

EFFECT OF PRE-EXPOSURE THERMAL TREATMENT
ON SUSCEPTIBILITY OF TYPE 304
AUSTENITIC STAINLESS STEEL
TO STRESS CORROSION

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INTRODUCTION

Among many industrial alloys, stainless steels find exceptionally broad applications. These range from household hardware to heavy industry components. However, there are many problems still unsolved which restrict further uses of these materials. In order to improve stainless steels and extend their uses, rather than to develop new alloys, much attention has been given to their metallurgical and corrosion characteristics.

One of the problems which restricts further applications is stress corrosion. This type of corrosive attack involves the combined effect of stress, either static or dynamic, and specific environmental conditions.

Stress corrosion cracking is defined as combined action of stress and corrosion which leads to cracking or embrittlement of metals.⁽¹⁾ Stress corrosion cracking is known to occur in all conventional austenitic stainless steels. The principal variables are stress, environment, time of exposure, and internal structure of the alloys. Other factors in stress corrosion cracking are

composition of the alloy, thermal and mechanical treatment, and surface condition. Each of these variables probably affects the nucleation time of cracks, the rate of crack propagation, and the type of cracks formed.

The path taken by a stress corrosion crack is determined mainly by the stress distribution near its advancing edges. ⁽²⁾ The type of propagation may consist of an intergranular, transgranular, or an intergranular-transgranular path. Intergranular cracking can be avoided by high temperature annealing, followed by rapid quenching, since the austenitic stainless steels are metallographically unstable when heated in the temperature range where carbide precipitation occurs. Transgranular cracking can be eliminated or reduced by stress relief annealing and by limiting the applied stress, since residual or a combination of residual and operating stresses are mainly responsible for this type of failure.

In general, as the residual stress or the applied stress increases, the greater is the acceleration and the rate of crack propagation. However, many failures caused by stress corrosion are

the result of an internal or residual stress rather than an applied operating stress. Therefore, in order to reduce or remove this susceptibility, the stress relief heat treatment can be done by using a combination of time and temperature capable of eliminating residual stress in the absence of subsequently applied stress of sufficient magnitude to cause damage. (3)

The purpose of this work is to investigate the effect of a specific type of pre-exposure heat treatment on the susceptibility of austenitic stainless steel, AISI type 304, to stress corrosion cracking in a corrosive environment of boiling aqueous solution of magnesium chloride.

The experimental procedure and the method of evaluation of susceptibility is based on the method which has already been described by Eckel. (4)

REVIEW OF LITERATURE

It is a well known fact that stress corrosion of austenitic stainless steel is identified by cracks which usually follow random paths in a branching pattern, or radiate from a pit or other focal point, or start at some other stress raising notch. On the microscopic scale the cracks are mostly transgranular. But, intergranular cracks are also observed.

Intergranular cracking usually results in material which is susceptible to intergranular attack caused by carbide precipitation.

Stress corrosion cracking has been observed in most commercial austenitic stainless steels when they are exposed to concentrated aqueous magnesium chloride solutions boiling at atmospheric pressure. The principal factors which determine the initiation and growth of stress corrosion cracks in austenitic stainless steels are stress, environment, time of exposure, and internal structure of the alloys. The latter is not well understood, but probably is of the form of structural discontinuities.

Many theories of the mechanism have been proposed to account for stress corrosion in

austenitic stainless steels, but no one theory explains all of the known and observable facts of the process.

Effect of Stress on Stress Corrosion Cracking

When work is done on a metal or alloy, a large portion is dissipated in the form of heat. However, a significant amount of this work is stored up by the metal as latent energy, or residual stress which raises the energy level. Such residual stress can be developed in the metal by welding, casting, heat treatment, forming, machining, grinding, plating, etc. (5)

Hines and Hoar (6) observed that austenitic stainless steel with residual stresses from quenching or straining, cracks more severely and fractures with no applied stress in a comparatively short time when exposed to certain environments. This was true in austenitic stainless steels, but not in all other steels or alloys. For example, quenching so increases the resistance to cracking compared to air cooling, in naval brass, that higher stresses were required to produce stress corrosion cracks. (7)

Many investigators tried to obtain a threshold stress, that is, a minimum stress required to produce stress corrosion cracking in austenitic stainless

steel, but the results have been inconclusive. Frank, Binder, and Brown⁽⁹⁾ found the order of yield strength as threshold stress. Harwood⁽⁷⁾ agreed with this and mentioned that stresses approximately equal to the yield strength are required to cause stress corrosion cracking. Frequently stresses of quite low magnitude are sufficient, thus the threshold stress depends mainly upon the physical nature of the medium, such as the temperature, the anion in the environment, and previous history of the material.

It is a well known fact that the stress stored in metallic material can be removed or reduced by the heat treatment using a combination of time and temperature. In other words, heat treatment can be applied for the purpose of avoiding stress corrosion cracking in the absence of subsequent applied stress. Hines and Hoar⁽¹⁰⁾ observed that a reduction of internal stress or applied stress delays the onset of cracking, but it does not prevent it indefinitely. Heeley and Little⁽¹¹⁾ observed that the application of heat treatment at 880°C (1616°F) for one to two hours efficiently restored the corrosion resistance of

the materials which had been impaired by heating in the range of 600°C to 750°C (1112°F to 1382°F).

The main effects of stress either applied or residual, on the nature, rate, and distribution of the corrosion reaction, in the stainless steel, have been summarized by Harwood⁽⁷⁾ as follows:

Residual or applied stress:

1. Increases the internal energy level of the metallic system and causes a possible shift of electrochemical potential in a more active direction.
2. Causes an intrinsic increase in the rate of corrosion.
3. Damages protective surface films.
4. Influences polarization reactions.
5. Changes the metallurgical characteristics of the metal system by promoting phase transformation, precipitation, etc.
6. Accelerates the rate of corrosion by purely mechanical effects.

Effect of Corrosive Environment on
Stress Corrosion Cracking

Almost all grades of austenitic stainless steels are susceptible to stress corrosion in various chloride solutions, regardless of whether they are stabilized or previously heat treated to resist attack. The chlorides in which cracking has been experienced are magnesium-, sodium-, lithium-, nickel-, manganese-, calcium-, and tin-chlorides. Edeleanu⁽¹²⁾ noted that all aqueous chlorides do not attack the stainless steel to the same extent. There must be some other factors in environment which will determine the initiation and propagation of crack.

Eckel and Williams⁽¹³⁾ observed that both oxygen and chloride must be present for the stress corrosion cracking to occur at high temperatures and pressures. That is, high oxygen concentration in solution is unable to attack the steel if the chloride ion concentration is extremely low, while high chloride ion does not affect stress corrosion cracking if the oxygen content is very small. These observations, however, apply only to chloride solutions containing not more than 2000 ppm chlorides. However, it is

noticeable that, as Harwood⁽⁸⁾ pointed out, oxygen must be present in sodium chloride solution for stress corrosion cracking to occur, but it may not be a requisite for cracking in concentrated magnesium chloride solution.

