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STRESS CORROSION CRACKING OF TYPE 304 STAINLESS STEEL

STATUS REPORT - MARCH 1, 1964

M. R. LOUTHAN, JR.

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STRESS CORROSION CRACKING OF TYPE 304 STAINLESS STEEL
STATUS REPORT - MARCH 1, 1964

by

McIntyre R. Louthan, Jr.

Approved by

P. H. Permar, Research Manager
Pile Materials Division

August 1964

E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA

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ABSTRACT

Stress corrosion cracking of type 304 stainless steel exposed in dilute chloride solutions is being investigated at the Savannah River Laboratory in attempts to develop a fundamental understanding of the phenomenon. This report describes the status of the stress corrosion studies that relate microstructure and dislocation substructure to transgranular stress corrosion cracking. Observations are reported which show that transgranular stress corrosion cracking, particularly during initial stages, occurs preferentially on the $\{111\}$ family of planes and that such cracking most probably occurs by preferential chemical attack at lattice defects.

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STRESS CORROSION CRACKING OF TYPE 304 STAINLESS STEEL
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INTRODUCTION

Stress corrosion cracking has caused failure of type 304 stainless steel reactor components and other types of plant equipment.⁽¹⁾ An investigation of the stress corrosion processes is in progress at Savannah River Laboratory to develop a fundamental understanding of the phenomenon.

Transgranular stress corrosion cracking in face-centered cubic alloys has been studied extensively since the early 1930's, but is still not fully understood. Most of the investigations have dealt with the effects of chemical environment, stress level, alloy content, heat treatment, deformation history, and temperature of exposure on the susceptibility of an alloy to stress corrosion cracking. From such investigations, several theoretical mechanisms for stress corrosion cracking have been developed. These mechanisms were reviewed by Barnartt⁽²⁾, who concluded that "the continuous electrochemical mechanism of cracking has several serious drawbacks, and the periodic electrochemical-mechanical mechanism appears to be more generally applicable". Several recent studies, beginning with those of Forty⁽³⁾, have emphasized the importance of lattice imperfections in the stress corrosion processes. Swann,⁽⁴⁾ Douglass, Thomas, and Roser,⁽⁵⁾ and Barnartt and Stickler⁽⁶⁾ used transmission electron microscopy to obtain evidence which they interpret as supporting the periodic electrochemical-mechanical mechanism. They show that alloys with low stacking fault energies* are, in general, susceptible to stress corrosion cracking and that increasing the stacking fault energy decreases the susceptibility to stress corrosion. These results give some experimental evidence for the alternative chemical-mechanical models proposed by Forty⁽³⁾ and Robertson and Tetelman⁽⁷⁾. Conversely, Tromans and Nutting⁽⁸⁾ studied stress corrosion cracking in thin foils of copper alloys and state that "cracking was found to proceed at a rate which would be consistent with a single-stage mechanism (continuous electrochemical attack) of the type suggested by Hoar and Hines⁽⁹⁾". Thus, it is apparent that differing opinions on the theoretical mechanisms for stress corrosion cracking still exist and further experimental evidence is required to define the mechanism.

This report describes the status of the stress corrosion studies at the Savannah River Laboratory. These studies relate microstructure and dislocation substructure to transgranular stress corrosion cracking.

* In face-centered cubic lattices, localized errors in second nearest neighbor relationships may result from plastic deformation or crystal growth. Such an error is called a stacking fault and the excess lattice energy per unit area of stacking fault is termed the stacking fault energy.

SUMMARY

Microstructural observations of the stress corrosion processes have established the following important points which appear to be pertinent to the mechanism for cracking.

- ✗ Planar arrays of dislocations and stacking faults provide sites for preferential electrochemical attack in type 304 stainless steels exposed to dilute NaCl solutions.
- ✗ Nucleation and propagation of stress corrosion cracks in type 304 and 304L stainless steels occur preferentially on the $\{111\}$ family of planes.
- ✗ Transgranular stress corrosion cracking was produced in specimens containing stacking faults that were anodic to the matrix, while intergranular cracking was observed in specimens containing stacking faults that were cathodic to the matrix.
- ✗ Stress corrosion cracks were produced in type 304 foils that were prepared for transmission electron microscopy prior to exposure to the crack-producing solutions. The formation of corrosion products accompanied this cracking.
- ✗ The surface condition of a specimen has an effect on the susceptibility to initiation of stress corrosion.

→ 8

top 8

DISCUSSION

EXPERIMENTAL PROCEDURES

The material used in this study was mainly from a single heat of type 304 stainless steel having the composition shown in Table I; however, several other heats of type 304 were also studied and one investigation was made using type 304L steel. Three general specimen designs were used:

- Square sheet samples approximately $1/2 \times 1/2 \times 0.060$ inch with one side dry ground with an alumina abrasive wheel and the edges and other side wet ground through 600 grit paper.
- U-bend samples with either mechanically polished, mechanically polished and electrolytically etched, or dry-ground surfaces.
- Thin foils (approximately 1000 \AA thick) prepared by wet grinding, mechanical polishing, and electrochemical thinning to the required thickness.

