

***ADVANCES IN
CORROSION SCIENCE
AND TECHNOLOGY
VOLUME 2***

ADVANCES IN CORROSION SCIENCE AND TECHNOLOGY

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***Edited by
Mars G. Fontana and Roger W. Staehle***

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PREFACE TO VOLUME 1

This series was organized to provide a forum for review papers in the area of corrosion. The aim of these reviews is to bring certain areas of corrosion science and technology into a sharp focus. The volumes of this series will be published approximately on a yearly basis and will each contain three to five reviews. The articles in each volume will be selected in such a way to be of interest both to the corrosion scientists and the corrosion technologists. There is, in fact, a particular aim in juxtaposing these interests because of the importance of mutual interaction and interdisciplinarity so important in corrosion studies. It is hoped that the corrosion scientists in this way may stay abreast of the activities in corrosion technology and *vice versa*.

In this series the term "corrosion" will be used in its very broadest sense. This will include, therefore, not only the degradation of metals in aqueous environment but also what is commonly referred to as "high-temperature oxidation." Further, the plan is to be even more general than these topics; the series will include all solids and all environments. Today, engineering solids include not only metals but glasses, ionic solids, polymeric solids, and composites of these. Environments of interest must be extended to liquid metals, a wide variety of gases, nonaqueous electrolytes, and other nonaqueous liquids. Furthermore, there are certain complex situations such as wear, cavitation, fretting, and other forms of degradation which it is appropriate to include. At suitable intervals certain of the review articles will be updated as the demands of technology and the fund of new information dictate.

Another important aim of this series is to attract those in areas peripheral to the field of corrosion. Thus, physicists, physical metallurgists, physical chemists, and electronic scientists all can make very substantial contributions to the resolution of corrosion problems. It is hoped that these reviews will make the field more accessible to potential contributors from these other areas. Many of the phenomena in corrosion are so complex

that it is impossible for reasonable progress to be made without more serious and enthusiastic interdisciplinary interest.

In addition to the discussion of scientific and technological phenomena the articles will also include discussions of important techniques which should be of interest to corrosion scientists.

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BIOLOGICAL CORROSION *

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INTRODUCTION

Ever since man began recovering metals from their ores and placing them in soil or aqueous environments, organisms have undoubtedly played a role in accelerating their corrosion. In 1891, the possibility that microorganisms might exert an influence on the corrosion of metals was mentioned by Garrett.¹ He postulated that the increase in the corrosive action of lead could be due to the ammonia, nitrites, and nitrates produced by bacterial action.

Gaines, in 1910,² suggested that the corrosion of iron in the soil and aqueous environments might be caused by sulfate-reducing, sulfur-oxidizing, and "iron" bacteria. The formation of deposits in water pipes by iron bacteria was reported by Ellis³ and Harder⁴ in 1919.

Although corrosion was generally associated with the presence of oxygen, the process of anaerobic corrosion was encountered several times before 1934. Convincing evidence that corrosion took place in oxygen-free environments and that bacteria were responsible for it was provided in 1934 by von Wolzogen Kühr and van der Vlugt.⁵ They had observed severe corrosion of cast iron water pipes and mains in communities north of Amsterdam, requiring pipes to be replaced every 2–3 years. The highly anaerobic soil in which these pipes had been placed was primarily polder land, land which had been reclaimed from the sea. The cast iron pipes were found to be subject to a particular type of corrosion called graphitiza-

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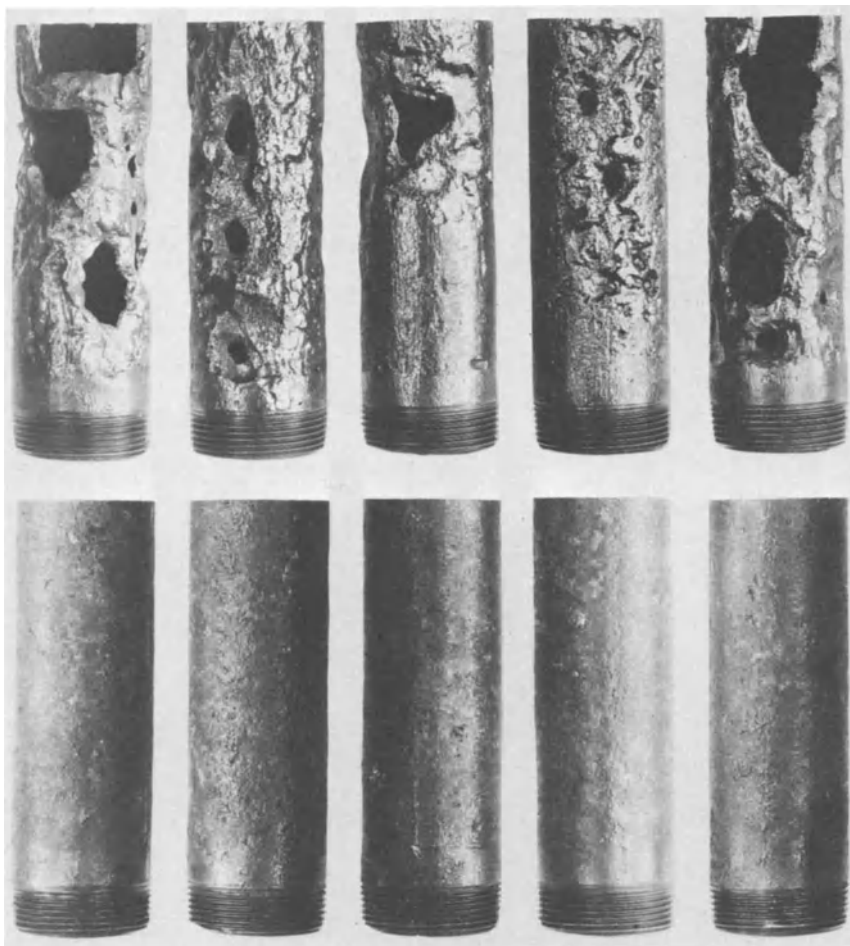


Fig. 1. Cast iron pipes showing graphitization before (top row) and after removal of corrosion products (bottom row) (courtesy of M. Romanoff, National Bureau of Standards).

tion, also referred to in the older literature as “spongiosis” or “iron canker.” The cast iron was found to be changed into a soft mass, which could be cut with a knife, similar to black lead or graphite, whence the name of the corrosion process. The term “spongiosis” referred to the porous nature of the cast iron, while the term “iron canker” reflected the rapid spread of the corrosion process. An example of graphitization is shown in Fig. 1.

In their classical paper, von Wolzogen Kühr and van der Vlugt proposed the so-called cathodic depolarization theory to account for this

corrosion process. The theory postulated that sulfate-reducing bacteria act as depolarizers or oxidizing agents by removing hydrogen from the surface of steel, thereby driving the anodic reaction, the dissolution of iron. The hydrogen had been previously shown to be utilized by the bacteria for the reduction of sulfate to sulfide. This theory will be discussed in greater detail.

Evidence for this type of corrosion in other countries continued to mount until it is now recognized as world-wide. Anaerobic corrosion, in which sulfate-reducing bacteria have been associated or implicated, has been found to take place in neutral anaerobic soils, in bays, marshes, lakes, and oceans, and beneath fouling material.

Structures which have been attacked include fuel holding tanks, pipelines (exterior and interior), pumps, well casings, ships hulls, and various industrial equipment where the reaction is near neutrality, the temperature moderate, and oxygen is absent or relatively absent. A few cases of corrosion at high temperatures have been reported to be due to thermophilic sulfate-reducing organisms.⁶

More recently, evidence has been obtained that microorganisms, including sulfate-reducers, were involved in fuel contamination and corrosion of integral wing tanks on jet aircraft.^{7,8} Often, the corrosion was severe enough to cause the perforation of wing tanks. Figure 2 illustrates this type of attack.

With the exception of cast iron, corrosion of steel and other metals by microorganisms is generally of the pitting type, often leading to perforation. The sulfide stress cracking of certain steels by hydrogen sulfide is well known.^{9,10} Microbiologically produced hydrogen sulfide in this type of corrosion is most likely. Stress corrosion of brass and copper by microbially produced ammonia is always a possibility.

Economically, the corrosion attributed to microorganisms is quite significant. In the United States in 1954, biological corrosion, primarily of buried pipelines, was estimated to cause a loss of between 500 and 2000 million dollars per year.¹¹ In the U.S. petroleum industry, sulfate-reducing bacteria were found to be responsible for more than 77% of the corrosion occurring in one group of producing wells.¹² In Great Britain for the year 1956, estimates were of the order of 20 million pounds for maintenance and replacement of underground pipelines.¹³ Booth¹⁴ in 1964 estimated at least 50% or more of the failures of buried metal to be due to microbiological causes. In Japan, corrosion loss to underground cables and pipelines was estimated in 1956 at 0.2 million dollars annually.¹⁵

Because of the variety of conditions encountered in natural environments, no standard rate of corrosion can be stated. Some unusually high

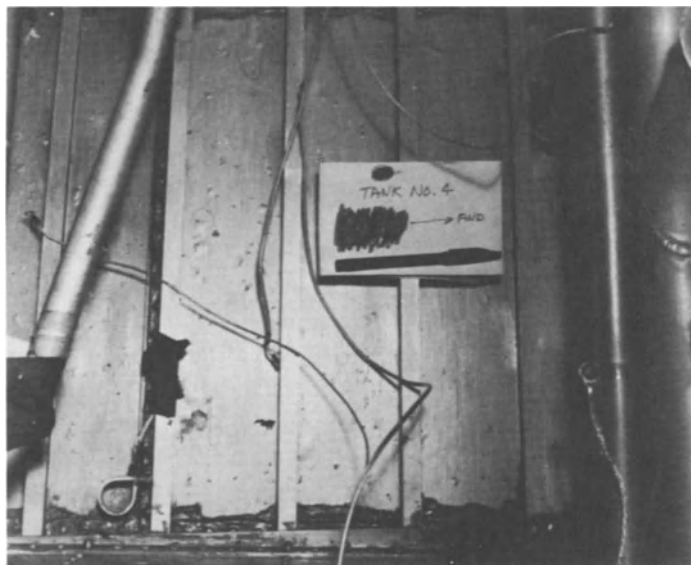


Fig. 2. Bottom of integral wing tank, showing extensive corrosion damage as a result of microbiological contamination (courtesy W. W. Boggs, Lockhead—Georgia Co., Marietta, Georgia).

rates of corrosion attributed to microorganisms have been encountered, however. Von Wolzogen Kühr, and van der Vlugt⁵ reported observing holes 2–3 cm in diameter in a 9-in. main which had been in a harbor for 15 years. Steel pipes 1 and 1.3 cm thick have been reported to have been penetrated within 9 and 8 years, respectively.^{16,17} Steel piling 1.5 cm thick immersed in marine mud has been penetrated in 12 years.¹⁸ More recent findings of even more severe corrosion (a 0.64-cm perforation, quite often in four years and sometimes within a year) have been mentioned by Booth.¹⁹ Anaerobic corrosion rates obtained in the laboratory are usually much smaller.

Although most of the studies on biological corrosion have been concerned with microorganisms, macroorganisms alone or in combination with microorganisms have been shown to play a role in this process.

ORGANISMS

Traditionally, organisms have been placed into two kingdoms: the plant kingdom and the animal kingdom. There are some instances where the organisms are classified as plants by botanists and animals by zoologists.

To overcome some of these objections, two classification systems which depart from this two-kingdom system have been proposed, the four-kingdom system of Copeland and, more recently, the five-kingdom system of Whittaker.²⁰ A brief outline of the four-kingdom system of Copeland is shown in Table 1.

Microorganisms

Microorganisms are usually considered to be organisms so small that they can be seen only with the aid of a light or electron microscope. They generally include certain fungal forms (yeasts and molds), protozoa, bacteria, the unicellular algae, rickettsiae, and viruses. They vary greatly in their nutritional requirements and tolerances to heat, light, pH, oxygen, moisture, etc. With the exception of the rickettsiae and viruses, which are parasitic and pathogenic, the other microorganisms are found in great abundance in the soil and natural bodies of water.

Fungi

The fungi are a heterogeneous group of plantlike organisms which do not contain chlorophyll and grow as saprophytes on nonliving organic material or as parasites on other living organisms. The fungal forms which are generally found alone or in association with corroding metals are primarily filamentous or yeastlike (nonfilamentous oval cells). Many of the fungal and yeastlike forms can be cultured quite readily on the surface of agar or in liquid medium. Identification of these forms is primarily based upon recognition of the reproductive bodies or spores (sexual and asexual) which may be produced. In several instances, spore formation can be induced only with difficulty if at all. In contrast to some bacteria, the fungi usually require some oxygen to grow. They may obtain their energy from a substrate (a carbohydrate, for example) by a fermentative (anaerobic) or an oxidative (aerobic) mechanism. Ethyl alcohol production by some yeastlike forms is a result of a fermentative mechanism. Various organic acids such as citric acid, oxalic acid, gluconic acid, etc., which may be corrosive to metals, are products of an oxidative metabolism.

The pitting of clad aluminum in two South African Air Force trainer aircraft, for example, has been reported by Copenhagen²¹ to be due to the fungus *Cerostromella* sp. The principal corrosion product was found to be aluminum acetate.

In addition to causing disease of humans, plants, and animals, fungi are responsible for the deterioration of many materials, including manu-

Table 1. Four-Kingdom Classification System of Plants and Animals

Kingdom, Monera (Procaryotic cells—bacteria and blue-green algae)Phylum I—*Schizophyta* (bacteria and related organisms)Class I—*Schizomycetes*

- Order I—*Pseudomonadales* (polar flagellated bacteria)
- Order II—*Chlamydo bacteriales* (sheathed bacteria)
- Order III—*Hyphomicrobiales* (budding bacteria)
- Order IV—*Eubacteriales* (true bacteria)
- Order V—*Actinomycetales* (branching bacteria)
- Order VI—*Caryophanales* (large, many-celled, filamentous bacteria)
- Order VII—*Beggiatoales* (oscillating bacteria)
- Order VIII—*Myxobacteriales* (slime bacteria)
- Order IX—*Spirochaetales* (spiral, flexous bacteria)
- Order X—*Mycoplasmatales* (pleuropneumonia-like organisms)

Class II—*Micrototabiotetes* (parasites, occur intracellularly)

- Order I—*Rickettsiales* (rickettsia; cause several human diseases transmitted by arthropods, e.g., Rocky Mountain Spotted Fever)
- Order II—*Virales* (viruses, plant, animal, and bacteria)

Phylum II—*Cyanophyta* (blue-green algae)Class I—*Myxophyceae* (*cyanophyceae*)*Kingdom, Protista* (Eucaryotic organisms without advanced tissue differentiated)Phylum I—*Mastigophora* (flagellated protozoa)Phylum II—*Rhizopoda* (amoeboid protozoa)Phylum III—*Ciliophora* (ciliate protozoa)Phylum IV—*Sporozoa* (spore-producing protozoa)Phylum V—*Myxophyta* (slime molds)Phylum VI—*Mycophyta** (fungi)Class I—*Phycomycetes* (nonseptate mycelium; algaelike fungi)Class II—*Basidiomycetes* [septate mycelium; sexual spores (basidiospores) borne on basidia, smuts, rusts, mushroom, puffballs]Class III—*Ascomycetes* [septate mycelium; sexual spores (ascospores) produced in asci or saclike structures]Class IV—*Fungi Imperfecti* (sexual spores not produced)Phylum VII—*Chlorophyta* (green algae)Phylum VIII—*Euglenophyta* (euglenoids)Phylum IX—*Chrysophyta*Class I—*Bacillariophyceae* (diatoms)Class II—*Chrysophyceae* (golden-brown algae)Class III—*Xanthophyceae* (yellow-green algae)

Table 1 (*continued*)

Phylum X— <i>Pyrrophyta</i> (fire algae)
Class I— <i>Cryptophyceae</i> (cryptomonads)
Class II— <i>Dinophyceae</i> (dinoflagellates)
Phylum XI— <i>Phaeophyta</i> (brown algae)
Phylum XII— <i>Rhodophyta</i> (red algae)
Phylum XIII— <i>Charophyta</i> (stoneworts)
<i>Kingdom, Metaphyta</i> (Multicellular green plants)
Phylum I— <i>Bryophyta</i> (mosses, liverworts, hornworts)
Phylum II— <i>Tracheophyta</i> (vascular plants)
Class I— <i>Pteridophytae</i> (ferns, club mosses)
Class II— <i>Gymnospermae</i> (naked seed-bearing plants)
Class III— <i>Angiospermae</i> (flowering plants)
Monocotyledons
Dicotyledons
<i>Kingdom, Metazoa</i> (multicellular animals)
Phylum I— <i>Porifera</i> (sponges) three classes
Phylum II— <i>Coelenterata</i>
Class I— <i>Hydrazoa</i> (hydroids)
Class II— <i>Scyphozoa</i> (jelly fish)
Class III— <i>Anthozoa</i> (corals, sea anemones)
Phylum III— <i>Ctenophora</i> (comb jellies)
Phylum IV— <i>Platyhelminthes</i> (flatworms) three classes
Phylum V— <i>Mesozoa</i> (degenerate flatworms)
Phylum VI— <i>Nemertinea</i> (ribbon worms)
Phylum VII— <i>Aschleminthes</i> (rotifers, nematodes) five classes
Phylum VIII— <i>Entoprocta</i>
Phylum IX— <i>Acanthocephala</i> (spiny-headed worms)
Phylum X— <i>Priapulida</i> (Cucumber-shaped marine worms)
Phylum XI— <i>Chaetognatha</i> (arrow worms)
Phylum XII— <i>Echiurida</i> (spoon worms)
Phylum XIII— <i>Sipunculida</i> (peanut worms)
Phylum XIV— <i>Mollusca</i> (clams, mussels, slugs, cuttlefish) six classes
Phylum XV— <i>Annelida</i> (segmented worms; earthworms, leeches)
Phylum XVI— <i>Arthropoda</i>
Class I— <i>Crustacea</i> (crayfish, crabs, barnacles)
Class II— <i>Chilopoda</i> (centipedes)
Class III— <i>Dipholoda</i> (millipedes)

Table 1 (*continued*)

Class IV— <i>Merostomata</i> (horseshoe crabs)
Class V— <i>Pycnogonida</i> (sea spiders)
Class VI— <i>Arachnida</i> (spiders, scorpions)
Class VII— <i>Insecta</i> (insects; bees, grasshoppers, flies, beetles, butterflies, etc.)
Phylum XVII— <i>Tardigrada</i> (water bears)
Phylum XVIII— <i>Onychophora</i> (claw-bearing worms)
Phylum XIX— <i>Pentastomida</i> (wormlike, blood-sucking parasites)
Phylum XV— <i>Brachiopoda</i> (lamp shells)
Phylum XXI— <i>Ectopoda</i> (polyzoa; bryozoa; moss animals)
Phylum XXII— <i>Phoronida</i> (phoronid worms)
Phylum XXIII— <i>Hemichordata</i> (acorn worms)
Phylum XXIV— <i>Pogonophora</i> (beard worms)
Phylum XXV— <i>Echinodermata</i> (starfish, sea urchins, sea lilies, sea cucumbers) five classes
Phylum XXVI— <i>Chordata</i>
Subphyla I— <i>Urochordata</i> (tunicates, sea squirts)
Subphyla II— <i>Cephalochordata</i> (lancelets or amphioxus)
Subphyla III— <i>Vertebrata</i> (fish amphibians, reptiles, birds, mammals)

* *Molds* are multicellular, filamentous fungi classed as *Phycomycetes*, *Ascomycetes* or *Fungi Imperfecti*; *Yeasts* are generally nonfilamentous fungi occurring as single cells or groups of cells which vary greatly in shape. Most all "true" yeasts (form sexual spores) are *Ascomycetes*; "false" yeasts (do not form sexual spores) are *Fungi Imperfecti*.

factured products, wood, fabrics, optical glass, paint films, plastics, etc. Several fungi which can utilize hydrocarbons as a carbon source have been associated with fuel contamination. Most of these fungi belong to the *Fungi imperfecti* (sexual spores not observed). One of the most prevalent forms isolated from fuels is *Cladosporium (Hormodendrum) resinae*. Hendey^{22,23} and Parbery²⁴ have reported on the corrosion of aluminum by this fungus.

Some fungi are extremely hardy and have been found growing in very unlikely environments, such as formalin²⁵ and electroplating baths.²⁶ Aside from their adverse effects on organisms and materials, they produce products of commercial importance such as antibiotics, vitamins, and enzymes.

Bacteria

Bacteria are small, unicellular organisms which reproduce by fission. The cells exist in any one of three basic shapes: rods, curved or spiral rods, and spheres. The spheres average about 0.5–1.0 μm (micrometers; microns)

in diameter; the rods from 0.2 to 1.5 μm in diameter and up to 10 or more μm in length. The variations among spiral forms are so great that averages mean little.

Bacterial cells possess a cell wall, a cytoplasmic membrane, nuclear material, and various types of inclusion bodies. Surrounding the cell wall may be a slime layer and often a capsule. Motile bacteria have appendages known as flagella which usually serve as a means of propulsion for the cell. In addition, some bacterial cells (primarily certain rod forms) form an endospore (spore with a cell). These are highly refractile spherical or oval shaped bodies, which are about the same diameter or larger than the cells in certain species. The spores, when transplanted to a suitable medium, germinate to form single cells again. Spores generally exhibit a high tolerance to heating and other inimical agencies.

With respect to their nutrition, bacteria are divided into two groups, heterotrophs and autotrophs. Heterotrophic bacteria may be defined as those microorganisms that obtain their energy and carbon from organic substances and assimilate carbon dioxide to only a limited extent. Autotrophic bacteria obtain their energy from light or by oxidation of one or more inorganic elements or compounds and their carbon by the assimilation of carbon dioxide. In addition to energy and carbon sources, bacteria require nitrogen, which some can get from atmospheric nitrogen, others from inorganic nitrogen salts, and others from organic nitrogen compounds. Water and various elements are also required for satisfactory growth and reproduction. Some bacteria require vitamins and other growth factors as well.

Certain environmental factors must also be favorable for bacterial growth to occur. These include pH , temperature, and oxygen tension. The optimum pH for growth of most bacteria is between 6.5 and 7.5, with the minimum–maximum range between 0 and 1 to greater than pH 9.0.

The extremes of temperature at which bacteria can grow are from -7.5 to $+75^\circ\text{C}$, and some even higher. Generally, bacteria are placed into three groups based upon their temperature requirements: psychrophiles, mesophiles, and thermophiles. Psychrophilic bacteria have the ability to grow at 0°C , mesophilic bacteria grow best (optimum growth rate) at 37°C , and thermophilic bacteria grow best at 55°C or higher.

Bacteria have also been grouped according to their ability or inability to grow in an environment containing atmospheric oxygen. Aerobic bacteria require atmospheric oxygen for growth, while anaerobic bacteria do not require oxygen. Facultative anaerobes, however, grow either aerobically or anaerobically. Some bacteria (microaerophilic) grow best in the presence of small amounts of oxygen.

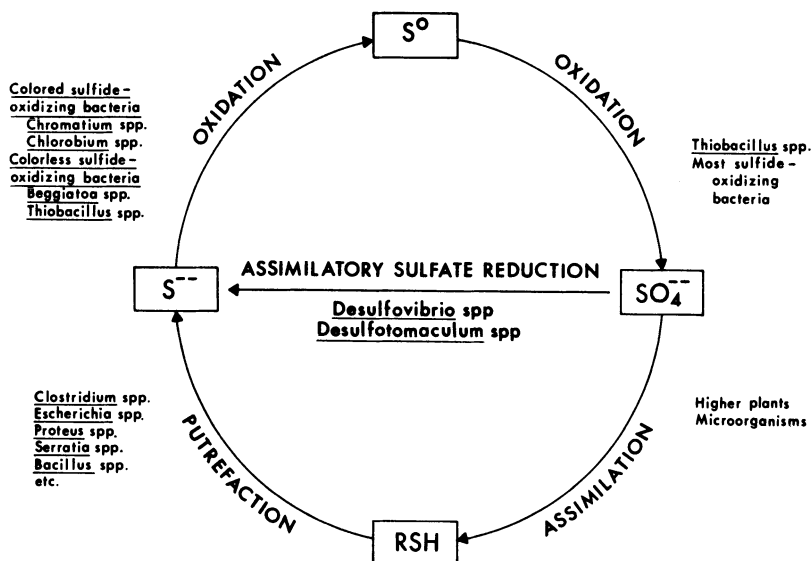


Fig. 3. Sulfur cycle. S° , elemental sulfur; S^{2-} , sulfide; SO_4^{2-} , sulfate; RSH , organic compounds, mainly sulfur-containing amino acids.

Three genera of bacteria most closely associated with microbial corrosion may be placed in either the strict anaerobic group or the aerobic group. These genera, in addition to their association with microbial corrosion, are also involved in sulfur transformations.

Bacteria Involved in Sulfur Transformations. In nature, the sulfur atom is passed through various stages of oxidation by water and soil bacteria (Fig. 3). Aerobic organisms in the genus *Thiobacillus*, which convert sulfur to sulfuric acid, and anaerobic organisms in the genera *Desulfovibrio* and *Desulfotomaculum*, which reduce sulfates to hydrogen sulfide, probably cause most of the corrosion attributed to microorganisms.

Thiobacilli. Bacteria in the genus *Thiobacilli* (previously, *Thiobacterium*) are classified within the order *Pseudomonadales*. They are small, rod-shaped cells (0.5 to 1 to 3.0 μm) which may be motile or nonmotile. Motility is due to a single polar flagellum. *Bergey's Manual*²⁸ lists nine species, most of which are aerobic. They derive their energy from the oxidation primarily of sulfur, thiosulfate, or both, the principal product being sulfate. The mechanism by which these bacteria attack sulfur and oxidize it to sulfate is still not completely understood.²⁹ *Thiobacillus concretivorus* (nitrate-utilizing) and *Thiobacillus thiooxidans* (nitrate-nonutilizing) require a pH

of 6.0 or lower for growth. These organisms can synthesize cell material (including vitamins, enzymes, protein, carbohydrates, etc.) from inorganic sources and carbon dioxide and can survive in sulfuric acid concentrations up to 10%.

Media containing sulfur and inorganic salts are used for the cultivation of these organisms.^{30,31} Growth is indicated by turbidity and an increase in acidity.

Desulfovibrio. Members of the genus *Desulfovibrio* (previously, *Spirillum*, *Microspira*, *Vibrio*, and *Sporovibrio*) are nonsporeforming, slightly curved rods (0.5–1 by 1–5 μm) which occur singly or in chains which have the appearance of spirals. The cells are usually motile by means of a single flagellum or a tuft of flagella at one end (Fig. 4) and produce a red fluorescence under UV light at 365 nm if treated with alkali. They, like the *Thiobacilli*, are also classified in the order *Pseudomonadales*. Differentiation among five recognizable species is based upon the types of flagellation,



Fig. 4. Electron micrograph of *Desulfovibrio desulfuricans* (mid-continent strain A) cells with a polar flagellum (magnification: $\sim 25,000\times$; reduced 30% for reproduction).

deoxyribonucleic acid composition, growth with certain carbon sources, resistance to *bis-p*-chlorophenyldiguanido-hexane diacetate (*Hibitane*), and requirement for sodium chloride.³²

These strictly anaerobic organisms bring about a process called dissimilatory sulfate reduction or "respiratory sulfate reduction" in which sulfate acts as a terminal electron acceptor (instead of oxygen in the aerobic forms of life) for their respiratory process. Hydrogen sulfide, the end product, is responsible for a number of unfavorable economic, ecological, and esthetic consequences.^{6,29,33} It has been stated that sulfate reduction is "one of the most commonly occurring and extensive microbiological processes on earth." The metabolic pathway of sulfate reduction in the cell is only partially known. The initial steps may be represented as



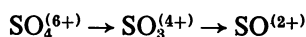
Sulfate is "activated" by ATP (adenosine triphosphate; an energy-rich compound found in all terrestrial organisms), to form a different nucleotide, adenosine-5-phosphosulfate (APS). The enzyme which activates this reaction is ATP-sulfurylase. Another enzyme, pyrophosphatase, removes the pyrophosphate (PP), hydrolyzing it to orthophosphate. This causes the equilibrium of reaction (1) to go to the right.

The APS is then reduced by the enzyme APS-reductase plus electrons from the hydrogen (via a hydrogenase, cytochrome system) to form sulfite and AMP (adenosine monophosphate).

The steps in the reduction of sulfite are generally unknown. Disulfur monoxide (S_2O) has been identified as a relatively stable gaseous product (in the absence of air and moisture) from *Desulfovibrio*,³⁴ possibly being produced from the almost immediate decomposition of SO :



SO could conceivably be an intermediate in the reduction of SO_4^{2-} , assuming two-electron reduction steps of sulfur:



Formerly, it was thought that these organisms were strict autotrophs, but recent evidence indicates that this belief may be mistaken.^{35,36}

Media for the cultivation of *Desulfovibrio* sp. generally include: (1) a source of electrons, hydrogen or organic donors such as lactate, (2) an electron acceptor, usually sulfate, (3) a buffer, usually monopotassium phosphate, (4) one or more inorganic salts, including ammonium chloride, a nitrogen source, and (5) a ferrous salt as an indicator of growth (H_2S

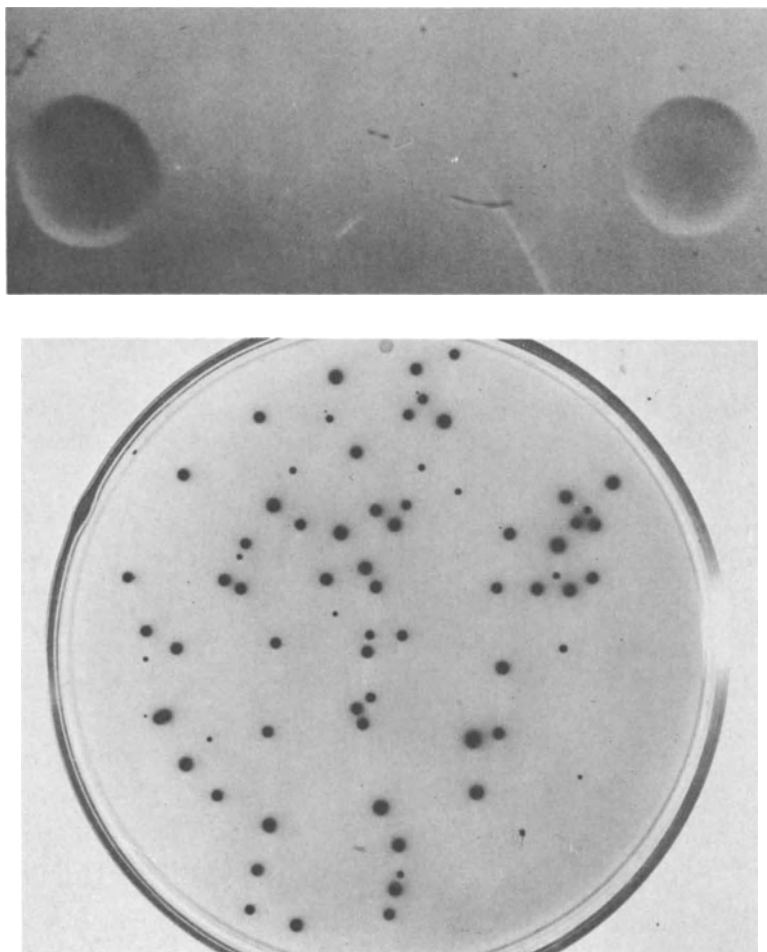


Fig. 5. (a) Colonies (~ 1 mm dia.) of *D. Desulfuricans* (mid-continent strain *A*) on trypticase soy broth plus 2% agar after seven-day incubation at room temperature in a hydrogen atmosphere. (b) Colonies of *D. Desulfuricans* (mid-continent strain *A*) on the same medium plus ferrous ions showing black precipitate around each colony. (From Iverson,³⁸ with permission of the American Society for Microbiology.)

formation).^{30,31,37} Yeast extract, which stimulates growth, and one or more redox-lowering agents, such as ascorbic acid or thioglycollic acid, may also be added. Agar (0.7%) may be added for growth in tubes which are sealed to prevent the entrance of air. Media for growth of the organism on the surface of agar plates (Fig. 5) have been reported.^{38,39} An agar plate with surface colonies of *D. desulfuricans* is shown in Fig. 5.

Desulfotomaculum. Organisms in the newly created genus *Desulfotomaculum* (previously, *Clostridium* and *Sporovibrio*) are motile, rod-shaped forms, which produce spores and which do not fluoresce in UV light with alkali. The flagella are distributed round the cell, which gives them a tumbling, wobbling movement in contrast to the polar flagellated *Desulfovibrio*, which move in more direct or straight paths. They are classified in the order *Eubacteriales*. Of the three species in this genus, only one is a thermophile: *Desulfotomaculum nigrificans* (formerly, *Clostridium nigrificans*). This organism is associated with sulfur spoilage of canned goods. Like the organisms in the genus *Desulfovibrio*, these organisms carry out a dissimilatory sulfate reduction.

Media used for the cultivation of *Desulfovibrio* may also be used for growth of *Desulfotomaculum*, but may not be as satisfactory.

Bacteria Involved in Iron Transformations. The so called "iron" bacteria are a miscellaneous group of bacteria which are associated with the oxidation of ferrous ions to ferric ions. As a result, masses of ferric hydroxide accumulate on or near the cells. In general, they are difficult to culture in the laboratory. Some are autotrophic, obtaining their energy directly from the oxidation of ferrous ions. The strict autotrophy of the others remains in doubt. Several algae also precipitate iron from ferricyanide wastes. Because of their association with iron transformations, they have been implicated in corrosion. Several of the iron bacteria have unusual morphological peculiarities, which have given rise to much confusion in their classification and identification. In addition to being associated with iron transformation, many of these organisms are also involved in sulfur transformations as well.

Some of the more commonly found forms will be discussed.

Ferrobacillus. *Ferrobacillus ferrooxidans*, the only species in this genus according to the latest *Bergey's Manual*,²⁸ is a short, motile (polar flagellum), rod-shaped cell which is a strict autotroph, deriving its energy by the oxidation of ferrous iron to the ferric state. It is very similar, if not identical, to *Thiobacillus ferrooxidans*, which also brings about this

oxidation in addition to the oxidation of sulfur and thiosulfate.⁴⁰ Originally, it was thought to differ from *Thiobacillus ferrooxidans* by its inability to oxidize thiosulfate.

The medium of Leathen and Bradley⁴¹ is one of a variety which is suitable for cultivation of this organism. An agar medium has also been described.⁴²

This organism, as well as certain *Thiobacilli*, are responsible for the leaching process of low-grade copper and uranium ores. They accelerate the oxidation of pyrite (FeS_2) to ferric sulfate and sulfuric acid, which in turn accelerates the rate of removal of either copper or uranium.⁴³

Gallionella. Of the species which precipitate iron, *Gallionella* is most commonly considered. The cells of organisms in this genus (of which *Bergey's Manual*²⁹ recognizes five species) in the order *Pseudomonadales* are kidney-shaped or rounded. Stalks are secreted by the cells from the concave side, which are transverse to the long axis of the cell. The slender, twisted stalks contain ferric hydroxide.

Cultivation in the laboratory is difficult and requires special techniques.⁴⁴ Recently, it has been reported to have been isolated in pure culture.^{45,46} These organisms are found in cool springs and brooks, which contain reduced iron in solution, and in the interior of pipes, where they have been found associated with other iron bacteria in tubercles, such as *Leptothrix* and *Crenothrix*.^{47,48}

Sphaerotilus. Organisms in this genus are placed in the order *Chlamydo bacteriales*, which includes other genera associated with iron deposition. These genera include *Crenothrix*, *Leptothrix*, and *Clonothrix*. All of these organisms are colorless, algaelike bacteria, which occur in trichomes (filaments).

Sphaerotilus natans, one of three species in this genus, is characterized by cotton or tassel-like growth attached to the bottom or side of sewage-polluted streams. The tassels are composed of trichomes of bacterial cells surrounded by a tubular, slimy sheath. In the presence of low organic matter and a considerable amount of ferrous compounds, the sheaths are brittle and glasslike in appearance due to deposition of ferric hydroxide in a hard colloidal form. Iron oxidation does not appear vital for growth of the organisms, however.⁴⁹

These organisms are the only filamentous iron bacteria that may be easily cultivated in the laboratory.⁴⁹ The use of sodium cyanodithioimido-carbonate as a selection agent for the isolation of *Sphaerotilus* appears to be quite successful.⁵⁰

Other Bacteria. A wide variety of bacteria produce hydrogen sulfide as a result of putrefaction. Members of the genus *Pseudomonas*, as well as other bacteria, produce mercaptans.⁵¹ Many bacteria also produce ammonia. Organic acids are produced by many bacteria in anaerobic or partially anaerobic environments. The cellulose-decomposing bacteria, for example, produce mainly acetic and butyric acids. All of these metabolic products are known to exert a corrosive effect on metals.

Many bacteria and higher organisms which produce slime may assist in the formation of oxygen concentration cells.

Certain bacteria in addition to *Desulfovibrio* and *Desulfotomaculum*, which are known to possess the enzyme hydrogenase (an enzyme capable of activating molecular hydrogen), may possibly be involved in corrosion processes. These would include (a) the hydrogen bacteria (*Hydrogenomonas*), organisms which obtain their energy by the oxidation of H_2 using oxygen as the electron acceptor, (b) the nitrate-reducing bacteria, which use nitrate as the final electron acceptor, and (c) the methane bacteria, which use CO_2 as the electron acceptor.⁵²

Algae

The algae are a heterogeneous group of plants found in sea and fresh water and damp places which are not differentiated into roots, stems, and leaves. They vary in size from microscopic species to seaweeds which may be over a hundred feet long.

Like higher plants, they are primarily autotrophic, obtaining their energy for growth from light. The photosynthetic process in algae is basically similar to that in higher plants in which water is the hydrogen donor and molecular oxygen is liberated. The oxygen liberated as a result of this mechanism certainly could accelerate corrosion processes.

A few strains of blue-green algae have been shown to reduce CO_2 with H_2 under anaerobic conditions in the light.⁵³ In this respect, they are similar to some of the bacteria mentioned previously.

Macroorganisms

A wide variety (about 2000 species) of larger organisms, primarily marine plants and animals, have been associated with the fouling of metals in sea water. The principal fouling animals include: barnacles, tubeworms, bryozoa (polyzoa), hydroids, mussels, and tunicates (sea squirts). The principal plants are algae. A series of well-illustrated catalogues of these

organisms is being published under the auspices of the Organization for Economic Cooperation and Development.⁵⁴

These organisms may exert both protective and detrimental effects on the corrosion process, which will be discussed under the mechanisms of corrosion.

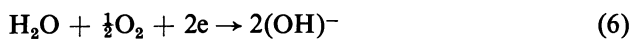
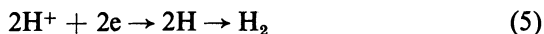
MECHANISMS OF BIOLOGICAL CORROSION

Corrosion in aqueous environments is now well established as an electrochemical process.

A metal in solution tends to ionize:



Removal of electrons by one or more mechanisms causes the reaction to go to the right (corrosion). Two principal mechanisms for removal of electrons are



The oxidizing agents (also referred to as depolarizing agents) involved in these mechanisms are hydrogen ions and oxygen, respectively.

If a plentiful supply of an oxidizing agent were present, the corrosion process would be expected to go on unimpeded, were it not for the formation of films of oxidation products which slow down one or both of the above reactions (4) and (5) or (6). Biological corrosion is simply a result of stimulation of these electrochemical processes.

Organisms may therefore stimulate corrosion by the production of oxidizing or depolarizing agents which are usually metabolic products or indirect products resulting from the action of these metabolic products on the metal.

Masses of microbial growth or higher organisms may also contribute or initiate corrosion by forming differential concentrations of depolarizing agents: differential oxygen or chemical concentration cells.

Certain anaerobic bacteria which can activate and utilize molecular hydrogen may remove hydrogen (electrons) from the surface of metal, accelerating reaction (5) to the right.

Interference by organisms with the formation or destruction of pro-

protective films either natural or applied or by the breakdown of corrosion inhibitors in closed systems could also greatly contribute to the overall corrosion rate.

Production of Oxidizing Agents

Acids (Hydrogen Ions)

Among the most corrosive products produced by microorganisms are various inorganic and organic acids. Those significant in accelerating corrosion are produced mainly under aerobic conditions. The production of sulfuric acid by various species in the genus *Thiobacillus* brings about the most impressive corrosion of metals as well as deterioration of concrete,⁵⁵ stone,⁵⁶ and rubber.⁵⁷ In pure cultures containing elemental sulfur, *Thiobacillus thiooxidans* may produce up to 10% sulfuric acid.

In addition to sulfur, other inorganic sulfur ions may be oxidized to sulfate. These include sulfide, thiosulfate, sulfite, tetrathionate, other polythionates, and thiocyanates.

In nature, thiobacilli are usually found in association with other organisms which convert sulfates to sulfides and sulfides to free sulfur.

In a peaty soil in England which was highly acid, it has been found⁵⁸ that at lower levels, hydrogen sulfide produced by the action of anaerobic sulfate-reducing bacteria was diffusing up to the aerated soil on top and there being oxidized to sulfuric acid by *Thiobacillus* species. Bitumen-covered steel gas pipes, cast-iron water mains, and steel bolts on fire hydrants were severely corroded in this soil during the first 22 years after its development as a residential area.

A more recent case of severe underground corrosion of copper tubing in southern Maryland was in all probability due to such a mechanism.⁵⁹ A bog was prepared for a building site by being excavated and piled to allow the water to drain. The bog soil was then spread over a large area and mixed with the underlying sandy clay soil. The pH of the soil was 2.0 and chemical tests indicated considerable free sulfuric acid.

Thiobacillus ferrooxidans (*Ferrobacillus ferrooxidans*) is responsible for accelerating the oxidation of pyritic (FeS_2) deposits in coal and gold mines with the formation of mine waters, high in acidity, which are very corrosive to pumping machinery and mining installations.⁶⁰

The production of organic acids by bacteria, which occurs under anaerobic or partially aerobic conditions, has been known to contribute to some cases of corrosion. The corrosion in the return water circuit of a

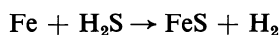
beet sugar factory was found to be due to acids produced by the growth of *Lactobacillus delbrueckii*.⁶¹ Etching of metals in the soil which were wrapped in a tar impregnated jute was due to the acids (mainly acetic and butyric acid) produced by cellulose-decomposing bacteria.⁶² In poorly buffered culture media, organic acids from a number of Gram negative bacteria caused extensive corrosion of iron.⁶³ Organic acids produced from fungi under aerobic conditions have been implicated in the corrosion of aluminum and other metals.^{22-24,64,65}

By superimposing the parameters of pH and Eh (redox-potential) for microbial life upon the Pourbaix diagram, it is possible to postulate whether microorganisms could be involved in the corrosion process, providing the metal ions and corrosion products are not toxic to the organisms.⁶⁶

Sulfur Compounds

Hydrogen Sulfide. Hydrogen sulfide is produced under anaerobic conditions by sulfate-reducing organisms, primarily those in the genus *Desulfovibrio*. The extensive corrosion of underground metallic structures, primarily iron and steel, and the internal corrosion of oil well piping, transport pipeline systems, and storage tanks by hydrogen sulfide have been serious problems for years.

The electrochemical corrosion of iron by hydrogen sulfide in an aqueous environment in the relative absence of oxygen can be expressed by the following overall equation:



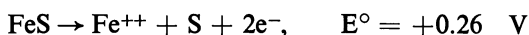
At pH values around 7 and above (a favorable pH for growth of *Desulfovibrio*), ferrous sulfide is precipitated very close to anodic areas to form a protective film.⁶⁷ The corrosion rate may be decreased considerably as a result of such a film. Booth and Tiller,⁶⁸⁻⁷⁰ from a study of polarization curves, have shown that the sulfide coating affords considerable protection against corrosion for a wide range of strains of sulfate-reducing bacteria.

Booth *et al.*⁷¹ have also observed that this protection is temporary and that on prolonged exposure to bacterial cultures, the film becomes detached, with a corresponding increase in the corrosion rate. The occurrence has also been observed by the author. The nature of the film appears to be variable. Meyer *et al.*⁷² have identified a film produced by H_2S -forming bacteria on mild steel as kansite (Fe_9S_8). Sardisco and Pitts⁷³ found the film to vary with concentration of H_2S in H_2S - CO_2 . At 0.00958 psia of

H₂S, the film consisted of troilite (FeS), pyrite (FeS₂), or mascalite (FeS_{1.965}), with very little kansite. At H₂S concentrations of 0.0544–3.25 psia, the film was found to consist of troilite, pyrite, or mascalite and a predominant amount of kansite. Kansite was found to be the least protective film in a pH region of 6.5–8.0,⁷⁴ possibly due to a defect solid structure.⁷² As HS⁻ is the predominant species in this pH region, it was postulated that the ion suppressed the formation of troilite and FeS₂.

The increase in corrosion rate following the disattachment of the film may be mainly due to the formation of a FeS/Fe couple. Cobb⁷⁵ first showed in 1911 that FeS forms galvanic cells with Fe, through use of the ferroxyl indicator. Stumper,⁷⁶ also noted a high corrosion rate of steel in direct contact with FeS. Ginter⁷⁷ had observed that sulfide-containing scale on corroded steel tanks was cathodic to the bare iron. A corrosion rate of 800 mpy was reported by Treseder⁷⁸ when this sulfide scale from corroded equipment was placed on a mild steel coupon in an air-free, quiescent H₂S laboratory test system (similar to the NACE sour corrosion test). In this test, laboratory-prepared FeS and FeS₂ (pyrite) showed rates of 3 and 26 mpy, respectively. More recently, Herzog,⁹ reported that the galvanic corrosion current density between a FeS/Fe couple was 0.01 mA/cm² (~2.4 g/m²/day).

From the standard electrode potential of Fe⁺⁺/Fe = 0.44 V and the free enthalpy of formation for FeS, $\Delta G_{298}^{\circ} = 32,500$ cal, Wranglen⁷⁹ found for the equilibrium



If sufficient ferrous ions were added to the culture medium to precipitate all of the sulfide formed by the bacteria in the medium rather than on the surface in the form of a film, Booth *et al.*⁷¹ found that the rate of corrosion was greatly increased. Earlier, Bunker,¹⁶ investigators at the National Chemical Laboratory (Teddington, England),⁸⁰ and Adams and Farrer⁸¹ had observed the rate of corrosion to be greatly enhanced by the presence of added ferrous ions to the medium. Further investigations by Booth *et al.*⁸² of this effect using nine pure strains of sulfate-reducing bacteria were only partially successful, however, as some patchy film formation was experienced.

There is further evidence that anaerobic corrosion may be primarily due to iron sulfide acting as a depolarizing agent rather than direct removal of hydrogen by the bacteria. Booth *et al.*⁸³ have shown considerable cathodic depolarization of mild steel by both bacterially produced and chemically

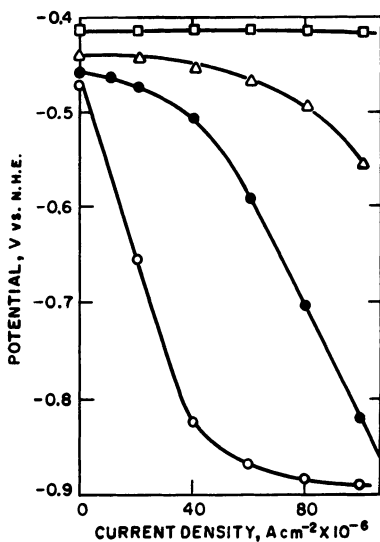


Fig. 6. Cathodic polarization curves for mild steel in static sterile suspensions of FeS in 1% NaCl at 25°C. ○, without FeS; ●, with 0.6 mM FeS; △, with 1.2 mM FeS; □, with 5 mM FeS. (From Booth *et al.*,⁸³ with permission of the British Joint Corrosion Group.)

produced suspensions of ferrous sulfide (Fig. 6). In their classic paper on the bacterial cathodic depolarization theory, von Wolzogen Kühr and van der Vlugt⁵ mentioned several times that FeS was present in the highly corrosive anaerobic soils that they studied. Workers at the National Chemical Laboratory, Teddington,⁸⁴ had also observed a greatly increased loss of weight in specimens of mild steel that were covered with a precipitate of ferrous sulfide compared to those that were not covered. It is commonly observed that around pipes corroding in waterlogged clay soils, blackening of the surrounding clay has taken place with a black crust of ferrous sulfide sometimes one or more inches thick over the corroded area.

It has been reported by Romanoff⁸⁵ that very little corrosion was found in pilings which were driven into the soil where sulfate-reducers would be expected to be present, in contrast to pipes buried in the soil where backfill occurred. A possible mechanism to explain this difference is as follows: In soils where sulfate-reducers are active, most of the hydrogen sulfide may be bound in the form of sulfides (other than iron sulfide) and possibly very little would be available to react with the iron. Harter and McLean,⁸⁶ for example, have noted the production of 2000 ppm of sulfide under waterlogged conditions without the release of H_2S from the soil. When the soils are disturbed, the "ecological equilibrium" may be upset so that an excess of hydrogen sulfide would be produced by growth of the sulfate-reducers, which then would be available to react with the iron to form ferrous sulfide and start the corrosive cycle. Growth of the sulfate-reducers

would be stimulated by the availability of fresh nutrients which would be made available to them as a result of increased decomposition of organic matter by aerobic macroorganisms. Harris⁸⁷ has shown a significant increase in the number of aerobic bacteria in a backfilled ditch over that in undisturbed soil adjacent to it at similar depths. In addition to providing nutrients, suitable anaerobic conditions would again be provided as a result of utilization of the oxygen by the microorganisms. If the soil was initially rich in iron sulfide, such differences in corrosion rates might not be observed. Corrosion in the undisturbed soil might be as high or higher than in the disturbed soil.

Ferrous sulfide may also be involved in the corrosion of aluminum, as Tiller and Booth⁸⁸ have shown. They found chemically prepared ferrous sulfide to have strong anodic and cathodic depolarizing action. Sulfides and sulfate-reducing organisms have been found in corrosion pits in simulated aluminum aircraft fuel tanks by Iverson.⁸⁹ Endtinger⁹⁰ has also found sulfides to be present in corrosion pits in aluminum alloys exposed to river water.

Hoar and Stockbridge⁹¹ have shown that films of cuprous sulfide on copper may be reduced to copper and hydrogen sulfide. It is possible that the cathodic reaction may involve a similar reduction of ferrous sulfide.

Sulfur. It has been found by Farrer and Wormwell⁹² that accelerated corrosion of mild steel took place under anaerobic as well as aerobic conditions in a suspension of sulfur 20% (w/v). In the previously mentioned tests by Treseder,⁷⁸ it was found that the corrosion rate of mild steel in contact with free sulfur was 1100 mpy. Elemental sulfur has been reported in soils where sulfate reduction has taken place.⁹³ Sulfur may be produced in soils by chemical means,^{18,94} as well as by sulfide-oxidizing bacteria²⁹ under intermittently aerobic and anaerobic conditions. Kansite, previously mentioned as a corrosion product, oxidizes to iron oxides and free sulfur when exposed to the atmosphere.⁷²

Mercaptans. Many bacteria, especially those in the genus *Pseudomonas*, are capable of producing mercaptans.⁵¹ The corrosive action of mercaptans is probably similar to that of hydrogen sulfide.

Other Agents

Oxygen production by algae in contact with noninhibitory metals in the presence of sunlight would be expected to increase the rate of corrosion.

Ammonia is produced by many microorganisms as a result of protein decomposition. The stress corrosion cracking of brass and copper by this

compound is well known.⁹⁵ Organic compounds with molecular weights of greater than 5000 were isolated by Blanchard and Goucher,⁹⁶ from various strains of *Pseudomonas* isolated from jet fuel. They were found to be corrosive to aluminum alloys used in aircraft manufacture.

Production of Differential Oxygen and Chemical Concentration Cells

It is well established that variations in the oxygen concentration or ion concentration on a metal surface can set up electric currents and that these currents play an important part in the corrosion of many metals.⁹⁷ Microorganisms, by virtue of their active metabolic processes, are ideally suitable to affect such changes, providing they are able to grow upon or very near the surface of a metal. Many microorganisms also have a natural tendency to adhere to surfaces, providing they are not toxic, where they may form films or masses of growth. The oxygen concentration under such a mass may become depleted due to physical exclusion of the oxygen and to utilization of oxygen as a result of the metabolic reactions of the microbial cells comprising the mass. When such a differential in oxygen concentration arises, a potential is formed between the poorly aerated metal surface under the mass and the more aerated regions surrounding the mass. Miller *et al.*⁹⁸ measured potential differences up to 60 mV between insulated, segmented aluminum surfaces covered by a fungal mat (anodes) and uncovered segments (cathodes). Metal goes into solution at the anodic areas of low oxygen concentration under the mass and the electrons combine with water and oxygen to form hydroxyl ions at the more oxygenated cathodic areas. This is illustrated in Fig. 7 with iron. The pitting type of corrosion observed on the internal surfaces of water pipes is believed to be due primarily to this mechanism. Tuberculation is usually associated with this pitting (Fig. 8), a tubercle or nodule of corrosion products and microorganisms being formed over each pit. The nonfilamentous iron bacterium *Gallionella*, and the filamentous types in the general *Crenothrix* and *Leptothrix*, are among the principal types found.^{47,48}

In addition, sulfate-reducing bacteria have also been isolated by the author and others^{16,99} from the tubercular material inside water pipes. This would seem to indicate that the environment at the base of and in the tubercles must be quite anaerobic and a considerable differential oxygen concentration cell effect would be expected if the water flowing through the pipe was well aerated. Of perhaps ever greater significance is the finding by Bunker¹⁶ and Butlin *et al.*⁹⁹ of considerable quantities of sulfide and sulfur

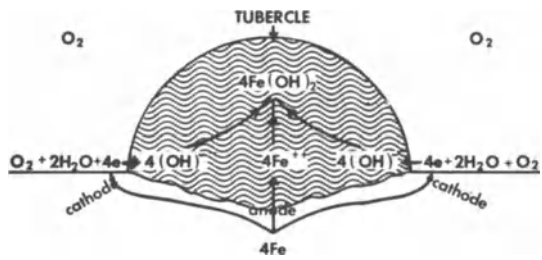


Fig. 7. Oxygen concentration cell.

in the tubercles, which were found to consist chiefly of hydrated ferroso-ferric oxide mixed with ferric hydroxide. The corrosion of iron by iron sulfide and sulfur, previously referred to, may be of even greater importance than the oxygen concentration cell effect.

A somewhat analogous situation was found in the pitting of aluminum tanks containing jet fuel.¹⁰⁰ The fungus *Cladosporium* and large numbers of a fuel-oxidizing bacterium *Pseudomonas aeruginosa* were found to be present in the tubercles. In addition, sulfate-reducing bacteria were isolated from

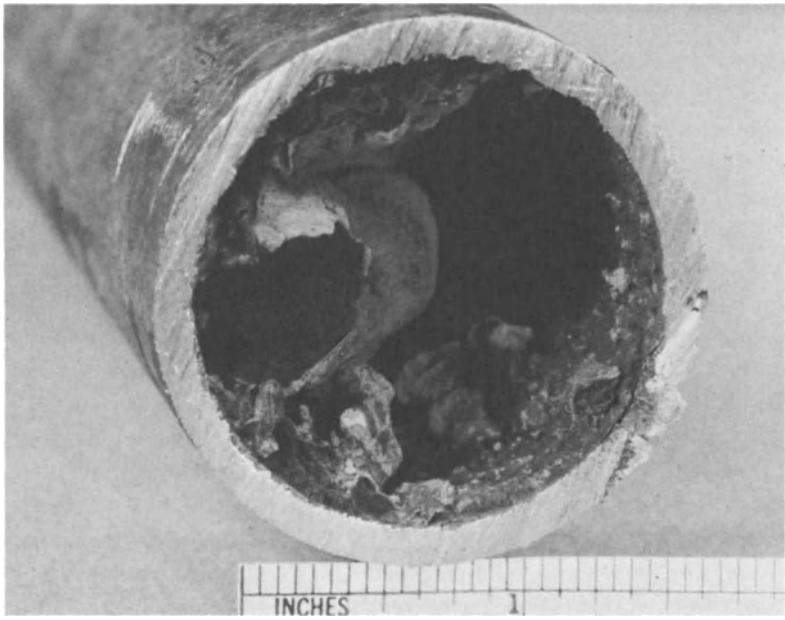


Fig. 8. Interior of steel water pipe showing extensive tuberculation.

one of the pits. The presence of sulfide on the corrosion of aluminum has previously been referred to.

The pitting that occurs under various fouling organisms, particularly barnacles, is probably due mainly to the formation of oxygen concentration cells, but again sulfate-reducing organisms may also be involved.

In addition to localized oxygen concentration cells, long line effects have been mentioned as possibly contributing to underground corrosion.¹⁰¹ A section of pipe in an anaerobic soil would be anodic to a section of pipe in an aerobic soil.

Chemical concentration cells or salt concentration cells are formed when two identical electrodes are in contact with a solution of differing composition.

Microorganisms, because of their active metabolic activities, have the ability to concentrate or dilute various ions. The technical difficulties encountered in studying the ionic concentration beneath a small mass of microorganisms on a metal surface probably account for the dearth of publications in this area.

Cathodic Depolarization

The fact that metals could corrode in a soil of neutral or near-neutral pH under anaerobic condition was a quite unexplained phenomenon until the work of von Wolzogen Kühn and van der Vlugt,⁵ who put forth conclusive evidence that sulfate-reducing bacteria were the cause of this anaerobic corrosion. They proposed a theory which stated that sulfate-reducing bacteria, which had previously been shown to contain the molecular-hydrogen-activating enzyme hydrogenase,¹⁰² removed hydrogen from the surface of iron and utilized it for the reduction of sulfate. As electrons were removed in this process, more iron went into solution. The mechanism of the theory is shown in ionic form in Table 2. At the time the theory was proposed, the hydrogen which formed at the surface was considered to exert a "polarizing" action at the cathode, with the resulting decrease in the electrochemical solution process of the iron. The organisms, by removing the hydrogen, would act as oxidizing agents or "depolarizing"* agents.

* In modern terminology, polarization is defined as the mathematical difference between the observed electrode potential under the set conditions of current density, etc. and the open-circuit or rest potential. A polarizing agent would be one which would increase this difference, and a depolarizing agent would be one which would reduce polarization on an electrode.

Table 2. Cathodic Depolarization Theory

I. $8\text{H}_2\text{O} \rightarrow 8\text{OH}^- + 8\text{H}^+$
II. $4\text{Fe} \rightarrow 4\text{Fe}^{++} + 8\text{e}$ (anode)
III. $8\text{H}^+ + 8\text{e} \rightarrow 8\text{H}$ (cathode)
IV. $\text{SO}_4^{--} + 8\text{H} \xrightarrow{\text{(bacteria)}} \text{S}^{--} + 4\text{H}_2\text{O}$ (cathodic depolarization)
V. $\text{Fe}^{++} + \text{S}^{--} \rightarrow \text{FeS}$ (anode)
VI. $3\text{Fe}^{++} + 6(\text{OH})^- \rightarrow 3\text{Fe}(\text{OH})_2$ (anode)

$$4\text{Fe} + \text{SO}_4^{--} + 4\text{H}_2\text{O} \rightarrow \text{FeS} + 3\text{Fe}(\text{OH})_2 + 2(\text{OH})^-$$

Considerable evidence has been proposed both for and against this theory.^{16,103-107} Much of this older literature on microbial corrosion has been thoroughly reviewed and evaluated by Starkey.¹⁰¹

Very little, if any of it, however, gave concrete affirmation or negation to the most important part of the theory, namely the step involving the direct removal of hydrogen by the bacteria and the coupling of this reaction with sulfate reduction.

The open-circuit potential of steel in the presence of sulfate-reducing bacteria has been shown by Hadley,¹⁰³ Spruitt and Wanklyn,¹⁰⁵ and Horvath¹⁰⁷ to rise initially to a more negative (active) value, followed by a drop to more positive (noble) values as in Fig. 9. The initial rise in potential of the steel may be due to the low redox-potential which the bacteria have produced about the time of their initial development. The drop in potential to a more noble value may have been due to the formation of a protective film of iron sulfide. The redox potential was found by Horvath¹⁰⁷ to drop from about +0.2 V to about -0.2 V.

Polarization studies were carried out by Horvath¹⁰⁷ on mild steel electrodes in Starkey's medium* inoculated with a strain of *D. desulfuricans* isolated from clay soil. Polarization curves in the sterile medium indicated strong anodic and cathodic polarization. Both anodic and cathodic curves

* Starkey's medium: K_2HPO_4 , 0.5 g; NH_4Cl , 1.0 g; Na_2SO_4 , 1.0 g; Na lactate (70% sol.), 5.0 g; distilled water, 1000 ml. Dissolve the ingredients and adjust the pH to between 7.0 and 7.5. Sterilize at 121°C for 20 min. This medium has a slight precipitate, which may be removed by filtration after sterilization, following which the medium may be resterilized. Prepare a 1% solution of $\text{FeSO}_4(\text{NH}_4)\text{SO}_6 \cdot 6\text{H}_2\text{O}$ and sterilize by steaming for 1 h on three successive days. Add 5 ml per 100 ml of medium just before use.

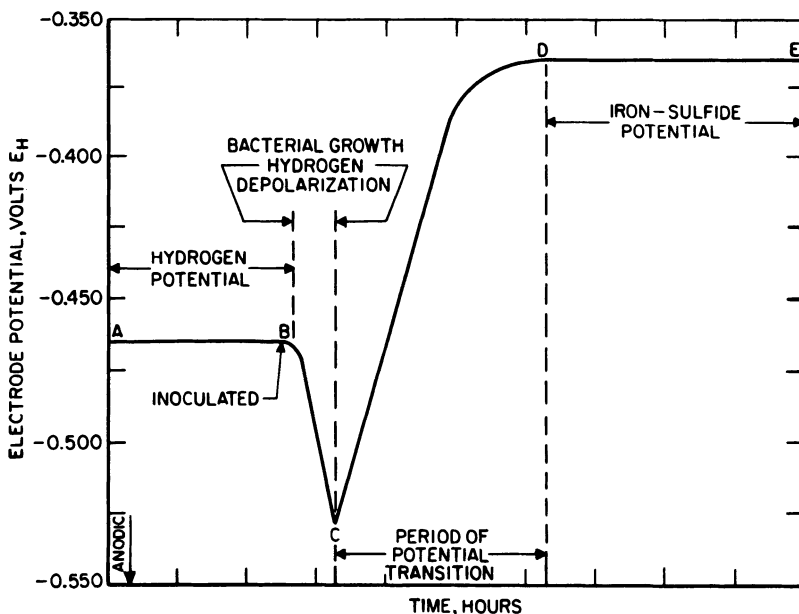


Fig. 9. Potential-time curve of mild steel electrode in modified Starkey's medium inoculated with *Desulfovibrio* (From Hadley.¹⁰⁸)

six days after inoculation indicated much less polarization, which was evidence of a marked increase in corrosion rate. With further increase of time, anodic and cathodic polarization was found to increase again, a greater increase in anodic than in cathodic polarization being reported. The decrease in the slope of the cathodic polarization curves was interpreted by Horvath as being due to the removal of hydrogen by the sulfate-reducing bacteria.

Booth and Tiller⁶⁸ employed two species of *Desulfovibrio*, *D. desulfuricans*, a hydrogenase-positive (benzyl viologen and sulfate as electron acceptors) species, and *D. orientis*, a hydrogenase-negative species (benzyl viologen as acceptor; low activity) in Butlin's medium supplemented with yeast extract and thioglycollic acid.* They observed, from the anodic polarization curves of both organisms, an early and small decrease in polarization followed by a rapid increase with time. A marked early decrease in cathodic polarization was observed only with the hydrogenase-positive strain (Fig. 10).

* Butlin's medium A plus supplements K_2HPO_4 , 0.5 g; NH_4Cl , 1 g; $CaSO_4$, 1 g; $MgSO_4 \cdot 7H_2O$, 2 g; Na lactate (70% sol.), 5 g; $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, 0.5 g; yeast extract, 1 g; thioglycollic acid, 0.1 g; distilled water, one liter.

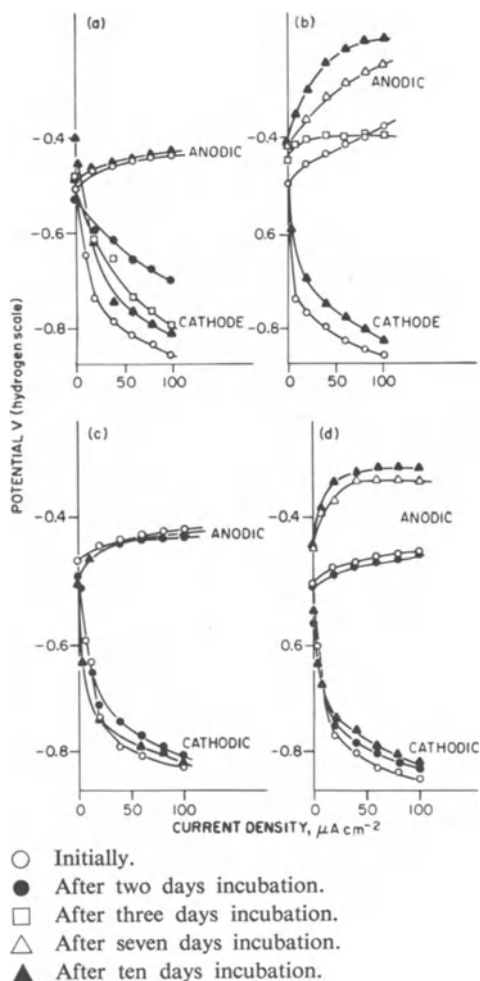


Fig. 10. Anodic and cathodic polarization curves for mild steel at 30°C. (a) Anode compartment sterile; cathode compartment inoculated with *D. desulphuricans* (Hildenborough). (b) Anode compartment inoculated with *D. desulphuricans* (Hildenborough); cathode compartment sterile. (c) Anode compartment sterile; cathode compartment inoculated with *D. orientis* (Singapore). (d) Anodic and cathodic polarization curves for mild steel at 30°C. Anode compartment inoculated with *D. orientis* (Singapore); cathodic compartment sterile. (From Booth and Tiller,⁶⁸ with permission of The Faraday Society.)

Essentially similar results were observed by Tiller and Booth⁶⁹ using two strains of a spore-forming, thermophilic sulfate-reducer, *Clostridium nigrificans* (*Desulfotomaculum nigrificans*).

A marked decrease in cathodic polarization after two days was observed with the hydrogenase-positive strain (benzyl viologen positive, sulfate negative). Very little, if any, change in the cathodic polarization of the steel electrode in the presence of the hydrogenase-negative strain (benzyl viologen and sulfate negative as electron acceptors) was found to occur.

Similar results were again found by Booth and Tiller,⁷⁰ using four halophilic strains of *D. desulfuricans*.

Marked decreases in cathodic polarization were observed with the three hydrogenase-positive strains (benzyl viologen positive; low with respect to sulfate) and an increase in cathodic polarization with the hydrogenase-negative strain (benzyl viologen and sulfate negative).

These changes in the cathodic polarization curves were also interpreted by Booth and Tiller as being due to the direct removal of hydrogen from the metal surface by the bacteria. In view of more recent work by Booth *et al.*⁸³ showing a marked decrease in polarization of steel by iron sulfide, the changes in the cathodic polarization curves attributed to direct hydrogen removal may also have been produced by the iron sulfide in the culture. Cathodic removal of hydrogen, if it did occur, was certainly of a transient nature.

Earlier results of Booth and Wormwell¹⁰⁸ had indicated a direct relationship between the hydrogenase activity (based on sulfate as the electron acceptor) and the corrosion rate, but later results by Booth *et al.*⁷¹ did not confirm this direct relationship. The hydrogenase-positive organisms, however, were always found to cause much more corrosion than the single organism *D. orientis* (Singapore), which was hydrogenase-negative.

More positive evidence that sulfate-reducing bacteria were directly involved in driving the corrosion reaction by hydrogen uptake from a steel surface was obtained by Iverson.^{109,110} Two steel electrodes (Fig. 11) were placed on the surface of a tris(hydroxymethyl)amino-methane buffered (pH 7) agar plate containing the redox dye, benzyl viologen (BV), as an electron acceptor instead of sulfate. A heavy concentration of hydrogenase-positive (benzyl viologen) bacterial cells (*D. desulfuricans*) had previously been placed on an area of the agar, so that only one of the electrodes was in direct contact with the cells. The plate with the electrodes was placed in a N₂ atmosphere and the current between the two electrodes recorded. A current density of 1 $\mu\text{A}/\text{cm}^2$ was sustained for 9 hr. On removal of the electrodes, a dense purple area of reduced BV was observed in the agar under the electrode (cathode) in contact with the cells. "Developing"

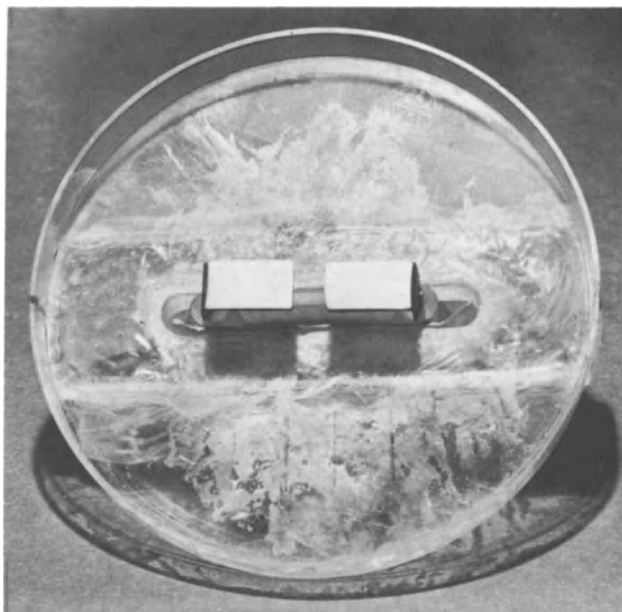
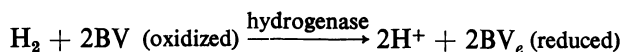
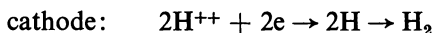


Fig. 11. Mild steel electrodes mounted in plastic petri dish cover.

the agar with ferricyanide only revealed ferrous ions in the agar under the electrode (anode) which was not in contact with the cells. Similar results were obtained in yeast extract 2% agar containing BV (Fig. 12a,b).

The reactions at the electrodes probably were



Booth and Tiller¹¹¹ maintained a steel electrode in a tris buffer solution at four fixed potentials [−0.65, −0.75, −0.85, and −0.95 V (NHE)]. Detectable increases in corrosion current densities at each of these potentials in the presence of *D. desulfuricans* cells plus BV over the current densities in the absence of the electron acceptor BV were observed. These increases were also found to be related to the hydrogenase activity of the cells. Greater current densities were found to be required in the presence of cells having a high hydrogenase activity than in the presence of cells with low hydrogenase activity. No increases in current density were observed with the hydrogenase-negative species *D. orientis*.

On a theoretical basis, Nelson¹¹² has calculated the corrosion rate of iron based on the rate of hydrogen formation by the direct reduction of water as a function of the electrode potential based on Stern's formula:

$$E = 0.670 - 0.147 \log i$$

where E is the potential on the hydrogen scale in volts of the iron electrode and i is the current in $\mu\text{A}/\text{cm}^2$ represented by the decomposition of water. Using potentials of steel in bacteria cultures from Booth and Tiller's data⁶⁸ within the range -0.45 to -0.6 V (NHE), corrosion currents of from

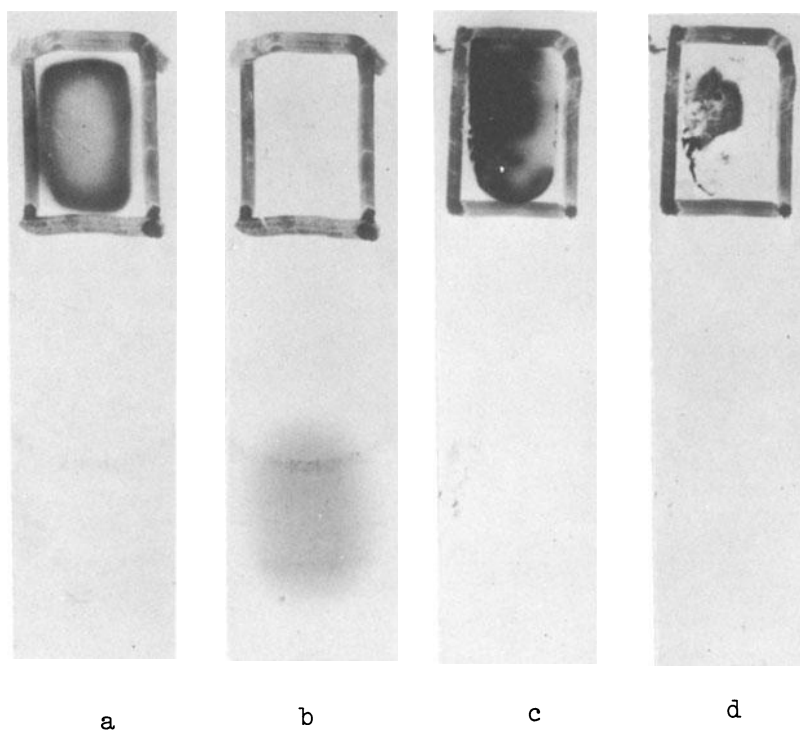


Fig. 12. Areas in agar under coupon indicating location of ferrous ions and reduced benzyl viologen (BV). (a) Yeast extract (YE) agar plus BV surface immediately after removal of mild steel coupon. Dark area (violet) caused by reduction of BV by *Desulfovibrio* cells. (b) Same plate, 15 min after addition of aqueous potassium ferricyanide (10% w/v) indicating the presence of ferrous ions at the anode (no cells). (c) YE agar minus BV immediately after removal of coupon showing dark area under cells. (d) Same plate 15 min after addition of potassium ferricyanide solution indicating ferrous ions at the same site. (From Iverson,¹¹⁰ with permission of *Nature*.)

0.05 to 0.4 $\mu\text{A}/\text{cm}^2$ (0.025–0.20 mpy) were obtained. These rates are close to the actual rate of 1 $\mu\text{A}/\text{cm}^2$ using BV as the electron acceptor.

In general, the evidence so far appears to indicate that part of the theory proposed by von Wolzogen Kühr and van der Vlugt to account for the anaerobic corrosion of iron, namely the removal of hydrogen from the surface of iron, may be a valid one, but certainly not of sufficient importance to account for the high corrosion rates observed in the soil.

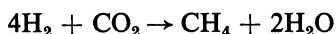
There is less evidence to support the part of the theory that states that this removal of cathodic hydrogen is coupled to the reduction of sulfate. Booth and Tiller,^{69,70} using resting (nongrowing) cells, indicated quite clearly that the hydrogenase and sulfate-reductase systems were not always coupled. Booth¹⁴ also reported a communication to him by Miller who had found that resting cells in the presence of sulfate rapidly took up hydrogen, whereas growing cells did not. When sulfate was replaced with BV, hydrogen absorption proceeded unimpeded with both resting and growing cells.

Using the technique previously described of placing electrodes on an agar surface, Iverson¹¹⁰ did not observe any constant unilateral flow of current ascribed to hydrogen utilization if sulfate was substituted for BV under conditions favorable to growth (yeast extract agar) or unfavorable to growth (tris buffer). Yeast extract was found by Iverson¹¹³ to provide excellent surface growth for *Desulfovibrio* (only a few strains tested) if it was incorporated in agar, providing an electron donor (H_2) and an acceptor (sulfate) were present. If one or the other were absent, little, if any, growth occurred. It therefore provided a good screening medium for possible electron donors and acceptors. Each batch was checked to verify the absence of both donors and acceptors.

Cells of *D. desulfuricans* on the surface of yeast extract (2%) agar in contact with steel in the absence of any added donor or acceptor (except the hydrogen on the metal surface) were found to produce an intense blackening¹¹⁰ (Fig. 12c,d). Formation of a black precipitate was also found to occur if a steel coupon was placed in a yeast extract broth culture of the identical strain as well as in the deaerated cell-free filtrate of the yeast extract broth culture. Analysis of this black precipitate indicated that it was Fe_3P . The cell-free filtrate was also capable of utilizing molecular hydrogen in the presence of benzyl viologen as an acceptor in a fashion similar to the intracellular hydrogenase in the bacterial cells.

The corrosion rate of a steel probe in a yeast extract culture was so small, however, that changes in resistance could not be detected with a very sensitive bridge circuit (<2.5 mdd).¹¹⁰

Corrosion by anaerobic bacteria other than sulfate-reducing bacteria has been reported by Kuznetsov and Panskava.⁵² They found that the methane-forming bacterium *Methanobacterium formicium* produced corrosion rates of iron greater than the control (0.24 mdd) in seven out of ten bacterially inoculated systems. They postulated a cathodic hydrogen utilization mechanisms with carbon dioxide as the electron acceptor:



Using benzyl viologen as an electron acceptor, hydrogen removal from aluminum has also been demonstrated by Iverson¹⁰⁹ and Tiller and Booth.⁸⁸

Summarizing the present available evidence, it appears therefore that the cathodic depolarization mechanism may not account for the major part of the anaerobic corrosion process. One highly probable mechanism which could account for the high corrosion rates observed in the field may be the depolarizing action of iron sulfide when in contact with iron or steel. The evidence for this mechanism was previously discussed.

Disruption of Protective Films

The corrosion of metals in natural environments is greatly inhibited to varying degrees by the formation of protective films of corrosion products. In the case of aluminum, the oxide film offers considerable protection, while in the case of iron, much less protection is provided by the oxide films. Although little studied, it seems reasonable to assume that a mass of microorganisms on the metal surface may prevent natural oxide film formation from taking place or removing these films once they have formed.

Certain macroorganisms, particularly purple sea urchins, have been reported to destroy steel H-beam piles in the ocean by removing the partially protective rust films through their abrasive action.¹¹⁴

Protective films of iron sulfide formed on steel in cultures of sulfate-reducing bacteria have been observed by Booth *et al.*⁷¹ to become detached. This detachment was varied with different strains of the organism.

Various applied protective organic coatings have been observed to become attacked by various organisms. Soil bacteria have been known to attack polyester, waxy, or asphalt coatings used to coat buried pipes.⁸⁷ Several organic coatings applied to aluminum fuel tanks have been shown to act as nutrients for bacteria and fungi.^{98,115}

Fouling organisms are known to damage protective coatings. Barnacle shells, for example, may cut into the coating as they grow. If barnacle shells are torn loose, the underlying coating usually comes off with it.

Breakdown of Corrosion Inhibitors

In closed aqueous systems, various corrosion inhibitors are frequently employed. An inhibitor such as chromate may also be inhibitory to microbial growth. Nitrite, an inhibitor for iron corrosion, was found by Lundgren and Krikszens¹¹⁶ to be utilized by nitrite-oxidizing bacteria (*Nitrobacter agilis*) and thereby rendered ineffective.

Nitrate, an inhibitor of aluminum corrosion, was found by Blanchard and Goucher⁹⁶ to be reduced to nitrite (ineffective as a corrosion inhibitor for aluminum) by hydrocarbon-oxidizing bacteria, primarily by *Pseudomonas aeruginosa*.

The utilization or inactivation by microorganisms of material in natural environments which may act as corrosion inhibitors could possibly enhance corrosion. Conversely, utilization or inactivation of oxidizing agents (oxygen), corrosive ions, or other corrodents by biological systems may, under certain circumstances, inhibit corrosion as well.¹¹⁷

Other Mechanisms

Hedrick *et al.*¹¹⁸ have proposed that the corrosion of aluminum alloys by microorganisms, particularly bacteria, is a result of the removal of metallic atoms (major and minor) from the basic structure of the alloy by extracellular enzyme activity. This working hypothesis was suggested by the observation that greater amounts of corrosion products were present in the environment containing a lesser quantity of nutrient.

Combinations of Mechanisms

Biologically stimulated corrosion in natural environments is in all probability due to a number of mechanisms, operating either simultaneously or in succession.

Corrosion of iron in the soil under anaerobic conditions, for example, could be partly due to iron sulfide-iron corrosion cells and to cathodic removal of hydrogen. If the soil becomes aerated, due to dehydration, oxidation of sulfide to sulfuric acid by *Thiobacilli*, in addition to the possible formation of oxygen concentration cells, might be expected to occur.

Results based upon laboratory studies to elucidate mechanisms of biological corrosion in natural environments may often be quite misleading, mainly due to the failure to reproduce the environment exactly. Unknowingly, corrosion systems set up artificially may introduce other or novel corrosion effects.

PREVENTION OF BIOLOGICAL CORROSION

Selection of Environment

As natural environments vary so widely in their corrosive properties, selection or modification of the environment so as to render it less corrosive should be the first consideration in corrosion prevention, where possible. Obviously, utilization of this principle affords greater promise of avoiding severe corrosion when metal structures are to be placed in the soil rather than in an aqueous environment.

Many tests, for example, have been proposed to determine the corrosiveness or "aggressiveness" of soils. Determination of soil resistivity and redox potential have been proposed^{106,119-122} as among the most significant tests. Burial and removal of test specimens is still the most reliable method if time is available. The test period may be shortened considerably through use of polarization tests for determining corrosion rates of test metals specimens *in situ*.^{123,124}

Modification of Environment

Mitigation of biological corrosion has been affected by changing the environment to a less corrosive one in a number of cases. When placing of metal structures in localized areas of anaerobic soil cannot be avoided, it may be possible to provide aerobic conditions (air is the cheapest inhibitor for sulfate-reducers) by surrounding the structure with gravel, providing there is adequate drainage. Modification of the soil or aqueous environments to alkaline^{125,126} or acid^{127,128} values has been shown to be effective as a means for control of sulfate-reducing bacteria.

Microbial Inhibitors

In certain closed systems (oil storage tanks, aircraft wing tanks, oil wells, heat exchangers, hot-water systems, cooling towers, etc.), inhibitors have been used with varying degrees of success in controlling corrosion. Chromates have been widely used as corrosion inhibitors. Part of their effectiveness is probably due to their strong inhibitory effects on sulfate-reducing bacteria.¹²⁹ Other inhibitors, such as chlorophenols, quaternary ammonium detergents, polyamines, acridine dyes, *bis-p*-chlorophenyldi-guanido-hexane diacetate (Hibitane, I.C.I.) and 2-2'-dihydroxy-5, dichlorodiphenyl methane (Panacide, B.D.H.) have also been found effective

inhibitors of sulfate-reducing bacteria. A comprehensive review of these and other inhibitors is given by Saleh *et al.*¹³⁰

Ethylene glycol monomethyl ether (EGME) and organoboron compounds have been demonstrated to be effective in controlling fuel contamination and resulting corrosion in aircraft fuel systems.^{131–133} In addition to being an excellent biostat, EGME is an excellent antiicing inhibitor. It is added to the fuel in a concentration of approximately 0.1%. It selectively partitions to the water which collects in the fuel tank.