High acidity of magnesium chloride solutions is favorable to stress corrosion of austenitic stainless steels. The addition of hydrochloric acid to boiling magnesium chloride solution decreases the time to failure,⁽³⁾ whereas making the solution alkaline with sodium hydroxide increases the time to cracking. However, lowering the initial pH of the corrosive medium apparently has no effect on the stress corrosion behavior of austenitic stainless steel in a sodium chloride environment.⁽¹³⁾

The temperature and the concentration of the corrosive solution also affect the susceptibility to stress corrosion cracking. Kirk, Beck, and Fontana⁽¹⁴⁾ observed that by reducing the temperature of the magnesium chloride solution the time necessary for the onset of cracking in AISI 347 and 316 stainless steels was increased. Higgins,⁽¹⁵⁾ Ishiwatari,⁽¹⁶⁾ and Greene⁽¹⁷⁾ observed that by

increasing the concentration of the magnesium chloride solution (with which the boiling temperature of the solution increases) the time for crack nucleation and the rate of crack propagation were decreased in AISI 304 and 347 stainless steels.

Effect of Structure and Composition of Stainless Steel on Stress Corrosion Cracking

The stress corrosion behavior of austenitic stainless steels varies with its composition and microstructure.

Edeleanu⁽¹²⁾ observed that when 18% Cr and 0.05% to 0.07% C stainless steel is exposed to 42% magnesium chloride solution, the susceptibility to stress corrosion cracking was decreased with increasing nickel content. Eckel⁽⁴⁾ showed that when the nucleation time for crack is plotted as a function of nickel content by arranging the various grades of austenitic stainless steels in the order of nickel content, type 304, 304L, 321, 347, and 310, the susceptibility is reduced with the increase in the nickel content.

Berwick⁽¹⁸⁾ observed that a lower carbon alloy is less susceptible to intergranular stress corrosion

cracking. He also observed that molybdenum bearing stainless steel has no tendency toward stress corrosion cracking in severely corrosive media after heat treatment.

Changes in microstructure from the prior history of the steel also affect susceptibility to stress corrosion cracking. Edeleanu⁽¹⁹⁾ mentioned that strain-induced martensite in austenitic stainless steel is attacked more preferentially by magnesium chloride solution and cracks can propagate along the martensite plates. However, Hines⁽²⁾ commented on this that martensite plates can act as a cracking path only when they lie in the cracking direction and the cracks can propagate across the martensite plates. It is evident that the stress induced martensite has some effect on susceptibility whether the effect is large or small.

Susceptibility can also be expected to depend upon the grain boundary condition of austenitic stainless steel, such as precipitation of carbide, orientation and stress concentrations, and the presence of slip line, deformation markings, etc. All these can result in active sites for pitting or corrosion attack.

Effect of Surface Condition on
Stress Corrosion Cracking

In general, stress corrosion cracking of austenitic stainless steels is related to pitting behavior, or breakdown of surface film due to electrochemical reaction with corrosive media.

Rhodin⁽²⁶⁾ observed that the behavior and the composition of the oxide film on stainless steel depend upon the alloy composition. He also observed the role of stress and said that stress causes the fracture but sometimes it helps the crystallization of the oxide film. In general, oxide film formed on stainless steel seems to be somewhat ductile but their ductility is decreased with increasing temperature and film thickness.

Gulbransen⁽²⁰⁾ observed that oxide films formed with dry oxygen are susceptible to stress corrosion cracking. He found thin whisker oxides on annealed stainless steel and stated that at or near the root of a whisker or a platelet, a small pit or narrow trench may form and this may lead to nucleation of a stress corrosion crack.

In the case of a stainless steel which has been stressed on the surface by quenching, stress corrosion was prevented by the removal of a thin surface layer. Klingel⁽²¹⁾ quenched a stainless steel, type 402, into oil from 1010°C (1850°F), then stress-relieved at 470°C (880°F) for two hours, and air cooled. There were no cracks on the surface when it was subjected to a solution of 6% sodium chloride, 0.5% acetic acid saturated with hydrogen sulfide and the balance water, at room temperature for 19 hours.

Kirk, Beck, and Fontana⁽¹⁴⁾ observed that the adsorption of chloride ions on the surface at breaks initiates cracking which leads to local anodic area.

Thus, the nucleation stage of the cracking process appears to be mainly determined by the condition of the surface and the passivating film.

Proposed Theories on the Mechanism of Stress Corrosion Cracking

There have been many proposed mechanisms of stress corrosion cracking in austenitic stainless steels. However, no single one completely explains the observed facts. Certainly none explains why

a ductile alloy fails in a brittle fashion when exposed to certain corrosive environments.

Harwood⁽⁷⁾ suggested that susceptibility of stress corrosion cracking is dependent of film forming properties and deformability of the metal, and implied that stress plays no direct part in crack propagation.

Logan⁽²²⁾ suggested that the propagation of crack depends upon the nature of oxide or corrosion film at the tip of the advancing crack as a result of the localized deformation. The film free metal will be anodic to the filmed metal along the cracks and thus localized intense corrosion can be maintained.

Hoar⁽²³⁾ suggested that initiation of cracks depends upon the mere exposure of bare metal to the corrosive medium and cracks propagate by the rapid dissolution of rapidly yielding metal at the advancing edge of the metal crack. The primary role of stress is to cause localized deformation at the root of the corrosion fissure.

Leu and Helle⁽²⁴⁾ emphasized the role of stress and suggested that stressing of austenitic stainless steel leads to a deformation of the material which results in slip. At the place where slip occurs

the oxide film present on the surface can be damaged, so that a corrosive attack at these sites is possible and the result is pitting. These pits act as stress raisers, so that mechanical cracking of the material is initiated.

Uhlig⁽²⁵⁾ suggested the role of stress is associated with the plastic deformation process occurring at the tip of the corrosion fissure. Deformation thus induces local change in composition at imperfection sites, such as dislocations, grain boundaries, etc., thus causing precipitation of carbides and/or nitrides or other segregation which provides the local cell necessary for continuous electrochemical dissolution.

It can be concluded that no one theory of the mechanism of stress corrosion cracking in austenitic stainless steel is satisfactory. However, it is generally agreed that stress corrosion occurs in two stages. The first stage is the nucleation or initiation stage of cracks. The second stage is the propagation of such crack. It must be concluded again that more extensive studies which could rationalize the mechanism in a better way are necessary.

EXPERIMENTAL PROCEDURE

Description of Apparatus

The apparatus used throughout this work consisted of two separate pieces of equipment. An electric resistance oven having a temperature range from 35°C to 180°C (95°F to 356°F) was used for the pre-exposure heat treatments. A standard corrosion testing apparatus consisting of a flask equipped with a reflux condenser was used to expose specimens to 42% magnesium chloride boiling at atmospheric pressure. This apparatus permitted exposure without any sensible change in the composition of the corrosive environment.