Samples prepared by each technique were exposed to boiling solutions of deionized water that contained small amounts of either NaCl, NaI, NiCl_2 , or LiCl. Additionally, several samples were exposed to solutions of deionized water - 42% MgCl_2 at 154°C . Both optical and electron microscopy were used to study the effect of exposure on the sample.

TABLE I

Analysis of Type 304 Stainless Steel, Heat 31614

<u>Element</u>	<u>%</u>
C	0.035
Si	0.38
Mn	1.03
S	0.020
P	0.020
Cr	18.35
Ni	9.14
Fe	Balance

OBSERVATIONS

Dry-Ground Samples

Specimens with dry-ground surfaces were used in these studies because previous work had shown that a dry-grinding operation produced a surface that was highly susceptible to stress corrosion cracking in dilute chloride solutions.⁽¹⁰⁾ The dry-grinding operation caused structural changes, indicated by strain markings in individual grains of the metal, to a depth of approximately two grains (Figure 1). No such changes were observed in specimens with wet-ground or polished surfaces

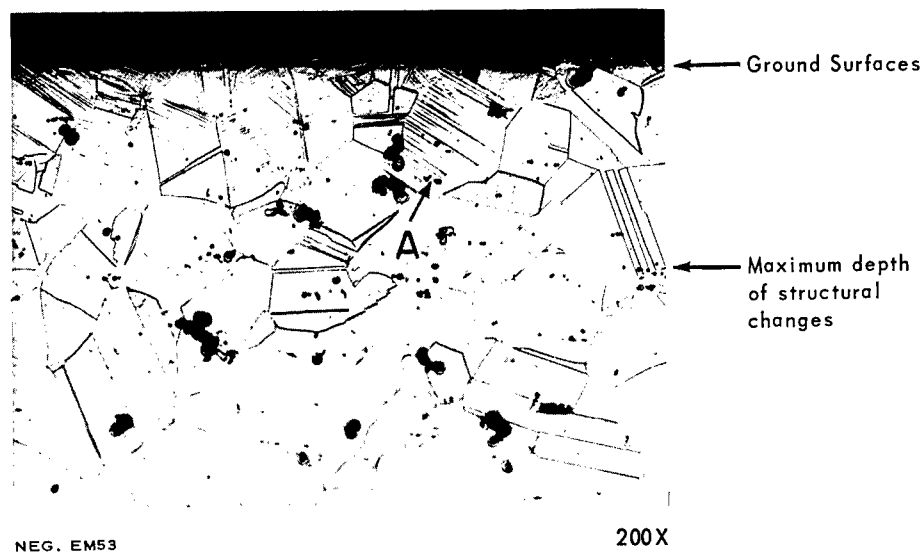
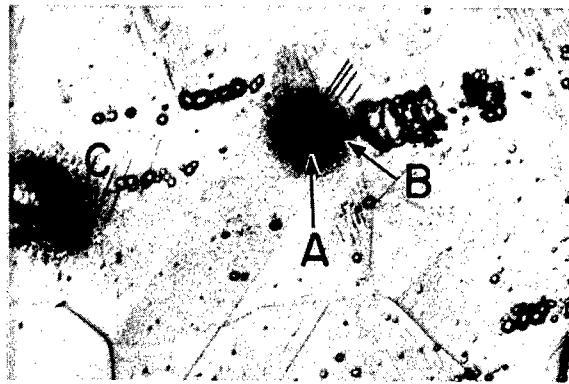


FIG. 1 STRUCTURAL CHANGES ACCOMPANYING DRY GRINDING
Note strain markings, such as shown at A, in the grains near the surface.

Observations of specimens before, during, and after exposures to solutions containing 100 ppm Cl^- (as NaCl or NiCl_2) at 100°C showed that stress cracking occurred in the following sequence. After an incubation period during which no visible changes were observed, dark corrosion spots appeared on the surfaces of the specimens. These spots were generally associated with inclusions (Figure 2) and developed on both dry- and wet-ground surfaces, on polished surfaces, and on polished-and-etched surfaces. The time required for these corrosion spots to form was influenced by surface preparation and varied from approximately 15 minutes for



NEG. EM142-5

500X

FIG. 2 DARK CORROSION AREA BEGINNING TO FORM AT INCLUSION
Region A is the inclusion and region B the corrosion area. Additional
corrosion buildup at another inclusion can be seen in region C.

dry-ground surfaces to several hundred hours for polished-and-etched surfaces. Reflection electron diffraction patterns from these corroded areas showed the presence of both Fe_2O_3 and MnFe_2O_4 (Table II), suggesting that the inclusion associated with the corrosion was MnS . The

TABLE II

Reflection Diffraction Pattern from Corroded Area(a)