Protective Coating

Insulating the metal surface from its environment by means of a coating is one of the most practical and effective preventative measures, especially in nonclosed systems where the environment cannot be controlled or where use of inhibitors would be too costly and ineffective. Coatings resistant to microbial attack are most desirable. Coal tar and asphaltic coatings have been quite successful in protecting underground steel structures and pipes.¹¹⁹ Portland cement coatings applied over steel have also been found to be quite effective.¹³⁴ The use of polyethylene sleeving has been reported to afford protection of cast-iron pipe in extremely corrosive environments.¹³⁵

Cathodic Protection

The use of cathodic protection in combination with coated metallic structures is probably the most effective method of preventing or decreasing corrosion in soil and aqueous environments, according to Booth.¹⁴ For the protection of ferrous metal, an additional (to -0.85 V) negative potential (-0.10 V) has been found by Booth¹¹¹ to confer cathodic protection on steel in the presence of bacterial cells.

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ELLIPSOMETRY IN CORROSION TECHNOLOGY

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INTRODUCTION

Ellipsometry is a technique for examining interfaces, in which use is made of the change in the polarization of light that occurs on reflection at an oblique angle of incidence. It may be used to determine either the optical parameters of one of the media involved, or, if an interfacial film is present, the thickness and optical properties of the layer. The attraction in applying the technique to corrosion studies is in measuring the thickness of corrosion films, and usually this can be done *in situ* with little or no interference to the reaction under investigation. Data on the optical properties of films may also be used as an aid in identifying film composition and, in some instances, as a powerful means of indicating differences in stoichiometry within a single-phase film. The sensitivity of the technique is of a high order, average film thicknesses being computable to within a few angstrom units, and the technique is applicable to films ranging from submonolayer thickness to many thousands of angstroms, depending in particular on the absorption coefficient of the film under study at the wavelength chosen. As a general rule, the technique can be used to measure the thickness of any films giving rise, when viewed in ordinary daylight, to interference colors.

Ellipsometry may be thought of as an extension of reflection metallography and, in particular, polarized light metallography. In these techniques, usually employing normal or near-normal incident light, contrast, defined as differences in intensity of reflected light, develops as a consequence of

such features as differences in composition, surface microroughening, and the orientation of crystal facets different from that of the specimen as a whole. Using plane polarized incidence light, the amount and specificity of contrast increases, and, for example, an optically isotropic medium such as copper will show less contrast than optically anisotropic ones such as beryllium and uranium. Assessment of relative absorption between light reflected from different crystallographic planes (pleochrism), and refracted (birefringence), is a standard petrological procedure.^{1,2} In ellipsometry, the surface under examination is generally viewed obliquely, and it is not usual to focus on the specimen and observe contrast in a qualitative manner, but rather to reflect a collimated beam of light and to measure homogeneous changes in the character of the reflected polarized light. If one were to focus upon the specimen, it would be observed that many features which previously showed no contrast would now begin to do so, and, for example, isotropic copper would show varying reflectivity with rotation of the incident polarized beam. In addition to the contrast produced by the substrate material, the presence of a film will also effect contrast, depending upon its thickness, and optical isotropy or anisotropy. In fact, the number of sources of contrast in oblique polarized light reflection become so numerous that if it were used as a standard metallographic technique, the results would be too difficult to interpret. However, by minimizing the number of variables, for example, by choosing an optically homogeneous substrate and a single, uniform thickness film, advantage can be taken of the considerable sensitivity of the technique, and this is exactly what is done in ellipsometry.

In corrosion studies, it is particularly useful to maintain the comparison between ellipsometry and polarized light metallography, because a brief examination using the latter method will show whether the overall field of examination is optically isotropic and hence whether a simple interpretation can be applied to the ellipsometric observations. In addition to this check on the validity of interpretation of the optical data, it is advantageous to make simultaneous examination using other techniques for measuring different parameters. For example, in studying adsorption reactions, it is helpful to combine low-energy electron diffraction or work function measurement with ellipsometry. In the aqueous corrosion field, it is of value to measure such quantities as electrode potential, corrosion current, and a range of metallographic and electron microscopic aspects, as well as film thickness and optical parameters of the film.

OPTICAL PROPERTIES OF METALS AND DIELECTRICS

As the discussion on ellipsometry given in this chapter is concerned with the interaction of polarized light with metal or alloy surfaces covered with dielectric or insulating films, it seems appropriate to introduce a section concerning some general characteristics of the optical properties of these materials.

The macro parameters involved in any discussion on optical properties are the refractive index n , which is a measure of the ability of a material to refract or bend a light beam, and the absorption coefficient k , which defines the attenuation in amplitude or intensity of the beam on transmission through a medium, and the variation of these two quantities with wavelength. The wavelengths usually considered range from the far-infrared ($\sim 50\text{ }\mu\text{m}$) through the visible (4000–8000 Å) to the ultraviolet. The energy of the incident beam can therefore be between 1/50 eV (50 μm) and many electron volts (UV), and over the visible range, which is most normally used, the energy varies from 1.5 to 3.0 eV. The different excitations produced in metals and dielectrics by interaction with light of these widely varying energies give rise to their characteristic optical properties.

Most ellipsometric work to date has been done using monochromatic, visible light, usually mercury green, sodium yellow or, more recently, the red light obtainable with laser sources. The wavelength finally chosen is, to a large extent, dictated not only by the availability of reliable high-intensity sources, but also the availability of optical components, such as quarter-wave plates, specifically made for use at a fixed wavelength. Such restriction upon wavelength is usually of little consequence in the determination of film thickness, but may become a problem in particular extended uses of the technique.

Metals by definition possess high reflectivities, for example, the approximate reflecting power of silver for green light is 94%, of copper 64%, carbon steel 58%, and gold 74%, and these and other metals become almost perfect reflectors in the infrared, the corresponding values at 9 μm being 99% for silver, 98.4% for copper, 93% for steel, and 98% for gold. This property is explained in terms of the interaction of the incident light with conduction electrons. These absorb and then reemit the incident photons with a small decrease in intensity due to electron interactions, which may be considered as effecting a viscous damping on the oscillations of the outer electrons of the irradiated material. As the energy of the incident beam increases, i.e., the wavelength falls, the interaction may be sufficiently strong to induce an internal photoelectric effect in which electrons from an

inner band level are excited to an outer level. With the noble metals, the excitation of a *d*-band electron gives rise to a specific absorption and hence color. The absorption in copper begins near 4600 Å and the metal therefore reflects the complimentary visible spectrum colors and is reddish in appearance. In gold, absorption begins at a lower wavelength, and hence more yellow can occur in the reflected light than with copper, giving gold its characteristic color. At ambient and more elevated temperatures, the absorption and refraction changes of metals with wavelength are not very sharp, and for ellipsometric measurements the choice of wavelength is not critical, except that higher wavelengths give higher reflectivities, which could in certain instances be important with respect to sensitivity. There are, however, particular situations to be avoided, such as the change in optical properties associated with metallurgical phase changes, the Curie transition temperature with magnetic materials, and even some instances of severe optical changes with temperature relatable to other physical characteristics. An extreme example is the reversible change in color of some beta brass compositions on heating from room temperature to about 300°C. In this context, it may be noted that ellipsometry, along with electro-reflectance studies, is used to obtain information on the electron distribution in the surface structure of metals by perturbing the surface in some manner, e.g., by the use of electric and magnetic fields, temperature, etc., and then measuring the corresponding changes in character of reflected light.^{3,4}

Dielectrics (and insulators), the physical classifications which describe corrosion films, have inherently low reflectivities, stemming from their very different outer electron configurations compared with metals. The more common dielectrics, such as glasses, are transparent over wide wavelength ranges, but, when considered over wavelengths from the ultraviolet to radio waves, they are characterized by periodic absorption and refractive index changes. This phenomenon has been known for glasses for a long time, Cauchy and Sellmeier having derived empirical equations⁵ to relate the changes with wavelength, and these formulas are still of use in certain ellipsometric and spectrophotometric studies.

The discontinuities in the refractive index and absorption coefficient dispersion relationships are associated with resonance effects between the incident light and the material being irradiated. At very high wavelengths, the resonance is associated with the natural frequency of vibration of the molecular and lattice structures. With decreasing wavelength of incident light, corresponding to the visible and ultraviolet regions, absorption occurs (as in metals) due to an internal photoelectric effect. Excitation of inner-band electrons to higher energy levels is restricted by the specific features

of the electron energy band structure. Such characteristics are determined by the interacting electrostatic forces within the lattice, dictated by the nature of the atomic species and the spacing between them. It follows that the band structure may, in some general way, be associated with heat of formation, band energies, etc. and recently Vijn⁶ gave examples of such correlations. Using published data on the optical properties of a range of inorganic semiconductors and insulators, a fairly linear relationship was shown to exist between the band gap measured in electron volts and the heat of activation. In general, the greater the heat of activation expressed as electron volts at 25°C, or the free energy of sublimation ΔG (in kilocalories per mole), the greater the band gap and thus the greater the energy of incident light needed to produce an internal photoelectric absorption effect—or the fundamental absorption edge or peak sometimes referred to. Alkali halides, such as lithium, calcium, and potassium fluorides, have high band gaps of 10–12 eV, while that of aluminum oxide is in the region 7–8 eV, and with germanium, silicon, cuprous oxide, lead sulfide, etc., the values are much lower, in the 1–2-eV region.

In noncubic crystals, both refractive index and absorption coefficient may be directional. In petrology, this variability of differential absorption coefficient is known as diachrism or pleochrism, while for refractive index, the corresponding term is anisotropy or birefringence, and crystals may be uniaxial or biaxial.² Monoclinic zirconium oxide, for example, has refractive indices of 2.13, 2.19, and 2.20 in the α , β , and γ directions in sodium light, while rutile, the hexagonal form of titanium dioxide, has refractive indices of 2.6 and 2.9. An additional feature to note is that excitation of an electron from the band structure characteristic of one part of a lattice, e.g., associated with the cupric ion in a cuprous oxide lattice, will result in the transfer of an electron to an energy band of an adjacent site, e.g., that of an oxygen ion.^{7,8}

Also falling in the group of intrinsic absorption phenomena are those features, seen also in metals, associated with transition from one allotropic modification to another. This is illustrated most readily in the straining of a lattice, e.g., of barium titanate, to a point at which a phase transition occurs. In the vicinity of this transition, the dielectric constant, and hence the refractive index, rises to high values. Transitions of this kind are known to occur in corrosion situations, examples being the change from the cubic to the monoclinic form of zirconium dioxide during the oxidation of zirconium in steam at elevated temperature, and with titanium in the anatase modification of titanium dioxide to rutile on heating in air. Probably the change from an epitaxial to a nonepitaxial film structure would also give

rise to similar changes in lattice optical properties, and in the ultimate, it should be possible to measure the strain introduced by the buildup of dislocations. In ellipsometric methods of assessing the thickness of a film forming in a given environment, the existence of a strong optical interaction between incident beam and film material, giving rise to strong refraction and absorption, may result in considerable uncertainty in the measurement or, mainly due to the high absorption coefficient, severely limit the range of thickness over which measurement is possible. Thus the strong absorption inherent in some oxides in the lower-wavelength ranges of the visible spectrum limits the useful measurement of film growth to a few hundred angstroms only. Even under such severe limitations, however, the ellipsometric method may still be one of the few open to use, other methods of assessment of the optical properties, such as absorption measurements by transmission in films having k_2 values in excess of 2.0, themselves being very restricted.

Superimposed upon the fundamental absorption and refraction dispersion characteristics of dielectrics already described are those changes induced by the defect state of the materials and which are implicit in the statement that many oxides are nonstoichiometric in composition. This is particularly relevant in corrosion processes, where films produced are usually nonstoichiometric. For example, in the oxidation of copper in air at temperatures a little above ambient, the predominant oxide formed is cuprous oxide. Near the oxide/metal boundary, however, the composition will tend to toward copper, whereas at the oxide/environment interface, the composition approaches that of cupric oxide, and indeed at temperatures of $\sim 200^\circ\text{C}$ and above, increasing amounts of the higher oxide are formed. Thus a composition gradient exists across the thickness of the film even though the overall lattice spacing is that of cuprous oxide. Cuprous oxide is a *p*-type semiconductor characterized by the presence of oxygen vacant sites and associated cupric ions (positive holes). At higher temperatures, such variations in stoichiometry (i.e., defect structure), have been shown by Wagner⁹ and Haufler¹⁰ to be the primary phenomenon determining oxidation rate; in corrosion processes, the presence of defects produced in a film intrinsically, and by the presence of impurity ions, is also of key importance.

Lattice defects affect optical properties by introducing local changes in the electron energy band structure, often giving rise to energy levels falling between the conduction and valence bands of the majority of the electrons in the medium. Either as a result of them accepting or donating electrons, the existence of these states in the normally forbidden zone allows

additional optical transitions to occur which appear as peaks in the absorption dispersion curve. Each peak is specific to a particular transition, and the wavelength at which it occurs and the intensity of the absorption produced provide indications of the distortions occurring in the lattice and the concentration of such distortions. Effects of this kind are produced by a wide range of lattice point defects, such as vacant lattice sites, substitutional impurities, interstitial ions, and also point defects associated with line defects such as edge and spiral dislocations. The correlation between the type and concentration of defects in substances and their macrooptical properties such as absorption coefficient and refractive index is at present not well-documented, but the magnitude of the changes would probably bear a direct relationship to the concentration of such defects. Where the change in stoichiometry of an oxide is small, for example, in the rutile form of titanium dioxide, then the corresponding changes in refractive index and absorption coefficient will also be small. However, as the absorption peak in the spectrum will occur in a region where the material is usually transparent, this change in absorption can usually be more readily detected than the change in refractive index or dielectric constant. The corresponding changes will be greater in materials showing much wider differences in composition, such as cuprous oxide, cuprous sulfide etc.

An appreciation of the defects of a particular dielectric film, together with experimentally determined data on the optical absorption in thin films, should therefore allow some inference to be drawn with relation to a particular corrosion process, and this aspect will be discussed in later sections dealing with the applications of the method.

A considerable literature now exists on the optical properties of materials, and further information in relation to metals and alloys may be found in the review article by Givens¹¹ and in a recent symposium,¹² while properties of dielectrics are described by Seitz.¹³

REFLECTION FROM A FILM-FREE SURFACE

From the preceding section dealing with optical parameters in terms of the interaction between the incident beam and the electron structure of the media involved, it might be expected that quantitative treatment of reflection could also be considered in these terms. At present, however, the process is more conveniently derived in terms of electromagnetic theory¹⁴ and the use of macrooptical properties such as refractive index and absorption coefficient. In this context, light is regarded as a disturbance of the

electromagnetic field propagating in a transverse manner with simple harmonic motion. The media involved are assumed to be optically isotropic, and the interface at which reflection occurs to be absolutely sharp and of no measureable thickness. Clearly, this is an idealized system, but it allows a mathematical representation of the general characteristics of reflection phenomena. The present section deals only with a film-free surface and the determinations of substrate optical constants, which are necessary data before dealing with the ellipsometric study of surfaces covered with film(s).

In any consideration of reflection and transmission by media which absorb light, it is necessary to introduce the concept of a complex refractive index $\bar{n}$, which consists of a term referring to refraction and another referring to absorption. The reason for this is connected with mathematical manipulation, and may be illustrated by considering the movement of a homogeneous wavefront AB approaching obliquely the surface formed by an absorbing medium (Fig. 1). The wavefront AB has just reached the metal surface, while a short time later, the same wavefront will have moved to CD . The disturbance originally at B will just have reached the interface at D , and its amplitude will not have diminished in the process. In contrast, the disturbance at A will now have traveled a distance AC through the metal, and in so doing, will have had its amplitude decreased by absorption. The amplitude of the wavefront decreases exponentially from D to C , even though the line CD represents the wavefront with respect to constant phase. This means that, except for the special case of normal incidence, the planes of equal phase and amplitude are not coincident. In the treatment of reflection by the electromagnetic theory, the object, therefore, is to determine

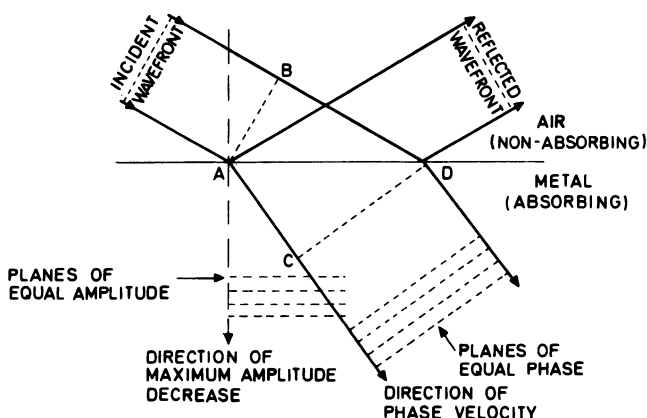


Fig. 1. Reflection and transmission of light at an air/metal interface.

changes in both phase and amplitude, and doing this mathematically requires the use of two coordinate systems. Hence complex notation is employed, such that $\bar{n} = n - ik$.

While the detailed mathematics of the electromagnetic treatment will not be given here, it may be noted that the derivation involves inserting certain boundary conditions into Maxwell's equations, which define the assumptions in electromagnetic theory. The boundary conditions assumed are that tangential components of both electric and magnetic vectors should remain continuous, and it is implied in this that no optical changes occur in the plane of the interface. Reference to the mathematical derivation can be found in publications by Heavens,¹⁵ Vasicek,¹⁶ and Winterbottom.¹⁷

In this discussion, as far as possible, the terminology adopted is that due to Muller,¹⁸ in order to avoid further complication in a field in which a wide variety of nomenclatures has been used.

In defining the equations, note should be taken of the fact that refractive index n and absorption coefficient k (also termed absorptivity) are assumed invariant with angle of incidence ϕ . The amplitude of incident and reflected components, both in the plane of incidence (p) and at right angles (s), are written as E^p , E^s , R^p and R^s , respectively. Thus reflection coefficients may be expressed as

$$r^p = R^p/E^p \quad \text{and} \quad r^s = R^s/E^s$$

For an environment and substrate which are both transparent, these reflection coefficients, on the basis of the electromagnetic theory, can be written in the form

$$\begin{aligned} r^p &= (n_3 \cos \phi_1 - n_1 \cos \phi_3)/(n_3 \cos \phi_1 + n_1 \cos \phi_3) \\ r^s &= (n_1 \cos \phi_1 - n_3 \cos \phi_3)/(n_1 \cos \phi_1 + n_3 \cos \phi_3) \end{aligned} \quad (1)$$

where ϕ_1 and ϕ_3 are the angles of incidence and reflection, respectively, and n_1 and n_3 are the refractive indices of environment and substrate, respectively. These are known as the Fresnel equations or coefficients.

For reflection at a substrate showing absorption, these same equations can be shown to remain valid provided that the refractive index term is replaced by the complex form $\bar{n} = n - ik$, with the consequence that the angle of refraction must also be expressed in complex form, $\bar{\phi}_3$. Thus

$$\begin{aligned} \bar{r}^p &= (\bar{n}_3 \cos \phi_1 - n_1 \cos \bar{\phi}_3)/(\bar{n}_3 \cos \phi_1 + n_1 \cos \bar{\phi}_3) \\ \bar{r}^s &= (n_1 \cos \phi_1 - \bar{n}_3 \cos \bar{\phi}_3)/(n_1 \cos \phi_1 + \bar{n}_3 \cos \bar{\phi}_3) \end{aligned} \quad (2)$$

A complex angle of refraction has no physical significance, but is used to assist in mathematical manipulation.

The reflected components $\bar{r}^p$ and $\bar{r}^s$ can be written in the form $|r^p| e^{i\delta_p}$ and $|r^s| e^{i\delta_s}$, showing that each contains both an amplitude and a phase component. Experimentally, it is possible to measure amplitude by determining the intensity, $|r^p|^2$ in the plane of incidence, and $|r^s|^2$ normal to this plane, but the measurement of phase presents difficulty due to lack of a reference phase and the fact that the reflected light is usually incoherent or only partially coherent. However, the reflection process can be analyzed in such a way that the waveform of the reflected beam, which is elliptically polarized, can be defined by the ellipticity $\bar{Z}$, given by

$$\bar{Z} = \bar{r}^p / \bar{r}^s = (|r^p| / |r^s|) e^{-2i(\delta_p - \delta_s)} = (\tan \psi) e^{i\Delta} \quad (3)$$

where $\Delta = \delta_p - \delta_s$ and $\tan \psi$ is the ratio of the resultant reflected amplitudes in the plane of incidence and normal to this plane (see Fig. 2).

One method of measurement stems directly from the definition of ellipticity as expressed in (3), as it is experimentally possible to measure both $\tan \psi$ and Δ using conventional optical techniques. Thus, even though the reflected light consists of a series of wavelets whose phase is not related, the difference in phase caused by a large number of such incoherent waves gives rise to the overall resultant phase change measured using optical components.

A second method consists in defining the shape of the resultant ellipse of vibration which is formed by the combination of two orthogonal components of unequal amplitude and phase (Fig. 2). The shape and orientation of this ellipse are mathematically connected with $\tan \psi$ and Δ by the relationships

$$\begin{aligned} \tan \Delta &= (\tan \beta)(\tan^2 \eta + 1) / (\tan \eta)(\tan^2 \beta - 1) \\ \tan \psi &= [(\sin^2 \eta + \tan^2 \beta \cos^2 \eta) / (\cos^2 \eta + \tan^2 \beta \sin^2 \eta)]^{1/2} \end{aligned} \quad (4)$$

where β is the ratio of the minor to the major axis of the ellipse and has values between 0 and 1, and η is the angle between the major axis of the ellipse and the normal to the plane of incidence, and has values between $\pm\pi/2$. Also, $\eta > 0$ for small angles of incidence ($\phi < \bar{\phi}$, the principal angle of incidence), and $\eta < 0$ for $\phi > \bar{\phi}$. It follows from this second method that measurement of the intensity of the reflected, elliptically polarized light at a number of fixed orientations can be used to define the shape and orientation of the ellipse. Indeed, by this method, if measured intensities

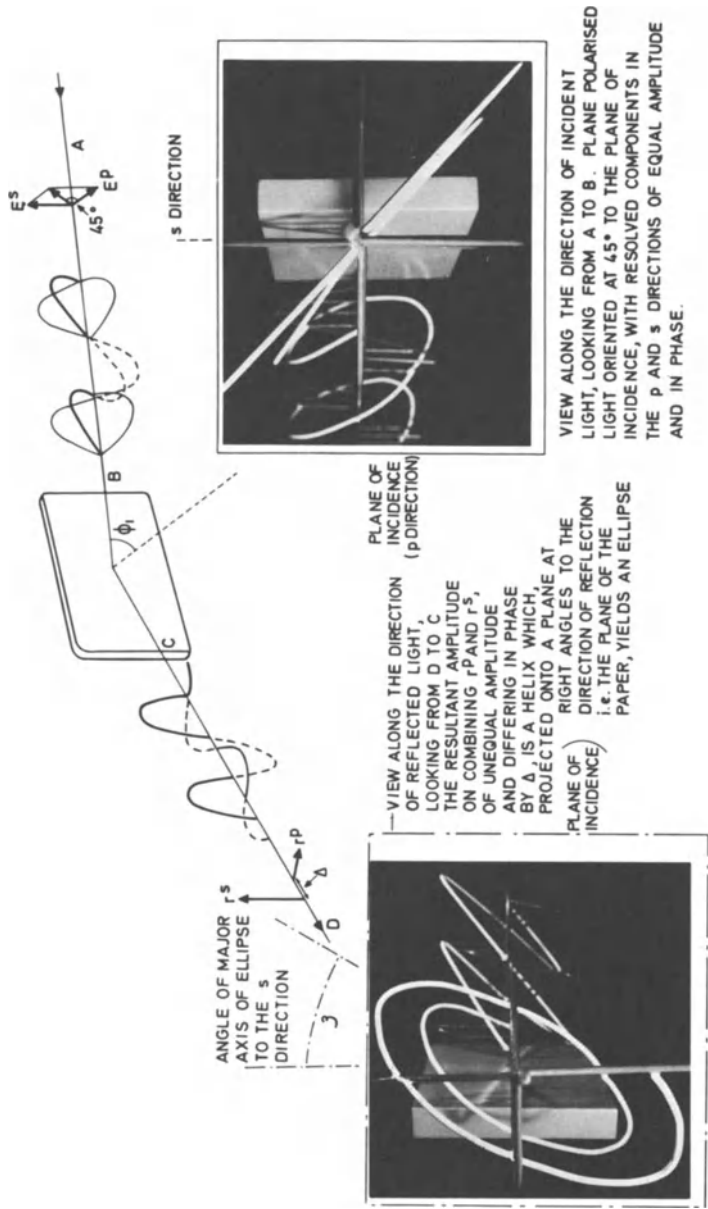


Fig. 2. Reflection of plane polarized light at an air/metal interface.

are related to the intensity of the incident beam, it is possible to determine the absolute size, in addition to the shape, of the ellipse.

Whichever method of determining $\tan \psi$ and Δ , or other related quantities, is adopted, an objective must be to solve the Fresnel equations. By combining equations of type (2) with type (3), and making use of Snell's law

$$n_1 \sin \phi_1 = \bar{n}_3 \sin \phi_3 \quad (5)$$

the equations relating reflection of polarized light at a film-free surface can be written

$$\bar{n}_3/n_1 = (\tan \phi_1) \{1 - [(4\bar{Z} \sin^2 \phi_1)/(1 + \bar{Z})^2]\}^{1/2} \quad (6)$$

or

$$\bar{Z} = \frac{\sin^2 \phi_1 - (\cos \phi_1) \{[(\bar{n}_3)^2/n_1] - (\sin \phi_1)^2\}^{1/2}}{\sin^2 \phi_1 + (\cos \phi_1) \{[(\bar{n}_3)^2/n_1] - (\sin \phi_1)^2\}^{1/2}} \quad (7)$$

These expressions, which do not contain a wavelength term, allow the computation of the complex refractive index of a film-free surface from an experimentally determined $\bar{Z}$ value, or alternatively, the ellipticity to be expected on reflection at a film-free surface of known optical constants. The ellipticity corresponding to a film-free surface is frequently written $\bar{Z}_0$ to distinguish this value from those measured on filmed surfaces.

Another method used to determine the optical parameters of metal surfaces is that involving the determination of the principal angle. At the principal angle, the phase retardation between parallel and reflected components equals 90° , and therefore the reflectivity in the plane of incidence falls to a minimum and the emergent light is almost wholly polarized in a plane normal to the plane of incidence, and completely plane polarized if the substrate is transparent. Thus an experimental arrangement is used in which an angle of incidence at which the phase change between r^p and r^s becomes 90° can be located. With this information, and the principal azimuth of the reflected ellipse of vibration at this angle, $\bar{n}_3$ can be evaluated.⁵ This is infrequently used in the ellipsometric study of films, mainly because of the difficulty in designing equipment with windows suitable for *in situ* examination of specimens over a range of angles of incidence, and because other methods are available, but is included in the present survey because it was used extensively in the past to measure the optical constants of film-free metal substrates.

The ellipticity corresponding to a particular metal can conveniently be plotted graphically in terms of $\tan \psi$ and Δ using a polar diagram,

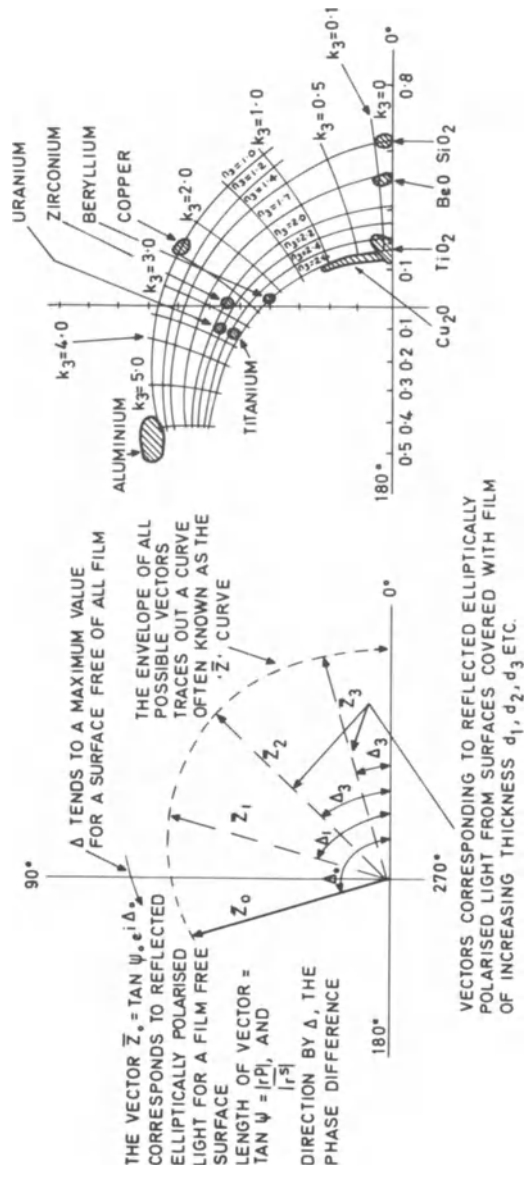


Fig. 3. Graphical method of representing reflected elliptically polarized light, showing approximate values of $\tan \psi$ and Δ for a number of metals and oxides at $\phi_1 = 75^\circ$ and $\lambda = 5461 \text{ \AA}$. Also marked is a calibration grid relating $\tan \psi$ and Δ to $n_3 - ik_3$, the data being computed from Eq. (6).

$\tan \psi = r^p/r^s$ being represented by the length of a vector and Δ by the angular rotation (Fig. 3). Plotted on this diagram are the results of calculations of Eqs. (6) and (7), the ellipticity values being represented only as the end point of the vector to avoid confusion on the final diagram. As defined here, reflection from dielectric surfaces gives rise to no phase change between parallel and normal components, whereas for a series of metals and alloys examined at $\phi_1 = 75^\circ$ and $\lambda = 5461 \text{ \AA}$, the phase change falls between 80 and 120° . For beryllium, zirconium, and a 70/30 copper/nickel alloy, this angle of incidence lies close to the principal angle. The experimental determination of these constants, including the problems of surface preparation and residual films, is described in a subsequent section.

REFLECTION FROM A FILM-COVERED SURFACE

The basis underlying ellipsometry is that the presence of a film overlying a substrate modifies the properties of obliquely reflected polarized light in a predictable manner, and that this change in the state of polarization can be correlated with the thickness and optical parameters of the film. In the case of a parallel-sided, optically isotropic film, the reflection process may be treated as in Fig. 4. The sequence of events can be subdivided into reflections at the various interfaces, each of which is describable in terms of the appropriate Fresnel reflection coefficients mentioned in the previous section, and transmission through the film layer. The latter will introduce a phase change and attenuation of amplitude, both of which will be dependent upon the thickness of the film. The expression for the resultant change of polarization on reflection will therefore involve the film thickness. In the following analysis, $\bar{r}_1$ and $\bar{r}_2$, $\bar{i}_1$ and $\bar{i}_2$, etc. refer to light traveling in one direction, and the dashed values to light in the opposite direction. The total amplitude of light reflected from the surface will be

$$\bar{R} = \bar{r}_1 + \bar{i}_1 \bar{i}_1' \bar{r}_2 e^{-2i\delta} + \bar{i}_1 \bar{i}_1' \bar{r}_1' \bar{r}_2^2 e^{-4i\delta} + \bar{i}_1 \bar{i}_1' (\bar{r}_1')^2 \bar{r}_2^3 e^{-6i\delta} + \dots$$

where δ is a measure of the phase and absorption change on transmission through the film, given by $2\pi\bar{n}_2(\cos \bar{\phi}_2)d/\lambda$. Writing $\bar{r}_1 = -\bar{r}_1'$ and using the Fresnel relationship $\bar{i}_1 \bar{i}_1' = 1 - \bar{r}_1^2$, the expression may be summed to yield

$$\bar{R} = (\bar{r}_1 + \bar{r}_2 e^{-2i\delta}) / (1 + \bar{r}_1 \bar{r}_2 e^{-2i\delta}) \quad (8)$$

This relationship applies both to light reflected in the plane of incidence (p)

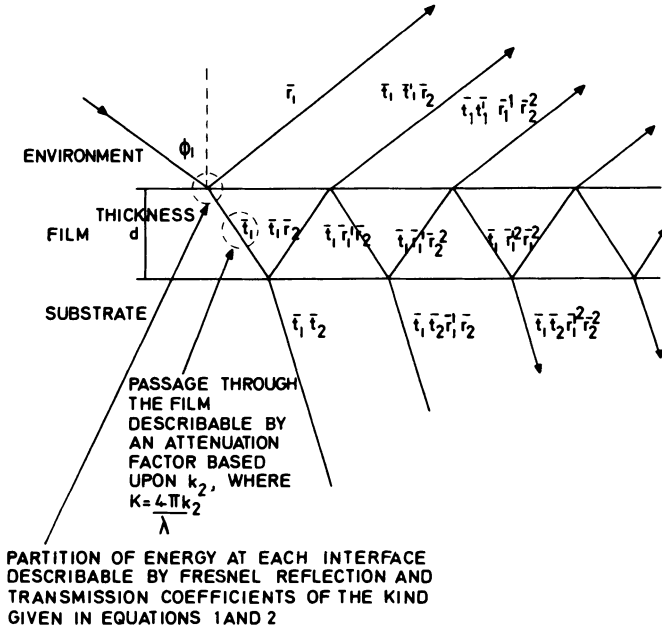


Fig. 4. Multiple reflection of light at a film-covered metal surface.

and normal to this plane (s), so that the overall reflection process may be written

$$\bar{Z} = (\tan \psi) e^{i\Delta} = \frac{\bar{r}^p}{\bar{r}^s} = \frac{(\bar{r}_{12}^p + \bar{r}_{23}^p e^{-2i\delta}) / (1 + \bar{r}_{12}^p \bar{r}_{23}^p e^{-2i\delta})}{(\bar{r}_{12}^s + \bar{r}_{23}^s e^{-2i\delta}) / (1 + \bar{r}_{12}^s \bar{r}_{23}^s e^{-2i\delta})} \quad (9)$$

where

$$\bar{r}_{12}^p = (\bar{n}_2 \cos \phi_1 - n_1 \cos \bar{\phi}_2) / (\bar{n}_2 \cos \phi_1 + n_1 \cos \bar{\phi}_2)$$

$$\bar{r}_{23}^p = (\bar{n}_3 \cos \bar{\phi}_2 - \bar{n}_2 \cos \bar{\phi}_3) / (\bar{n}_3 \cos \bar{\phi}_2 + \bar{n}_2 \cos \bar{\phi}_3)$$

$$\bar{r}_{12}^s = (n_1 \cos \phi_1 - \bar{n}_2 \cos \bar{\phi}_2) / (n_1 \cos \phi_1 + \bar{n}_2 \cos \bar{\phi}_2)$$

$$\bar{r}_{23}^s = (\bar{n}_2 \cos \bar{\phi}_2 - \bar{n}_3 \cos \bar{\phi}_3) / (\bar{n}_2 \cos \bar{\phi}_2 + \bar{n}_3 \cos \bar{\phi}_3)$$

The rigorous derivation of this expression has been described by Winterbottom,¹⁷ Mowat and Muller,¹⁹ Heavens,¹⁵ and others. Other mathematical approaches to the summation of the resultant reflection, also yielding Eq. (9), have included the equivalent beam method introduced by Fry²⁰ and the matrix approach.^{21,22} The latter method is of interest because of the relative ease with which the calculation may be extended to reflection from multilayer parallel films. The process of reflection at an interface

can be written (using symbols referred to in Fig. 3) as

$$\begin{pmatrix} 1/\bar{t}_1 & \bar{r}_1/\bar{t}_1 \\ \bar{r}_1/\bar{t}_1 & 1/\bar{t}_1 \end{pmatrix} \quad (10)$$

and that of transmission through a film as

$$\begin{pmatrix} e^{i\delta} & 0 \\ 0 & e^{-i\delta} \end{pmatrix}$$

and the overall reflection can be expressed as three matrices:

$$\begin{aligned} & \begin{pmatrix} 1/\bar{t}_1 & \bar{r}_1/\bar{t}_1 \\ \bar{r}_1/\bar{t}_1 & 1/\bar{t}_1 \end{pmatrix} \begin{pmatrix} e^{i\delta} & 0 \\ 0 & e^{-i\delta} \end{pmatrix} \begin{pmatrix} 1/\bar{t}_2 & \bar{r}_2/\bar{t}_2 \\ \bar{r}_2/\bar{t}_2 & 1/\bar{t}_2 \end{pmatrix} \\ &= \frac{e^{i\delta}}{\bar{t}_1\bar{t}_2} \begin{pmatrix} 1 + \bar{r}_1\bar{r}_2e^{-2i\delta} & \bar{r}_2 + \bar{r}_1e^{-2i\delta} \\ \bar{r}_1 + \bar{r}_2e^{-2i\delta} & \bar{r}_1\bar{r}_2 + e^{-2i\delta} \end{pmatrix} \end{aligned} \quad (11)$$

The reflection coefficient can be extracted from this expression as the ratio of the second to the first element of the first column, i.e.,

$$R = (\bar{r}_1 + \bar{r}_2e^{-2i\delta})/(1 + \bar{r}_1\bar{r}_2e^{-2i\delta})$$

For a two-layer situation, it is only necessary to multiply Eq. (11) by

$$\frac{e^{i\delta_2}}{t_3} \begin{pmatrix} 1 & 0 \\ 0 & e^{-2i\delta_2} \end{pmatrix} \begin{pmatrix} 1 & \bar{r}_3 \\ \bar{r}_3 & 1 \end{pmatrix}$$

giving a resultant

$$R = \frac{\bar{r}_1 + \bar{r}_2e^{-2i\delta} + \bar{r}_1\bar{r}_2\bar{r}_3e^{-2i\delta_2} + \bar{r}_3e^{-2i\delta}e^{-2i\delta_2}}{1 + \bar{r}_1\bar{r}_2e^{-2i\delta} + \bar{r}_2\bar{r}_3e^{-2i\delta_2} + \bar{r}_1\bar{r}_3e^{-2i\delta}e^{-2i\delta_2}} \quad (12)$$

where δ may be defined as $n_2'(\cos \phi_2') d'/\lambda$ and δ_2 as $n_2''(\cos \phi_2'') d''/\lambda$, the single and double primes identifying the film optical constants and thicknesses of the two layers. As in the example for reflection at a single film, reflection in planes parallel and perpendicular to the plane of incidence would be determined by substitution of the appropriate Fresnel coefficients [see Eqs. (2)].

MEASUREMENT OF ELLIPTICALLY POLARIZED LIGHT

Methods commonly used in the measurement of the ellipticity of polarized light are dealt with here, as these give some impression of accuracy and precision, and allow a better perspective to be obtained of the

derivation of film thickness and optical properties in terms of measured ellipticity levels which is described in following sections.

A method of measurement is required for the general case of elliptically polarized light depicted in Fig. 2. This can be represented as separate components in the p and s planes, having amplitudes differing in height and also differing in relative phase. The resultant wave motion traces out a helical path through space, and the projection onto a plane at right angles to the direction of travel forms an ellipse, the ellipse of vibration. The geometric relationships between the relative amplitude and phase differences of the p and s components and the shape and orientation of the ellipse has already been given, [see Eqs. (4)]. The two basic methods of measurement use either the principle of compensation or that of intensity measurement. In the first case, the phase difference between p and s components is removed by passing the light through an optical system which produces an exactly equal and opposite phase difference. The resulting light consists of two components which are in phase, yielding a resultant plane polarized vibration, for which methods of determination are readily achieved. In the intensity method, the shape of the ellipse is determined by measurement of the intensity of light in different vibration directions. Both of these methods allow the shape and orientation of the ellipse to be defined, but not its absolute size. Additional information can be gained by determining this last parameter, which involves the measurement of the ratio of incident to reflected intensity in one or more planes.

Compensator Methods

A range of methods has been described by Jerrard,²³ together with their relative sensitivities of detection of $\tan \psi$ and Δ . In the simplest form of the apparatus, three basic components are required, the plane polarizer P , the compensator Q , and the analyzer A , the latter in fact being simply another plane polarizer but traditionally called an analyzer to distinguish its function from that of the polarizer. A typical component layout is shown in Fig. 5. A collimated beam of monochromatic light is directed onto the polarizer whose azimuth is set at 45° to the plane of incidence (the p direction) in order to produce resolved components in the p and s directions which are equal in amplitude and phase. On reflection from the specimen, which may be regarded as producing vibration in the p and s directions, the light is changed in amplitude and phase as shown in Fig. 2.

The light is then passed through a compensator (of the Babinet-Soleil type, for example) whose vibration directions are also set in the p and s

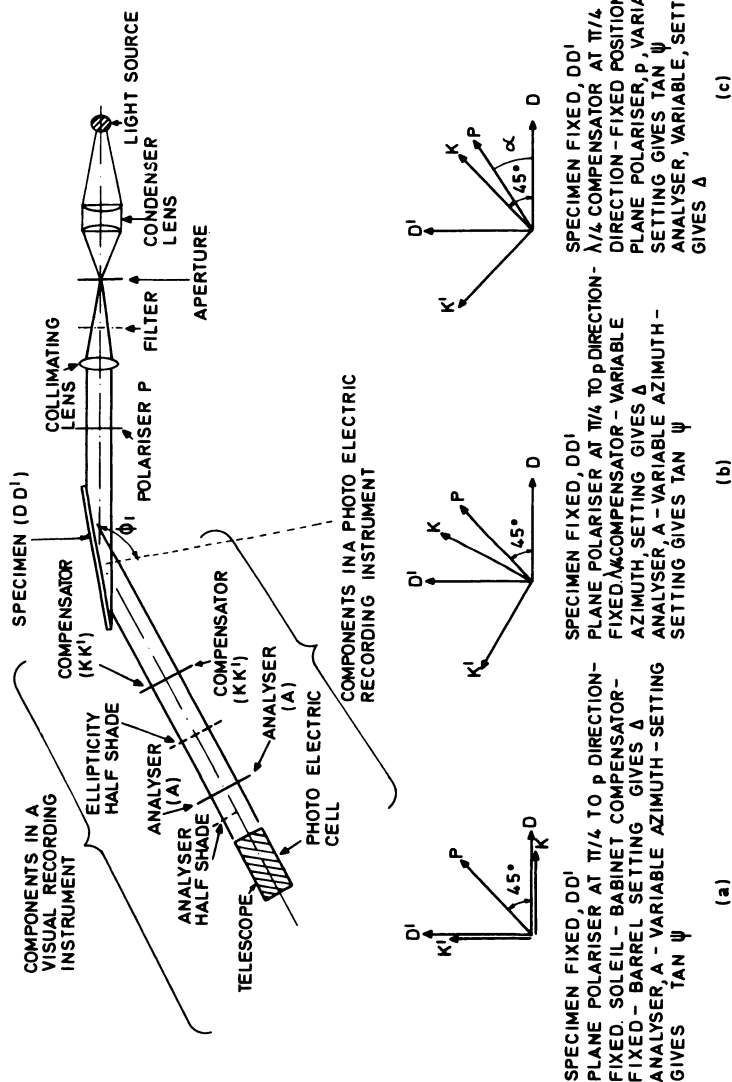


Fig. 5. Components in a simple ellipsometer and different component settings for measurement of reflected elliptically polarized light using the compensator principle.

planes. This component is constructed in such a way that, by operating a micrometer, one can alter the thickness of one element of the compensator with respect to another, producing a continuously variable phase delay between the p and s directions.²⁴ By appropriate adjustment of this component, a phase difference Δ equal and opposite to that caused on reflection can be produced, rendering the resultant light plane polarized. This is then passed through a further calibrated analyzer, which is rotated to the crossed position at which the light is totally extinguished, hence locating the vibration direction of the restored plane polarized light. The tangent of the angle between this direction and the s direction defines $\tan \psi$.

Continuously variable-phase Babinet-Soleil-type compensators are quite expensive, and similar sensitivities can be obtained using a cheaper, fixed-phase-delay compensator in which the effective phase delay can be continuously varied by rotation of the component in a plane normal to the direction of the reflected light beam. Such a component is the quarter-wave plate, which is an optical element producing two vibration directions having a phase retardation between them of $\lambda/4$ or 90° for the particular wavelength for which they are calibrated. Such elements introduce no difference in amplitude between relative vibration directions. The principle underlying the quarter-wave-plate method, known also as the Sénarmont compensator method, is shown diagrammatically in Fig. 6. When the reflected elliptically polarized light is passed through the quarter-wave plate, set with vibration directions parallel to p and s directions (as in the upper diagram of Fig. 6), the phase difference between these two planes becomes $\Delta + (\pi/2)$. If the quarter-wave plate is then rotated through 90° , the phase delay changes to $\Delta - (\pi/2)$. This means that rotation of the quarter-wave plate Q through 90° has effectively produced a phase change from $+\pi/2$ to $-\pi/2$, i.e., of 180° . At some intermediate setting of the Q axes of vibration of the plate between the p and s directions, an effective phase difference can be produced which equals and opposes Δ , not only providing a measure of the value of Δ , but leaving plane polarized light which can provide a direct value of $\tan \psi$. The relevant orientation of the components is shown in Fig. 5(b). Thus with the incident light set at 45° to the plane of incidence, the axes of the quarter-wave plate are rotated until plane polarized light is restored. The vibration direction of the analyzer is not shown, but this will be set at right angles to the vibration direction of the restored plane polarized light.

In another variation of the method (Fig. 5c), the quarter-wave plate Q is fixed with one of its axes at 45° to the plane of incidence. In this case, the polarizer P is rotated until the resultant polarization effects produced on

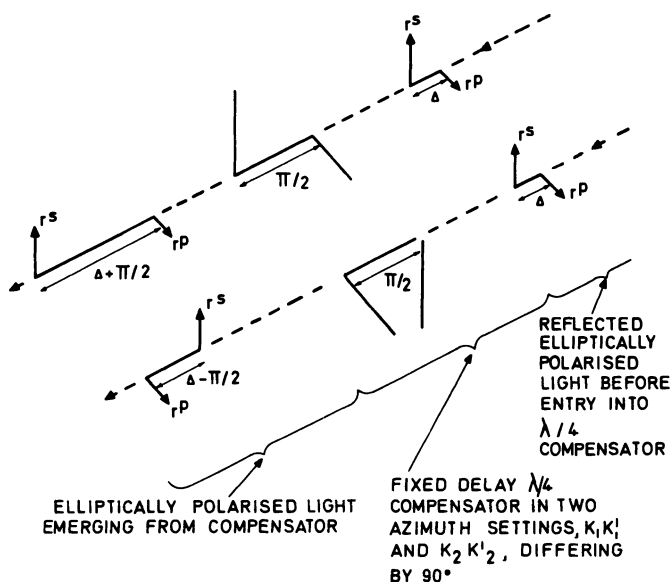


Fig. 6. Use of a variable-azimuth, fixed-delay compensator (arrangement b in Fig. 5) for the analysis of elliptically polarized light. Rotation of the fixed-delay compensator through 90° produces a 180° phase change. At some intermediate $\lambda/4$ setting to those indicated, the effective phase delay produced by passage through this component can be made equal and opposite to Δ , hence bringing about "restored" plane polarized light.

reflection and subsequent passage through Q yield plane polarized light. With this arrangement, the change in position of the polarizer from its original setting at 45° to the plane of incidence gives $\tan \psi$, and the rotation of the analyzer yields the phase difference Δ .

In the discussion so far, it has been tacitly assumed that all the settings can be made satisfactorily, i.e., that components can be rotated until restored plane polarized light has been achieved; however, in practice, some criterion is needed to indicate that these settings have in fact been realized. In the examples quoted, the correct settings have only been reached when the restored plane polarized light is completely extinguished by use of the analyzer. If the compensation is not complete, some residual light will be passed through the analyzer. When a photoelectric detection system is being used, the setting is achieved by successive adjustment of compensator and analyzer (in the first two methods) or polarizer and analyzer if the third system is used (Fig. 5), until the minimum intensity of light is trans-

mitted. In this condition, the various optical components are in the required settings. The same procedure can be used if visual methods of analysis are being employed, but the sensitivity of the system will be of a low order, as the eye cannot discern intensity changes at very low intensity levels. To allow the maximum sensitivity of the eye to be used, which varies from one observer to another, half-shade systems are employed which enable settings to be made at moderately high intensity levels.²⁴ These will not be described here, but it can be noted that half-shade devices are available which balance only when plane polarized light is being passed through the element. One such device is known as the Tronstad ellipticity half-shade²⁵ and another as the Nackamura bi-plate, both of which can be used to indicate when a compensator or polarizer setting has been achieved which yields restored plane polarized light. Once this has been accomplished, the half-shade can be moved out of the field of view so that the plane of the polarized light can be located using the analyzer. The analyzer may also be fitted with a half-shade device to improve the accuracy of this final measurement. It is usual to focus the telescope directly upon the half-shades in order to achieve the best null point, i.e., matching of intensities in the two halves of the field of view.

Quarter-wave plates are usually made for use with light of the wavelength of the mercury green line ($\lambda = 5461 \text{ \AA}$), because the eye is usually most sensitive to changes to green light, and such components are therefore extensively used in visual recording instruments. They are usually constructed of mica or quartz, and by appropriate choice of the thickness d , the phase retardation can be set for any wavelength, this retardation being given for a plate cut from a uniaxial crystal by the value of $(2\pi/\lambda)(n_e - n_o)d$, where λ is the wavelength, and n_o and n_e are the refractive indices of the plate for ordinary and extraordinary rays respectively. With appropriate correction factors,²⁶⁻²⁸ quarter-wave plates made for one particular wavelength may be employed as compensators at other known wavelengths. An achromatic quarter-wave plate, based upon the Fresnel rhomb principle, has been described by King,²⁹ which promises to be a useful component for ellipsometric studies, as the variation in phase retardation can be kept to less than 0.4° over a range of wavelengths from the visible down to $3300 \text{ \AA}$.

The precision of ellipticity measurement, especially in rapidly changing conditions, can be greatly increased by the use of automatic techniques for determining both polarizer and analyzer settings (assuming the method of Fig. 5c is being used). Ord and Wills^{30,31} constructed an instrument in which both polarizer and analyzer are driven by stepping motors, and the orienta-

tions necessary to give minimum transmission through the analyzer are selected by a computer coupled to the output of a photomultiplier. Detection and storage of the null position, to a precision of 0.01° , can be achieved in 1 sec. In studying film growth during corrosion reactions, the computer can be programmed to plot the null positions on an X - Y recorder and to store all the experimental data for later printing, punching on cards, or replotting for comparison with theoretical curves.

Precision of measurement using photoelectric recording can be improved by employing modulated response systems.³²⁻³⁴ A component, either the polarizer or the analyzer, is rotated about the null position to produce varying signals. Instead of moving actual components physically as in the Ord and Wills instrument, the movement of the plane of polarization is effected by means of a Faraday cell.³⁵ This is a device which makes use of the rotation in plane of polarization of light produced by certain substances in the presence of a magnetic field. These materials, which include some glasses, are those having a high Verdet constant. By using a solenoid wound around the core of such a material to produce the required magnetic field, rotations of a few degrees can be obtained with considerable precision. By using a Faraday modulator, the accurate setting of the polarizer or analyzer for a null response can be determined electrically. In the absence of any other component, however, it is still necessary to drive one of the components by hand, or some kind of servo mechanism, in order to reach the desired point of balance. To avoid the necessity of this time-consuming operation, use can be made of an ADP-type of compensator. In certain crystals, the phase retardation between ordinary and extraordinary rays can be varied by means of an electric field applied across the material—the Pockels effect. Materials showing this high electrooptical response include ammonium dihydrogen phosphate (ADP), potassium dihydrogen phosphate (KDP), and a range of phosphates and arsenates.³⁶ Using such components, it is possible to make large phase retardation changes, and when they are included in a Faraday-modulated recording system, it is possible to completely automate measurements on elliptically polarized light using the compensator/null method.³⁷⁻³⁹

These developments in ellipsometry measurement have been discussed by Winterbottom³⁵ while the present level of sophistication is typified by the ellipsometer described by Layer,⁴⁰ who has reached a precision of measurement of 0.01° in ~ 0.1 msec.

It can be seen that compensator methods of measurement, depending upon the type of instrumentation employed (i.e., manual or automatic), can reach a precision of measurement varying from $\sim 1^\circ$ to 0.01° , in times

varying from 1 min using a visual measuring system to fractions of milliseconds for automatic techniques. Usually, only relative changes in polarization are important and the instrumental methods described provide all the necessary information. In order to determine accurate absolute values of reflected elliptically polarized light, however, it is necessary to eliminate various errors in the system. For example, for the wavelength in use, the quarter-wave plate may not provide a retardation of exactly 90° , or windows placed between the specimen and the optical components, necessary in *in situ* studies of corrosion reactions, may possess birefringence. Errors in quarter-wave-plate systems have been discussed by Holmes and Feucht⁴¹ and McCrackin.⁴² Many of the errors arising in components and in alignment of the system can be taken into account in the method of analysis employed. There are, for example, four positions of the polarizer, four positions of the quarter-wave plate, and two of the analyzer that will allow a null position to be obtained, making a total of 32 possible combinations of setting for P and A which allow the determination of $\tan \psi$ and Δ . By taking all such measurements, many of the errors in a system can be detected and corrected. McCrackin has developed a computer program that not only computes film thickness and optical constants—referred to later—but also determines any instrument errors and makes appropriate corrections. The correction factors include inexactness of the phase retardation of the quarter-wave plate, tilt in the mounting of the quarter-wave plate, and any variation of the specimen from the vertical. In order to apply such corrections, measurements are necessary at some of the 32 possible combinations leading to a null reading, which are referred to as zones. Such multiple measurements are possible on specimen surfaces in film-free or stable-film condition, but usually it is only possible to take measurements at one of the 32 settings when a corrosion reaction is being monitored and the film thickness is continuously varying.

Intensity Methods

Since the intensity of a light beam is given by the square of its amplitude, measurement of the intensity of an elliptically polarized beam at various azimuths will define the shape of the ellipse, and if comparison is made with the intensity of the incident light, the size, as well as the shape, will be determined. Such intensity levels can be measured by passing the elliptically polarized light through a rotating polarizer into a photoelectric detector. Measurement of the intensity in the p and s directions will give $\tan \psi = (I^p/I^s)^{1/2}$, while the ratio of the minor to major axes of the ellipse

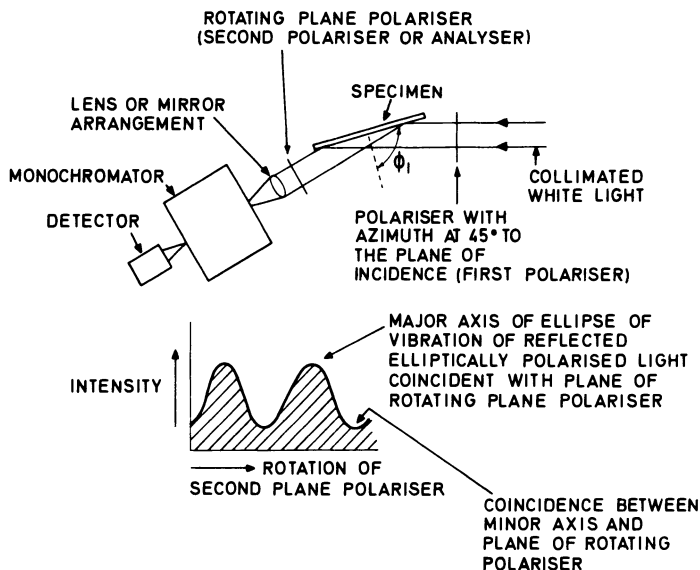


Fig. 7. Arrangement for measuring reflected elliptically polarized light using an intensity method. Applicable for use at different wavelengths if white light source and monochromator employed.

will be given by

$$\tan \beta = (I_{\min}/I_{\max})^{1/2}$$

To ascertain the phase retardation Δ from this data, it is necessary to measure the orientation of ellipse, and defining this as the angle η between the major axis of the ellipse and the normal to the plane of incidence, i.e., the s direction, Δ is given by Eq. (4).

A more general relationship between the intensity and $\tan \psi$ and Δ is given by

$$I = \cos^2(\beta' + \psi) + \sin(2\beta') \sin(2\psi) \cos^2(\Delta/2) \quad (13)$$

where β' is defined as the angle between the plane of polarization of the rotating analyzer and the plane of incidence. Thus, $\tan \psi$ and Δ can be determined by taking intensity measurements at two or more well-defined azimuths of the analyzer.

An experimental arrangement suitable for carrying out intensity measurements is shown in Fig. 7. Collimated light is plane polarized, usually at an azimuth of 45° to the plane of incidence, before illuminating the sample. After reflection, the light passes through a second rotating polarizer (the

analyzer) and the intensity of light emerging is detected by a photocell or photomultiplier. It is usual to use a modulated beam of light to increase the signal-to-noise ratio of the detector. If a white light source is employed, then a monochromator may be interposed after the rotating analyzer so that measurements at different wavelength can be made. The technique is equally applicable to infrared and ultraviolet studies provided that suitable

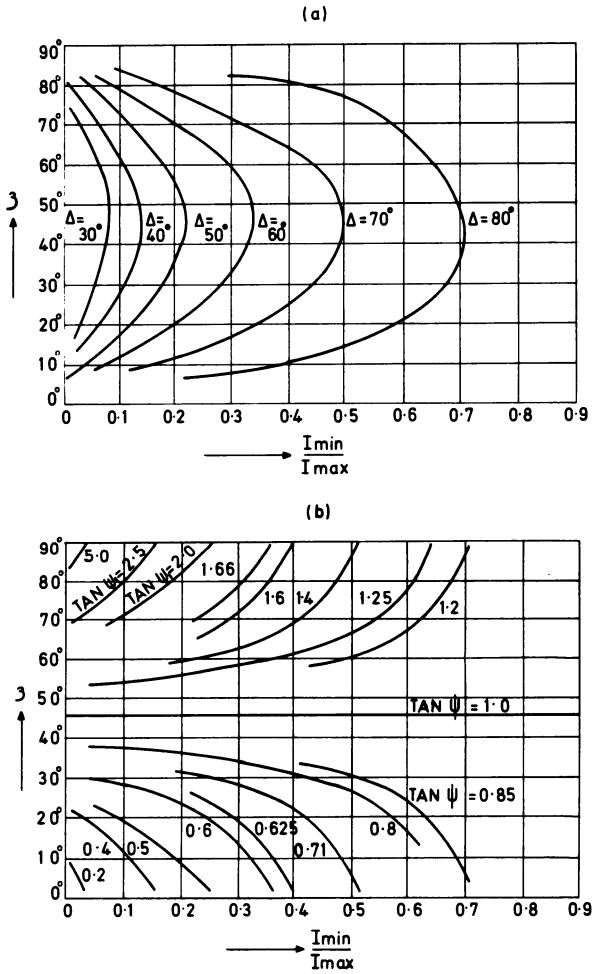


Fig. 8. Relationship between elliptically polarized light expressed as $\tan \psi e^{i\Delta}$ and the shape and orientation of the ellipse of vibration defined by η and $I_{\min}/I_{\max}$, i.e., computation of Eqs. (4).

light sources and detectors are used, and that the polarizing components are suitably transparent to the wavelengths being employed.

The interrelationship between compensation and intensity methods can be judged from the graphs given in Fig. 8, which represent Eq. (4), the relationship between the orientation of the ellipse of vibration and the ratio $I_{\min}/I_{\max}$ in terms of $\tan \psi$ and Δ . It can be seen that it is possible by intensity methods to measure Δ with good accuracy between $+45^\circ$ and 90° for all $I_{\min}/I_{\max}$ and in other ranges if $I_{\min}/I_{\max}$ is between 0.15 and 1.0, i.e., where the ellipse is 'fat.' For the range $\Delta = 0-45^\circ$, the ellipses become very thin and more difficult to measure with accuracy, especially in the limiting situation where $I_{\min}/I_{\max}$ goes to zero, i.e., the light is plane polarized. In contrast, the compensation method retains full sensitivity except for the limiting situation where $\tan \psi \rightarrow 0$. It follows that, although the regions of maximum sensitivity for the measurement of elliptically polarized light are rather different for the two techniques, a generally higher overall level of sensitivity is inherent in the compensator or null method. To achieve an accuracy in Δ of $+0.01^\circ$ by the intensity method requires the measurement of both η and $I_{\min}/I_{\max}$ to one part in 10^4 , and although this can be achieved, more precise methods are required than the one of measuring the variables directly from the recorder trace provided by a photomultiplier.

COMPUTATIONAL TECHNIQUES

Earlier sections have been concerned with the mathematical relationships between macro parameters, such as film optical properties and film thickness, and the properties of the reflected elliptically polarized light, and also with the accuracy of experimental measurement of the elliptically polarized light in terms of $\tan \psi$ and Δ . It now remains to describe how experimentally determined values of these parameters are translated into film thickness values. As in the interpretation of electrical methods of studying surface films, e.g., variation of impedance with frequency, where an equivalent electrical circuit is assumed to exist, the results are interpreted in terms of a model which is believed to represent closely the actual situation being studied. The usual model is that of a single, optically homogeneous, parallel-sided film which, in the majority of situations, is sufficiently close to the experimental case to yield sensible results. In some experimental situations, it may be necessary to refine the model, as in the case of two optically different, homogeneous, parallel-sided films in contact. In other

systems, the composition of the film varies continuously from film/environment interface to metal/film interface, and is best interpreted in terms of a series of parallel-sided films of successively varying optical constants. These various situations will be discussed later, but as the primary consideration in this section is of computational techniques, the simplest case of the single, optically homogeneous, parallel-sided layer is considered.

It will be assumed that the optical constants of the environment n_1 and of the substrate $n_3 - ik_3$ are known. In practice, the environment is usually vacuum ($n_1 = 1.0$) or a some gaseous or liquid medium. In the case of liquids, the refractive index can usually be found by reference to handbooks of physical constants, but it can be readily measured using a refractometer. Care needs to be exercised, however, if the environment is absorbing, or becomes absorbing due to the presence of reaction products. The latter situation may often be taken into account by assuming that the absorbing species exists in a finite layer in which the absorption level can be ascertained or assumed. A simpler method is to choose a wavelength at which the liquid is nonabsorbing.

The determination of $n_3 - ik_3$ is conditioned by the type of experiment and the accuracy required. A large body of literature on metal optical constants exists, but it is not always certain to what surface structural condition the data related. Wide differences in structure exist between "perfect" and actual conditions. For many purposes, it is realistic to make measurements of the thickness of surface films forming on metals or alloys in an as-rolled or some other "practical" condition, e.g., as abraded or mechanically polished, and in these instances, it is necessary to make measurements of the corresponding $n_3 - ik_3$ value.

For more fundamental studies, it is good practice to achieve as near a perfect surface as possible, where the structure in the surface layers is as close as possible to that of the material in depth, apart from inherent changes associated with the interfacial free energy. Ellipsometry is ultimately sensitive enough to detect very small coverages of even the first monolayer of surface reaction product to form, and the experimental problems arise, not only in achieving a suitable initial condition of the surface, but also in bringing to bear techniques capable of confirming that such a condition has been achieved by the use of such methods as low-energy electron diffraction techniques and Auger-electron spectroscopy.

Conveniently, the characteristics of the elliptically polarized light reflected from a metal surface follow well-defined trends, and therefore the approach toward cleaner and cleaner surfaces is readily observed. Reference to Fig. 3(a) shows that the angle Δ increases with decreasing

film thickness, and if experimentally determined $\tan \psi$ and Δ results are plotted for successively cleaner surfaces, then a characteristic $\bar{Z}$ trace will be produced.

In corrosion work, it is worth bearing in mind that if a sample is prepared with a "technical" as opposed to a "perfect" surface, and if corrosion takes place, consuming part of the technical surface (e.g., etching), then a change in the substrate optical constants will occur in addition to any film growth.

Assuming that n_1 and $n_3 - ik_3$ are known, and constant, the objective in the interpretation of the results is the solution of the basic ellipsometric equation (9) for the film thickness d , and also determination of $n_2 - ik_2$. The relationship may be more simply written as

$$\tan \psi \text{ and } \Delta \text{ are functions of } n_1, n_2 - ik_2, n_3 - ik_3, d, \lambda, \text{ and } \phi$$

but by prior determination of $n_1, n_3 - ik_3, \lambda$, and ϕ , the "knowns" and "unknowns" may be written

$$\tan \psi \text{ and } \Delta \text{ (for a particular } \lambda \text{ and } \phi) \text{ are functions of } n_2, k_2, d$$

i.e., two measured quantities and three unknowns.

If we take the special case of a transparent film, where k_2 is zero, the relationship becomes a quadratic of the form⁴¹

$$C_1(e^{-2i\delta})^2 + C_2(e^{-2i\delta}) + C_3 = 0 \quad (14)$$

where C_1, C_2 , and C_3 are complex numbers dependent upon the refractive indices, angle of incidence, and measured $\tan \psi$ and Δ values. The correct value of δ , computed by the relationship

$$-2i\delta = -4\pi n_2(\cos \phi_2) d/\lambda \quad (15)$$

is that which consists of a real value only and does not contain an imaginary component. In practice, experimental errors will result in both computed thicknesses being complex. The thickness including the smallest imaginary component is selected as the correct solution, the real part being taken as the thickness and the magnitude of the imaginary part is arbitrarily taken as a measure of error. Such calculations have been programmed^{42,43} in Fortran for IBM 704, 7090, and 7094 computers.

While this direct method of calculation can be used for transparent films of known refractive index, and can be extended to those of unknown refractive index if measurements are made at more than one level of thick-

ness, it is not acceptable in the more usual situation of an absorbing film on an absorbing metal substrate. To resolve this situation, fresh experimental data are required. Ideally, an independent measure of the film refractive index is all that is necessary, varying the refractive index of the environment, altering the angle of incidence, and so on. In many instances, an interpretation can be obtained graphically. Whatever the particular approach adopted, graphical methods are useful, not only for the general situation of absorbing films on absorbing substrates, but for transparent films on absorbing substrates, and a brief description of the situations in which these methods are useful is appropriate at this point. The purpose here is to match the range of experimentally determined $\tan \psi$ and Δ curves with sets of curves computed using Eq. (9). In certain optical situations, the form of curve is very specific and matching of experimental and theoretically derived curves is unambiguous and readily done—frequent reference is made to curve fitting in the literature. In other situations, there is ambiguity, and the situation is made additionally complicated by, for example, nonuniformity of film thickness, or optical anisotropy in the film.

Graphical Methods

The graphical methods described in this chapter are based upon plots of the type shown in Fig. 3(a). Mention has already been made of the fact that the locus of vectors of reflected elliptically polarized light starts from a position on the polar plot corresponding to the clean metal surface and then describes a spiral, the shape being specific to set values of n_1 , n_2 , $n_3 - ik_3$, and ϕ (Fig. 9). The curves may spiral either clockwise or anticlockwise, the latter being associated with substrates for which the start point falls most distant from the origin and additionally there is a small refractive index difference between film and environment. With absorbing films, the curves form a spiral which eventually decreases to a limiting value corresponding to reflection wholly from the film (see Fig. 10).

To illustrate the care that should be exercised in curve matching by determining a set of theoretically derived ellipticity values using a set of trial optical constants in Eq. (9), which are expected to correspond to the experimentally determined ones, reference is made to Fig. 11, in which a series of curves are plotted for absorbing films of varying refractive index and absorption coefficient. The difference in shape of the curves for a wide range of refractive index ($n_2 = 2.0 \rightarrow 3.0$) is small for a given film absorption coefficient, although the latter can be estimated irrespective of refractive

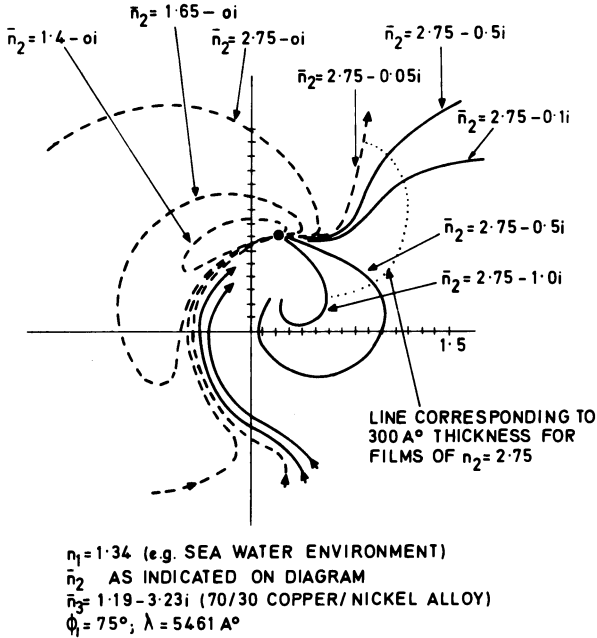


Fig. 9. Locus of vectors corresponding to elliptically polarized light reflected from a metallic surface covered with film of different optical properties.

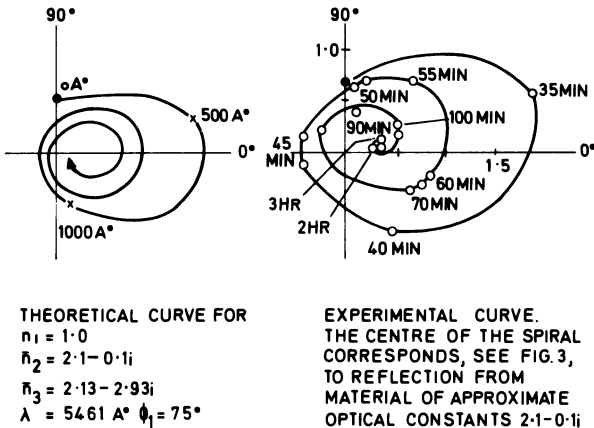


Fig. 10. Ellipsometry data relating to the formation of thick zirconium dioxide films on commercial-purity zirconium exposed to steam at 400°C and 1500 psi and then quenched in water after the stated times. Samples washed in water, then acetone, then dried. Readings taken on samples exposed to air.

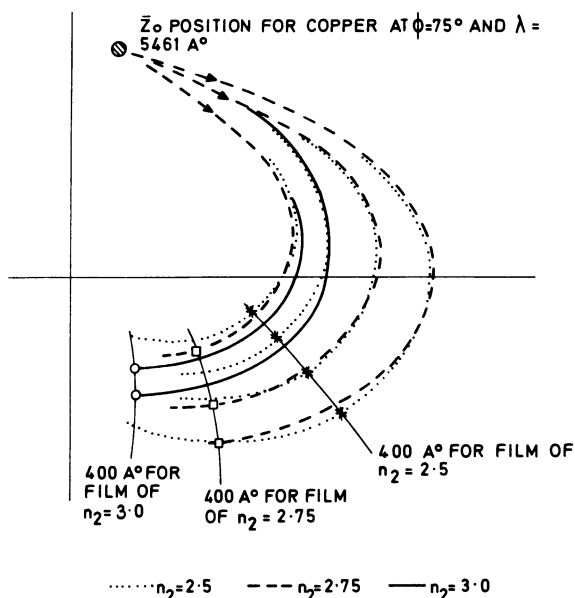


Fig. 11. Similarity in shape of locus of vectors corresponding to elliptically polarized light reflected from copper assumed covered with film of differing refractive index and adsorption coefficient.

index level. The situation in practical corrosion problems is made even more uncertain by films which often depart widely from the single, homogeneous, parallel-sided layer model, a few examples being illustrated in Fig. 12.

However, this does not mean that curve fitting to ascertain at least an approximate refractive index level is not possible, but a series of computations for film growth on the substrate being studied, and for a particular environment, will soon show whether any ambiguity is likely to arise. Assuming that matching can be achieved for a specific set of curves produced for a specific set of experimental parameters, then the film thickness corresponding to the experimentally derived $\tan \psi$ and Δ values can be obtained by reference to a theoretically derived curve. The precision of interpretation will depend upon many factors, but estimates to a few angstroms in several hundreds or thousands of angstroms are possible. In a specific example, that of cuprous oxide on copper, the film refractive index of which is high (2.70–2.75) (oxides usually having high dielectric constants and therefore refractive indices), a change of 5 Å at the 200–300 Å level will result in changes of Δ of 5°. Assuming that Δ can be measured

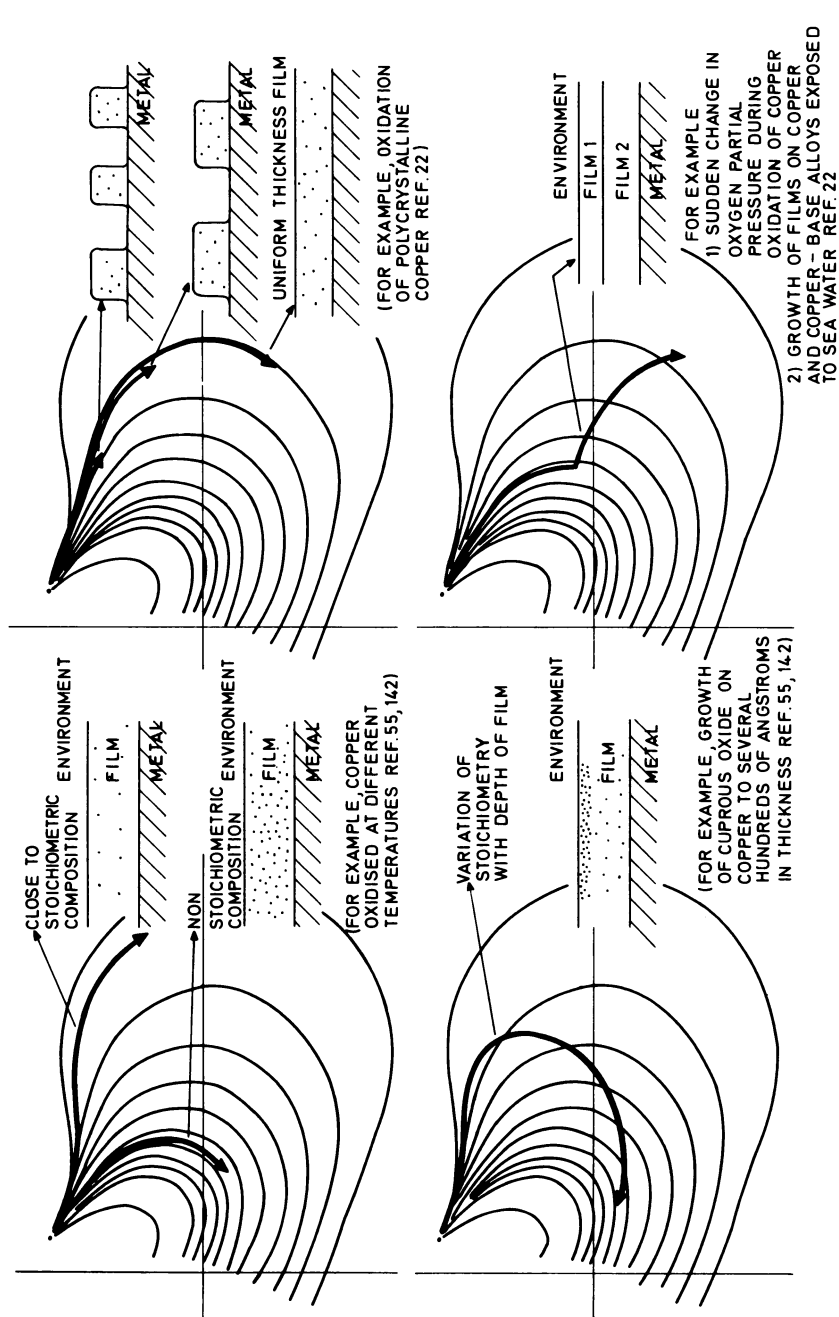


Fig. 12. Various shapes of the locus of vectors corresponding to reflected elliptically polarized light from surfaces covered with different types of film. Based upon copper examined at $\phi_1 = 75^\circ$ and $\lambda = 5461 \text{ \AA}$, but of general relevance.

to $\pm 0.01^\circ$, this leads to an apparent precision of measurement corresponding to $\pm 0.05 \text{ \AA}$. This may be significant with respect to very thin surface films, but when dealing with thicker corrosion films (about several hundred angstroms), many factors contribute to the change in ellipticity, and such high measurement precision is of doubtful value. With decreasing difference in refractive index between film and environment, the precision of interpretation decreases, and in the situation where no difference exists, the ellipsometric method is invalid. If the difference between n_1 and n_2 becomes less than about 0.5, it may be necessary to obtain appreciably greater precision of measurement than can be achieved, for example, by using visual methods of recording. One method of increasing sensitivity in such a case is to reflect the light between parallel plates of the substrate under study, such that the reflected elliptically polarized light is no longer represented by $(\tan \psi)e^{-i\Delta}$, but by $(\tan \psi)^n e^{-ni\Delta}$ where n is the number of reflections, a method used by Stromberg *et al.*⁴⁶ and others.^{47,48} On first consideration, this would seem a simple way of improving accuracy by as many times as the light can conveniently be made to reflect, but certain limitations are inherent in the method. For example, $(\tan \psi)^n$ becomes very small, due to the almost complete suppression of reflection in the plane of polarization r^p , which eventually leads to a "thin" ellipse of reflected polarized light, which is difficult to measure. Also, the absolute reflectivity of light in the s direction falls off rapidly with increasing n , decreasing the final intensity and producing a detection problem. Multiple reflections where $n = 2 \rightarrow 5$ can usefully be employed in ellipsometry, however, and for reflectivity measurement alone, especially near normal incidence, many more reflections may be used.

The implication of the preceding paragraphs is that graphical methods may be used directly to interpret experimentally determined $\tan \psi$ and Δ values, but with ambiguity in certain situations. An analysis of the graphical method shows that the sensitivity of the method in the detection of films is of a high order, especially for oxide films, and that this sensitivity is decreased as n_1 and n_2 become closer in value, requiring improved accuracy, and that ultimately the ellipsometric method becomes inappropriate as the two values become identical. At this stage, it is logical to extend the discussion to methods of interpretation usable where graphical methods alone are inadequate. Before proceeding with this stage, however, a short account will be given of the interrelationship between ellipsometry and the measurement of reflectivity, as it will assist in describing, even in those instances where curve fitting is applicable, the various changes in reflectivity which are encountered in practice.

REFLECTIVITY MEASUREMENTS

By definition, the reflectivity of a surface at oblique angles of incidence is given by $R = |r^p|^2 + |r^s|^2$, and will therefore vary with film thickness. This, indeed, forms the basis of spectrophotometric methods of studying films, as first described by Constable^{49,50} and later put into wide use by Young.⁵¹ Examples of the variation of R with the thickness of a transparent film, for $\phi = 0$ and 75° , are illustrated in Fig. 13. It can be seen that the variation of reflectivity with increasing thickness is less regular, and also shows greater overall changes in reflectivity, when using oblique as opposed to normal incidence. Also, the nodes in reflectivity, which are the parameters required in spectrophotometric techniques, occur at relatively large film thickness increments, so that the sensitivity of the method is appreciably lower than obtained by ellipsometry. These nodes are caused by interference minima in the p and s planes. The first occurs in the s plane, and as this is the component least attenuated in amplitude on reflection, interference removes the greatest component of intensity in the reflected light. This minimum in reflected light occurs as $\tan \psi$ tends to infinity, which is inherently a difficult condition to measure, and this fact makes the measurement problem even more difficult. A similar decrease in reflectivity occurs as r^p tends to zero by interference, $\tan \psi$ tending to zero at the same time. For absorbing films, this cyclic behavior in reflectivity still occurs, but at a decreased overall level of reflectivity.

It is relevant at this juncture to note that a change in reflectivity is itself a useful indicator of change in thickness, and may produce a sensitivity of thickness determination comparable to that of ellipsometric observation.^{47,48} Calculation of the individual reflectivity changes occurring in the p and s directions shows that particular advantage may occur from confining measurement to the r^p component, at least for single reflection or a few multiple reflections between parallel plates of the substrate. Alternatively, the smaller incremental changes in the r^s component can be studied using many (10, 20, or more) multiple reflections between parallel plates. In these circumstances, the multiple reflection process so attenuates the r^p component that the emergent light is essentially of intensity $|r^s|^{2n}$ and plane polarized, and no polarizing component is necessary in the system to select the r^s component for intensity measurement. There are many examples of electreflectance studies in the literature, especially as applied to thin-film situations.⁵²⁻⁵⁴

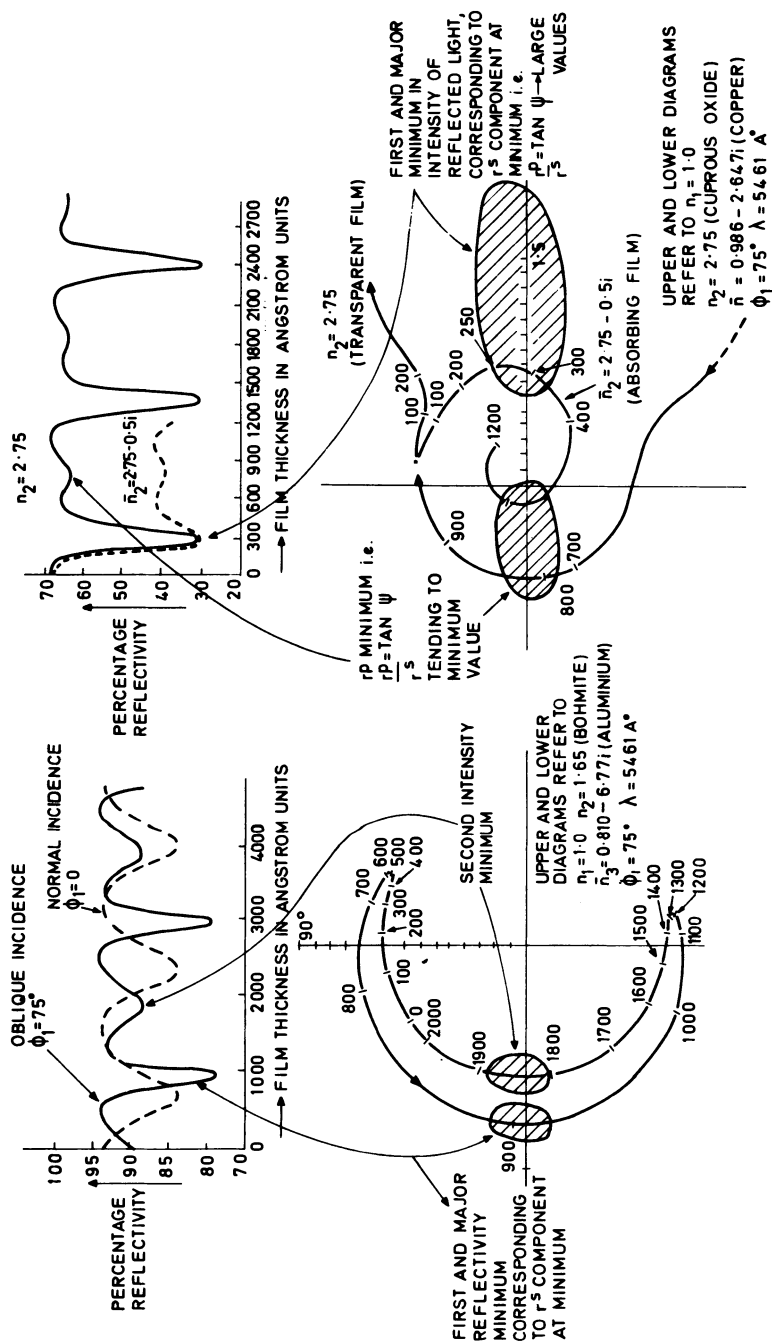


Fig. 13. Comparison of reflectivity and ellipsometry data for growth of film on highly and moderately reflecting metal substrates.