Materials and Specimens

The material used in this work was austenitic stainless steel, AISI type 304. It consisted of sheet stock 0.0625 inches thick with an ASTM 2B finish, and was supplied by the United States Steel Corporation. The heat analysis of the steel is as follows:

Carbon-----	0.05%	Copper-----	0.18%
Manganese----	1.59%	Nickel-----	9.4%
Phosphorus---	0.030%	Chromium----	18.7%
Sulfur-----	0.025%	Molybdenum---	0.36%
Silicon-----	0.56%		

Specimens were prepared from the sheet stock sheared to a length of 5.0 inches and a width of 0.625 inches. They were cut in the direction transverse to the rolling direction. After the shearing operation, each specimen was milled longitudinally to a width of 0.50 inches. A hole 0.172 inches in diameter was drilled 0.50 inches from each end of each specimen. Each specimen was bent around an one-inch diameter mandrel and the ends secured with a stainless steel screw so that the inside dimension at the open end of the U was one inch.

Pre-Exposure Heat Treatment

Two pre-exposure heat treatment temperatures and two pre-exposure heat treatment time intervals were employed prior to exposure to the corrosive environment. Specimen Group A, consisting of nine specimens, was placed in the oven for 24 hours at

154°C (309°F) and atmospheric pressure. Group D, consisting of nine specimens, was treated the same way, but held for two hours in the oven.

Specimen Group B, consisting of nine specimens, was placed in the oven for 24 hours at 140°C (284°F) at atmospheric pressure. Group C, consisting of seven specimens, was treated the same way, but held for two hours in the oven.

All specimens were exposed to boiling 42% magnesium chloride aqueous solution without cooling from the pre-treatment temperature.

Corrosive Environment

An aqueous solution of magnesium chloride containing 42% $MgCl_2$ by weight, boiling at 154°C (309°F) and atmospheric pressure was used as the corrosive medium. This solution was obtained by placing 500 grams of magnesium chloride ($MgCl_2 \cdot 6H_2O$) in a flask and then adding demineralized water until its adjusted boiling point reached 154°C (309°F).

Each specimen was exposed to this solution for a pre-determined length of time without cooling after the pre-exposure heat treatment. Only one specimen

was exposed in each fresh batch of the solution, which was then discarded. No specimen was re-exposed a second time.

Metallographic Examination

After each specimen was exposed to the corrosive environment for a pre-determined length of time, the specimen was washed thoroughly with hot water and dried. Each specimen was then ground with the 400 and 600 grit paper on a stationary flat surface lubricated with flowing water, polished on a low speed rotating lap covered with wool-broad-cloth with application of aluminum oxide powder in water, and again fine polished with gamal cloth with an application of levigated alumina in water, and then electrolytically etched to reveal the microstructure and crack pattern.

The etching was done by placing a bent portion of each specimen in a chromic acid solution (10 gm. of CrO_3 + 100 cc. demineralized water), and applying three volts and three amperes for 150 seconds.

The depth of the deepest crack was measured microscopically in microns using a filar eyepiece.

In order to insure accurate measurements from the edge of each specimen, a light source was placed in front of the microscope slightly higher than the level of the specimen under examination. This illuminated the surface so that the edge could be positively located.

RESULTS

The measured maximum crack depths are tabulated in Table I for specimen Groups A and D, and in Table II for specimen Groups B and C. The data for each group were expressed graphically by plotting the maximum crack depth as a function of the logarithm of exposure time for the Groups A, D, B, and C, in Figures 1, 2, 3, and 4, respectively.

The straight line in each plot was used to describe the relationship between crack depth and exposure time. The constants for each line were obtained by statistical methods. The equation expressing the relationship⁽⁴⁾ between crack depth and exposure time is:

$$\log t = D/M + \log t_0 \quad (1)$$

where t is the time of exposure in minutes, D is the maximum crack depth in microns, M is the slope of the straight line, a function of the rate of crack propagation, and t_0 is the exposure time required for crack nucleation.

The least square method was applied to obtain the values of the constants, M and t_0 , and the straight

lines. The least square line approximating the set of points $(X_1, Y_1), (X_2, Y_2), \dots, (X_n, Y_n)$ has the equation

$$Y = a_0 + a_1 X$$

The constants a_0 and a_1 are determined by solving simultaneously the equations:

$$\bar{Y} = a_0 N + a_1 \bar{X} \quad (2)$$

$$\overline{XY} = a_0 \bar{X} + a_1 \bar{X}^2$$

where $Y = \log t$, $X = D$, $a_0 = \log t_0$, $a_1 = 1/M$, and $N =$ the number of specimens in each group. The constants M and t_0 can, if desired, be found from the equations:

$$\log t_0 = \frac{(\bar{Y})(\bar{X}^2) - (\bar{X})(\overline{XY})}{N\bar{X} - (\bar{X})^2} \quad (3)$$

$$M = \frac{N\bar{X}^2 - (\bar{X})(\overline{XY})}{N\overline{XY} - (\bar{X})(\bar{Y})} \quad (4)$$

The equations obtained by the above method which correspond to equation (1) for each group are as follows:

$$\text{Group A: } \log t = -0.87 + 0.00223 D$$

$$\text{Group B: } \log t = -0.55 + 0.00198 D$$

$$\text{Group D: } \log t = -0.49 + 0.0019 D$$

$$\text{Group C: } \log t = -0.22 + 0.0016 D$$

From these equations straight lines were located on the plots of Figures 1, 2, 3, and 4, which represent the data obtained.

The values of constants M and t_0 determined from equations (3) and (4) are tabulated in Table III. The time required for complete crack penetration and the time required from crack nucleation to complete crack penetration of each specimen group are also shown in Table III.

The rate of crack propagation was plotted in terms of percent penetration in Figure 5 according to the equation: (4)

$$dD/dt_p = \frac{0.4343 M}{t - t_0},$$

which shows that the rate of crack propagation is inversely proportional to the exposure time after crack nucleation, and that crack propagation acts to relieve stresses in the U-bend specimen.

DISCUSSION OF RESULTS

The data obtained from the present investigation show scattering around the straight line expressing the relationship between the maximum crack depth and the logarithm of exposure time. There are three principal sources of error in the experimental method which account for a large portion of this scattering.

First, some non-uniformity of the specimen surface caused by the cutting operations. Second, some non-uniformity of the stress distribution in the material caused by the plastic deformation from the bending process. And third, two dimensional observation of the three dimensional cracks results in tunneling of the crack path, as shown earlier.⁽⁴⁾

The data obtained (see Table III) from the present investigation show that the specimens subjected to the pre-exposure heat treated (PEH-treated) for the longer time, 24 hours, at the higher temperature, 154°C (Group A), initiates cracks in a shorter time, but the rate of crack propagation is lower. Thus the complete breakdown of the specimen requires a longer time. While with shorter pre-exposure times and lower temperatures of

pre-exposure (two hours and 140°C, respectively, for Group C specimens) cracks nucleate after a longer time of exposure in the corroding medium. The time for complete crack penetration is shortened.

