

**METALLURGICAL SOCIETY CONFERENCES**

VOLUME

**4**

**PHYSICAL METALLURGY  
OF STRESS CORROSION  
FRACTURE**

Edited by **THOR N. RHODIN**

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# **PHYSICAL METALLURGY OF STRESS CORROSION FRACTURE**

**Edited by THOR N. RHODIN**

**A Symposium**

**arranged and sponsored by**

**Committee on Corrosion-Resistant Metals,**

**Institute of Metals Division,**

**The Metallurgical Society,**

**and**

**Pittsburgh Section,**

**American Institute of Mining,**

**Metallurgical, and Petroleum Engineers.**



**Presented in Cooperation with the Electrochemical Society,  
National Association of Corrosion Engineers, and the  
American Society for Testing Materials**

**PITTSBURGH, PENNSYLVANIA, APRIL 2-3, 1959**



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## PREFACE

The symposium on the Physical Metallurgy of Stress Corrosion Fracture, arranged by the Committee on Corrosion-Resistant Metals of The Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, was held at Pittsburgh in April, 1959. It followed a sequence of such conferences initiated by the symposium on the same subject sponsored by the American Society for Testing Materials in 1944 and continued by a symposium on the same subject by the Electrochemical Society in 1954. Important contributions to understanding stress corrosion cracking were made by the National Conferences held in Philadelphia in 1944 and in Boston in 1954. However, the problem has grown significantly in the last five years, relative both to the expanding scope of its occurrence for an increasing number of materials and environments and in the seriousness of the technological implications involved.

Today the pressure of major advances in concepts of design is seriously pushing against the operational limits of many engineering materials. This is particularly true for the problem of stress corrosion where the demands of technology on the development of new materials are particularly critical in such areas as power generation, chemical processing, and nuclear technology. Fortunately, important advances have also been made concurrently in our knowledge of the solid state and particularly of the role of imperfections in mechanical deformation and in chemical reactivity. New design requirements are placing an increasing challenge on the solid state scientist to know more about the general relationships between stress, structure, strength, and the chemistry of crystalline solids. The conclusion is becoming more certain as technology advances that major solutions to this problem and others like it will depend on a unified insight into the metallurgical, physical, and chemical factors involved. It seemed that this conference could contribute most effectively to the specific problem of stress corrosion failure by bringing together investigators from these different fields of interest and by focussing consideration on the underlying relationship among the various factors involved. On the other hand, no meaningful contri-

bution can be made without the realistic insight of the experienced metallurgical and design engineer.

For this reason effort was made to approach the problem in two ways. The first half of the symposium, under the leadership of A. M. Pound and H. H. Uhlig, was concerned mainly with general principles relating the three basic factors of stress, fracture, and chemical reactivity. No effort was made to emphasize the consideration of practical engineering environment or the complicated behavior of new alloys. The second half of the program was addressed directly towards clarification of the mechanisms of stress corrosion cracking in terms of specific environments and materials. These latter sessions were lead by F. L. LaQue and E. J. Kreh.

The main objective of the symposium was to provide a forum for discussion among specialists from divergent fields and experiences in the solid state sciences and in the technology of materials. The papers were preprinted and the complete and edited discussion material is included in this publication of the proceedings.

Advances in the science of materials develop with understanding of the fundamental aspects of the behavior of solids. Areas contributing to understanding of the stress corrosion phenomena especially cover a broad field in physical metallurgy, electrochemistry, applied mechanics, metal physics, and surface chemistry. It was not expected that this symposium, representative as it was of such varied interests, would evolve a universal corrosion mechanism or a new super material. However, the general discussion did result in special emphasis on the following aspects:

1. Relationship between stress and chemical reactivity.
2. Concept of embrittlement by localized corrosion.
3. Interactions between the initiation and propagation stages of cracking and the influence of crystallography.
4. Effect of specific alloy compositions and chemical environments on failure mechanisms.
5. Application of dislocation movement to crack growth.

