nitrate, sulfate, and calcium. A significant difference in the constants C and M was found to exist with the presence of each impurity. It was not determined, how-

ever, if a change in pH resulted from the addition of the impurity compounds. Hence, a further study is required in order to determine the pH of the corrosive media and the effects of its changes.