Other data, obtained by Greene,⁽¹⁷⁾ on the same steel exposed to 42% MgCl₂ at 154°C without the PEH-treatment shows that the nucleation time of the crack is much longer (2.3 minutes) than any obtained in the present investigation. Also, the rate of crack propagation is much more rapid (738 micron/log t) in spite of the longer nucleation time of the crack.

The nature of the film on the surface of the stainless steel resulting from the PEH-treatment may cause the differences in the nucleation time of cracks. In addition to the comparison of the time for crack nucleation, it is observed that at the constant oven temperature of PEH-treatment, the nucleation time is shortened with increasing the time of PEH-treatment, while for the constant time of PEH-treatment, the time for nucleation of crack is shortened by raising the oven temperature. From this, it may be said that the increase in time of PEH-treatment changes the thickness of the surface

film, and the rise in oven temperature will change the physical and structural natures of the surface film.

Although no attempt has been made to identify the film formed on the surface of stainless steel by the PEH-treatment, previous work indicates what may have occurred.

Rhodin⁽²⁶⁾ has observed that increased temperature causes oxide films on stainless steel to become thicker, more crystalline, and less protective. Gulbransen⁽²⁰⁾ observed that the crystal habits of film growth could consist of a platelet type of growth and suggested that crack nucleation was promoted by pit formation at the root of these platelets. This type of film may, or may not, form on the surface of the specimens which were PEH-treated. Exposure of the steel to the atmosphere at elevated temperatures may have resulted in changes which produced less protection. It may have increased the thickness of the film and changed its characteristics. An increase in thickness caused by the pre-exposure temperature would be expected to decrease the ductility of the surface film formed on the stainless steel, as Rhodin observed.

This decrease of ductility could result in a shorter crack nucleation time.

Changes in the alloy during the PEH-treatment could also account for the difference in nucleation time between the specimens PEH-treated and non-PEH-treated before subjecting them to the corrosive medium. Herrnstein⁽²⁷⁾ observed, on the same steel, type 304, that abrupt changes in the slope of the strain-temperature curve occurred in the temperature range between 95 and 145°C. This phenomenon may occur during the PEH-treatment at the oven temperatures 140°C and 154°C. Such changes in the alloy may rupture the film formed by PEH-treatment, so that it enhances the corrosive attack of the bare metal. Structural changes within the alloy which cause the discontinuities observed by Herrnstein have not been identified but are believed to be associated with interstitials such as nitrogen.

The slope M of the straight lines in Figures 1, 2, 3, and 4 is a function of the rate of crack propagation. The values obtained show that the rate of crack propagation is decreased by an increase in the time or temperature of the PEH-treatment. This could

result from partial stress relief. It appears more likely that it is related to structural changes within the alloy. Such structural changes can be expected to be time and temperature dependent. Thus a longer time or a higher temperature should result in the structural changes being more nearly completed.

It should be noted that the PEH-treatment at the same temperature as the corrosive medium (154°C) reduced the time for crack nucleation and the rate of crack propagation. The pre-treatment probably changed the nature of the protective film, rendering it less protective. It also may have caused structural changes to approach more closely to equilibrium, thus reducing the rate of crack propagation. Each of these factors probably contributed to observed changes in nucleation time and rate of crack propagation.

As shown elsewhere^(15,16,17), the crack nucleation time and the rate of crack propagation are both decreased by increasing the concentration of the magnesium chloride solution. Those data and the data obtained from this investigation suggest that temperature is a more important variable than concentration of the magnesium chloride.

SUMMARY AND CONCLUSIONS

The effect of a specific type of pre-exposure heat treatment on susceptibility of austenitic stainless steel, AISI type 304, to stress corrosion cracking has been evaluated in terms of time for crack nucleation and the rate of crack propagation by subjecting the U-bend specimen to magnesium chloride solution after pre-exposure heat treatments.

From the results of the present investigation, it can be concluded that:

The linear relationship between the maximum crack depth and the logarithm of time of exposure is applicable to AISI 304 heat treated at 140°C (284°F) and 154°C (309°F) for two hours and 24 hours.

This type of pre-exposure heat treatment promotes the crack nucleation and retards the rate of crack propagation.

The decrease in crack nucleation time may be caused by changes in the nature of the surface film during the pre-exposure heat treatment.

The retardation of the rate of crack propagation may be caused partially by the reduction

of internal stress during the pre-exposure heat treatment and partially by permitting internal structural changes in the alloy to approach completion.

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BIBLIOGRAPHY

1. Uhlig, H. H., Corrosion Handbook, John Wiley and Sons, New York, N. Y., 6th printing, p. 569 (1958).
2. Hines, J. G. and Hugill, R. W., "Metallographic and Crystallographic Examination of Stress Corrosion Cracks in Austenitic Cr-Ni Steels," Physical Metallurgy of Stress-Corrosion Fracture (T. N. Rhodin), Met. Soc., AIME, Met. Soc. Conf., Vol. 4, Interscience Publishers, New York, N. Y. (1959).
3. LaQue, F. L., Symposium on Stress Corrosion Cracking of Austenitic Cr-Ni Stainless Steels, ASTM Special Report No. 264, p. 1 (1960).
4. Eckel, J. F., "Stress Corrosion Crack and Growth in Austenitic Stainless Steels," Bulletin of Va. Poly. Inst., Vol. LV, No. 3 (1962).
5. ASTM, Metal Handbook, supplement (1955).
6. Hines, J. G. and Hoar, T. P., "The Stress-Corrosion Cracking of Austenitic Stainless Steel," J.I.S.I., Vol. 184, p. 166 (1956).
7. Harwood, J. J., "The Influence of Stress on Corrosion," Corrosion, Vol. 6, p. 249 (1956).
8. Harwood, J. J., "The Mechanism of Stress Corrosion Cracking of Austenitic Stainless Steel," Symposium on Stress Corrosion Cracking of Austenitic Cr-Ni Stainless Steels, ASTM Special Report No. 264, pp. 22-67 (1960).
9. Scheil, M. A., Symposium on Stress Corrosion Cracking of Metals, ASTM-AIME, p. 395 (1944).
10. Hoar, T. P. and Hines, J. G., "Stress Corrosion of Stainless Steel," J.I.S.I., Vol. 182, p. 124 (1956).