"d" Values	"d" Values of Fe_2O_3	"d" Values of MnFe_2O_4
3.74	3.68	
3.12		3.01
2.57		2.56
2.20	2.20	
2.07	2.07	
1.86	1.84	
1.73		1.73
1.66	1.69	
1.62	1.59	1.64
1.52		1.50
1.46	1.45	1.44
1.31	1.31	
1.26	1.26	
1.16	1.16	
1.08	1.10	
1.04	1.05	
1.00	0.99	0.98

(a) Samples used in these studies had dry-ground surfaces and were exposed approximately 24 hours to a deionized H_2O and 100 ppm Cl^- (as NaCl) solution at 100°C . The diffraction studies were made with the corrosion product in situ on the specimen surface.

corroded areas grew larger with continued exposures, and cracks subsequently occurred in these regions on the dry-ground surfaces. The NiCl_2 solutions were more aggressive than NaCl solutions since the NiCl_2 solutions generally produced cracking in less time than NaCl solutions of similar chloride concentrations. No cracking was observed on wet-ground, polished, or polished-and-etched surfaces, although corrosion spots were observed.

Corrosion spots similar to those observed on samples exposed to the NaCl and NiCl_2 solutions were observed on samples exposed to dilute boiling solutions of LiCl and NaI and in samples exposed to boiling tap water. However, no cracking was produced in any of the specimens exposed to these solutions after as much as 500 hours exposure.

This work corroborated previous observations in which the above cracking sequence was observed in ground samples exposed to dilute NaCl solutions.⁽¹⁰⁾

The cracks in the dry-ground samples were principally transgranular and formed pronounced Widmanstätten patterns in several cases (Figure 4). Grain boundary and twin boundary cracking were also observed in limited regions (Figure 3).



NEG. EM2

250X

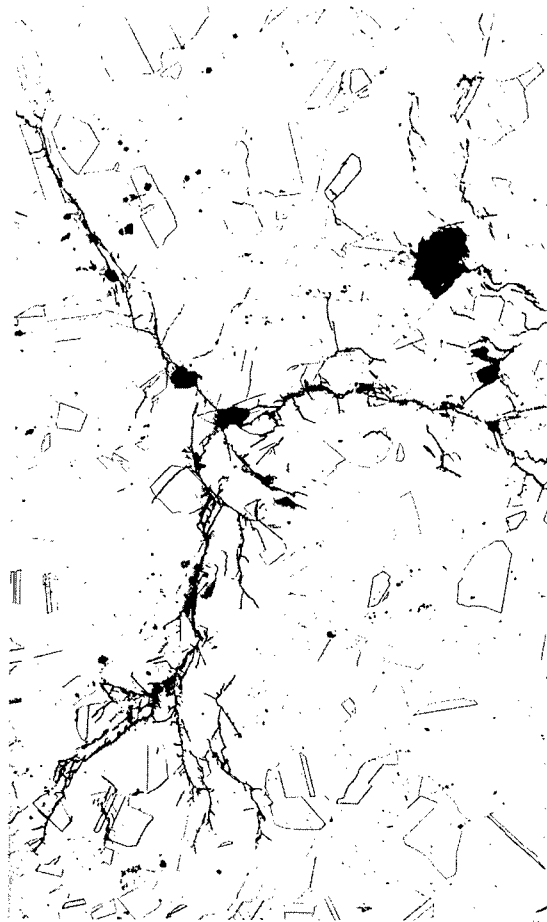
FIG. 3 STRESS CORROSION CRACK PROPAGATION ALONG GRAIN AND TWIN BOUNDARIES. Note regions A, B, and C.



NEG. EM20

200X

- a. Note the Widmanstätten pattern of the crack. (Specimen polished parallel to sample surface.)



NEG. EM11

60X

- b. Note the pits associated with cracks. (Specimen polished parallel to the sample surface.)



NEG. EM16

125X

- c. Note that the cracks often change directions at grain and twin boundaries. (Specimen polished perpendicular to the sample surface.)

FIG. 4 TYPICAL STRESS CORROSION CRACKS IN GROUND SAMPLES

Although the dry-grinding operation was observed to increase the susceptibility to stress corrosion cracking, no direct relationships between the structural changes that occurred upon grinding and stress corrosion cracking were noted. The cracks were observed to follow the strain markings in some regions (Figure 5, region A), but did not follow the markings in others (Figure 5, region B). Electron microscopy of several cracks did not reveal any structural change in the matrix immediately in advance of the crack tip; however, indications of a second phase were observed adjacent to the crack (Figure 6). This structure was not seen in all samples and the possibility exists that it was produced by replication artifacts. However, Douglass, et al.⁽⁵⁾ recently reported that ferrite (α -Fe) was present along the crack walls of several stress corrosion cracks examined by transmission electron microscopy.