DETERMINATION OF FILM OPTICAL PROPERTIES

Returning to the problem of interpretation where graphical methods of solution alone are impracticable, the most obvious method of clarifying the situation is by a determination of film refractive index. For the thicker films, where electron diffraction is applicable ($> \sim 50 \text{ \AA}$), and the film is crystalline, the composition of the layer can be identified. If this corresponds to a well-defined single compound, then it is likely that the refractive index of the bulk material will have been determined and be available in the literature. A considerable volume of such data on mineralogical materials is in existence, and a range of values for specific, commonly encountered oxides is listed in Table 1. Such values can be used to calculate the optical changes produced by thin films of the same material, except in certain situations where the lattice can be appreciably distorted. This can occur with very thin films undergoing epitaxial growth, or with thicker films showing wide variations in stoichiometry. In certain cases, correspondence between thin-film and bulk refractive index values can be assumed, for example, the refractive index of cuprous oxide a few hundred angstroms thick has been found comparable to that measured on bulk material.⁵⁵ On the assumption that the refractive index changes little between thin and thick films, measurements can be made on absorbing films grown to a level at which reflection occurs wholly from film material (see Fig. 10), but the method may be rendered additionally difficult by virtue of the low level of reflectivity from dielectrics and the usually uneven environment/film interface, which does not reflect in a specular manner. In the case of films formed in liquid, and in particular, aqueous environments, the presence of bound water inside the film, as with the hydrated form of corrosion films, may give rise to very large changes in bulk refractive index.

Various additional methods that have been devised to determine the refractive index of thin films in order to assist in the interpretation of ellipsometric data will now be discussed.

The Liquid Immersion Method

This method is based upon the principle that when the refractive index of the environment equals that of the film, the ellipticity of the resultant reflected beam will be independent of the film thickness.

In this technique, a range of filmed samples is used in a range of liquid media of varying refractive index until a medium is found in which the ellipticity is constant. The method presupposes that the refractive index of the film remains constant with thickness and that the films are not affected

Table 1. Optical Constants of a Range of Metals and Films Encountered in Corrosion Situations¹

Metal		Film	
Iron	2.98 — 3.83 <i>i</i>	Fe ₂ O ₃	3.46 — 1.07 <i>i</i>
	3.06 — 3.67 <i>i</i>	Fe ₃ O ₄ ⁽³⁾	2.58 — 0.28 <i>i</i>
	3.50 — 3.66 <i>i</i>		2.5 — 0.3 <i>i</i>
	3.35 — 3.84 <i>i</i>		2.6 — 0.4 <i>i</i> (<i>k</i> ₂ = 0.2–0.7) ⁽²⁾
Aluminum	0.76 — 5.49 <i>i</i>	Al ₂ O ₃ ⁽⁴⁾	1.61 — 0 <i>i</i>
	0.81 — 5.47 <i>i</i>		1.68 — 0 <i>i</i>
	1.0 — 6.7 <i>i</i>		(<i>k</i> ₂ = 0–0.5) ⁽²⁾
	0.81 — 6.77 <i>i</i>		
Copper	0.99 — 2.62 <i>i</i>	Cu ₂ O	(2.35, 2.5) — (0.14–0.15) <i>i</i>
	1.00 — 2.40 <i>i</i>		2.70 — 0 <i>i</i>
	1.101 — 2.165 <i>i</i>		2.80 — 0.165 <i>i</i> (<i>k</i> ₂ = 0–1.5) ⁽²⁾
Titanium	2.53 — 3.38 <i>i</i>	TiO ₂ (Rutile)	2.76 — 0 <i>i</i>
	2.41 — 3.24 <i>i</i>		2.40 — 0.17 <i>i</i> (<i>k</i> ₂ = 0–0.5) ⁽²⁾
Zirconium	—	ZrO ₂	2.1 — (0.05–0.4) <i>i</i> (<i>k</i> ₂ = 0.05–0.4) ⁽²⁾
Uranium	1.50 — 1.87 <i>i</i>	UO ₂	1.95 — 0.01 <i>i</i> ⁽⁵⁾
	2.11 — 3.4 <i>i</i>		2.2 — (0–0.3) <i>i</i> ⁽⁶⁾
			2.25 ⁽⁷⁾ (<i>k</i> ₂ = 0–1.0) ⁽²⁾
Beryllium	2.72 — 2.33 <i>i</i>	BeO	1.8 — (0–0.2) <i>i</i>
	2.66 — 2.36 <i>i</i>		(<i>k</i> ₂ = 0–0.2) ⁽²⁾
Silver ⁽⁸⁾	0.069 — 3.429 <i>i</i>	Silver sulfide	3.04 — (0.42–0.53) <i>i</i>
Nickel	1.79 — 1.83 <i>i</i>	NiO _x , <i>x</i> ≥ 1	3.5 — (various) <i>i</i>
Tantalum	2.05 — 2.3 <i>i</i>	Ta ₂ O ₅	(2.22–2.25) — 0 <i>i</i>
	3.30 — 2.3 <i>i</i>		anodization
Niobium	3.60 — 3.60 <i>i</i>	Nb ₂ O ₅	2.37 — 0 <i>i</i> ⁽⁷⁾
Silicon	4.05 — 0.028 <i>i</i>	SiO ₂	1.45 — 0 <i>i</i> ⁽⁹⁾
			1.47 — 0 <i>i</i> ⁽¹⁰⁾
			1.362 — 0 <i>i</i> ⁽⁷⁾

¹ Data refer to optical constants employed in ellipsometric examinations, the wavelength of light corresponding to mercury green ($\lambda = 5461 \text{ \AA}$) unless otherwise stated.

² Indicates approximate range of absorption coefficient encountered in corrosion films formed under a range of environmental conditions.

³ Passive films.

⁴ See also Table 2.

⁵ Sodium light.

⁶ Anodization.

⁷ Air oxidation.

⁸ All data at 5500 $\text{\AA}$.

⁹ Gaseous oxidation.

¹⁰ Steam.

Table 2. Refractive Index of Anodic Films Formed on Aluminum¹

Electrolyte	Refractive index
Bisulfate melts	1.748
Ammonium borate, 3% (15 hr)	1.723
Ammonium borate, 3%	1.700
Oxalic acid	1.669
Oxalic (one year in atmosphere)	1.658
Chromic acid	1.650
Sulfo-salicylic acid (+H ₂ SO ₄)	1.636
Oxalic acid (hard coating)	1.634
Phosphoric acid	1.628
Sulfuric acid	1.619
Boric acid + formamide	1.591
Boric acid + H ₂ SO ₄	1.573

¹ From Tajima and Mori.¹⁵⁸ Data refer to sodium light, and were obtained on stripped films using the Becké line method.

in any way by the immersion media. This technique has been used successfully on aluminum filmed by anodizing, natural corrosion, and thermal oxidation.^{56,57} The results of other work on aluminum filmed in a range of environments are listed in Table 2 to illustrate the wide differences in refractive index produced by different forming conditions. This is an extreme case where the porous films occlude a high water and anion content but, nevertheless, similar effects are not unknown in corrosion situations. The effect of estimating film thickness using the high refractive index appropriate to dehydrated forms of oxide will always be to give a thickness figure which is too low.

Becké Test

The range of transparent, or translucent, immersion media is limited in refractive index to values of $n < 1.8$, and thus rules out the method for many of the oxides of the common structural materials, which have n_2 in excess of 2.0. The range of measurement can be considerably extended if the film can be removed from the surface and subjected to the standard petrological method of assessing refractive index known as the Becké method.⁵⁸ In this technique, the film, embedded in a medium of known refractive index, is examined by transmission microscopy. A bright line is seen around the film and the movement produced on racking the

microscope up and down is measured. The line moves toward the medium of higher refractive index as the microscope is racked upward, out of focus. Where a sufficient range of media is available, an accuracy of measurement of the difference in refractive index between one medium and another of within a second or even a third decimal place can be obtained. The method has the advantage, that, by using sulfur/selenium mixtures, levels of refractive index between 2.0 to 3.0 may be ascertained. Since such media need to be cast around the film, there is a possibility that the properties of the film may be altered (as they may be by the initial stripping), and in practice, the Becké line is difficult to observe on films only a few hundred angstroms in thickness.

Interferometry

The successful stripping of a film from a specimen allows the possibility of a single film thickness measurement by interferometry, where the film can be mounted on a glass slide, silvered, and used as one plate in a multiple-beam interferometer. Although the accuracy of this method is claimed, on glass surfaces, to be 1/50 of a fringe (one fringe = $\lambda/2$), e.g., $\sim 5 \text{ \AA}$ at $5461 \text{ \AA}$,⁵⁹ the inherent roughness of the surface of many oxides, such as that which occurs due to differential rates of oxidation on the different crystal orientations of polycrystalline materials, often prevents such accuracy from being achieved, and a precision of even an order of magnitude from the theoretical is difficult to obtain. Nevertheless, the method has been successfully used to measure the refractive index of oxide films.

The Brewster Angle Method

For a transparent film, the reflectivity of the p component of light falls to zero at the Brewster angle ϕ , and Abeles⁶¹ has pointed out that at this angle the reflectivity from both filmed and unfilmed substrates is constant. Experimentally, therefore, it is necessary to determine the angle of incidence at which the reflectivity of p light falls to a minimum for both an unfilmed surface and surfaces covered with different film thicknesses. With an accuracy of reflectance measurements of $\pm 0.5\%$, and values of n_3 and k_3 in the region of 2.0, the refractive index of a nonabsorbing film, can be estimated to a few percent if n_2 is about 2.0. Heavens and Kelly⁶² have put forward evidence to show that tantalum oxide formed by anodizing evaporated deposits in $N/10$ sodium sulfate produces a nonuniform film in which the refractive index varies linearly with thickness from 1.95 to 2.15.

Calculation

The optical properties of solids, briefly mentioned in an earlier section, have been widely considered theoretically in terms of the classical theory of optics based upon Maxwell's equations, and subsequently in terms of quantum theory, and reviews of the present state of knowledge can be found in the work of Seitz¹⁴ and, more recently, of other authors,^{11,63,64} as well as in a report of a conference on the optical properties and electronic structure of metals and alloys.¹² Lorentz's classical theory treatment¹⁴ leads to the equation

$$(\bar{n}^2 - 1)/(\bar{n}^2 + 2) = \frac{4}{3}\pi P\alpha \quad (16)$$

where $\bar{n}$ is the real refractive index, P the number of oscillators per unit volume, and α is the polarizability of such oscillators. The number of oscillators P will be in the region of 10^{22} per cm^3 and will be related to molecular weight and density. The important problem in the calculation is in determining the polarizability of the oscillators. Bockris *et al.*⁶⁵ have used the formulas developed for diatomic molecules to calculate the refractive index of $\text{NiO}_{1.5}$ – $\text{NiO}_{1.7}$, and have shown that it varies from 3.3 to 3.7.

MEASUREMENTS ON FILMS LESS THAN 50 Å IN THICKNESS

As shown in the preceding section, ellipsometric methods are applicable for the detection of films down to a few angstroms in thickness. An obvious application of the method has therefore been in the study of the first stages of reactions between metals and their environment, e.g., the adsorption of a first monolayer onto a clean metal from a gaseous or liquid environment. There are particular advantages, in corrosion, in the study of very thin films as produced in passivity, and by adsorbed inhibitors, for example, and these necessitate special attention to the problems of thin-film examination.

These problems are to a certain extent specific to thin films as compared to other, more general, applications of the technique. For example, it is necessary to measure the reflected elliptically polarized light with a greater precision than in other circumstances; the measurement of film refractive index is less critical, but interpretation is usually made more difficult by surface roughness and optical anisotropy within the film.

The first consideration in such a case is the relevance of the basic ellipsometric equation (9) to the situation created by a film only a few

molecular layers in total thickness, or even less than one monolayer. There are at least two ways of checking the applicability of the theory, one being the practical one of comparing the data from ellipsometric observation with that obtained by other methods not subject to the same problems of interpretation, the other being theoretical, and based upon a different model in which the surface film is considered as discrete particles rather than a continuous homogeneous layer.

An early indication of the applicability of the method to thin films came from the work of Feacham and Tronstad in 1934, who measured the thickness and anisotropy of fatty acid films formed on mercury. Deryaguin and Zorin⁶⁷ studied adsorption and surface condensation of vapors near to saturation on to glass, including both polar and nonpolar liquids, and obtained a series of adsorption isotherms. More recently, Bartell and Betts⁶⁸ and Miller and Berger⁶⁹ observed close agreement between ellipsometric and radioactive tracer methods when assessing the monolayer adsorption of polar molecules on metal surfaces.

Smith⁷⁰ has extended this type of measurement to the simultaneous observation of elliptically reflected light, surface tension, and contact potential for molecules of known dimensions at and below monolayer coverage on mercury. An objective of this work was to ascertain whether changes in $\tan \psi$ and Δ were linearly proportional to coverage, or to the square root of coverage as proposed by Hall.⁷¹ Smith concluded that, for approximately isotropic molecules, the first-order Drude equation⁷ $\Delta = \bar{\Delta} - \alpha d$, where d is an arithmetic mean thickness, is accurately valid for coverages of between 0.05 and 1, and suggests that the square-root relationship may apply to films that form patches or islands with dimensions larger than the wavelength of the light used. There is, therefore, adequate experimental evidence to show that ellipsometric observation of the films yields meaningful results, and that the problems are those concerned with deciding the appropriate refractive index, the influence of optical anisotropy, etc.

The corresponding theoretical approach to reflection from very thin films has been considered by Strachan,⁷² who treated the case of reflection at a surface covered with a monomolecular film. This layer was considered as a "two-dimensional" assembly of scattering centers producing a surface distribution of oscillators. The resultant equations characterize reflection in terms of the scattering indices of the oscillators rather than of the refractive index used in the treatment of the process as a three-dimensional model, but the two sets are essentially similar. Sivukhim⁷³ has presented a similar treatment.

REFLECTION FROM ANISOTROPIC MEDIA

As remarked earlier, many metals and corrosion products are optically anisotropic, and this might be expected to decrease the very high level of sensitivity inherent in the method, and in a few extreme instances, this can in fact occur. The theoretical treatment of such situations has been considered by Mallemaun and Suhner⁷⁴ and Blodgett,⁷⁵ but the resulting equations are more cumbersome than Eq. (9) and difficult to correlate with experimental observation. Blodgett's studies of multiple films of barium stearate indicated that the refractive index varies with direction between that in the plane of the surface and that normal to this surface. More recently, Cathcart and Petersen⁷⁶ instanced an extreme example of anisotropy in the oxidation of copper. On single crystals, the thin cuprous oxide formed at moderately low temperatures was crystalline, highly oriented, and subject to large epitaxial stresses. By rotating the specimen in its own plane, variations of average film thickness of from 180 to 260 Å were apparent from computation using Eq. (9), when manifestly the film remained of constant thickness throughout the rotation. The anisotropy which gives rise to such errors is readily detectable by normal polarized light metallographic examination. Its effects can be considerably minimized by working with a randomly oriented microcrystalline substrate, in which case the corrosion product will likewise be randomly oriented. In these circumstances, the experimentally determined optical constants of substrate and film will refer to a mean value for the various crystallites. Examples relating to the variation of $\tan \psi$ and Δ with orientation of samples of anodized microcrystalline titanium have been published to indicate the magnitude of this effect, which clearly needs careful consideration before absolute film thicknesses and optical properties can be estimated. Errors due to this cause can in particular be expected in those situations where a marked anisotropy occurs in the crystallographic characteristics of either substrate or film. An example has been described by Franklin and Stirland,⁷⁷ who showed that the pore size and distribution in anodically formed alumina, which vary with orientation of the substrate crystal, can lead to optical anisotropy.

REFLECTION FROM FILMS OF NONUNIFORM THICKNESS

In many corrosion situations, especially when a polycrystalline structure is involved, the reaction rate is orientation-dependent, with the result that the film being measured is nonuniform in thickness over the area

illuminated by the light beam, which may vary from tens to hundreds of square millimeters. In the extreme case of films with submonolayer coverage, $\tan \psi$ and Δ are linearly related to coverage, at least for the case of random nucleation. For thicker films, the situation has been assessed by measurement of the thickness of evaporated films in the form of homogeneous planar deposits and islands of various dimensions,²² and, to a first order of approximation, the ellipsometrically determined film thickness represents, conveniently, the arithmetic mean of the thicknesses present. The situation may not always be so straightforward, however, as, for example, specific substrate orientations may lead to enhanced film growth as compared with others, but such a configuration falls into the rather specific case of a preferred crystallographic structure, and needs more care in interpretation.

Another possible film configuration is the formation of spherically shaped particles which, although having dimensions of several tens of angstroms, so that their crystallographic habit is readily detectable by electron diffraction, are undetectable by ellipsometry. Other irregular features, such as localized mounds of corrosion product, will remain undetected if they do not contribute to specular reflection. In well-advanced corrosion reactions such as these, the ellipsometric technique will only allow analysis of those areas still contributing to specular reflectivity, which may in fact be limited to those at a particular orientation. In such situations, measurements of absolute reflectivity between incident and reflected planes become meaningless, although the intensity method of estimating the shape, as opposed to the absolute size, of the reflected elliptically polarized light is still valid.

REFLECTION FROM SURFACES OF VARYING ROUGHNESS

The surfaces encountered in most corrosion situations will depart appreciably from the perfect planar surface assumed in theoretical models, the closest approach to theory probably occurring with evaporated deposits on glass or cleaved single-crystal surfaces, and with electropolishing, the latter at least giving some localized regions of atomic smoothness. The theoretical treatment of surface roughening has been considered by Fenstermaker and McCrackin,⁷⁸ Kruger,⁷⁹ and Berreman.⁸⁰ One procedure has been to consider various well-defined geometric models, examples being the square-ridge, triangular-ridge, and pyramid models, on the assumption that these extend over the whole surface being illuminated, the effective refractive index of the surface layer being calculated using the Maxwell-

Garnet relationship. This was derived originally to ascertain the effective optical constants of evaporated layers, which were assumed to consist of packed spheres with air spaces in between. If the volume fraction of spheres is written as q , the refractive index of each sphere as $\bar{n}$, and that of the spaces as unity, then the effective refractive index of the layer $\bar{n}_e$ is given by

$$(\bar{n}_e^2 - 1)/(\bar{n}_e^2 + 2) = q(\bar{n}^2 - 1)/(\bar{n}^2 + 2) \quad (18)$$

On this basis, the effective optical constants for different surface roughness configurations have been calculated and shown to lead to considerable error, the inference being that very smooth surfaces are necessary for all measurements of optical constants and that, in following a corrosion reaction where surface roughening might be occurring, the effective optical constants of the substrate will vary, in addition to any optical changes due to film growth. It is important, however, to stress at this stage that no experimental work has been reported on the magnitude of the errors introduced by such regular roughening of the surface under examination. Kruger,⁷⁹ in studying the optical changes on iron during anodic polarization, has reported Δ changes in potential regions corresponding to activation which are consistent with surface roughening. Small differences in apparent optical constants have been reported for mechanically polished surfaces, dependent upon the orientation of the direction of polishing to the plane of incidence, but it is not possible to separate the effects of surface roughening from those of damage to the crystallographic structure introduced by polishing and also of polishing contaminant embedded in the surface.

Probably the same generalization can be made for surface roughening as for film roughening and inhomogeneity, i.e., that there is a size and regularity effect. Thus, for surfaces containing obvious macropitting, the roughening produced does not lead to specular reflection, and the analyzed reflected elliptically polarized light can be interpreted in terms of filming behavior over the remainder of the surface. Some guidance on the problem can be drawn from the similarity in derivation of the equations of elliptically polarized light and those of interference phenomena, and the fact that change of the state of interference colors can be detected visually for very small thickness changes should provide a useful indicator to the effect of surface roughening. In practice, the same interference colors can be produced, at constant applied voltage, on anodized titanium whether it is electropolished or deeply etched. While this can hardly be advanced as very strong evidence that microroughening is likely to introduce only small error into ellipsometry measurements, it is not an error of the large order

of magnitude implicit in the calculations of Fenstermaker and McCrackin. The fact remains, however, that for very regular surface roughening effects, such as may occur in the activation of single-crystal surfaces, optical anomalies are likely to occur, and this is of particular significance in studies of anodic passivity.

INSTRUMENTATION

Mention has already been made of the principles of measurement of reflected elliptically polarized light and the accuracy attainable, and it seems appropriate now to describe some of the equipment and reaction cells commonly employed, prior to discussing the type of information that can be derived from the application of the technique.

Commercial ellipsometers are available, one from Gaertner Scientific Corp. Chicago, Ill. and another from O. C. Rudolph and Sons, Caldwell, N.J., and both are available in a range of configurations. Whether it is better to have the plane of incidence horizontal or vertical is a moot point and depends on the problem under investigation. A vertical plane is convenient for studying reflection from liquid surfaces, but there are mechanical problems in counterbalancing the optical benches onto which the components are attached. An essential component is the polarizer,²⁴ which can either be the dichroic type, of which Polaroid (in various forms) is the most common example, or the birefringent type, such as the calcite, or Glan Thompson, prism. The latter is the best form of polarizer, but is expensive, especially when large apertures are required. For some applications, however, the characteristics of the Polaroid type are adequate, this material having the advantage of being much cheaper, and aperture size is not a restriction. The Glan Thompson prism can be used over the range from 2000 Å to 2 μm (and also at 50 μm). For intermediate wavelength ranges, grid-type polarizers are appropriate.⁸¹ Polarizing materials are mounted in divided circles so that azimuths of the plane of vibration can be accurately ascertained. The cost of such components varies with the accuracy obtainable, those readable to 0.01° being much more costly than those to 0.1°. Counter methods of setting the orientations are also employed, and these may have a precision equivalent to seconds of arc. The quarter-wave plate, another commonly used component, is constructed from mica or quartz in such a way that the phase retardation between orthogonal components of a light beam is 90° at a specific wavelength. In practice, this may not be precisely achieved, and methods of correction for errors

in this component have already been described. King²⁹ has discussed the properties of the Fresnel rhomb, which serves as a quarter-wave plate over a wide range of wavelengths, but this is not at present in commercial production. The quarter-wave plate is mounted in a divided circle in the same way as the polarizer. All these components, together with others, such as the Babinet–Soleil compensator and Faraday cells, can be purchased from a wide range of optical manufacturers.

In studying film formation on materials during particular corrosion reactions, it is a particular attraction of the technique that it can be carried out on the surface *in situ*. In such cases, a reaction chamber is required which is fitted with windows to allow the entry and exit of the polarized light beam. Vessels of this kind have been constructed for the study of a wide range of reactions, including gaseous reactions under near-vacuum, atmospheric pressure, and pressure levels up to 300 psi. Extensive use has also been made of apparatus for investigating electrochemical reactions in aqueous media, even in such extreme environments as flowing, high-pressure water up to 600 psi. These various types of cell pose problems in material of construction, but common to all is the need to employ strain-free, non-birefringent windows. For a wide range of applications, especially for comparative work, it is sufficient to use good-quality, strain-free glass. Winterbottom⁸² has discussed the requirements for plane parallelism and surface finish of high-quality windows. Methods of attaching windows which involve the use of pressure at the periphery are inadmissible for situations in which very accurate absolute values of Δ and $\tan \psi$ are to be determined.

ALIGNMENT AND CALIBRATION OF ELLIPSOMETERS

The alignment of the optical system is basically the straightforward process of ensuring that the centers of all the optical components lie on a common optical axis (in two directions at right angles—with a horizontally dispersed ellipsometer, this means in the plane of incidence and normal to this plane) and this requires that sufficient adjustment is available in the optical benches and components. It is also important with components such as polarizers and quarter-wave plates to set the face of the elements accurately normal to the optical axis, and there are optical devices available for doing this. A further requirement is to establish that the pivot point for the one optical bench (in a horizontal unit) or both (in a vertical one) is at the intersection of the optical axes of both optical benches. Dependent

upon the light source employed, the incident beam is collimated and made monochromatic—either by virtue of the light source chosen (e.g., laser), by filters, e.g., as with a mercury vapor lamp, or by using white light and a monochromator—and the next step is that of calibrating the vibration directions of the various optical components. The standard method makes use of reflection from a dielectric surface of known refractive index, and the fact that at the Brewster angle, given by $\tan \phi_B = n$, the component of light in the plane of incidence becomes zero.⁵ Using this method, if the collimated, nonpolarized light is reflected from the dielectric surface through the polarizer and onto a photoelectric detector, then only at one angle of incidence, the Brewster angle, will the reflected light be completely extinguished by rotation of the polarizer. At this position, the plane of polarization of this component is accurately horizontal, and it is convenient to rotate the element within the divided circle until the setting is reasonably close to zero. An alternative method is to pass the incident light through the polarizer before reflection at either a dielectric or metal surface, and then through an ellipticity half-shade, analyzer, and telescope (if a visual method is being employed) or a photoelectric cell. The principle involved in this case is that only when the plane of the incident polarized light is in the plane of incidence, or at right angles to it, will the reflected light, for any setting of the angle of incidence, be plane polarized. It is essential in both methods to set the reflecting surface either accurately horizontal or vertical depending upon the type of ellipsometer, and this can be done conveniently using optical levers. Using the second method, it will not be known whether the setting of plane of polarization is in the plane of incidence or normal to this plane, but this can be determined at a later stage.

Once the vibration direction of one component has been determined, or better, those of both polarizer and analyzer, it is straightforward to use these to find the axes of, say, the quarter-wave plate, Babinet-Soleil compensator, or whatever further optical elements are being used, and to set the various axes in the azimuths required for the method of measurement selected (e.g., Fig. 5a-c). Once this has been done, the next step, if, for example, a compensator system has been selected, is to align the two optical benches and, with no specimen present, record the readings of the various elements corresponding to the extinction of light passing through the system. If, in the system adopted, the components to be varied are the polarizer and analyzer (Fig. 5c), then this could yield the zero values P_0 and A_0 . The equipment is then moved to the angle of incidence required, and the corresponding polarizer and analyzer settings for extinction of emergent light on reflection from a specimen are found. If these values are

P and A , then, for a quarter-wave-plate compensated system, the required characteristics of the reflected elliptically polarized light would be given by $\tan \psi = \tan(P - P_0)$ and $\Delta = 2(A - A_0)$. An approximate check on this calibration is to make measurements on the reflection from polished gold or platinum, or some other metal providing negligibly small room-temperature film characteristics, and to check that the $\tan \psi$ and Δ values in comparison to those published in the literature. This is of necessity a simplification of one basic method, but, without recourse to a detailed calibration procedure for a range of possible ellipsometric methods, is sufficient to indicate the ease with which even the simple visual or photo-electric recording ellipsometer may be used. Variations needed for improved accuracy and speed of recording have already been described.

APPLICATIONS TO CORROSION STUDIES

Little progress could be made in attempting to understand corrosion phenomena without recourse to methods of defining the progress of reactions, and a wide range of techniques is used to help delineate the processes involved. It follows that any method of assessing the extent of reaction at any point in time will be of great use, and for many years, the advantages of ellipsometry in making measurements of the earliest stages of reaction have been appreciated. Farsightedly, Tronstad⁸³ wrote in 1933 of the considerable impact that the technique could have in evaluating such processes as passivation, adsorption, and surface migration, and he indicated the progress that might be made. Much of the evidence put forward now seems now rather obvious, but the ideas were proposed at a time when considerable doubt existed on the importance, or even the presence, of surface films on naked surfaces invisible to the eye. Subsequently, it has been demonstrated that the technique can yield information relating to the very early stages of reaction between metal and environment, even including the formation of the first monolayer of the film and, at the other extreme, to the much thicker films found in practical corrosion environments where such films determine the rate of any subsequent reaction. Natural corrosion reactions are electrochemical in origin,⁸⁴ and on first consideration, it might be thought that a technique assessing a relatively large area incorporating both local anodes and cathodes would have limited application, and that it would provide no more than a measure of the overall reaction product formed. This limitation can to a large extent be removed by the separate study of the anodic and cathodic polarization characteristics

of the metal involved in the corrosion reaction, using, for example, potentiostatic or galvanostatic techniques, as is evident from the literature. The range of application of ellipsometry is considerable, and was recently described in terms of its usefulness to corrosion science and engineering.⁸⁵ In the present chapter, it is proposed to group all these applications together, and to discuss the progress that has been made in applying ellipsometry to such subjects as adsorption, passivity, and anodizing, and to indicate likely lines of future development. In some instances, simultaneous measurements, using alternative techniques, have been made in order to define in more detail the processes involved in a reaction, and this may have required not only sophisticated and expensive equipment, but also groups of, rather than individual, investigators. This does not in any way mean that this will be the trend for all future ellipsometric investigations, as wide opportunities still exist for the application of the simple equipment to corrosion science and engineering subjects. A few of the many possible corrosion-related applications of the technique are the influence of residual surface films on the wetting of surfaces by solders, the effects of air-formed oxides developed during fabrication on subsequent friction characteristics, or on the characteristics of cathodically deposited metals, the stability of surface films during the anodic evolution of oxygen and other gases, the influence of outdoor exposure on metal tarnishing reactions, and the adsorption of organic corrosion inhibitors. At present, however, as far as the published literature is concerned, the majority of applications of ellipsometry to corrosion have been concerned with sensitive techniques for monitoring the very first stages of reactions, and the classification of bare metal surfaces.

Bare Metal Surfaces

Although the optical constants of most metals have now been determined over a wide spectral range, and the data available relate to material in various surface crystallographic conditions, in most instances, it is desirable to make some direct measurement at the start of an investigation, as none may be appropriate for the particular corrosion situation to be investigated. The ease with which this can be done will depend, for example, on the type of metal and whether it is necessary to study the reaction on as near a perfect surface as obtainable, or on a "technical" surface such as bright rolled, extruded, mechanically abraded, or polished. Various methods of arriving at a standard surface have been tried, including cleaning under high vacuum, but the most usual procedures are either to study evaporated deposits or to remove surface films from mechanically polished

or electropolished surfaces, by hydrogen reduction under high vacuum, positive-ion bombardment, high-temperature dissociation, or, in the case of aqueous reactions, by the cathodic reduction of surface films where possible. One of the difficulties of establishing absolute optical constants is that of knowing when a clean surface has been obtained. From purely ellipsometric data, it is known that the characteristics of reflected elliptically polarized light show a well-defined trend (Figs. 3 and 9–13) and it is always possible to decide whether a treatment process has produced a cleaner surface than was present previously, but not whether the ultimate limit of cleanliness has been reached. For this reason, it is necessary to introduce alternative and simultaneous methods of assessing surface condition. Muller *et al.*,⁸⁶ Melmed *et al.*,⁸⁷ and Carroll and Melmed⁸⁸ have employed low-energy electron diffraction and combined this with ellipsometry to study gaseous adsorption processes. Similarly, it is to be expected that ellipsometry and Auger-electron spectroscopy could be combined to define clean surfaces and subsequent adsorption phenomena or the early stages in thin-film formation. Smith⁷⁰ has correlated ellipsometric, work function, and contact potential measurements.

For the study of gaseous reactions, the preparation of evaporated films under high-vacuum (10^{-9} Torr or better) was sufficient for Dettorre *et al.*⁸⁹ to make observations on the initial stages of adsorption of oxygen on copper. Meyer and Bootsma⁹⁰ investigated absorption of oxygen on silicon by preheating samples to 1250°C under high vacuum, while Archer and Gobeli⁹¹ studied oxygen absorption on freshly cleaved (111) faces of silicon. Less exacting preparation techniques have proved sufficient for reproducible studies on the growth of thicker reaction products, such as oxide films several hundred angstroms thick. For example, Young *et al.*⁹² electropolished copper single crystals and, after a careful reduction of the residual film by heating in purified dry hydrogen for 1 hr at 500°C, carried out oxidation studies in the range 150–200°C. A similar sequence has been used on microcrystalline copper oxidized in the same temperature region.⁵⁵ With the strongly passivable metals, such as iron alloys, aluminum, and titanium, it is more difficult to achieve a clean surface on wrought material, and some compromise must be reached. Volenik,^{93,94} for example, used chemical polishing and etching techniques to prepare dilute iron–silicon alloys, while Menard⁹⁵ and Johnson and Tao⁹⁶ made use of the absorption of oxide films into titanium that occurs at elevated temperature under high vacuum to procedure a clean surface.

The study of metals in liquid environments presents its own particular advantages and disadvantages. Many surface films can be cathodically

reduced in neutral or acid solution, but the treatment should be restricted to surfaces initially covered with very thin films so that on cathodic treatment the reduced metal does not adhere as a high-surface-area matt coating which will be neither reflective nor typical of the required planar surface. Further, the process should also be carefully controlled to minimize hydrogen uptake by the cathode surface, or surface roughening where metal activation occurs in acid solutions. Certain metal oxides, for example, titanium⁹⁷ and other refractory metal oxides, cannot be reduced even with extended and high-current-density cathodic treatment, and there is a danger that such cathodic charging will contaminate existing residual surface films with hydrogen and that subsequent anodic reactions will be influenced by proton penetration. In such circumstances, it is probably appropriate to study reactions on mechanically or anodically polished metal surfaces. Cathodic cleaning has been extensively employed for the cleaning of noble metals, and a number of investigators have cleaned platinum by flaming in air (heating to red heat) and then cathodically reducing the surface, a technique which leads to reproducible anodic charging cycles, as observed both potentiostatically and ellipsometrically.⁵³

Adsorption Phenomena

From electrochemical studies, it can be deduced that the adsorption of inhibitors, such as benzoate on iron, may be effective in producing inhibition even before the first complete monolayer has formed on the surface, the inference being that adsorption at a few specifically active sites is capable of controlling the progress of the corrosion reaction. The ellipsometric technique would seem, in this case, to offer the direct possibility of measurement of such processes, as proposed in the early 1930's. In fact, however, there is as yet little reported data of this kind, although a number of ellipsometric studies on adsorption have been carried out, including, in addition to those mentioned previously, a study of oxygen adsorption on tungsten by Carroll and Melmed, using both ellipsometry and LEED, and the comparative investigation of ellipsometry, surface tension, and contact potential for various organic adsorbates on mercury.⁷⁰ Bootsma and Meyer⁹⁸ have measured the physical adsorption of krypton, xenon, methane, silane, and nitric oxide on germanium and silicon surfaces at low temperatures, while Archer and Gobeli⁹¹ have studied oxygen adsorption on cleaved silicon surfaces. Deryagin and Zorin⁶⁷ have reported an optical investigation of the adsorption of various organic species onto optically polished glass surfaces using an ellipsometric method. More closely related

to the inhibitor field are the studies by Pimbley and MacQueen⁹⁹ of the desorption of stearic acid from platinum and nickel surfaces, by Miller and Berger⁶⁹ of the adsorption of caproic and benzoic acid vapors on chromium, and by Stromberg *et al.*¹⁰⁰ and Bornong and Martin^{101,102} of a range of organic molecules, also on chromium. In several of these investigations, use was made of external calibration of the ellipsometer using a barium stearate wedge. In one such case, chromium was evaporated onto a slide to a thickness of 100 Å and successive layers of barium stearate were deposited using the technique of Blodgett.¹⁰³ Each complete monolayer of barium stearate has a thickness of 24.3 Å, and it was shown that the relationship between change of analyzer setting and thickness of barium stearate was linear, with a slope of 1.07° per monolayer using the Pimbley and MacQueen experimental arrangement. This method presupposes that the refractive index of the barium stearate wedge and organic adsorbate are the same, but provided the differences are small, the error in estimation of film thickness is also small, and the method removes the need for computation of Eq. (9). The Miller and Berger results are particularly informative, as these authors made a comparative study of ellipsometric and radio-tracer methods, some indication of the agreement found being given in Table 3.

An example of a less rigorous, but nevertheless useful, application of ellipsometry arose in the fabrication of brass sheets that had been dried, after pickling, by means of sawdust. It was discovered that natural oil was being leached from the pine wood and transferred to the brass sheet,

Table 3. Adsorption of Tagged Caproic Acid Vapor by Chromium Plate (Ferrottype)*

Absorption time, min	Film thickness, Å	
	Radiotracer	Ellipsometer
30	4.1	4.4
45	—	7.8
60	9.0	9.2
135	9.8	10.0
3900	11.2	10.9

* After Miller and Berger.⁶⁹

thereby imparting useful lubricant properties. After extraction of the oil from the wood, it was diluted to various concentrations in carbon tetrachloride. After dipping clean brass sheet into these solutions, ellipsometric examination revealed changes in Δ proportional to oil concentration.

Passivity

Passivity is an extensively investigated phenomenon, but the distinctions between passivity and adsorption on the one hand, and electropolishing and anodic oxidation on the other, are often small, and a discussion of the contribution that ellipsometry has and might be expected to make to the topic is somewhat arbitrary. By definition, the phenomenon is one in which the corrosion rate of a metal, on being taken to progressively more noble electrode potentials, undergoes a decrease, sometimes slight, and often dramatic. Subsequently, the rate may slowly increase with further rise in potential, or rise very rapidly (transpassivity). Each metal-environment system requires to be considered separately, for many electrochemical oxidation reactions may contribute to such a decrease in corrosion rate, but the effects are usually brought about by the formation of a surface phase and it is logical to expect ellipsometry to be a valid technique for the detection of such a phase. The method has particular advantages in that measurements can be made *in situ* as the potential of the surface is changed, a condition which cannot be met if the applied potential has to be switched off and the specimen removed, as in examination by such techniques as low-energy electron diffraction or Auger-electron spectroscopy. Even though many electrochemical and other methods of examination have been brought to bear on the subject, uncertainty still exists on the mechanism of passive film formation, which may be electrocrystallization, chemical precipitation, or valence change to an existing oxide structure, depending upon the metal/solution system under investigation. It is also often uncertain whether the rate-controlling surface phase is an adsorbed layer or a three-dimensional oxide layer and also what its exact composition is at a given potential level. A complicating factor is that the surface condition is a dynamic one, possibly consisting of a continuing slow dissolution with constant readsorption in the case of an adsorbing layer, or film dissolution at the film/electrolyte interface with continuous film growth at the metal/film boundary.

It is of interest to review the ellipsometric literature concerned with passivity, which already covers a wide range of materials, including iron, stainless steel, chromium, nickel, platinum, titanium, aluminum, and gold,

against this background. For the most part, it is concerned with the measurement of thickness, and the rate of formation and dissolution, of the films which exist over the passive potential range, and which in most instances are very thin, ranging from an adsorbed layer to a few tens of angstroms. There has been a tendency in this past work to report only the film thickness data obtained and not the method of interpretation chosen, i.e., the refractive index used or whether roughening of the substrate has taken into account, and more attention could usefully be focused on this aspect in future work. By considering the optical parameters of the film as well as its thickness, especially over a range of wavelengths, it may be possible to derive information on film composition. McBee and Kruger¹⁰⁴ have reported preliminary data for iron, but considerably more information of this kind needs to be collected. Electroreflectance spectra from passivated iron electrodes, such as reported by Ebiko *et al.*,¹⁰⁵ are another approach to the problem of defining this kind of information.

Some of the first applications of ellipsometry to passivity can be attributed to Tronstad,⁸³ who made *in situ* observations on iron, stainless steel, and nickel in alkaline solutions in the early 1930's. He deduced that passivity was associated with the growth of oxide films of fairly high average refractive index (~ 3.0), of thickness 20–40 Å. By making the passivated surface cathodic, it was observed that the film was only partially reducible and that by alternate activation and repassivation, the thickness of a passive film could be increased to ~ 80 –100 Å. Tronstad considered the complications likely to be introduced by surface roughening, but deduced that this effect did not influence the results, commenting that films of 100 Å should produce first-order interference colors when observed at grazing angle of incidence, and confirming this when the samples were withdrawn for examination. This experimental evidence on film formation was put forward to support the oxide theory of passivation. Later, in collaboration with Hoverstad,¹⁰⁶ similar observations were made on aluminum immersed in chromic, nitric, and sulfuric acids.

The next important stage in ellipsometric examination of passivity was that described by Andreeva,¹⁰⁷ who provided information on the change in film coverage of several metals during passivation as the electrode potential was made progressively more noble using both potentiostatic and galvanostatic techniques. A number of features which are common to many passive systems can be illustrated by reference to work on massive polished chromium.¹⁰⁷ The thickness of passive film formed in acid solutions is less than that in neutral solutions—by 30–50%—and a similar effect has been shown independently for titanium.¹⁵² On raising the electrode

potential from its natural, open-circuit potential in sulfuric acid, the surface first becomes covered with a film several hundreds of angstroms in thickness, which decreases to only a few tens of angstroms in the passive potential region, and rises again to several hundred angstroms in the region of transpassivity. Chromium also becomes covered with a thick film on cathodic polarization. The extent to which roughening of the substrate may have influenced these results is not known, but the evidence is for the presence of a prepassive film during activation, as reported by Bockris *et al.*⁶⁵ for nickel in sulfuric acid, and also as observed on iron and copper.¹⁵² Although the evidence for such a film is generally inconsistent with previous conceptions of metal activation, many corrosion reactions involve an oxidation/dissolution process, and many etchants are based upon an accelerated oxidation/dissolution reaction, an aspect which will be considered in more detail later.

Over the potential ranges giving rise to activation, passivity, and transpassivity, different electrochemical reactions will become dominant and changes in composition as a result of increasing oxidation will occur. For this reason, each combination of material and environment needs to be considered as a separate case. For nickel, Bockris *et al.* proposed that the semiconducting properties of the prepassivation film change in a manner which induces passivity, inferring that a modification of an existing film occurs on raising the electrode potential into the passive region. Andreeva suggests that the increase in film thickness on chromium on passing from the passive to the transpassive condition can be accounted for by the volume increase in changing from CrO or Cr_2O_3 to CrO_2 .¹⁰⁷ Whatever mechanism of composition change is assumed to occur on raising the electrode potential, e.g., whether it is a diffusionless phase change in an existing oxide, or a completely dynamic process involving dissolution of one phase and its replacement by another of different composition, there are likely to be changes in optical parameters, either continuous or discontinuous, which will directly affect the properties of reflected elliptically polarized light. Bockris *et al.*⁶⁵ interpret their results in terms of a prepassive film which remains relatively constant in thickness at passive potentials but undergoes marked changes in optical absorptivity. The same results may be interpreted as a decrease in film thickness over the passive potential range, as found by Andreeva for chromium and titanium, or alternatively, Andreeva's results may justify interpretation in terms of a change in film optical constants.

Kruger^{108,109} has examined the passivation of iron in nitrite solutions containing dissolved oxygen and has shown that oxide was present even

before a passive potential was reached, and that further growth (and/or alteration) was required before a passive potential could be achieved. However, when such a potential was reached, a three-dimensional film of greater than 30 Å thickness was present. On the basis of previously published work, Kruger assumed that the initial oxide film was Fe_3O_4 , which, during passivation, changed, at least in part, to produce an outer layer of $\gamma\text{-Fe}_2\text{O}_3$. This process has not been verified directly by optical methods, but the film optical constants during passivation were shown to approximate to $2.5 - 0.3i$, a value close to that found for the oxide film formed by oxidizing iron in air.¹¹⁰ Subsequently, further examinations of the phenomenon by Ord and DeSmet¹¹¹ and Kruger and Calvert¹¹² has shown that the passive layer on iron cannot be represented solely as a single homogeneous layer and that, kinetically, at least three stages of growth are involved. Kruger and Ambrose¹¹³ have looked for changes in optical properties of the passive film in chloride-containing electrolytes at potential levels known to induce breakdown and pitting attack. The kinetics of film growth were the same both in the presence and absence of halide, provided that the electrode potential was lower than a critical potential (related to the critical pitting potential for iron as defined by Nagayama and Cohen¹¹⁴), but at more noble potentials, the presence of chloride accelerated the growth of a film of different composition. The onset of localized breakdown with increased anodic current flow was not accompanied by any observable change in reflected polarized light, at least during the earlier stages. This could mean that chloride ions attack the surface film in a very localized and subtle way, and there is evidence from dispersion measurements that this is so.¹⁰⁴

Similar ellipsometric investigations to those reported on iron have not been published on other readily passivable materials, and, for example, it should be rewarding to examine in more detail the passivation of both titanium and aluminum and to examine the effect of halide additions on the film breakdown during and subsequent pitting attack. A good deal of work has been undertaken on the passivation of noble metals, including gold^{115,116} and platinum,¹¹⁷⁻¹²³ this work mainly designed to distinguish differences between adsorbed films and three-dimensional phase oxide films.

Further analysis of the phenomenon of passivity seems possible using optical techniques of progressively improved refinement, the sensitivity of modern ellipsometers still leaving scope for further improvement, provided that interpretation can keep pace with the more accurate data provided. In this connection, information on the effect of the electrical double layer on the reflectance from, and ellipticity changes produced by, electrolyte/conductor interfaces^{124,125} will be of great value.

Electropolishing and Anodic Oxidation

These processes show many of the characteristics of anodic passivation, but are discussed separately, not only because of the high levels of current density involved, usually mA/cm² to A/cm² rather than μ A/cm², but because the films grown are usually thicker. Electropolishing as such has received scant attention, an exception being the recent publication by Novak *et al.*¹²⁶ on copper. In this work, a complication arises from the absorption of green light by copper ions passing into solution, but the authors were able to show that electropolishing involves two films, one an adherent solid film of at least 40 Å in thickness, next to the metal, and the other a displaceable viscous layer of electrolyte highly concentrated in metal ions of about 2000–3500 Å in thickness. These results accord well with the Hoar–Farthing¹²⁷ concept of anodic polishing of copper, but seem counter to observations made using cadmium red light¹⁴³ to minimize the absorption effect arising from the presence of copper ions in solution, in which the change in Δ reading at the onset of polishing was in the opposite direction to that described by Novak *et al.*, suggesting a thinning of the surface film at the onset of polishing.

Anodizing in its more usual context, namely the application of high anodic potentials in order to form oxide layers of considerable thickness, has received considerable attention, not only on theoretical grounds, but because of the considerable commercial interest in the dielectric and insulating properties of anodically formed films. In many ways, optical studies on the process are relatively easy to pursue, the changes in reflected light being much larger than in any of the applications discussed so far, sometimes showing Δ changes of 360° or more, rendering precision of measurement much less important. Further, it is usually easy to determine the absorption coefficient of the film, although this will necessarily be an average value for the entire film. The fact that the absorption coefficient can be ascertained allows the possibility of measuring changes in absorption properties with wavelength as a means of identification of the film composition as well as its thickness. Some of the systems investigated include aluminum in ammonium tartrate,^{56,57} aluminum in ammonium pentaborate and ammonium pentaborate–ethylene glycol,¹²⁸ tantalum, niobium, and silicon in sulfuric acid,^{129–131} and uranium in ethylene glycol/ammonia/water.²² Examples relating to titanium are illustrated in Fig. 14. In most instances, the results form closed loops, showing that the film absorption coefficient is zero, and this allows the film refractive index to be determined accurately, with the result that the elliptically polarized light measurements can be

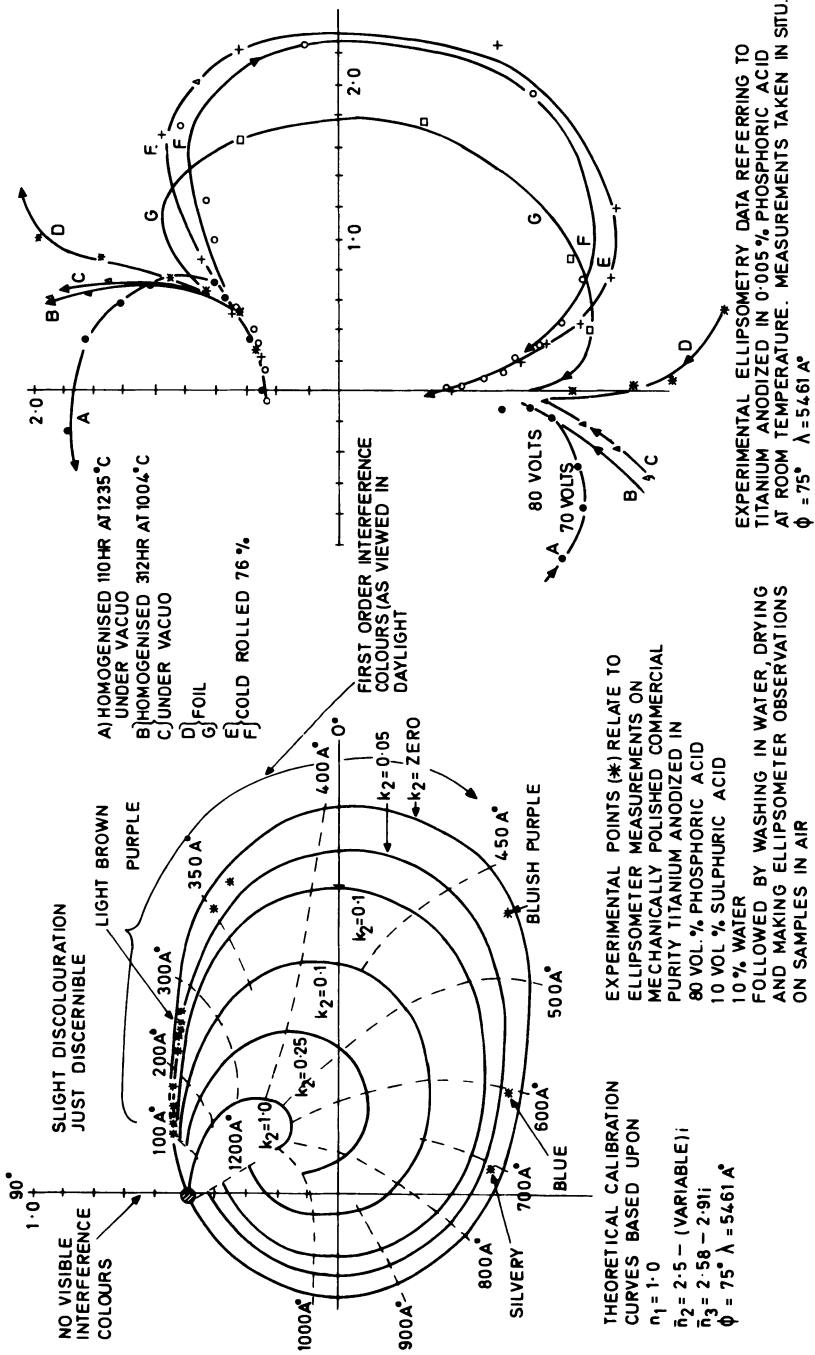


Fig. 14. Ellipsometry data obtained on commercial-purity titanium anodized in different electrolytes.

accurately interpreted in terms of film thickness values. Dell'Oca and Young¹³¹ studied a less straightforward example relating to tantalum in dilute solutions of phosphoric acid, in which two distinct layers form due to the migration of both metal and oxygen ions simultaneously, and at approximately equal rates, and showed that these layers could be distinguished by analysis of the ellipsometry results. An exception to this general finding, i.e., that low-absorptivity films are formed, arises when impurities are present, either in the substrate or in the anodizing electrolyte, which become occluded in the film and give rise to absorption in their own right or promote impurity absorption in the host oxide lattice. An example is silicon in aluminum oxide films, which gives rise to a wide absorption band, with the result that specimens go dark brown or black in appearance. The darkening of anodized aluminum alloys containing silicon, and especially of high-silicon-content brazing alloys, is a well-known phenomenon in the metal finishing industry and has to be avoided in most applications.

Anodic Protection

Since anodic protection is merely a practical application of anodic passivity, it may seem unnecessary to list the topic separately as a subject that may benefit from the application of ellipsometric techniques. However, not only is it becoming an increasingly important practical method in the chemical industry, but it also tends to involve situations that would not normally receive the attention of the corrosion science investigator. By the very nature of its practical application, the environments involved are mainly strong, hot acids, and exposure times of years have to be considered. The current density is usually intermediate between those found in passivity and in electropolishing, namely a few tens or hundreds of $\mu\text{A}/\text{cm}^2$, but, in the case of titanium, only a small proportion of this current is associated with film growth and metal dissolution, the remainder being due to gas evolution. It is of interest to measure the variation in thickness of anodically developed films with acid concentration, temperature, and time for both stationary and continuously refreshed electrolytes at a range of anodic voltages. In the case of titanium,¹⁵³ the film formed in dilute sulfuric and phosphoric acids at 40–60°C and voltages of up to 12 V is measured in terms of a few tens to hundreds of angstroms over long exposure times. With increasing acid concentration, the film dissolution rate increases, and accompanying this increase is a corresponding thickening of the anodic film to many tens of microns. Such adherent film layers may have a complex composition, but mainly consists of blue colored titania indicative of non-

stoichiometric composition. Apart from assisting in explaining these and related phenomena, such as the film changes which may be responsible for the onset of the micropitting sometimes observed, from a practical standpoint, the measurement of the thickness of anodically formed films is a useful aid in assessing the anodic throwing power of a protection system.

Electrochemical Machining

Yet another application of electrochemistry that is of increasing practical importance and requires a basic understanding that might stem from ellipsometric study is electrochemical machining. Suitable electrolytes are those that induce a low anodic breakdown voltage and, having brought about metal activation, will sustain very high current densities at low voltages. Such an attribute is most commonly found in the halides, and the subject is thus an extension of the halide breakdown of passive films referred to earlier.

Cathodic Reactions

The very nature of many cathodic reactions (i.e., reduction of films) means that ellipsometry is likely to be used less extensively here than for anodic film-forming reactions. Barrett and Parsons⁵⁴ refer to the change of reflectivity corresponding to hydrogen absorption on platinum. Andreeva¹⁰⁷ records an increasing thickness of film on several passivable metals when cathodically polarized in acid solutions, but whether this is associated with activation of the metal, hydride formation, or some other factor has not been detailed. El-Sayed and Leach⁹⁷ have considered the effect of proton entry into titanium oxide films during cathodic reaction in weakly alkaline solution, and find evidence, in the change of reaction rate with electrode potential, for the existence of a Ti_2O_3 phase which probably only exists under cathodically held potentials.

Natural Corrosion Reactions

Aqueous Reactions

The subject of aqueous corrosion is enormously large and complex, a fact readily testified to by the standard treatises available on the subject. The formation of films and their role in influencing subsequent reaction is of paramount importance, and the galvanic nature of the process as first put forward by U. R. Evans is generally accepted as accounting for all

aqueous corrosion processes. For this reason, the surface of a corroding metal has to be considered as an array of anodes and cathodes, though in terms of actual coverage of surface, the relative anodic and cathodic areas may be extremely small. Apart from certain fairly well-defined situations, this complicated pattern of growth means that natural corrosion films are less homogeneous than those formed under more controlled potential conditions, and usually grow to levels of thickness above the limit of detection of the ellipsometer, although, by use of long wavelengths, this range could well be extended considerably beyond that used to date. Against this background, it is easy to understand the so far limited application of the technique to natural corrosion reactions. It is debatable whether it is fundamentally a better approach to consider the basic steps in a corrosion reaction by means, for example, of the separate study of anodic and cathodic polarization—even in this case, local galvanic actions can be a complication—or to study the overall natural reaction. As the following examples will illustrate, the interpretation of the observed film formation is exceedingly complicated, but new sidelights can be cast on the reactions involved which might otherwise not have been detected or would perhaps have been difficult to put in perspective, and there is no doubt that direct measurements upon natural reactions have contributed significantly to the understanding of natural corrosion mechanisms.

This is well illustrated by reference to observations on aluminum. Winterbottom¹⁶ first pointed out that Tronstad and Hoverstad's results¹⁰⁶ for film growth on immersion in nitric acid could not be adequately fitted to theoretically computed $\tan \psi$ and Δ values for various formulations of isotropic film. Subsequently Barrett^{56,57} examined film formation on aluminum in distilled water at 50–75°C and observed results, similar to Tronstad's, which did not conform with a simple film-growth model. The films formed had a relatively low refractive index and were therefore amenable to measurement by the liquid immersion method. Those formed in hot water had an apparent refractive index of 1.50 or less, at least on the side adjacent to the solution, and were therefore thought of as a microporous form of either Bayerite or Böhmite. To account for the particular shape of the experimentally determined $\tan \psi$ and Δ curves, it was necessary to postulate models involving variations in coverage or refractive index across the surface, or a film of lower refractive index compared to that near the metal adjacent to the electrolyte and in which both layers increase in thickness during the overall corrosion process.

Aluminum containing small additions of iron and nickel has been developed as a corrosion-resistant material for use in low-temperature,

water-cooled reactors, but in practice, a few samples have been encountered which exhibited a very much lower corrosion rate compared to the majority of the material. One difference in the two types of material, readily detectable by ellipsometry, was the fact that the most protective films were optically absorbing to mercury green light. In a study of the doping of aluminum oxide films to minimize ionic diffusion rates, on the basis of the Wagner-Hauffe valence predictions, high-valence elements were found to produce an absorbing form of alumina, and silicon in particular was, under certain conditions, able to effect a decrease in corrosion rate. This example highlights the possible use of ellipsometry as a method of monitoring success in achieving impurity doping in practice. The use of mercury green light was, fortuitously, successful in detecting the presence of silicon in alumina, but in the more general application of the detection of film modifications, it is necessary to be able to select wavelengths over a wide range, dependent upon the defect spectra of the oxide in question and the specificity of the dopant itself.

Other metals singled out for optical study of natural corrosion reactions include copper and copper-base alloys.^{22,132} On exposure to chloride-containing solutions, including natural seawater, copper and various brasses were shown to develop first a single film layer of cuprous oxide, and then, at a later stage, a second film, composed of Atacamite, formed over the first film. From optical observations, it was apparent that the initial cuprous oxide was far more strongly absorbing to green light than, for example, cuprous oxide formed in a natural tarnishing reaction, and this was another example of a nonstoichiometric, possibly microporous, film which exists on the surface during a corrosion reaction where metal dissolution, and consequently movement of the metal/film interface, is occurring. Optical measurements are here providing an indication of a very dynamic situation, which is slowed down by the subsequent formation of a much thicker outer layer. This second layer has been observed to have variable optical characteristics which, in the case of natural seawater, seem to be related to the location and time of year of sampling.

The natural corrosion of iron has received comparatively little attention by ellipsometric techniques. In a study aimed at minimizing the corrosion of mild steel in low-pressure boiler equipment, Ashworth *et al.*¹³³ examined filming behavior in citric acid solutions and the subsequent influence of the addition of ammonia and/or oxidizing agents such as sodium bromate. As might be expected, the dissolution rate is decreased as the alkalinity is adjusted to pH 10, but the growth of oxide increases with time of exposure. The addition of a strong oxidizing agent effectively stops both dissolution

and film growth, and also produces a sudden discontinuity in the average film absorption coefficient, but the exact significance of this, probably due to a modification of the film material adjacent the electrolyte, has not been established in any detail.

Optical measurements have also proved of value in monitoring the early stages of magnetite formation on mild steel exposed to water at high temperatures and pressure.¹³³ Thus at pressures up to 100 psi (temperature 175°C), the growth rate conforms to a logarithmic relationship with time of exposure over 24-hr periods. At higher temperatures and pressures, the reaction is characterized by an outer layer which occurs first as a random deposit of fairly massive magnetite crystals, depending upon electrolyte flow rate and temperature, and eventually forms a much thicker film than the inner layer first observable. The growth process has some comparable features to that observed on aluminum and described above, in that after long times, both inner and outer layer probably grow simultaneously, but at this stage, the outer layer is so thick that ellipsometry using visible light is no longer practicable. During the early stages of formation of the outer film, the ellipsometric observations mostly refer to the properties and thickness of the inner layer, but a stage is eventually reached where there is uncertainty about the relative contributions from the inner and outer layers.

In situ measurements on the formation of corrosion films on other metals, such as the reactor alloys based upon zirconium and hafnium, would seem to be entirely practicable provided suitable window materials can be obtained for the reaction vessel. Results on zirconium exposed to steam at 400°C and 1500 psi, removed from the environment for measurement, have been reported by Wilkins¹³⁴ using a spectrophotometric method, and ellipsometer measurements have also been reported.¹³⁵ The latter work has shown that large differences in optical absorptivity of the monoclinic zirconia can be detected between materials exposed to the same environment, and in other, unreported work relating to oxidation in air,¹⁵³ differences in the absorption coefficient of films formed on the same material for different conditions of oxidation have been observed. The origin of these absorption coefficient changes has not been investigated, but in common with the changes in film absorption coefficient associated with the oxides of titanium, vanadium, and niobium,¹³⁶ it seems likely that these are connected with a change in the defect structure of the film.

Outdoor Exposure

Another field where ellipsometry has found application is in monitoring the surface films on metals exposed over long periods to atmospheric cor-

rosion. It has proved practicable to make observations every six months on a range of anodized titanium surfaces, and over a period of years, small but progressive increases in oxide thickness have been noted.¹⁵³ The method appears to be feasible for other metals and alloys which show a high resistance to weathering and form only a thin film.

Influence of Films on Mechanical Properties (Including Stress Corrosion and Corrosion Fatigue)

The influence of surface films and surface condition on the mechanical properties of metals and alloys is well known, and Andrade,¹³⁷ has surveyed the magnitude of the effects for naturally formed surface films. In the related fields of stress corrosion and corrosion fatigue, the presence of a film provides not only some indication of the extent of corrosion, but the film probably plays an intrinsic role in the subsequent relaxation of stress from within the metal, for example, the manner in which it stops or accommodates an edge dislocation moving to the surface. Thus, for many corrosion processes, the mechanical as well as the electrical properties of the surface films are important. Ellipsometry may well be used to interpret photoelasticity changes within a surface film, as well as changes due to film growth, and thus application of the technique is likely to contribute to a detailed understanding of the basic processes involved in these complex reactions. Studies of this kind relating to stress corrosion are in progress.¹³⁸

Gaseous Oxidation

This section is largely concerned with tarnishing reactions and reactions at moderately elevated temperatures, as the early stages of adsorption of gaseous species has been discussed. Gaseous oxidation is one of the fields in which ellipsometry was first applied, and it is probably even now one of the most widely investigated. Much of the early work relates to copper, Winterbottom¹³⁹ making use of the rigorous calculation of optical properties [Eq. (9)] to estimate the thickness of the cuprous oxide films producing interference tints on copper. Subsequently, Lustman and Mehl¹⁴⁰ used ellipsometry to determine the rate of growth of oxide at different crystallographic orientations of the substrate, a topic subsequently reexamined by Cathcart and Petersen,⁷⁶ who encountered problems associated with the presence of optical anisotropy due to large epitaxial stresses in the crystalline, highly oriented films. Lustman and Mehl also noted that the optical absorption coefficient of copper oxide varied with the conditions of forma-

tion, and also with the growth of film with time in any set of reaction conditions, and compared this with the variation in electrical conductivity noted earlier by Ruther and Bohnke.¹⁴¹ Similar variations were also observed in a later investigation^{135,142} using randomly oriented microcrystalline copper, and some indication of the range of optical inhomogeneity found has already been illustrated in Fig. 12. Taking these factors into account, the average film optical absorption coefficient of cuprous oxide reveals a change in composition from Cu_2O to CuO , bulk cuprous oxide of stoichiometric composition having a k_2 value for green light close to zero¹⁴³ and, as might be supposed, from its natural black color, cupric oxide showing absorption over a considerable region of the visible spectrum. Together with supplementary information to show that the absorption changes observed by experiment cannot be attributed to grain boundary defects, temperature, lattice strain, or a shift of the fundamental absorption edge for cuprous oxide, these results enable the average film absorption changes to be interpreted. Using measured absorption level increases for films formed in air from room temperature up to 200°C and at temperatures in the region of 250°C , various proportions of cuprous and cupric oxide have been deduced both by electrometric reduction¹⁴⁴ and electron diffraction studies. Poor correspondence was observed between ellipsometric and Coulometric methods of film-thickness estimation for films formed in the $150\text{--}200^\circ\text{C}$ range,¹⁵² possibly associated with the reduction characteristics of highly nonstoichiometric oxide films. Coulometric methods of estimating film thickness at any stage in a reaction process have been used to help define the oxide refractive index in other systems, notably iron. Systematic changes in film absorption coefficient in films grown on dilute copper alloys, including binary alloys containing aluminum, gallium, and germanium, have interpreted as indicating that the centers responsible for absorbing green light are probably positive holes. Copper oxidized to the same thickness of cuprous oxide film but of differing average film absorption coefficient and hence stoichiometry, has a different electrode potential, and it was concluded that differences in stoichiometry revealed as changes in average film absorptivity across the planar surface of a specimen were one of the possible origins of pitting attack when copper is exposed to certain aggressive electrolytes.¹³⁵

There is considerable scope for further work on the copper/cuprous oxide/cupric oxide system and on dilute alloys using the ellipsometric method to indicate the relative stoichiometric composition of oxide phases. Hardesty¹⁴⁵ has shown that the technique is a useful method of assessing the acceleration in oxidation brought about by trace quantities of either hydrogen sulfide or sulfur dioxide, and there seems no reason why it should

not be applied to defining aspects of other reaction systems such as the copper/cuprous sulfide/cupric sulfide system formed when copper is exposed to sulfur at moderately elevated temperature.

Ellipsometry has also been applied to the oxidation of a range of metals, which will not be described in detail here because of space considerations. These include iron and a range of steels,^{110,146} iron-silicon alloys,¹⁴⁷ silicon,¹⁴⁸ the nitriding of chromium,¹⁴⁹ the oxidation of uranium in air,¹⁵⁰ and the reactions between carbon dioxide and beryllium, uranium, and uranium monocarbide crystals and between carbon monoxide and uranium.¹⁵¹

Indeed, whenever a situation arises in which thin, "tarnish"-type films (i.e., films giving rise to interference colors) are formed, it is possible that optical methods of film thickness measurement and the determination of optical properties by ellipsometric techniques may prove advantageous.

CONCLUSIONS

Although the basis of ellipsometric techniques has been known for some 80 years, their application to corrosion studies was not appreciated for about half this period. At this stage, Tronstad, among other investigators, demonstrated the power of the technique in contributing to the study of passivation, oxidation, surface migration, etc. phenomena, and later, Winterbottom took over as almost the sole figure in further developing and exploiting the technique. It has not been until the last 20 years that ellipsometry has become more widely used, and at the present time there is a tremendous impetus to the application of the method to many aspects of the corrosion field. Results to date can already be said to have contributed significantly to an improved understanding of many topics, but there seems little doubt that if the technique can be extended to not only measurement of film thickness, but to the determination of the optical spectra of thin films, and if these data can be interpreted in terms of their composition and electrical characteristics, then the corrosion scientist will indeed have available a most powerful technique. This ultimate objective apart, there is still a need for the further development of both instrumental and interpretational techniques. Very sophisticated and precise ellipsometer methods have been developed, but suitable equipment for the corrosion scientist is not generally available. Whether it is better for ellipsometer specialists and corrosion scientists to work together or to have one worker with an overall, but usually less extensive knowledge of both fields, is always a debatable question, and both situations have developed. At the present time, most

investigators have to spend considerable time developing a technique before applying it, which must surely slow down the rate of application. On the interpretation side, most optical data are still largely interpreted on the basis of parallel-sided, optically homogeneous films even when this is frequently not the situation. Theoretical studies of the form of reflected elliptically polarized light from different film configurations, including random inhomogeneities in both substrate and film, would be welcomed. Given the correct interpretation of the optical parameters of a corrosion situation, or, to draw a parallel with electrical methods of interpretation, the equivalent optical circuit, progress also needs to be made in the correlations between the optical dispersion properties of the more common oxides and such properties as composition and electrical conductance, before the ultimate objective of correlating film properties with electrode potential, and electrochemical phenomena generally, can be achieved.

Notwithstanding the long-term objectives just outlined, the technique has a place in more limited corrosion investigations—the corrosion engineering problems—and is surely worth adding to the general range of physical techniques, such as microscopy, electron diffraction, scanning electron microscopy, and electron probe microanalysis, which are currently available to the corrosion scientist and technologist.

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STRESS-CORROSION CRACKING OF HIGH-STRENGTH ALUMINUM ALLOYS

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INTRODUCTION

High-strength aluminum alloys are of considerable importance in our technologically advanced society. Perhaps the best-known application is in the aerospace industry, where the high-strength aluminum alloys are the engineer's mainstay for rockets, spacecraft, aircraft, and hydrospace vehicles. Table 1 lists the chemical compositions for the commonly used high-strength aluminum-base alloys. Composition limits for several of these alloys are shown in Fig. 1. Typical applications for each of these alloys are listed in Table 2. The heat treatments for the various tempers of these alloys are given in Table 3. Mechanical properties of the alloys are listed in Table 4. (Data in Tables 1–4 were obtained from Refs. 1–45a.) The highest-strength aluminum alloys are those based on the Al–Cu–Mg (2000 series) and Al–Zn–Mg–Cu (7000 series) alloy systems. Since these alloys are the most widely used for today's high-performance structures, this chapter will concentrate on them.

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Table 1. Chemical Composition Limits of Commercial Aluminum Alloys¹

Alloy	Zinc	Magnesium	Copper	Iron	Silicon	Manganese	Chromium	Titanium	Others	
									Each	Total
2014	0.25	0.20-0.8	3.9-5.0	0.7	0.50-1.2	0.40-1.2	0.10	0.15	0.05	0.15
X2020	0.25	0.03	4.0-5.0	0.4	0.40	0.30-0.8	—	0.10	0.05 ²	0.15
2021	0.10	0.02	5.8-8.8	0.3	0.20	0.20-0.40	—	0.02-0.10	0.05 ³	0.15
2024	0.25	1.2-1.8	3.8-4.9	0.50	0.50	0.30-0.9	0.10	—	0.05	0.15
2124	0.25	1.2-1.8	3.8-4.9	0.30	0.20	0.30-0.9	0.10	—	0.05	0.15
2219	0.10	0.02	5.8-8.8	0.30	0.20	0.20-0.40	—	0.02-0.10	0.05 ⁴	0.15
2618	—	1.3-1.8	1.9-2.7	0.9-1.3	0.25	—	—	0.04-0.10	0.05 ⁵	0.15
5052	0.10	2.2-2.8	0.10	0.45 Fe + Si	0.10	0.15-0.35	—	0.05	0.05	0.15
5083	0.25	4.0-4.9	0.10	0.40	0.40	0.30-1.0	0.05-0.25	0.15	0.05	0.15
5086	0.25	3.5-4.5	0.10	0.50	0.40	0.20-0.7	0.05-0.25	0.15	0.05	0.15
X5090	0.20	6.0-8.0	0.25	0.50	0.50	0.35	0.05-0.30	0.015	0.05 ⁶	0.15
5454	0.25	2.4-3.0	0.10	0.40 Fe + Si	0.50-1.0	0.05-0.20	0.20	0.05	0.05	0.15
5456	0.25	4.7-5.5	0.10	0.40 Fe + Si	0.50-1.0	0.05-0.20	0.20	0.05	0.05	0.15
6061	0.25	0.8-1.2	0.15-0.40	0.7	0.40-0.8	0.15	0.04-0.35	0.15	0.05	0.15
6066	0.25	0.8-1.4	0.7-1.2	0.50	0.9-1.8	0.6-1.1	0.40	0.20	0.05	0.15
6070	0.25	0.50-1.2	0.15-0.40	0.50	1.0-1.7	0.40-1.0	0.10	0.15	0.05	0.15
6151	0.25	0.45-0.8	0.35	1.0	0.6-1.2	0.20	0.15-0.35	0.15	0.05	0.15
7001	6.8-8.0	2.6-3.4	1.6-2.6	0.40	0.35	0.20	0.18-0.35	0.20	0.05 ⁷	0.15
	4.0-5.0	1.0-1.8	0.10	0.40	0.35	0.20-0.70	0.06-0.20	0.01-0.06	0.05 ⁷	0.15
X7007	6.0-7.0	1.4-2.2	0.25	0.40 Fe + Si	0.40	0.05-0.25	0.01-0.06	0.05 ⁸	0.05 ⁸	0.15
7039	3.5-4.5	2.3-3.3	0.10	0.40	0.30	0.10-0.40	0.15-0.25	0.10	0.05	0.15
7049	7.2-8.2	2.0-2.9	1.2-1.9	0.35	0.25	0.20	0.10-0.22	0.10	0.05	0.15
X7050	5.7-6.7	1.9-2.6	2.0-2.8	0.15	0.12	0.10	0.04	0.06	0.04 ¹⁷	0.10
7075	5.1-6.1	2.1-2.9	1.2-2.0	0.50	0.40	0.30	0.18-0.35	0.20	0.05	0.15
7076	7.0-8.0	1.2-2.0	0.3-1.0	0.60	0.40	0.30-0.80	—	0.20	0.05	0.15
AZ74	5.5-6.5	2.1-2.5	0.7-1.0	0.50	0.40	0.10	0.15-0.25	0.10	0.05 ⁹	0.15
7079	3.8-4.8	2.9-3.7	0.40-0.8	0.40	0.30	0.10-0.30	0.10-0.25	0.10	0.05	0.15
X7080	5.0-7.0	1.5-3.0	0.50-1.50	0.40	0.30	0.10-0.70	0.25	0.20	0.05	0.15
7175	5.1-6.1	2.1-2.9	1.2-2.0	0.20	0.15	0.10	0.18-0.30	0.10	0.05	0.15
7178	6.3-7.3	2.4-3.1	1.6-2.4	0.50	0.40	0.30	0.18-0.35	0.20	0.05	0.15
X7475	5.2-6.2	1.9-2.6	1.2-1.9	0.12	0.10	0.06	0.18-0.25	0.06	0.05	0.15
Cladding alloys										
1230 ¹⁰	0.10	—	0.10	0.7 Fe + Si	0.05	—	—	0.05	—	—
6003 ¹¹	0.20	0.8-1.5	0.10	0.6	0.35-1.0	0.08	0.35	0.10	0.05	0.15
7008 ¹²	4.4-5.5	0.7-1.4	0.05	0.10	0.10	0.05	0.12-0.25	0.05	0.05	0.10
7011 ¹³	4.0-5.5	1.0-1.6	0.05	0.20	0.15	0.10-0.30	0.05-0.20	0.05	0.05	0.15
7072 ¹⁴	0.8-1.3	0.10	0.10	0.7 Fe + Si	0.10	—	—	0.05	0.05	0.15
Welding wires										
2319	0.10	0.02	5.8-6.8	0.30	0.20	0.20-0.40	—	0.10-0.20	0.05 ¹⁵	0.15
4043	0.10	0.05	0.30	0.8	4.5-6.0	0.05	—	0.20	0.05 ¹⁶	0.15
4145	0.20	0.15	3.3-4.7	0.8	9.3-10.7	0.15	0.15	—	0.05	0.15
5039	2.4-3.2	3.3-4.3	0.03	0.40	0.10	0.30-0.50	0.10-0.20	0.10	0.05 ¹⁶	0.10

¹Composition in weight percent maximum unless shown as a range²X2020 contains cadmium 0.10-0.35, lithium 0.90-1.7³2021 contains zirconium 0.10-0.25, vanadium 0.05-0.15, cadmium 0.05-0.20, tin 0.03-0.08⁴2219 contains zirconium 0.10-0.25, vanadium 0.05-0.15⁵2618 contains nickel 0.9-1.2⁶X5090 contains beryllium 0.001-0.02, boron 0.001-0.050⁷7005 contains zirconium 0.06-0.20⁸X7007 contains zirconium 0.05-0.25⁹AZ74 contains silver 0.3-0.5¹⁰Cladding on alclad 2024¹¹Cladding on alclad 2014¹²High-strength cladding for 7075 and 7178¹³High-strength cladding for 7075, 7079 and 7178¹⁴Cladding on alclad 2219, 6061, 7075, 7079 and 7178¹⁵2319 contains zirconium 0.10-0.25, vanadium 0.05-0.15, beryllium 0.0008 maximum¹⁶4043 and 5039 beryllium content for welding electrodes will be 0.0008 maximum¹⁷X7050 contains zirconium 0.08-0.15

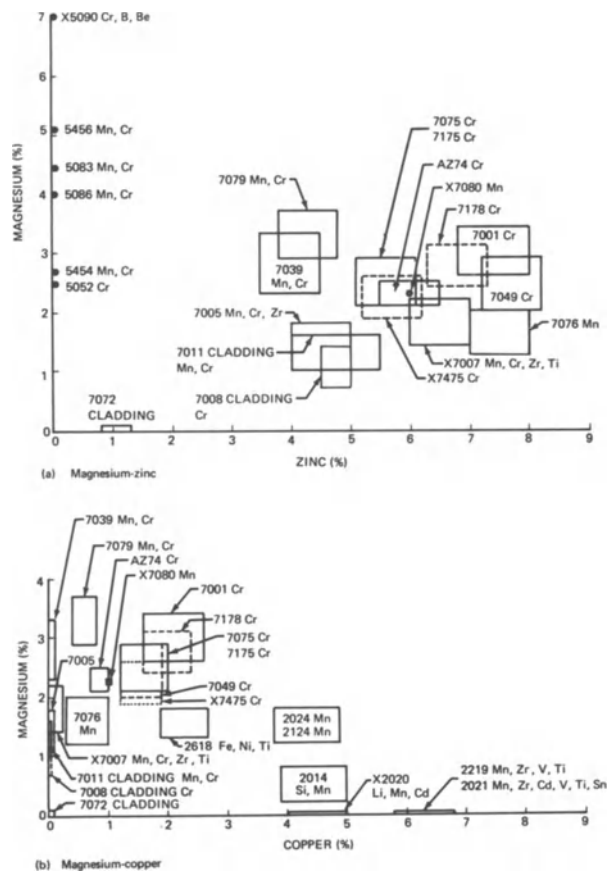


Fig. 1. Chemical compositions of some commercial aluminum alloys (Zn, Mg, and Cu). Only nominal compositions are shown for X7080 and the 5000-series alloys. Primary recrystallization retardants are also indicated for each alloy.

In their service environment, many of the high-strength aluminum alloys can, under specific conditions, fail at stresses far below the yield strength, due to stress-corrosion cracking (SCC). The large potential losses in load-carrying capability due to SCC can be appreciated by noting the low SCC threshold stresses in many of the alloys in Table 4. Since such cracking often occurs below gross yielding, it is appropriate to use linear elastic fracture mechanics analysis. It is a basic tenet of fracture mechanics that rapid mechanical crack propagation will occur when the stress intensity near the tip of a flaw equals or exceeds a critical value K_{Ic} , which is the

Table 2. Typical Applications for Wrought Aluminum Alloys

Alloy	Typical applications
2014	Truck frames, aircraft structures
X2020	Structural use at high temperatures (to 400° F)
2021	High-strength weldments, cryogenics
2024	Aircraft structures
2124	Aircraft structures
2219	Structural use at high temperatures (to 600° F), high-strength weldments
2618	Aircraft engines
5052	Sheet metal work, hydraulic tube
5083	Unfired welded pressure vessels, marine, auto, aircraft, cryogenics, armor, TV towers, drilling rigs, transportation equipment, missile components
5086	
X5090	Potential use as aircraft structural sheet material
5454	Welded structures, pressure vessels, marine service
5456	High-strength welded structures, storage tanks, pressure vessels, marine applications
6061	Heavy-duty structures requiring good corrosion resistance, truck and marine, railroad cars, pipelines
6066	Forgings and extrusions for welded structures
6070	Heavy-duty welded structures, pipelines
6151	Moderate-strength intricate forgings for machine and auto parts
7001	High-strength structures
7005	Welded, brazed or soldered assemblies
X7007	High-strength weldments
7039	Welded cryogenic and missile applications, armor plate
7049	Forgings for aircraft and other structures
X7050	Aircraft and other structures
7075	Aircraft and other structures
7076	Aircraft propellers
7079	Structural parts for aircraft; authors do not recommend usage for forgings
X7080	Was intended for massive forgings for aircraft
7175	Forgings for aircraft and other structures
7178	Aircraft and other structures
X7475	Sheet alloy for aircraft and other structures

fracture toughness of the material. With this in mind, we can define stress-corrosion cracking of high-strength aluminum alloys as environmentally induced subcritical crack growth under static tensile stress. This definition excludes purely mechanical cracking at stress intensities higher than critical. Also excluded is subcritical crack growth due to grain-boundary sliding and creep; these phenomena can occur in vacuum and the help of an environment is not needed as it is in the case of SCC. Fatigue and corrosion fatigue are also excluded from this chapter, because we are considering only static and not cyclic stresses.