11. Heeley, E. J. and Little, A. T., "Corrosion Resistance of Some Austenitic Cr-Ni Steel of 18/8/Ti Composition," J.I.S.I., Vol. 182, p. 241 (1956).
12. Edeleanu, C., "Transgranular Stress Corrosion in Cr-Ni Stainless Steel," J.I.S.I., Vol. 173, p. 140 (1953).
13. Eckel, J. F., "Stress Corrosion of Austenitic Stainless Steel in High Temperature Water," J. Am. Soc. Naval Engrs., Vol. 68, p. 93 (1956).
14. Kirk, W. W., Beck, F. H., and Fontana, "Stress Corrosion Cracking of Austenitic Stainless Steel in High Temperature Chloride Water," Physical Metallurgy of Stress Corrosion Fracture (T. N. Rhodin), Met. Soc. AIME, Met. Soc. Conf., Vol. 4, Interscience Publishers, New York, N. Y. (1959).
15. Higgins, J. P., "Evaluation of Susceptivity of AISI 304 to Stress Corrosion Cracking in Terms of Crack Nucleation and Crack Propagation," Unpublished Thesis, M. S., Met. Engr., Va. Poly. Inst. (1962).
16. Ishiwatari, T., "Evaluation of Susceptivity of AISI 347 to Stress Corrosion Cracking in Terms of Crack Nucleation and Crack Propagation," Unpublished Thesis, M. S., Met. Engr., Va. Poly. Inst. (1962).
17. Greene, A. B., Unpublished data.
18. Berwick, I. D. G., "A Case History of Stress Corrosion Cracking of Austenitic Stainless Steel," Corrosion, Vol. 12, p. 634t (1956).
19. Edeleanu, C., "The Phenomena of Stress Corrosion Cracking in Austenitic Stainless Steel," Stress Corrosion Cracking and Embrittlement (W. D. Robertson), John Wiley and Sons, New York, N. Y., p. 126 (1956).

20. Gulbransen, E. A. and Copan, T. P., "Effect of Stress and Environment on the Microtopology of the Corrosion Product," Physical Metallurgy of Stress Corrosion Fracture (T. N. Rhodin), Met. Soc. AIME, Met. Soc. Conf., Vol. 4, Interscience Publishers, New York, N. Y. (1959).
21. Klingel, G., "Stress Corrosion Cracking of Stainless Steel," Metal Progress, Vol. 69, p. 77, April (1956).
22. Logan, H. L., "Studies of Stress Corrosion Cracking of Austenitic Stainless Steel," Welding Journal, Am. Welding Soc., Vol. 37, No. 10, p. 463s (1958).
23. Hoar, T. P. and Hines, J. G., "Stress Corrosion Cracking of Austenitic Stainless Steels in Aqueous Chloride Solution," Stress Corrosion Cracking and Embrittlement (W. D. Robertson), John Wiley and Sons, New York, N. Y., p. 107 (1956).
24. Leu, K. W. and Helle, J. N., "On the Mechanism of Stress Corrosion of Austenitic Stainless Steel in Hot Aqueous Chloride Solution," Corrosion, Vol. 14, No. 5, p. 249t (1958).
25. Uhlig, H. H., "New Perspectives in the Stress Corrosion Problem," Physical Metallurgy of Stress Corrosion Fracture (T. N. Rhodin), Met. Soc. AIME, Met. Soc. Conf., Vol. 4, Interscience Publishers, New York, N. Y. (1959).
26. Rhodin, T. N., "Oxide Films on Stainless Steel," Corrosion, Vol. 12, No. 3, p. 123t (1956).
27. Herrnstein, W. H., "Effect of Nitrogen on the Strain Behavior of AISI 304 Stainless Steel under Low Stress in the Temperature Range 80° to 170°C," Unpublished Thesis, M. S., Met. Engr., Va. Poly. Inst. (1962).

VITA

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TABLE I

Stress Corrosion Cracks in AISI 304 Stainless
Steel Exposed to 42% MgCl₂ Boiling at 154°C
and Atmospheric Pressure After
Pre-Exposure Heat Treatment

<u>Pre-Exposure Heat Treatment</u>	<u>Specimen Number</u>	<u>Exposure Time (min)</u>	<u>Maximum Crack Depth (micron)</u>
<u>Group A</u> Treated at 154°C for 24 hrs at atm.	6	20	1090
	9	30	1032
	2	30	1129
	7	40	1061
	1	60	1100
	4	60	1178
	5	80	1236
	3	100	1295
	8	150	1353
<u>Group D</u> Treated at 154°C for 2 hrs at atm.	6	20	1005
	3	30	1110
	9	30	1120
	4	40	1071
	1	60	1071
	7	60	1207
	2	80	1334
	10	100	1227
8	100	1265	

TABLE II

Stress Corrosion Cracks in AISI 304 Stainless
Steel Exposed to 42% MgCl₂ Boiling at 154°C
and Atmospheric Pressure After
Pre-Exposure Heat Treatment

Pre-Exposure Heat Treatment	Specimen Number	Exposure Time (min)	Maximum Crack Depth (micron)	
<u>Group B</u> Treated at 154°C for 24 hrs at atm.	5	20	1012	
	10	30	1032	
	3	30	1120	
	7	40	1032	
	8	50	1139	
	1	60	1149	
	9	80	1149	
	2	110	1314	
	11	150	1363	
	<u>Group C</u> Treated at 154°C for 2 hrs at atm.	3	15	969
		5	20	969
2		30	1012	
4		30	1071	
6		40	1090	
1		50	1129	
7		80	1363	

TABLE III

Stress Corrosion Constants for AISI 304
Stainless Steel Exposed to 42% MgCl₂
Boiling at Atmospheric Pressure after
Pre-Exposure Heat Treatment

Specimen Group	Heat Treatment	M (micron/log t)	t ₀ (min)	t _{max} (min)	t _{max} - t ₀ (min)
A	154°C, 24 hrs	448	0.134	496.6	496.47
B	140°C, 24 hrs	505	0.282	409.2	408.92
D	154°C, 2 hrs	527	0.310	349.6	349.29
C	140°C, 2 hrs	607	0.605	219.6	218.99