Although the Committee on Corrosion-Resistant Metals is concerned primarily with the physical metallurgical aspects of corrosion-resistant metals, it was apparent that effective consideration of the stress corrosion phenomena must overlap into the fields of electrochemistry and into the engineering behavior of materials. It seemed appropriate to plan and execute the program in cooperation with the following three technical societies which have also been concerned with the broad implications of the phenomena: the Electrochemical Society, the National Association for Corrosion Engineers, and The

American Society for Testing Materials. The symposium committee was fortunate to have the interest and assistance of advisors from all three of these societies. Arrangements for the foreign visitors were made possible by a grant from the National Science Foundation.

The support of the people and organizations involved in the publication of these proceedings is gratefully acknowledged. It is hoped that this volume will serve to introduce the reader to some of the more recent thinking in research on stress corrosion fracture and on related advances in the field of the science of materials.

Thor N. Rhodin  
*Editor*

Ithaca, New York  
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## New Perspectives in the Stress Corrosion Problem

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### Summary

Stress corrosion cracking is damage resulting from a complex interplay of tensile stress, corrosion, and crack-sensitive paths through a metal or alloy.

Pure metals do not stress corrosion crack in any environment. In alloys, impurities may enter the mechanism of cracking, as for example, in austenitic stainless steels for which interstitial nitrogen is important in imparting susceptibility. Impurities, however, are not responsible for stress corrosion cracking of all solid-solution alloys. Brass, Cu<sub>3</sub>Au, Ag-Au, and Mg-Al alloys are among those which stress corrosion crack no matter how pure. Stress corrosion cracking can be prevented by cathodic protection or sometimes by use of corrosion inhibitors.

Two similar kinds of cracking are observed in which corrosion apparently does not enter the mechanism, and which therefore are not true examples of stress corrosion cracking. The first includes *hydrogen cracking*, e.g., of martensitic stainless steels or 9% nickel steels. The second is illustrated by cracking of single crystals of Mg<sub>3</sub>Sn without applied stress which fail along octahedral planes on exposure to distilled water. Along the same lines, Zn-Al alloys crack in moist atmospheres. In common with stressed plastics which crack in certain organic solvents, failure occurs by a mechanism which appears to be the reduction of surface energy by adsorption along walls of the crack. It is proposed that this second kind be called *interfacial stress cracking* or *stress-sorption cracking*.

For stress corrosion cracking, the crack-sensitive paths, as in Cu-Al alloys, may be formed at grain boundaries as a result of cooling from the melt, heat treatment, or aging. The grain boundary is anodic to the grain and cracking involves an electrochemical mechanism. Electrochemical cells in other alloys can form as a result of plastic deformation, illustrated by Cu<sub>3</sub>Au or austenitic stainless steels. Lattice defect sites produced by cold work become either anodic or cathodic to the remainder of the alloy, depending on properties of atoms which concentrate at such sites. In either case, dissolution of anodic material accounts for crack

\* Presented by Dr. Uhlig.

propagation in presence of certain electrolytes. In  $\text{Cu}_3\text{Au}$ , the crack-sensitive paths appear to line up with dislocation loops, and it is proposed that this is also the case for austenitic stainless steels, which accounts for the tortuous paths often observed for stress corrosion cracks in this alloy. It is shown that localized composition gradients account for crack-sensitive paths rather than increased energy of metal atoms displaced from their lattice positions, or formation of new lattice structures.

The specific effects of certain chemical species in causing stress corrosion cracking suggests that the electrochemical mechanism alone is not sufficient to account for crack propagation. It is proposed that selective adsorption of ions which lower the surface energy of the crack operate conjointly with electrochemical action along paths where defects predominate and where compositional gradients exist. This results in a discontinuous rate of crack formation by alternate physical parting and electrochemical action.