The significance of a phase change preceding the propagation of a stress corrosion crack is apparent if one considers the role of hydrogen in crack propagation. Several investigators ~~(11-13)~~ have presented evidence to show that hydrogen pickup and stress corrosion are fundamentally related and suggest that hydrogen embrittlement occurs during the stress corrosion processes. In this event, hydrogen should diffuse into the metal more rapidly than the crack propagates. The diffusion rate of hydrogen in γ -Fe is approximately 3×10^{-9} cm/sec at 154°C ~~(12)~~, and crack propagation rates approximately three orders of magnitude faster than this have been observed ~~(11-13)~~ (Table III). However, the diffusion rate of hydrogen in α -Fe is approximately 5.5×10^{-5} cm/sec at 154°C ⁽¹³⁾ $\rightarrow 14$

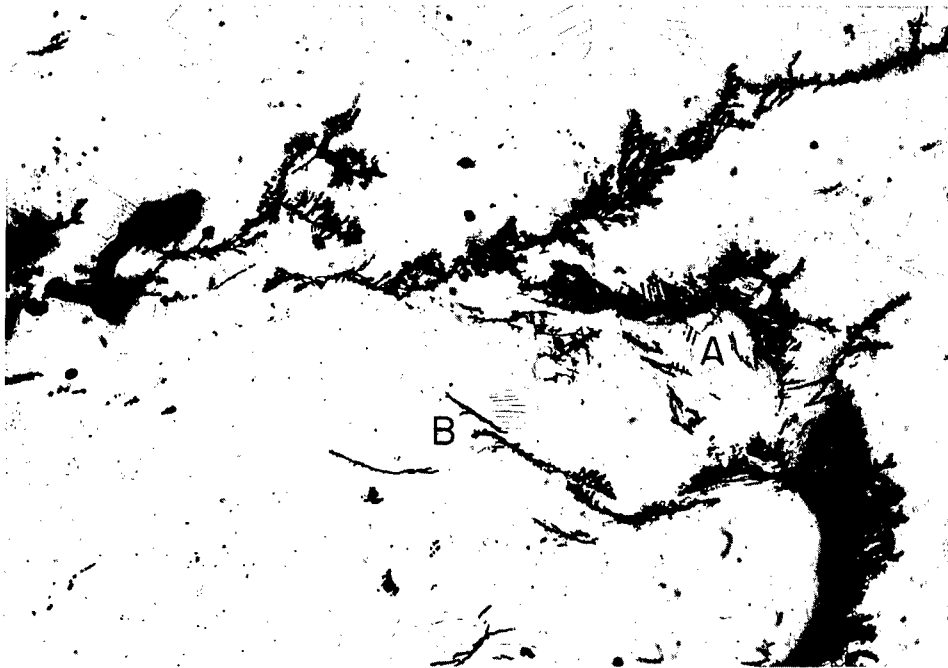
Snippet out referen a numbers

TABLE III
Crack Propagation Rates in Stainless Steel

Investigator	Time of Exposure, seconds	Temp. of Exposure, $^\circ\text{C}$	Crack Depth, cm	Approximate Crack Propagation Rate, cm/sec (a)
Eckel ⁽¹⁴⁾	5,600	154	0.160	3.5×10^{-5}
Edeleanu ⁽¹⁵⁾	3,600	154	0.127	3.5×10^{-5}
Uhlig and White ⁽¹⁶⁾	1,080	154	0.040	3.7×10^{-5}
Louthan	3,600	154	0.100	2.8×10^{-5}

(a) An approximate crack propagation rate was calculated by dividing the crack depth by the time of exposure.

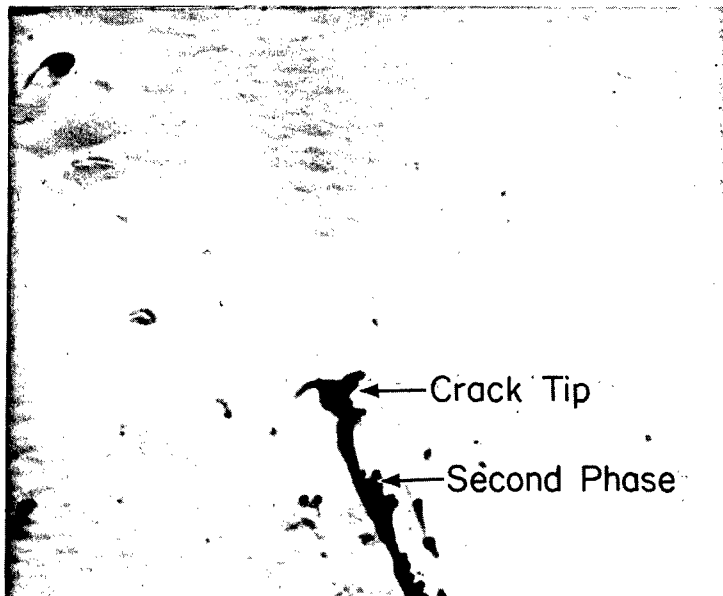
P14



NEG. EM18

200X

FIG. 5 RELATIONSHIP BETWEEN STRAIN MARKINGS RESULTING FROM DRY GRINDING AND THE DIRECTION OF CRACK PROPAGATION



NEG. 1523A

33,000X

FIG. 6 TIP OF STRESS CORROSION CRACK IN TYPE 304 STAINLESS STEEL. Note the indication of a second phase along the crack wall.