The main purpose of this paper is to present and critically review the quantitative stress-corrosion data that are now available. The fracture mechanics approach has, in the past few years, allowed us to design quantitative stress-corrosion tests^{46,47} and to compare environmental and metallurgical effects on a quantitative basis, as will be shown in the following sections. Before such modern testing techniques had been developed, the conventional and more qualitative time-to-failure (TTF) tests had been used⁴⁸ for almost half a century to assess the susceptibility to stress corrosion

Table 3. Heat Treatments for Commercial Aluminum Alloys

Alloy	Temper	Temperature (°F)		Artificial aging treatment
		Solution treatment	Water quench	
Sheets and plates				
2014	-T4, -T42, -T451 ¹ -T6, -T62, -T651 ¹	935	R.T.	None
		935	R.T.	18 hr 320° F
		935	R.T.	10 hr 350° F
X2020	-T6, -T651 ¹	960	R.T.	18 hr 320° F
2021	-T6, -T81 ² (sheet) -T6, -T81 ² (plate)	985	R.T.	16 hr 325° F
		985	R.T.	24 hr 325° F
2024	-T3, -T351 ¹ , -T36 ³ -T4, -T42 -T6, -T62 -T81 ³ , -T851 ¹ -T86 ³	920	R.T.	None
		920	R.T.	None
		920	R.T.	9 hr 375° F
		920	R.T.	12 hr 375° F
		920	R.T.	8 hr 375° F
2124	-T851 ¹	920	R.T.	12 hr 375° F
2219	-T31 ³ , -T351 ¹ , -T37 ³ -T42 -T62 -T81 ³ , -T851 ¹ -T87 ³ (sheet) -T87 ³ (plate)	995	R.T.	None
		995	R.T.	None
		995	R.T.	36 hr 375° F
		995	R.T.	18 hr 350° F
		995	R.T.	24 hr 325° F
		995	R.T.	18 hr 350° F
6061	-T4, -T451 ¹ -T6, -T651 ¹	985	R.T.	None
		985	R.T.	18 hr 320° F
7005	-T6, -T63, -T6351 ¹	870	R.T. or Air cool	Proprietary
X7007	-T6	870	Note 4	96 hr R.T. + 16 hr 275° F
7039	-T6 -T61 -T63 -T64	900	?	72 hr R.T. + 48 hr 240° F
		750	160-180	48 hr R.T. + 16 hr 170° F + 14 hr 320° F
		870	Note 4	72 hr R.T. + 8 hr 225° F + 16 hr 300° F
		750	160-180	48 hr R.T. + 16 hr 170° F + 12 hr 300° F
X7050	-T7X1 -T7X2 -T7351	900	R.T.	4 hr 250° F + 9 hr 325-335° F
		900	R.T.	4 hr 250° F + 24 hr 325-335° F
		890	R.T.	24 hr 250° F + 24 hr 325° F (Tentative)
7075	-T6, -T651 ¹ -T76, -T7651 ¹ -T73, -T7351 ¹	900	R.T.	24 hr 250° F or 4 hr 205° F + 8 hr 315° F
		900	R.T.	3-5 hr 250° F + 15-18 hr 325° F
		900	R.T.	6-8 hr 225° F + 24-30 hr 325° F or 6-8 hr 225° F + 14-18 hr 335° F ⁵
7079	-T6, -T651 ¹	830	R.T.	5 days R.T. + 48 hr 240° F or 6-10 hr 200° F + 24 hr 250° F
7178	-T6, -T651 ¹ -T76, -T7651 ¹	875	R.T.	24 hr 250° F
		875	R.T.	3-5 hr 250° F + 15-18 hr 325° F
X7475	-T61 -T761	—	—	Proprietary
		—	—	Proprietary
Extrusions				
2014	-T4, -T42, -T451X ¹ -T6, -T62, -T651X ¹	935	R.T.	None
		935	R.T.	18 hr 320° F or 10 hr 350° F
2024	-T351X ¹ -T42 -T62 -T851X ¹	920	R.T.	None
		920	R.T.	None
		920	R.T.	16 hr 375° F
		920	R.T.	11-12 hr 375° F
2219	-T351X ¹ -T42 -T62 -T851X ¹	995	R.T.	None
		995	R.T.	None
		995	R.T.	36 hr 375° F
		995	R.T.	18 hr 375° F

¹Stress relieved by cold stretching (to produce permanent set of 1.5% to 3% for sheet and plate) subsequent to solution heat treatment and prior to any elevated-temperature precipitation treatment.

²Preaged 1 hr at 300° F after quenching and stretched a maximum of 1.5% before artificial aging.

³Cold working subsequent to the solution heat treatment and prior to any elevated-temperature precipitation treatment is necessary to secure the specified properties for this temper.

⁴Quench rate not greater than 200° F/sec.

Table 3 (continued)

Alloy	Temper	Temperature (°F)		Artificial aging treatment
		Solution treatment	Water quench	
6061	-T4, -T451X ¹ -T6, -T651X ¹	985 985	R.T. R.T.	None 8 hr 350° F
6066	-T4, -T451X ¹ -T6, -T651X ¹	990 990	R.T. R.T.	None 8 hr 350° F
6070	-T4 -T6	1,025 ⁶ 1,025 ⁶	R.T. R.T.	None 8 hr 350° F or 18 hr 320° F
7001	-T6, -T651X ¹ -T75	870 870	R.T. R.T.	24 hr 250° F Proprietary
7005	-T53, -T5351 ¹	870	R.T. or air cool	Proprietary
7075	-T6, -T651X ¹ -T76, -T7651X ¹ -T73, -T7351X ¹	870 870 870	R.T. R.T. R.T.	24 hr 250° F or 5 hr 210° F + 4 hr 250° F + 4 hr 300° F 3-5 hr 250° F + 18-21 hr 320° F 6-8 hr 225° F + 6-8 hr 350° F or 6-8 hr 225° F + 14-18 hr 335° F ⁵
7079	-T6, -T651X ¹	830	R.T.	5 days R.T. + 48 hr 240° F or 6-10 hr 200° F + 24 hr 250° F
7178	-T6, -T651X -T76, -T7651X	870 870	R.T. R.T.	24 hr 250° F 3-5 hr 250° F + 18-21 hr 320° F
Forgings				
2014	-T4 -T6 -T61 -T652 ⁷	935 935 935 935	140-160 140-160 212 140-160	None 10 hr 340° F 5-14 hr 350° F 10 hr 340° F
2024	-T4 -T6 -T852 ⁷	920 920 920	R.T. R.T. R.T.	None 18 hr 375° F 11 hr 375° F
2219	-T6 -T852 ⁷	995 995	R.T. R.T.	26 hr 375° F 18 hr 350° F
2618	-T61	985	212	20 hr 390° F
6061	-T6	985	R.T.	8 hr 350° F
6066	-T6	990	180 max	8 hr 350° F
6151	-T6	960	R.T.	10 hr 340° F
7039	-T6	900	R.T.	48 hr 250° F
7049	-T73	875	140	48 hr R.T. + 24 hr 250° F + 14 hr 320° F ⁸
X7050	-T73	890	140-160	24 hr 250° F + 8 hr 350° F (Tentative)
7075	-T6, -T652 ⁷ -T73 -T7352 ⁷ -T736	880 880 880 ?	140-160 140-160 140-160 ?	24 hr 250° F 6-8 hr 225° F + 8-10 hr 350° F 6-8 hr 225° F + 6-8 hr 350° F Proprietary
7076	-T6	875	?	14 hr 275° F
AZ74	.61	870	85-105	11 hr 320° F or 24-28 hr 250° F + 6-9 hr 320° F
7079	-T6, -T652 ⁷ -T611	830 830	R.T. 175-185	6 hr 200° F + 48 hr 240° F 6 hr 200° F + 48 hr 240° F
X7080	-T7	880	212	Proprietary
7175	-T66 -T736	? ?	R.T. R.T.	Proprietary Proprietary
7178	-T6, -T652 ⁷	870	R.T.	24 hr 250° F

⁵Second heat treatment may be used only if a heatup rate of 25° F per hour to the aging temperature is used.

⁶By suitable control of extrusion temperature, product may be quenched directly from extrusion press to provide specified properties for this temper. Some products may be adequately quenched in airblast at room temperature.

⁷Stress relieved by cold compression to a permanent set of 2% to 5% subsequent to solution heat treatment and prior to any elevated-temperature precipitation treatment.

⁸A heating-up rate of 50 to 75° F per hour is recommended.

Table 4. Mechanical, Fracture, and Stress-Corrosion Properties for Several Aluminum Alloys

Alloy-temper	Thickness (in.)	Axis ¹ of test spec	Minimum tensile strength		Min elong (% in 2 in. or 4D)	Range in plane-strain fracture toughness K _{IC}			Estimated Stress-corrosion threshold stress		
			Ultimate (ksi)	0.2% yield (ksi)		Long. (ksi√in.)	Long. trans (ksi√in.)	Short trans (ksi√in.)	Long. (ksi)	Long. trans (ksi)	Short trans (ksi)
Plates											
2014 T451 2014 T651	0.500-1.000 0.500-1.000	LT LT	58 67	36 59	14 6	≈ 40 21-28	≈ 38 19-27	17-25 16-19	-- 45	-- 30	-- 8
X2020-T651	1.275	LT	75	70	1.5	18-23	15-21	---	> 57	> 56	34
2021 T81	0.500-1.000	LT	≈ 67	≈ 59	3	26-37	21-34	---	> 48	> 46	35
2024 T351 2024 T62 2024 T851 2024 T86	0.500-1.000 0.500-3.000 0.500-1.000 0.500	LT LT LT LT	63 63 66 70	42 50 58 64	8 5 5 4	≈ 45 27 20-32 22	≈ 40 26 20-32 21	20-26 --- 16-24 ---	35 > 50 > 50 ---	20 > 50 > 50 ---	< 8 43 40 ---
2124-T851 ¹	1.001-1.449	LT	66	57	5	28	24	23	> 50	> 50	30
2219-T351 2219-T37 2219-T62 2219-T87	0.250-2.000 0.040-2.000 0.250-1.000 0.250-1.000	LT LT LT LT	46 49 54 64	28 37 36 51	10 6 8 7	> 40 ≈ 40 50 26-29	> 40 ≈ 34 36 24-28	--- 33 --- 26-30	--- --- > 34 > 44	--- --- --- ---	--- < 10 > 32 > 41
RR-58	0.250	LT	≈ 56	≈ 45	≈ 6	27-34	26	---	> 44	---	> 40
5083-H112 5083-H321	0.250-1.500 0.188-1.500	L L	40 44	18 31	12 12	≈ 40 ≈ 45	≈ 38 ≈ 45	--- ---	--- > 25	--- ---	--- > 25
5456-H112 5456-H321	0.250-1.500 0.625-1.250	L L	42 46	19 33	12 12	≈ 38 ≈ 45	≈ 36 ≈ 45	--- 30-33	--- ---	--- ---	--- ---
6061-T651	0.500-1.000	LT	42	35	9	≈ 50	≈ 50	32-35	> 38	---	> 36
7001-T75	1.275	LT	77	66	4	19-26	17-23	---	> 56	---	25
7005-T6351	0.250-3.000	LT	47	38	7	≈ 50	---	---	≈ 29	≈ 29	< 20
X7007-T6		--	--	--	--	44	37	---	--	--	--
7039-T6151 7039-T63 7039-T64	0.250-2.000 --- up to 1.500	LT --- LT	55 --- 60	45 --- 51	10 --- 9	48 44-45 > 40	40 36-37 ≈ 40	25-35 20-25 30-34	-- > 42 ---	-- 35 ---	< 5 < 8 < 5
X7050-T7351	--	--	--	--	--	36	30	26	--	--	--
7075-T651 7075-T7651 7075-T7351	0.500-1.000 0.500-1.000 0.250-1.000	LT LT LT	78 71 69	68 60 57	7 6 7	25-33 31 30-41	19-31 23-26 24-35	15-20 22 19-21	50 > 49 > 50	45 > 49 > 48	< 8 25 > 43
X7475-T7351	2.6	LT	≈ 59	≈ 49	--	52	---	35	> 50	> 48	> 43
7079-T651	0.250-1.000	LT	74	65	8	25-34	22-28	15-18	> 55	40	< 8
7178-T651 7178-T7651	0.500-1.000 0.500-1.000	LT LT	84 73	73 62	6 6	21-27 26-30	18-23 21-28	14-21 17-19	55 > 52	38 > 52	< 8 25
Forgings											
2014-T4	0.0-4.000	D.F.	L	55	30	11	--	--	--	--	7
	0.0-1.000 0.0-1.000 1.001-2.000 1.001-2.000	D.F. D.F. D.F. D.F.	L T L T	65 64 65 64	56 55 56 55	6 3 6 2					

Table 4 (continued)

Alloy-temper	Heat treat thickness (in.)	Product form ²	Grain dir ¹	Minimum tensile strength		Min elong (% in 2 in. or 4D)	Range in plane-strain fracture toughness K _{IC}			Estimated Short trans stress-corrosion threshold stress (ksi) ³
				Ultimate (ksi)	0.2% yield (ksi)		Long. (ksi√in.)	Long. trans (ksi√in.)	Short trans (ksi√in.)	
Forgings										
2014-T6	2.001-3.000	D.F.	L	65	55	6	25-34	18-30	15-19	<8-10
	2.001-3.000	D.F.	T	63	54	2				
	3.001-4.000	D.F.	L	63	55	6				
	3.001-4.000	D.F.	T	63	54	2				
	4.001-5.000	H.F.	L	62	54	7				
	5.001-6.000	H.F.	L	61	53	7				
	7.001-8.000	H.F.	L	59	51	6				
	7.001-8.000	H.F.	LT	59	51	2				
2124-T852	0.0-4.000	D.F.	L	63	56	12	26	18	16	≈ 15
	0.0-4.000	D.F.	T	59	52	3				
	0.0-4.000	H.F.	L	63	56	8				
	4.000-5.000	H.F.	L	61	55	8				
	5.000-6.000	H.F.	L	59	54	8				
2219-T6	4.0 max	D.F.	L	58	38	8	≈ 36	≈ 34	---	> 32
	4.0 max	D.F.	T	56	36	4				
2219-T852	4.0 max	H.F.	L	62	50	6	---	---	---	> 38
2618-T6	4.0 max	D.F.	L	58	45	4	---	---	---	> 40
	4.0 max	D.F.	T	55	42	4				
5083-H112	4.0 max	D.F.	L	40	18	16	---	---	---	
	4.0 max	D.F.	T	39	16	14				
5456-H112	4.0 max	D.F.	L	44	20	16	---	---	---	
6061-T6	4.0 max	D.F.	L	38	35	7	---	---	---	> 36
	4.0 max	D.F.	T	38	35	5				
6061-T652	8.0 max	H.F.	L	37	34	8	---	---	---	> 36
6066-T6	4.0 max	D.F.	L	50	45	8	---	---	---	> 26
6151-T6	4.0 max	D.F.	L	44	37	10	---	≈ 33	---	
	4.0 max	D.F.	T	44	37	6				
7039-T64	0.0-4.000	D.F.	L	57	48	8	---	---	---	< 10
	0.0-4.000	D.F.	T	54	45	4				
7049-T73	0.0-1.000	D.F.	L	72	62	7	32-34	---	18-29	45
	0.0-1.000	D.F.	T	71	61	3				
	1.001-2.000	D.F.	L	72	62	7				
	1.001-2.000	D.F.	T	70	60	3				
	2.001-3.000	D.F.	L	71	61	7				
	2.001-3.000	D.F.	T	70	60	3				
	3.001-4.000	D.F.	L	71	61	7				
	3.001-4.000	D.F.	T	70	60	2				
	4.001-5.000	D.F.	L	70	60	7				
	4.001-5.000	D.F.	T	68	58	2				
	4.001-5.000	H.F.	L	67	56	7				
	7075-T6	0.0-1.000	D.F.	L	75	64				
0.0-1.000		D.F.	T	71	61	3				
1.001-2.000		D.F.	L	74	63	7				
1.001-2.000		D.F.	T	71	61	3				
2.001-3.000		D.F.	L	74	63	7				
2.001-3.000		D.F.	T	70	60	3				
3.001-4.000		D.F.	L	73	62	7				
3.001-4.000		D.F.	T	70	60	2				
4.001-5.000		H.F.	L	69	58	7				
5.001-6.000		H.F.	L	68	56	6				

Table 4 (continued)

Alloy-temper	Heat treat thickness (in.)	Product form ²	Grain dir ¹	Minimum tensile strength		Min elong (% in 2 in. or 4D)	Range in plane-strain fracture toughness K _{IC}			Estimated Short trans stress-corrosion threshold stress (ksi) ³
				Ultimate (ksi)	0.2% yield (ksi)		Long. (ksi√in.)	Long. trans (ksi√in.)	Short trans (ksi√in.)	
Forgings										
7075-T73	3.0 max	D.F.	L	66	56	7	27-35	21-26	19-25	>43
	3.0 max	D.F.	T	62	53	3				
	3.001-4.000	D.F.	L	64	55	7				
	3.001-4.000	D.F.	T	61	52	2				
	4.001-5.000	D.F.	L	62	53	7				
	4.001-5.000	D.F.	T	59	51	2				
	4.001-5.000	H.F.	L	62	53	7				
	5.001-6.000	D.F.	L	61	51	6				
	5.001-6.000	D.F.	T	58	50	2				
	5.001-6.000	H.F.	L	61	51	6				
7076-T61	4.0 max	D.F.	L	70	60	9				≈ 7
AZ74.61	2.0 max	D.F.	L	≈ 71	≈ 61	≈ 4	--	--	--	≈ 45
	2.0 max	D.F.	T	≈ 69	≈ 59	≈ 3				
	3.0 max	H.F.	L	≈ 69	≈ 58	≈ 9				
7079-T6	0.0-1.000	D.F.	L	72	62	7	25-30	23-35	18-25	<8-6
	0.0-1.000	D.F.	T	71	61	5				
	1.001-2.000	D.F.	L	72	62	7				
	1.001-2.000	D.F.	T	70	60	5				
	2.001-3.000	D.F.	L	71	61	7				
	2.001-3.000	D.F.	T	70	60	4				
	3.001-4.000	D.F.	L	71	61	7				
	3.001-4.000	D.F.	T	70	60	4				
	4.001-5.000	D.F.	L	70	60	7				
	4.001-5.000	D.F.	T	68	58	3				
	4.001-5.000	H.F.	L	70	60	9				
	5.001-6.000	D.F.	L	70	59	7				
	5.001-6.000	D.F.	T	68	58	3				
	5.001-6.000	H.F.	L	69	59	7				
	7.001-8.000	H.F.	L	67	57	9				
		7.001-8.000	H.F.	LT	66	53				
X7080-T7	6.0 max	D.F.	L	65	57	6	32-39	20-29	20-26	25-15
	6.0 max	D.F.	T	65	56	3				
	6.0 max	H.F.	L	65	55	10				
7175-T66	3.0 max	D.F.	L	86	76	7	26-33	24	17-26	<8
	3.0 max	D.F.	T	77	66	4				
7175-T7365 ⁴	0.0-3.000	D.F.	L	76	66	7	32-36	32	23-33	35
	0.0-3.000	D.F.	T	71	62	4				
	0.0-3.000	H.F.	L	73	63	9				
	3.001-4.000	D.F.	L	73	63	7				
	3.001-4.000	D.F.	T	70	60	4				
	3.001-4.000	H.F.	L	71	61	9				
	4.001-5.000	D.F.	L	70	61	7				
	4.001-5.000	D.F.	T	68	58	4				
	4.001-5.000	H.F.	L	68	57	8				
	5.001-6.000	D.F.	L	68	58	7				
	5.001-6.000	D.F.	T	65	55	4				
		5.001-6.000	H.F.	L	65	54				
7175-T73652 ⁴	0.0-3.000	D.F.	L	73	63	7	--	--	--	35
	0.0-3.000	D.F.	T	68	55	4				
	0.0-3.000	H.F.	L	71	61	9				
	5.001-6.000	D.F.	L	65	55	7				
	5.001-6.000	D.F.	T	62	49	4				
	5.001-6.000	H.F.	L	63	51	8				

¹LT Long transverse
L Longitudinal
T Transverse

²D.F. Die forged
H.F. Hand forged

³ When two numbers are shown, the first is the threshold stress in 3.5% NaCl alternate immersion and the second is the threshold in an inland industrial environment.

⁴ Tentative minimum mechanical properties—applicable to parts with a maximum cross sectional area of approximately 100 in.²

of high-strength aluminum alloys. Smooth specimens are also used to determine a threshold stress σ_{SCC} below which stress-corrosion cracking is not observed within a given time.⁴² Using this technique, metallurgists have been remarkably successful in developing aluminum alloys that combine high strength and resistance to stress-corrosion cracking, and a number of reviews have been published that adequately cover what smooth specimen testing has contributed to our understanding of stress-corrosion cracking of high-strength aluminum alloys.^{49–51} Today, however, quantitative SCC data are equally needed for alloy development, fundamental studies of SCC, and advanced design. Already, quantitative SCC data based on fracture mechanics analysis are indispensable for the design of pressure vessels in the aerospace industry, and efforts are under way to introduce the same concepts to other designs as well. Therefore, throughout this chapter we will attempt to state not only whether an alloy will crack in a given environment, but also how fast it cracks at any given crack-tip stress intensity. Only for comparisons and where important aspects of SCC of high-strength aluminum alloys have not yet been quantitatively dealt with will we resort to the results of the conventional, smooth-specimen tests.

Likewise, we will not give a detailed account of all the models proposed to explain the phenomenon of stress-corrosion cracking. Rather, we shall focus attention on those theories that allow quantitative predictions which can be compared with experimental results.

Although stress-corrosion cracking of high-strength aluminum alloys has been studied for more than 50 years and the last few years have seen much progress, it is safe to say that this very complex phenomenon is still far from being thoroughly understood. At this point, a short historical note concerning the first usage of high-strength aluminum alloys in an aerospace application seems appropriate. In 1906, the principle of precipitation hardening was discovered with an Al–Cu–Mg alloy that could be described as a forerunner to the modern 2024-T3 alloy.⁵² Soon, the Al–Cu–Mg alloy was in use for the rigid airship, Zeppelin. However, the search for even higher strength-to-density ratios went on and in 1923, the very high-strength Al–Zn–Mg alloys, forerunners to the modern 7000-series alloys, were developed.⁵³ The first shipment of Al–Zn–Mg parts made for the Zeppelin factory was never used because the parts cracked during transport to the factory. The cracks were apparently caused by stress-corrosion cracking under the combined influence of residual tensile stresses and the moisture of the air.⁵⁴

It is useful to recall this early incident because, as this report is being prepared, we are nearing a highly relevant anniversary: It has now been

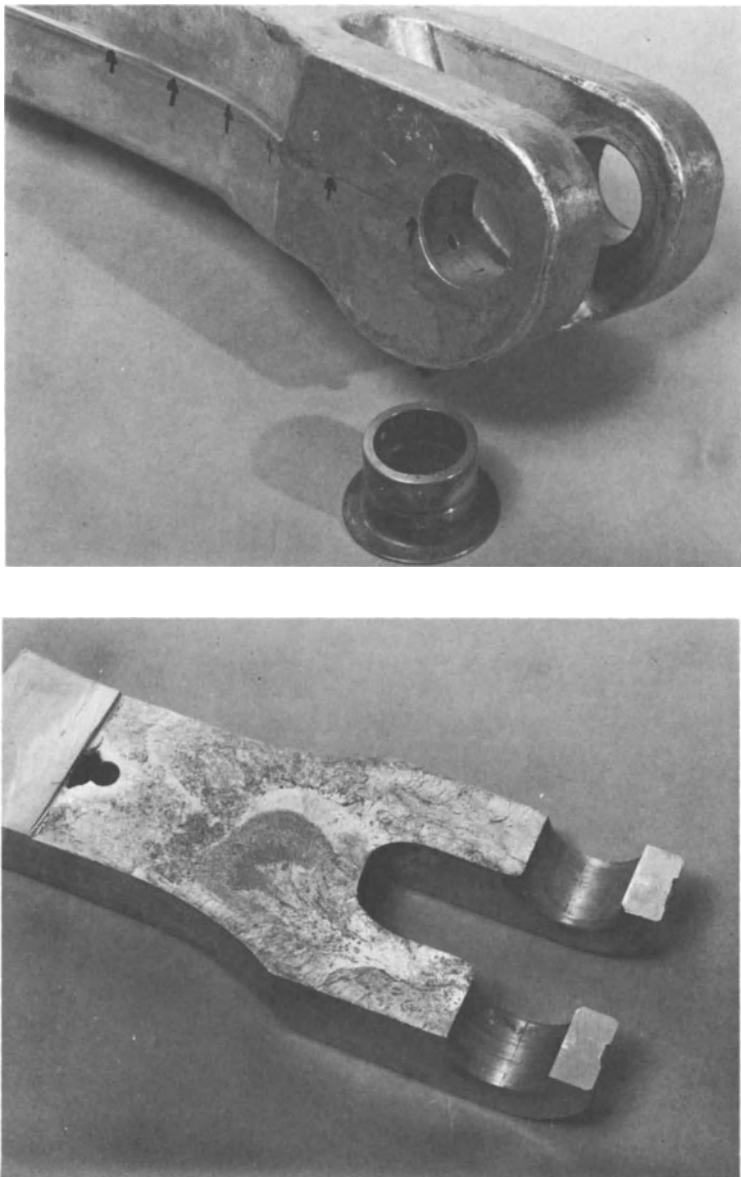


Fig. 2. Typical stress-corrosion fracture along the parting plane of a 7079-T6 die forging. The crack initiated at the faying surface between the flanged bushing and the hole.

almost half a century since this first actual airframe structural material, made of a high-strength Al-Zn-Mg alloy, failed because of stress-corrosion cracking. It is worthwhile to note the three most important factors associated with this early failure, because they are exactly the same factors that are responsible for the majority of the stress-corrosion failures in today's high-strength aluminum alloys, as evidenced by the experience of the U. S. Air Force, the U. S. Navy, and the NASA—Apollo program. These factors are: the introduction of a new alloy with higher yield and tensile strength than alloys previously used, residual or assembly stresses in the alloy, and exposure to the moisture of the air. From the early days of the Zeppelin to the present days of the Apollo moon missions, the majority of the stress-corrosion failures of high-strength aluminum alloys in aerospace structures can be traced back to a combination of these three factors. A typical example of a stress-corrosion failure is shown in Fig. 2.

In the following sections, the authors will describe the conditions under which SCC failures can occur. It is the authors' hope that metallurgists, scientists, and engineers can use the information presented here to further develop, understand, and safely use the high-strength aluminum alloys.

MECHANICAL ASPECTS (THE EFFECTS OF STRESS)

In this section, we will discuss those aspects of stress-corrosion testing that are peculiar to the high-strength commercial aluminum alloys by virtue of the pronounced effect of grain shape and orientation on the stress-corrosion performance of these alloys.

Grain Shape and Orientation

Since stress-corrosion cracking in aluminum alloys is always intergranular, the stress-corrosion performance of these alloys is strongly related to the local grain shape and orientation with respect to the applied stresses. Typical grain shapes and orientations in plate products are illustrated in Fig. 3. Figure 4 shows a typical intergranular stress-corrosion crack in a specimen stressed in the short transverse direction. The grain orientations in the standard wrought forms are indicated schematically in Fig. 5. For hand and die forgings, grain shape and orientation can vary widely throughout the part, and cross sectioning is required to determine local grain shape and orientation. Grain flow in a typical die forging is illustrated in Fig. 6, which shows a cross section perpendicular to the parting plane.

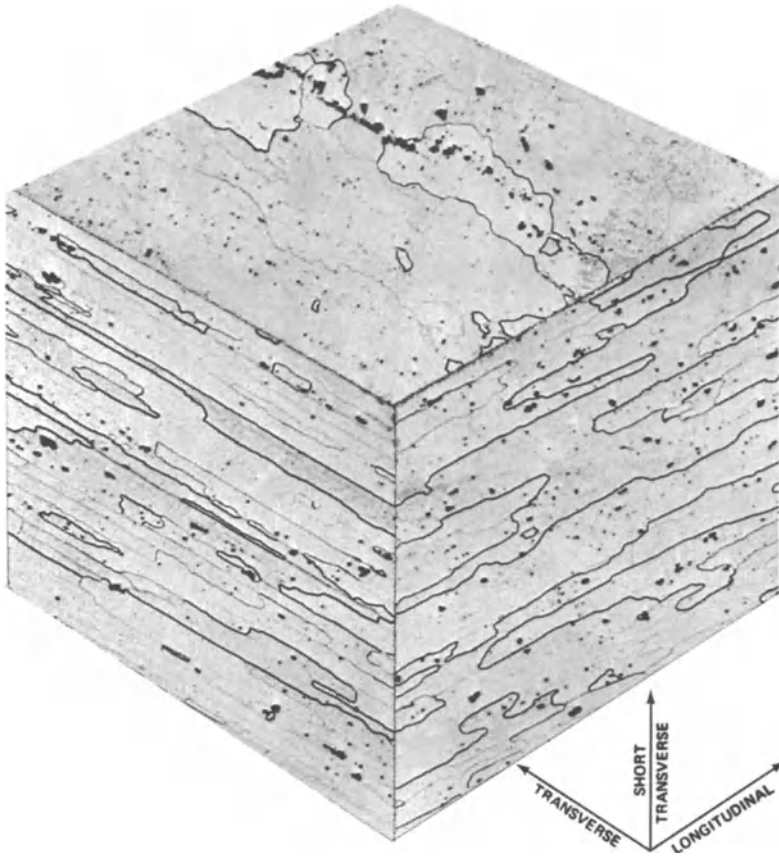


Fig. 3. Typical microstructure of 0.25-in.-thick 7075-T651 plate. Longitudinal, transverse, and short transverse directions are indicated.

Because it is important to relate stressing direction and grain flow directions in aluminum alloys, two systems have been devised to relate these two parameters. In one system, used primarily for testing smooth specimens, the three stressing directions are designated simply by denoting whether the stress is parallel to the longitudinal (L), long transverse (LT), transverse (T), or short transverse (ST) directions as defined in Fig. 5.

Another system has been devised that is particularly useful for pre-cracked specimens. This system specifies both the cracking plane and crack propagation direction. It uses three letters (L , T , W) to indicate the three mutually perpendicular directions: L for the longitudinal direction, T for the thickness direction, and W for the width direction. The crack plane is



Fig. 4. Typical intergranular stress-corrosion crack in 0.25-in.-thick 7075-T651 plate stressed in the short transverse direction.

identified by the direction normal to the crack. The crack propagation direction is identified by one of the three directions, *L*, *T*, or *W*. Figure 7 illustrates the various possible double cantilever beam (DCB) specimen orientations in plate material. Using this system, cracks propagating in the parting plane of die forgings would correspond to *TL* and *TW* cracks in plate.

The Sources of Stress

Tensile stresses are always necessary for SCC to occur. Service stress-corrosion failures in susceptible aluminum alloys usually result from sustained, unintentionally induced stresses or residual short transverse or transverse tension stresses acting at the surface. A typical source of an unintentionally induced stress resulting from assembly is illustrated in

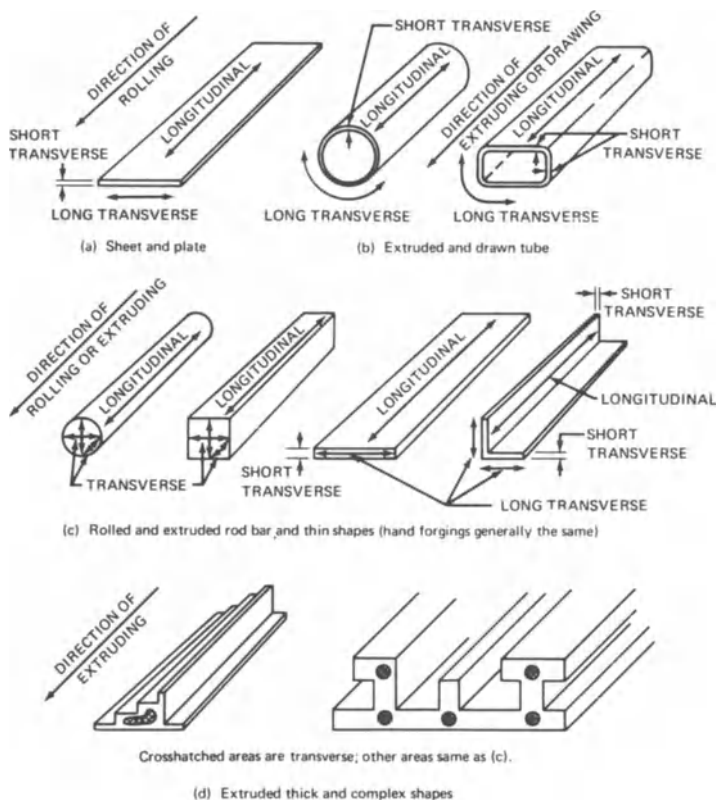


Fig. 5. Grain orientations in standard wrought forms (after Spuhler and Burton⁵⁶).

Fig. 8. Residual stresses usually result from quenching after solution heat treatment. An example showing the magnitude and sense of such stresses is shown in Fig. 9. The problem usually arises when machining operations expose the material under high residual tension stresses. In some parts of complicated geometry, cooling rates may vary from area to area during quenching due to variations in section size or formation of steam pockets. This can lead to surface residual tension stresses even without subsequent machining operations. Since design loads are seldom of the sustained type, they are not usually the cause of stress-corrosion cracking. There are exceptions to this rule, however, and stress-corrosion cracking often occurs in hydraulic parts or pressure vessels where pressurization may last for long periods of time. Other exceptions are interference fitted bushings and fasteners.

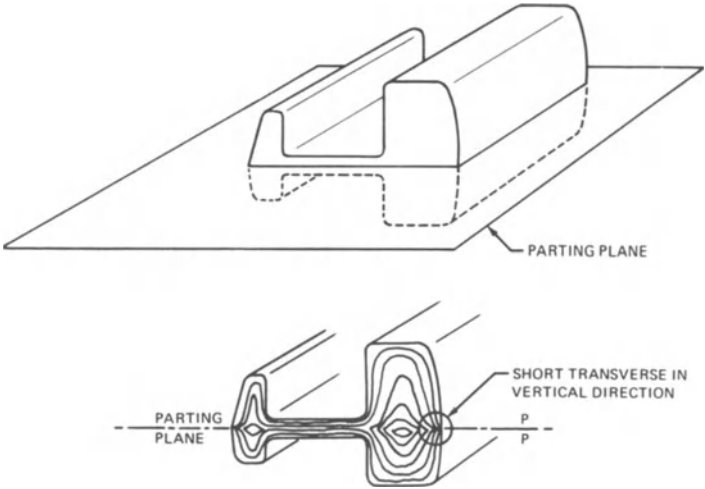


Fig. 6. Schematic representation of the grain flow in a section of a typical die forging.

Although it is probably less common, it is worth noting that once a stress-corrosion crack has initiated, the formation of voluminous corrosion products within the crack itself can help in maintaining high stresses at the crack tip. This phenomenon has been observed in several high-strength aluminum alloys.^{44,45,45b}

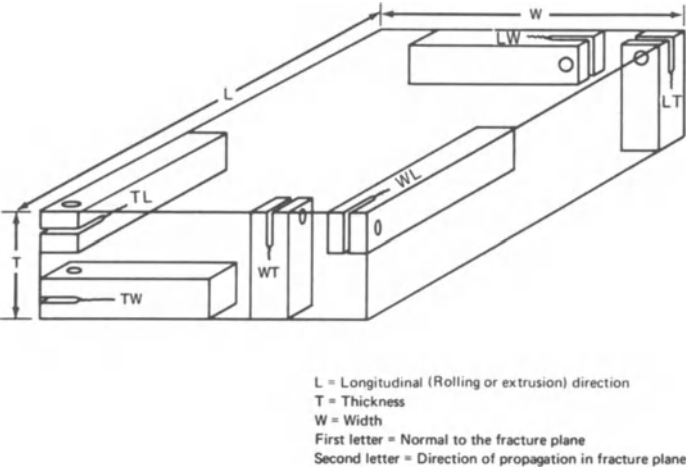


Fig. 7. Some possible double-cantilever-beam (DCB) specimen orientations in plate material.

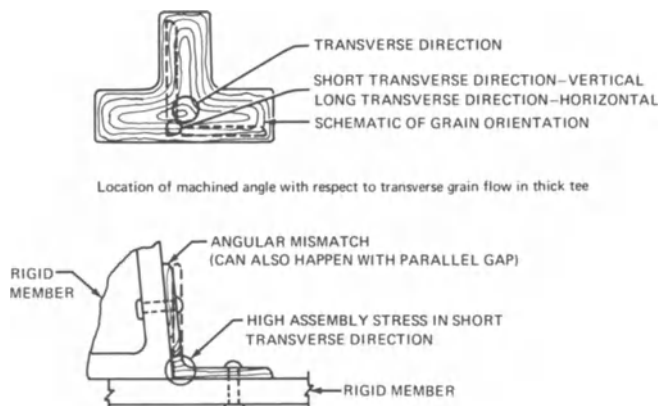


Fig. 8. Illustration of one way in which locked-in short transverse assembly stresses can result (after Spuhler and Burton⁵⁵).

Two other forms of corrosion in high-strength aluminum alloys, namely intergranular and exfoliation corrosion, are related to SCC inasmuch as the attack also occurs along grain boundaries. The role of stress is different, as discussed in the following subsections.

Intergranular Corrosion

Intergranular corrosion occurs even when there are no stresses present. This form of corrosion consists of localized attack in which a narrow path is corroded out preferentially along the grain boundaries of a metal. The mechanism is electrochemical and depends on the presence of local cells at grain boundaries. The local cells are usually caused by the presence in the grain boundaries of second-phase precipitates. During the formation of intermetallic second-phase precipitates along the grain boundaries, an adjacent denuded zone is formed that has a different solution potential. The precipitate may be anodic, such as Mg_5Al_8 , in which case it corrodes preferentially; or it may be cathodic, such as $CuAl_2$, in which case it does

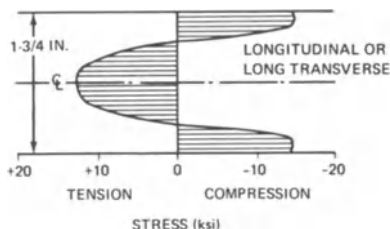


Fig. 9. Typical residual stress pattern in 7075-T6 plate given a cold-water quench and not stress-relieved (after Spuhler and Burton⁵⁵).

not corrode, but stimulates corrosion of the adjacent denuded zone. In either case, selective grain-boundary corrosion occurs. The degree of susceptibility of an alloy to intergranular attack can thus vary appreciably, depending on its microstructure (in particular, the amount, size, and distribution of the second phase), which is of course the result of its metallurgical history and thermal treatment. Heat treatments that cause precipitation throughout the grain tend to diminish the tendency to intergranular attack. It is significant that under specific conditions, Al-Mg-Si and Al-Mg-Cu alloys may suffer intergranular corrosion, but not SCC.^{51,56-58}

Exfoliation Corrosion

Exfoliation corrosion is a specific type of selective attack that proceeds along multiple narrow paths parallel to the surface of a metal. Generation of corrosion products forces the layers apart and causes the metal to swell. Flakes of metal may be pushed up and even peel from the surface. Exfoliation corrosion is most common in the heat-treatable Al-Cu-Mg, Al-Zn-Mg-Cu, and Al-Mg alloys, but it has also been observed in Al-Mg-Si alloys. This form of corrosion is associated with a marked directionality of the grain structure. Figure 10 shows an example of exfoliation corrosion in a high-strength aluminum alloy. Applied stresses are not necessary for exfoliation to occur. However, in alloys susceptible to SCC, the corrosion-product-wedging action undoubtedly contributes to the propagation of the exfoliation attack. It is important to note that some alloys not susceptible to SCC (Al-Mg-Si) may suffer exfoliation corrosion.⁵⁶ If the grain structure is equiaxed, exfoliation corrosion does not usually occur.

Smooth-Specimen Test Techniques

Traditionally, SCC data for aluminum alloys have been obtained by exposing smooth, stressed specimens to a corrosive environment.⁵⁹ Time to failure (TTF) is then plotted as a function of the applied gross section stress as illustrated in Fig. 11. Note that there appears to be a stress below which no stress-corrosion failures occur. This estimated threshold stress σ_{SCC} depends on the particular alloy, temper, grain direction, environment, and testing time; it is referred to as the smooth-specimen stress-corrosion threshold stress. Most of the available threshold stresses are listed in Table 4. Determination of the threshold stress is not a simple matter and usually requires exposure of a number of specimens stressed to each of several

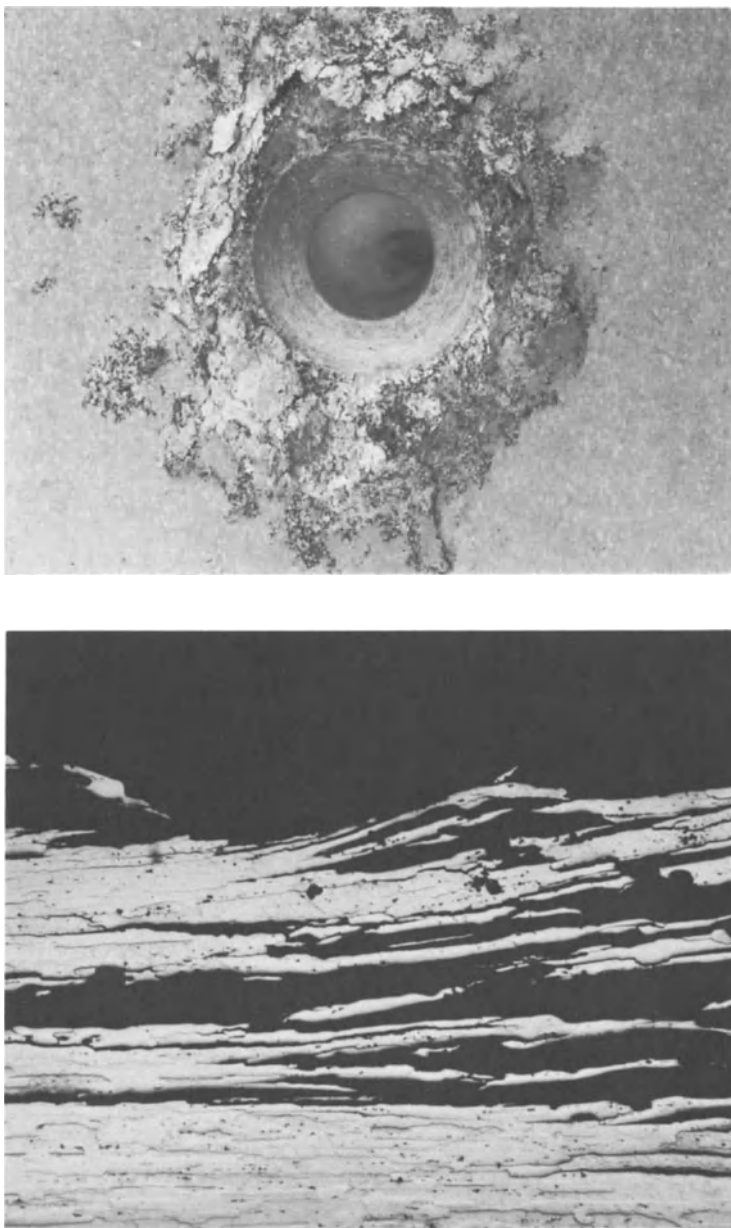


Fig. 10. Intergranular exfoliation attack around the countersink area of a fastener hole in 0.5-in.-thick 7075-T651 plate. The cross section shows the lifting of the metal grains resulting from the wedging action of the corrosion products within the intergranular crevices.

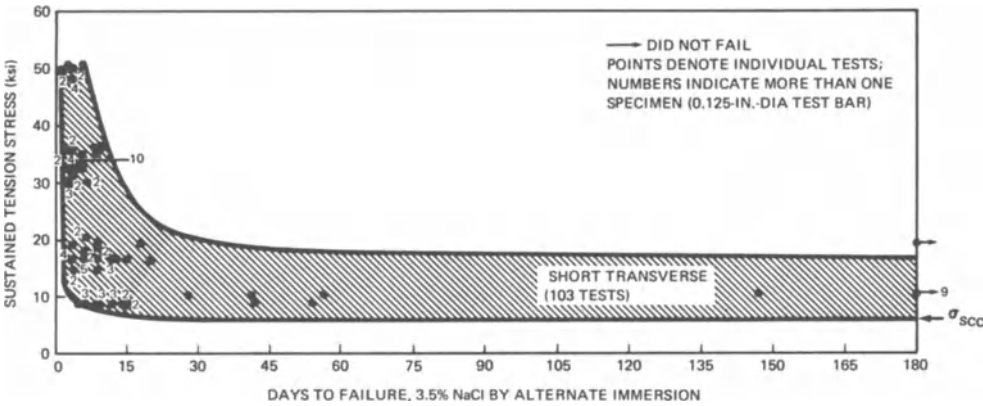


Fig. 11. Smooth-specimen stress-corrosion data for 0.25- to 3.0-in.-thick 7075-T6 plate illustrating the time-to-failure (TTF) method of obtaining threshold stresses (σ_{SCC}). For the short transverse direction, the threshold stress of 7075-T6 obtained using this technique is about 7 ksi. (After Sprowls and Brown.⁴²)

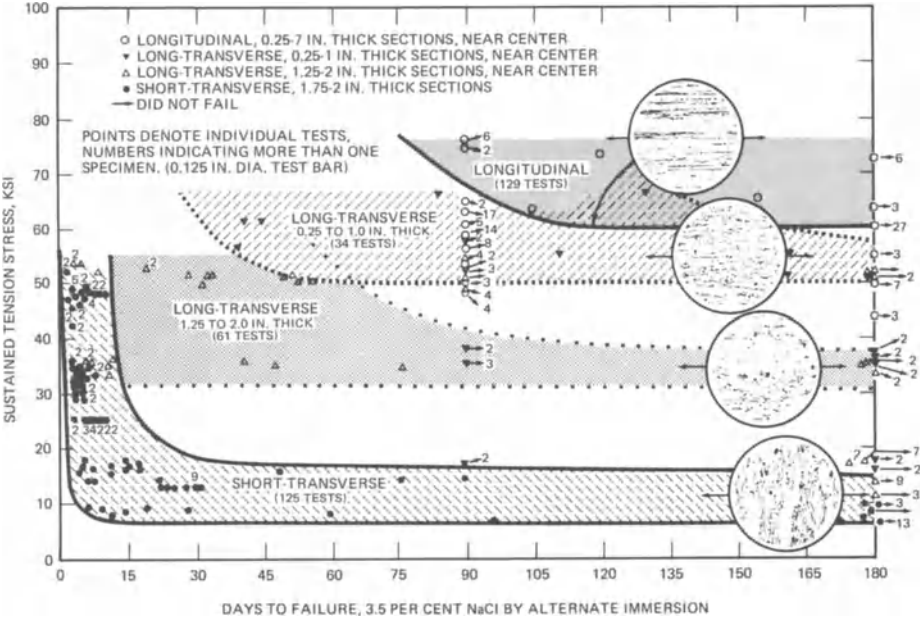


Fig. 12. Smooth-specimen stress-corrosion data for 7075-T6 extruded sections illustrating the effect of grain geometry on TTF data (after Sprowls and Brown.⁴²).

stress levels. The most widely used testing procedure involves alternate immersion in an aqueous 3.5% NaCl solution. Specimens are immersed 10 min followed by a 50-min drying period in air. Test times range from 30 to 180 days in aggressive environments like the alternate immersion test. In less aggressive environments, such as industrial atmospheres, testing times of not less than three years are required.

Failure is usually defined as either actual fracture of the specimen or the visual appearance of the first crack at some nominal magnification. It is often necessary to conduct metallographic examination on specimens at the conclusion of testing to verify test results, since failure can result from deep pitting or general corrosion rather than SCC. In addition, while some specimens may not appear to have failed by the previously defined failure criterion, sharp, intergranular stress-corrosion cracks may be found during the metallographic examination, thus indicating failure. The important influence of grain shape and orientation with respect to the stressing direction on the SCC threshold of smooth specimens is illustrated in Fig. 12 and 13.

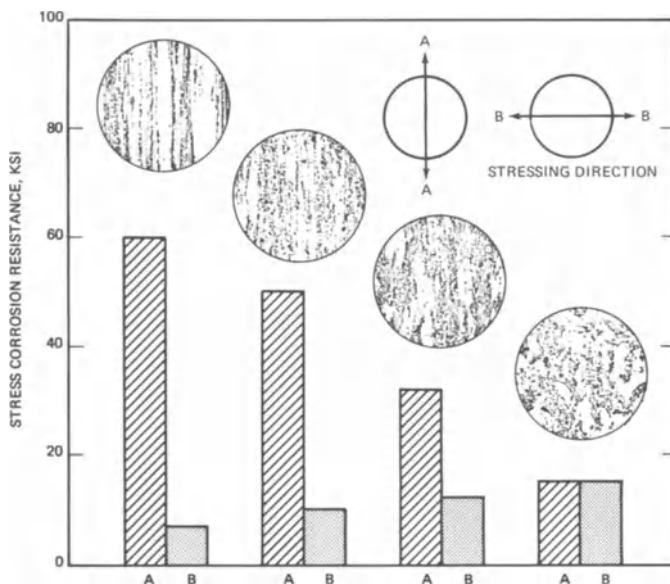


Fig. 13. Effect of grain geometry and stressing direction on resistance to stress-corrosion cracking (SCC) for 7075-T6 extrusions. This same trend is applicable to other manufactured forms of 7075-T6 and also to other high-strength aluminum alloys in a susceptible temper. (After Sprowls and Brown.⁶¹)

Note in Fig. 12 that both the threshold stress and TTF decrease as the stressing direction is changed from the longitudinal to the short transverse direction. There are two reasons for this behavior. First, the stress-corrosion cracking path is shortest for short transverse stresses, as illustrated in Fig. 14. Second, in the short transverse direction, the tensile stresses are more nearly perpendicular to the grain boundaries, and it has been shown that susceptibility to stress-corrosion cracking is a function of the resolved stress component acting normal to the grain boundaries.^{60,61} Despite the lower threshold stress in the short transverse direction, it is important to note that even in longitudinal SCC specimens, cracks can initiate easily on boundaries that are perpendicular to the applied stress.⁶² However, for cracks of this orientation, there is no available continuous intergranular path perpendicular to the stressing direction. Therefore, these cracks have great difficulty propagating by stress corrosion. Nevertheless, such shallow stress-corrosion cracks only one or two grains deep could be responsible for initiating fatigue cracks in longitudinally stressed members.

Smooth-specimen stress-corrosion testing during the last six decades has provided very useful data. It has, however, a number of severe limitations, some of which are listed below. To estimate the threshold stress σ_{SCC} :

1. Many specimens are required to estimate threshold levels.
2. Loading fixtures and stressing frames are required.
3. Smooth-specimen threshold stresses cannot be used to determine whether a stress-corrosion crack can grow in a notched or cracked specimen or part of a structure containing a flaw, since a notch or crack will intensify the local stress level above the nominal applied stress.
4. Extremely long testing times are required to estimate threshold stresses in some environments, such as industrial atmospheres.
5. Estimates of threshold stresses are of little use in studies of the fundamental mechanisms of stress-corrosion cracking, because the time-to-failure (TTF) testing has the following additional limitations: (a) Smooth-specimen TTF data include both the initiation and propagation phases of stress-corrosion cracking and do not usually allow their separation. (b) Time-to-failure data (when they include complete fracture) are affected by the fracture toughness of the material, since in tougher materials, cracks must grow to larger dimensions before reaching the critical length.

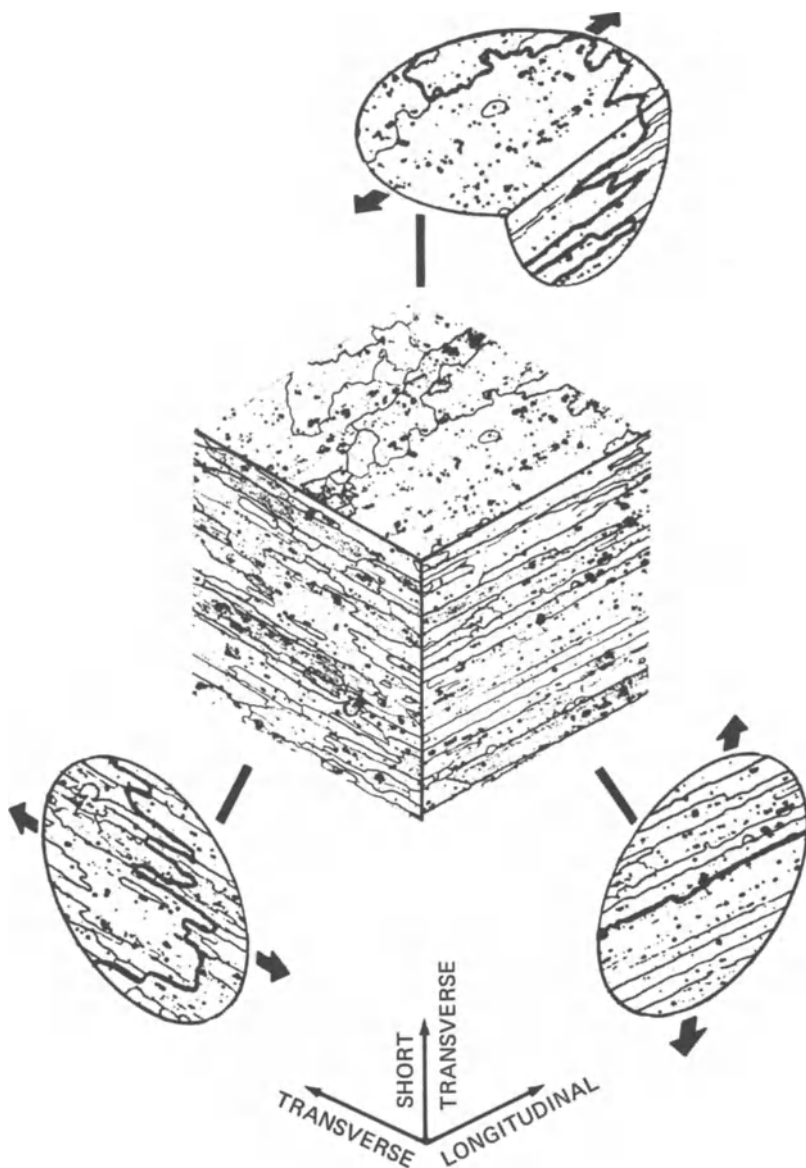


Fig. 14. Effect of stressing direction on the intergranular stress-corrosion crack path in a susceptible high-strength aluminum alloy.

Precracked-Specimen Test Techniques

There are several methods of obtaining stress-corrosion data from aluminum alloys using precracked specimens. One involves testing a series of fatigue-precracked specimens using constant loads to achieve a series of plane-strain stress-intensity K_I levels below the plane-strain fracture toughness K_{Ic} . If the cracks propagate by stress corrosion, the K_I level increases until K_{Ic} is reached and failure occurs. By plotting time to failure against initial applied-stress intensity, an apparent threshold can be determined, which is denoted K_{ISCC} .^{*} This test method is illustrated in Fig. 15. It is essentially a time-to-failure test where precracked specimens are used instead of smooth ones and the results are plotted against stress intensity instead of cross-section stress.

This method overcomes some of the objections against smooth-specimen TTF testing listed in the preceding section, since with the test results, it is possible to predict whether cracks in flawed structures can propagate by SCC. Since stress-corrosion crack growth rates in aluminum alloys can be extremely slow, failure times can be extremely long; if impatient investigators select too short testing times, erroneously high K_{ISCC} values can result. Threshold K_I levels can be estimated by mechanically fracturing precracked specimens after they have been exposed at a series of K_I levels for a sufficiently long time. Subsequent examination of the fractured specimens allows the determination of the K_I levels above which growth is observed and below which no growth is observed. For any of these tests, either the bent-beam, single-edge-notch, or surface-flaw type of specimen can be used, although it is usually difficult, if not impossible, to test the short transverse direction using such specimens unless very thick material is available.

The methods described above have been used in recent years by a number of investigators to overcome some of the disadvantages associated with smooth-specimen time-to-failure testing.^{35,36,63-66} In addition to the establishment of a K_{ISCC} using this technique, some of the first crack-velocity measurements have been made from additional fractographic observations. A more convenient and accurate technique for measuring crack growth rates as a function of the applied crack-tip stress intensity is outlined next.

^{*} It is assumed that at stress intensities below K_{ISCC} , either no crack growth or no failure occurs.

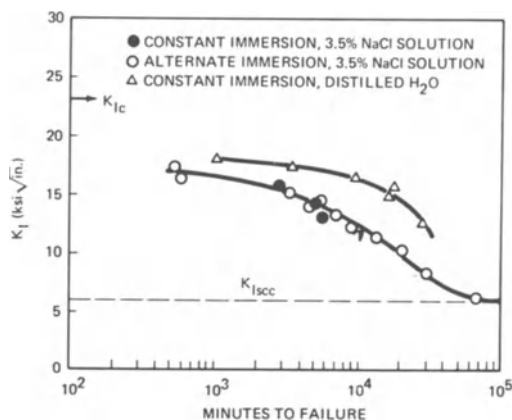


Fig. 15. Precracked-specimen stress-corrosion data for short transverse 7075-T651 plate illustrating the TTF method of obtaining " K_{ISCC} ." Using this technique, a " K_{ISCC} " of about 6 ksi in.^{1/2} is obtained. (After Mulherin.⁶³)

Crack Velocity As a Function of Stress Intensity

Obviously the knowledge of the stress-corrosion crack velocity as a function of the crack-tip stress intensity would constitute more complete and detailed information than either TTF or K_{ISCC} . The double-cantilever-beam (DCB) specimen provides the most economical and convenient method for measuring such crack velocities at known stress-intensity levels. This specimen is illustrated in Figs. 16 and 17.

Stress intensities for this DCB specimen can be calculated using a curve of compliance versus crack length and the equations^{66a}

$$G = (P^2/2b) dc/da \quad (1)$$

$$K_I = (GE)^{1/2} \quad (2)$$

where G is the crack extension force or strain energy release rate, P is the load, b is the specimen thickness, c is the specimen compliance (reciprocal stiffness) when the crack length a is measured from the load point (centerline of loading bolt), and E is the modulus of elasticity (10.5×10^6 for high-strength aluminum alloys).

Alternatively, an approximate analytical expression for compliance as a function of crack length can be obtained using beam theory. However, it has been shown^{66b} that in addition to the bending and shear deflections

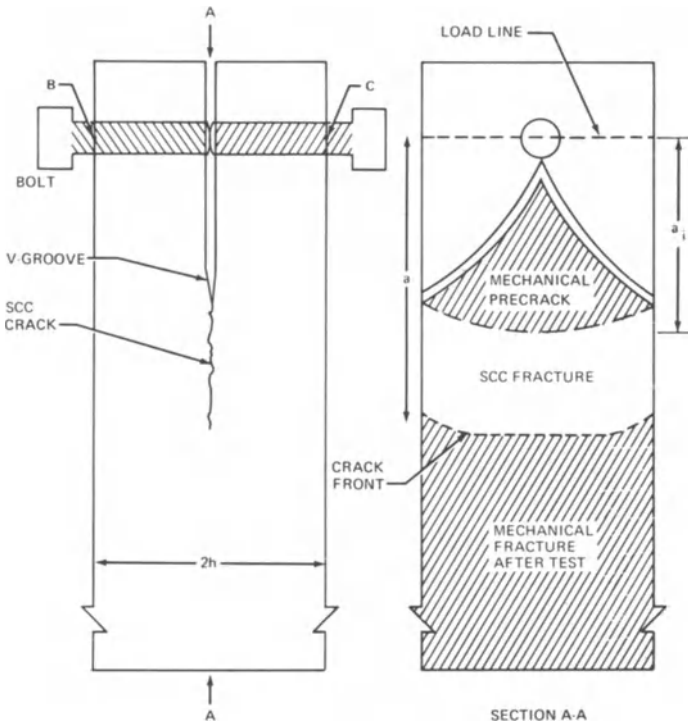


Fig. 16. DCB specimen used to determine stress-corrosion crack velocity as a function of applied stress intensity K_I (after Speidel^{44b}).

that may be calculated from beam theory, some deflection also occurs because of rotations at the assumed built-in end of the beam. By treating this contribution to compliance as an increase in crack length, the following expression for compliance was obtained^{66b}:

$$c = (2/3EI)[(a + a_0)^3 + h^2a] \quad (3)$$

where I is the moment of inertia of one of the arms, $I = bh^3/12$; a_0 is an empirical rotation correction equal to $0.6h$; and h is one-half the specimen height.

The value of a_0 was determined to be approximately $0.6h$ from calibration bars of heights from 4 to $\frac{1}{2}$ in. over 10 in. of effective crack length.^{66b} By differentiating Eq. (3) with respect to a , substituting into Eqs. (1) and (2), and noting that

$$P = \delta/c \quad (4)$$

where δ is the total deflection of the two arms of the DCB specimen at the load point, the following expression for K_I can be derived:

$$K_I = \delta E h [3h(a + 0.6h)^2 + h^3]^{1/2} / 4 [(a + 0.6h)^3 + h^2 a] \quad (5)$$

It should be noted from Eq. (5) that in DCB specimens with constant δ , the stress intensity decreases as the stress-corrosion crack grows. This is illustrated in Fig. 18.

To perform a stress-corrosion test using this specimen, the loading bolts are turned until a crack is introduced and propagated mechanically through the chevron crack starter. Crack opening displacement δ (measured between points *B* and *C* in Fig. 16) and precrack length a_i are then measured. They can be used with Eq. (5) to determine K_{Ic} . The stressed specimen is then exposed to the corrosive environment, and the crack length a

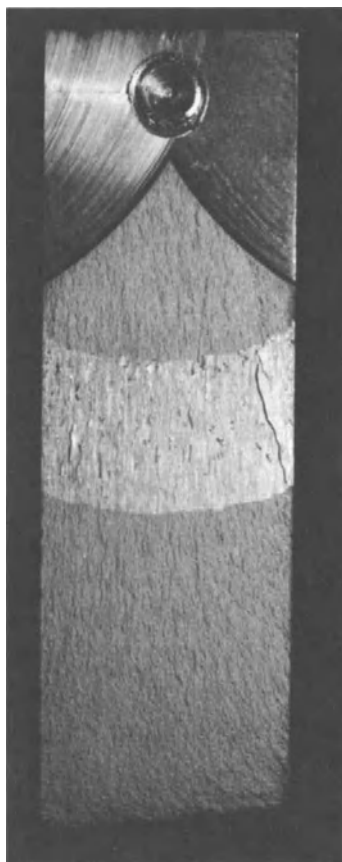


Fig. 17. Typical DCB specimen that has been broken open after testing. The mechanical precrack, stress-corrosion fracture, and post-test mechanical fracture are clearly evident (after Speidel^{44a}).

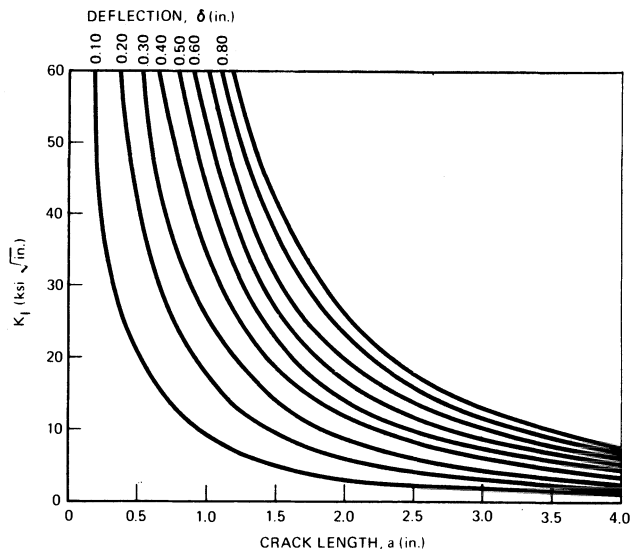


Fig. 18. K_I versus crack length for several deflections in aluminum alloy DCB specimens with a $2h$ value of 1 in. (after Hyatt⁷⁰).

is measured on the two sides of the specimen as a function of time. The crack-tip velocity is measured from the slopes of the crack length versus time curve. Stress intensities corresponding to each measured velocity can be calculated from Eq. (5) if the corresponding a and δ are known. The crack length at which growth ceases (if this occurs) is then used to calculate K_{ISCC} . The procedure is illustrated schematically in Fig. 19.

The DCB specimen is ideally suited to testing the short transverse direction of high-strength aluminum-alloy materials because the intergranular nature of stress-corrosion cracking in these alloys prevents the stress-corrosion cracks from running out of plane. Thus, in a *TL* or *TW* DCB specimen machined from plate material as shown in Fig. 7, the stress-corrosion crack will propagate down the midplane of the plate material rather than veer off, as it often does in magnesium alloys, titanium alloys, and steel. This is shown dramatically in Fig. 20, where an intercrystalline liquid-metal embrittlement (LME) crack has propagated straight along the center plane of a 1-ft-long *TL* DCB specimen of a high-strength aluminum alloy.

Most of the quantitative stress-corrosion data presented in the following sections were obtained using DCB specimens of the *TL* (short transverse) orientation. A typical result is given in Fig. 21, which shows the velocity of the tip of a stress-corrosion crack in the alloy 7075-T651 as a function of the applied crack-tip stress intensity. This is one of the key figures of

this chapter and the reader should carefully examine it before going on. It summarizes much of the progress that has recently been made with the new and quantitative stress-corrosion tests. Note that at low stress intensities, the crack-tip velocity is strongly stress-dependent. This part of the crack velocity versus stress-intensity curve (V - K curve) is labeled region I. At higher stress intensities, the crack-tip velocity is almost independent of stress. This plateau of the V - K curve is labeled region II. It is important to note that the slope in region I, when measured on a single specimen, has always been found to be finite, at least down to very low velocities

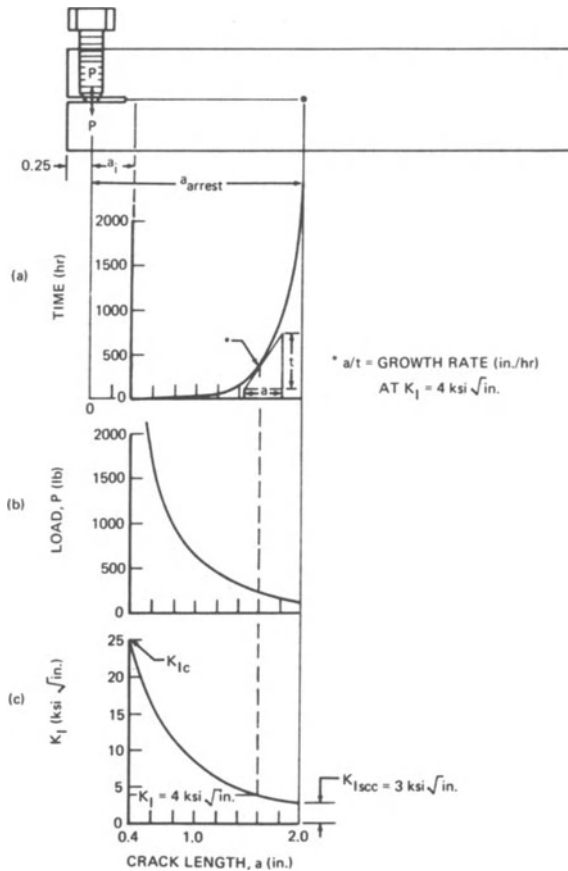


Fig. 19. Effect of crack growth on load and stress intensity under constant crack opening displacement conditions ($\delta = 0.010$ in.) in a 1- by 1- by 5-in. aluminum alloy DCB specimen (after Hyatt⁷⁰).

(10^{-8} to 10^{-9} cm/sec). This means that at the present time, no true lower limit of stress intensity (K_{ISCC}) has been observed below which stress-corrosion cracks do not propagate. Thus, minimum growth rates depend primarily on the patience of the observer. Therefore, the assumption of a K_{ISCC} value for aluminum alloys based on data shown in Fig. 15 and 21 is tech-

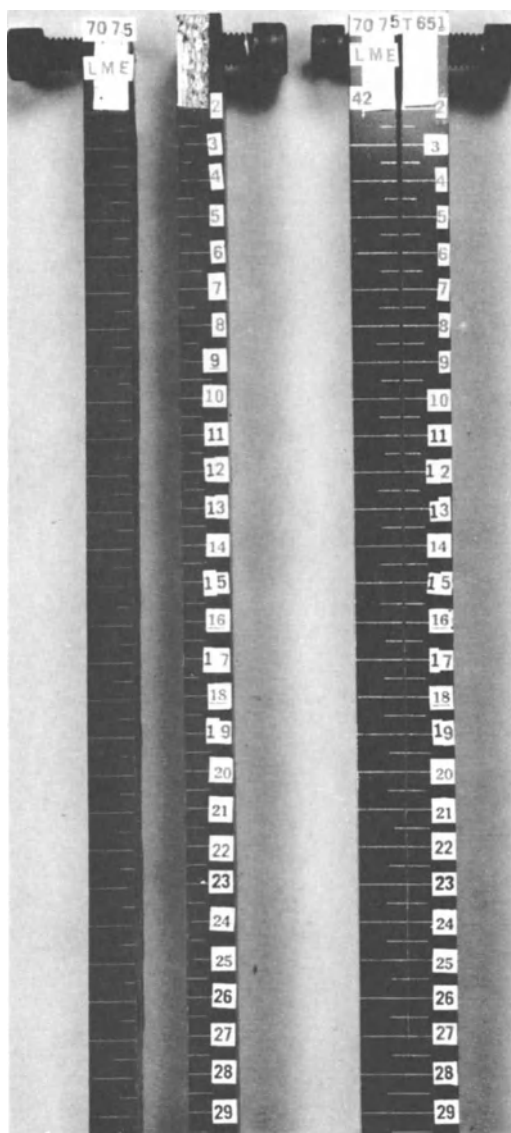


Fig. 20. TL DCB specimen 1 ft long from 7075-T651 plate used for liquid-metal embrittlement studies. The intercrystalline nature of the cracking and the elongated grain structure in the specimen have combined to keep the crack in the midplane of the specimen. (After Speidel.^{44a})

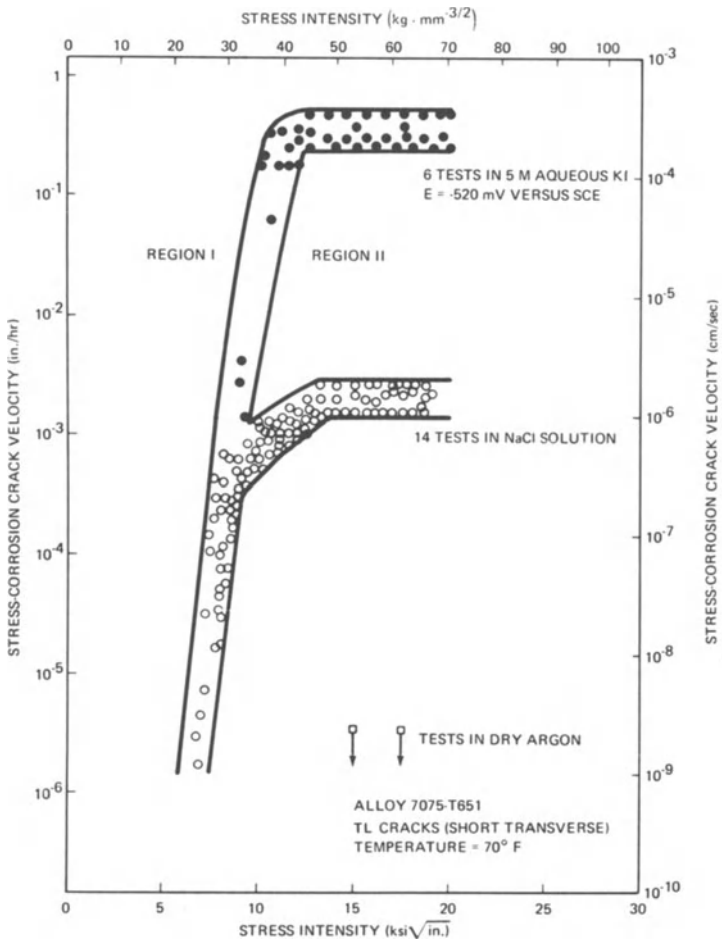


Fig. 21. Typical V - K curves for 7075-T651 obtained using TL DCB stress-corrosion specimens. Regions I (stress-intensity-dependent) and II (stress-intensity-independent) are clearly evident, as is the finite slope of the curve in region I. Note also the several orders of magnitude variation in growth rate possible in different environments. The “ K_{ISCC} ” value for 7075-T651 from these tests is just less than $7 \text{ ksi in.}^{1/2}$.

nically incorrect unless sufficiently long times are used to obtain threshold or K_{ISCC} data.

However, it is worth noting that crack growth rates become negligible at low K_I levels. We therefore propose that “ K_{ISCC} ” be defined as the stress intensity at which the stress-corrosion crack-tip velocity reaches 10^{-8} cm/sec , or about $1.4 \times 10^{-5} \text{ in./hr}$. This is the lowest crack-tip velocity

that can conveniently be measured within 30 days. It also happens to correspond to the crack growth rate that one would observe if everywhere along the crack front one atomic bond would fracture every second. According to the data shown in Fig. 21, the " K_{ISCC} " for alloy 7075-T651 in NaCl solution would be just below 7 ksi in.^{1/2}.

It is obvious from Fig. 21 that regions I and II of the V - K curve are affected differently by the environment. The fastest cracking was observed in a 5 M aqueous KI solution under potentiostatic conditions at -520 mV versus the saturated calomel electrode (SCE). Much lower crack velocities were observed in aqueous NaCl solutions under open-circuit conditions. For the alloy 7075-T651, stress-corrosion crack velocities are identical for specimens completely immersed in saturated NaCl solution and for specimens alternately immersed in 3.5% NaCl solution. Thus, the data presented in Fig. 21 have been obtained for the same alloy, crack orientation, and environment as the data in Fig. 11 (smooth-specimen TTF) and in Fig. 15 (precracked-specimen TTF, K_{ISCC}). These three figures, therefore, represent a fair comparison of the results obtained with the three different SCC testing methods for high-strength aluminum alloys.

The scatter in the SCC data presented in Fig. 21 is typical for different specimens and different heats of alloys with the same nominal composition and the same heat treatment. The scatter of the velocity data in region II is less than a factor of two; the stress intensity in region I is measured with an accuracy of ± 1 ksi in.^{1/2}. The scatter is much reduced if data from only one plate or one specimen are presented.

The velocity versus stress-intensity data for 7075-T651 in NaCl solutions shown in Fig. 21 have been generated with DCB specimens from four different plates. The velocity data in the plateau region (region II) agree very well with other published data,⁶⁸⁻⁷⁰ including seven different heats.⁷⁰ According to Fig. 21, alloy 7075-T651 should cease to stress corrode within reasonable times at stress intensities just below 7 ksi in.^{1/2}. This agrees well with a " K_{ISCC} " of about 6 ksi in.^{1/2} derived from the TTF data in Fig. 15. It seems, then, that the V - K curve shown in Fig. 21 for 7075-T651 alloy in NaCl solutions is fairly well established and reproducible, provided the tests are always done with proper care to avoid residual stresses and corrosion-product wedging.

It should be noted that for this particular alloy, the V - K curve is nearly identical for specimens that are continually immersed and for those that are alternately immersed.⁷⁰ Little or no difference between the effects of continual and alternate immersion has also been observed in time-to-failure tests on precracked specimens of 7075-T651.⁶³

For each alloy–environment combination, the stress-corrosion crack velocity versus stress-intensity curve can have a different position in the V – K diagram. Generally, it must be established experimentally and only very seldom can it be predicted. The effects of environment on the V – K curve are treated in the next Section, while the metallurgical effects and attempts to interpret and predict parts of the V – K curve are given in the subsequent two Sections.

Relationship between Data from Smooth and Precracked Specimens

Since the precracked-specimen approach is fairly new in stress-corrosion testing of aluminum alloys, it seems appropriate to discuss briefly some of the suggested relationships between stress-corrosion results from smooth and precracked specimens of high-strength aluminum alloys.

One suggested means for merging the two types of data⁷¹ is illustrated in Fig. 22. In this figure, both the SCC threshold stress for smooth specimens and the threshold stress intensity K_{ISCC} for precracked specimens are plotted versus flaw depth. The generalized equation $K = \sigma(\pi a)^{1/2}$ relating stress intensity K_I , stress σ , and flaw size $2a$, has been used to construct the K_{ISCC} lines in Fig. 22. There are two implications from this type of plot. First, to avoid stress-corrosion cracking, 7075-T6510 should not be stressed at levels above the smooth-specimen threshold stress (7 ksi), regardless of the flaw size in the material. Second, when relatively large flaws are present, 7075-T6510 should not be stressed at levels above those defined by the threshold stress-intensity K_{ISCC} . The approximate K_{ISCC} value for

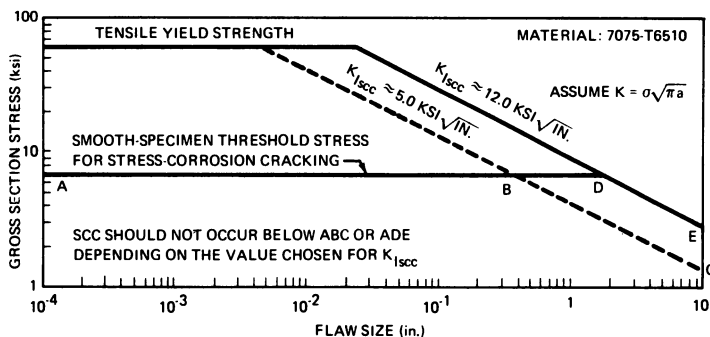


Fig. 22. Suggested method for combining stress-corrosion data on smooth and precracked specimens for predicting when stress-corrosion cracking will occur (after Kaufman *et al.*⁷¹).

7075-T6510 from Ref. 71 used to construct Fig. 22 is much higher than would be expected from the data for 7075-T651 in Fig. 15 and 21. Therefore, we have added a second K_{ISCC} line based on a value of 5 ksi in.^{1/2} to show the effect of a lower K_{ISCC} value on this type of plot.

While not particularly useful for design purposes, this type of plot does illustrate the fact that susceptible aluminum alloys are subject to failure at stress-intensity levels below the apparent K_{ISCC} , provided the stress level is above the smooth-specimen threshold stress. This fact in itself shows that the " K_{ISCC} " values in Fig. 22 are not the lower limit of stress intensity below which stress-corrosion cracking cannot occur. The reasons for this are threefold. First, as pointed out in the preceding section, even at low stress intensities and extremely low growth rates, a threshold stress intensity for aluminum alloys has not yet been observed. This is different from the observed behavior of magnesium alloys, titanium alloys, and steels in neutral aqueous halide solutions, where apparently a true K_{ISCC} exists. Second, the reason that SCC is observed below the " K_{ISCC} " in specimens with very small flaws or no apparent initial flaws (Fig. 22) is that other forms of corrosion can occur. These could be either pitting or intergranular corrosion, both of which can provide stress-raisers that could increase the effective stress intensity to levels where the growth rate is sufficiently high to cause eventual failure. (Note that pitting or intergranular corrosion may also cause changes in the local solution chemistry and thus influence the V - K curve, see the next section and the discussion section on SCC cracking in Al alloys.) Stress-corrosion failures in alloy 7039-T6 have occurred at extremely low stress levels, i.e., at stress levels below the 7-ksi level typical of that observed for other susceptible 7000-series alloys.⁷² It is significant in this context that SCC cracks in 7039-T6 have been observed to initiate at pits resulting from corrosion in laboratory air of Mg_2Si particles along grain boundaries.⁶² A number of other factors could also provide effective stress intensities higher than those calculated. These include local plastic deformation, cracked intermetallic particles, and residual stresses. Third, the assumption $K_I = \sigma(\pi a)^{1/2}$ in Fig. 22 is an oversimplification. It would be more appropriate to adjust K_I values with a correction factor that takes into account the depth of the flaw with respect to the specimen size. For the relatively small specimens generally used in stress-corrosion testing, this factor is not insignificant and could increase appreciably the actual crack-tip stress intensities over those shown in Fig. 22 for the flaw depth listed there.

A quantitative example is given as follows: Assume that a crack is present on one face of a smooth tension specimen of square cross section,

resulting effectively in a single-edge-notched tension specimen. Assume also that a growing stress-corrosion crack in a round tension specimen simulates a single-edge notch in a specimen of square cross section. Then the equation $K_I = \sigma_g(\pi a)^{1/2} Y$ for a single-edge-notched specimen⁷³ can be used to calculate a family of K_I versus crack-depth curves for various gross stress levels. Such a family of curves is shown in Fig. 23 for a square specimen whose cross-sectional area was made equal to that of a round, 0.25-in.-diameter tension specimen of the type commonly used for stress-corrosion testing purposes. Thus, the stress levels in Fig. 23 are similar to those for a round tension specimen of 0.25-in. diameter.

If an effective K_{ISCC} around 5 ksi in.^{1/2} is assumed, then it would be possible, according to Fig. 23, to achieve this K_I level at gross stresses of 20 ksi with a flaw only 0.014 in. deep. For stresses above 40 ksi, a crack depth of only about 0.004 in. is sufficient to achieve a K_I level of 5 ksi in.^{1/2}. It certainly seems reasonable that such shallow flaws could readily be attained during a stress-corrosion test by simple intergranular attack or pitting. The K_I would increase with crack depth, according to Fig. 23, and stress-corrosion crack growth rate would increase with this increasing K_I level, according to Fig. 21. Failure would occur at a critical stress intensity.

At the lower stresses, say the threshold stress of 7 ksi, a sharp crack nearly 0.062 in. deep is required to attain a K_I level of 5 ksi in.^{1/2}. For a

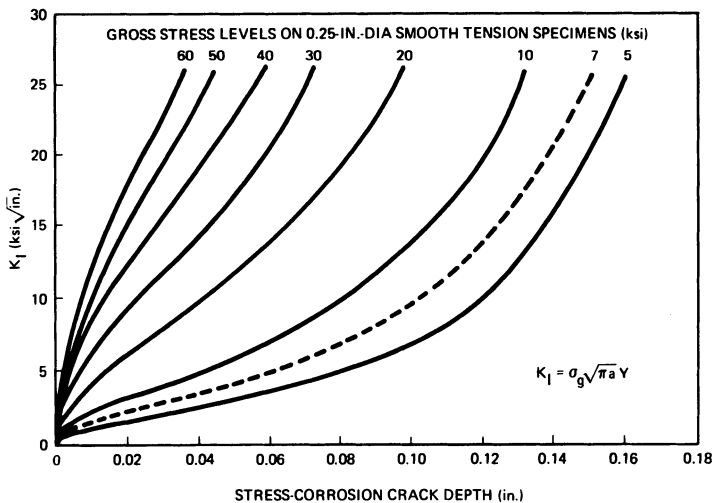


Fig. 23. Approximate stress intensity versus crack depth curves for single-edge-notched tension specimens loaded to different gross stress levels (after Hyatt⁷⁰).

gross stress below the threshold, say 5 ksi, a 0.080-in.-deep flaw is required to achieve a K_I level of 5 ksi in.^{1/2}. Such flaw depths are an order of magnitude greater than those required at the higher gross stresses, and it can easily be visualized that at some low stress (the threshold stress), the crack depth required for reaching a K_I level where significant growth rates can be achieved is so deep that, in the normal alternate-immersion test periods for smooth specimens, failure will not occur. In addition, at these lower stresses, general corrosion or pitting corrosion can proceed at a rate sufficient to blunt out any sharp, slow-growing intergranular crevices, thus making the effective K_I level even lower than that shown in Fig. 23. This combination of events simply prevents the crack from propagating a sufficient distance to cause failure within the usual testing times.

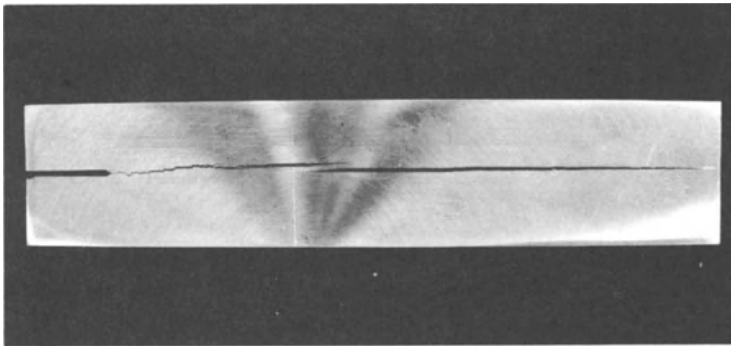
Experimental Difficulties in Testing Precracked Specimens

Experience gained with many hundreds of tests to date has shown that there are a number of experimental problems that must be overcome if accurate V - K curves are to be obtained. These problems are discussed below.