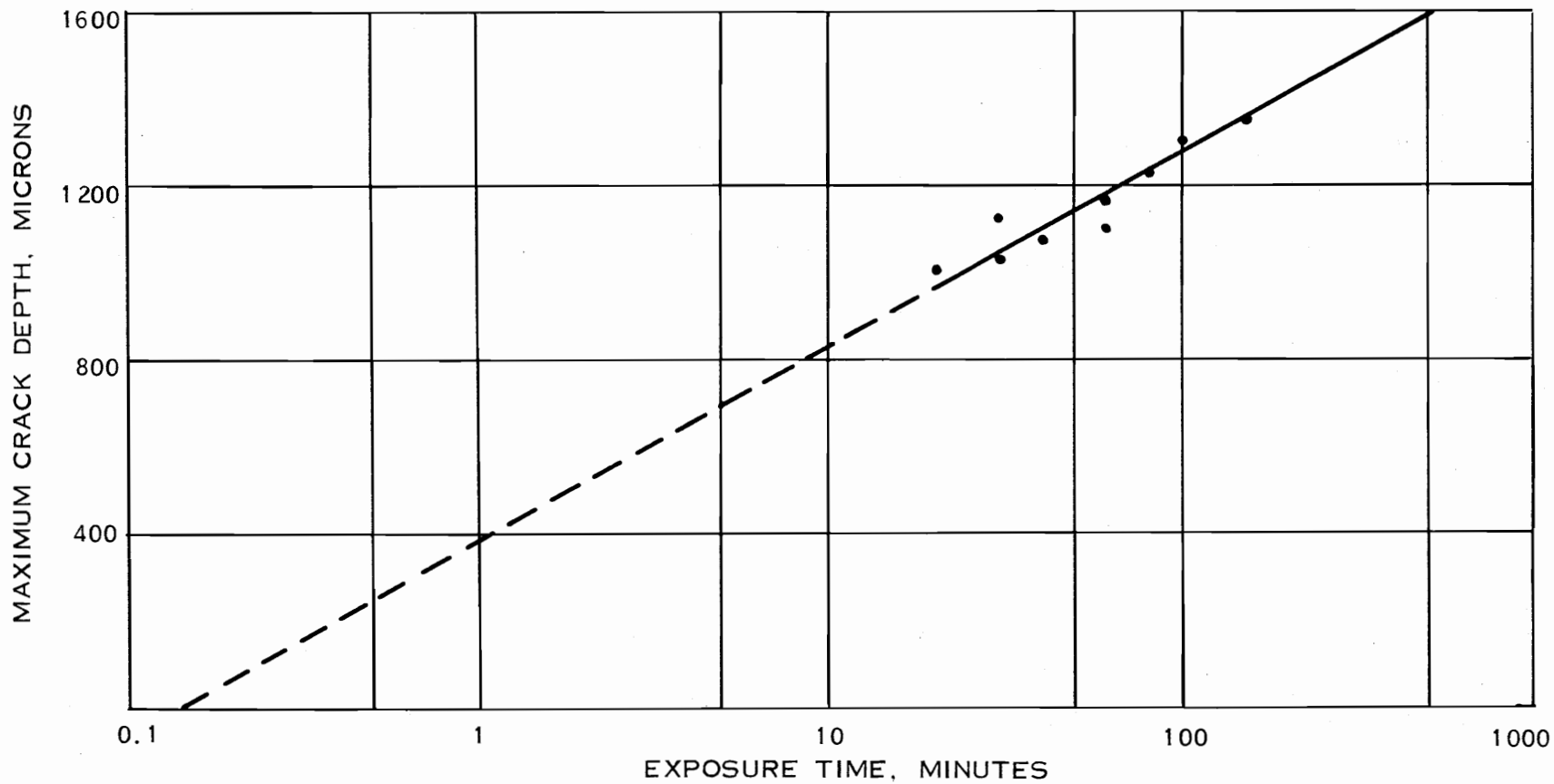


FIGURE 1. CRACK NUCLEATION AND GROWTH IN AISI 304 STAINLESS STEEL EXPOSED TO 42%
 $MgCl_2$ AFTER PRE-EXPOSURE HEAT TREATMENT AT 154°C FOR 24 HOURS - GROUP A

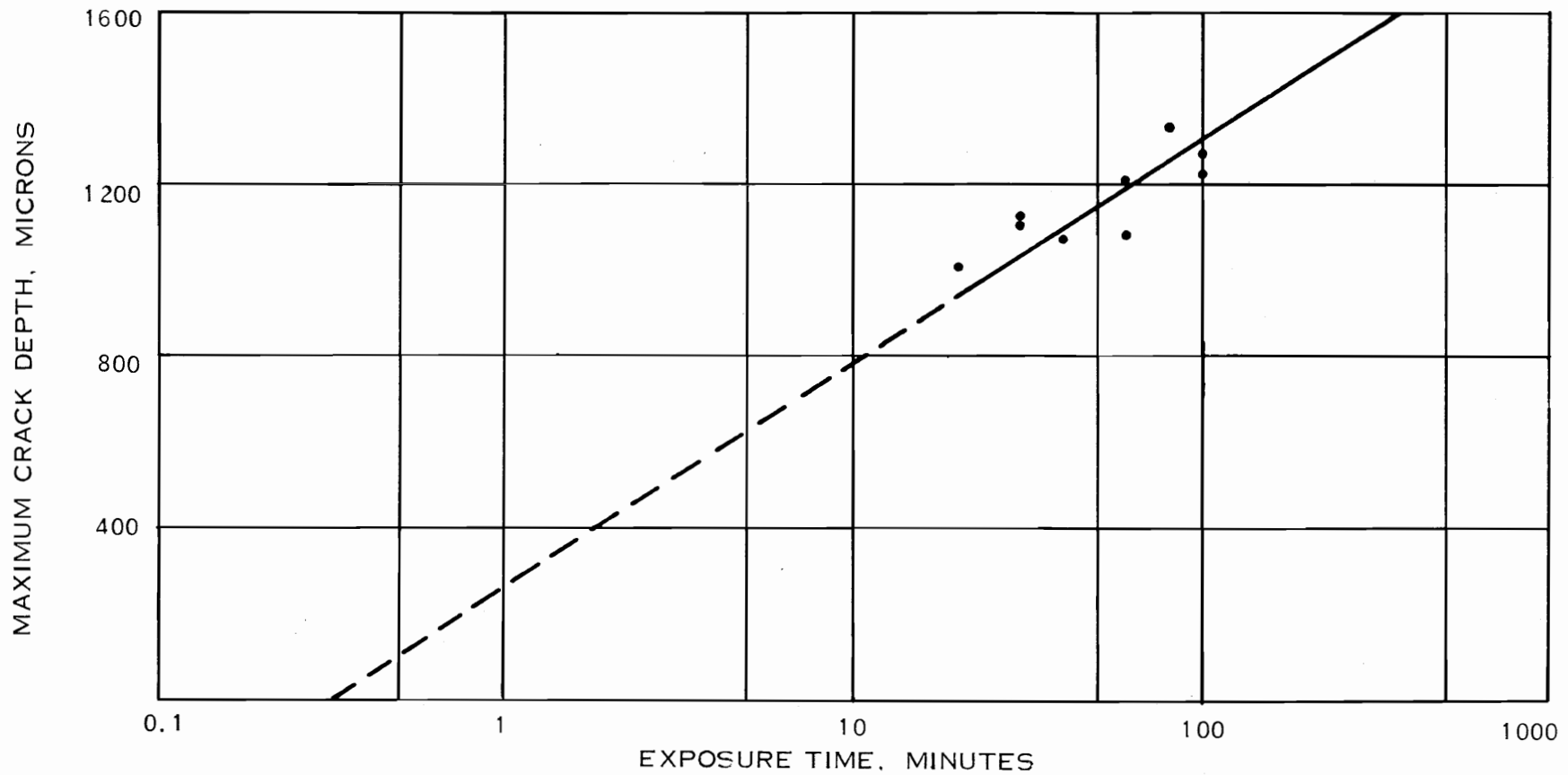


FIGURE 2. CRACK NUCLEATION AND GROWTH IN AISI 304 STAINLESS STEEL EXPOSED TO 42% $MgCl_2$ AFTER PRE-EXPOSURE HEAT TREATMENT AT 154°C FOR 2 HOURS - GROUP D