[which is of the same order of magnitude as the observed crack propagation rates. Thus, if a $\gamma \rightarrow \alpha$ -Fe transformation does precede stress corrosion crack propagation, a fundamental relationship between hydrogen embrittlement and stress corrosion cracking could be rationalized.]

[Cathodic Charging Experiments]

Several type 304 stainless steel samples were cathodically charged with hydrogen to investigate the possible relationship between hydrogen embrittlement and stress corrosion cracking. Replicas of these samples were made at various time intervals and were examined by electron metallography to determine the effect of hydrogen.

[The as-charged samples exhibited no evidence of a second-phase precipitate or cracking; however, after aging approximately 3-1/2 hours at room temperature, incipient precipitation was observed (Figure 7a), and after 5-1/2 hours second-phase platelets (or needles) were seen (Figure 7b). This precipitate was not identified; however, it was probably the same phase that Vaughan, et al.,⁽¹¹⁾ described as iron hydride. Cracking often occurred in the specimen surface during second-phase precipitation and such surface cracks were observed adjacent to the second phase both within the grains (Figure 7c), and along grain boundaries (Figure 7d). These observations agreed with the previous work, which showed that the formation of transgranular cracks accompanied precipitation of a second phase.

To elucidate the effect of the hydrogen ion in the charging experiments, [samples were also charged in tritiated water. These samples contained the precipitate upon removal from the charging bath; thus, no aging was required to develop the platelets. Furthermore, type 304 specimens with surface conditions that were susceptible to stress corrosion in chloride solutions in normal water did not stress crack in tritiated water solutions. These results corroborate previous investigations,⁽¹¹⁾ which have shown that susceptibility of austenitic steels to stress corrosion cracking may be related to the incubation time required for second-phase precipitation after hydrogen charging: alloys with long incubation periods stress cracked, whereas alloys with little or no incubation time did not crack. The full significance of these observations is not yet apparent.] however, work along these lines is continuing at SRL.

→ 16

NEG. 1419B

4500X

a. Specimen aged $3\frac{1}{2}$ hours
after charging.

NEG. 1417A

4500X

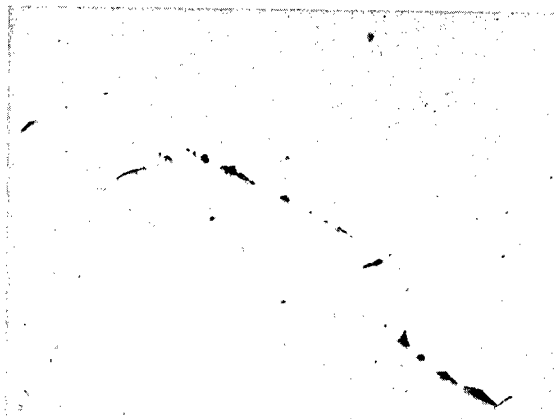
b. Specimen aged $5\frac{1}{2}$ hours
after charging.



NEG. 1448D

3400X

c. Cracking occurring within grains.



NEG. 1448B

3400X

d. Cracking occurring at grain boundaries.

FIG. 7 SECOND-PHASE PRECIPITATION AND CRACKING IN THE SURFACES OF CATHODICALLY CHARGED TYPE 304 STAINLESS STEEL SPECIMENS

U-Bend Samples

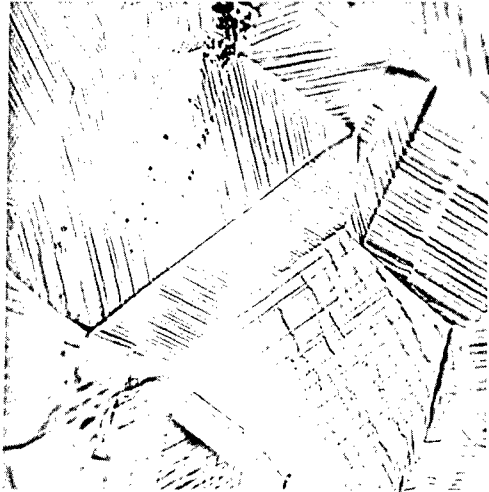
U-bend samples of type 304L stainless steel were exposed for a maximum of 250 hours in boiling solutions of 100 ppm chloride (added as NaCl), and for 5, 15, and 30 minutes in 42% MgCl₂ at 154°C. These samples had been annealed at 1010°C for 1 hour and water quenched, then polished through 1-micron diamond dust, and bent into the U-shape prior to exposure. No apparent attack occurred in the samples exposed to the NaCl solutions; however, in the samples exposed to the MgCl₂ solutions cracking occurred in the following manner:

- Initially, corrosion pitting occurred in localized areas (Figure 8a).
- The pitting was followed by extension of the corrosion to form linear traces of corrosion product on the sample surfaces; these traces were often parallel to observable slip traces (Figure 8b).
- Additional exposure caused cracking to occur in the corroded regions (Figure 8c).
- At still greater exposures, the small cracks within each grain connected to form the branching, transgranular cracks shown in Figure 8d. By this time the crystallographic nature of the cracks was not readily apparent. However, the branches often changed directions at grain boundaries, and many of the branches were parallel to slip lines.