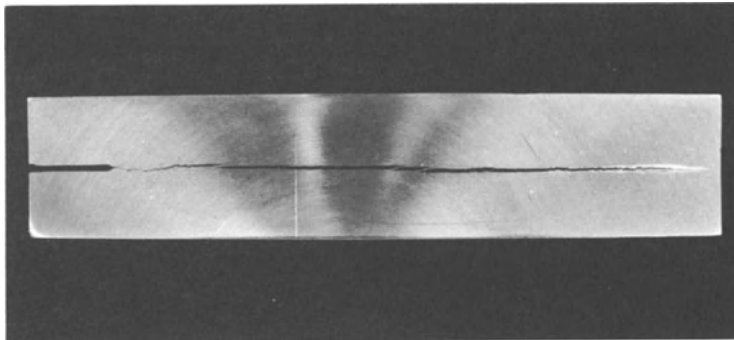
Residual Stresses

When DCB specimens are machined from heat-treated, quenched, and aged material that has not been stretched or compressively stress-relieved after quenching, residual stresses can cause large errors in K_I levels calculated from Eq. (5). Error is introduced by the bowing apart of the DCB specimen arms due to the residual compressive stresses on the surface of the specimen. Bowing in a DCB specimen is illustrated in Fig. 24. This bowing action results in an increased crack opening displacement (COD) at the crack tip and hence an increased K_I level. The effectiveness of these residual stresses in causing crack propagation should not be underestimated, since cracks have been observed to propagate completely through DCB specimens even though the specimens were unloaded and the loading bolts removed after the initial crack had been popped in (Fig. 24). Crack growth rate data for such specimens are often independent of the applied K_I level calculated using crack length, deflection at the loading bolt, and Eq. (5). Either the K_I level in these specimens is being maintained in region II of the V - K curve (Fig. 21), or residual stresses keep the crack-tip stress intensity constant.

If DCB specimens are heat treated and quenched at high rates, they will contain residual compressive stresses on all surfaces. These stresses



(a) Side 1



(b) Side 2

Fig. 24. Bowing of DCB specimen arms due to residual surface compressive stresses from the quenching operation. This specimen was machined from 1-in.-thick 7075-T651 plate and reheat-treated to a highly susceptible condition (860°F, cold-water quenched, aged 72 hr at 158°F). Crack propagation in this specimen was caused solely by the residual quenching stresses from reheat treatment, since the loading bolt was removed after pop-in. (After Hyatt.⁷⁵)

retard the growth of the stress-corrosion crack near the surface. Therefore, the growing stress-corrosion crack will bow out and lead in the center. Bowing of the crack front causes errors in the stress intensity calculated from Eq. (5) because the position of the crack front through the thickness of the specimen is not known. Bowing of the crack front in a specimen containing residual stresses is shown in Fig. 25. In extreme cases, the stress-corrosion crack may propagate only in the center of the specimen, where it can reach a considerable length without ever reaching the surface where it could be observed. This is illustrated in Fig. 26.

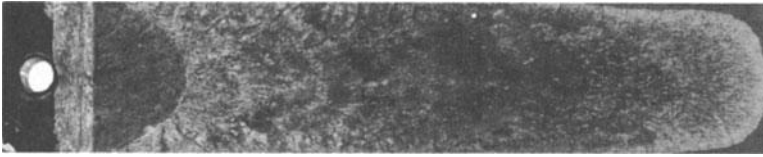


Fig. 25. Crack-front bowing in a DCB specimen due to residual surface compressive stresses from the quenching operation. Both the pop-in and stress-corrosion cracks are severely bowed. This specimen was machined from 7075-T651 plate and reheat-treated to the T6 condition (860°F, cold-water quenched, aged 24 hr at 250°F). (After Hyatt.⁷⁶)

Similar problems are encountered if DCB specimens are machined from hand or die forgings containing quenched-in residual stresses; the K_I levels calculated for such specimens based on Eq. (5) are not valid. In this connection, the effect of residual stresses on the behavior of DCB specimens has clearly demonstrated the important role that quenched-in residual stresses can play in the propagation of stress-corrosion cracks in actual parts. Thus, in many cases, it may be extremely dangerous to predict growth rates in an actual part based on a K_I level calculated from assumed loads and crack geometry. Local geometry changes in the part (similar to the bowing action in DCB specimens) may be keeping the K_I level much higher than that calculated.

The majority of the quantitative stress-corrosion data reported in this chapter for the high-strength aluminum alloys were obtained from plate material that was stretcher-straightened to remove residual stresses. This is indicated in the temper designation, TX51, for stretcher-straightened material.

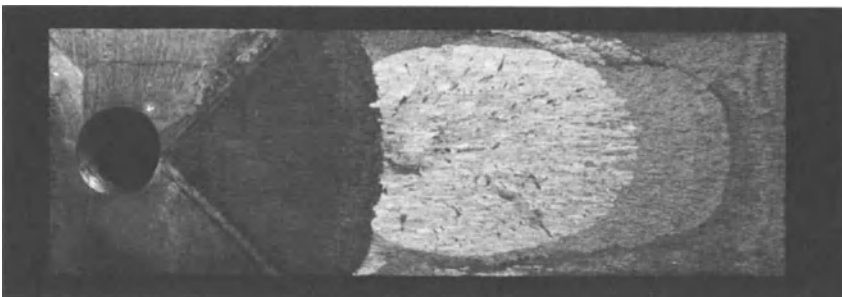


Fig. 26. Extreme example of the effect of residual quenching stresses on crack growth in aluminum alloy DCB specimen. Crack growth from the pop-in crack has occurred only in the interior of this reheat-treated, nonstress-relieved specimen.

Corrosion-Product Wedging

The buildup of corrosion products in the crack of a DCB specimen can cause stresses at the crack tip. These stresses can reach an intensity higher than the crack-tip stress intensity applied by external loading. This has been observed in both 2000- and 7000-series alloys.^{44,45,70} Thus, K_I values calculated from Eq. (5) can be in error. In extreme cases, the corrosion-product-wedging action can be so severe that the loading bolts are lifted free, with the entire stress being supplied by the corrosion products.^{44,70}

There are two ways to determine that corrosion-product wedging has not introduced errors into the measured V - K curves. First, the DCB specimen can be unloaded after the test and the deflection at the load line can be remeasured and compared to the deflection at the beginning of the test. If the two are nearly equal, no substantial amount of corrosion products has accumulated in the crack. Second, when, at low applied crack-tip stress intensities, the crack growth rate becomes immeasurably small, one can conclude that corrosion-product wedging is insignificant.

Specimen Orientation and Grain Flow

Grain flow in forgings varies with location in the part. Because stress-corrosion cracks are intergranular in high-strength aluminum alloys, they follow the grain flow (see Fig. 27). Therefore, care must be taken to ensure that DCB specimens are machined from forgings in such a way that they are loaded normal to the grain flow. If they are not loaded in this manner, growth rates several orders of magnitude slower than those in the short transverse direction can result. For example, growth rates were more than four orders of magnitude slower for *WL* (long transverse) DCB specimens machined from 7079-T651 plate than for *TL* (short transverse) DCB specimens (see Fig. 28).

Crack Branching

Generally, stress-corrosion cracks in commercial high-strength aluminum alloys in the *TL* and *TW* directions do not branch. The same is true in forgings if cracks grow along a direction of pronounced grain flow. If, however, an equiaxed grain structure exists, macroscopic crack branching is possible under certain conditions⁷⁷:

1. The V - K curve must show a K_I -independent region (e.g., region II in Figs. 21 and 28).

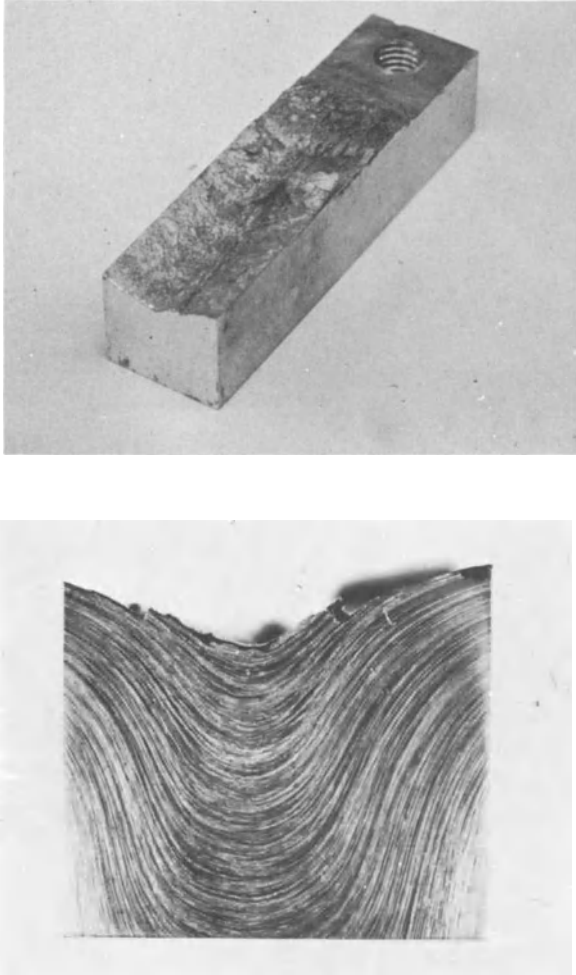


Fig. 27. DCB specimen from a 7175-T66 die forging illustrating the tendency for stress-corrosion cracks to follow the grain flow.

2. The crack-tip stress intensity at the point of branching must be at least 1.4 times the stress intensity at which region II begins (point *B* in Fig. 28).

Note that these conditions are necessary, but not sufficient, for branching.

A macroscopically branched stress-corrosion crack in a DCB specimen from a forging of 7079-T6 is shown in Fig. 29. Branching occurred on only

one side of the specimen, where the grain structure was equiaxed (Fig. 30). On the other side of the same specimen, the grain structure was elongated and the crack did not branch.

Stress-corrosion-crack branching can be a real problem in testing high-purity, high-strength aluminum alloys because these alloys are generally recrystallized and have an equiaxed grain structure. An example is shown in Fig. 31.

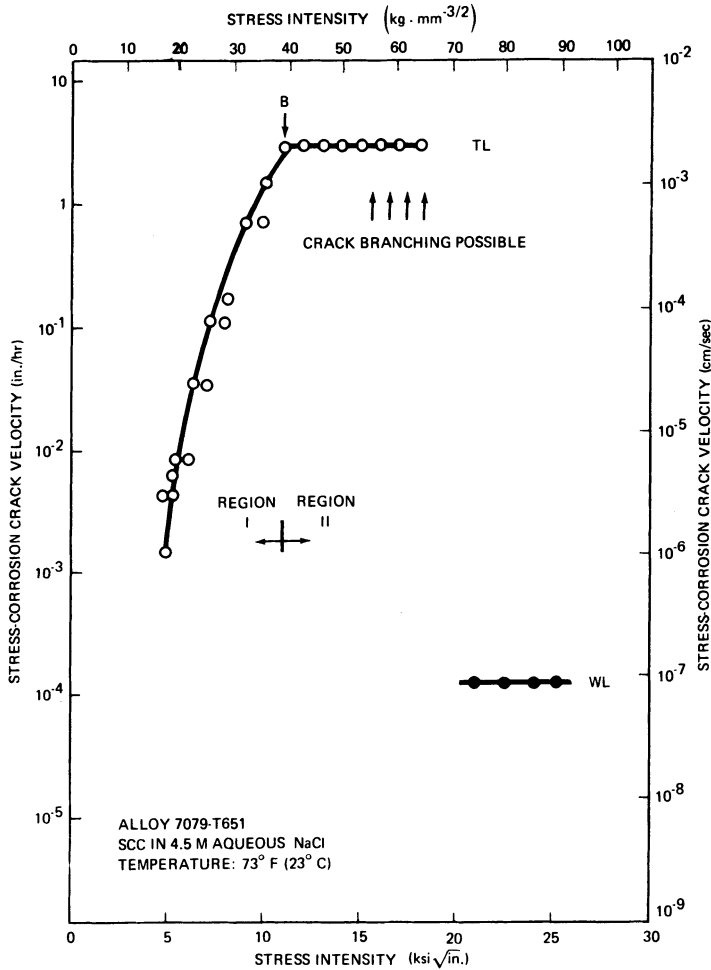


Fig. 28. Effect of specimen orientation on V - K curves of 7079-T651. Crack velocities in region II are four orders of magnitude faster for the short transverse (TL) orientation than for the long transverse (WL) orientation.

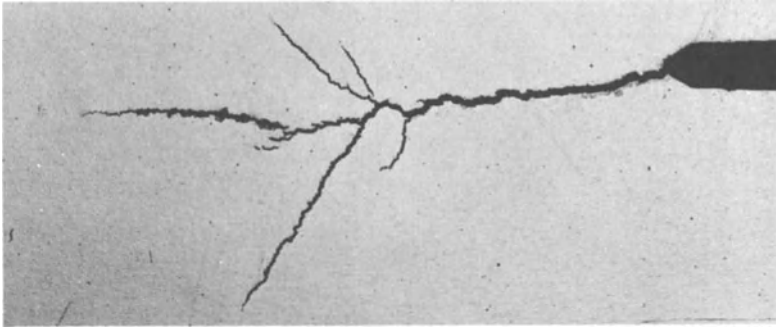


Fig. 29. Branching of a stress-corrosion crack on one side of a DCB specimen machined from a large 7079-T6 die forging.

Stress-corrosion-crack branching is a problem because cracks grow away from the symmetry plane of the specimen and therefore the K_I values obtained from Eq. (5) are invalid. This problem can be overcome by applying an initial stress intensity low enough to avoid branching.

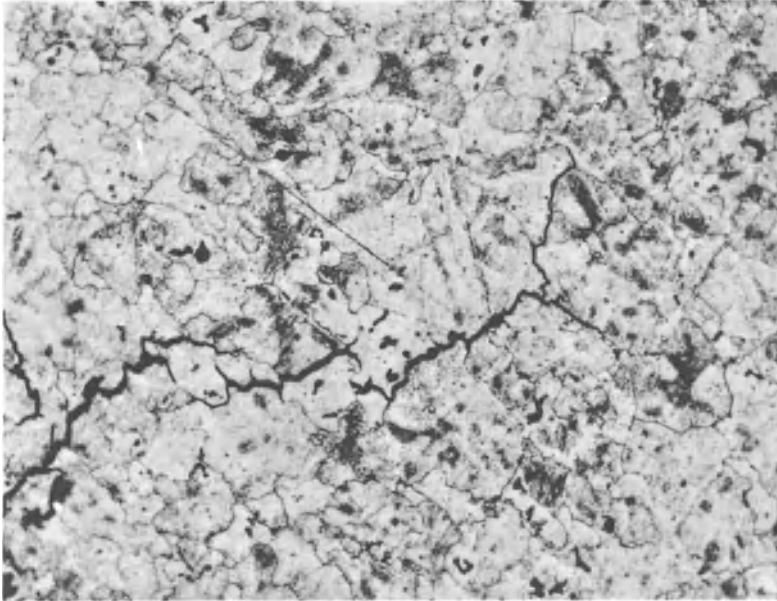


Fig. 30. Equiaxed microstructure on the branched side of the DCB specimen shown in Fig. 29 (200 $\times$).

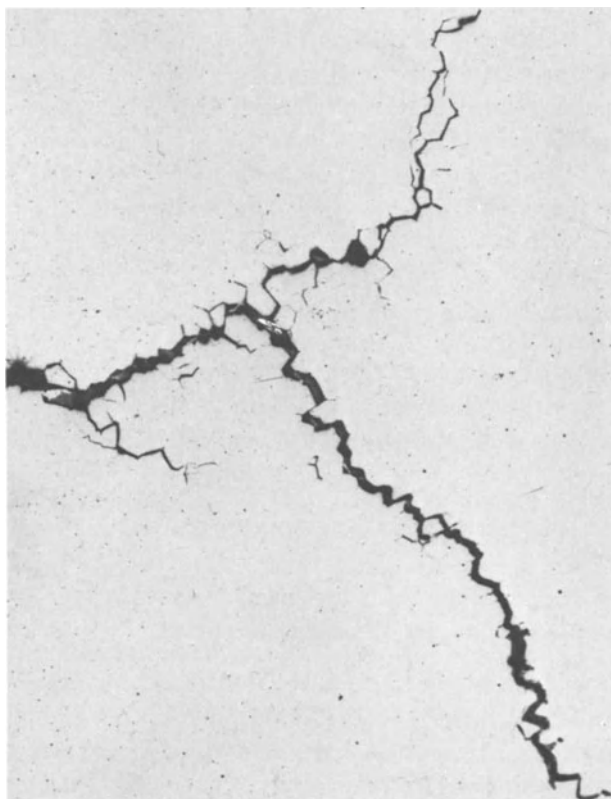


Fig. 31. Branching of a stress-corrosion crack in a high-purity alloy having a recrystallized and equiaxed grain structure.

Delamination

When specimens with precracks in *LT* and *WT* orientations are SCC tested, delamination (grain-boundary separation along *TL* and *TW* planes) can occur. This can effectively blunt the crack, thus invalidating the calculated stress intensity.⁶⁴

Short Testing Times

Stress-corrosion crack growth rates observed in aluminum alloys can be extremely slow (10^{-5} in./hr or less, 10^{-7} cm/sec or less). Therefore, long testing times may be required to accurately determine the lower end of the *V-K* curve. Long testing times can be a problem, either because data are required immediately or because testing facilities cannot be tied up for long

periods of time. Moreover, it has often not been realized that instead of a K_{ISCC} , region I of the V - K curve must be determined; i.e., cracks often do not stop even though they may slow down considerably. For these reasons, short test runout times can lead to erroneously high K_{ISCC} values. Too short testing times could cause significant problems when it becomes necessary to ensure integrity in aluminum-alloy pressure vessels for use in deep-space probes (three-year mission to Mars and back, for example).

Relating Laboratory Data to Crack Growth in Service

Under service conditions, the environment as well as the stress level varies with time. Therefore, laboratory data should be supplemented with tests conducted in actual and simulated service environments.

Advantages of Precracked Specimens for SCC Testing

The use of precracked DCB specimens for stress-corrosion testing of aluminum alloys has several advantages.

1. Measurement can be made of the stress-corrosion crack-tip velocity as a function of the crack-tip stress intensity. Thus, while smooth-specimen data cannot be used to evaluate failure times of flawed structures or to prescribe loads below which unintentionally flawed structures will not fail in a given time, precracked specimen data can be used for these purposes. It is not intended that precracked specimens should replace all smooth specimens for stress-corrosion testing of aluminum alloys. Rather, such precracked-specimen data are a valuable addition to the smooth-specimen threshold data in the same way that fatigue crack growth data are a valuable addition to the standard S - N fatigue curves for different alloys.⁷⁰ And, like fatigue crack growth data, actual stress-corrosion crack growth data can be useful for setting inspection intervals and for monitoring a variety of structures. In addition, " K_{ISCC} " values can be used to establish loads which ensure that structures containing possible undetectable flaws will operate safely in corrosive environments during their design lifetimes. Specific examples where precracked-specimen data (rate and K_{ISCC} data) have actually been used are given below (p. 159).

2. Use of DCB specimens can eliminate scatter due to the initiation of stress-corrosion cracks in smooth specimens. This raises hopes that for the first time reproducible test results can be obtained in different laboratories.

3. The DCB specimen can be used equally well for fundamental studies and alloy development and design, making communications between these various disciplines much easier.

4. The simple design, low cost, portability, and self-stressing capability of the DCB specimen, and the ease with which data are generated from this specimen, are the keys to its eventual widespread use.

5. When testing smooth tension specimens for SCC, it is good testing practice to expose unstressed specimens simultaneously with stressed specimens, since stressed specimens could fail simply by cross-section reduction due to intergranular, pitting, or general corrosion. Such a double check is not needed with DCB specimens because all possible effects of corrosion can be studied on the unstressed part of the same specimen after the test. Thus, when the DCB specimen is broken open after a SCC test, the crack face will show not only the depth of the SCC crack, but also the depth of pits and intergranular corrosion in the unstressed part of the specimen.

Some Advantages of Smooth-SCC Specimens

Smooth-specimen stress-corrosion tests measure a sequence of phenomena in one test. i.e., initiation and propagation of cracks, and this can be an advantage for practical applications. In cases where crack initiation takes up a major part of the time to failure, smooth specimens are useful to simulate service behavior of a flawless structure. In addition, a wealth of smooth-specimen data have been generated over the past several decades for most of the high-strength aluminum alloys currently in use. This makes the use of smooth-specimen test techniques attractive in alloy development since the new alloy can be compared directly with the well-known alloys already in service. However, alloys can be rated equally well using crack growth rate data at known K_I levels, and it is thought that such test techniques will eventually be preferred over the smooth-specimen test technique for many applications.

Some Specific Applications of Precracked-Specimen Data

The use of threshold stress intensity data in actual design is probably best illustrated in the case of pressure vessels for the U. S. space program.^{35,36,64,65} In such cases, the relationships connecting fracture toughness (K_{Ic}), threshold stress intensity level (K_{ISCC}), applied stress intensity level (K_{Ii}), operating stress (σ_{op}), and proof test pressure ($\sigma_{op} \times \text{proof test factor } \alpha$) are illustrated in Fig. 32.

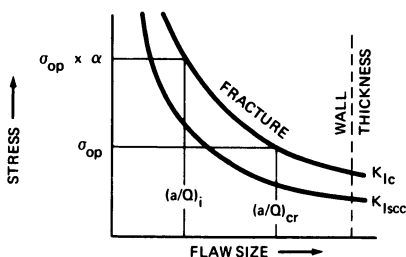


Fig. 32. Use of K_{Ic} and K_{ISCC} criteria in pressure-vessel and critical-burst design (after Lorenz³⁶).

In this particular instance, vessels successfully passing a proof test at the $\sigma_{op}\alpha$ stress level are presumed to have defects not larger than $(a/Q)_i$ (Fig. 32). Any preexisting defects larger than $(a/Q)_i$ would cause bursting since the intersection of the $\sigma_{op}\alpha$ horizontal line with the vertical projection of a flaw larger than $(a/Q)_i$ would fall to the right of the K_{Ic} curve or into the fracture region.

At the operating stress level σ_{op} , a pre-existing flaw as large as $(a/Q)_i$ would remain stationary under sustained load because the resultant K_{Ii} is smaller than the K_{ISCC} , as seen from the fact that the intersection of the σ_{op} and $(a/Q)_i$ lines falls to the left of the intersection between the K_{ISCC} curve and the σ_{op} line. If the vessel were subjected to cyclic loading at σ_{op} , the initial flaw $(a/Q)_i$ would grow in size by fatigue until it reached the $(a/Q)_{cr}$ size, at which point bursting would occur.

In a thinner-walled pressure vessel, the critical flaw size $(a/Q)_{cr}$ may be larger than the wall thickness (Fig. 33). In this case, the vessel would be safe to operate at σ_{op} sustained load just as in the previous case; again, the maximum initial flaw size $(a/Q)_i$ that could remain after proof test is smaller than what would be required to generate K_{Ii} above the K_{ISCC} level. If this vessel were subjected to cyclic loading, the flaw would again grow in size, but the pressure vessel would leak and depressurize rather than burst because the wall thickness is less than the critical flaw size $(a/Q)_{cr}$. In both cases, a relatively short fatigue-crack extension could increase the crack-tip stress intensity above K_{ISCC} , resulting in failure by SCC even

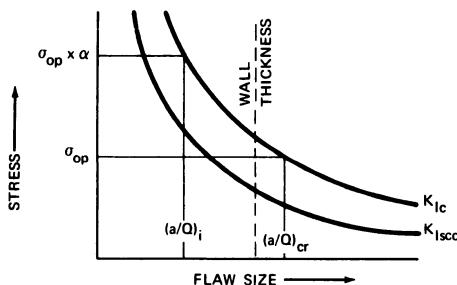


Fig. 33. Use of K_{Ic} and K_{ISCC} criteria in pressure-vessel and leak-before-burst design (after Lorenz³⁶).

without further cycling. If the V - K curve for the material-environment combination were known, it would be possible to predict quantitatively the remaining lifetime of the pressure vessel.

V - K curves have actually been used in setting inspection intervals for structural parts known or suspected to contain flaws. In one case,⁷⁸ serious stress-corrosion problems arose in a large, machined 7075-T6 forging used to transmit loads from the wing to the fuselage of a fighter aircraft. An attempt was made to determine inspection intervals such that the largest undetectable flaw could not grow to a critical size between inspections. To set a realistic inspection interval, the small amount of stress-corrosion crack growth rate data for 7075-T6 available at the time⁶³ was examined. An equation for the growth rate da/dt as a function of K was determined, and the time necessary for growth from initial to critical flaw size for given load conditions was determined by integrating the expression between the appropriate limits. This work was carried a step further⁷⁸ by incorporating into the crack growth equation a term accounting for simple intergranular corrosion, which, in the assumed model, precedes the rapid stress-accelerated corrosion stage. Further modifications to the formula incorporated the smooth-specimen stress-corrosion threshold stress and an initiation term.

This early work illustrated the need for more stress-corrosion crack growth rate data as a function of stress intensity in several commonly encountered environments. It also illustrated the need for more data on the rates of intergranular attack, since this mode of corrosion may precede the stress-accelerated form of cracking. Much of the data in the next section should be useful in this regard and should make analysis of the type just described both more quantitative and more accurate.

EFFECTS OF ENVIRONMENT

In this section, an attempt is made to present the known quantitative experimental data concerning the effect of environment on the growth of stress-corrosion cracks in high-strength aluminum alloys. Most of these data come from very few sources, and many results of quantitative stress-corrosion tests are presented here for the first time.

The environment has a most important effect on the nucleation and growth of subcritical cracks in high-strength aluminum alloys. Actually measured crack velocities in a single alloy may range over more than nine orders of magnitude, depending solely on the environment that fills the

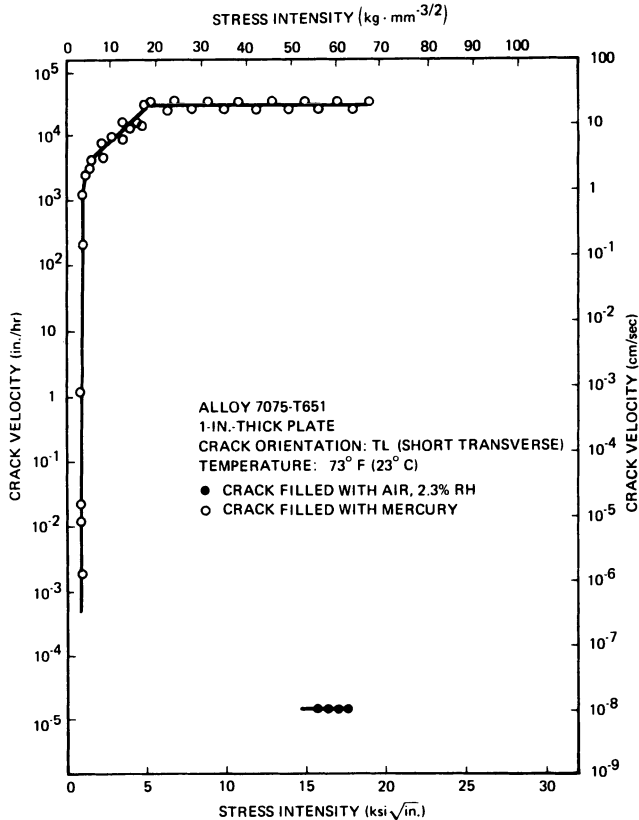


Fig. 34. Fastest and slowest subcritical crack growth measured in a high-strength aluminum alloy.

crack. This is illustrated in Fig. 34, which shows both the fastest and slowest subcritical crack velocities ever measured in a high-strength aluminum alloy. Note the big difference in stress-independent velocities due to different environments. Note also that the shape (but not the position) of the V - K curve for cracks filled with a liquid metal is very similar to the shape of the V - K curve for cracks filled with aqueous halide solutions, as shown in Fig. 21.

Throughout this section, it must be kept in mind that stress-corrosion cracks are influenced not only by the environment, but also by the microstructure of the alloy and by the crack-tip stress intensity. The effect of metallurgical (microstructural) parameters is exemplified by the large reduction of the crack growth rate when the crack orientation is changed with respect to the preferred orientation of the grain boundaries, as il-

illustrated in Fig. 28. The effect of the crack-tip stress intensity on crack-tip velocity is obvious at low K_I levels, as can be seen from Figs. 21, 28, and 34, and many of the following illustrations. Thus, for a meaningful comparison of the effects of various environments on stress-corrosion crack growth rates, the metallurgical and mechanical parameters should be known and controlled. A simple and reliable method to assess the effect of various environments on stress-corrosion cracking is to measure only the stress-independent region II of the V - K curve, the so-called "plateau velocity." For detailed studies, it is of course necessary to measure the full V - K curve as a function of the environment.

Gaseous Environments

Gaseous environments are among the most important ones to consider, since obviously the use of high-strength aluminum alloys in air is widespread. The qualitative tests of yesteryear (time-to-failure) have indicated that the water vapor content of gaseous environments might have a specific effect on SCC.⁷⁹ It is therefore mandatory for quantitative stress-corrosion tests that the water content of all gases investigated be known and controlled.

Hydrogen Gas

Aluminum alloys do not appear to be embrittled to any appreciable extent by high-purity hydrogen gas at ambient temperature.⁸⁰ Tensile strength and ductility of alloys 6061-T6 and 7075-T73 are not substantially reduced when the test environment is changed from helium to hydrogen of 10,000-psi pressure, and the same is true for notched specimens of these alloys.⁸¹ No loss in mechanical properties and no change in fracture behavior is observed when alloy 7039-T61 is tested in hydrogen up to 10,000 psi.⁸²

The effect of high-pressure, high-purity hydrogen gas on subcritical crack growth of aluminum alloy 2219-T6 was studied with surface-flawed, part-through-crack specimens,⁸⁵ as outlined earlier (p. 138). The results of such tests are shown in Fig. 35. These results indicate that the threshold stress-intensity factor (K_{TH}) for this alloy exposed to hydrogen gas at 5200 psi was about 28 ksi in.^{1/2} for specimens from 0.75- and 1.00-in.-thick plates. Corresponding data for weld metal in welded specimens indicated that the threshold stress intensity was about 26 ksi in.^{1/2} for the hydrogen environment. Since these tests proved that base metal and weldments of 2219-T6E46 aluminum alloy retain their load-carrying capability in pressurized hydrogen gas at stress intensities of more than 80% of their respective

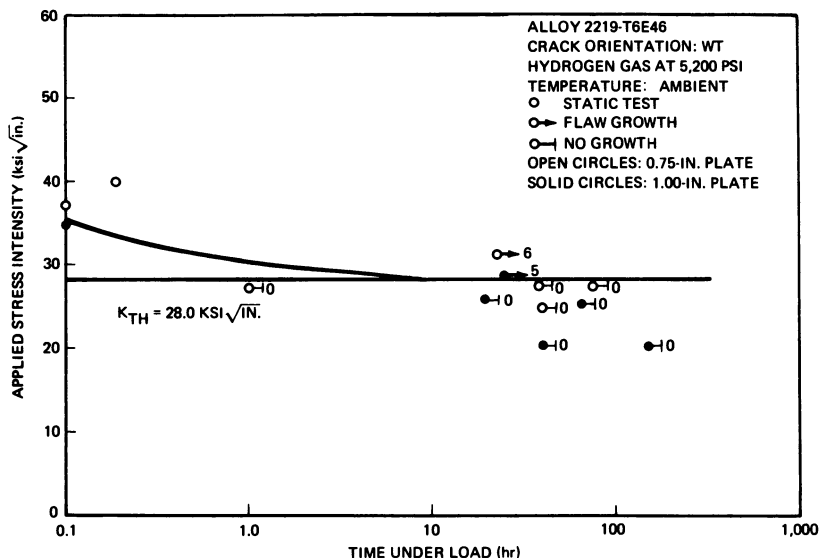


Fig. 35. Sustained-load crack growth in pure hydrogen gas. The numbers next to the points indicate the extent of crack growth in thousandths of an inch. (After Lorenz.³⁵)

fracture toughness values, the alloy is recommended for pressure vessels containing hydrogen gas.³⁵

Four of the most widely used high-strength aluminum alloys showed no crack growth when precracked, stressed to near K_{Ic} , and exposed to dry hydrogen for 47 days, as illustrated in Fig. 36. The hydrogen gas used was at room temperature and 1-atm pressure. The relative humidity was less than 0.01%. The fact that no crack growth could be observed indicates that the crack growth rate was smaller than 4×10^{-6} in./hr. Note in Fig. 36 that after a long period of no growth in dry hydrogen, crack growth starts immediately when the relative humidity is increased to 100%.

Crack-tip velocity as a function of crack-tip stress intensity in moist hydrogen gas is shown in Fig. 37 for the same four high-strength aluminum alloys. Note that the V - K curves show the familiar shape, a stress-dependent part at low stress intensities (region I) and a stress-independent part (region II, plateau) at higher stress intensities. The plateau velocities of the four alloys are rather similar, about 10^{-3} in./hr. Characteristically, region I of the V - K curve of the copper-lean alloys 7079 and 7039 extends to lower stress intensities than does region I of the copper-rich alloys 7075 and 7178. Thus, the latter two alloys could be called more resistant to subcritical crack growth in the moist hydrogen atmosphere. Microscopic

examination of the crack faces shows typical intercrystalline stress-corrosion cracks, indistinguishable from those obtained in many other environments.

Remember that no subcritical crack growth was observed in dry hydrogen gas of 1-atm pressure. The maximum growth rates that could have escaped detection are indicated in Fig. 37. In summary, it can be said that it is the water content of low-pressure hydrogen that causes stress-corrosion cracking in susceptible high-strength aluminum alloys.

Argon

Figure 38 summarizes stress-corrosion cracking of five susceptible, commercial high-strength aluminum alloys in gaseous argon that contained less than 1 ppm oxygen, hydrogen, and nitrogen. As can be seen by comparing Figs. 36–38, there are a number of similarities between SCC in hydrogen and in argon. These similarities have also been observed in a number of other gases, including air:

1. Stress-corrosion cracks neither initiate nor propagate in the dry gases.

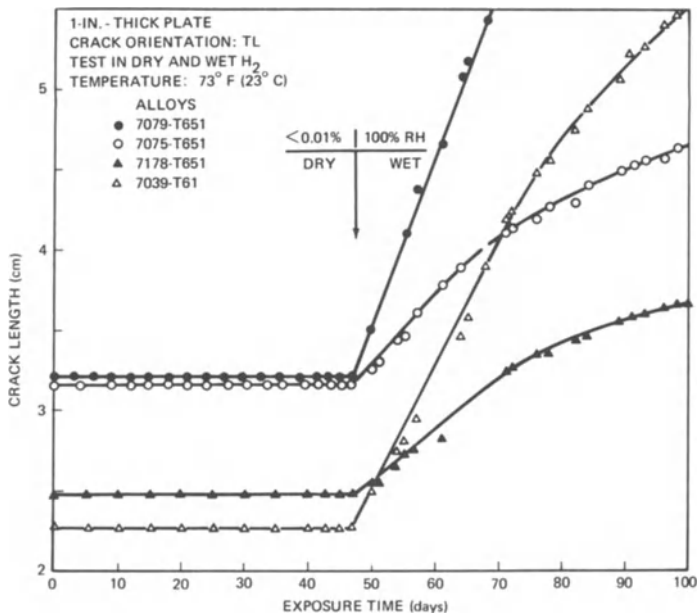


Fig. 36. Effect of humidity on stress-corrosion crack growth of high-strength aluminum alloys in hydrogen gas (after Speidel^{44a}).

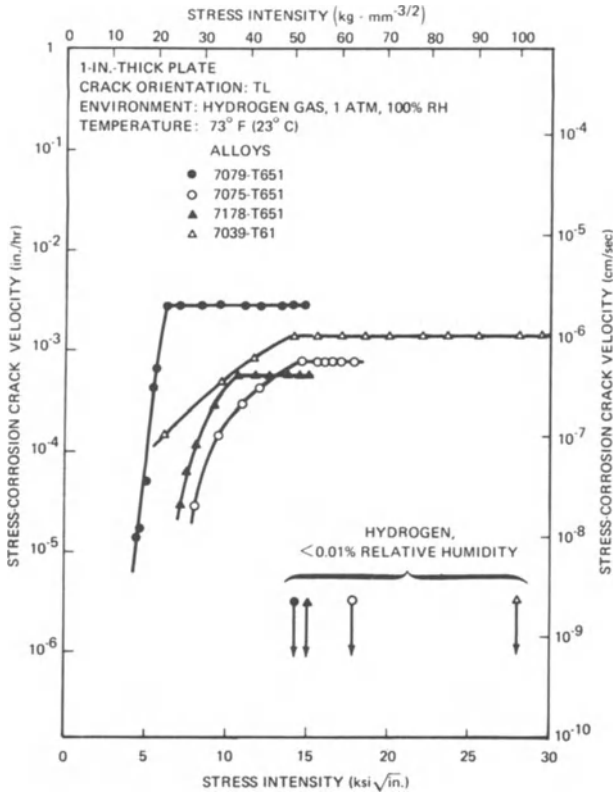


Fig. 37. Stress-corrosion crack velocity of four high-strength aluminum alloys, plotted as a function of crack-tip stress intensity in moist and dry hydrogen gas.

2. Stress-corrosion cracks are initiated immediately from precracks stressed to near K_{Ic} in the wet gases (Fig. 36).
3. In gases containing 100% relative humidity, crack growth occurs with a velocity of about 10^{-3} in./hr in the stress-independent region II of the V - K curve.
4. The stress-dependent crack velocity in region I of the V - K curve is strongly influenced by the metallurgical parameters, with alloy 7079-T651 being most susceptible, followed by 7039-T61, 7178-T651, and 7075-T651.

Note that stress-corrosion cracks in wet argon are faster by far than in dry hydrogen (compare Figs. 38 and 37).

Dry argon is sometimes used as an inert reference environment when the effect of other environments on subcritical crack growth is investigated. It is therefore of interest to know quantitatively the crack propagation rates in dry argon, since they could be used as a baseline. For the alloys mentioned in Fig. 38, no crack growth was observed in dry argon and the growth rate that could have escaped detection was less than 3×10^{-6} in./hr. We suspect that most commercial high-strength aluminum alloys will behave similarly and will exhibit no stress-corrosion crack growth in dry argon. As a significant exception, however, a high-purity ternary Al-Mg-Zn alloy showed subcritical crack growth in dry argon with a crack velocity of about 10^{-8} in./hr. These data are incorporated in Fig. 39. Note that more aggressive environments, such as moist air, greatly accelerated crack growth in the

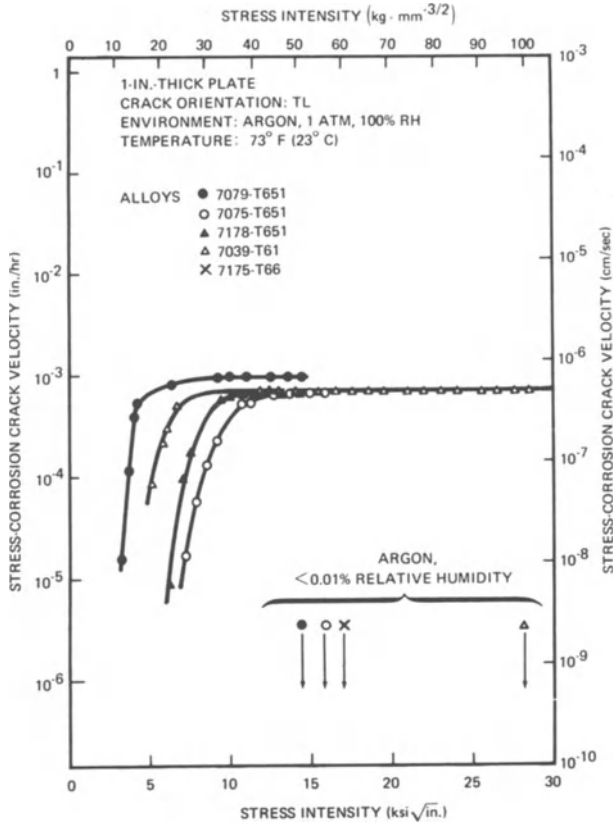


Fig. 38. Stress-corrosion crack propagation of high-strength aluminum alloys in moist and dry argon.

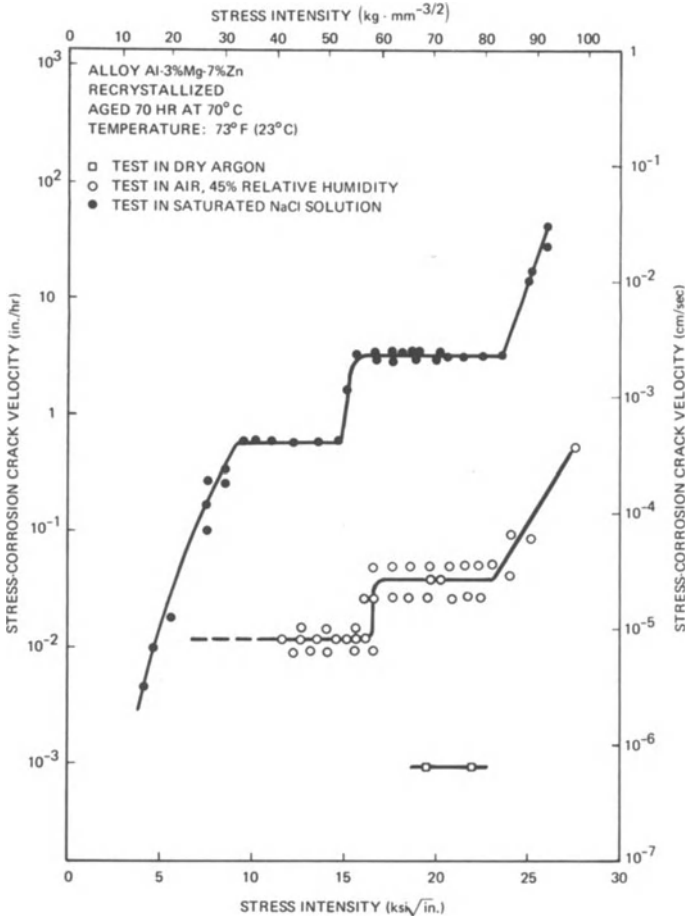


Fig. 39. Propagation of stress-corrosion cracks in a high-purity Al-Mg-Zn alloy exposed to dry argon, moist air, and a saturated NaCl solution.

alloy. This indicates that even in the high-purity alloy, subcritical crack growth is environment-sensitive and therefore is rightly called stress-corrosion cracking.

The recrystallized high-purity alloy in Fig. 39 shows two velocity plateaus and a stress-dependent velocity at the highest stress intensities. This latter region of the V - K curve is labeled region III and it has not yet been observed in commercial high-strength aluminum alloys, although it is quite common with other material-environment combinations. Because of this anomalous behavior and because of the exceptional crack growth

in dry argon, the engineer and practical metallurgist need to pay only limited attention to the results of stress-corrosion studies with the rather academic high-purity aluminum alloys of recrystallized, equiaxed grain structure. Commercial high-strength aluminum alloys are of superior stress-corrosion resistance even in the critical short transverse direction.

Nitrogen

Alloy 7075-T651 is reported to show no crack growth in dry nitrogen.⁸³ This fact and the behavior of many alloys in air (discussed below) make it highly probable that stress-corrosion cracking of susceptible high-strength aluminum alloys in nitrogen follows the same rules as outlined for argon and hydrogen in the preceding paragraphs.

Air

Stress-corrosion cracks of susceptible high-strength aluminum alloys in air follow the same rules as outlined above for argon and hydrogen. However, since moist air is doubtless the most widespread environment in which high-strength aluminum alloys are used, a more detailed review of the present knowledge is appropriate.

Dry Air (less than 0.01% relative humidity). Neither initiation nor propagation of stress-corrosion cracks is observed with the alloys 7079-T651, 7039-T61, 7039-T64, 7178-T651, 7075-T651, 7075-T7651, 7075-T7351, 7175-T66, 2024-T351, and 5456-H321.⁴⁴ The propagation that could have escaped detection is slower than 3×10^{-6} in./hr, based on microscopic observations of large DCB specimens that were precracked, stressed to near K_{Ic} , and exposed to air for 56 days. Neither the specimen surface nor the crack face (after the DCB specimens were broken open mechanically) showed any sign of intercrystalline crack growth detectable with a low-power microscope. This is significant because it shows that no intergranular separation (e.g., due to creep) occurs in the absence of traces of water. These data are incorporated in Fig. 40. Stress-corrosion cracks that initiate and grow in moist air can be stopped by transferring the specimens to dry air, as has been done with alloy 7075-T651.⁴⁴

Moist Air. Stress-corrosion test results of several high-strength aluminum alloys in air with 100% relative humidity are presented in Fig. 40. A comparison of Fig. 37, 38, and 40 reveals that the behavior of stress-corrosion cracks in air is analogous to that in argon and hydrogen as outlined above. Note in Fig. 40 that the plateau velocities are around 10^{-3}

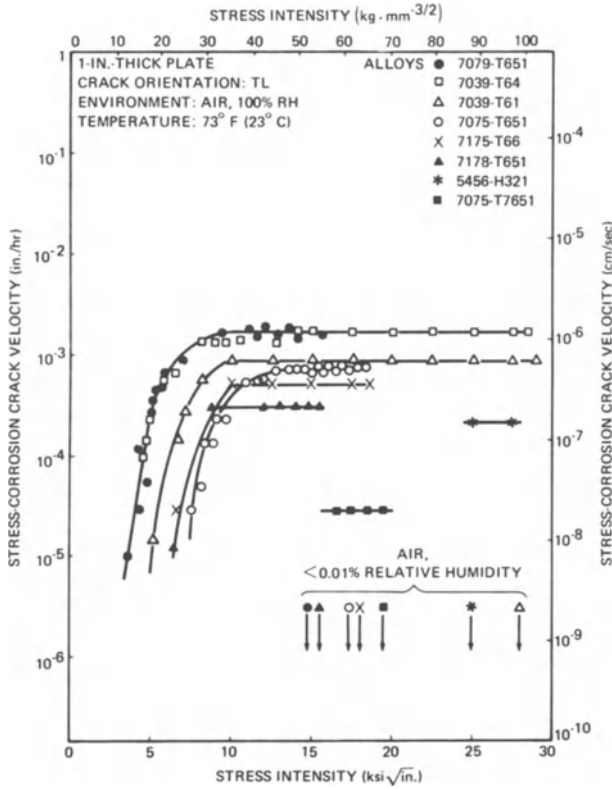


Fig. 40. Stress-corrosion crack propagation in high-strength aluminum alloys exposed to moist and dry air.

in./hr and that the V - K curves of alloys 7079 and 7039 extend to lower stress intensities than the V - K curves of alloys 7075, 7175, and 7178.

The obvious analogies between SCC of high-strength aluminum alloys in various dry and moist gases indicate that it is the water vapor rather than the individual gases that causes, SCC. The effect of water vapor concentration on subcritical crack growth in gaseous environments has been quantitatively determined for a number of high-strength aluminum alloys in moist air.⁴⁴ Figure 41 illustrates the effect of water content of the air on the velocity of stress-corrosion cracks in the stress-independent region of the V - K curve for the widely used alloy 7075-T651. These results indicate that the stress-corrosion crack velocity in the plateau region (region II) depends linearly on the water vapor content of the air. It would be of interest to know how the stress-dependent velocity in region I is affected by the moisture of the air. However, because of the very slow crack growth

rates involved, no systematic experimental data are available at this time. Figure 42 summarizes the present knowledge on stress-corrosion crack growth rates in air and also puts it in perspective with respect to crack growth observed in aqueous halide solutions. The crack velocity versus stress-intensity curves of specimens tested in air with 40% or higher relative humidity join the scatter band (from Fig. 21) of specimens tested in aqueous halide solutions at low stress intensities. The crack growth rate data (Fig. 42) in air of 27% relative humidity indicate that lowering the humidity in air may displace region I of the V - K curve to higher stress intensities.

Outdoor Exposure

Stress-corrosion cracks in specimens exposed to the outdoors can be alternately filled with gases and liquids due to rainy and dry periods. Figure 43 shows the growth rate of stress-corrosion cracks in a number of susceptible high-strength aluminum alloys exposed on a rooftop in Seattle, Washington. The V - K curves are very similar to those for moist gases presented in the preceding section. The plateau crack velocity of alloy

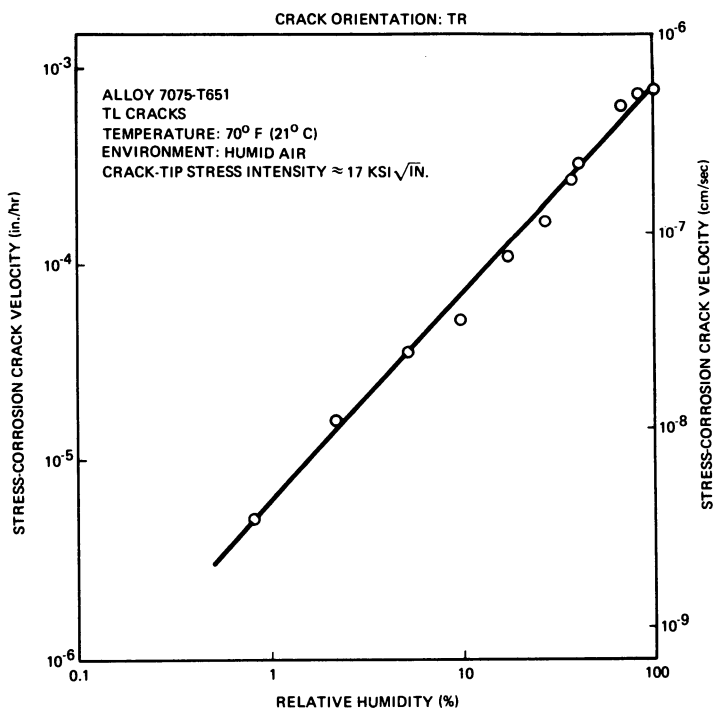


Fig. 41. Effect of humidity of air on stress-independent stress-corrosion crack velocity of a high-strength aluminum alloy (after Speidel^{44a}).

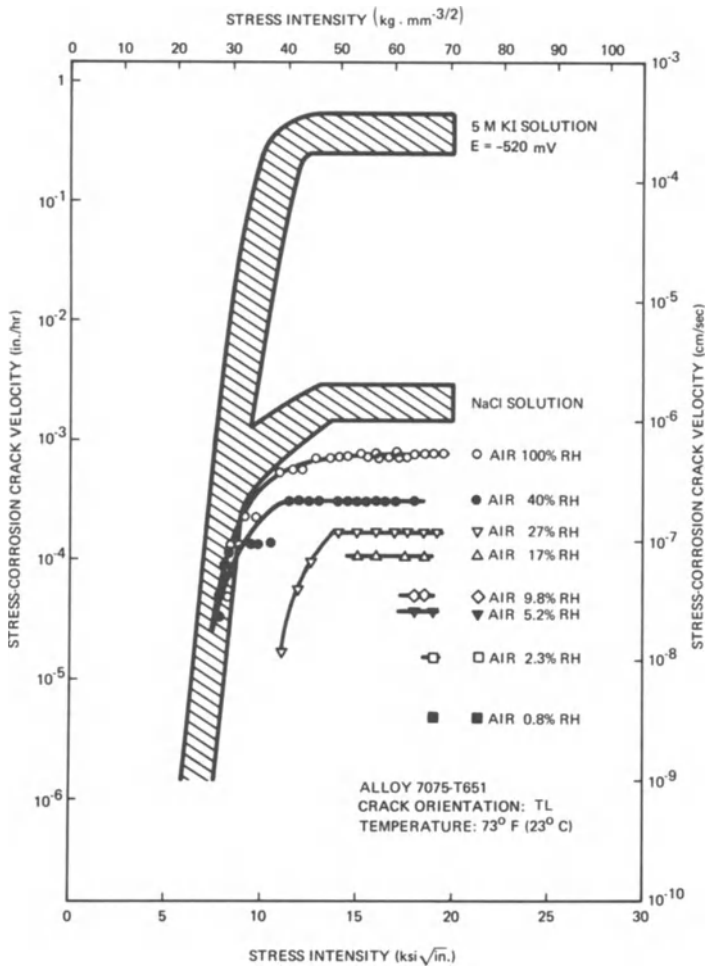


Fig. 42. Effect of humidity and stress intensity on stress-corrosion crack velocity of a high-strength aluminum alloy.

7075-T651 equals about the value expected from Fig. 41 for the prevailing relative humidity. Alloy 7079 again shows the fastest crack growth rate down to the lowest stress intensity, once more confirming that this alloy is by far the most SCC-susceptible one among the commonly used high-strength aluminum alloys, a fact that only too well correlates with its known poor service behavior. The excellent stress corrosion resistance of alloy 2219-T87 in an outdoor environment is immediately obvious from Fig. 43.

Smooth SCC test specimens of many high-strength aluminum alloys have been exposed in the stressed condition to both seacoast and inland atmospheres. Typical results are shown in Fig. 44.⁴² Note that in the seacoast atmosphere, all alloys listed seem to have the same smooth-specimen threshold stress of 7 ksi. However, in the inland industrial atmosphere, alloy 7079-T6 cracks not only fastest, but also at the lowest stress levels. This is consistent with the results shown in Fig. 43 for precracked specimens, as well as with the service behavior of the alloy. A different kind of com-

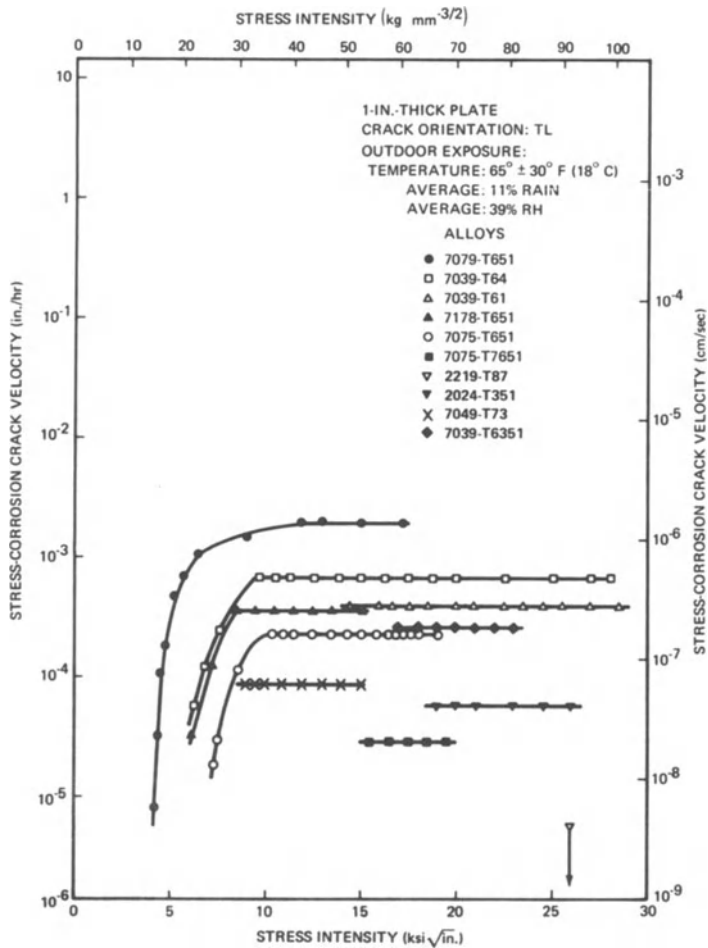


Fig. 43. Effect of outdoor exposure and stress intensity on stress-corrosion crack velocity of several high-strength aluminum alloys.

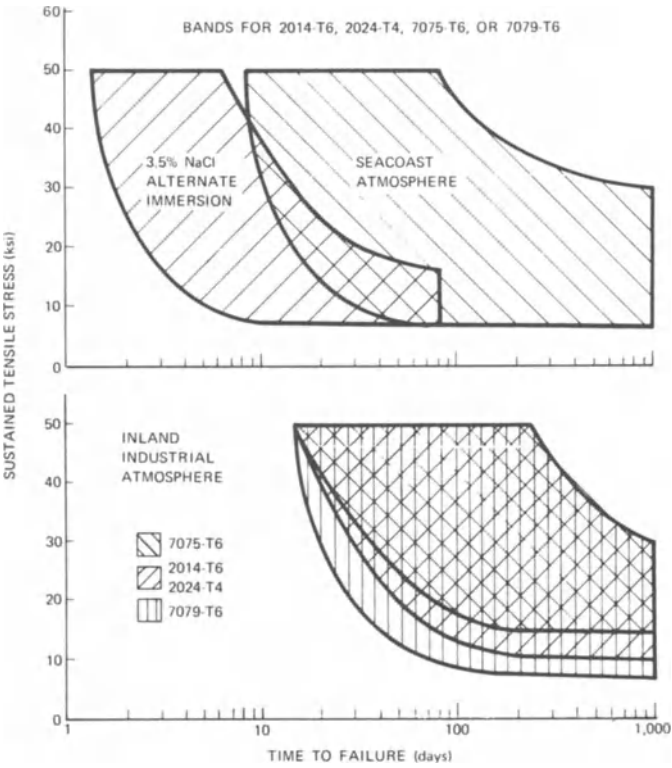


Fig. 44. Time to failure by stress corrosion of smooth specimens stressed in the short transverse direction and exposed to three different environments (after Sprowls and Brown⁴²).

parison of the SCC resistance of high-strength aluminum alloys in various atmospheres is shown in Fig. 45; the probability of failure of smooth SCC test specimens is compared for four different alloys in three different environments. Note the significant high percentage of failure of alloy 7079-T6 specimens in an industrial atmosphere when stressed to only 15% of their yield strength. If more attention is given to such data, the incidence of SCC service failures in future designs can be greatly reduced. Unfortunately, the smooth-specimen threshold stress level from 3.5% NaCl alternate-immersion tests cannot always be relied upon to assess the SCC susceptibility of high-strength aluminum alloys, and the results of such tests do not indicate any difference between many alloys when tested in the critical short transverse direction (see Table 4). Here is a clearcut case where the method of determining V - K curves using precracked specimens is not only

cheaper and faster than other methods, but it also shows quantitatively just how much more susceptible than other alloys 7079-T6 really is (see Figs. 37, 38, 40, and 43).

Aqueous Solutions

Since the preceding sections pointed out that water can be a stress-corrosion agent for high-strength aluminum alloys, it might be suspected that all aqueous solutions would cause SCC of susceptible high-strength aluminum alloys. With very few exceptions, this is indeed true. No effective inhibitor has yet been found to prevent a stress-corrosion crack from growing in a susceptible high-strength aluminum alloy exposed to an aqueous solution. Buffered solutions with a high *pH*, although they reduce SCC when compared to neutral solutions, often cause other severe corrosion problems, such as alkaline attack. Therefore, a stress-corrosion threat always exists when susceptible alloys are stressed and exposed to aqueous solutions.

Distilled Water

Many high-strength aluminum alloys exhibit almost identical crack growth rates whether tested in gaseous atmospheres of 100% relative

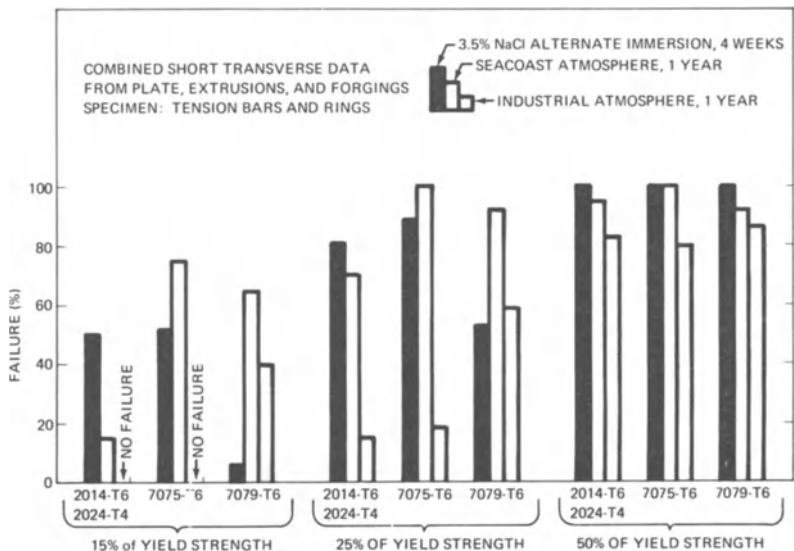


Fig. 45. Comparison of the probability of failure of smooth stress-corrosion specimens in several environments (after Sprowls and Brown⁴²).

humidity or tested in distilled water. Thus, the V - K curves shown in Fig. 40 for moist air also apply to crack growth in distilled water, with the exception of crack growth for alloy 7079-T651. This is apparent from a comparison of Figs. 40 and 46. The latter figure shows the velocity of stress-corrosion cracks as a function of stress intensity for two widely used high-strength aluminum alloys in distilled water. While the plateau velocity for alloy 7075 is about the same in distilled water as it is in moist air, stress-corrosion cracks in alloy 7079 are faster when the alloy is immersed in water. Region I is not affected by a transition from moist air to immersion in distilled water.

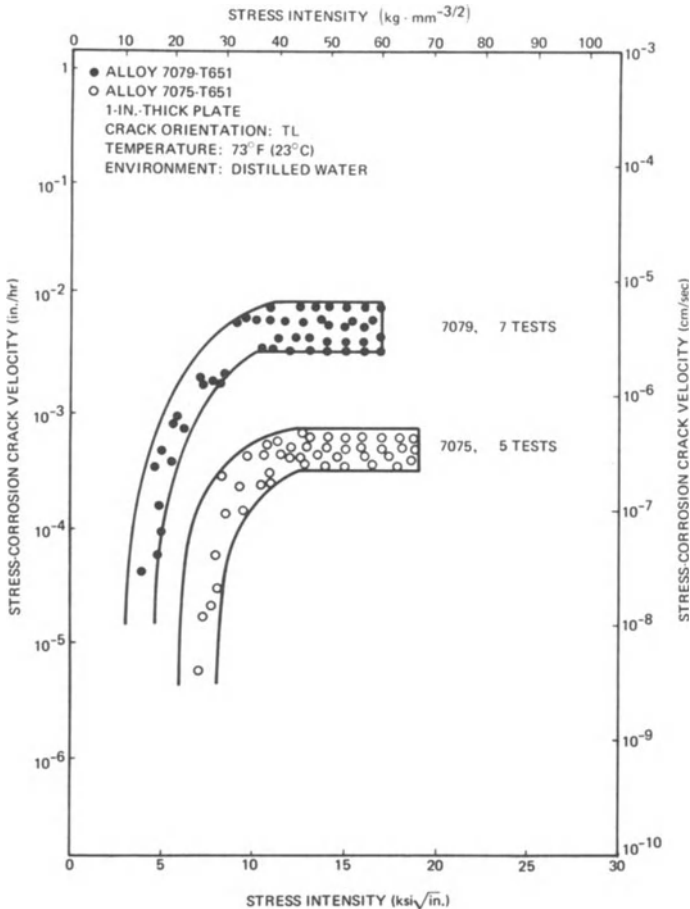


Fig. 46. Effect of stress intensity on stress-corrosion crack velocity in two high-strength aluminum alloys immersed in distilled water.

Neutral Aqueous Salt Solutions

In this section, aqueous solutions of pH 4–9 containing a variety of cations and anions are considered. The few cations quantitatively tested to date (i.e., Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ca^{++} , Al^{3+} , NH_4^+) do not appear to have any specific effect on the growth of stress-corrosion cracks,^{44a} except that they influence the solubility product and thus can govern the concentration of specific anions. Hg^{++} and H^+ are exceptions to this rule: Hg^{++} can cause fast intergranular corrosion and possibly stress corrosion by the deposition of mercury. H^+ is discussed below (p. 190).

The effect of various anions on stress-corrosion crack growth in high-strength aluminum alloys is illustrated in Fig. 47. Quite obviously, only chloride, bromide, and iodide accelerate the growth of stress-corrosion cracks above and beyond the velocity measured in water. Note that none of the nine other anions mentioned in Fig. 47 showed any tendency to catalyze stress-corrosion cracking, even under extreme metallurgical, mechanical, and electrochemical conditions. Such extreme conditions include (1) the most susceptible alloys (such as 7079-T651), (2) stress-intensity levels near K_{IC} , and (3) applied anodic potentials from -1.8 to $+14$ V versus the saturated calomel electrode.⁴⁴ Note also in Fig. 47 that neither the halide ion F^- nor the pseudohalide ion SCN^- accelerates SCC in a manner similar to the other halide ions. For these reasons, the observed acceleration of stress-corrosion crack growth by chloride, bromide, and iodide ions can be called unique or “specific.”

Aqueous Solutions Containing Chloride, Bromide, and Iodide Ions

The acceleration of stress-corrosion cracks by chloride, bromide, and iodide is of importance for several reasons. First, the ubiquity of these halides in marine environments makes it a necessity to know their influence on cracking if susceptible alloys are to be used in such environments. Second, aqueous chloride solutions are widely used for accelerated stress-corrosion tests, and it is surprising how little was known until recently about what phenomena are accelerated by chloride solutions and how much so. Third, chloride, bromide, and iodide are the unique pitting agents for aluminum and its alloys; therefore, they can influence not only propagation, but also initiation of stress-corrosion cracks by causing stress-raisers.

Acceleration of stress-corrosion crack growth by chloride, bromide, and iodide depends strongly on metallurgical, mechanical, electrochemical, and other environmental parameters that must be controlled if a meaningful

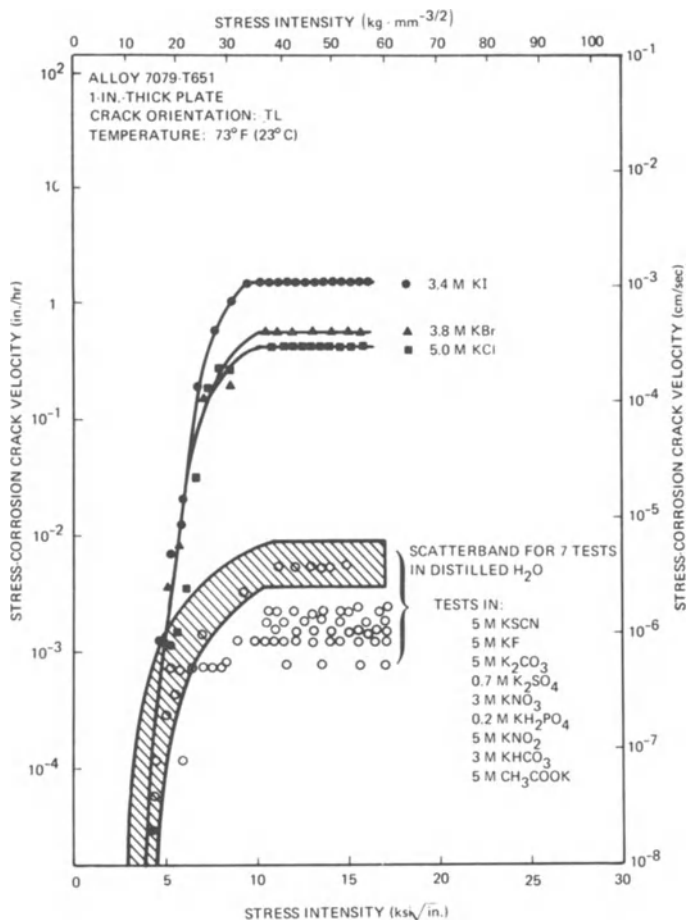


Fig. 47. Influence of various anions on stress-corrosion crack velocity of a high-strength aluminum alloy immersed in aqueous solutions (after Speidel^{44a}).

quantitative stress-corrosion test is to be attempted. The effects (on SCC acceleration by halides) of most of the above parameters are interrelated, making stress-corrosion cracking of high-strength aluminum alloys in aqueous halide solutions an extremely complex subject. The complexity of the subject has only recently become clear through the use of quantitative stress-corrosion experiments. A few selected examples of the results are given below.

Metallurgical parameters affecting the acceleration of stress-corrosion cracks by chloride, bromide, and iodide have not been studied systematically.

The behavior of individual alloys, however, is known to some extent. Under open-circuit conditions, stress-corrosion cracks in alloy 7079-T6S1 grow several hundred times faster in concentrated halide solutions than in distilled water, as shown in Fig. 47. Stress-corrosion cracks in alloy 7075-T6S1 grow only about five times faster in concentrated chloride solutions than in distilled water, as can be seen by comparing Figs. 21 and 46. Chloride additions accelerate stress-corrosion cracks more in alloy 7175-T66 than in alloy 7075-T6S1 under open-circuit conditions (Fig. 48). Stress-corrosion cracks in alloy 7178-T6S1 propagate about 10 times faster in concentrated NaCl solutions than in distilled water, as illustrated in Fig. 49. Note that

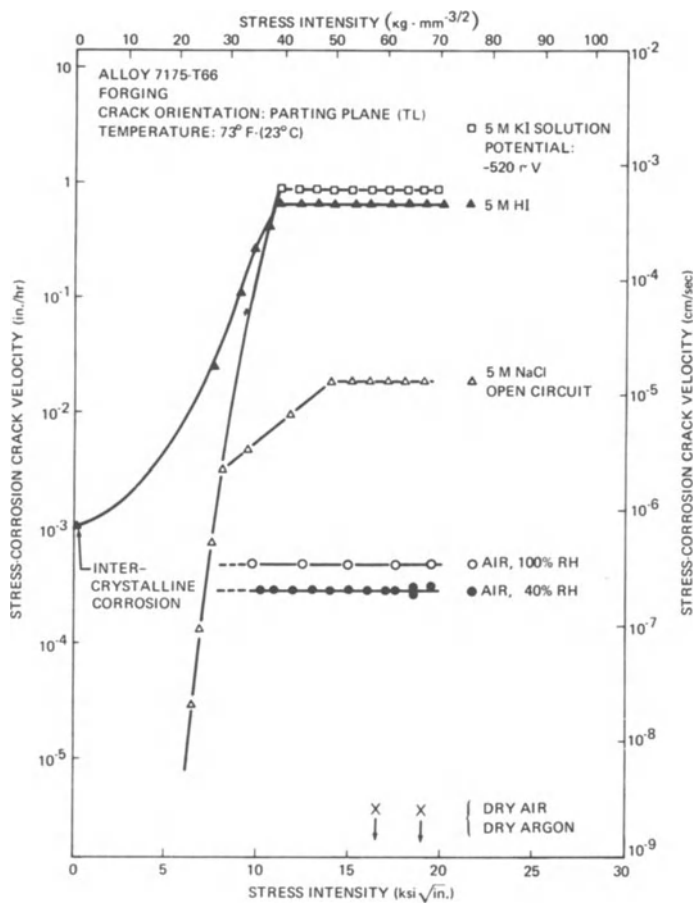


Fig. 48. Effect of stress intensity on stress-corrosion crack velocity of a high-strength aluminum alloy exposed to various environments.

in all cases mentioned, only the stress-independent plateau velocity is affected by the presence of the halides; the smaller velocities in region I at low stress intensities are not much affected by halide additions. A more complicated influence of halide additions on the velocity of stress-corrosion cracks has been observed with alloy 7039-T64 under open-circuit conditions (see Fig. 50). Taking the V - K curve for tests in distilled water as a baseline, it can be seen that chloride additions accelerate the stress-corrosion crack growth from the transition between regions I and II up to the highest stress intensity. Iodide additions, however, do not accelerate stress-corrosion

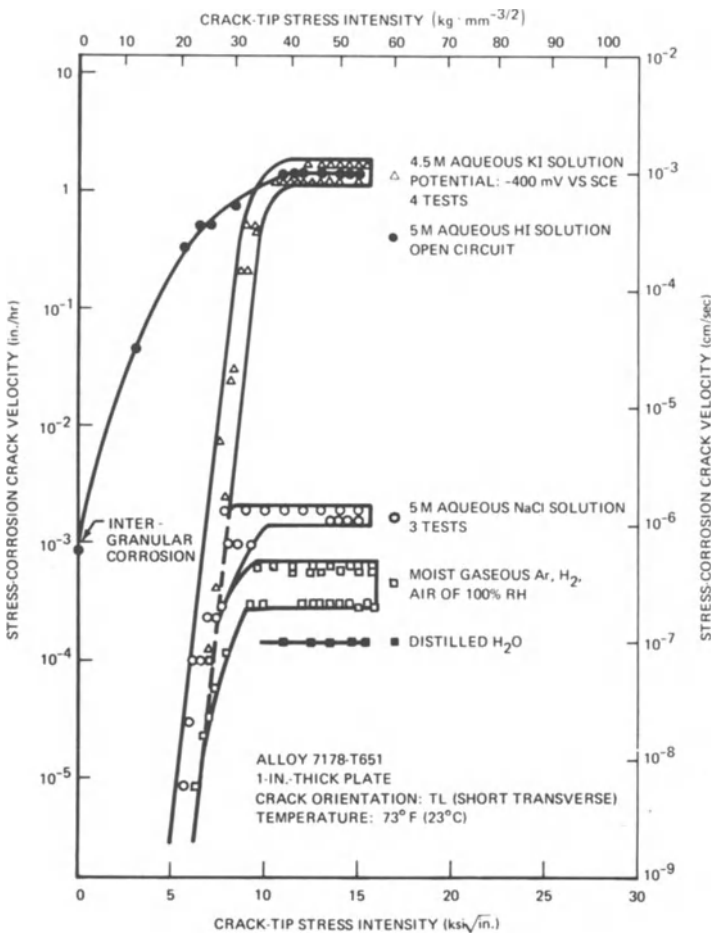


Fig. 49. Effect of stress intensity on stress-corrosion crack velocity in a high-strength aluminum alloy exposed to various environments.

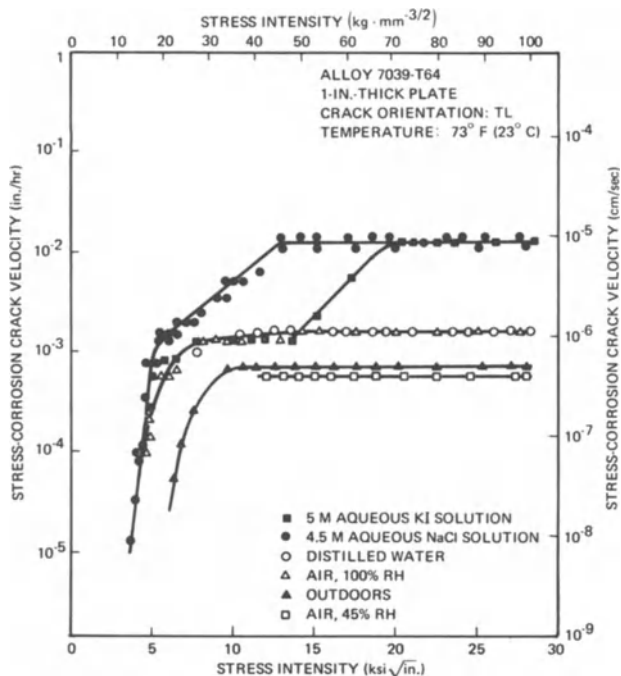


Fig. 50. Effect of stress intensity on stress-corrosion crack velocity in a high-strength aluminum alloy exposed to various environments.

crack growth unless a stress intensity of about $14 \text{ ksi in.}^{1/2}$ is exceeded. This behavior is perfectly reproducible with many specimens from the one plate tested thus far (specimens from different plates will have to be tested to determine if this SCC behavior is typical for alloy 7039-T64).

When an anodic electrochemical potential is applied, the acceleration of stress-corrosion cracks due to halide additions is sometimes greatly enhanced, as shown for alloy 7075-T651 in Fig. 21. This figure shows that under potentiostatic conditions in halide solutions, stress-corrosion cracks in the stress-independent region II are very much accelerated, and yet velocities do not seem to be affected in the lower end of region I of the V - K curve. The implications for accelerated stress-corrosion tests in the laboratory are obvious. A similarly large increase in stress-corrosion crack velocity due to an applied anodic potential in concentrated chloride, bromide, and iodide solutions has been observed with alloy 7175-T66 (Fig. 48), alloy 7178-T651 (Fig. 49), and a high-purity ternary alloy (Fig. 51). Note in Fig. 51 that neither of the stress-dependent velocity regions I and III

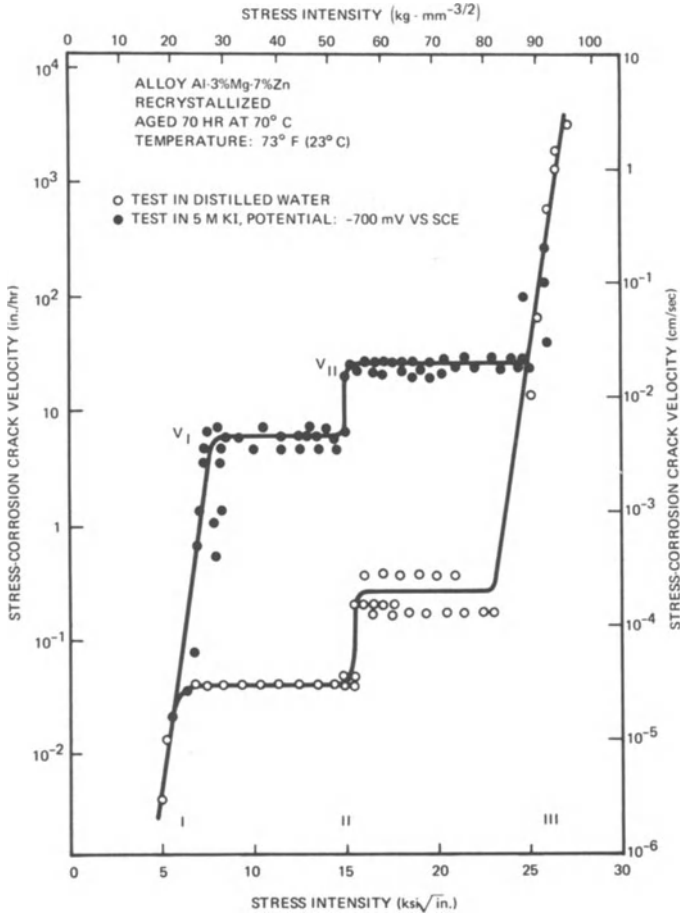


Fig. 51. Stress-corrosion crack velocity in a high-purity ternary aluminum alloy as a function of stress intensity and environment (after Speidel^{44a}).

seems to be affected by the presence of the halide. However, the crack velocity in the two plateau regions of the V - K curve is increased a hundredfold. The corresponding figure 52 shows how these plateau velocities of the high-purity alloy depend on the iodide concentration in the bulk aqueous solution. Small additions of iodide do not measurably increase the crack velocity until a concentration of more than 2×10^{-2} mole/liter is reached. Above that, the crack velocity increases linearly with the halide concentration. (Remember that these tests were made under potentiostatic conditions and refer only to the plateau velocity.)

The effect of halide ion concentration on crack velocity has also been studied systematically for the commercial alloy 7079-T651 under controlled potentiostatic conditions. Results are reported in Figs. 53 and 54. Here again, the presence of the halide affects only region II of the V - K curve, and the crack velocity in this region depends linearly on the halide ion concentration when concentrations of 2×10^{-2} mole/liter are exceeded. Such data provide a quantitative basis for fundamental studies of the mechanisms of stress-corrosion cracking and for the design of accelerated stress-corrosion tests.

Mechanical parameters affecting the acceleration of stress-corrosion cracks by chloride, bromide, and iodide shall be illustrated by two examples. The first is shown in Fig. 55, where the stress-corrosion crack velocity of alloy 7039-T64 in aqueous iodide solutions is plotted as a function of the crack-tip stress intensity. Consider only the V - K curve for room temperature (23°C). Starting from very low stress intensities, the velocity increases (region I) as the stress is raised. At a crack-tip stress intensity of about $7.5 \text{ ksi in.}^{1/2}$, a plateau is reached; i.e., the stress-corrosion crack velocity remains constant as the stress intensity is further increased to about $13.5 \text{ ksi in.}^{1/2}$. A comparison with Fig. 50 shows that this low plateau velocity is the same for both distilled water and concentrated iodide solutions. If, however, the stress intensity exceeds $13.5 \text{ ksi in.}^{1/2}$, the stress-corrosion crack growth becomes more than 2000 times faster, and a second, higher plateau in the V - K curve is measured. This complicated, but reproducible

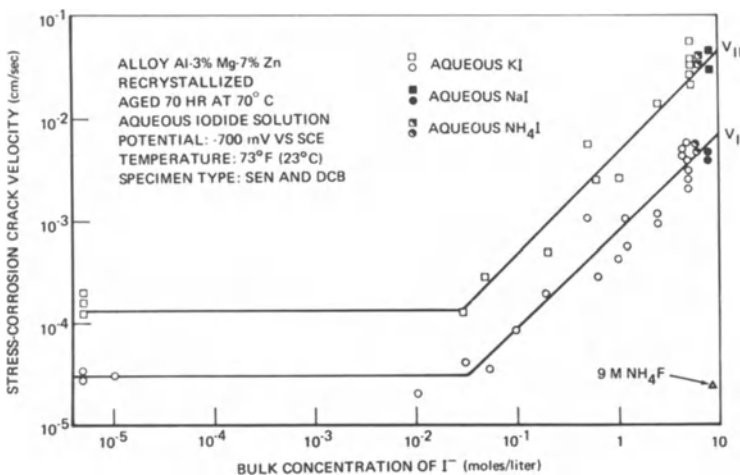


Fig. 52. Effect of iodide concentration on stress-corrosion crack velocity in a high-purity ternary aluminum alloy.

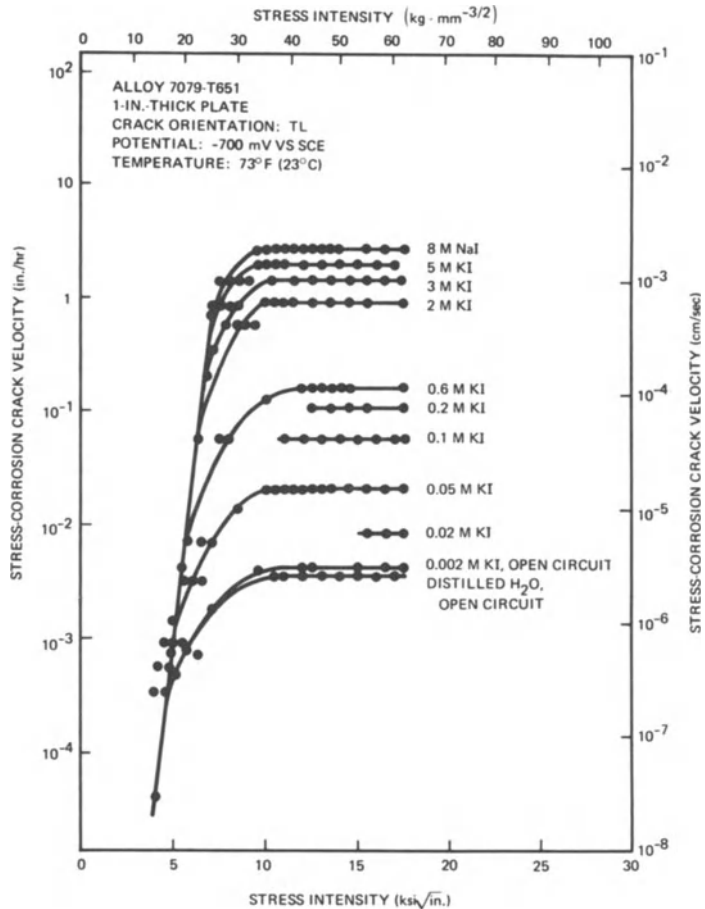


Fig. 53. Stress-corrosion crack velocity in a high-strength aluminum alloy immersed in aqueous solutions of various iodide concentrations.