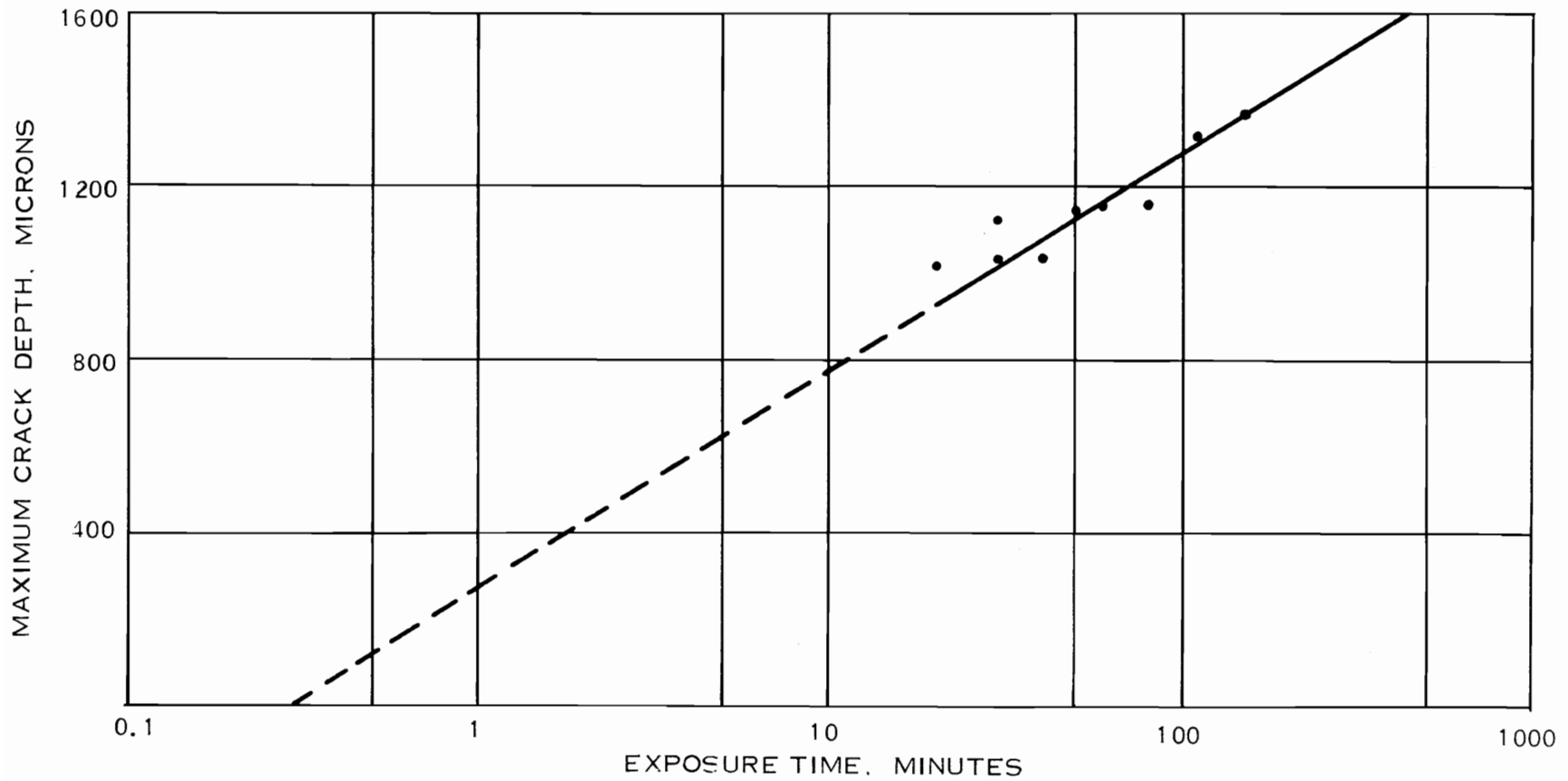


FIGURE 3. CRACK NUCLEATION AND GROWTH IN AISI 304 STAINLESS STEEL EXPOSED TO 42% $MgCl_2$ AFTER PRE-EXPOSURE HEAT TREATMENT AT 140°C FOR 24 HOURS - GROUP B