Since both slip lines and twins were clearly visible in these samples and since both of these features represent {111} traces (intersections of {111} planes with the surface), one-surface stereographic analysis could be used to determine the orientation of many of the grains and the traces of stress corrosion cracks could be indexed. In all cases examined, the traces of the stress corrosion cracks, during the initial stages of cracking, were on the {111} family of planes.

These results indicate that stress corrosion cracking occurs preferentially along the {111} family of planes, particularly during the initial stages of corrosion. Since stress corrosion cracking and the two principal modes of deformation in austenitic stainless steel, slip and twinning, all occur on the {111} planes, a relationship between stress corrosion cracking and deformation is probable. → 19

Details of the work involving the crystallographic nature of stress corrosion are given in Reference 17.



NEG. EM268

425X

a. Initial pitting in very localized regions. Exposure 5 minutes.



NEG. EM270

425X

b. Extension of pits to form linear traces of corrosion parallel to slip lines. Exposure 15 minutes.



NEG. EM271

425X

c. Initiation of cracks (dark centers) within lines of corrosion. Several cracks have joined to form a single branched crack in the center of the field. Exposure 15 minutes.



NEG. EM275

425X

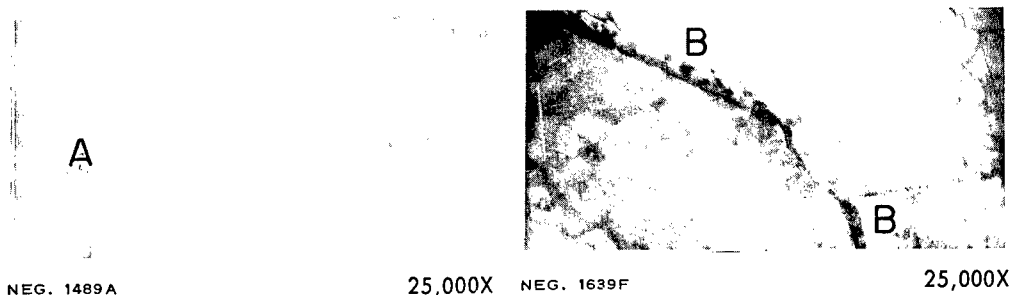
d. Pattern of well-developed cracks. Exposure 30 minutes.

FIG. 8 SEQUENCE OF CRACK INITIATION IN TYPE 304 STAINLESS STEEL U-BEND SPECIMEN IN BOILING $MgCl_2$

Thin Foils

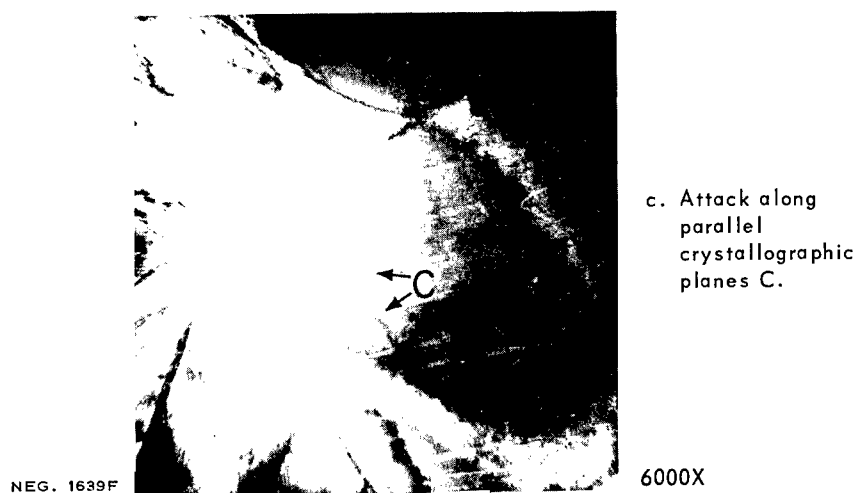
Lattice defects, such as dislocations and stacking faults, may be observed directly by transmission electron microscopy of thin foils of the metal. For stainless steel, the thickness of the foil must be $\sim 1000 \text{ \AA}$ (i.e., 4×10^{-3} mil). Samples of type 304 stainless steel were thinned by mechanical polishing to a thickness of 3 mils or less and then electropolished in a $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solution until the sample was thin enough for electron transmission. The samples were then "corroded" in boiling solutions of 100-ppm NaCl for varying periods of time.

The electropolishing caused preferential chemical attack to occur at stacking faults, grain boundaries, and along certain crystallographic planes (Figure 9). This preferential attack was not noted in all regions, but occurred to some extent in almost every sample. The stacking faults were generally more reactive than the other sites of preferential attack and in some cases were completely dissolved.



a. Attack at a stacking fault A.

b. Attack along a grain boundary B.