V-*K* curve indicates that the acceleration of stress-corrosion cracks by halide ions under the conditions noted in Fig. 55 depends on the crack-tip stress intensity even in the plateau region of the *V*-*K* curve. Note that the *V*-*K* curve below 13.5 ksi.in.^{1/2} is not affected by the presence of the iodide, while above that stress intensity, the *V*-*K* curve is shifted to much higher crack velocities due to the presence of the halide ions.

As a second example of the effect of mechanical parameters on the acceleration of stress-corrosion cracks by halides, consider the difference between region I and region II of the *V*-*K* curve. It follows from any of the

Figures 47–50 or 53 that an investigator measuring the effect of halide ions on stress-corrosion crack growth would find almost no influence at stress intensities near the lower end of the V – K curve, even at applied anodic potentials. He would, however, find a very significant effect of the chloride, bromide, and iodide concentration on the crack growth rate if he had applied a high stress intensity. A time-to-failure test would include a halide-dependent growth time and a halide-independent growth time, together with a probably halide-dependent initiation time. For such reasons, time-to-failure tests can never be of any merit in fundamental studies of stress-corrosion cracking. Clearly, the knowledge of the full V – K curve is necessary to describe the effect of chloride, bromide, and iodide on stress-corrosion cracking of high-strength aluminum alloys. In the following sections, we will show that even this is not enough and that other influential parameters should also be taken into account.

Although time-to-failure tests should not be used in basic SCC studies, they can be used in some cases as a first approximation to indicate whether an environment will cause rapid failure of a part under stress. A summary of such TTF test results is given in Table 5.^{62,84} Note in Table 5 that for alloy 7075-T651, the shortest failure times are always measured in chloride-containing solutions.

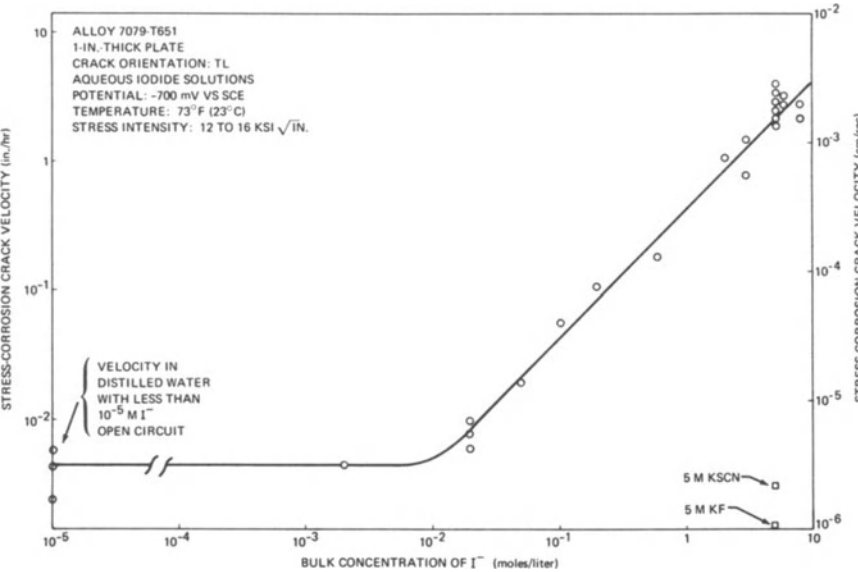


Fig. 54. Effects of iodide concentration on stress-corrosion crack velocity in a high-strength aluminum alloy (after Speidel^{64a}).

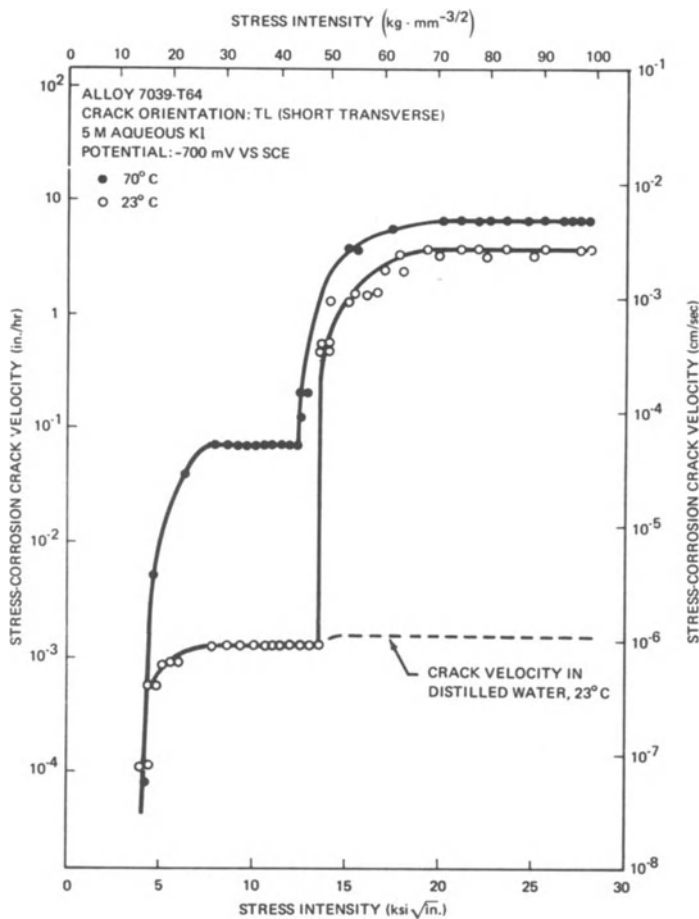


Fig. 55. Stress-corrosion crack velocity versus stress-intensity curve, showing two plateaus.

Effect of Electrical Potential

The effect of an applied electrical potential on stress-corrosion cracking is of interest for several reasons. In actual service, aluminum alloys could be coupled to dissimilar metals and form either the anode or the cathode of an electrolytic cell. An anodic potential is often applied to stress-corrosion test specimens to accelerate laboratory tests. Moreover, the effect of applied electrical potentials is studied in an attempt to understand the mechanisms involved in the SCC process of high-strength alu-

Table 5. Time to Failure by Stress-Corrosion Cracking of Aluminum Alloys in Various Aqueous Environments (After Hunter⁸⁴)

Concentration	Solutions	Nominal pH	Adjusted with	Median failure time (days) ¹				
				7075-T651	2219-T37	7039-T63	7075-T7351	2219-T87
Halide Ions								
1 N	NaCl	2	HCl	3	19	No test	18 NS	54 NS
1 N	NaCl	7	NaOH	47	28	14	---	---
1 N	NaBr	2	HBr	10	---	No test	---	60 NS
1 N	NaBr	7	NaOH	>60	---	9	---	---
1 N	NaI	2	HI	12	No test	No test	---	32 NS
1 N	NaI	7	HI	---	---	10	---	---
1 N	KHF ₂	2	---	34	---	No test	---	---
1 N	NaF	7	HF	---	---	19	---	---
Complex Anions								
1 N	NaNO ₃	2	HNO ₃	---	---	No test	---	---
1 N	NaNO ₃	7	NaOH	---	---	60	---	---
1 N	NaNO ₃	9	NaOH	---	---	No test	No test	No test
1 N	Na ₂ CrO ₄	2	CrO ₃	---	---	No test	---	---
1 N	Na ₂ CrO ₄	7	CrO ₃	---	---	60	---	---
1 N	Na ₂ CrO ₄	9	NaOH	25	---	No test	No test	No test
1 N	Na ₂ SO ₄	2	H ₂ SO ₄	40 B	---	No test	---	---
1 N	Na ₂ SO ₄	7	NaOH	---	---	No test	---	---
1 N	Na ₂ SO ₄	9	NaOH	---	---	No test	No test	No test
0.5 N	Na ₂ SO ₄ + 0.5 N NaNO ₃	2	H ₂ SO ₄	56 Q	---	No test	---	---
0.5 N	Na ₂ SO ₄ + 0.5 N NaNO ₃	7	NaOH	---	---	No test	No test	No test
0.5 N	Na ₂ SO ₄ + 0.5 N Na ₂ CrO ₄	2	H ₂ SO ₄	---	>60	No test	---	---
0.5 N	Na ₂ SO ₄ + 0.5 N Na ₂ CrO ₄	7	H ₂ SO ₄	---	---	No test	No test	No test
1 N	NaHCO ₃	9	---	---	---	No test	No test	No test
1 N	NaHSO ₄	1	---	17 Q	---	No test	34 NS	---
1 N	Na ₂ HPO ₄	9	---	---	---	No test	No test	No test
1 N	NaH ₂ PO ₄	4	---	---	---	No test	---	---
1 N	NaH ₂ PO ₄	4	H ₂ SO ₄	---	---	No test	No test	No test
1 N	NaC ₂ H ₃ O ₂	4	CH ₃ COOH	6 B	---	No test	No test	No test
Sodium Chloride + Oxidizing Acids								
1 N	NaCl	2	HNO ₃	1	7	No test	7 NS	7 NS
1 N	NaCl	2	H ₃ PO ₄	1	8	No test	No test	No test
1 N	NaCl	2	H ₂ SO ₄	1	8	No test	2 NS	9 NS
1 N	NaCl	2	CrO ₃	60	>60	No test	42 NS	21 NS
4 N	NaCl + 0.5 KNO ₃	0.4	HNO ₃	1	1	No test	19 NS	25 NS
Sodium Chloride + Complex Anion								
0.5 N	NaCl + 0.5 N NaNO ₃	2	HNO ₃	8	---	No test	---	---
0.5 N	NaCl + 0.5 N NaNO ₃	7	NaOH	60	---	No test	---	---
0.5 N	NaCl + 0.5 N Na ₂ SO ₄	2	H ₂ SO ₄	2 Q	No test	No test	4 NS	5 NS
0.5 N	NaCl + 0.5 N Na ₂ SO ₄	7	NaOH	21 Q	6	No test	>60 NS	>60 NS
0.5 N	NaCl + 0.5 N Na ₂ CrO ₄	2	HCl	10 B	1	No test	52 NS	22 NS
0.5 N	NaCl + 0.5 N Na ₂ CrO ₄	7	HCl	26	33	No test	---	---
Ammonium Salts								
1 N	NH ₄ Cl	7	NH ₄ OH	15	23	No test	52 NS	---
1 N	NH ₄ NO ₃	7	NH ₄ OH	---	---	No test	No test	No test
1 N	(NH ₄) ₂ SO ₄	7	NH ₄ OH	---	---	No test	No test	No test
1 N	(NH ₄) ₂ CrO ₄	7	CrO ₃	---	---	No test	No test	No test
Miscellaneous								
1 N	NaCl + 10 ml/l 30% H ₂ O ₂	5.5	---	4	3	No test	22 NS	6 NS
1 N	NaCl + 1 N AlCl ₃	2	HCl	4	16	No test	10 NS	4 NS
1 N	Na ₂ SO ₄ + 10 ml/l 30% H ₂ O ₂	5.8	---	15	>60	No test	31 NS	---
1 N	Na ₂ SO ₄ + 1 N Al ₂ (SO ₄) ₃	2	H ₂ SO ₄	> 60 Q	---	No test	---	---

¹ Short transverse tensile specimens were stressed to 75% of their yield strength and exposed by continuous immersion at 80° to 85° F. Tests were terminated at the end of 60 days. Therefore, absence of failure does not necessarily indicate immunity to stress-corrosion cracking, particularly in the less corrosive solutions. Median failure times shown are for three specimens.

--- No failures after 60 days of testing

B Borderline susceptibility to SCC

Q SCC questionable because of high strength losses in unstressed and corroded specimens

NS Failures not due to SCC

minum alloys. Finally, cathodic protection is sometimes used to prevent initiation and growth of stress-corrosion cracks.

Figure 56 illustrates the effect of electrical potential on stress-corrosion crack growth of a high-purity ternary aluminum alloy. (Remember that the effect of stress intensity and iodide concentration on stress-corrosion crack growth of this alloy has already been presented in Figs. 39, 51, and 52.) Figure 56 refers only to the stress-independent plateau velocity V_1 . Consider first the potential dependence of the crack growth rate in neutral 5 M KI solution. The open-circuit potential of this alloy is about -1100 mV versus the saturated calomel electrode, corresponding to a crack velocity of 2×10^{-4} cm/sec. If a more negative potential is applied, crack growth rate is reduced; this is called cathodic protection. If a more positive potential is applied, the crack growth rate increases sharply until the pitting potential is reached between -700 and -600 mV. A further

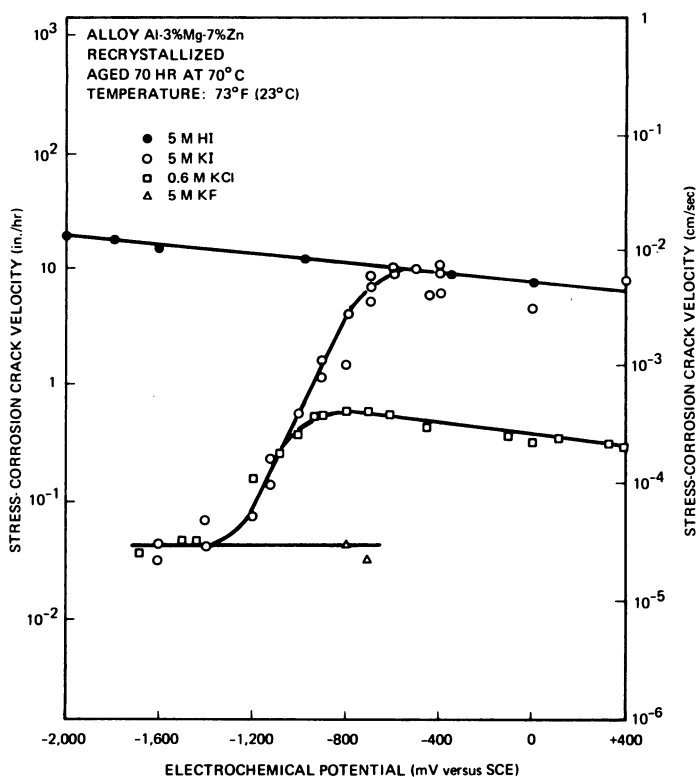


Fig. 56. Effect of electrical potential on stress-corrosion crack velocity in a ternary aluminum alloy.

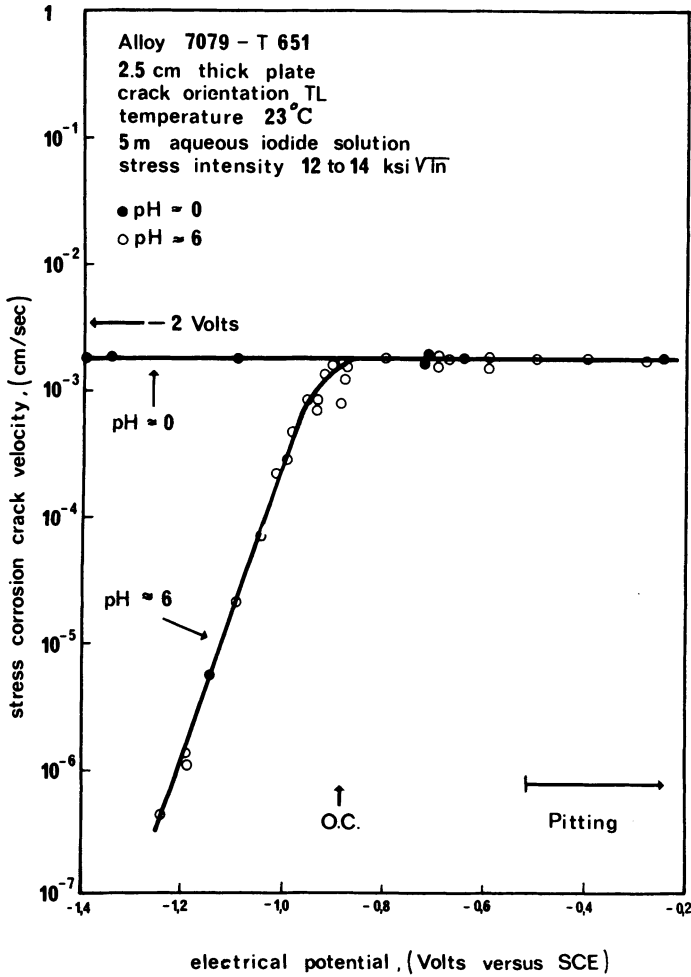


Fig. 57. Effect of electrical potential on stress-corrosion crack velocity in a high-strength aluminum alloy.

increase of the potential has no significant effect on crack growth. However, the level to which the crack velocity is increased by an applied anodic potential depends on the chloride, bromide, and iodide concentration in the solution. This is apparent in Fig. 56. The limited data available for the high-purity alloy indicate that cathodic protection does not completely stop crack growth. However, it does reduce the crack growth rate in chloride, bromide, and iodide solutions to that normally observed in distilled water

or fluoride solutions. Next, consider the potential dependence of the crack growth rate in the very acidic 5 M HI solution, which is also illustrated in Fig. 56. In this acidic solution, cathodic protection is obviously impossible. Experience shows that this is true for many other high-strength aluminum alloys, too. An example for the commercial alloy 7079-T651 is given in Fig. 57. This alloy has an open-circuit potential of ≈ -880 mV, and cathodic protection causes a markedly reduced crack growth rate. No such protection is possible in the strongly acidic 5 M HI solution.

Figures 56 and 57 show once more the complexity of the subject of stress-corrosion cracking of high-strength aluminum alloys. We knew before that the acceleration of stress-corrosion cracks in aqueous solutions by halide ions depends on crack-tip stress intensity and metallurgical parameters. Now we learn that it also depends on electrical potential and pH . Most of these effects are interrelated, and the effect of temperature will complicate the subject even more. Obviously, the fundamental aspects of the phenomenon of stress-corrosion cracking will never be understood through studies that limit themselves to one facet of it. A background in metallurgy, fracture mechanics, and chemical and electrochemical kinetics appears to be indispensable for any team that wants to make progress toward an understanding of stress-corrosion cracking.

Effect of pH

Qualitative studies on the effect of pH on stress-corrosion cracking of high-strength aluminum alloys abound. There is general agreement that the occurrence of SCC in chloride solutions is markedly reduced as the solution is made increasingly alkaline.⁵¹ Sometimes, it is possible to prevent SCC of aluminum alloys by restricting their application to an environment with a pH larger than a fixed minimum.⁸⁵ Acidifying the solution usually reduces the time to failure. Typical results for smooth specimens are shown in Fig. 58.⁸⁶

A more detailed description of the effect of pH is possible through quantitative studies of the crack growth rate as a function of stress intensity and environment. Figure 59 illustrates the effect of pH on the V - K curve of a susceptible high-strength aluminum alloy in concentrated aqueous iodide solutions. It can be seen that the plateau velocity is not affected by a sharp decrease of the pH under the experimental conditions listed in Fig. 59. The stress-dependent crack velocity in region I, however, is strongly affected since the whole V - K curve is shifted to lower stress intensities in the acidic solution. Note in Fig. 59 that the stress-corrosion crack growth rate at a

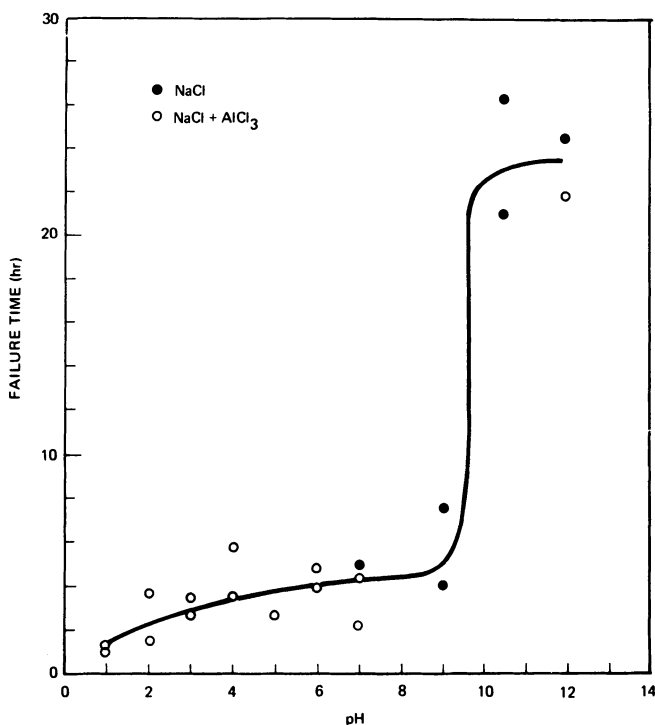


Fig. 58. Effect of pH on time to failure by stress-corrosion cracking of aluminum alloy 7075-T6 (after McHardy and Hollingsworth⁸⁶).

a stress intensity of $15 \text{ ksi in.}^{1/2}$ is not affected by a pH change from 11 (buffered) to 0. Precracked specimens stressed to a stress intensity of $5.5 \text{ ksi in.}^{1/2}$, however, would show a large difference in crack growth rate when exposed to solutions of pH 11 and 0. This observation shows once more that the measurement of the full velocity versus stress-intensity curve is necessary for quantitative stress-corrosion experiments. Statements like "lowering the pH accelerates the propagation of stress-corrosion cracks"⁸⁷ should be qualified by indicating the region of the V - K curve which is affected.

Figures 48 and 49 give two more illustrations of the fact that the effect of pH on stress-corrosion crack velocity in region II of the V - K curve can be negligible and that region I is shifted to lower stress intensities when the halide solution is acidified. Figure 60 presents results from more systematic studies showing that the effect of pH upon region II velocity is indeed immeasurably small up to pH 11 under the experimental conditions listed. However, it should be kept in mind that under different electro-

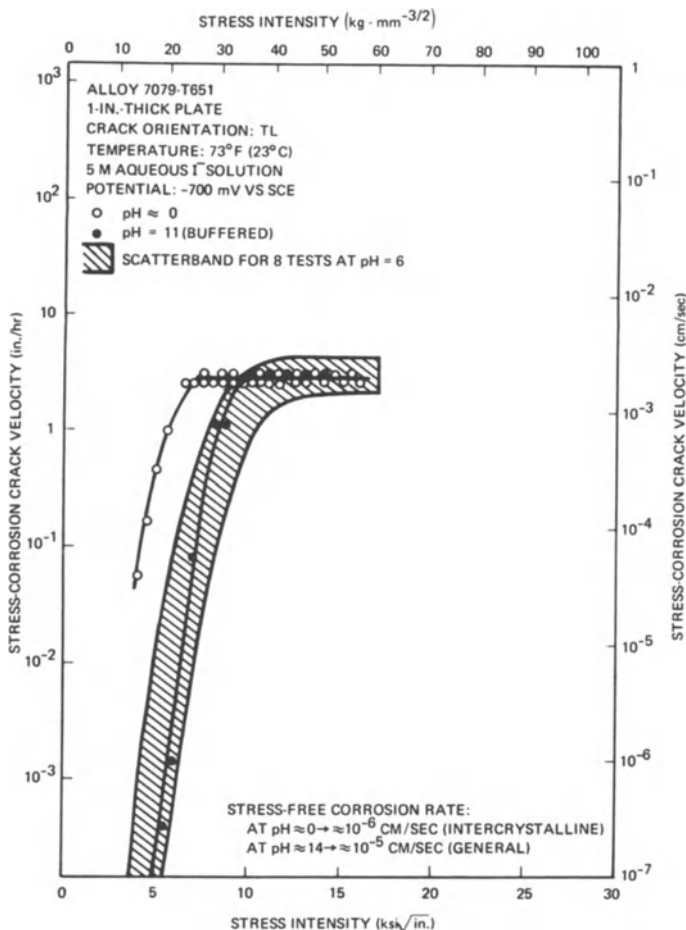


Fig. 59. Effect of stress intensity and pH on the velocity of stress-corrosion cracks in a high-strength aluminum alloy.

chemical conditions, lowering the pH of the bulk solution can increase the crack growth rate even in the plateau region. This can best be seen in Fig. 56 and 57. On the anodic side, the effect of pH on region II crack growth is negligible. At more negative potentials, e.g., -1400 mV, region II crack growth is increased by several orders of magnitude.

The solution chemistry within a narrow crack can be very different from the chemistry of the bulk solution. This was pointed out convincingly many years ago.⁸⁸ Consider an aluminum alloy in a neutral 0.5 M NaCl solution. If the metal contains a crack filled with the solution, aluminum

chloride is formed in the crack. The aluminum chloride can hydrolyze and acidify the medium. Theoretical calculations predict a pH of 3.5 in the crack under such conditions. Direct measurements of electrolyte from a narrow crevice yielded pH values of 3.2–3.4.⁸⁸ Such tests have recently been repeated, with the same results.⁸⁹ Therefore, studies of the fundamental aspects of stress-corrosion cracking will have to take into account both the chemistry of the bulk solution and the solution within the crack.

Effect of Temperature

It is not merely of academic interest to know the effect of temperature on stress-corrosion cracking of high-strength aluminum alloys. Ships, aircraft, and pressure vessels might experience a more severe stress-corrosion problem when operating in the tropics than when operating in polar areas.

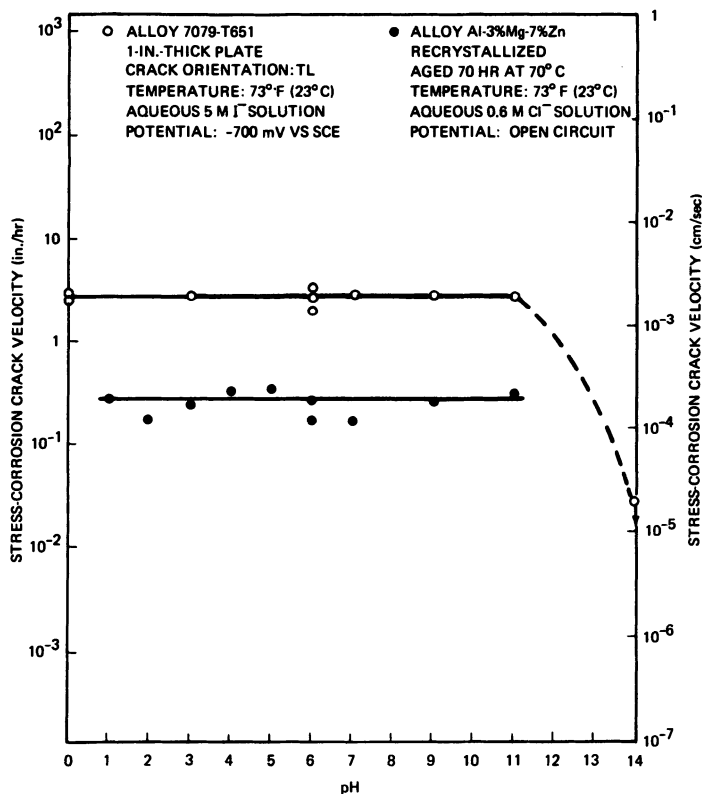


Fig. 60. Effect of pH on region II velocity of stress-corrosion cracks in two aluminum alloys.

Furthermore, aerodynamic heating of future aircraft makes it desirable to know the effect of temperature on environment-induced subcritical crack growth of the materials used.

For many years, it has been known that higher temperatures can cause a decrease of the time to failure by stress corrosion of susceptible aluminum alloys. Time-to-failure data for alloy 7039-T64 are shown in Fig. 61.⁹⁰ The difficulties encountered in interpreting such data are not small and become more clear when time-to-failure data are compared with quantitative measurements of the velocity of stress-corrosion cracks as a function of stress intensity and temperature.

Figure 62 shows the effect of temperature and stress intensity on the velocity of stress-corrosion cracks in alloy 7079-T651. It is apparent that an increase in temperature causes not only faster cracking in region II of the V - K curve, but also a shift of region I to lower stress intensities. That is to say, at higher temperatures, cracks grow not only faster, but also at lower stresses. The logarithm of the crack growth rate is plotted versus the reciprocal temperature in Fig. 63. It appears that the stress-corrosion crack

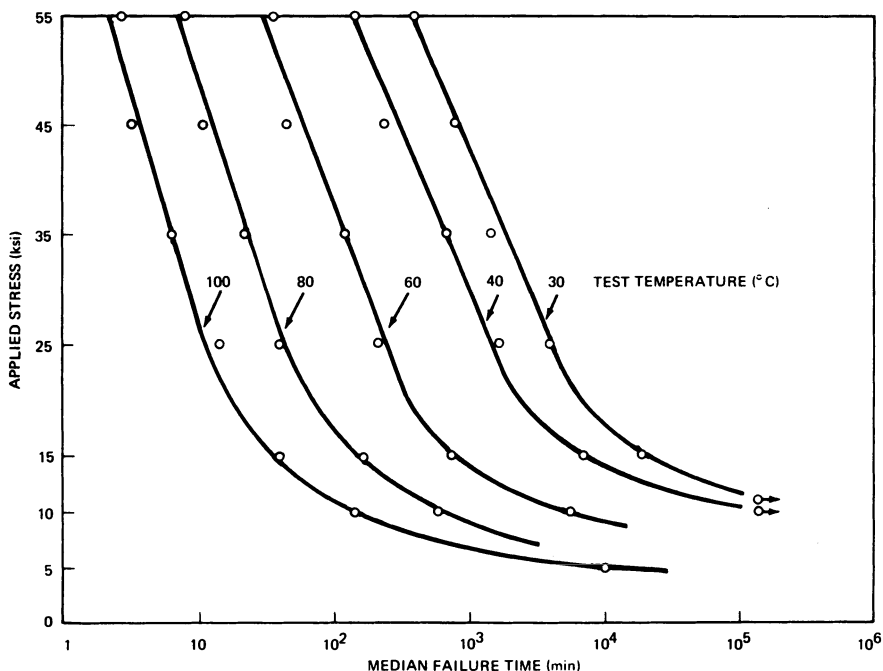


Fig. 61. Effect of stress and temperature on time to failure by stress-corrosion cracking of alloy 7039-T64 (after Helfrich⁹⁰).

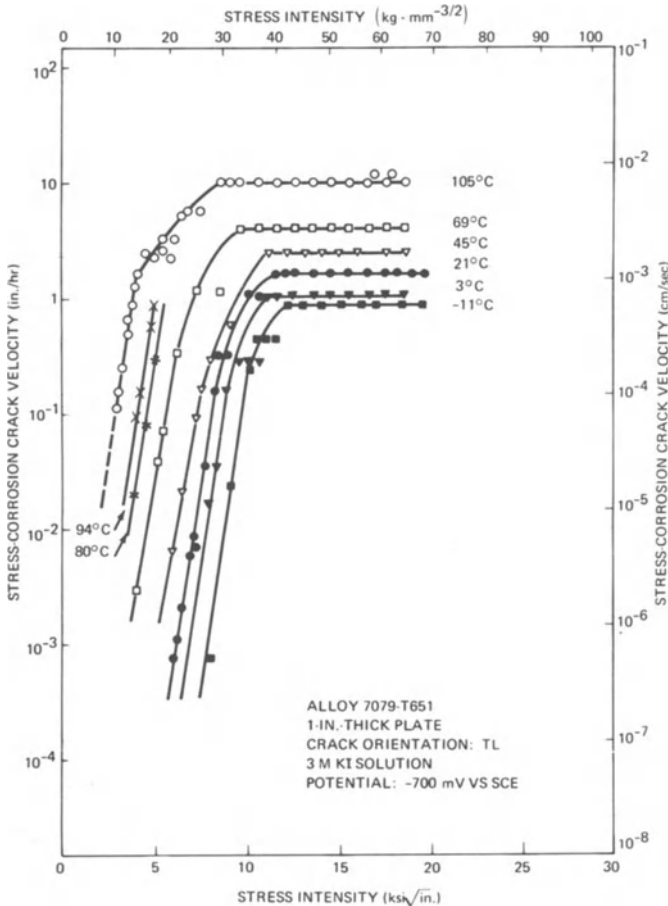


Fig. 62. Stress-corrosion crack velocity in alloy 7079-T651 as a function of stress intensity and temperature (after Speidel^{44a}).

velocity in the plateau region (II) can be approximated by the following equation:

$$V = V_0 \exp(-Q/RT) \quad (6)$$

where V is velocity, V_0 is an experimental constant, Q is the activation energy, R is the gas constant, and T is temperature.

The stress-corrosion crack velocity in region I of the V - K curves of Fig. 62 fits the following empirical equation:

$$V = V_0 \exp[(-Q + bK_1)/RT] \quad (7)$$

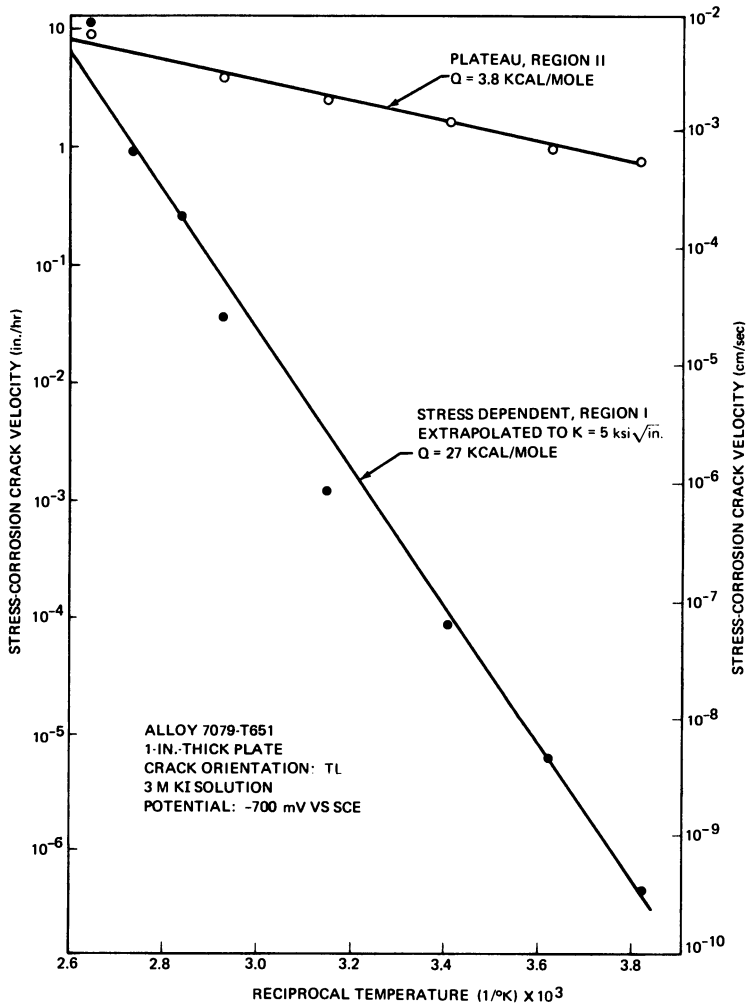


Fig. 63. Determining the apparent activation energy of the thermally activated stress-corrosion crack growth illustrated in Fig. 62 (after Speidel^{44a}).

where V_0 , Q , and b are experimental constants and K_1 is the stress intensity.

The apparent activation energies are $Q = 3.8 \text{ kcal/mole}$ for region II crack growth and $Q = 27 \text{ kcal/mole}$ for region I crack growth. A time-to-failure test would integrate over region I and region II of the V - K curve as well as over the transition between the two regions. It would be expected, therefore, that TTF tests would yield apparent activation energies some-

where between 3.8 and 27 kcal/mole, but biased toward the larger value because most of the lifetime of a smooth stress-corrosion specimen is probably spent in the slow-growth region. Historically, activation energies measured with TTF tests indeed follow that description.

Quite different experimental results have been obtained for alloy 7039-T61, as shown in Fig. 64. This alloy exhibits very slow crack growth at room temperature in concentrated iodide solutions, and has an extended flat plateau (region II) of the V - K curve. This stress-independent plateau crack velocity is thermally activated with an apparent activation energy of

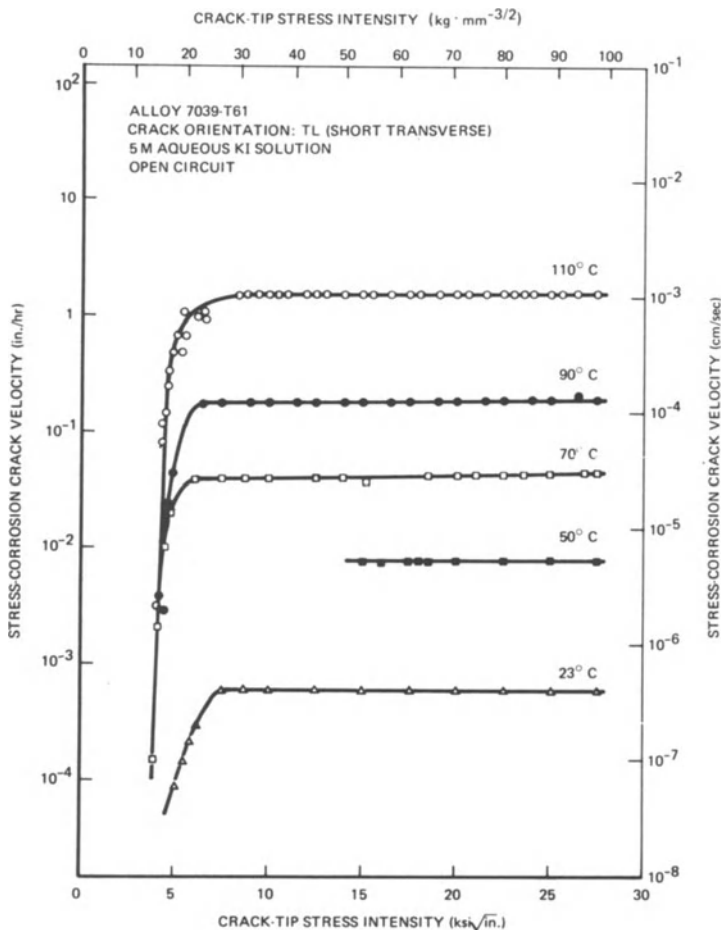


Fig. 64. Effect of stress intensity and temperature on stress-corrosion crack velocity of alloy 7039-T61.

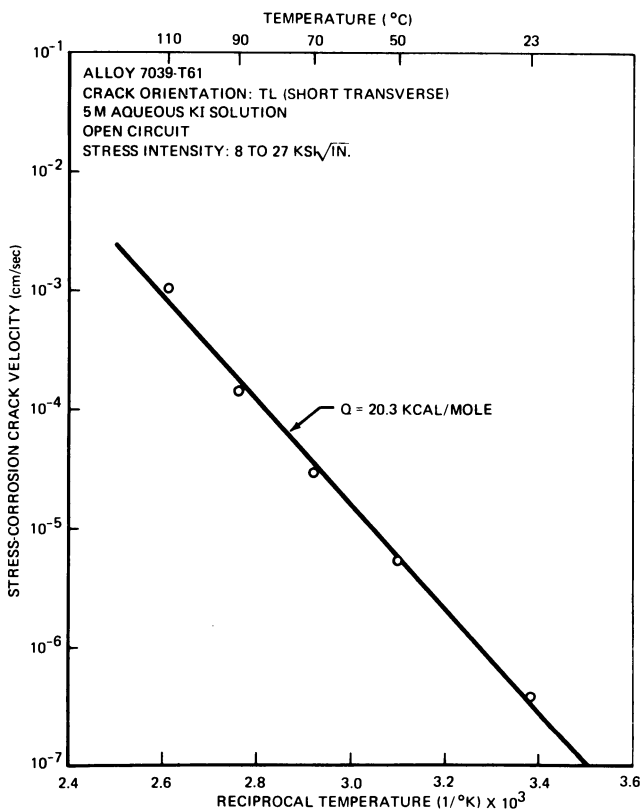


Fig. 65. Arrhenius plot of the thermally activated stress-corrosion crack growth shown in Fig. 64.

20.3 kcal/mole, deduced from Fig. 65. This activation energy for the region II velocity is by far higher than the one measured for alloy 7079-T651 (Fig. 63). Such a large difference of activation energies seems to indicate that a different process might be rate-controlling, a notion supported by the observation that the plateau velocity in alloy 7039-T61 is independent of halide-ion concentration at room temperature under open circuit. This is in sharp contrast to the observations reported earlier for alloy 7079-T651.

The two different activation energies observed for region II crack growth seem to be particular for the thermal activation of two different processes: a halide-ion concentration-controlled crack velocity (3.9 kcal/mole) and a halide-independent crack velocity (20.3 kcal/mole). Recall that alloy 7039-T64 had two vastly different plateaus in its V - K curve, one dependent on the iodide concentration, the other independent of it (Fig.

55). Preliminary experimental results on temperature dependence indicate that the plateau independent of iodide concentration is indeed thermally activated, with an apparent activation energy $Q = 20$ kcal/mole, whereas the plateau dependent on iodide concentration has an apparent activation energy $Q = 4$ kcal/mole. This indicates that the thermal activation of stress-corrosion crack growth is intimately related to crack-tip stress intensity, a fact that could have never been revealed with time-to-failure tests. Further investigations of this phenomenon are of interest.

Effect of Solution Viscosity

The effect of the viscosity of a 2 M aqueous KI solution on the velocity of stress-corrosion cracks in alloy 7079-T651 is illustrated in Fig. 66. The viscosity of the solution was varied by additions of glycerol. It appears that viscosity affects only the plateau of the V - K curve, and region I crack growth is not influenced. Figure 67 plots plateau crack velocities from Fig. 66 versus solution viscosity. They scatter around a straight line with the slope -1 on the double-logarithmic plot, indicating that the stress-corrosion crack velocity is linearly related to the reciprocal solution viscosity.

The results presented in Fig. 66 are based on tests with only one specimen per solution. A scatter band of about the same width as those shown in Figs. 21 and 46 could be expected if many tests were run under identical conditions. Note, however, in Figs. 66 and 67 that increasing the viscosity lowers the crack velocity by more than two orders of magnitude. Therefore, the observed effect is much larger than the expected experimental scatter.

Acids

HCl, HBr, and HI. It is known that acidified chloride, bromide, and iodide solutions cause rather short times to failure in stress-corrosion tests of smooth specimens, as illustrated in Table 5. This could be due to a short initiation time⁹¹ or fast crack propagation (see the discussion of the effect of pH). The effect of an aqueous 50% HI solution on crack propagation in alloy 7079 is shown in Fig. 59. Concentrated aqueous HBr and HCl solutions up to 10 moles/liter have the same effect.⁴⁴ The effect of pure, water-free HCl, HBr, and HI on stress-corrosion crack growth has not yet been measured.

H₂SO₄. H₂SO₄ containing 2.6% H₂O does not cause any stress-corrosion crack growth in precracked and stressed specimens of alloys 7079-T651 and 7075-T651 when such specimens are immersed in the acid for

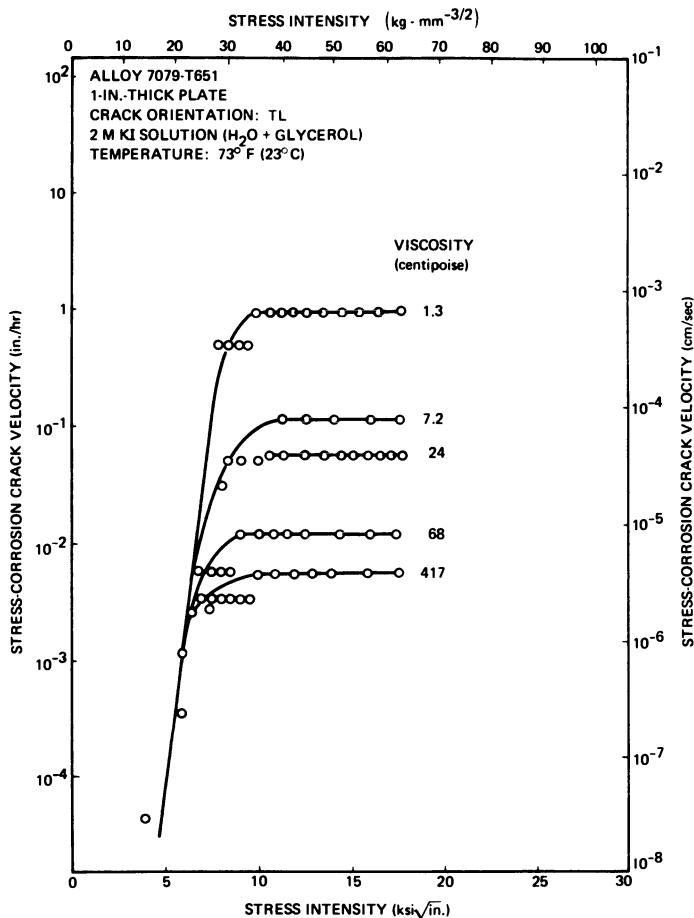


Fig. 66. Stress-corrosion crack velocity of a high-strength aluminum alloy as a function of stress intensity and solution viscosity (after Speidel^{44a}).

22 days.⁴⁴ It is thought that the well-known properties of H_2SO_4 as a drying agent play a role.

HNO₃ and Inhibited Red Fuming Nitric Acid (IRFNA). The few experimental data available on the effect of concentrated nitric acid (70.9%) on the growth of SCC cracks in alloy 7079-T651 indicate that the crack velocity is equal to or close to that measured in distilled water,⁴⁴ as illustrated in Fig. 46. Smooth specimens of a number of high-strength aluminum alloys were tested in hot (165°F) IRFNA.⁹² The results are illustrated in Fig. 68.

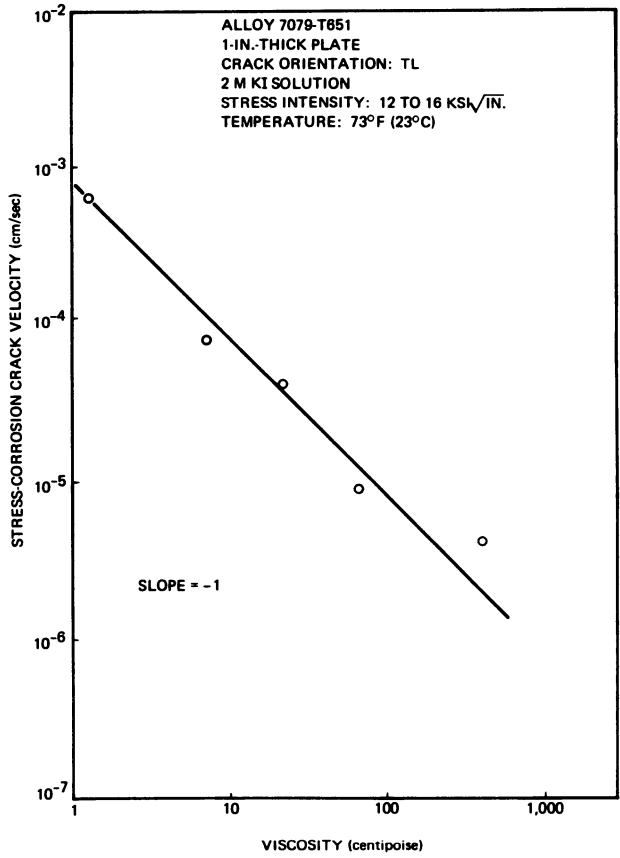


Fig. 67. Effect of solution viscosity on stress-corrosion crack velocity in region II (after Speidel^{44a}).

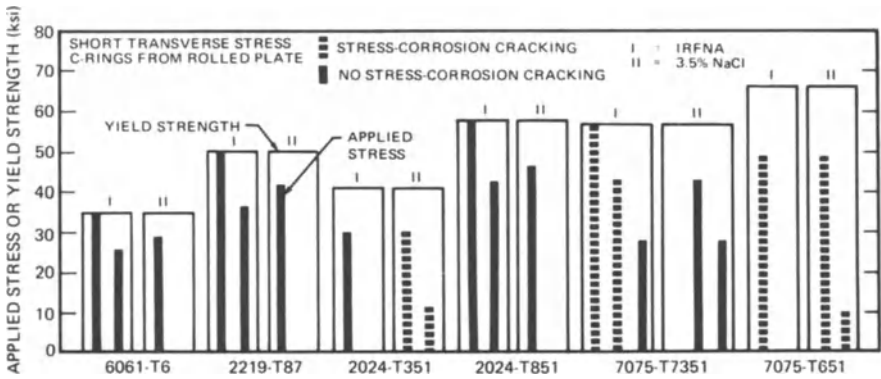


Fig. 68. Comparison of smooth-specimen resistance to SCC of various alloys in inhibited red fuming nitric acid at 165°F and in 3.5% NaCl alternate immersion (after Lifka⁹²).

Note that the highly stressed 7075-T7351 specimens that were resistant in 3.5% NaCl failed in the hot IRFNA, as did 7075-T651. Alloys 6061-T6, 2024-T851, and 2219-T87 apparently are resistant to SCC in IRFNA.

H_3PO_4 . H_3PO_4 containing 14.7% H_2O causes intercrystalline corrosion in alloy 7079-T651. The corrosion rate is about 10^{-5} cm/sec and does not appear to be accelerated by stress in DCB specimens precracked in the TL orientation and stressed to near K_{IC} .⁴⁴

Nitrogen Tetroxide

Nitrogen tetroxide has been considered as a liquid rocket propellant. However, certain high-strength aluminum alloys are susceptible to environment-induced subcritical crack growth in N_2O_4 .³⁶ The effect of applied stress intensity on growth of surface flaws in alloy 2021 exposed to N_2O_4 is shown in Fig. 69.³⁶ The numbers next to the data points indicate the extent of crack growth in thousandths of an inch. It is apparent that subcritical crack growth occurs at stress intensities much lower than $K_{IC} = 32.5$ ksi in.^{1/2}. The fact that the threshold stress intensity K_{TH} is only 10.0 ksi in.^{1/2} for alloy 2021-T81 is quite likely to create functional problems if the alloy is used to make pressurized N_2O_4 storage vessels.

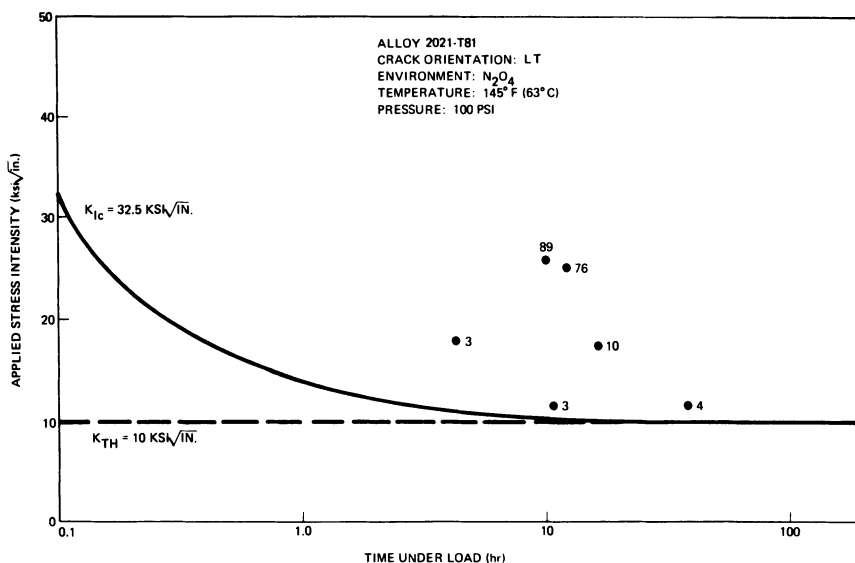


Fig. 69. Subcritical crack growth of an aluminum alloy in N_2O_4 .³⁶ The numbers next to the points indicate the extent of crack growth in thousandths of an inch. (After Lorenz.³⁶)

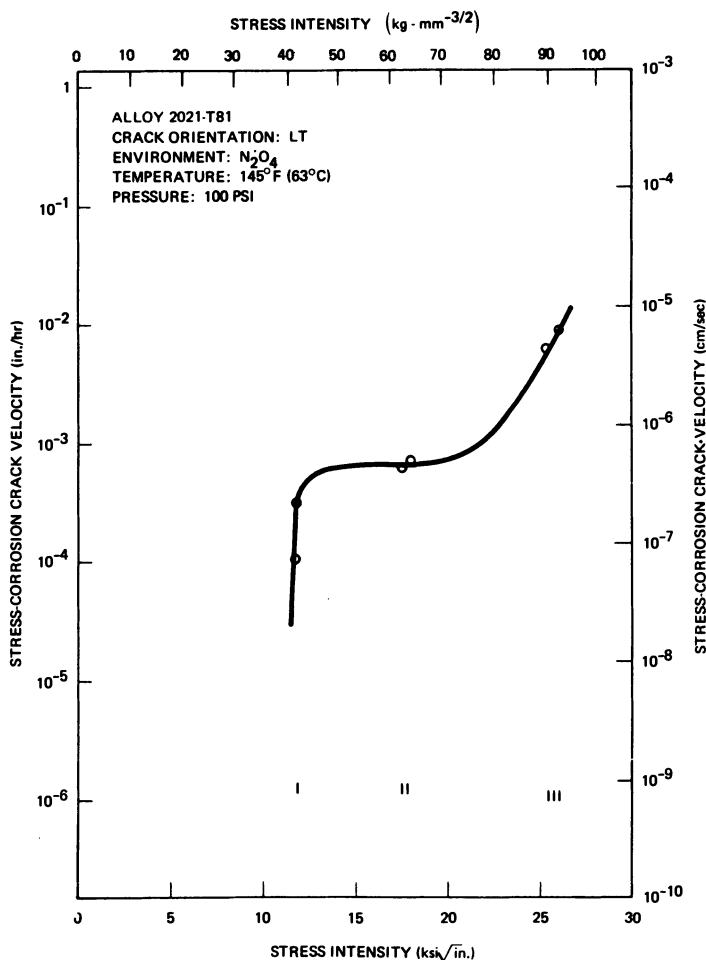


Fig. 70. Stress-corrosion crack velocity as a function of stress intensity for an aluminum alloy in N_2O_4 , replotted from data in Fig. 69 and Ref. 36.

In Fig. 70, the author's³⁶ original average experimental growth rates have been replotted to get a V - K curve. This curve was drawn through the experimental data points, showing the familiar region I (stress-dependent) crack growth, region II (plateau, stress-independent), and region III crack growth, but more experimental data would be needed to confirm this shape of the V - K curve for alloy 2021-T81 in N_2O_4 . It would be of special interest to determine whether a threshold stress intensity exists, as assumed in Fig. 69, or whether region I in Fig. 70 extends to lower stress intensities.

Organic Liquids

Stress-corrosion cracking of high-strength aluminum alloys in oil has been known for some time, but only recently has the growth of stress-corrosion cracks been quantitatively studied as a function of crack-tip stress intensity in various organic liquids.^{44,83,93} One of the first published results is shown in Fig. 71, where the crack growth rate of alloy 7075-T651 in ethanol is plotted as a function of the plane strain crack-tip stress intensity. A linear relationship between crack velocity and stress intensity was reported for alloy 7075-T651 in both ethanol and carbon tetrachloride. From the intersection of the straight line with the stress axis, K_{ISCC} was estimated to be 7–9 ksi in.^{1/2} in ethanol and 10–12 ksi in.^{1/2} in carbon tetrachloride.⁸³ It was thought that crack propagation was not due to traces of water in the organic liquids.^{83,93} Note that these results were generated with cracks in the *WL* orientation and that the cracking mode was observed to be mixed transgranular and intergranular.⁸³

Figure 72 illustrates the effect of stress intensity on crack-tip velocity of stress-corrosion cracks in alloy 7075-T651 immersed in a wide variety of organic liquids. Note that for the six different reagent-grade alcohols,

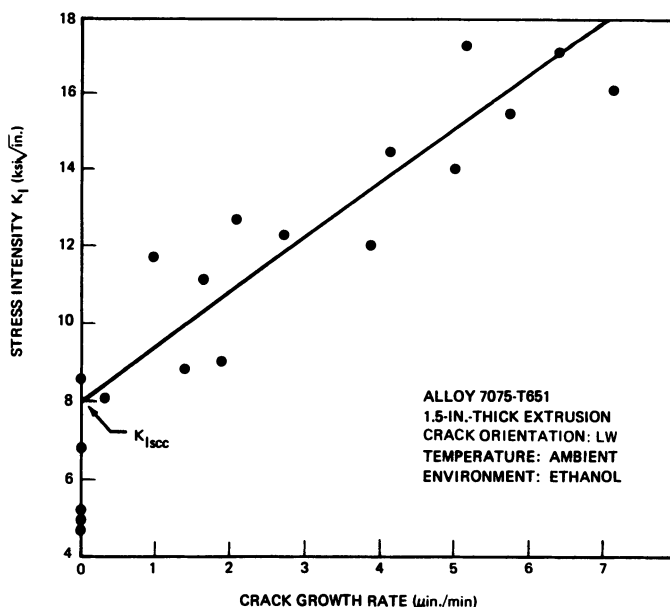


Fig. 71. Effects of stress intensity on stress-corrosion crack growth rate of a high-strength aluminum alloy immersed in ethanol (after Proctor and Paxton⁸³).

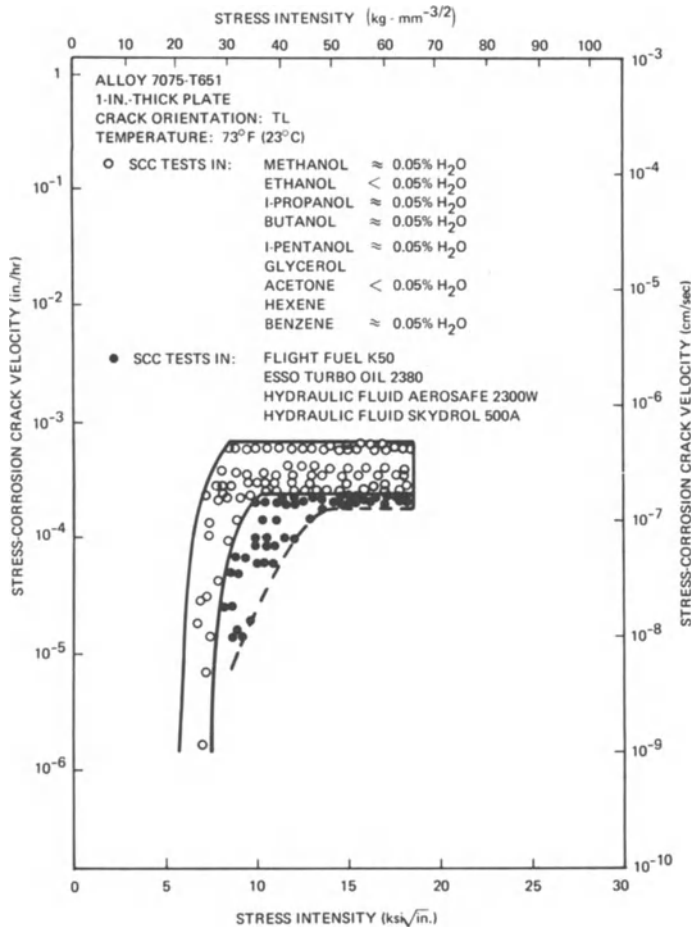


Fig. 72. Effect of various organic liquids on subcritical crack growth in a high-strength aluminum alloy.

as well as for acetone and hexene, the experimental data fall into a scatter band almost identical to that for SCC data in distilled water (Fig. 46). It might be speculated, therefore, that the water content of the organic liquids indicated in Fig. 72 is sufficient to cause stress-corrosion cracking. A number of the alcohols and acetone were therefore tested in a much dryer condition. A reduction of the water content of the alcohols and the acetone by a factor of 10 resulted in a reduction of the crack growth rate by a factor of 10. Adding water during the test caused the crack velocity to increase again. This is illustrated for butanol in Fig. 73. It seems, there-

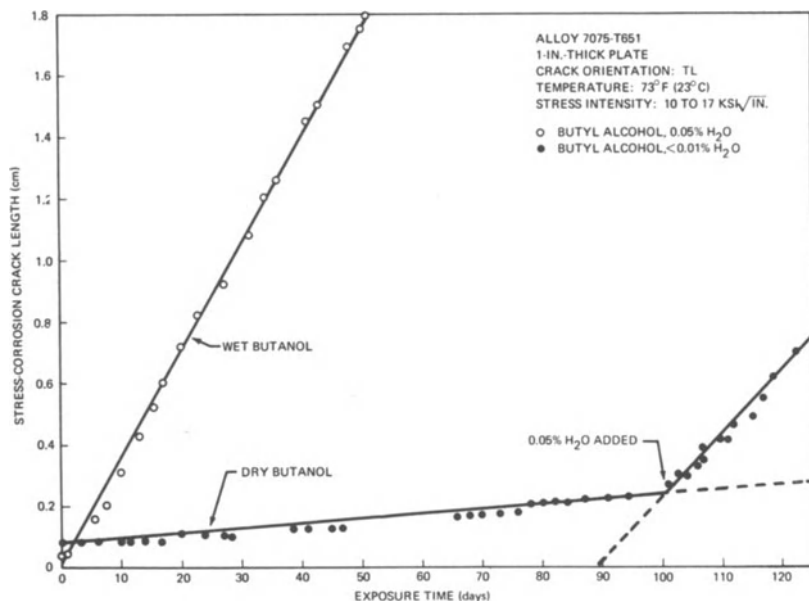


Fig. 73. Stress-corrosion crack growth in a high-strength aluminum alloy immersed in dry and wet butanol.

fore, that the stress-corrosion crack velocities of about 4×10^{-4} in./hr for alloy 7075-T651 in organic liquids are due to the water. Although this velocity is reduced by an order of magnitude when dryer liquids are used, there is no proof that the organic liquids are not also stress-corrosion agents with perhaps a much lesser associated crack velocity. Thus, while the effect of extremely pure organic liquids on SCC of high-strength aluminum alloys remains unknown, crack propagation caused by ordinary reagent-grade organic liquids can be attributed to the water content of these liquids.

A comparison of the data presented in Figs. 71 and 72 reveals that they agree essentially. The highest velocity reported in Fig. 71⁸³ at a stress intensity of 17 ksi in.^{1/2} falls into the center of the scatter band of Fig. 72 at the same stress intensity. The K_{ISCC} of 8 ksi in.^{1/2} reported in Fig. 71 corresponds to the transition from the plateau velocity to region I crack growth near 8 ksi in.^{1/2} in Fig. 72. This is the stress intensity at which the crack velocity in a DCB specimen rapidly decreases with increasing crack length. It is somewhat surprising that the quantitative results from partly transgranular *WL* cracks should agree so well with results from clearly intergranular cracks of the *TL* orientation.

Results of a systematic study of the effect of water additions on stress-corrosion crack growth in high-strength aluminum alloys are reported in Fig. 74 and 75. Figure 74 shows that the water influences mainly the plateau region of the V - K curve; region I crack growth at very low stress intensities is hardly influenced by the water. The effect of the water content of the methanol on the plateau velocity is shown in Fig. 75. Note that both pure water and dry methanol cause visible corrosion of the immersed aluminum-alloy specimens. Small water additions to the the methanol inhibit the corrosion

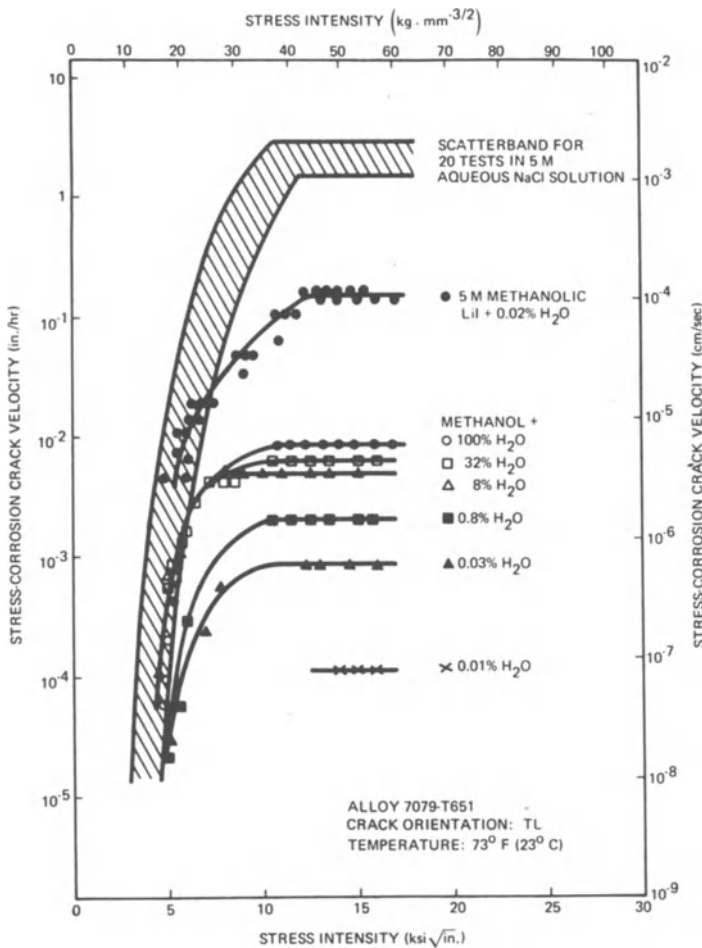


Fig. 74. Effect of stress intensity on velocity of stress-corrosion cracks in a high-strength aluminum alloy immersed in various methanolic environments.

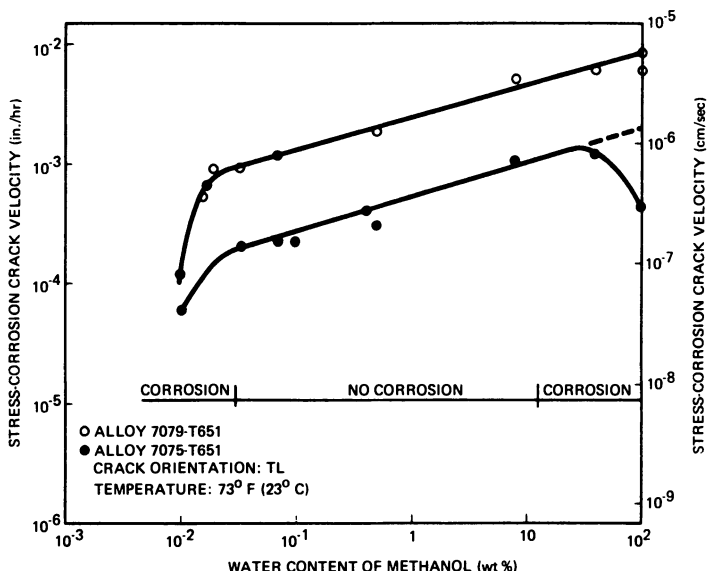


Fig. 75. Velocity of stress-corrosion cracks in a high-strength aluminum alloy as a function of water content in methanol.

markedly. Under such conditions, an increasing water content results in an increasing stress-corrosion crack growth rate.

Stress-corrosion crack growth rates of *TL* cracks of alloys 7075-T651 and 7079-T651 immersed in carbon tetrachloride are not measurably accelerated when the water content is increased from 0.0012% to 0.009%.⁴⁴ The measured plateau crack growth rates equal about 9×10^{-8} cm/sec. Surprisingly, this is less than one-tenth the crack velocity reported for partly transcrystalline *WL* cracks of alloy 7075-T651 in carbon tetrachloride.⁸³

Halide additions to organic solutions can greatly accelerate stress-corrosion cracks of susceptible high-strength aluminum alloys immersed in such solutions.⁴⁴ An example is given in Fig. 74, which shows the velocity of stress-corrosion cracks in alloy 7079-T651 immersed in a 5 M methanolic solution of LiI. The plateau velocity in this solution is more than two orders of magnitude higher than in a iodide-free solution of the same water content. Characteristically, region I crack growth at low stress intensities is not affected by either the iodide or the water additions. The few experimental data available concerning the effect of halide concentration on region II crack velocity in methanol are presented in Fig. 76. The acceleration of stress-corrosion cracks due to iodide in methanol appears to parallel

the observations made in aqueous solutions, i.e., no acceleration up to a threshold, followed by a linear increase of the crack velocity with iodide concentration in excess of about 2×10^{-2} mole/liter.

Included in Fig. 72 are the results of stress-corrosion crack growth measurements on alloy 7075-T651 immersed in four different organic liquids often used in aircraft. These liquids are flight fuel, engine oil, and two hydraulic fluids. They all contain traces of water. It is not surprising that the velocities of stress-corrosion cracks observed in these media are similar to those measured in the other water-containing organic liquids. It is of particular interest to note that subcritical crack growth of alloy 7075-T651 in flight fuel, engine oil, and hydraulic fluids (Fig. 72) is almost the same as in moist air of about 30% relative humidity (Figs. 41 and 42).

Liquid Metals

All high-strength aluminum alloys are susceptible to intergranular liquid-metal embrittlement (LME). The following liquid metals have been found to embrittle aluminum alloys: Hg, Ga, Na, In, Sn, and Zn.⁹⁴ The effect of liquid mercury on subcritical crack growth of high-strength

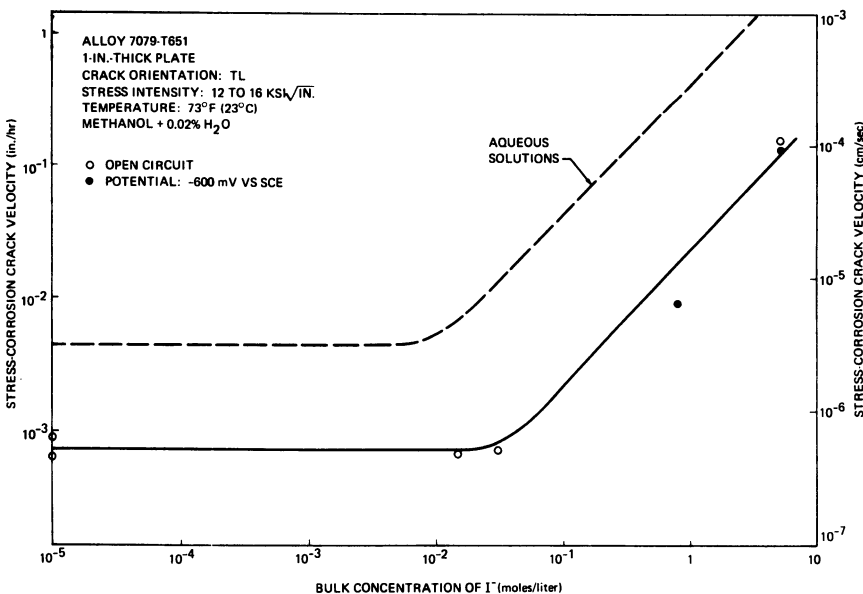


Fig. 76. Effect of iodide concentration on velocity of stress-corrosion cracks in a high-strength aluminum alloy immersed in methanolic solutions.

Table 6. Fracture Toughness of High-Strength Aluminum Alloys in Dry Air (K_{Ic}) and in Mercury ($K_{I_{LME}}$) at Ambient Temperature

Alloy	Fracture toughness			
	in mercury		in dry air	
	$K_{I_{LME}}$ (TL)		K_{Ic} (TL)	
	(ksi√in.)	(kg · mm ^{-3/2})	(ksi√in.)	(kg · mm ^{-3/2})
2024-T351	1.8	6.4	20-26	71-92
2024-T851	1.9	6.7	16-24	56-85
2024-W	5.8	20		
6061-T6	2.4	8.5	32-35	110-120
7039-T61	1.4	4.9	25-35	88-120
7079-T651	1.1	3.9	15-18	53-64
7075-T651	0.84	3.0	15-20	53-71
7075-T7651	1.0	3.5	22	78
7075-T7351	1.1	3.9	19-21	67-74
7178-T651	0.81	2.8	14-21	50-74
7178-T7651	1.0	3.5	17-19	60-67
7178-W	3.6	13		

aluminum alloys at room temperature has been intensively investigated. In contrast to the historical time-to-failure test, the fracture mechanics approach allows quantitative measurement of crack-tip velocity as a function of crack-tip stress intensity. Figure 20 shows a typical intergranular LME crack of the *TL* orientation. This specimen was of alloy 7075-T651 and the crack was filled with mercury at room temperature. The corresponding *V-K* curve is shown in Fig. 34. Note the very fast crack growth rate in the stress-independent region II of the *V-K* curve. The LME crack growth rate of most high-strength aluminum alloys is about 10⁴ in./hr. This crack velocity is too high to be followed visually. Thus a high-speed movie camera was used to obtain these data. Note the transition between region II and the strongly stress-dependent region I crack growth. At very low stress intensities, the crack velocity is so strongly stress-dependent that it is almost meaningful to speak of a threshold stress intensity $K_{I_{LME}}$ below which crack growth is not measurable. Table 6 reports the measured $K_{I_{LME}}$ data for many high-strength aluminum alloys that were embrittled by mercury at room temperature.

METALLURGICAL ASPECTS AND ALLOY DEVELOPMENT

Aluminum–Magnesium Alloys (5000 Series)

Wrought, strain-hardened Al–Mg alloys are used because they combine corrosion resistance with good formability, weldability, and medium strength. Alloy compositions for several common 5000-series alloys are

listed in Table 1. Typical applications for these alloys are given in Table 2. Mechanical, fracture, and corrosion properties are listed in Table 4.

Aluminum can accommodate more than 17% magnesium in solid solution. This is illustrated by the extent of the single-phase alpha region in the Al-Mg phase diagram (Fig. 77). Despite magnesium's high solubility in aluminum, the Al-Mg alloy system does not show appreciable precipita-

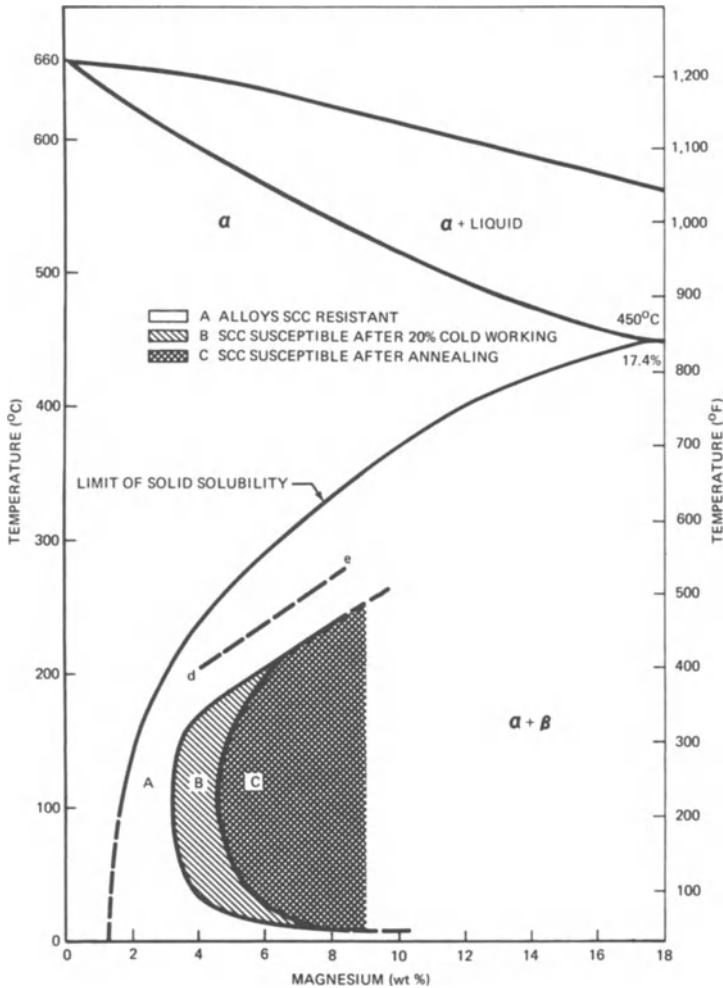


Fig. 77. Aluminum-rich portion of the Al-Mg phase diagram showing the effect of magnesium content and elevated-temperature exposure on susceptibility to SCC. Specimens were exposed to the various temperatures for two years. (Plotted from data in Refs. 95 and 96.)

tion hardening during aging at lower temperatures unless the magnesium content is greater than about 9%. Instead, considerable strength in alloys of this system can be achieved through working operations such as cold rolling.

Temper Designations

Commercial Al-Mg alloys are strengthened primarily by strain hardening. A brief description of the symbols used to indicate the amount of strain hardening is given below.

Strain-hardened commercial alloys are identified by the letter H in their temper designation. The first digit following the H indicates whether the material has been strain hardened only (H1), strain hardened and then partially annealed (H2), or strain hardened and then stabilized (H3). The digit following H1, H2, or H3 indicates the final degree of strain hardening. These digits range from 0 (annealed) to 8 (full work hardened, or about 75% reduction of area). The third digit, when used, indicates a variation of the two-digit H temper. For example, H323, H343, H116, and H117 apply to products specially fabricated to have acceptable resistance to SCC or exfoliation resistance. For more detailed information about temper designations, see Ref. 2.

Relationship between Microstructure and SCC

Ingots of commercial Al-Mg alloys are homogenized in the single-phase alpha region shown in Fig. 77. Rapid cooling from the single-phase region results in a supersaturated solid solution. One might expect, therefore, that substantial precipitation hardening should be possible. This is not observed in the composition range of the commercial Al-Mg alloys. It is thought that the poor precipitation hardening is due to the lack of GP zones. During annealing or heat treatment in the two-phase region, the supersaturated solid solution decomposes and precipitates occur as a transition phase β' (plates on $\{100\}$ and $\{120\}$) and as the equilibrium phase β (Mg_5Al_8).^{97,98} These precipitates generally nucleate heterogeneously at grain boundaries and dislocations, and therefore they are not distributed on a scale fine enough to cause significant precipitation hardening.

The precipitation reaction is sluggish at room temperature. It is accelerated by deformation (cold work), by exposure to elevated temperatures, and by higher magnesium content. Each of these factors plays an important role in determining the susceptibility to SCC of Al-Mg alloys. The effect of each of these variables on the susceptibility to SCC of Al-Mg alloys is illustrated in Figs. 77-81.

It is generally believed that these effects can be explained by the formation of a continuous grain-boundary film of Mg_5Al_8 . The Mg_5Al_8 phase is strongly anodic to the Al-Mg solid solution matrix in most electrolytes.⁹⁹ Thus, if a continuous film of beta grain-boundary precipitate occurs and if the proper environment is present, a susceptibility to intergranular or exfoliation attack will exist. It is thought that if sustained tensile stresses are also present, SCC can occur. Although this has been observed for many 5000-series alloys, such a correlation between susceptibility to intergranular corrosion and SCC might be fortuitous. And it should be kept in mind that this simple and sometimes helpful explanation for the relationship between microstructure and intergranular corrosion may not be applicable to explain SCC, as pointed out earlier (p. 132).

If it is true that a continuous film of grain-boundary precipitates causes susceptibility to SCC in 5000-series alloys, then two ways of producing a resistant microstructure are conceivable. The first method involves keeping the grain boundaries free of precipitates. Even for alloys containing more than 7% magnesium, this can be achieved simply by air cooling

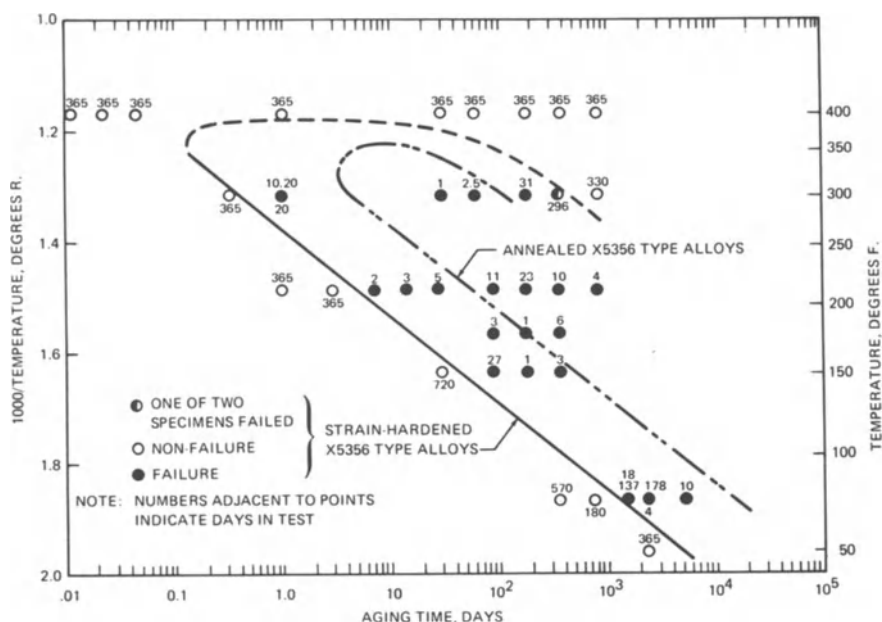


Fig. 78. Effects of time and temperature on sensitization to SCC in an Al-5.15% Mg-0.03% Cu-0.22% Fe-0.11% Sc-0.11% Mn-0.10% Cr-0.10% Ti alloy. Data were obtained on simple beam specimens loaded to 75% of yield strength and exposed to the 3.5% NaCl alternate-immersion test. (After Dix *et al.*⁹⁶)

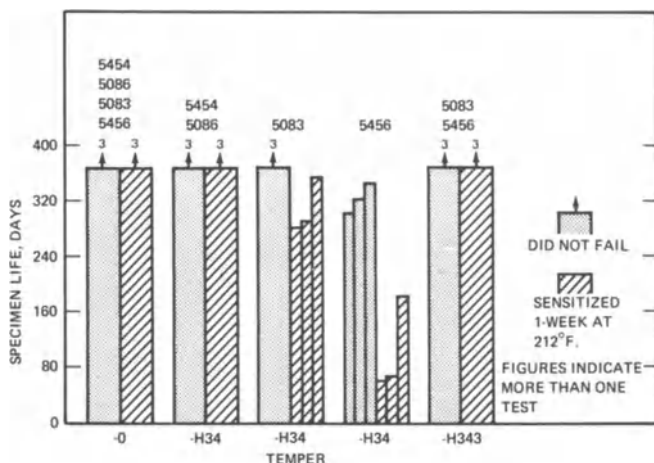


Fig. 79. Stress-corrosion resistance of stressed preformed specimens of several alloys of Al-Mg-Mn alloy sheet (0.064 in.) exposed to 3.5% NaCl solution by alternate immersion. In the O temper, alloys with Mg content up to 5.5% (5456) exhibit an excellent resistance to SCC. Strain-hardened and stabilized tempers such as H34 have a low resistance when Mg content is in the 4.0–5.5% range, as in alloys 5083 and 5456. Special tempers such as H343 have been developed to provide a high resistance to SCC for the latter alloys. (After Rutemiller and Sprowls.^{99a})

from the normal annealing temperature range. Such a clean grain boundary is shown in Fig. 82 for an alloy containing 8% magnesium.