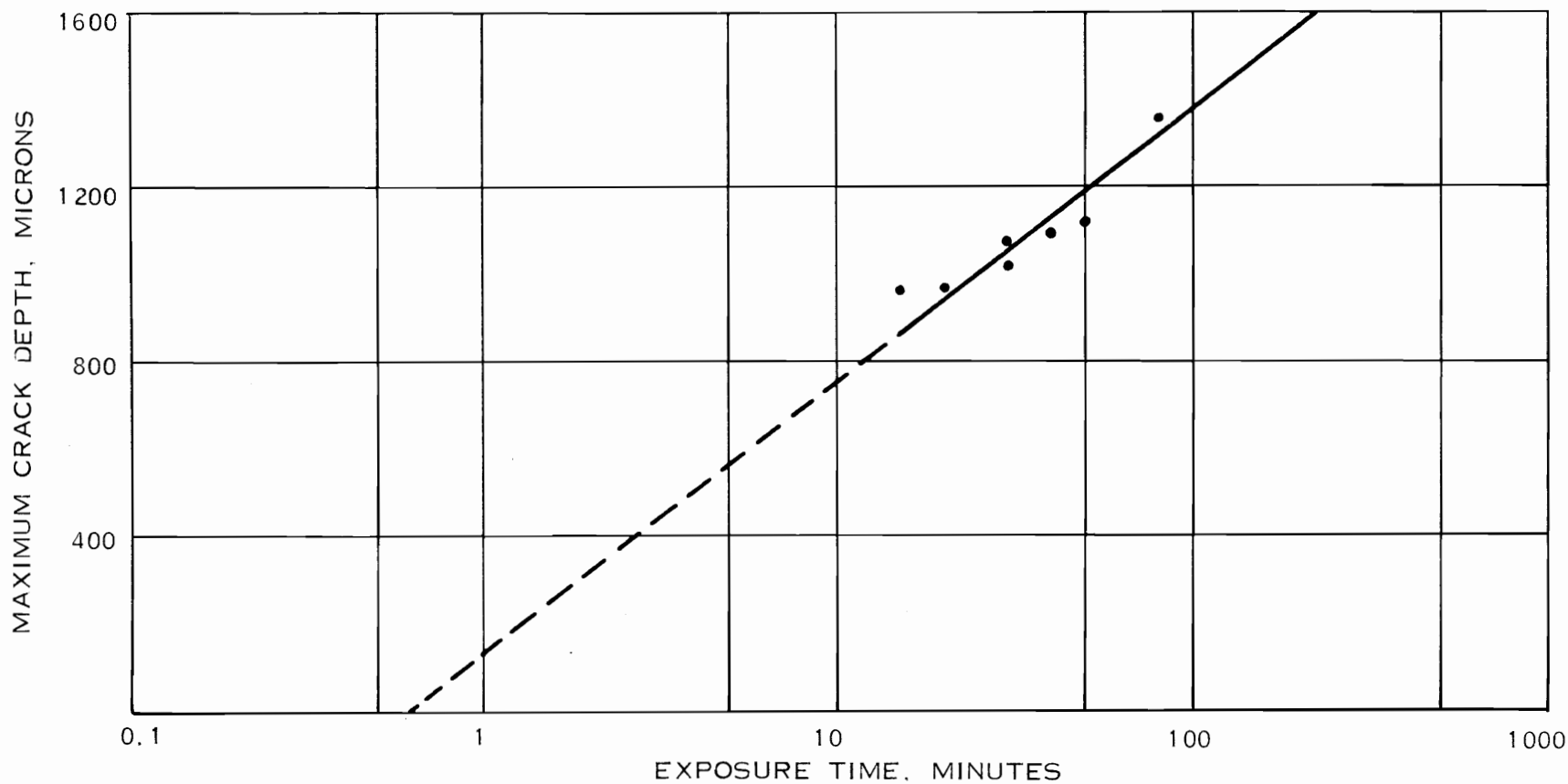


FIGURE 4. CRACK NUCLEATION AND GROWTH IN AISI 304 STAINLESS STEEL EXPOSED TO 42% $MgCl_2$ AFTER PRE-EXPOSURE HEAT TREATMENT AT 140°C FOR 2 HOURS - GROUP C

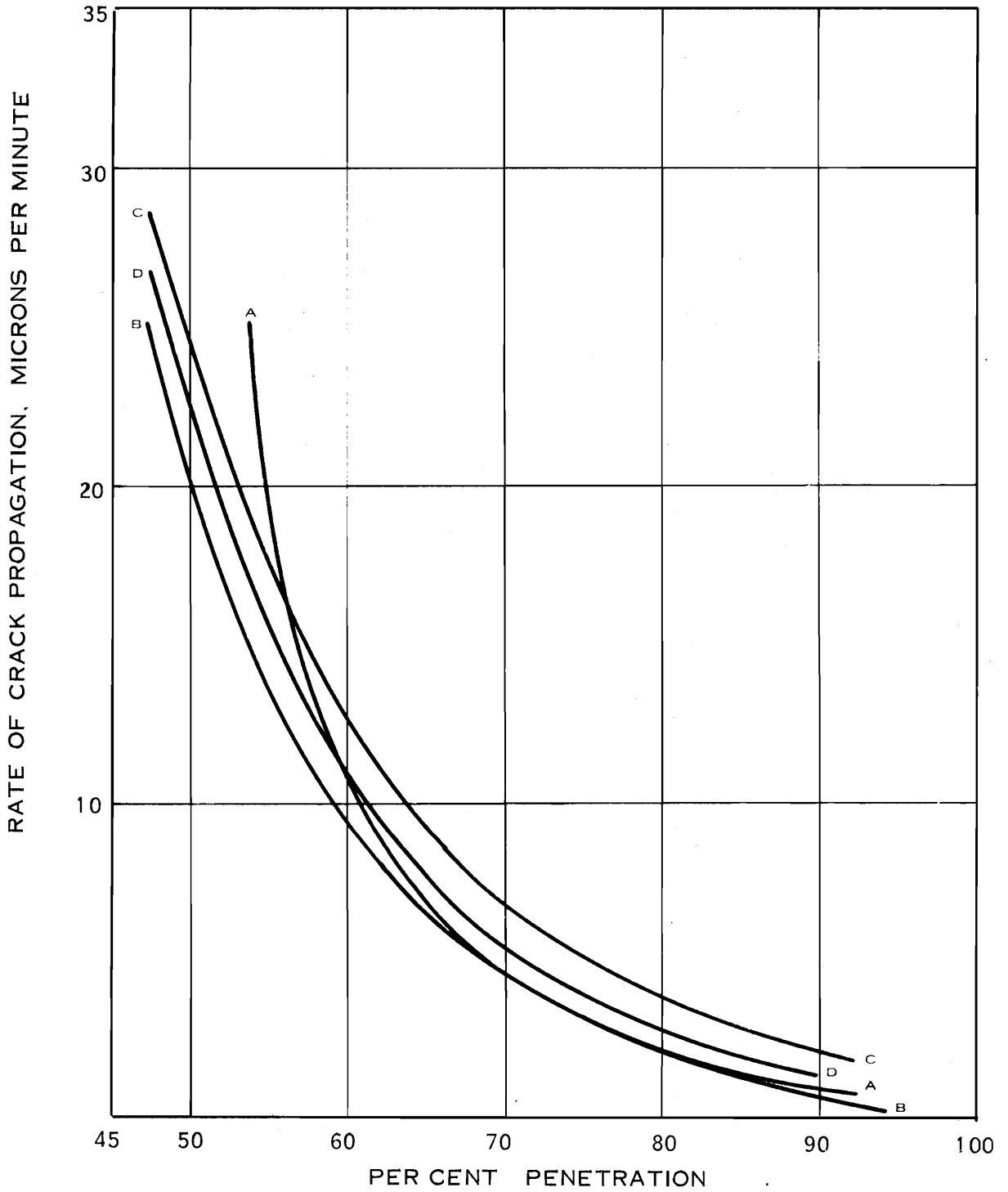


FIGURE 5. CRACK PROPAGATION RATES IN TERMS OF PERCENT PENETRATION FOR GROUPS A, B, C AND D

ABSTRACT

The effect of a specific type of pre-exposure heat treatment on the susceptibility of AISI type 304 stainless steel to stress corrosion cracking was studied in terms of time for crack nucleation and rate of crack propagation. U-bend specimens were exposed to 42 weight percent magnesium chloride aqueous solution after pre-exposure heat treatments at 140°C and 154°C. The straight-line relationship between maximum crack depth and logarithm of exposure time expressed by the empirical equation $\log t = \log t_0 + D/M$ was obtained. The stress corrosion constants derived from the empirical equation indicate that this type of pre-exposure heat treatment promotes crack nucleation because of the formation of less protective surface films, and retards the rate of crack propagation because of effects on internal structural changes within the alloy.