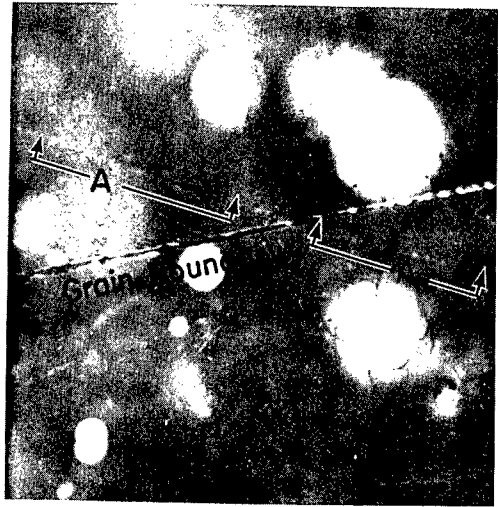


c. Attack along parallel crystallographic planes C.

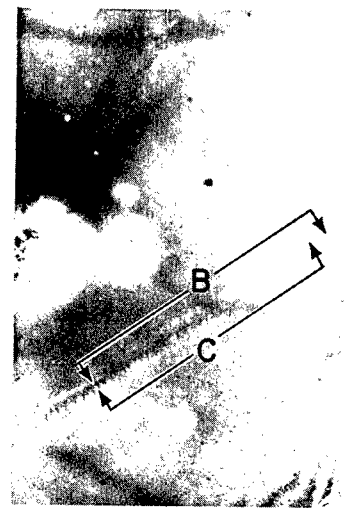
FIG. 9 TRANSMISSION ELECTRON MICROGRAPHS OF ELECTROPOLISHED TYPE 304 STAINLESS STEEL. Note the preferential attack (light, high-transmission regions) at various structural features. This attack was the result of the electrochemical thinning of the foils.

Exposure of the thinned foils to the chloride solutions caused preferential pitting that was distinct from the attack during electropolishing to occur in certain regions (Figure 10). This preferential pitting formed linear traces which changed directions at grain boundaries (Figure 10a), and was often parallel to arrays of dislocations (Figure 10b). This arrangement indicates that the array of pits was formed along the $\{111\}$ planes since the dislocation arrays are known to form on the $\{111\}$ planes in stainless steel. In addition to the pitting attack during the NaCl exposures,

→ top 20



a. Attack at a grain boundary and pitting A forming a linear trace which changed directions at the grain boundary.



b. Preferential pitting B forming a trace which was parallel to a planar array of dislocations C.

FIG. 10 EFFECT OF EXPOSURE OF TYPE 304 STAINLESS STEEL FOIL TO A BOILING SOLUTION OF 100 PPM CHLORIDE. The pitting attack occurred during exposure.

Further preferential attack was observed at stacking faults, planar arrays of dislocations, and along $\{111\}$ planes with no obvious defects. This attack formed crack-like voids in the metal similar to stress corrosion cracks. The following observations were made.

- ✓ The frequency of cracking increased with increasing exposure to the chloride solutions.
- ✗ Electrochemical attack accompanied crack growth. This can best be seen in Figure 11 where corrosion products were identified in the vicinity of the crack tip.
- ✓ Cracks already in existence propagated during subsequent exposures (Figure 12).
- ✗ Cracks propagated preferentially along planar arrays of dislocations and along stacking faults.

Similar foils exposed to deionized water not containing chloride additions did not show the profuse cracking observed in the foils exposed to the chloride solutions. *end*

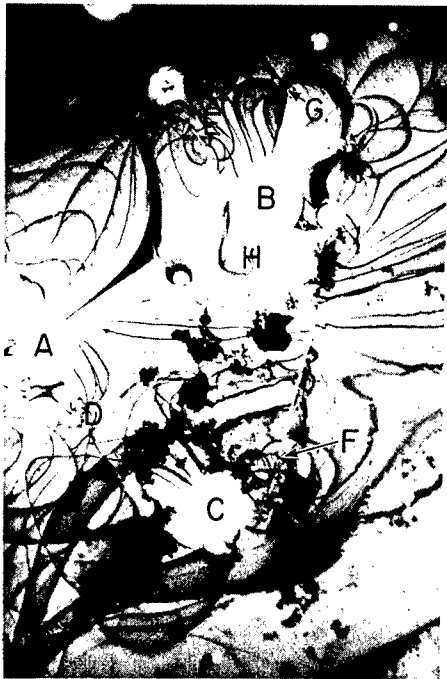
Additional foils were examined which were prepared from samples that had been cold rolled to 10% reduction in area and annealed one-half hour at 600°C. The stacking faults and martensite needles in these foils were left in relief during the thinning operation (Figure 13), showing that they were cathodic to the matrix. This contrasts the anodic