This method of ensuring resistance to SCC by avoiding continuous grain-boundary films has always been successful with alloys containing less than about 3% magnesium. The composition range of such alloys falls into region A of Fig. 77. The alloys have excellent resistance to SCC and intergranular corrosion. In alloys of higher magnesium content, however, a network of continuous grain-boundary precipitates can develop from a very slow precipitation at ambient temperatures. As shown in Figs. 77 and 78, temperatures in the 100–350°F range accelerate the development of such a network and thus make these alloys susceptible to SCC. To simulate long-time atmospheric temperature aging, a “sensitizing treatment” consisting of heating at 212°F for seven days is often used. At ambient temperatures, it is not known how fast continuous networks will develop, but the probable time is from several years to as long as 50 years. However, under equal metallurgical and exposure conditions, it will take much longer to develop a network in an alloy with a low magnesium content (i.e.,

5086 with 4.0% Mg) than in an alloy with a high magnesium content (i.e., 5456 with 5.1% Mg). To avoid SCC and especially exfoliation corrosion, this factor should be given serious consideration, and it should lead to a choice of 5086 over 5456 unless the extra strength of 5456 is needed.¹⁰⁰ (See also Fig. 79.)

A second method of producing a SCC-resistant microstructure involves extensive precipitation throughout the grains. Under these conditions, magnesium-rich precipitates in the grain boundaries tend to be discontinuous.⁸⁵ If, instead of a narrow, continuous grain-boundary film of Mg_5Al_8 , wide bands of grain-boundary precipitate as well as extensive general precipitation are present, resistance to SCC is intermediate.⁵¹ In this case, it is thought that the improved resistance results from a reduced current density for the anodic Mg_5Al_8 precipitate, caused by the increase in anode/cathode ratio.⁵¹

To achieve general precipitation in the grain interior, severe plastic deformation followed by annealing just below the solid-solubility level is required. Cold work alone or cold work followed by insufficiently high

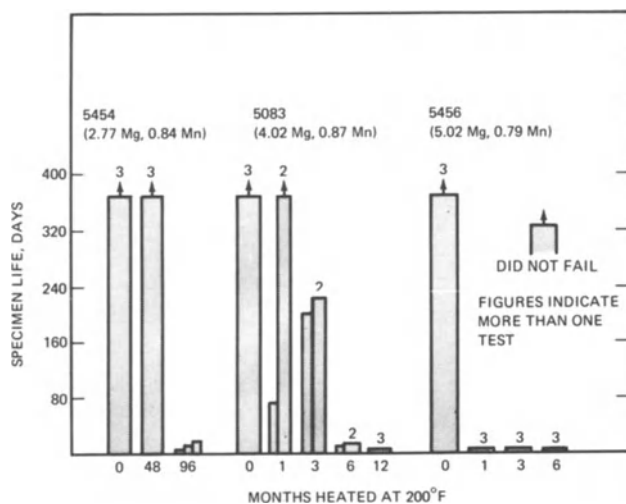


Fig. 80. Effect of heating on resistance to SCC of stressed, preformed specimens of Al-Mg-Mn alloy sheet (0.064 in.) exposed to 3.5% NaCl solution by alternate immersion. Strip specimens of O temper sheet were plastically deformed at room temperature prior to the 200°F exposure. Only the lower-magnesium-content alloy 5454 maintained a high resistance to SCC after prolonged heating at 200°F. (After Sprowls and Brown.⁵¹)

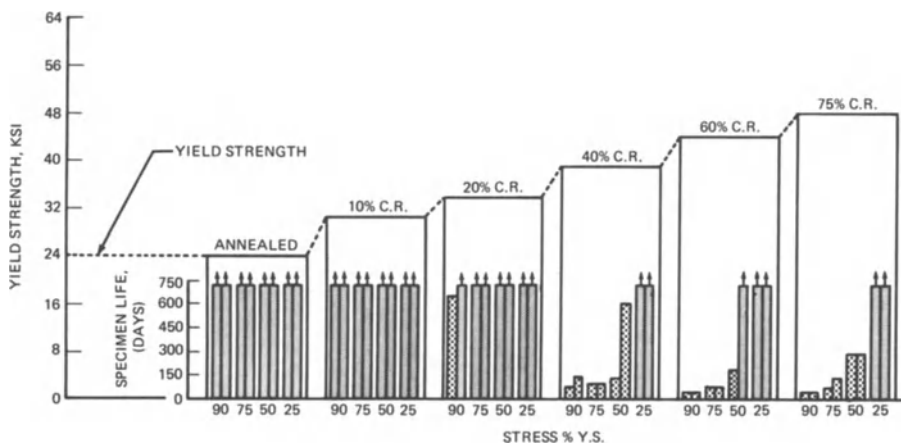


Fig. 81. Effect of cold reduction on yield strength and stress-corrosion resistance of Al-5.16% Mg-0.11% Mn-0.11% Cr-0.09% Cu alloy sheet (0.064 in.) exposed one week at 212°F. Sheet specimens were stressed by bending in constant deformation fixtures and exposed to 3.5% NaCl solution by alternate immersion. Bar graphs represent lives of individual specimens. (After Sprowls and Brown.⁶¹)

annealing temperatures stimulates precipitation of a continuous grain-boundary film. This is illustrated in Fig. 83, where, despite a high dislocation density from cold working, only grain-boundary precipitation has occurred during subsequent annealing at regions *B* and *C* of Fig. 77. The resulting low resistance to SCC from such a treatment is illustrated in Fig. 81.

One method of achieving a SCC-resistant microstructure in Al-Mg alloys containing 4–8% magnesium has been described as follows¹⁰¹: After homogenizing in the alpha solid-solution region (800–1050°F) (Fig. 77), the alloys are hot rolled and annealed between 600–800°F to remove the effects of work hardening. After cooling, the supersaturated solid solution is cold worked at temperatures below 500°F, with a reduction in cross section of at least 20%. This cold-worked material is then subjected to thermal treatment to produce the extensive general precipitation of the beta phase required to improve resistance to SCC. This treatment consists in heating to a temperature between 400 and 525°F (line *d–e* in Fig. 77) for a period of from 2 to 24 hr. As the position of line *d–e* in Fig. 77 indicates, a microstructure resistant to SCC results. Then, to achieve the desired strength, the material is cold worked, with a reduction in cross section of between 10 and 80%.

To stabilize the strength of this cold-worked material, it may be given a further thermal treatment at a relatively low temperature. Strength is slightly reduced, but age softening—a change that often occurs in cold-worked Al-Mg alloys—is effectively deterred.

These and other treatments provide tempers with increased stress-corrosion resistance. Examples are the H321, H323, H343, H116, and H117 tempers for Al-5% Mg alloys 5083 and 5456.^{1,85,100,102,103}

SCC and Exfoliation Corrosion in Commercial Aluminum–Magnesium Alloys

The authors are not aware of any service stress-corrosion problems with Al-Mg alloys containing <3.5% magnesium. Stress-corrosion cracking in Al-5% Mg alloy rivets has occurred, however, after exposure of the material to tropical temperatures.¹⁰⁴ The failures occurred at the junction



Fig. 82. Precipitate-free grain boundary in an Al-8% Mg alloy after air cooling from the single-phase α field.



Fig. 83. Grain-boundary precipitates in an Al-8% Mg alloy that was cold worked 20% and annealed in region C of Fig. 77.

of the shank and head, where the rivet had been severely cold worked during driving.

Stress-corrosion crack growth rate data for alloy 5456 in the more resistant H321 temper have been presented for the short transverse direction (see Table 7). The growth rates observed were very slow, but nevertheless, the alloy is not immune to SCC. This alloy is also susceptible to exfoliation and intergranular corrosion, as the Navy has experienced in a number of marine vessels where pitting, exfoliation, and intergranular corrosion occurred in the bottom of the bilge.¹⁰⁰ The alloy 5086-H32 can also be susceptible to these forms of attack, although its lower magnesium content makes it much less of a problem. To eliminate these problems with the H321 temper, two new tempers designated H116 and H117 are recommended.¹⁰⁰ These tempers apparently eliminate the continuous grain-boundary film

of Mg_5Al_8 . All production lots are examined metallographically and compared with standard photomicrographs to verify that each lot has a microstructure that is predominantly free of a continuous grain-boundary network of Al-Mg precipitate.¹⁰⁰

In addition to metallographic examination techniques, accelerated-corrosion tests for determining susceptibility to exfoliation corrosion in 5000-series alloys have recently been developed.¹⁰⁵⁻¹⁰⁷ One method, designated the seawater acetic acid test (SWAAT), involves a week-long exposure in an acidified salt fog at 120°F. The test cycle involves 30 min of continuous spraying followed by 90 min with the spray off.¹⁰⁶ This test has recently been adopted by the U. S. Navy upon recommendation of the Aluminum Association as a method of predicting exfoliation corrosion resistance in the Al-Mg alloys for boat and ship hull construction.^{106,106a}

Another accelerated test for exfoliation and intergranular corrosion susceptibility under consideration for incorporation in future specifications involves total immersion of the alloy for 24 hr in a solution of 1 M am-

Table 7. Short Transverse Stress-Corrosion Properties of Some High-Strength Aluminum Alloys

Alloy	Plateau velocity in saturated NaCl solution (in./hr)	Plateau velocity in distilled water (in./hr)	" K_{Isc} " (ksi $\sqrt{in.}$) ¹⁾	Smooth specimen stress-corrosion threshold stress (ksi) ⁴⁾
2014-T451	3×10^{-3} 2)		< 8	
2014-T651	8×10^{-4} 2)		< 7	8
2024-T351	9×10^{-4} 2)	3×10^{-4} 2)	8	7
2024-T4	1×10^{-3} 2)			< 8
2219-T37	3×10^{-3} 2)		< 8	< 10
2219-T87	$< 5 \times 10^{-6}$ 3)	$< 5 \times 10^{-6}$ 3)	≈ 26	> 41
5456-H321	1×10^{-4} 2)	1×10^{-4} 2)		
6061-T651	$< 5 \times 10^{-6}$ 3)	$< 5 \times 10^{-6}$ 3)	≈ 32	> 36
7039-T6151	8×10^{-4}	8×10^{-4}	4	< 5
7039-T6351	2×10^{-3}	2×10^{-3}	5	< 8
7039-T64	1×10^{-2}	2×10^{-3}	4	< 5
7049-T73	9×10^{-5}	9×10^{-5}		45
7075-T651	2×10^{-3}	5×10^{-4}	7	7
7075-T7651	3×10^{-5}	3×10^{-5}	< 20	25
7075-T7351	5×10^{-6}		≈ 21	> 43
7079-T651	2	6×10^{-3}	4	6
X7080-T7	6×10^{-5}			15
7175-T66	2×10^{-2}	5×10^{-4}	6	7
7175-T736	1×10^{-4}			≈ 35
7178-T651	2×10^{-3}	5×10^{-4}	7	7
7178-T7651	3×10^{-6}		≈ 17	25

1) " K_{Isc} " measured in NaCl solution at stress-corrosion crack velocity of 10^{-5} inches/hour

2) Stress-corrosion cracks grow only in alternate immersion

3) No stress-corrosion crack growth observed

4) Measured in 3.5% NaCl alternate immersion (30 days) or inland industrial environment (1 year), whichever is lower

monium chloride, 0.25 *M* ammonium nitrate, 0.01 *M* ammonium tartrate, and 3 g/liter hydrogen peroxide maintained at 150°F.¹⁰⁷ This test, designated the ASSET immersion test, is somewhat simpler to perform than the SWAAT test and requires a considerably shorter test period. Materials showing exfoliation or intergranular attack in either of these tests are considered unacceptable for boat or ship hull construction.^{106,107}

Manganese and chromium additions to aluminum alloys with 6 and 7% magnesium improve resistance to stress corrosion.¹⁰⁸ Reasons for this behavior are not certain, but manganese is known to increase precipitation in Al-Mg alloys,¹⁰⁹ and both manganese and chromium inhibit the formation of equiaxed grains and promote the formation of elongated grains.⁵¹ The addition of manganese is also helpful because a given strength can be achieved with a lower magnesium content,¹⁰² thus reducing the SCC threat.

5000-Series Alloy Development

X5090 is a recently developed Al-7% Mg strain-hardened and stabilized alloy. The composition limits for this alloy are shown in Table 1. As noted earlier, cold-rolled and stabilized tempers of Al-Mg alloys with magnesium contents above 5% usually are extremely susceptible to stress-corrosion cracking. This problem apparently has been overcome with the X5090 alloy, which was developed specifically to provide an alloy with the improved strength afforded by a magnesium content greater than 5% and a high resistance to SCC in the temper-rolled and stabilized conditions. Processing techniques for this alloy are still proprietary, and the only known difference between X5090 and other Al-Mg alloys besides its higher magnesium content is the addition of small amounts of beryllium and boron (Table 1).

The corrosion and stress-corrosion resistance of X5090 is being determined using two techniques. One method involves exposing preformed, long-transverse U-bend specimens to a marine atmosphere. To date, specimens of X5090 in about the H34 temper have been exposed more than five years in this atmosphere without failure.¹¹⁰ Other specimens in the H36 and H38 tempers have been exposed for nearly three years without failure.¹¹⁰

During the development of X5090, an accelerated laboratory test for stress-corrosion susceptibility was also developed. In this test, long transverse tension specimens are dead-weight loaded to 80% of their 0.2% yield stress and exposed to an aqueous 7% NaCl + 0.006 *N* NaHCO₃ solution. During testing, an external anodic current is applied. An empirical correla-

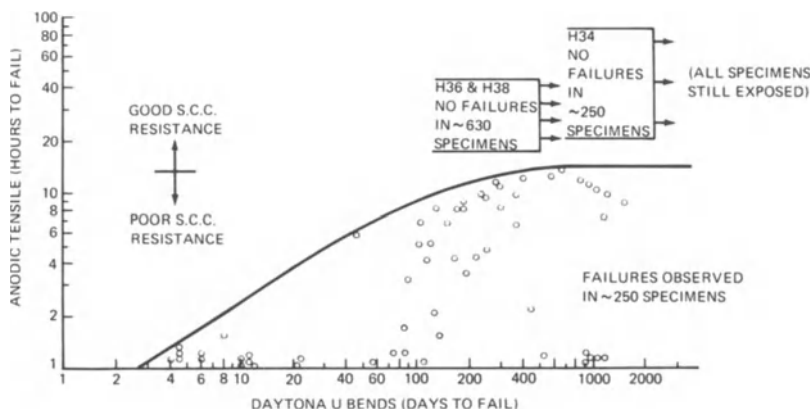


Fig. 84. Accelerated anodic tensile life versus marine-atmosphere exposure life of U-bend specimens of alloy X5090 (after Ford and Pryor¹¹⁰).

tion between the life of the specimen in the anodic tensile stress-corrosion test and the life of U-bend specimens exposed to the marine atmosphere has been observed and is shown in Fig. 84. On the basis of this correlation, it has been concluded that material with an anodic tensile life greater than 13–15 hr will not fail when exposed to the marine atmosphere, and therefore it has excellent, practical stress-corrosion resistance.¹¹⁰ The X5090 alloy in the H38 temper typically has an anodic tensile life of 20–25 hr, while less strain-hardened tempers show correspondingly longer lives. In actual practice, production lots of X5090 are evaluated using the anodic tensile test.¹¹⁰

In addition to excellent stress-corrosion resistance, X5090 apparently also possesses excellent resistance to general and localized corrosion, including pitting and exfoliation. Five-year test results from a 20-year test program being conducted in a marine atmosphere have been reported.¹¹⁰ These results indicate that X5090 exhibits pitting resistance equal or superior to that of 5086-0 and 5086-H34, which are known to possess excellent resistance to pitting corrosion. Whereas bare 2024-T3 and 7075-T6 test panels have shown typical exfoliation corrosion, X5090 has been found to be essentially resistant to marine atmospheric exfoliation corrosion after five years' exposure.

Mechanical, fracture, and fatigue properties of X5090 in the H34 and H38 tempers are compared with properties for several other commercial alloys, including the new high-strength clad 7000-series alloys, in Table 8. The strength advantage of X5090 over 5086 and 5052, and the similarity in strength between X5090 and 2024-T3 and 2014-T3, should be noted.

Table 8. Properties of Several Commercial Sheet Alloys

Alloy-temper	Thickness (in.)	Minimum tensile strength ¹		Min elong ¹ (%)	Transverse (WL) fracture toughness K_{IC} for 0.063-in. sheet ² (ksi $\sqrt{\text{in.}}$)	Flexure fatigue limit at 10^8 cycles ³ (ksi)	Density (lb/cu in.)
		Ultimate (ksi)	0.2% yield (ksi)				
X5090-H34	0.060	≈ 56	≈ 37	≈ 11	71	≈ 18.0	0.095
X5090-H38	0.060	≈ 66	≈ 50	≈ 7	74	22.0	0.095
5052-H34	0.051-0.113	34	26	6	≈ 120	18.0	0.097
5052-H38	0.032-0.128	39	32	4	89	---	0.097
5086-H34	0.051-0.249	44	34	6	≈ 120	---	0.096
5086-H38	0.006-0.020	50	41	3	---	---	0.096
2014-T3	0.040-0.249	59	36	14	---	---	0.101
2014-T6	0.040-0.249	66	58	7	54-60	---	0.101
2024-T3	0.021-0.049	64	42	15	90-110	18	0.100
2024-T36	0.020-0.062	67	50	8	67-90	19	0.100
2024-T81	0.010-0.249	67	58	5	50-57	---	0.100
2024-T86	0.020-0.062	70	62	3	47-48	---	0.100
6061-T6	0.021-0.249	42	35	10	91-120	13	0.098
7178-T6	0.045-0.249	84	73	8	43-57	≈ 20	0.102
7178-T76	0.045-0.249	75	64	8	54	≈ 20	0.102
7075-T6	0.040-0.125	78	68	8	54-69	20	0.101
7075-T76	0.125-0.249	73	62	8	---	---	0.101
X7475-T61	0.040-0.249	≈ 75	≈ 64	≈ 9	65-110	---	0.101
X7475-T761	0.040-0.249	≈ 71	≈ 60	≈ 9	75-110	---	0.101
7079-T6	0.040-0.249	74	65	8	69-89	≈ 20	0.099
Alclad 2014-T3	0.040-0.249	57	35	15	102-113	15	---
Alclad 2014-T6	0.040-0.249	64	57	8	50-68	15	---
Alclad 2024-T3	0.021-0.062	59	39	15	80-103	13	---
Alclad 2024-T36	0.020-0.062	61	47	8	68-90	13	---
Alclad 2024-T81	0.010-0.062	62	54	5	57-62	13	---
Alclad 2024-T86	0.020-0.062	64	58	3	46-54	13	---
Alclad 7178-T6	0.045-0.062	78	68	8	45-47	≈ 13	---
Alclad 7178-T76	0.045-0.062	71	60	8	≈ 54	---	---
Alclad 7075-T6	0.040-0.062	72	62	8	55-68	13	---
Alclad 7075-T76	0.125-0.187	68	57	8	---	---	---
Alclad 7079-T6	0.040-0.062	69	60	8	62-70	≈ 8	---
7011 alclad 7178-T6	0.045-0.062	81	70	8	37	≈ 16.5	---
7011 alclad 7178-T76	0.045-0.062	73	62	8	---	---	---
7011 alclad 7075-T6	0.040-0.187	75	65	8	48	≈ 17.5	---
7011 alclad 7075-T76	0.040-0.062	70	59	8	---	---	---
7011 alclad 7079-T6	0.040-0.249	72	63	8	50	≈ 14	---
7008 alclad 7075-T6	0.040-0.062	≈ 76	≈ 66	8	≈ 54-69	---	---
7008 alclad 7075-T76	0.040-0.249	≈ 71	≈ 61	8	---	---	---
7008 alclad X7475-T61	0.040-0.249	≈ 73	≈ 63	≈ 8	≈ 65-110	≈ 16.5	---
7008 alclad X7475-T761	0.040-0.249	≈ 70	≈ 59	≈ 8	≈ 75-110	≈ 16.5	---

¹Data are for long-transverse grain direction except for 5052 and 5086 (longitudinal direction). Minimum for X5090 obtained by subtracting 3 ksi from typical data for X5090 from reference 111. Minimum for other alloys taken from references 2 and 193, 194, 195, 196, 197.

²Data taken from references 11, 20, 111, 192, and 198.

³Data taken from references 112 and 192.

Note also the lower density of X5090 compared with the other 2000- and 7000-series alloys and the high fatigue properties of X5090 compared with the regular alclad materials.

To more fully characterize X5090, test data in several other areas are required. These include: low-temperature mechanical and fracture properties, corrosion characteristics in industrial atmosphere, corrosion charac-

teristics after various exposure times at several elevated temperatures that may be encountered in service or during assembly (adhesive bonding cycles), fatigue crack growth rate properties in various environments, and fatigue tests of built-up structural panels to determine whether the smooth fatigue properties adequately reflect actual performance in structural applications.

Aluminum–Magnesium–Silicon Alloys (6000 Series)

Alloys of the 6000 series are used in applications requiring intermediate strength and a high resistance to corrosion and stress-corrosion cracking. Alloy compositions for several common 6000-series alloys are listed in Table 1. Typical applications for these alloys are given in Table 2. Heat treatments for these alloys can be found in Table 3. Mechanical, fracture, and corrosion properties are listed in Table 4.

Commercial alloys based on the ternary system Al–Mg–Si (6000 series) are strengthened by precipitation hardening. This hardening is achieved by solution heat treatment at 970–990°F, followed by quenching and artificial aging at temperatures between 320 and 350°F. After aging 10–20 min in this temperature range, the first needlelike zones with a composition of approximately Mg_2Si can be detected, which grow to a length of about 1000 Å, a diameter of 60 Å, and a density of 5×10^{15} needles/cm² as the hardness maximum is approached.^{113,114} The high strength of the Al–Mg–Si alloys in this condition is due to the interaction of dislocations with the finely dispersed needlelike zones. Some 6000-series alloys (e.g., 6061) can be considered as pseudo-binary alloys Al–Mg₂Si. Other alloys, such as 6151, 6066, and 6070, contain excess silicon for additional strength. Small amounts of silicon, such as 0.2%, increase the strength of an 0.8% Mg_2Si alloy by 8000–12,000 psi; larger amounts of silicon are less beneficial.¹⁰⁹ In addition to excess silicon, alloys 6066 and 6070 contain additions of copper and manganese to increase strength; these two alloys develop the highest strength levels in this class of alloys.

Excess silicon tends to lower slightly the resistance to stress corrosion, but the resistance is still relatively high.⁵¹ Manganese and chromium additions to 6000-series alloys control grain size and increase both strength and ductility.¹¹⁵ Chromium and manganese additions have also been shown to minimize intercrystalline attack in acid–salt or salt–peroxide solutions, especially in the presence of small amounts of the tramp element iron.¹¹⁵ Copper is also a beneficial addition for increased strength, but amounts greater than about 0.5% reduce the resistance to corrosion.¹¹⁶

Although the Al-Mg-Si alloys are highly resistant to corrosion and to stress-corrosion cracking,^{51,115} certain abnormal thermal treatments can make these alloys susceptible to stress-corrosion cracking in the naturally aged T4 condition. This occurs when a high solution-heat-treating temperature is used, followed by a slow quench.^{51,117} Even in this condition, SCC on transverse 6061-T4 specimens has occurred only on highly stressed, plastically deformed (preformed) specimens and not on tensile-type specimens stressed to 75% of the yield strength. Aging the slowly quenched 6061-T4 material to the T6 temper eliminates the SCC tendency.⁵¹

The excellent stress-corrosion resistance of 6061-T6, even in the short transverse direction, has been confirmed by the double-cantilever-beam test.^{44,45} (see Table 7). Even when stressed to crack-tip stress intensities near K_{Ic} , no subcritical crack growth was observed in air, water, salt solution, or alternate immersion in NaCl solution. Moreover, the resistance of 6061-T6 to liquid-metal embrittlement by mercury was high compared to that of other aluminum alloys (Table 6).

It is known that Al-Mg-Si alloys can be susceptible to intergranular corrosion even when they are immune to SCC.^{51,56-58} This was again confirmed with a 6061-T6 alloy by using a *TL* DCB specimen loaded to just below K_{Ic} in an environment where rapid intergranular corrosion occurs. After the test, the specimen was broken open and it was observed that the depth of intergranular attack in the region of very high stresses was the same as that in the unstressed parts of the specimen.^{44,45} Thus, proposed explanations for the intergranular corrosion in these alloys⁵¹ based on the formation of local cells due to grain-boundary precipitates of Mg_2Si ¹¹⁸ or pure silicon¹¹³ are not applicable to SCC. Nor can these models be used to explain the observed fact⁵¹ that short transverse specimens from rolled plate or transverse specimens from rods of excess-silicon alloys such as 6070-T6 and 6066-T6 are susceptible to SCC, whereas specimens of 6061-T6 are not. The formation of local cells due to grain-boundary precipitates of silicon could, however, explain the increased susceptibility to intergranular corrosion of excess-silicon alloys.⁵¹

Aluminum-Copper-Magnesium Alloys (2000 Series)

Al-Cu-Mg alloys were the first heat-treatable, high-strength aluminum alloys and today they are still among the most popular and useful. Chemical compositions for the most widely used commercial 2000-series alloys are listed in Table 1. Typical applications are given in Table 2; heat treatments, in Table 3; and mechanical, fracture, and corrosion properties, in Table 4.

Al-Cu and Al-Cu-Mg alloys derive their high strength from precipitation hardening. This is achieved by solution heat treatment, followed by rapid cooling and either natural aging at room temperature (T4 temper) or artificial aging at intermediate temperatures (T6 temper). Cold working after the quench further increases strength, resulting in the T3 temper and, when artificially aged, the T8 temper.

Physical Metallurgy

Heat treatment, microstructure, and precipitation hardening of the multicomponent commercial 2000-series alloys can be understood to some extent by studying the underlying binary alloy system, Al-Cu. The phase diagram of the aluminum-rich part of the system is shown in Fig. 85. Aluminum can hold up to 5.7% copper in solid solution. The 2000-series alloys are solution heat-treated between 920 and 995°F. At that temperature, most of the alloying additions go into the FCC solid solution, as evident from Fig. 85. Through rapid cooling to room temperature, a solid solution supersaturated with copper, vacancies, and other alloying additions can be obtained. During aging at temperatures from ambient to the solid-solubility limit (Fig. 85), the supersaturated solid solution decomposes and, under certain conditions, this can lead to a considerable strengthening of the alloy. The distribution of copper in the alloy is also of primary influence on the resistance to intergranular corrosion and stress-corrosion cracking.

The thermodynamically stable end product of the decomposition of the supersaturated Al-Cu solid solution is a two-phase structure containing the saturated FCC solid solution α and the equilibrium phase θ , which has a tetragonal crystal lattice and the approximate composition CuAl_2 . Because of differences in the crystal structures, the equilibrium phase θ is not coherent with the FCC solid solution. The high interface energy ($> 1000 \text{ ergs/cm}^2$)¹¹⁹ results in a high activation energy for nucleation of θ ; this is why a series of metastable phases with lower activation energy for nucleation can be formed before equilibrium is attained. The precipitation sequence has been studied thoroughly and is generally given in the following way^{97,119,120}:



The GP zones are two-dimensional, disk-shaped, copper-rich layers of about 50 Å diameter, coherent with the matrix and parallel to $\{100\}$ planes. θ'' symbolizes ordered coherent platelets that are parallel to $\{100\}$ planes

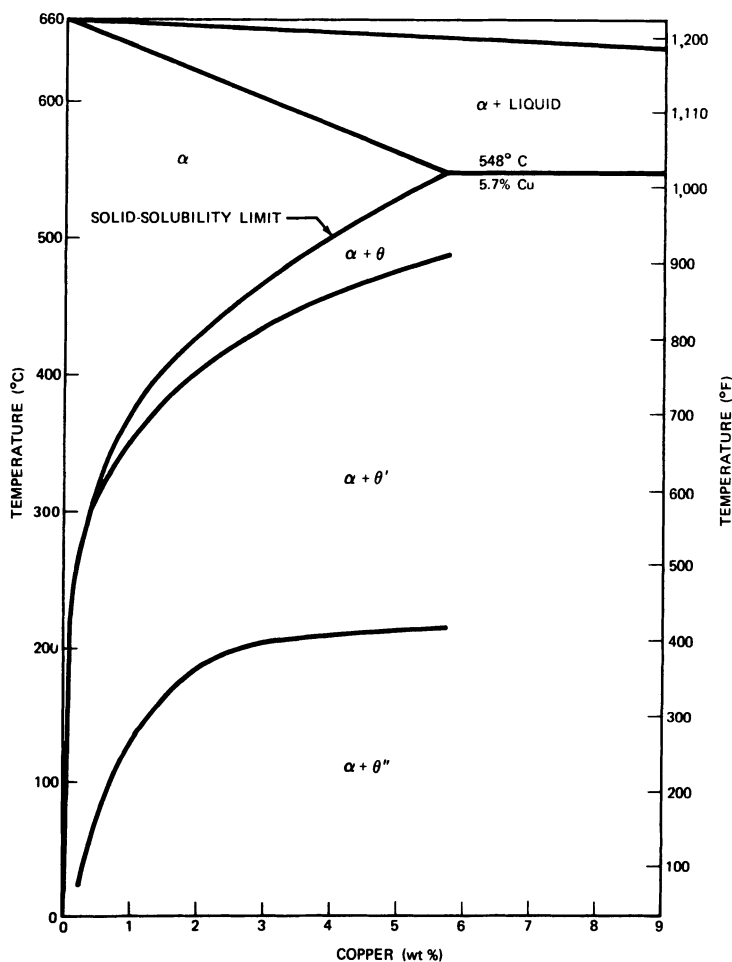


Fig. 85. Aluminum-rich portion of the Al-Cu phase diagram showing meta-stability lines for the θ'' , θ' , and θ phases (from data in Refs. 95 and 119).

of the matrix. They are up to 100 Å thick and have diameters up to 1500 Å. θ' is a semicoherent transition phase of the composition CuAl_2 . θ' platelets have a typical diameter of more than 1000 Å and a thickness of ~ 300 Å. They are parallel to the $\{100\}$ planes of the matrix.

The regions of metastability of θ'' and θ' are indicated in Fig. 85. It can be seen that for alloys with more than 1% copper, it is possible to go through the full aging sequence both during "natural" aging at room temperature and "artificial" aging between 320 and 390°F. That is to say, it

would be possible if the alloys were ideal crystals without dislocations and grain boundaries. However, precipitation from real, supersaturated aluminum-base alloys cannot even be qualitatively understood with the knowledge of the stable and metastable phase diagrams only. Knowledge of the role of lattice defects as nucleation sites is indispensable for an understanding of kind and distribution of precipitates as a function of solution temperature, quench rate, plastic deformation, aging temperature, and so on. Lattice defects that affect nucleation and growth of precipitates are: vacancies, dislocations, grain boundaries, and other precipitates.

Five mechanisms of nucleation are of importance in Al-Cu alloys¹¹⁹: (1) formation of θ at grain boundaries, (2) formation of θ' at dislocations, (3) formation of GP zones and θ'' at vacancies, (4) transition $\theta'' \rightarrow \theta'$, (5) transition $\theta' \rightarrow \theta$.

Competition between these reactions as functions of time, temperature, alloy composition, and defect structure is best presented in the form of nucleation diagrams. These are available in the literature for binary Al-Cu alloys.¹¹⁹ Nucleation diagrams for commercial alloys are not yet available, although they could be very helpful in relating heat treatment, microstructure, and resistance to corrosion.

Before any quantitative correlations between heat treatment, microstructure, and resistance to SCC of high-strength aluminum alloys can be made, certain relationships must be known. Metastable as well as stable phase diagrams, nucleation diagrams, and V - K curves for each alloy and heat treatment must be understood. It will become obvious in the following sections that our present knowledge of all these relationships is spotty at best.

Additions of magnesium to Al-Cu alloys accelerate and intensify precipitation hardening. Therefore, some commercial 2000-series alloys contain up to 1.8% magnesium, e.g., the alloy 2024. In such ternary and higher-order alloys of considerable copper content (about 4% Cu), two parallel precipitation sequences occur at the same time.⁹⁷ The first one is the same as that indicated above for the binary Al-Cu alloys, although its kinetics are affected by further alloy additions. The other precipitation sequence can be summarized as follows:

Solid solution $\rightarrow$ GPB zones $\rightarrow$ S phase

The GPB zones are coherent, spherical particles with a diameter of about 16 Å. They are ordered, containing magnesium and copper planes parallel to the $\{100\}$ planes of the matrix.^{97,121} Like the GP zones and the θ'' phase of the Al-Cu system, they can nucleate at vacancies. The GPB

zones have the approximate composition Cu–Mg. The *S* phase is lath-shaped and is preferentially nucleated at dislocations just as the θ' phase in the Al–Cu alloy. It is at least partially incoherent with the matrix and has the approximate composition Al_2CuMg .

It is surprising that a quantitative evaluation of the processes occurring during the standard thermomechanical treatment of such widely used alloys as 2024 is not yet available. A simplified qualitative description of the thermomechanical treatment for this alloy is as follows. At the solution-treatment temperature, most of the alloying elements are in solid solution. The manganese-rich and other intermetallic particles, however, are not soluble. These particles aid in retarding movement of grain boundaries, resulting in retention of the elongated grain structure formed during fabrication of the wrought product. Rapid cooling from the solution-treatment temperature leads to a supersaturated solid solution with the copper, and the magnesium distributed almost homogeneously throughout the matrix. In this condition, even the grain boundaries are free of precipitates, as illustrated in Fig. 86. If cooling rates during quenching are slower than about 1000°F/sec, the nucleation and growth of a copper-rich phase can occur at grain boundaries, leaving a zone depleted of copper adjacent to the boundary.

During subsequent aging at room temperature, which leads to the T4 and T3 tempers, the GP and GPB zones precipitate homogeneously throughout the matrix. The interaction of these particles with dislocations is responsible for strengthening the naturally aged tempers.

During artificial aging at 375°F, strength increases further by precipitation of the phases θ'' , θ' , and *S*. Plastic deformation after quenching and prior to artificial aging leads to a finer distribution of the semicoherent phases θ' and *S*, which nucleate preferentially at dislocations. During the initial stages of artificial aging, the noncoherent copper-rich phases θ and *S* nucleate and grow preferentially at grain boundaries, leading to copper-depleted regions adjacent to the grain boundary. Strength initially decreases during artificial aging due to partial reversion of the GP and GPB zones. As aging continues, a maximum in strength is reached when the alloy contains numerous small particles of the phases θ'' , θ' , and *S*. During precipitation, these copper-rich particles form throughout the grain (Fig. 87). This general precipitation depletes the entire matrix of copper, and thus the material no longer contains a preferentially depleted region adjacent to the grain boundaries.

The 2000-series alloys can contain additions of manganese, silicon, iron, nickel, lithium, cadmium, tin, zirconium, vanadium, and titanium

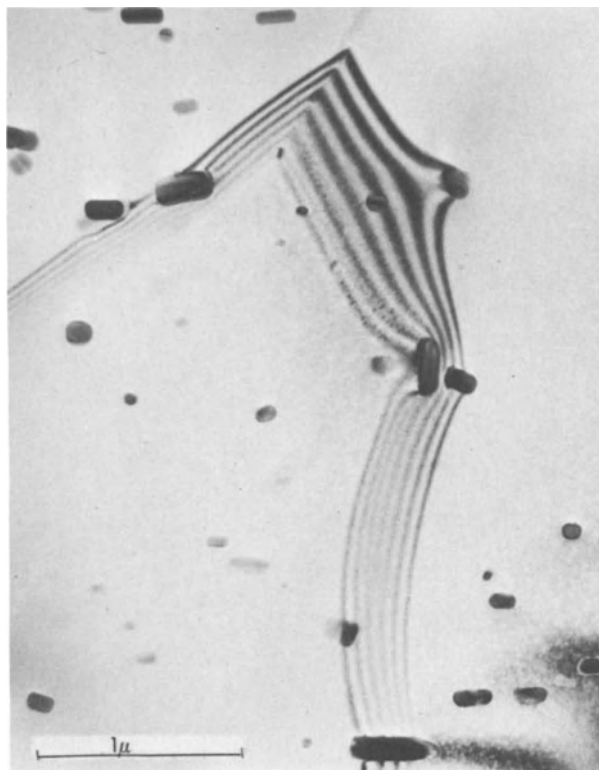


Fig. 86. Microstructure of a rapidly quenched 2024 alloy showing the absence of any visible Al-Cu-Mg precipitates. Note the larger recrystallization-retarding, manganese-rich intermetallic particles. (After Speidel.¹⁴⁴)

for specific applications. The most widely used 2000-series alloys, 2024 and 2014, contain additions of magnesium and manganese for increased strength. Reductions in fabrication characteristics and ductility with manganese additions limit the concentration of this element to about 1% in commercial alloys. Additions of cobalt, chromium, and molybdenum to the wrought Al-4Cu-0.5Mg type of alloy increase the tensile properties on heat treatment, but they do not offer a distinct advantage over manganese.¹⁰⁹

Silicon additions, as in 2014, are utilized to make Al-Cu-Mg alloys more amenable to artificial aging.¹¹⁶ Iron and nickel additions, as in 2618, improve the strength of Al-Cu-Mg alloys at elevated temperatures. This results from the presence of the intermetallic phase FeNiAl_9 , which forms during solidification and is insoluble during subsequent heat-treatment

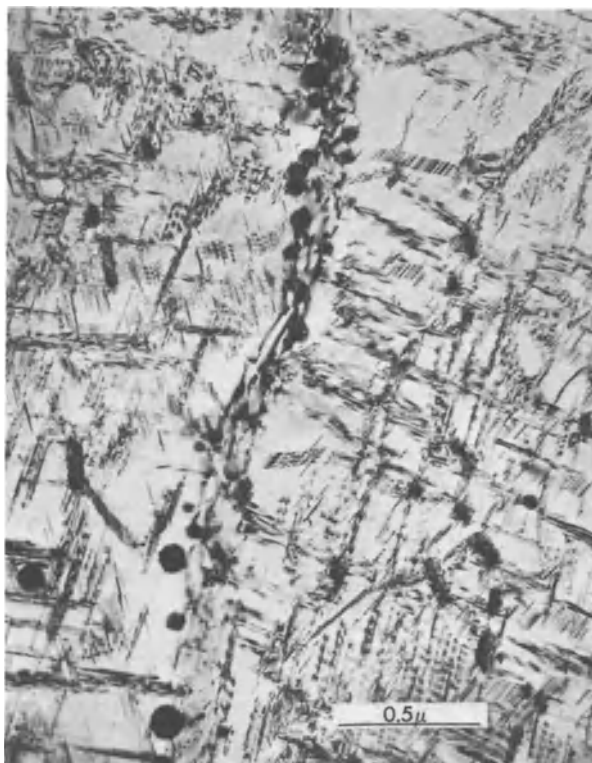


Fig. 87. General precipitation in a 2024 alloy after quenching and aging at 392°F for 22 hr.

operations. These particles reduce the grain size of the final product and, by stabilizing this grain size, also improve the creep strength of the alloy. The particles have little effect on the mode of precipitation hardening other than to increase the density of dislocations in their neighborhood on quenching (due to a different coefficient of thermal expansion), thus locally increasing the quantity of heterogeneously nucleated *S* precipitates.¹²² The British equivalent of 2618 in RR.58; this alloy is being used extensively in the Concorde, the British–French supersonic transport. Lithium and cadmium additions, as in X2020, accelerate artificial aging and increase strength. In addition, lithium reduces density and appreciably increases the modulus of elasticity—for example, 11.4×10^6 psi in compression versus 10.5×10^6 psi for 2024.^{109,116,123}

The lower-magnesium-content alloys like 2014 and 2219 are weldable and have been used in a number of space-vehicle applications in place of

the heavier, lower-strength, but readily weldable alloys such as 5456 and 5083, which were used on Saturn I. Alloy 2014, for example, was used in the Titan II, and in the S-II second stage and S-IVB third stage of Saturn V, while 2219 was used for the S-IC booster stage of Saturn V.

In an attempt to provide even higher-strength weldable aluminum alloys with good cryogenic toughness, alloy 2021 has been introduced.¹²⁴ Alloy 2021 is a complex alloy requiring close control of 11 elements. As in the case of 2219, the basic hardening of 2021 is provided by precipitation of a transition Al-Cu phase. However, nucleation of the hardening phase during elevated temperature aging is stimulated in 2021 by additions of cadmium and tin.¹²⁵ The result is a slightly higher strength than that of 2219. Of the other additions in 2021, manganese provides supplementary strengthening and aids in the control of grain size during fabrication. Titanium is an ingot grain refiner that is added together with zirconium and vanadium to minimize weld cracking. An upper limit is placed on magnesium content to avoid formation of the insoluble Mg_2Sn phase, which interferes with precipitate nucleation.¹²⁵

Unlike other 2000-series alloys, 2021 is subject to reduced yield strength in the final heat-treated material if it is cold worked prior to artificial aging; this results from an alteration in precipitate nucleation.¹²⁴ The harmful effects of cold working, such as stretcher straightening to flatten and stress-relieve quenched plate, can be minimized by stretching after a preaging treatment of 1 hr at 300°F. The preaging treatment establishes the precipitate pattern prior to straightening.¹²⁵ The temper designation for 2021 preaged, stretched a maximum of 1.5%, and artificially aged is T81.¹²³

Susceptibility to Stress-Corrosion Cracking

In the naturally aged T3 and T4 tempers, 2000-series alloys such as 2024, 2014, and 2219 are highly susceptible to SCC in the short transverse direction (Table 4). Even in the artificially aged T6 temper, 2014 is susceptible. Examples of in-service stress-corrosion cracking of these alloys attesting to this susceptibility can be found in recent literature.^{50,126} For example, stress-corrosion cracking of machined 2024-T4 parts has occurred fairly recently on the Saturn V Apollo moon rocket.

Typical V - K curves for these three alloys are shown in Fig. 88. Cracking in both regions I and II (defined earlier) is apparent, and the data indicate that " K_{ISCC} " is below 7 ksi in.^{1/2}. Similar V - K curves for the naturally

aged 2024 and 2219 alloys and the artificially aged 2014-T6 alloy agree well with the fact that all these alloys have similar low stress-corrosion resistance based on time-to-failure data (Table 4 and Fig. 44). In addition, the survival rate data in Fig. 45 show that 2014-T6 and 2024-T4 have similar low resistance when stressed in the short transverse direction.

Data for alloy RR.58 (2618) are shown in Fig. 89. The high apparent K_{ISCC} value is in line with the high smooth-specimen threshold stress reported for this alloy (Table 4). The fact that the maximum growth rates reported for RR.58 (Fig. 88) are nearly an order of magnitude greater than those of the susceptible alloys 2024-T3, 2014-T6, and 2219-T37 (Fig. 88) is somewhat surprising.

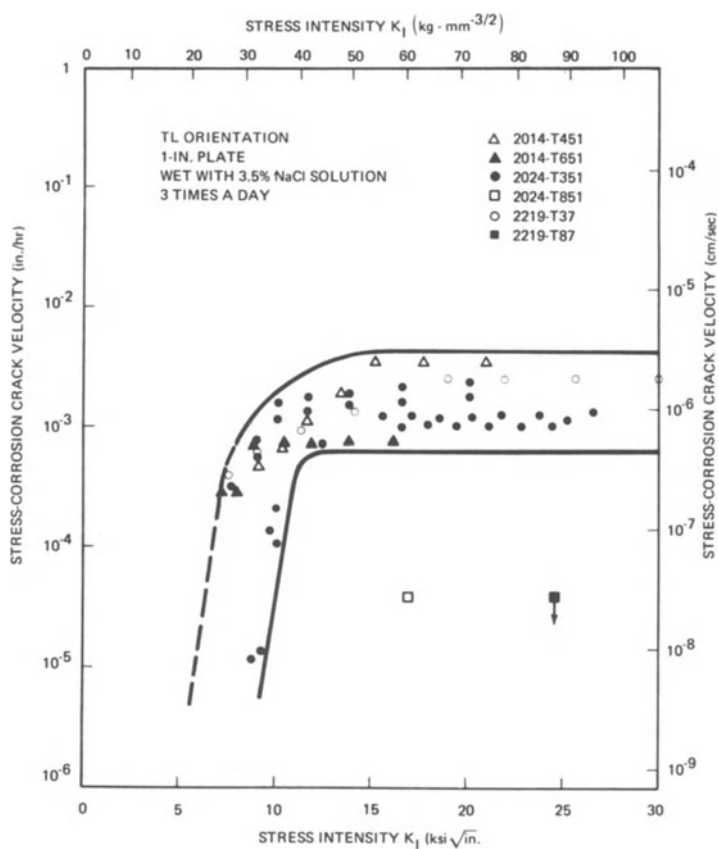


Fig. 88. Typical V - K curves for some 2000-series alloys obtained using TL DCB stress-corrosion specimens.

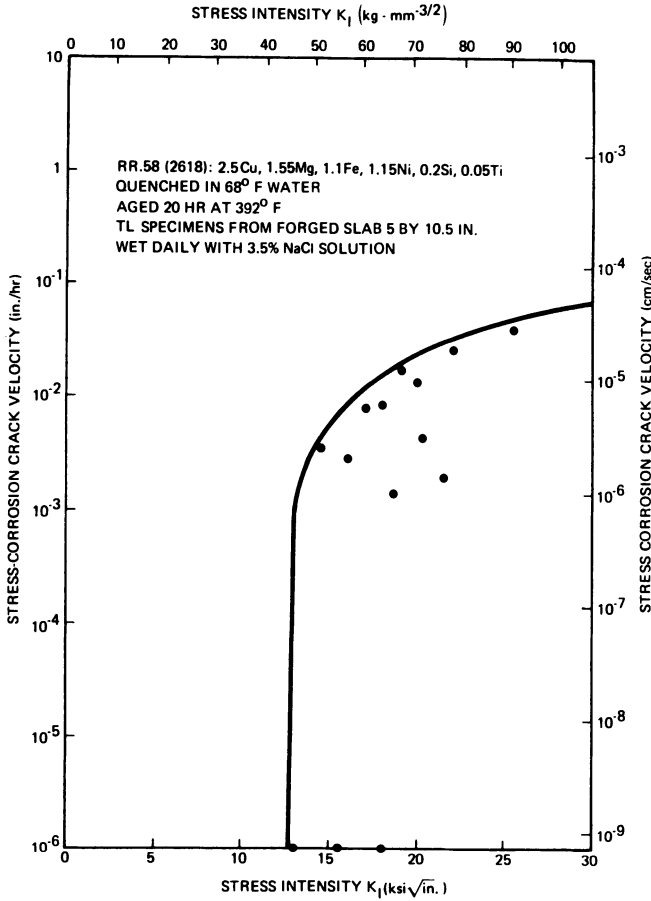


Fig. 89. V - K data for alloy RR.58 (2618-T6) (after Baxter.¹²⁷)

Effects of Quench Rate

Corrosion and apparently also stress-corrosion properties of such 2000-series alloys as 2024-T3 and -T4 are strongly influenced by the quench rate from the solution-treatment temperature. Quench rates that can be achieved with various thicknesses and quench water temperatures are shown in Figs. 90 and 91, and the effect of quench rate on the mechanical properties as well as type and extent of corrosion in 2024-T4 sheet is shown in Fig. 92. At the fastest quench rates, only pitting attack occurred. As quenching rate decreased below 1000°F/sec, the type of attack became increasingly intergranular. This susceptibility to intergranular corrosion after slow quenching has been explained on the basis of localized electro-

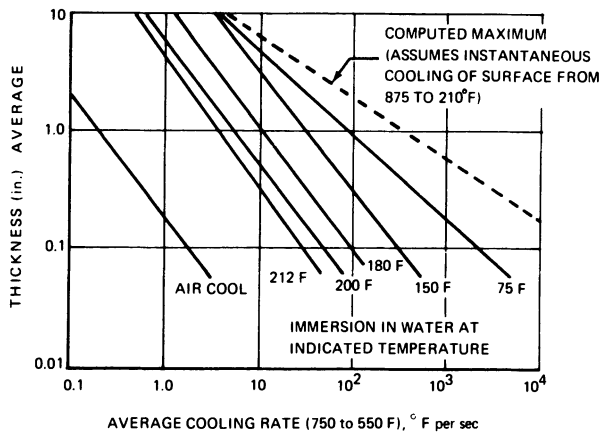


Fig. 90. Effects of thickness and quench-water temperature on average cooling rates at midplane of aluminum-alloy sheet and plate quenched from solution temperatures (after Hunsicker¹²⁸).

chemical effects associated with the formation of copper-rich grain-boundary precipitates and adjacent depleted zones that form during the quench.^{129,130} Note that tensile properties do not serve as a criterion for determining whether quench rates were slow enough to cause susceptibility to intergranular attack, since tensile properties are virtually independent of the quench rate over the range studied. The data on loss in tensile strength

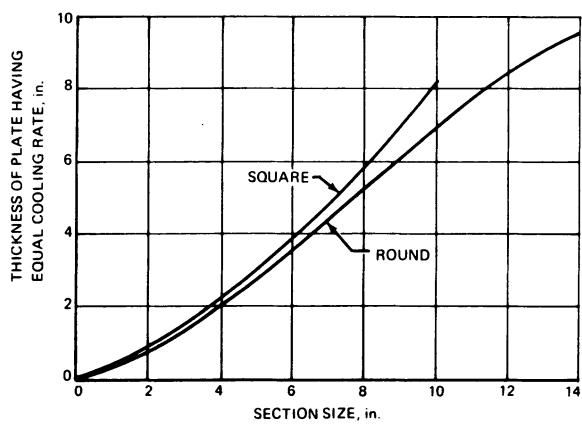


Fig. 91. Experimentally determined correlation between average cooling rates (750–550°F) of rod and square bars to plates. Rates were measured at centers of sections. (After Hunsicker.¹²⁸)

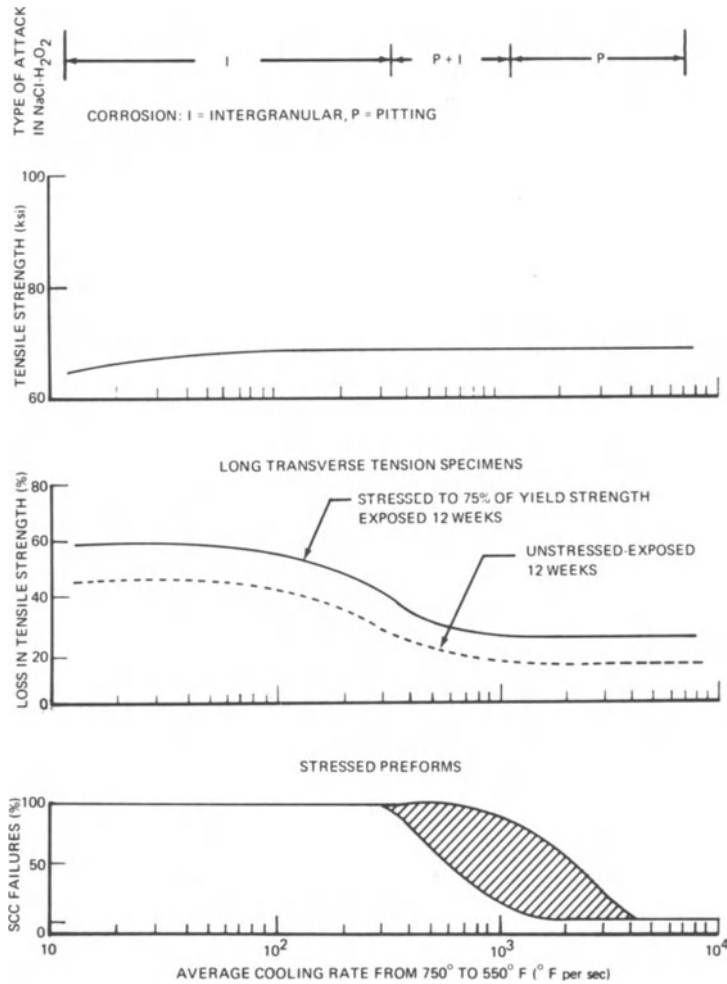


Fig. 92. Effect of quenching rate on tensile properties and corrosion resistance of 2024-T4 sheet specimens exposed to alternate immersion in 3.5% NaCl solution (after Hunsicker¹²⁸ and Lifka⁹²).

for the stressed and unstressed specimens shown in Fig. 92 indicate that stress has accelerated the intergranular attack (slow quench rates) and pitting attack (rapid quench rates) about equally. This, plus the fact that the data are for long transverse sheet specimens, makes it difficult to deduce the effects of quench rate on stress-corrosion resistance. The data in Fig. 92 for stressed preforms show more clearly the effect of quench rate on stress corrosion resistance and indicate that SCC can occur in specimens quenched

at rates below about 3000°F/sec even though the type of attack in unstressed specimens quenched above 1000°F/sec is pitting corrosion.

Additional data on the effects of quench rate and susceptibility to SCC obtained using transverse specimens are shown in Fig. 93. These data also indicate a potential susceptibility to SCC for quench rates above 1000°F/sec if stress levels are sufficiently high. Other evidence for binary Al-Cu and ternary Al-Cu-Mg alloys indicates that they can indeed be susceptible to SCC even if they are not susceptible to intergranular corrosion (Fig. 94) in a NaCl-H₂O₂ solution.

Some data are also available on the effects of quench rate on stress-corrosion crack velocity.⁴⁵ TL-type 2024-T4 DCB specimens were tested after quenching at two different rates (80 and 330°F/sec). It was shown that crack velocities at given *K_I* levels in the more slowly quenched specimen were as much as two times higher than for the most rapidly quenched specimen. This result is not unexpected, based on the data in Figs. 92 and 93.

The significant effects of quench rate on susceptibility to intergranular attack (as well as SCC and exfoliation corrosion) in 2024-T3 and -T4 products mean that in thickness ranges where quench rates cannot be kept above about 1000°F/sec, severe intergranular corrosion problems may occur in service. Examination of Fig. 90 reveals that for plate products quenched in 70°F water, the greatest thickness that can be quenched at or above 1000°F/sec is 0.25 in. Thus, it is recommended that 2024 products

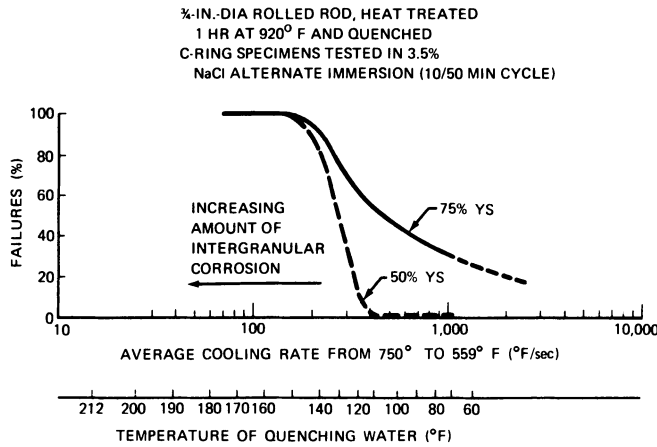


Fig. 93. Effect of cooling rate on the degree of intergranular attack and short transverse stress-corrosion cracking of heat-treated and quenched 2024-T4 (after data from Walsh¹⁸¹).

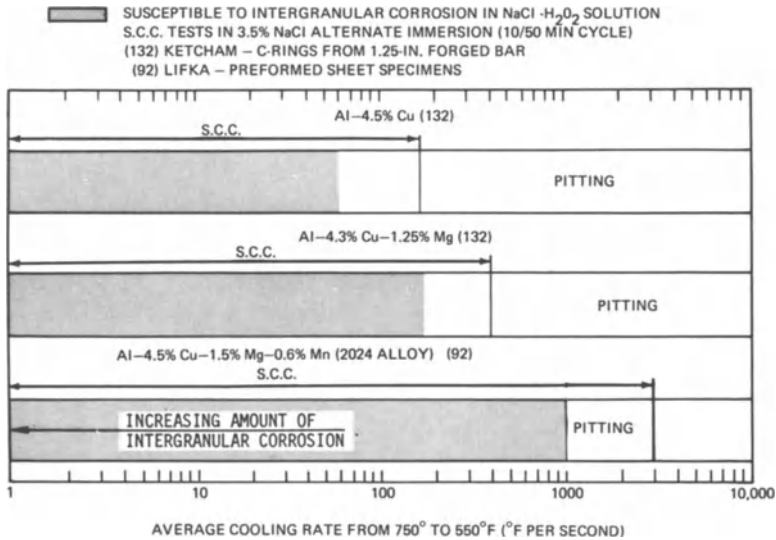


Fig. 94. Effect of quenching rate on susceptibility to intergranular corrosion and SCC for some 2000-series alloys (after Sprowls and Brown⁵¹).

thicker than about 0.25 in. should be used only in the artificially aged tempers (T6X and T8X)¹¹⁶ unless adequate surface protection can be provided.

Effects of Artificial Aging

The effects of artificial aging on the mechanical and fracture properties of 2024-T3 are shown in Fig. 95. Strength increases and toughness decreases as the material is aged to the T8 temper. The effects of artificial aging on the corrosion and stress-corrosion properties of 2024 are shown in Fig. 96. These data show that during artificial aging, susceptibility initially increases, reaches a maximum, and then decreases. Similar trends have been observed when potential differences between grains and grain-boundary regions are measured as a function of aging time.¹²⁹ These potential differences have been related to preferential grain-boundary precipitation of copper-rich phases during the initial stages of artificial aging and the associated formation of a copper-depleted region that is anodic to the grain centers. In a corrosive environment such as sodium chloride solution, these anodic depleted regions can corrode preferentially by an electrochemical process.^{129,130} The maximum potential difference between grain margins and grain centers occurs at some intermediate aging time. At longer aging times,

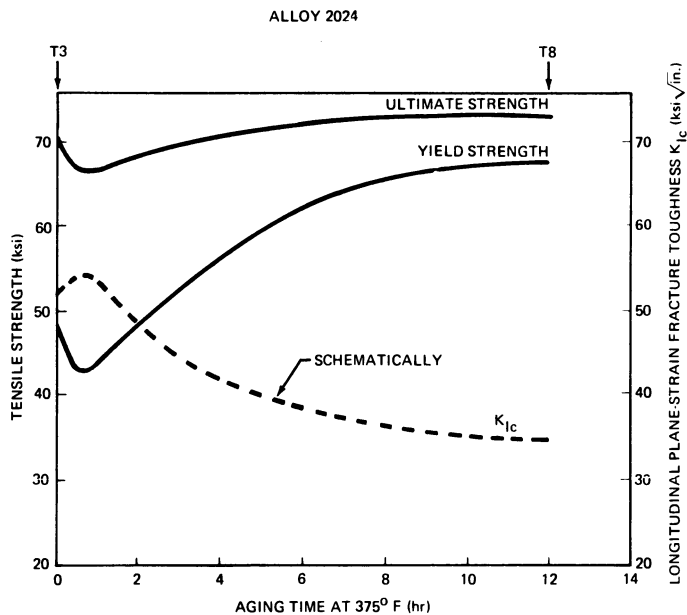


Fig. 95. Effects of artificial aging on the mechanical and fracture properties of alloy 2024. The T3 and T8 tempers are indicated by arrows.

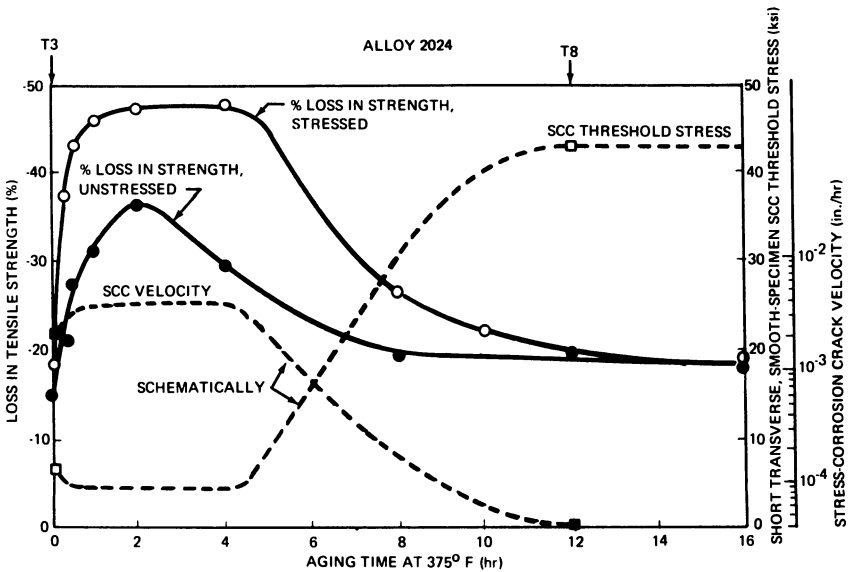


Fig. 96. Effects of artificial aging on the corrosion and stress-corrosion properties of alloy 2024 in NaCl solution. The T3 and T8 tempers are indicated by arrows.

continued formation of precipitates within the grain centers begins to equilibrate the potentials in the two regions. After further aging, when virtually complete precipitation has occurred both at the grain boundaries and within the grains, the difference in potential between the two areas is reduced to almost zero. These results have been used to explain the improved resistance to intergranular attack of the T6X and T8X tempers for alloy 2024, since in these tempers, the alloy has been aged at 375°F sufficiently long to minimize potential differences between grain-boundary margins and grain interiors.^{129,130}

Corrosion behavior similar to that shown in Fig. 96 occurs when 2024-T3 is subjected to temperatures above or below the normal artificial aging temperature of 375°F. For example, if thin-gauge 2024-T3 sheet that has been rapidly quenched is exposed to 266°F, the sensitization to intergranular attack occurs as shown in Fig. 97. For higher temperatures, times required for sensitization are shorter. Figure 98 summarizes data obtained over a range of temperatures.¹³³ These data are of interest since it is often necessary to subject 2024-T3 to medium temperatures (around 250°F) during curing of certain adhesively bonded structures. In addition, temperatures around 250°F are near the skin stagnation temperature of aircraft operating at Mach 2. The data in Fig. 97 for 266°F indicate that the alloy becomes susceptible to intergranular attack after only about 5 hr of exposure. Thus, if temperatures of 266°F were encountered during 2024-T3 processing, strict controls on allowable exposure times would have to be made to ensure against sensitization to intergranular attack.

Actual stress-corrosion crack growth rate data have recently been obtained using *TL* 2024-T351 DCB specimens which had been exposed to temperatures as low as 250°F.¹³⁴ The results are shown in Fig. 99 for a K_I level of 20 ksi in.^{1/2}. Crack velocity was observed to increase after very short exposure times at 250°F, with a maximum increase in growth rate (about 50%) occurring between 15 and >300 hr, in agreement with the trends observed in Fig. 97 based on strength losses of pre-exposed sheet tension specimens. What is surprising about the data in Fig. 99 is that the DCB specimens were machined from 1-in.-thick 2024-T351 plate and therefore could not have been quenched faster than about 150°F/sec, according to Fig. 90. The material was thus put into a condition of high susceptibility to intergranular attack, even before exposure to 250°F. Despite this situation, however, exposure at 250°F increased crack velocity in the same way that 266°F exposure increased susceptibility to intergranular attack of thin, rapidly quenched sheet (Fig. 97).

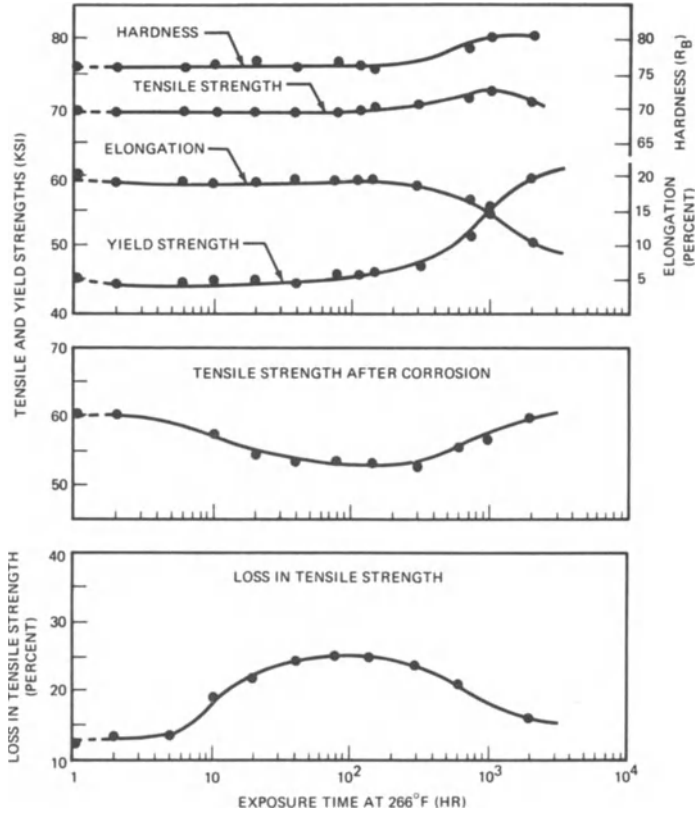


Fig. 97. Effect of exposure time at 266°F on mechanical properties and corrosion characteristics of longitudinal 2024-T3 sheet (0.057 in.) specimens. Corrosion specimens were stressed to 80% of their tensile yield strength and periodically immersed for 48 hr in a 5% NaCl solution containing 0.3% H₂O₂. (After Robertson.¹⁸³)

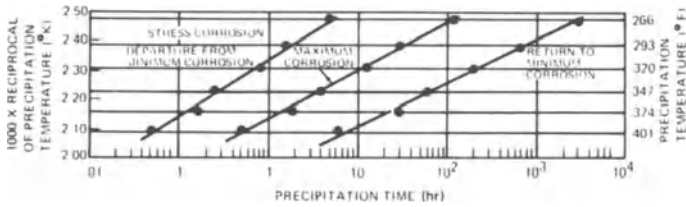


Fig. 98. Effect of temperature on the time required for sensitization to stress corrosion of 0.057-in.-thick 2024-T3 sheet (after Robertson¹⁸³).

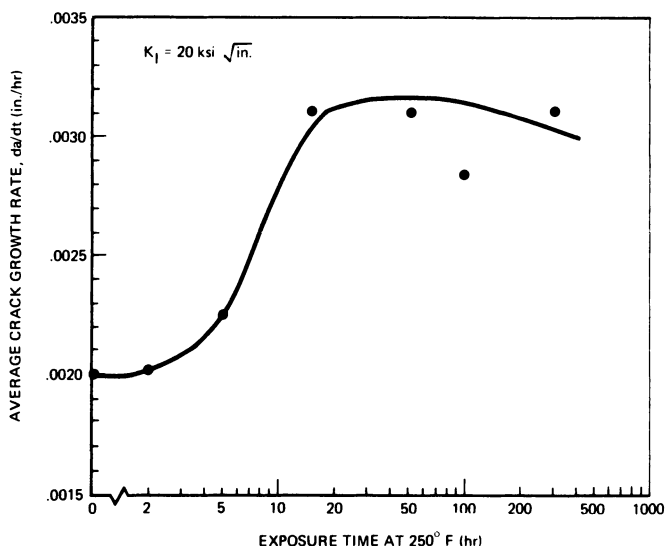


Fig. 99. Effect of exposure time at 250°F on the region II stress-corrosion crack velocity in TL DCB specimens from 1-in.-thick 2024-T351 plate. (After Hyatt and Quist.¹³⁴)

Rapid Tests for Determining Susceptibility to Intergranular Attack and SCC Resistance

An electrochemical test has recently been developed for predicting the stress-corrosion performance of 2219 alloy products in the T851 and T87 tempers.¹³⁵ The test offers an attractive possibility of evaluating the performance of 2219 products quickly as an alternate or supplement to the conventional 30-day alternate-immersion test in 3.5% sodium chloride solution. The test can be completed in less than 1 hr and requires only a simple measurement of solution potential of an unstressed specimen in a mixture of absolute methyl alcohol and carbon tetrachloride. Typical potential-time data for 2219 specimens in the T351 to T851 temper range aged for various periods at 350°F are shown in Fig. 100. Note the large difference in potential (over 200 mV) that this test provides between borderline and resistant material after potentials have stabilized. Correlations of solution potential with stress-corrosion performance of 2219 alloy products in the T851 and T87 tempers are shown in Figs. 101 and 102. With an acceptance criterion of -750 mV for both tempers, only materials resistant to SCC are accepted. Borderline as well as susceptible materials are rejected.

The mechanism of the reaction of 2219 with methyl alcohol-carbon tetrachloride solutions involves selective attack of the Al-Cu solid solution

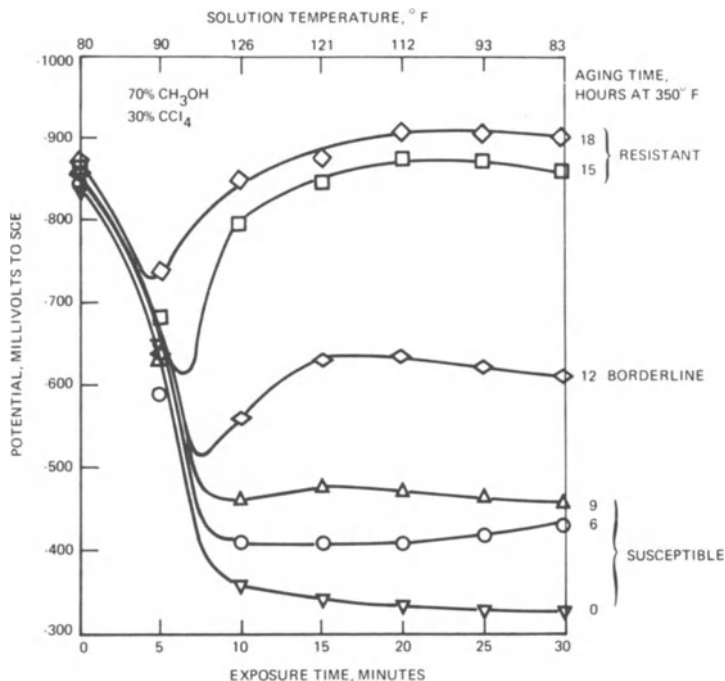


Fig. 100. Time-potential curves in $\text{CH}_3\text{OH}-\text{CCl}_4$ solution for 2219-T351 plate aged for various periods at 350°F up to the T851 temper (18 hr at 350°F) (after Horst *et al.*¹³⁵).

and redeposition of the dissolved copper on the specimens. In susceptible materials, copper deposits as a continuous mass because the selective intergranular attack on these specimens provides a mechanical means for the adherence of the depositing copper. This adherent copper film makes susceptible material behave as a copper electrode, which agrees with the fact that copper in a solution of 50% methyl alcohol and 50% carbon tetrachloride has a potential of around -300 mV. In resistant specimens, copper deposits as minute individual particles that are undercut and floated off. These specimens therefore tend to behave as aluminum electrodes, which agrees with the fact that pure aluminum in a solution of 50% methyl alcohol and 50% carbon tetrachloride has a potential of around -1100 mV.

Recently, a rapid test method for determining the resistance to exfoliation corrosion has been developed by ASTM Task Group G01.05.02—T.G.8. This test method is applicable to Al-Cu (2000 series) and Al-Zn-Mg-Cu (7000 series) alloys. The test, designated EXCO test, specifies total

immersion of freshly etched specimens in a solution of the following composition:



Testing times required are 48 hr for 7000-series alloys and 96 hr for 2000-series alloys. Specimens having a high resistance to exfoliation should show no visible blistering or delamination after exposure to this test.

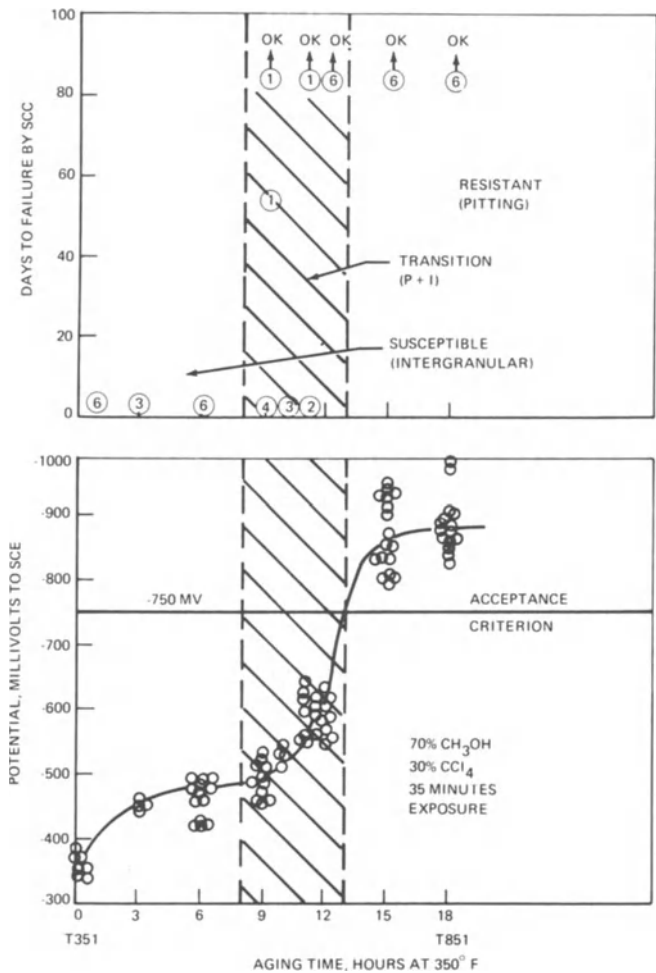


Fig. 101. Correlation of solution potential with stress-corrosion performance of 2219-T851 alloy plate. In the upper plot, the small numbers inside circles indicate the number of specimens tested. (After Horst *et al.*¹³⁵)

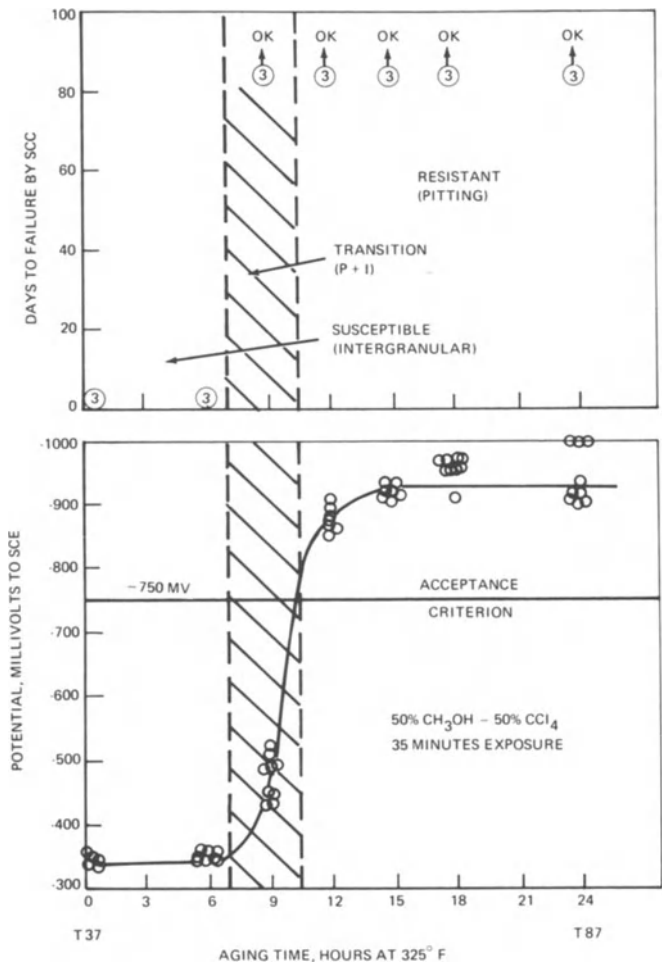


Fig. 102. Correlation of solution potential with stress-corrosion performance of 2219-T87 alloy plate. In the upper plot, the small numbers inside circles indicate the number of specimens tested. (After Horst *et al.*¹³⁵)

Aluminum–Zinc–Magnesium and Aluminum–Zinc–Magnesium–Copper Alloys (7000 Series)

The precipitation-hardened 7000-series alloys are used in applications requiring the highest strengths. Composition limits for this series of alloys are shown in Table 1. Typical applications for these alloys are given in Table 2, and mechanical, fracture, and corrosion properties are listed in Table 4.

Physical Metallurgy

The high strength of the 7000-series alloys is due mainly to their zinc and magnesium content. Aluminum can hold significant amounts of zinc and magnesium in solid solution at the solution-treatment temperatures (830–900°F). On rapid quenching, a supersaturated solid solution can be retained at room temperature; it decomposes on subsequent aging. If a fine distribution of precipitates is formed during aging, significant strengthening occurs. A typical microstructure of such an alloy after aging to peak strength is shown in Fig. 103. The strength levels that can be obtained depend on the concentrations of zinc and magnesium, as shown schematically in Fig. 104. Strength maximum can be achieved conveniently by aging at approximately 250°F for 24–48 hr (T6 tempers). Aging at higher temperatures, e.g., 320–350°F, causes overaging and thus reduces strength.

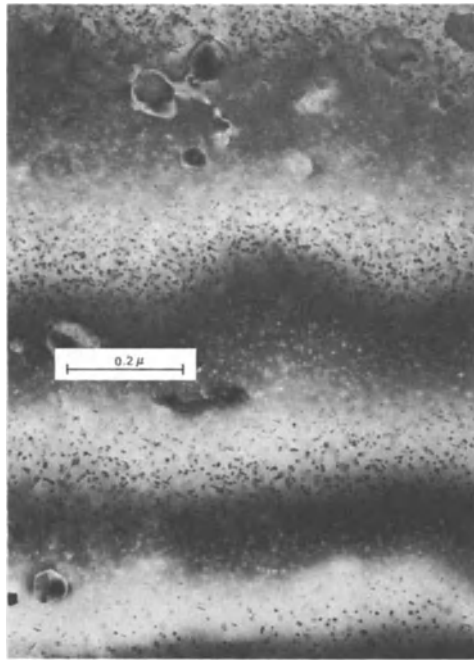


Fig. 103. Typical transmission electron micrograph of an Al-Zn-Mg-Cu-Cr 7075-type alloy aged to the peak strength or T6 condition. The smaller hardening precipitates and the larger recrystallization-retarding, chromium-rich intermetallic particles are clearly evident.

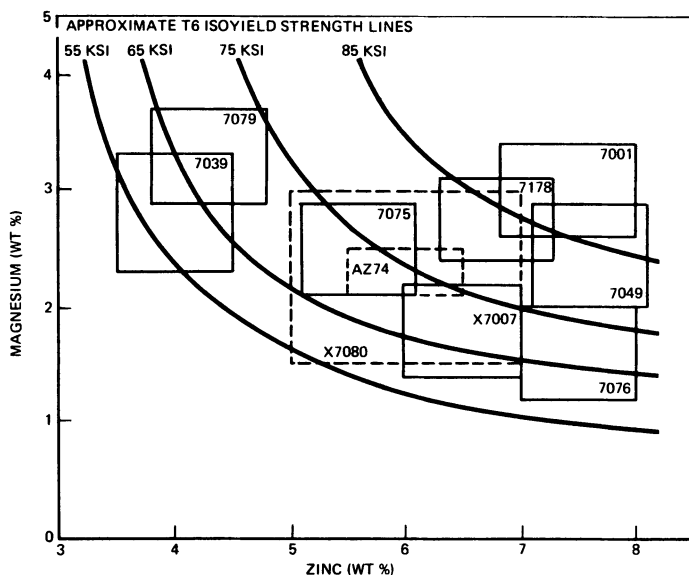


Fig. 104. Composition limits and approximate strength relationships for commercial Al-Zn-Mg-Cu alloys in the T6 temper.

The precipitation sequence in this alloy system depends on composition, but may be represented as^{121,136}

Solid solution $\rightarrow$ spherical GP zones $\rightarrow$ ordered GP zones

$\rightarrow \eta'$ (semicoherent) $\rightarrow \eta$ (MgZn_2) + T ($\text{Mg}_3\text{Zn}_3\text{Al}_2$)

Aging times and temperatures that produce the maximum hardening characteristic of the T6 temper produce zones having an average diameter of 20–35 Å. Particles of the transition η' precipitate which are partially coherent on $\{111\}_{\text{Al}}$ planes can also be detected in the T6 temper. During overaging at higher aging temperatures, zone growth and an increase in the amount of η' occur. With increased time or higher temperature, the η' converts to η (MgZn_2) or, in cases where T is the equilibrium phase, is replaced by T ($\text{Mg}_3\text{Zn}_3\text{Al}_2$). Phases η' and η are frequently present in grain boundaries, especially after slow cooling from the solution-heat-treatment temperature. Grain-boundary precipitates can also form during aging, as illustrated in Fig. 105.

Copper additions up to 1% do not appear to alter the basic precipitation mechanism. In this range, the strengthening effects of copper are

modest. Higher copper contents afford greater precipitation hardening, with some contribution of copper atoms to zone formation, as indicated by an increased temperature range of zone stability. Copper is limited to a low amount in some Al-Zn-Mg alloys, such as 7039 and X7007, to improve weldability.

Possibly the most important additions to the Al-Zn-Mg-Cu alloys are chromium, manganese, and zirconium. The addition of small amounts of the high-melting-point elements chromium, manganese,¹³⁷ and zirconium¹³⁸ to wrought Al-Zn-Mg or Al-Zn-Mg-Cu alloys raises the recrystallization temperature and changes the grain shape from an equiaxed to an elongated shape with much more irregular boundaries.¹³⁷ In combination with chromium, manganese additions lead to an even more pronounced elongation of grain structure.¹³⁷

Chromium, manganese, and zirconium form intermetallic particles that are not soluble at the solution-treatment temperature. These particles pin grain boundaries, thus retarding recrystallization and partly preserving the elongated grain structure formed during forging, extruding, or rolling. These chromium- and manganese-rich intermetallic particles can be seen in Fig. 105 (marked *A*). Before such additions were made to 7000-series

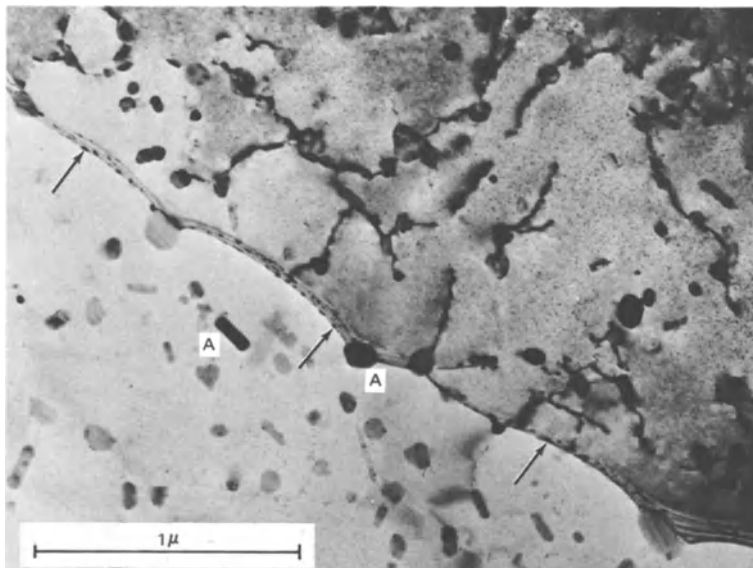


Fig. 105. Transmission electron micrograph of an Al-Zn-Mg-Cu-Cr 7075-type alloy in the T6 temper showing grain-boundary precipitates (arrows), chromium-rich intermetallics (*A*), and the smaller hardening precipitates.

alloys, the recrystallized, equiaxed grain structures in wrought products resulted in alloys with extremely poor stress-corrosion properties. The equiaxed grain structure of such a high-purity ternary Al–Mg–Zn alloy is shown in Fig. 106. This should be compared with the elongated grain structure of commercial 7000-series alloys shown in Figs. 3 and 4. Such recrystallized alloys exhibit the highest stress-corrosion crack growth rates ever observed in high-strength aluminum alloys.⁴⁴ An example was shown earlier in Figs. 39 and 51.