### Introduction

Perhaps no subject illustrates more spectacularly the interplay of metallurgical and chemical factors on damage to metals than does stress corrosion cracking. Metals of high strength and more than enough ductility, applied in support of conservative stresses, fail catastrophically by cracking when placed in contact with certain chemical environments. The chemical species responsible for weakening the metal lattice or grain boundaries are specific to each metal and fortunately are few in number. In most environments, atoms of the severely stressed lattice hold together with reasonable efficiency and follow the predicted stress-strain relations. Our present discussion concerns important exceptions to the rule.

Is stress corrosion cracking an example of corrosion in the normal sense? It is true that corrosion products need not be visible, and weight loss can be negligibly small. Yet the technique of cathodic protection, which makes use of external electric currents to neutralize corrosion currents and which is successfully employed to stop rusting, tarnishing, pitting, dezincification, and intergranular corrosion cracking can also be used to prevent most instances of stress corrosion cracking. Corrosion inhibitors can also tame the chemical environments that otherwise, like Delilah, shear the locks that give strength to Samson-like metals. On the other hand, the corrosivity of an environment is not a guide to the possible damage it exacts by stress corrosion cracking—many moderately or severely corrosive environments have no effect whatsoever in this direction. Calcium nitrate, for example, is not a corrosive chemical in the ordinary sense of the term, and is readily handled in steel equipment. However, a hot, concen-

trated solution, especially if ammonium nitrate is also present, in contact with previously cold-worked steel cracks thick sections of the metal in a short time. Paradoxically, nitrates added in small amounts to an alkaline boiler water are used to inhibit the stress-corrosion cracking (caustic embrittlement) otherwise produced by the caustic solution at severely stressed portions of the boiler. Corrosion phenomena, in other words, accompanying stress corrosion cracking are not simple. This is further illustrated by the lack of any reasonable classification of chemicals that are active in causing cracking. In the case of steels, the known damaging environments are: alkalis; nitrates; a mixture of  $\text{SbCl}_3$ ,  $\text{HCl}$ , and  $\text{AlCl}_3$  in a hydrocarbon solvent;<sup>1</sup> hydrogen cyanide;<sup>2</sup> and anhydrous liquid ammonia;<sup>3</sup> the first three of these produce failure along grain boundaries of the stressed metal. For cyanides the fracture is transgranular, and for ammonia information is not yet available. Whatever the constituent of these very different environments may be, or the common reaction that induces preferential corrosion along certain paths in the stressed metal, is certainly not self-evident. The complexity of the reaction is, moreover, indicated by the fact that very many chemicals, whether closely related or not to the damaging species, so far as present experience goes, do not cause stress corrosion cracking of steel.

The essential presence of tensile stress further illustrates the complexity of the problem. A structural metal thoroughly annealed and free of applied stress can often exist in harmony with otherwise damaging chemical species with no more observed attack than superficial corrosion of the surface. And, furthermore, if the metal is stressed in such a way that the surface stresses are all compressive rather than tensional, the metal will support the applied stresses adequately without cracking, and the superficial corrosion rate may not suffer appreciable change. The lower the applied or residual tensile stress, the longer is the observed time for cracking. A threshold stress below which cracking will not occur at all has been sought for and reported to exist for some metals, but doubt has been expressed that such threshold stresses are real and, in any case, there seems to be general concurrence in the view that they should not be relied upon in engineering design.

Metallurgically, the problem is not simpler. Heat treatment or aging of metals or alloys can often induce either susceptibility or immunity. Temperatures and times are specific to each metal, and the

TABLE I  
Typical Data for Effect of N and C on Susceptibility of Austenitic Stainless Steels to Stress-Corrosion Cracking in Boiling 42%  
MgCl<sub>2</sub> (154°C)