NEG. 1714D

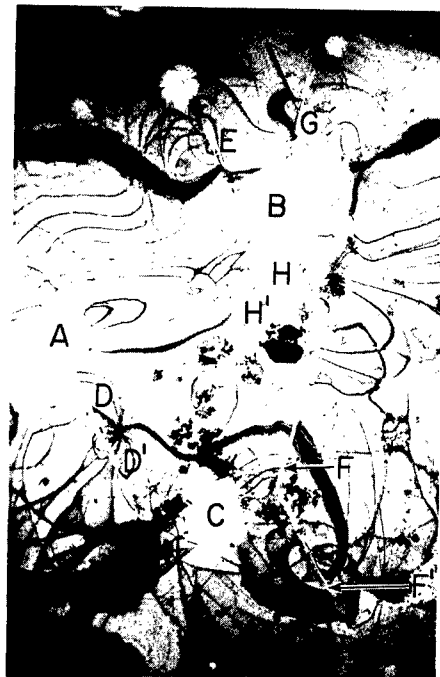
11,100X

FIG. 11 TIP OF CRACK PRODUCED IN TYPE 304 STAINLESS STEEL FOIL DURING 15-MINUTE EXPOSURE TO DILUTE NaCl SOLUTION AT 100°C. Corrosion product was identified by selected-area electron diffraction in the vicinity of the crack tip and a stacking fault is apparent at A.



NEG. 1714C

6700X



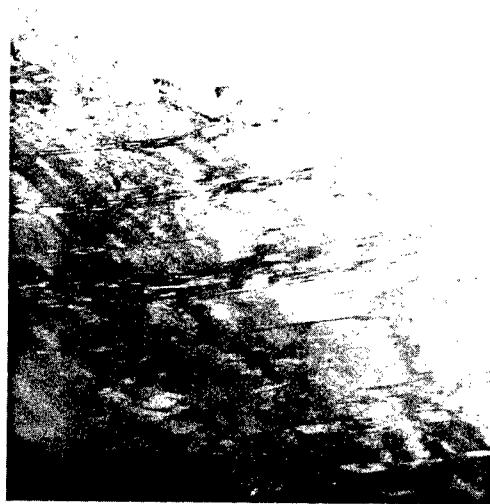
NEG. 1715B

6700X

a. After 15-minute exposure.

b. After 25-minute exposure.

FIG. 12 PROPAGATION OF EXISTING CRACKS IN TYPE 304 STAINLESS STEEL FOIL DURING EXPOSURE TO A SOLUTION OF DEIONIZED WATER AND 100 PPM CHLORIDE (as NaCl) AT 100°C. Note that after 15-minute exposure cracks in the foil propagated from holes A, B, and C ended at points D, E, F, G, and H, and that after 25-minute exposure the cracks had propagated to D', E', F', and H'.



NEG. 1718C

5500X

FIG. 13 EFFECT OF COLD WORK AND ANNEALING ON THE THINNING CHARACTERISTICS OF TYPE 304 STAINLESS STEEL. Note that stacking faults and martensite needles were left in relief during thinning of a type 304 stainless steel specimen, which was 10% cold rolled and annealed 1/2 hour at 600°C prior to thinning.

behavior of stacking faults in foils prepared from samples as-quenched from 1010°C, since preferential electrochemical attack of the stacking faults occurred during thinning of these foils. In addition to the differences in chemical attack during thinning, the cold-rolled and heat-treated specimen cracked intergranularly during exposures to 42% MgCl₂ solutions, while specimens as-quenched from 1010°C cracked transgranularly when exposed to similar solutions.

CONCLUSIONS

The observations to date have not established a mechanism for stress corrosion cracking; however, they have shown that:

- Corrosion accompanies stress corrosion cracking and that preferential corrosion occurs at stacking faults and dislocation pileups.
- Cracking preferentially occurs on the {111} family of planes.
- Surface condition has an effect on the initiation of stress corrosion cracks.
- The relative reactivity of stacking faults to the matrix appears to be important in determining the path of crack propagation.

FUTURE PROGRAM

Investigations will continue in attempts to establish a fundamental understanding of the stress corrosion processes. Several programs are currently either underway or being initiated.

- Stress corrosion tests are being made of several heats of types 304, 304L, and 316L stainless steels in 100-ppm chloride solutions and in 42% MgCl₂. The relative susceptibilities of these different heats of steel will be compared to their dislocation substructure, stacking fault energy, impurity content, fabrication history, and mechanical properties.
- Thin foils prepared from cold-rolled type 304 stainless steel having various heat treatments will be exposed to dilute chloride solutions and the attack will be compared by transmission electron microscopy.

- The effect of anode-to-cathode ratio on the corrosion rate will be compared to determine if anodic dissolution could occur rapidly enough to account for the very rapid rates of crack propagation observed in type 304 stainless steels exposed to (a) dilute NaCl solutions and (b) concentrated MgCl₂ solutions.
- The work will be expanded to include other 300 series stainless steels, 400 series steels, copper alloys, and aluminum alloys where necessary to assist in formulating a fundamental mechanism for stress corrosion cracking.

These studies will be altered, expanded, or dropped in accord with the results and progress made in each phase of the investigations.

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