Code	Major phase as quenched	Cr, %	Ni, %	C, %	N, %	Annealed and sheared		Cold-rolled, sheared		
						No. of Specimens tested	Cracking time, hr.	Reduction of thickness, %	No. of specimens tested	Cracking time, hr.
18-8 and Type 304										
A	$\alpha$	18.4	8.7	0.012	<0.001	2	>260	80	2	>260
H45	$\alpha$	18.4	8.1	0.004	0.005	3	>260	80	3	>260
C	$\gamma$	18.5	8.5	0.013	0.15	13	1.2 $\pm$ 0.3			
H44	$\gamma$	18.6	8.0	0.15	0.002	4	2.4 $\pm$ 0.4	80	3	0.8 $\pm$ 0.4
Com. 304A	$\gamma$	18.4	8.6	0.08	0.04	37	1.4 $\pm$ 0.4	35	11	0.7 $\pm$ 0.2
Com. 304B	$\gamma$	18.8	9.2	0.06	0.05	4	0.2 $\pm$ 0.1	35	4	0.3 $\pm$ 0.1
20-20 and Type 310										
NRL	$\gamma$	18.7	20.6	0.01	0.002	3	>200	80	3	>200
E2	$\gamma$	21.3	17.5	0.01	0.115	5	149 $\pm$ 49	80	3	59 $\pm$ 16
H	$\gamma$	18.2	20.4	0.17	0.005	2	>300	80	2	>300
Com. 310A	$\gamma$	24.7	21.4	0.05	0.04	5	20 $\pm$ 3	30	13	5.3 $\pm$ 1.5
Com. 310B	$\gamma$	24.8	19.5	0.03	0.05	4	5.5 $\pm$ 1.8	30	4	5.2 $\pm$ 1.2



metallurgical changes accomplished by such treatments are not always understood.

Pure metals, significantly, are immune to stress corrosion cracking in all environments. Pure aluminum is immune, e.g., to NaCl solutions that produce cracking in alloys of aluminum with copper or magnesium. Pure magnesium does not crack by stress corrosion, although some of its alloys are susceptible to moisture itself. Stressed pure copper will not crack in ammonia atmospheres, but on being alloyed with 0.1 or 0.2% phosphorus, antimony, arsenic, or silicon, it becomes susceptible.<sup>4</sup> Pure iron or steel that has been decarburized in wet hydrogen no longer suffers intergranular stress corrosion cracking in hot, concentrated, nitrate solutions.<sup>5,6</sup> Stressed nickel of commercial purity may crack in aqueous or fused caustic alkalis at elevated temperatures,<sup>7</sup> but it is reasonable to conclude from first principles, as discussed later, that all metals rigidly pure, including nickel, should be immune to stress corrosion cracking. Exceptions would be expected only when the environment itself at elevated temperatures diffuses impurities into the metal, thus causing it to become susceptible.

Impurities can also be important in alloys. For example, stressed stainless steels of 18% Cr-8% Ni composition do not crack in boiling 42% MgCl<sub>2</sub> within a 250- to 300-hr test period if the nitrogen or carbon contents are about 0.015% or less<sup>8,9</sup> (Table I). Two commercial 18-8 stainless steels in the same test cracked within 0.2 to 1.4 hr. For the stable, austenitic 20% Cr-20% Ni stainless steels, nitrogen apparently is the impurity largely responsible for susceptibility to cracking and carbon is beneficial. Severely cold-worked alloys containing about 0.002% N did not crack within the maximum test period of 250 hr, whereas a similar alloy containing 0.115% N cracked within 59 hr. Two cold-rolled, commercial 25% Cr-20% Ni (Type 310) alloys cracked within a little over 5 hr.

However, impurities do not always enter the mechanism and are not always necessary to susceptibility of solid solution alloys. Graf<sup>10</sup> pointed out that Ag-Au, Cu-Au, and Mg-Al alloys are subject to stress corrosion cracking, no matter how pure. Bakish and Robertson<sup>11</sup> also observed that single crystals of pure Cu<sub>3</sub>Au stress corrosion crack in FeCl<sub>3</sub> solution. In addition, it is clear from the results of many investigations,<sup>12</sup> including tests on single crystals,<sup>13,14</sup> that brass will stress corrosion crack in NH<sub>3</sub> atmospheres, independent of impurities in the alloy.