The difficulty in propagating stress-corrosion cracks perpendicular to the elongated grains is primarily responsible for the improved stress-corrosion performance of longitudinal or transverse specimens of alloys containing chromium, manganese, or zirconium, as outlined in the section on mechanical aspects (the effects of stress). Another very important effect of these elements is that they increase quench sensitivity in 7000-series alloys, as illustrated in Fig. 107. It can be seen that chromium causes by far the highest quench sensitivity. Thus, chromium-containing alloys like 7075 and 7178 are very quench-sensitive (Fig. 108). Primarily for this reason

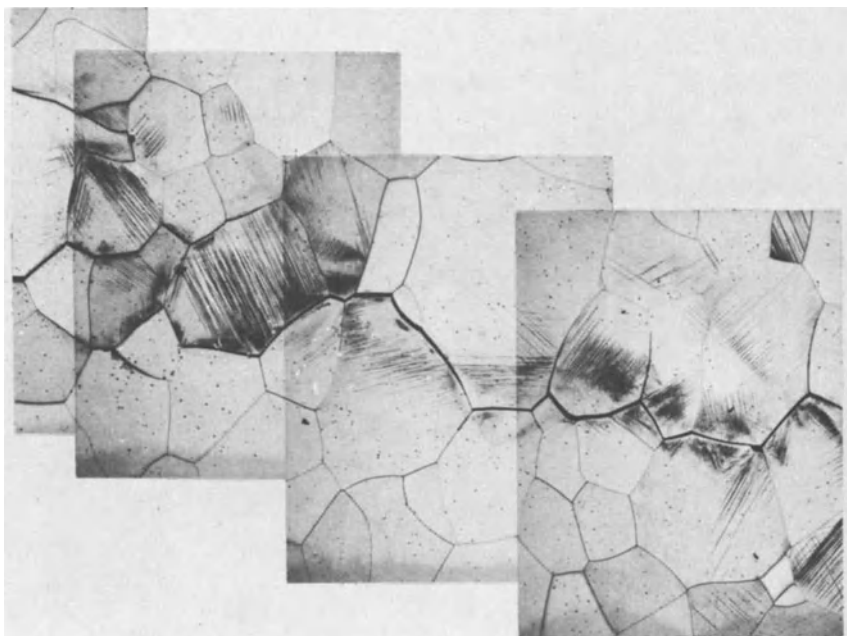


Fig. 106. Stress-corrosion crack in an equiaxed, high-purity Al–Zn–Mg alloy. Plastic deformation along the crack path was made visible after the SCC test by decorating the dislocations with precipitates and subsequently etching. (After Engell and Speidel.¹³⁹)

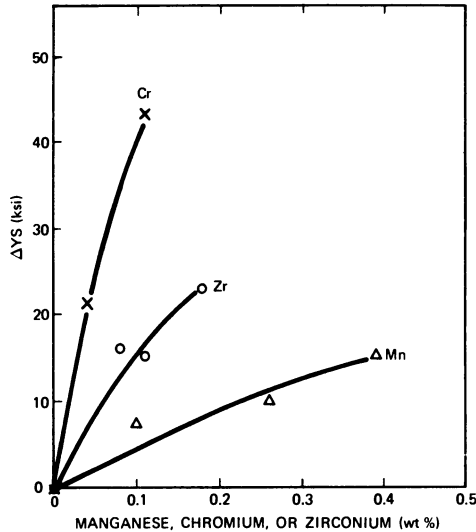


Fig. 107. Influence of chromium, zirconium, and manganese on quench sensitivity of a high-strength Al-6.8% Zn-2.5% Mg-1.2% Cu alloy as measured by the drop in peak yield strength when the quench rate is decreased from 90 to 9°F/sec (after Thompson and Levy¹⁴⁰).

the 7075-T6 and 7178-T6 alloys are generally limited to heat-treated section thicknesses of about 3 in. Quench rates in thicker sections are too slow to provide good mechanical properties. Copper additions and increased zinc and magnesium contents also increase quench sensitivity slightly.

Small amounts of iron and silicon are also present in the commercial Al-Zn-Mg-Cu alloys as tramp elements. While these elements have little effect on stress-corrosion resistance, their presence is a primary factor in determining the fracture toughness properties of these alloys. High iron

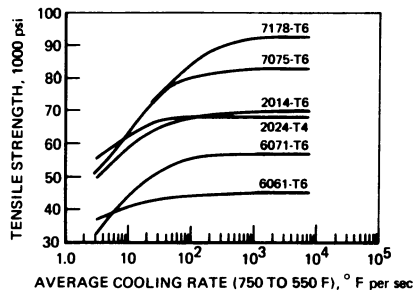


Fig. 108. Tensile strength as a function of cooling rate during quenching for several high-strength commercial aluminum alloys (after Hunsicker¹²⁸).

and silicon contents (still within the allowable composition limits in Table 1) can drastically lower fracture toughness, while low iron and silicon contents can increase toughness markedly.^{141,142} In addition, it has recently been shown that the tramp elements iron and silicon increase quench sensitivity in 7000-series alloys.¹⁴³ Thus, decreasing iron and silicon contents help minimize quench sensitivity as well as increase fracture toughness.

Susceptibility to Stress-Corrosion Cracking

While some of the previously mentioned compositional factors can increase stress-corrosion resistance in the longitudinal and transverse grain directions, they cannot appreciably increase short transverse stress-corrosion resistance. Indeed, susceptibility to SCC in the short transverse direction has been the cause of nearly all SCC service failures of high-strength aluminum alloys up to this time. A typical example of such a stress-corrosion crack is shown in Fig. 109.

The stress-corrosion properties of most of the 7000-series alloys in the short transverse direction are now quantitatively known. Figures 110 and 111 show stress-corrosion crack velocity as a function of crack-tip stress intensity for these alloys. These data, together with the stress-corrosion properties given in Table 7, can be used to quantitatively rate the stress-corrosion performance of the various 7000-series alloys.

Note the inferior stress-corrosion resistance of the low-copper-content alloys 7079-T651 and 7039-T61 and -T64. Note also that alloy 7079-T651 shows by far the highest stress-corrosion crack velocity of the commercial 7000-series alloys at all stress intensities. This is consistent with the fact that the majority of service SCC failures have occurred with this alloy. Such large differences in performance between the various 7000-series alloys in the T6 temper are not reflected in the SCC threshold data from smooth-specimen time-to-failure tests. The poor service performance of 7079-T6 could, however, be anticipated from the per cent survival data shown earlier in Fig. 45. These low survival rates⁴² and, more important, the newer quantitative stress-corrosion results (Figs. 110 and 111 and Table 7) and actual service experience itself, dictate that alloy 7079-T6 be eliminated from future use where there is any possibility of sustained applied or residual tensile stresses in the short transverse direction. Other alloys with good strength in thick sections and better stress-corrosion resistance should be used in its place. Such alloys are now available or under development, as outlined below (p. 264). Past experience suggests that the stress-corrosion resistance of alloys now under development should be charac-

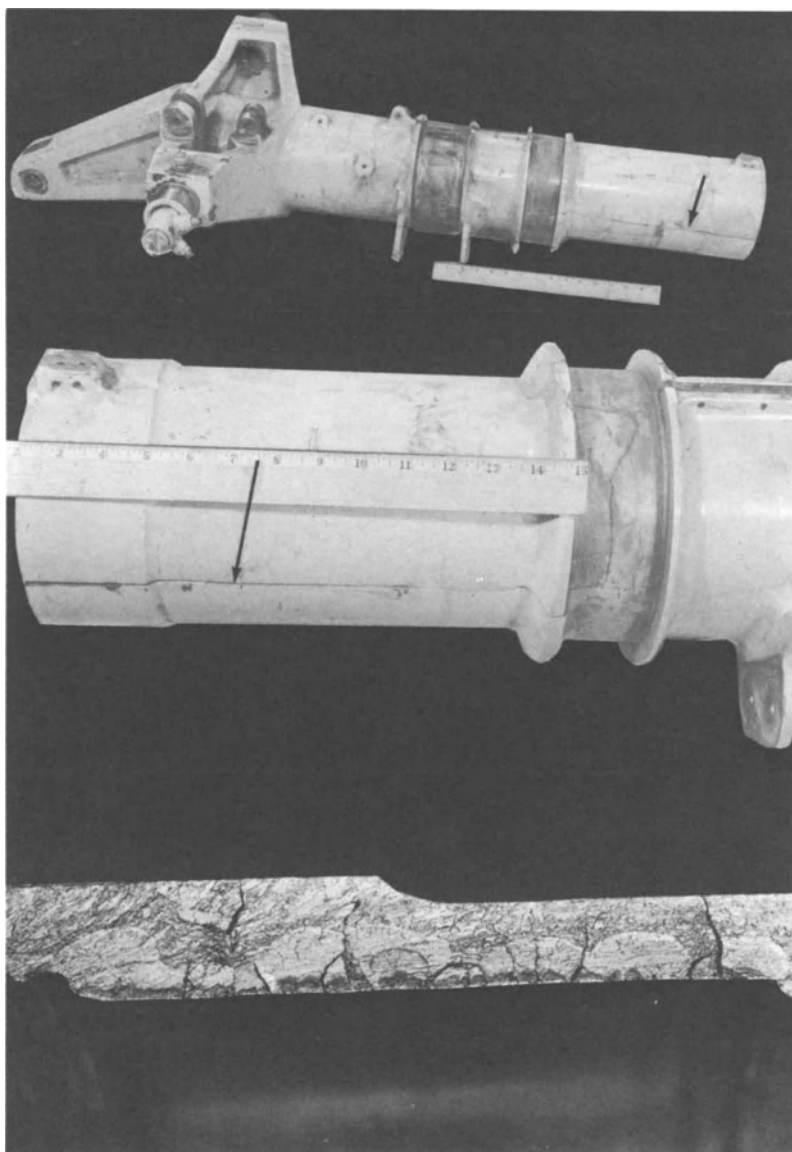


Fig. 109. Typical stress-corrosion cracks in a large 7079-T6 die forging.

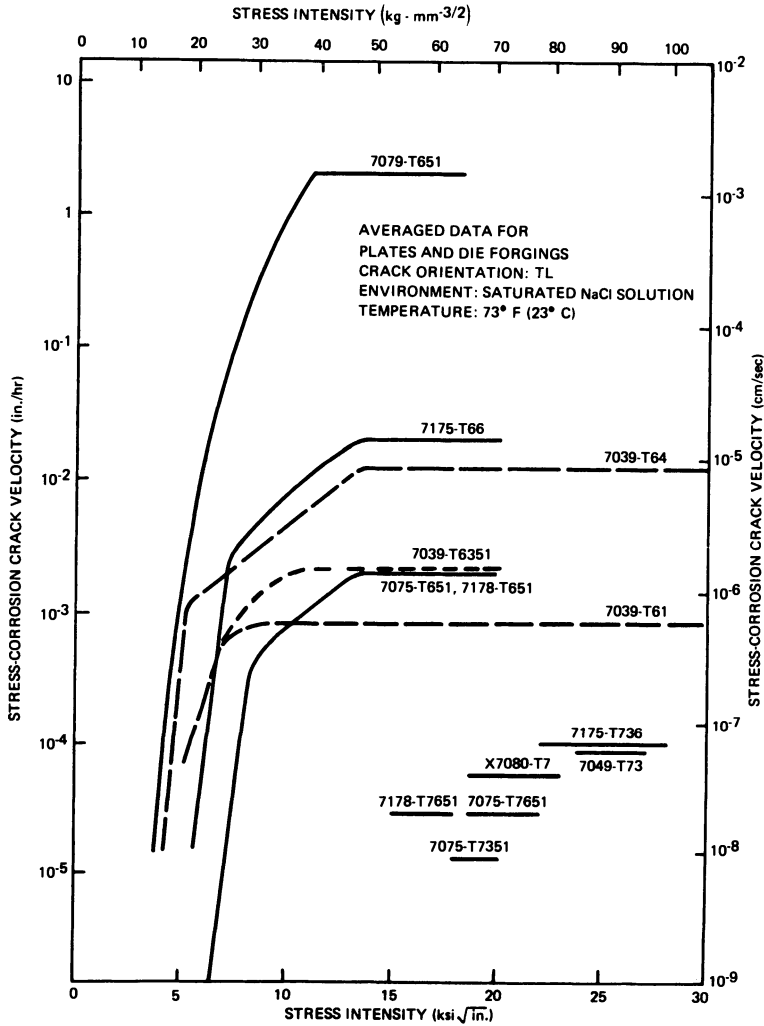


Fig. 110. Effect of stress intensity on stress-corrosion crack velocity for several high-strength aluminum alloys immersed in saturated aqueous NaCl solutions.

terized not only by their smooth-specimen SCC threshold stresses, but also by their SCC crack velocity versus stress intensity curve. This would provide a more quantitative basis for alloy selection.

Effects of Quench Rate

The rate of cooling from the solution-treatment temperature through a critical temperature range (750–550°F) has a pronounced effect on both

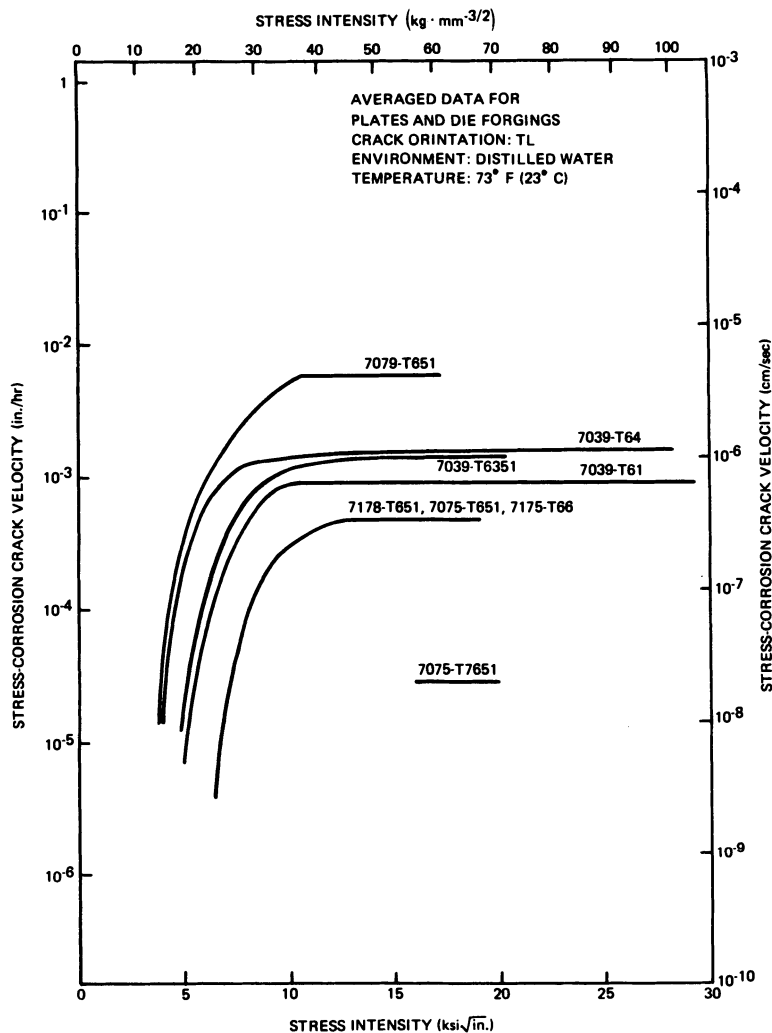


Fig. 111. Effect of stress intensity on stress-corrosion crack velocity for several high-strength aluminum alloys immersed in distilled water.

the resistance to corrosion and the characteristics of the corrosive attack for copper-bearing 7000-series alloys like 7075-T6. The effect of quench rate on the mechanical properties and type and extent of corrosion in long transverse 7075-T6 sheet specimens is shown in Fig. 112. Rapid cooling produced immunity to intergranular corrosion and to stress-corrosion cracking; cooling rates greater than about 200°F/sec also produced maximum tensile properties. Decreasing the cooling rate to about 40°F/sec

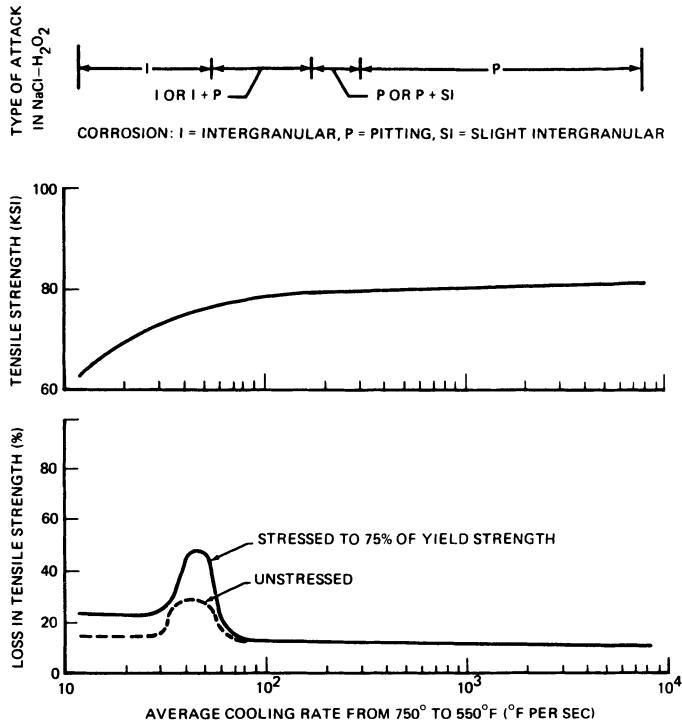


Fig. 112. Effects of quenching rate on tensile properties and corrosion resistance of 7075-T6 sheet. Stressed and unstressed specimens were exposed to alternate immersion in 3.5% NaCl solution for 12 weeks before testing. (After Hunsicker.¹²⁸)

results in the formation of coarse precipitates of η' or η phase in the matrix and in the grain boundaries, resulting in a marked reduction in strength and a high degree of susceptibility to intergranular attack and stress-corrosion cracking.⁵¹ Further decreases in cooling rate nearly eliminate susceptibility to SCC, but result in drastic strength losses.

It should be noted that the beneficial effects of high quench rates mentioned above for 7075-T6 sheet are relatively insignificant for plate and other products thick enough to permit stressing in the short transverse direction relative to the grains. Thus, even drastically quenched (>1000 °F/sec) short transverse specimens of 7075-T6 machined from 2-in.-thick plate stress-corrosion crack in sodium chloride solution at stresses as low as 11 ksi even though they are not susceptible to intergranular attack in the absence of applied stress.⁵¹ In fact, it has been found that such specimens are not appreciably more resistant than similar specimens quenched at

rates slow enough that they are susceptible to intergranular attack in the absence of stress.⁵¹

For copper-free 7000-series alloys, the behavior is generally opposite to that just described and resistance to stress-corrosion cracking in sodium chloride solutions is favored by a low cooling rate, as by cooling in air.^{143a,143b}

Effects of Overaging

As shown in the preceding section, all high-strength 7000-series alloys are susceptible to SCC when aged to peak hardness (T6 temper) and stressed in the short transverse direction. Furthermore, composition changes cannot increase appreciably the stress-corrosion resistance in the short transverse direction. As in the case of the 2000-series alloys, the only effective means of improving short transverse SCC resistance in 7000-series alloys is by artificial aging at fairly high temperatures (325–350°F). The relationship generally found between precipitation hardening and resistance to SCC is illustrated in Fig. 113. Note that during aging, the minimum resistance to SCC is reached before peak hardness is achieved. Overaging beyond peak hardness improves resistance to SCC.

Figure 114 presents quantitative data illustrating the stress-corrosion crack velocity of alloys 7075 and 7178 as a function of overaging time after a prior T651 treatment. Note that overaging for 25 hr at 320°F reduces the crack velocity by nearly three orders of magnitude. This degree of

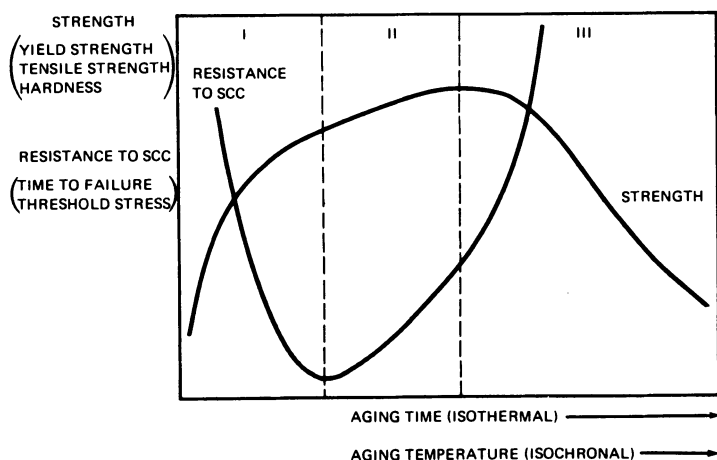


Fig. 113. Relationship between strength and stress-corrosion resistance during aging of high-strength, 7000-series alloys (after Speidel¹⁴⁴).

overaging causes a decrease in strength of only about 14% (Fig. 115), yet the short transverse fracture toughness is increased appreciably (Fig. 114). This same overaging treatment also considerably improves resistance to exfoliation corrosion. Figure 116 shows the effect of overaging on stress-corrosion crack velocity versus stress intensity for alloy 7178. Increasing overaging decreases the velocity in region II (plateau), as is also shown in Fig. 114. The slow growth rates in the overaged material necessitate extremely long test times to determine the entire V - K curve. Therefore, it is not known at the present time whether overaging affects only the stress-independent velocity in region II or whether it also influences the stress-dependent velocity in region I. Thus, the effect of overaging on K_{ISCC} remains unknown for alloys 7075 and 7178.

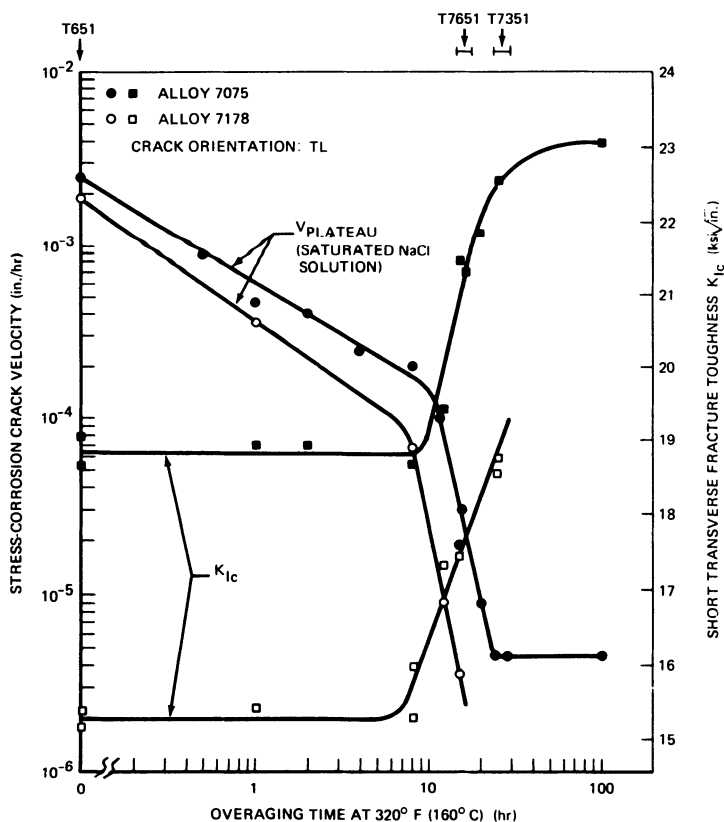


Fig. 114. Effect of artificial aging at 320°F on the toughness and stress-corrosion crack velocity of 7075-T651 and 7178-T651 plate. The T651, T7651, and T7351 tempers are indicated with arrows.

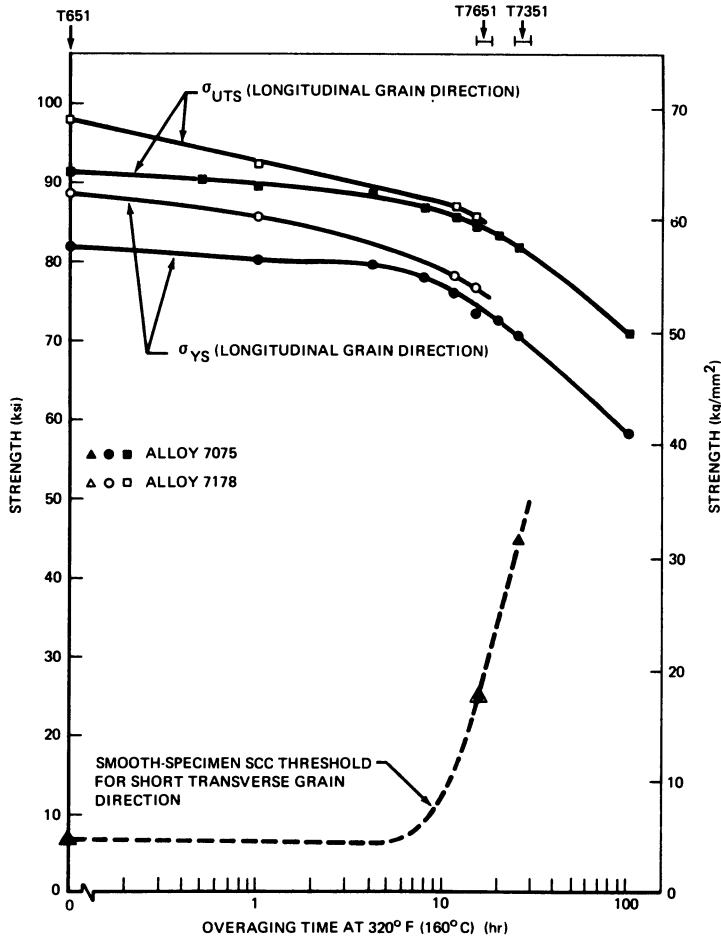


Fig. 115. Effect of artificial aging at 320°F on the strength and smooth-specimen SCC threshold of 7075-T651 and 7178-T651. The T651, T7651, and T7351 tempers are indicated with arrows.

The effect of overaging on the velocity of stress-corrosion cracks in alloy 7079-T651 is known in more detail. Figure 117 shows V - K curves for 7079 as a function of overaging time after a prior T651 treatment. Note that for this alloy, overaging has very little effect on the plateau velocity. Note that overaging does displace region I of the V - K curve to higher stress intensities. In this way, a fairly high " K_{ISCC} " can be achieved (Fig. 118). However, strength losses accompanying such overaging (Fig. 118) would prevent use of this alloy as a structural material. Therefore the

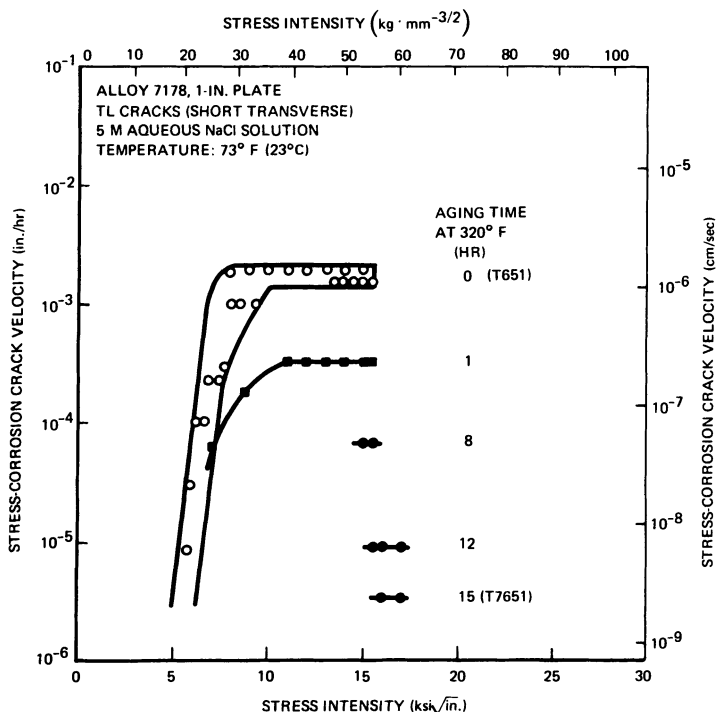


Fig. 116. Effect of artificial aging at 320°F on the stress-corrosion crack velocity versus stress-intensity curves for 7178-T651 plate (after Speidel^{44a}).

commercial overaging practices (T76 and/or T73) used for alloys 7075 and 7178 cannot be applied successfully to alloy 7079.

Over the past few years, a number of commercial overaging heat treatments have been developed for several high-strength 7000-series alloys.^{10,14,145,146} The tempers developed for alloys 7075 (T76 and T73) and 7178 (T76) and their effects on mechanical and stress-corrosion properties are shown in Figs. 114 and 115. The T76 tempers for 7075 and 7178 were developed primarily to improve resistance to exfoliation corrosion. Note that the overaging time used for the T76 tempers in Fig. 114 corresponds to the region in the curves where rapid changes in stress-corrosion velocity with aging time were observed. This would indicate that careful control during overaging to the T76 temper is required to ensure a uniformly resistant product. On the other hand, Fig. 114 indicates that the T73 heat treatment for 7075 will always provide a high degree of stress-corrosion resistance, regardless of minor deviations in the heat-treatment practice.

A drawback of the T73 temper, however, is the loss of strength of about 14% compared to the T6 temper. Through careful control of heat-treating variables and other processes, a T736 temper for alloys 7175 and 7075 has been developed that provides strengths equivalent to those of 7075-T6 and stress-corrosion resistance intermediate between that of the T76 and T73 tempers.^{7,14,146} Other partially overaged alloy-temper combinations providing improved exfoliation and stress-corrosion resistance are 7001-T75 and X7475-T761. Specific properties for these alloys and tempers can be found in Tables 4 and 7 and Fig. 110.

The strength and stress-corrosion resistance of the various overaged

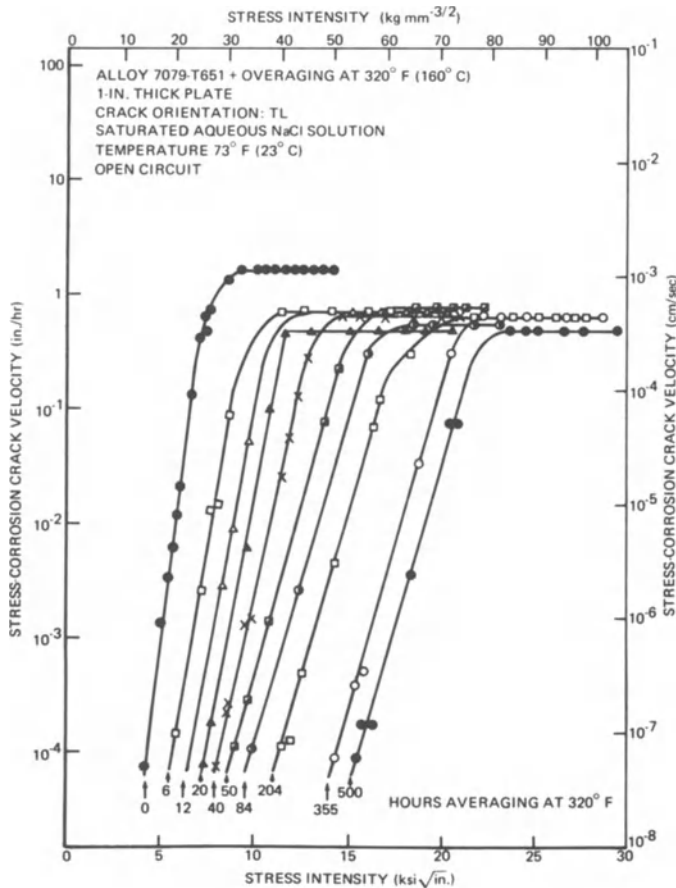


Fig. 117. Effect of overaging on the velocity of stress corrosion cracks in alloy 7079 immersed in NaCl solution (after Speidel^{44a}).

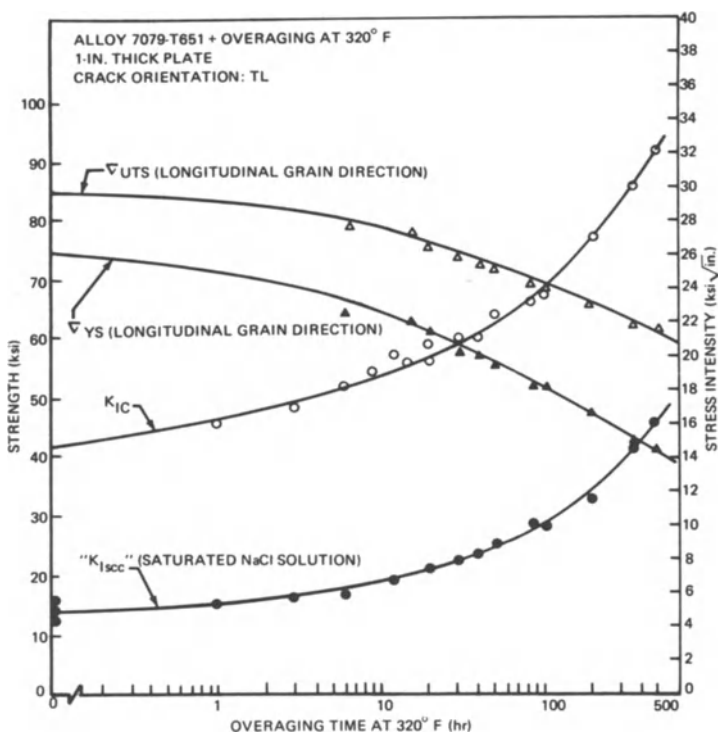


Fig. 118. Effect of overaging on strength, toughness, and stress corrosion resistance of alloy 7079. (Note that " K_{ISCC} " was measured at a crack velocity of 2×10^{-4} in./hr.). (After Speidel.^{44a})

7000-series alloys are usually verified by measuring hardness and electrical conductivity.¹⁴⁷ Smooth tensile specimens, *c*-rings, or other coupons of 7075-T73 are guaranteed to pass a 30-day, alternate-immersion stress-corrosion test when stressed in the short transverse direction up to 75% of the guaranteed yield strength. With the observed crack growth rates presented in Fig. 114, the stress-corrosion resistance of the T73 temper (as well as the T76 and T736 tempers) could be verified with DCB specimens in the same or less time. Another method of rapidly verifying the T73 temper for 7075 is being investigated. It is based on the measurement of solution potentials in methyl alcohol-carbon tetrachloride solutions.¹⁴⁸ Such a test has already been developed for 7178-T76 and 7075-T76 sheet and plate and shows promise as a quality control test to estimate exfoliation and stress-corrosion performance.¹⁴⁸ The test procedures and solutions are similar to those discussed above (p. 241) for 2219-T851 and T87; again the test requires less than an hour. Test results are shown in Figs. 119 and 120.

Note that alloys exhibiting MeOH/CCl_4 potentials less than about -400 mV versus SCE are always found to be exfoliation-resistant, while electrical conductivity values greater than 38% IACS do not always ensure that the product is resistant. It is not yet known whether this test can be applied to extrusions and other products.

A new and rapid method for testing resistance to exfoliation corrosion (EXCO test) has been described above (p. 242).

It should be noted that for alloys with low copper content, such as 7039 and X7007, overaging treatments are not nearly as effective as they are for other 7000-series alloys. Alloys with low copper content can be artificially aged to have a high resistance to SCC in the longitudinal and long transverse directions, but they are still highly susceptible in the short transverse direction.⁵¹

Other overaged intermediate copper-content alloys such as X7080-T7 have presented additional problems in that the threshold stresses developed after lengthy exposures to industrial environments (three years or more) are lower than those determined from the standard 3.5% NaCl alternate-immersion test. Thus, this boiling-water-quenchable, thick-section-forging alloy initially showed an adequate threshold stress of 25 ksi in alternate-immersion. Later, a lower threshold stress of 15 ksi was measured in an industrial environment.¹⁴⁹ Since these data were published, X7080-T7 has

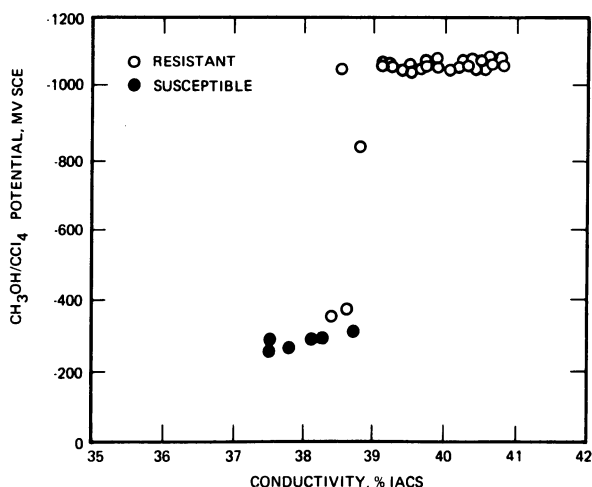


Fig. 119. Comparison of the ability of electrical conductivity and $\text{CH}_3\text{OH}-\text{CCl}_4$ potential to distinguish between the exfoliation-resistant and susceptible conditions of 36 production lots of 7178-T76 sheet (after Horst and Lifka¹⁴⁸).

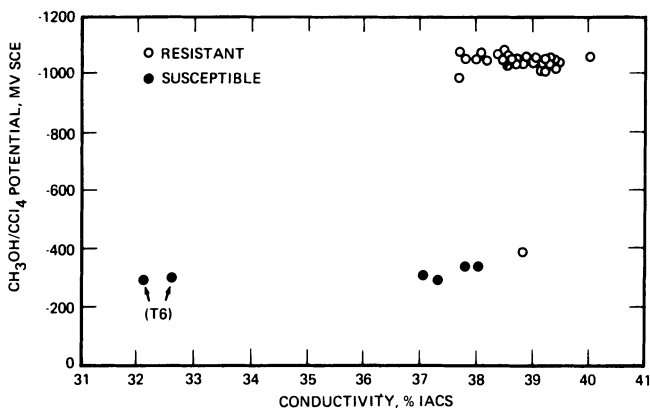


Fig. 120. Comparison of the ability of electrical conductivity and $\text{CH}_3\text{OH}-\text{CCl}_4$ potential to distinguish between the exfoliation-resistant and susceptible conditions of 31 production lots of 7075-T76 sheet and plate and four experimentally aged lots of 0.6-in. 7075-T76 plate (after Horst and Lifka¹⁴⁸).

essentially been removed from the list of candidate thick-section, high-strength, SCC-resistant alloys.

Figures 113–118 show that improved resistance to SCC through overaging is accompanied by a loss in strength. It has been the goal of several recent research projects to achieve a high degree of stress-corrosion resistance without incurring significant strength losses. One technique aimed at achieving this goal has been through the addition of small amounts of silver to these alloys.

Silver Additions

The effects of silver have been extensively investigated because it was reported that silver additions increased the maximum strength attainable by Al–Zn–Mg–Cu alloys that were aged above 250°F,^{138,150–158} and because silver reportedly increased the lifetime of smooth specimens tested in accelerated stress-corrosion tests.^{159,160} Others¹⁶¹ also reported that silver-bearing alloys aged above 300°F had higher resistance to short transverse SCC than similar silver-free material aged below 300°F. As a result of this work, at least one 7075-type alloy containing silver is available commercially (the German alloy AZ74.61). Other alloys containing silver are currently under development.¹⁶² Those investigators finding silver additions beneficial have attributed the improvement to a stimulation of nucleation of the η' phase that forms in the medium temperature range (250–450°F),

particularly in the region of grain boundaries.^{152,154} This stimulated nucleation minimizes the width of the grain-boundary precipitate-free zones (PFZ), which some investigators believe leads to stress-corrosion susceptibility in these alloys.¹⁶³⁻¹⁶⁷ These PFZ's result from either vacancy or solute depletion at grain boundaries during quenching, and their width depends on several quenching and aging parameters.^{168,169} However, many of the workers investigating silver additions have found no significant increases in strength or stress-corrosion resistance in overaged alloys due to the presence of this element.^{51,149,170,171} Much of this confusion regarding the effect of silver additions on strength was eliminated when it was pointed out that the higher-temperature overaging treatments performed in much of the earlier work were carried out using thin products or small pieces that were heated rapidly to the aging temperature in either oil or salt baths.¹⁴⁹ It has since been clearly demonstrated¹⁴⁹ that under these conditions, silver-bearing alloys do indeed maintain higher strengths than silver-free alloys (Fig. 121). However, virtually the same strengthening effect can be achieved in silver-free alloys by exposing them for appropriate times near 200°F so that GP zones can grow to sizes that will not revert (redissolve) during subsequent aging at higher temperatures. The necessary exposure time near 200°F is short enough in 7075-type alloys that it can be attained during normal production heating rates to the artificial aging temperature.¹⁴⁹

In addition to the dependence on the rate of heating to the aging temperature, the effect of silver additions on strength depends on the quench rate.^{149,172,173} Specifically, silver additions increase quench sensitivity of

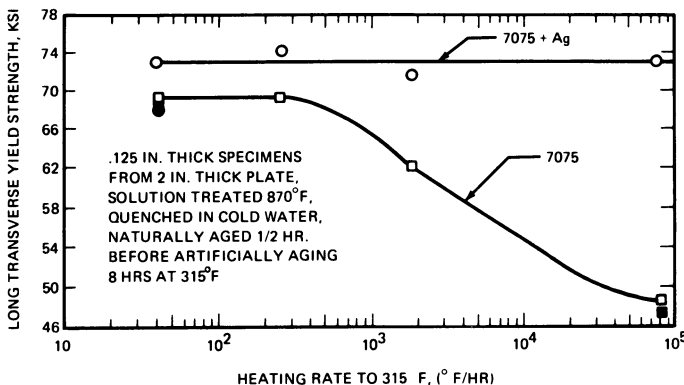


Fig. 121. Effect of rate of heating to the artificial aging temperature on the yield strength of 7075 and 7075 + 0.3% Ag (after Staley¹⁴⁹).

7075-type alloys containing either chromium or manganese.¹⁴⁹ On the other hand, silver additions to chromium- and manganese-free 7075-type alloys containing zirconium can improve strength slightly, even at fairly slow quench rates (2°F/sec).¹⁴⁹ However, high strength alone is not sufficient and to achieve adequate stress-corrosion resistance in silver-free or silver-bearing 7075-type alloys containing chromium, manganese, or zirconium, overaging is required. Thus, again, aging temperature and not chemical composition is the most important factor governing short transverse SCC resistance in these alloys.¹⁴⁹ If they are aged for sufficient times at 325°F, high SCC resistance can be achieved. The length of time at 325°F depends on alloy composition. Chromium-bearing 7075-type alloys develop a high resistance to stress-corrosion cracking after relatively short exposure periods at 325°F, whereas chromium-free 7075-type alloys containing either manganese or zirconium require longer aging times. In spite of the slower aging rate of chromium-free alloys containing manganese and/or zirconium, the strengths of 7075-type alloys with the various additions are comparable after the alloys are aged to have good resistance to SCC.¹⁴⁹ It was concluded that silver-bearing 7075-type alloys could not be aged to a higher strength than 7075-T73 and yet maintain equal resistance to stress-corrosion cracking.¹⁴⁹ Thus several investigators have recommended that development work on silver-bearing Al-Zn-Mg-Cu alloys be discontinued.^{149,170} No further alloy development work has been carried out in the United States, although silver-bearing alloys are still being investigated in Great Britain¹⁶² and Australia.¹⁷⁴ It seems worthwhile, however, to determine if silver-bearing alloys can be made resistant to exfoliation corrosion with less overaging and therefore higher strength than silver-free alloys.

New Alloy Development

With the introduction of the overaged T73 temper for 7075, many of the stress-corrosion problems in the 7075 alloy exposed to the more common environments were eliminated. Although the overaged 7075-T73 offers significant stress-corrosion resistance, the lower strength accompanying overaging can result in weight penalties in certain high-performance structures. This weight penalty is particularly severe in thick-section applications because in addition to strength losses resulting from overaging (about 14%), the chromium in 7075 imparts a high degree of quench sensitivity to the alloy. Thus, strength drops off rapidly with decreasing quench rate (increasing thickness). Efforts have continued toward developing alloys with good stress-corrosion resistance and even higher strengths.

A recent advance toward this goal has been the introduction of 7175-T736 and 7075-T736 alloys for die forgings. The 7175 alloy is essentially a cleaned-up version of 7075, containing lower concentrations of the tramp elements iron and silicon and therefore providing significant increases in fracture toughness. The mechanical processing and aging parameters used in achieving the T736 tempers are proprietary, but these alloy-temper combinations provide the highest strength consistent with adequate stress-corrosion resistance of any die-forging alloy available today, at least up to thicknesses of 3 in. (Table 4). These alloy-temper combinations are now available in both hand and die forgings in thicknesses up to 6 in.

The chromium content in the 7175 and 7075 alloys and the high attendant quench sensitivity causes a rapid drop in mechanical properties as thicknesses increases beyond 3 in. Thus there is still a need for a good thick-section alloy with high strength, high resistance to SCC, and good fracture toughness. It is with this aim that most of the current aluminum-alloy development in this country has been carried out.

One thick-section-forging alloy introduced several years ago was X7080-T7. This alloy was for use in parts up to 6–8 in. thick. One attractive feature of X7080-T7 is that it is boiling-water-quenchable. This quenching technique is desirable because it minimizes residual quenching stresses and distortion problems during subsequent machining operations. The boiling-water quench was made possible by the low degree of quench sensitivity in X7080-T7 achieved by virtue of its low copper content and the replacement of chromium with manganese. As mentioned earlier, this alloy also showed adequate stress-corrosion resistance when tested by 3.5% NaCl alternate immersion, having a short transverse threshold stress of 25 ksi. However, subsequent testing in outdoor industrial environments showed that stress-corrosion failures in short transverse specimens occurred at stresses as low as 15 ksi.¹⁴⁹ This discrepancy between 3.5% NaCl alternate-immersion and industrial environment test results has been a common problem in other low-copper-content alloys, such as 7079-T6 (Fig. 45). In any case, since the industrial environment results for X7080-T7 were published, much less interest has been shown in this alloy for thick-section-forging applications, especially in view of the good results currently being obtained on several experimental thick-section alloys.

A promising stress-corrosion-resistant material available in thicknesses up to 5 in. is the recently introduced 7049-T73 alloy. This chromium-bearing alloy contains about the same zinc content as 7001 and about the same magnesium and copper content as 7075 (Fig. 1). This alloy possesses

strength properties essentially equivalent to those of 7079-T6 in thicknesses up to 5 in. (Table 4). In addition, 7049-T73 shows excellent stress-corrosion resistance with a smooth stress-corrosion threshold stress of about 45 ksi (Table 4). Thus 7049-T73 provides mechanical properties comparable to those of 7079-T6 and stress-corrosion resistance comparable to that of 7075-T73. In addition, this alloy does not require special processing; therefore, existing dies for die forgings can be used if changes from a susceptible material such as 7079-T6 or 7075-T6 to the more stress-corrosion-resistant 7049-T73 material are desired.

Despite the availability of 7175-T736, 7075-T736, and 7049-T73, work aimed at developing an improved high-strength, stress-corrosion-resistant alloy for use in very thick sections has been under way for the past few years.^{74,140,149,175-186a}

In a Boeing program, the contract objective was,⁷⁴ "A minimum tensile yield stress of 70,000 psi, a minimum short transverse stress-corrosion threshold stress of 25,000 psi, good toughness and fatigue properties, and a quench sensitivity such that the properties can be maintained in thick plate and forgings." The nominal composition of the recommended alloy (designated alloy 21) is shown in Table 9 and plotted in Fig. 122. Alloy 21 is essentially a 7075-7178 alloy low in copper, with zirconium and manganese replacing chromium. The low copper content and replacement of the chromium with zirconium and manganese was aimed at minimizing quench sensitivity. Recommended composition limits for this alloy were: 5.9-6.9% Zn, 2.2-2.9% Mg, 0.7-1.5 Cu, 0.10-0.25% Zr, 0.05-0.15% Mn, 0.05% max Cr, 0.20% max Fe, 0.20% max Si, 0.10% max Ti.

Although minimum-property goals for thick sections have been lowered slightly in two more recent programs,^{140,181-186a} overall goals are similar to those just described. The stated objective is:

"The development of a high-strength general purpose forging aluminum alloy. The alloy shall be capable of production using presently available commercial processes and heat treatment, and it shall have the following properties (minimum values, not typical values):

1. A minimum longitudinal 0.2% yield stress of 72,000 psi in 3-in.-thick plate
2. A minimum longitudinal 0.2% yield stress of 63,000 psi in 8-in.-thick forgings
3. A minimum short transverse stress corrosion threshold stress of 25,000 psi (as measured in alternate immersion salt solution tests)
4. A minimum toughness K_{Ic} of 35,000 psi in.^{1/2}
5. A minimum fatigue strength equal to that of 7075-T6.

Table 9. Chemical Compositions of Thick-Section Experimental and Commercial Alloys

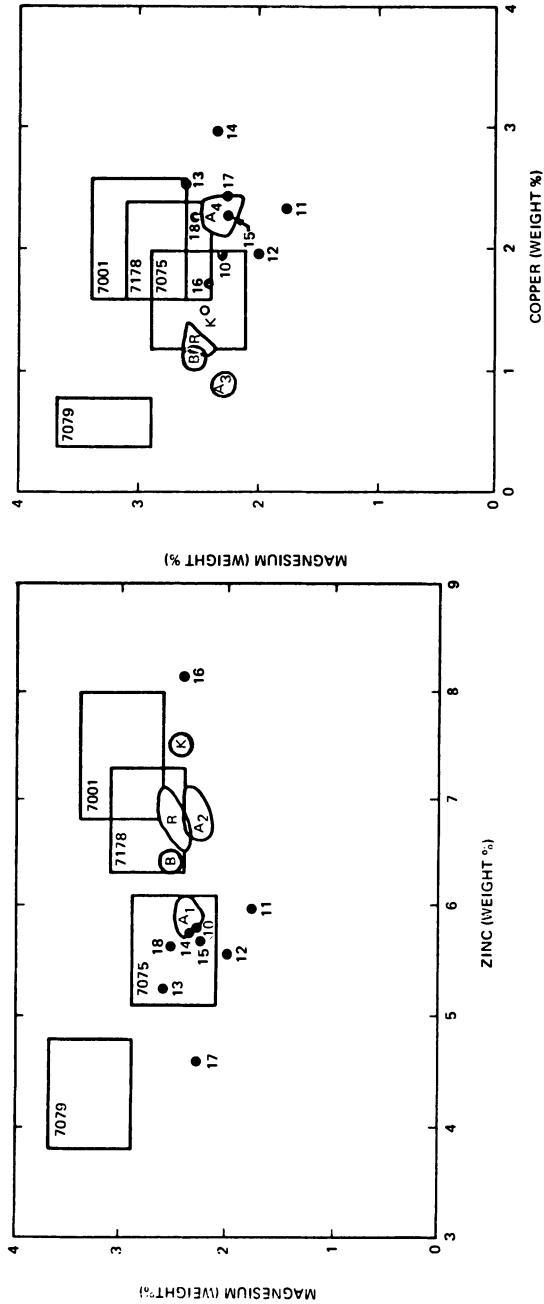
Alloy	Zn	Mg	Cu	Fe	Si	Ti	Be	Mn	Cr	Zr	Ni	V ^a
Boeing Alloy 21	6.40	2.55	1.10	0.13	0.06	0.02	0.001	0.10	<0.01	0.13	<0.01	-
Reynolds Alloys												
1	6.87	2.56	1.22	0.07	0.05	0.04	0.002	< 0.01	< 0.01	0.08	-	-
2	6.58	2.39	1.22	0.07	0.05	0.03	0.002	< 0.01	< 0.01	0.11	-	-
3	6.72	2.46	1.18	0.06	0.03	0.05	0.002	< 0.01	< 0.01	0.18	-	-
4	6.66	2.42	1.20	0.07	0.04	0.03	0.004	< 0.01	0.04	< 0.01	-	-
5	6.97	2.60	1.39	0.06	0.05	0.03	0.002	< 0.01	0.11	< 0.01	-	-
6	6.54	2.41	1.23	0.07	0.04	0.02	0.001	0.10	< 0.01	< 0.01	-	-
7	6.87	2.60	1.21	0.08	0.04	0.03	0.001	0.26	< 0.01	< 0.01	-	-
8	6.76	2.61	1.22	0.08	0.04	0.02	0.001	0.39	< 0.01	< 0.01	-	-
9	6.62	2.35	1.21	0.08	0.04	0.03	0.002	0.35	0.05	0.06	-	-
10	6.85	2.41	1.15	0.08	0.04	0.03	0.001	0.31	0.05	0.13	-	-
11	6.90	2.42	1.19	0.07	0.04	0.04	0.002	< 0.01	0.04	0.08	-	-
12	6.51	2.38	1.17	0.08	0.03	0.06	0.002	< 0.01	0.05	0.13	-	-
13	6.78	2.63	1.23	0.08	0.05	0.04	0.002	0.30	< 0.01	0.11	-	-
14	6.57	2.41	1.18	0.08	0.03	0.05	0.001	0.51	0.10	0.16	-	-
15	6.64	2.38	1.20	0.06	0.05	0.03	<0.001	< 0.01	< 0.01	< 0.01	-	-
16	7.11	2.61	1.39	0.06	0.04	0.03	<0.001	< 0.01	0.12	< 0.01	-	-
Alcoa Alloys												
A	5.90	2.20	2.40	-	-	-	-	0.34	0.01	-	-	-
NAVAIR 3	5.69	2.39	2.36	0.09	0.08	0.02	-	0.28	0.00	0.00	-	-
NAVAIR 4*	5.95	2.46	2.44	0.10	0.03	0.03	-	0.01	0.00	0.11	-	-
NAVAIR 5	6.86	2.17	2.32	0.12	0.05	0.07	-	0.33	0.00	0.00	-	-
NAVAIR 6	6.64	2.13	2.45	0.09	0.07	0.03	-	0.01	0.09	0.10	-	-
NAVAIR 7	6.67	2.37	2.27	0.09	0.05	0.02	-	0.16	0.00	0.10	-	-
NAVAIR 8	6.63	2.33	2.35	0.09	0.05	0.03	-	0.15	0.06	0.00	-	-
NAVAIR 9	7.06	2.25	2.12	0.12	0.05	0.07	-	0.33	0.00	0.00	-	-
NAVAIR 10	7.10	2.40	2.33	0.07	0.04	0.03	-	0.01	0.00	0.11	-	-
1	6.04	2.30	2.31	0.07	0.05	0.01	0.000	0.00	0.00	0.00	0.00	0.12
2	6.01	2.35	2.39	0.08	0.05	0.02	0.000	0.00	0.04	0.00	0.00	0.12
3	6.09	2.42	2.42	0.09	0.06	0.04	0.000	0.13	0.00	0.00	0.00	0.12
4	5.80	2.46	2.22	0.09	0.05	0.04	0.000	0.00	0.00	0.12	0.00	0.15
5	5.82	2.32	2.21	0.09	0.04	0.03	0.000	0.00	0.05	0.13	0.00	0.00
6	5.86	2.38	2.15	0.24	0.05	0.04	0.000	0.00	0.00	0.01	0.28	0.01
7	5.78	2.28	2.46	0.10	0.05	0.03	0.000	0.00	0.00	0.13	0.00	0.15
9 (NAVAIR 4)*	5.96	2.30	2.37	0.08	0.04	0.03	0.000	0.03	0.00	0.12	0.00	0.00
10	5.77	2.30	1.94	0.08	0.05	-	-	-	-	0.11	-	-
11	5.95	1.75	2.31	0.09	0.05	-	-	-	-	0.12	-	-
12	5.54	1.99	1.95	0.06	0.04	-	-	-	-	0.11	-	-
13	5.24	2.59	2.54	0.07	0.04	-	-	-	-	0.12	-	-
14	5.76	2.32	2.96	0.09	0.04	-	-	-	-	0.11	-	-
15	5.67	2.25	2.27	0.20	0.06	-	-	-	-	0.10	-	-
16	8.10	2.41	1.72	0.06	0.04	-	-	-	-	0.13	-	-
17	4.60	2.26	2.42	0.07	0.04	-	-	-	-	0.11	-	-
18	5.61	2.52	2.24	0.08	0.05	-	-	0.17	-	0.11	-	-
X7080	5.88	2.29	0.90	0.13	0.08	<0.02	-	0.32	0.01	-	-	-
Kaiser Alloy 7049	7.50	2.45	1.48	0.13	0.07	<0.10	-	0.01	0.16	-	-	-

-indicates that the element was present in only minor amounts and was not quantitatively measured

*Alcoa MA 15

The Reynolds approach^{140,185-186a} is to utilize a base composition very similar to that of alloy 21 but with just slightly higher zinc content (Table 9 and Fig. 122). The approach (stated in Ref. 185) is:

“...to improve toughness by minimizing insolubles and assuring complete solid solution. To that latter aim, Cu was kept to a minimum level consistent



SYMBOL	SOURCE	ALLOY	ADDITIONS
B	BOEING	21	Zr, Mn
R	REYNOLDS	1-16	Zr, Mn, Cr
K	KAISER	7049	Cr
A ₁	ALCOA	X7080	Mn
A ₂	ALCOA	ALLOY A	Mn
		NAVAIR 3, 4	Zr, Mn
		1-9	Zr, Mn, Cr, V, Ni
	ALCOA	NAVAIR 5-10	Zr, Mn, Cr
	ALCOA	10-18	Zr, Mn

(a) Magnesium-zinc plot

SYMBOL	SOURCE	ALLOY	ADDITIONS
B	BOEING	21	Zr, Mn
R	REYNOLDS	1-16	Zr, Mn, Cr
K	KAISER	7049	Cr
A ₃	ALCOA	X7080	Mn
A ₄	ALCOA	ALLOY A	Mn
		NAVAIR 3-10	Zr, Mn, Cr
		1-9	Zr, Mn, Cr, V, Ni
	ALCOA	10-18	Zr, Mn

(b) Magnesium-copper plot

Fig. 122. Chemical compositions of thick-section experimental and commercial alloys in relation to 7079, 7075, 7178, and 7001.

with achieving the desired stress corrosion resistance. In order to meet the mechanical property criteria, quench sensitivity had to be kept to a minimum. This was achieved by reducing the concentration of the recrystallization retardants Cr, Mn, and Zr.

An alloy designated No. 2 was the most promising based on preliminary stress-corrosion results.^{186,186a} At the conclusion of the Reynolds program, an alloy having the following composition was recommended: 6.4–7.1% Zn, 2.2–2.8% Mg, 1.1–1.4% Cu, 0.08–0.18% Zr, 0.12% max Fe, 0.10% max Si, 0.05% max Ti, 0.03% max Cr, 0.10% max Mn.

The Alcoa programs^{149,175–184d} involve a much broader range of zinc and magnesium content and most of the Alcoa alloys contain medium to high amounts of copper (Table 9 and Fig. 122). In addition, these alloys contain manganese, zirconium, chromium, vanadium, nickel, and iron. For this series of alloys, however, all vanadium-bearing materials have been dropped because of low elongations resulting from the formation of extremely coarse primary intermetallic particles of $Al_{12}Mg_2V$.¹⁸² Vanadium additions also introduced an unfavorable degree of quench sensitivity.¹⁸² It was concluded that vanadium additions, or even contamination by small amounts of this element, should be avoided. The (Fe + Ni)-bearing alloy has also been eliminated from further consideration because of low elongations.¹⁸⁴ Test results from some of the remaining alloys have led to the following recommended tentative composition limits for a new alloy designated MA-15: 5.75–6.75% Zn, 2.0–2.5% Mg, 2.1–2.5% Cu, 0.09–0.15% Zr, 0.12% max Fe, and 0.10% max Si.¹⁷⁸ The initial enthusiasm offered by the performance of MA-15 has been moderated by the less-promising stress-corrosion performance of closely related compositions. Therefore, for the optimum combination of strength in thick sections, resistance to stress-corrosion cracking, and fracture toughness, the following composition limits for MA-15 have been proposed: 5.5–6.5% Zn, 1.9–2.4% Mg, 2.25–2.75% Cu, 0.08–0.14 Zr, 0.12% max Fe, 0.10% max Si, 0.04% max Ti.^{184b} Slightly modified composition limits have recently been registered with The Aluminum Association as X7050 (see Table 1).

The final recommended composition limits from the Alcoa, Boeing, and Reynolds programs are compared with the composition limits for Kaiser's 7049 alloy and 7075 alloy in Fig. 123.

Comparison of the Various Thick-Section Alloys with Commercially Available Alloys

Figure 124 compares the strengths of the various thick-section alloys in plate form with typical long transverse yield strengths for plate of the

commercial alloys 7079-T651, 7075-T651, and 7075-T351. The strengths are plotted as a function of quench rate; arrows showing quench rates for plates of various thicknesses quenched in water at four temperatures are also shown to better illustrate the relationship between thickness and cooling rate.

Before the various alloys in Fig. 124 are examined more closely, a few words should be said about the heat treatments and relative stress-corrosion resistances of the alloys plotted. Aging treatments and smooth-specimen stress-corrosion threshold stresses for the alloys shown are listed in Table 10. The lower curve in Fig. 124 for the chromium-free, zirconium-bearing Reynolds alloy 2 was based on extrapolated aging curve data from

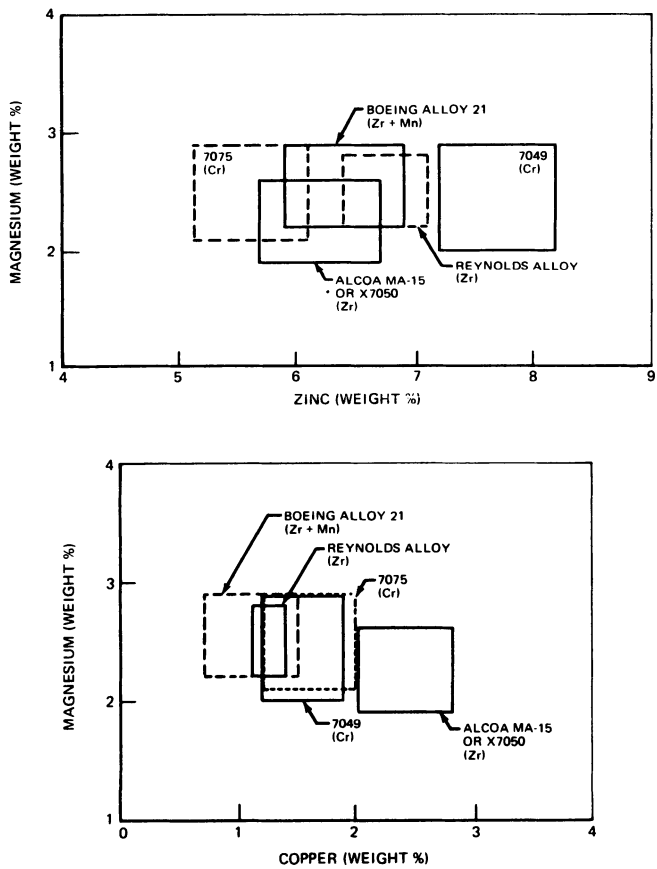


Fig. 123. Composition limits for some new and experimental high-strength aluminum alloys.

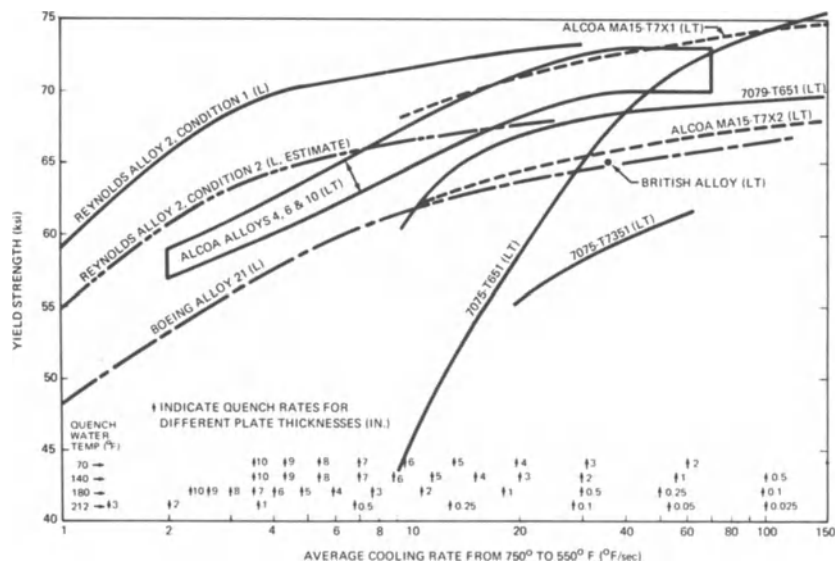


Fig. 124. Effect of quench rate (thickness and quench-water temperature) on the mechanical properties of several experimental alloys and commercial alloys 7079-T651, 7075-T651, and 7075-T7351. All properties are for plate material. Grain directions are as indicated (*L* = longitudinal, *LT* = long transverse).

Ref. 140 and is presented to show strength properties of this alloy in a more overaged condition (T6 + 24 hr 325°F instead of T6 + 18 hr 325°F). This was done because other available stress-corrosion data (Table 11) for similar chromium-free alloys tested in an industrial environment indicate that the T6 + 18 hr 325°F treatment may not provide an SCC threshold stress as high as 25 ksi.

Based on the data in Table 11, the threshold stresses for the manganese- and zirconium-bearing 7375 alloy* are less than 26 ksi. Longer exposure may lower this threshold even further. Thus, with a lesser degree of overaging (T6 + 18 hr 325°F), 7375 + 0.34% Mn, 7375 + 0.12% Zr, and the similar Reynolds alloy 2 may not have adequate stress-corrosion resistance in industrial environments. Note also in Table 11 that the threshold stress for 7075, which contains chromium, is about 42 ksi. This is expected since the T6 + 24 hr 325°F temper is essentially the T73 treatment and the threshold stress for 7075-T73 is greater than 40 ksi.

The most important aspect of Fig. 124, however, is that the data in-

* 7375 is a chromium-free version of 7075.

Table 10. Aging Treatments and Stress-Corrosion Resistance of Experimental- and Commercial-Alloy Plate

Alloy	Aging treatment	Short transverse SCC threshold stress (ksi)	
		3.5% NaCl alternate immersion	Industrial atmosphere
Reynolds alloy 2			
Condition 1	24 hr 250° F + 18 hr 325° F	≈ 25	?
Condition 2	24 hr 250° F + 24 hr 325° F	?	?
Alcoa alloy 4	24 hr 250° F + 24 hr 325° F	≈ 25	?
Alcoa alloy 6	24 hr 250° F + 18 hr 325° F	≈ 25	?
Alcoa alloy 10	24 hr 250° F + 25 hr 325° F	≈ 25	?
MA15-T7X1	4 hr 250° F + 9 hr 325-335° F	≈ 25	?
MA15-T7X2	4 hr 250° F + 24 hr 325-335° F	≈ 45	?
Boeing alloy 21	24 hr 250° F + 35 hr 325° F	≈ 35	?
British alloy	unknown	≈ 30	?
7075-T7351	24 hr 250° F + 27 hr 325° F	45	45
7075-T651	24 hr 250° F	7	14
7079-T651	48 hr 240° F	7	6

dicade a significant step forward in the development of better high-strength, stress-corrosion-resistant materials. All the experimental alloys in Fig. 124 show significant strength increases over 7075-T7351 and even over 7075-T651 for thicknesses greater than about 3 in. (using 70°F quench-water temperatures). Strengths for all the experimental alloys are also comparable with or superior to those for 7079-T651. Even more important is the significant improvement in stress-corrosion properties of the experimental alloys over those for the 7079-T651 and 7075-T651 alloys (Table 10).

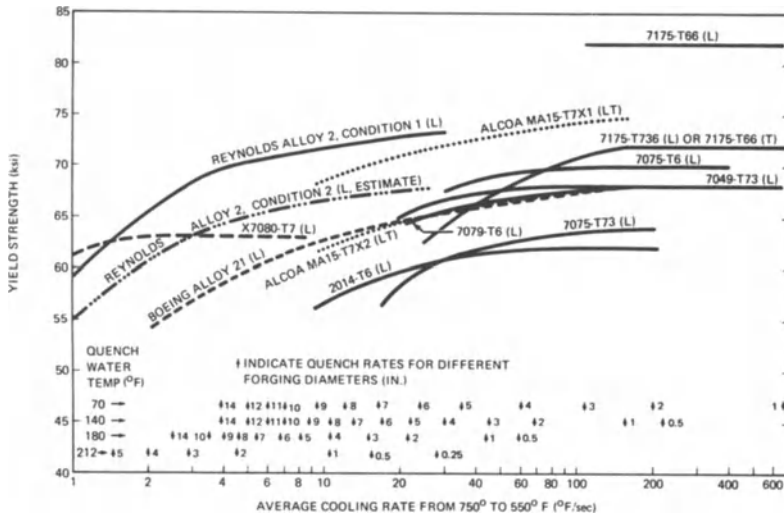
To put the relative merits of the various experimental alloys into more complete perspective, it is necessary to compare these alloys not only with the commercially available plate alloys, but also with the commercially available forging alloys. Figure 125 makes this comparison in a manner similar to that of Fig. 124. To construct Fig. 125, the typical yield strengths of Reynolds alloy 2 plate, Alcoa MA15 plate, and Boeing alloy 21 die forgings were compared with typical properties for die forgings of the commercially available materials. The typical yield strengths for all the

Table 11. Stress-Corrosion Resistance of Short Transverse Specimens from 2-in.-Thick Plate Exposed in New Kensington Atmosphere

Alloy	Heat treatment ¹	Short transverse yield strength (ksi)	Days to failure after exposure at indicated stress level (ksi)							
			18	26	34	38	42	46	50	54
7075	T6 + 24 hr at 325° F	61.5	OK	OK	OK	OK	OK	489	494	477
7375 + Zr	T6 + 24 hr at 325° F	63.0	OK	447	462	120	364	141	92	92
7375 + Mn	T6 + 24 hr at 325° F	65.3		435	196	214	181	113	102	92

Data taken from reference 149

¹Quench rate from solution treatment was 60° F/sec from 750° to 550° F



commercially available die forgings were obtained by adding 6 ksi to the minimum-allowable-strength properties for each thickness (typical properties are commonly 6 ksi above minimums for the high-strength aluminum alloys). This strength value was then plotted at a cooling rate determined by the thickness and quench-water temperature commonly used to quench each alloy. In all cases for the die forgings, cooling rates were determined assuming cylindrically shaped forgings. Arrows indicating different quench rates for various forging diameters and quench-water temperatures are shown in Fig. 125 to better illustrate the relationship between thickness and cooling rate. For this plot, the following quench-water temperatures were used for the forging alloys: 70°F for 7175-T66, 7175-T736, 7079-T6, and Boeing alloy 21; 140°F for 7075-T6, 7075-T73, 7049-T73, and 2014-T6; and 212°F for X7080-T7.

To compare the commercial and experimental alloys, their relative resistance to SCC should be known. Stress-corrosion properties for the various alloys are shown in Table 12 and available stress-corrosion crack growth rate data from Refs. 44, 45, 74, and 186a are shown in Fig. 126.

Table 12. Aging Treatments and Stress-Corrosion Resistance of Experimental- and Commercial-Alloy Forgings

Alloy	Aging treatment	Short transverse SCC threshold stress (ksi)	
		3.5% NaCl alternate immersion	Industrial atmosphere
Reynolds alloy 2			
Condition 1	24 hr 250° F + 18 hr 325° F	≈ 25	?
Condition 2	24 hr 250° F + 24 hr 325° F	?	?
MA15-T7X1	4 hr 250° F + 9 hr 325-335° F	≈ 25	?
MA15-T7X2	4 hr 250° F + 24 hr 325-335° F	≈ 45	?
Boeing alloy 21	24 hr 250° F + 35 hr 325° F	≈ 35	?
7175-T736	Proprietary { 24 hr 250° F +	≈ 35	≈ 35
7049-T73	48 hr R.T. + { 14 hr 320° F	45	45
7075-T73	24 hr 250° F + 27 hr 325° F	45	45
X7080-T7	Proprietary	25	15
7175-T66	Proprietary	7	?
7075-T6	24 hr 250° F	7	14
7079-T6	48 hr 240° F	7	6
2014-T6	18 hr 320° F	7	10

The combined data of Table 12 and Figs. 125 and 126 point out the excellent properties of 7175-T736 for thinner sections and 7049-T73 for thicker sections, especially to those familiar with the numerous in-service stress-corrosion problems of 7075-T6, 2014-T6, and particularly 7079-T6 forgings. Not until fracture toughness and stress-corrosion testing of all experimental alloys is complete and minimum allowable properties have been established will it be possible to judge whether these alloys offer real advantages over 7175-T736 and 7049-T73 in section thicknesses up to 5 in. Based on estimates of minimum mechanical properties for MA-15 (X7050) however, it does appear that this alloy will offer some advantages for very thick sections (Fig. 127). Comparative mechanical, fracture, and stress-corrosion data for X7050, 7049, and an alloy of the Boeing-Reynolds type are now being obtained by Alcoa on identical die forgings under identical test conditions.^{186c}

It should be added here that current work on chromium-free 7000-series alloys is also being carried out in Europe. In Italy, work on two promising Zr + Mn alloys (Zergal-3 and Zergal-4) is being conducted.¹⁷¹ Zergal-3 is being tested in the form of sheet, extrusions, and forgings, while Zergal-4 is being developed specifically for forgings.¹⁷¹ In England, a chromium-free, (Ag + Zr)-bearing alloy is being investigated.¹⁶² The chemical compositions of these three alloys are compared with Alcoa's MA15, Reynold's alloy 2, and Boeing's alloy 21 in Table 13. With the exception of the high copper content in MA15 and the silver addition in the British alloy, the chemical compositions of these alloys are very similar.

Although strength data as a function of thickness and quench rate were not available for Zergal-3 and Zergal-4, one strength data point for 2.75-in.-thick plate of the British alloy was available.¹⁸⁷ This data point has been plotted in Fig. 124, assuming the British alloy was quenched in 70°F water. The strength of this alloy seems to be very similar to that of other silver-free experimental alloys being developed in the United States.

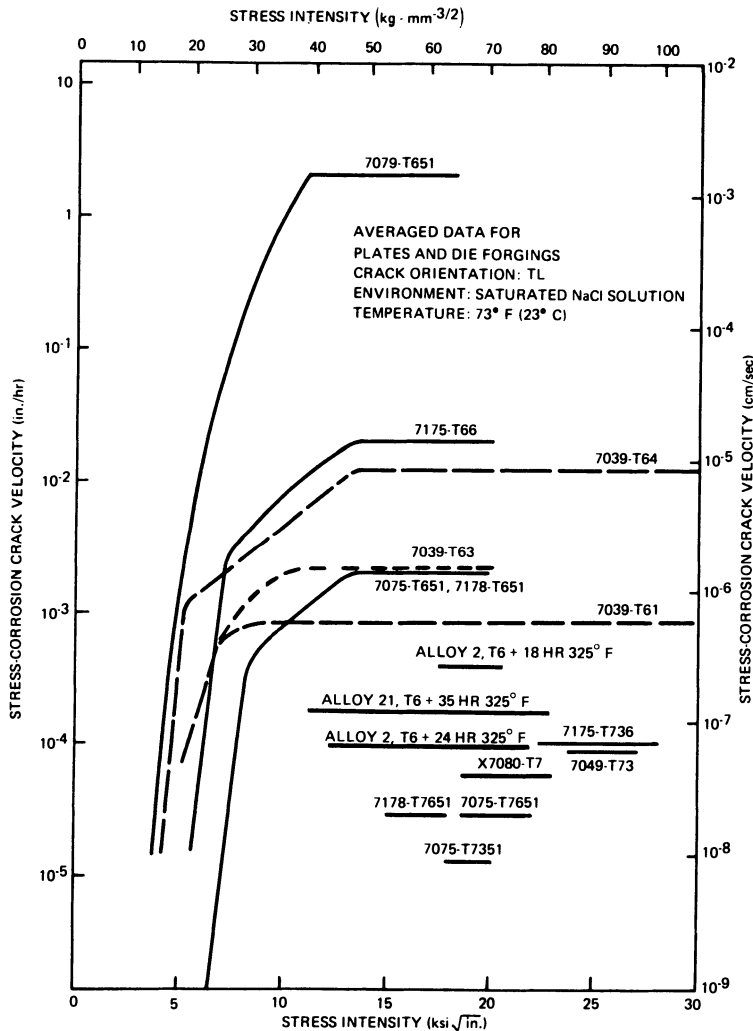


Fig. 126. Effect of stress intensity on stress-corrosion crack velocity for several commercial and experimental aluminum alloy.

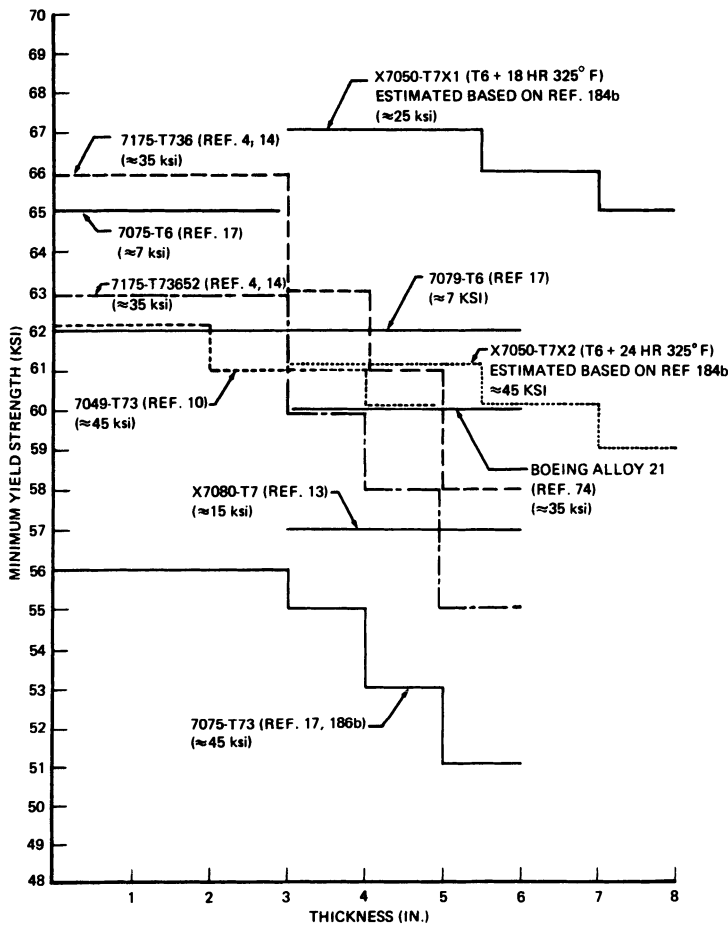


Fig. 127. Minimum longitudinal yield strength values for die forgings of several alloys. Minima for all alloys except MA-15 are based on die-forging data. Minima for MA-15 were based on long transverse plate data. The approximate smooth-specimen stress-corrosion threshold stress for each alloy is shown in brackets.

Table 13. Chemical Compositions of Some Experimental European and American Alloys

Alloy	Zn	Mg	Cu	Cr	Mn	Zr	Ag	Ti	Fe	Si
Zergal-3	6.0	2.5	1.5	0.05 max	0.20	0.18	---	0.06	0.25 max	0.20 max
Zergal-4	6.0	2.3	0.8	0.05 max	0.20	0.18	---	0.06	0.25 max	0.20 max
British alloy	6.1	2.8	1.0	---	---	0.13	0.30	---	0.17	0.07
Alcoa MA15	6.0	2.15	2.50	---	---	0.11	---	0.04 max	0.12 max	0.10 max
Reynolds alloy 2	6.58	2.39	1.22	<0.01	<0.01	0.11	---	0.03	0.07	0.05
Boeing alloy 21	6.40	2.55	1.10	<0.01	0.10	0.13	---	0.02	0.13	0.06

Recent aluminum-alloy development studies have used, with two exceptions^{74,170} stress-corrosion tests with smooth specimens only. The measurement of stress-corrosion crack velocity as a function of crack-tip stress intensity could, however, be a more useful approach, for reasons discussed earlier.

Thermomechanical Processing

It is well known that for some aluminum alloys, such as those of the Al-Cu-Mg type, plastic deformation at room temperature after quenching and before aging can increase strength properties after normal aging treatments. However, for Al-Zn-Mg-Cu alloys such as 7075-T6, room-temperature deformations from 0 to 20% after quenching and prior to aging have resulted in properties after aging that are not much different from those of material directly aged after quenching.

On the other hand, work on an Al-Zn-Mg-Cu alloy has shown that if it is hot-deformed (20% at 248°F) before the normal aging treatment at 248°F, strength can be increased without noticeable decreases in ductility.¹⁸⁸ This work has prompted others¹⁸⁹ to employ multistage aging cycles in combination with plastic deformation after the first stages of aging at low temperatures and before a subsequent higher temperature aging (Fig. 128). Using the technique, the strength of Al-5% Zn-1% Mg and Al-4% Zn-2.7% Mg (+Cr, Mn, Zr) alloys was increased significantly with little decrease in ductility. Based on these results, it was suggested that it may be possible to decrease magnesium content in an Al-Zn-Mg-Cu alloy to increase stress-corrosion resistance and at the same time use thermomechanical treatments of the type shown in Fig. 128 to maintain high strength levels. The prospects are intriguing and some work is being carried out in this direction.¹⁸⁹ To date, however, we are aware of no real breakthrough in this area.

In another program, thermomechanical treatments of 3- to 4-in.-thick 7075 blocks involving a two-step overaging/press forging operation are claimed to result in improved strength and stress-corrosion resistance.¹⁹⁰ However, close examination of the data reveals that stress-corrosion specimens machined from the thermomechanically processed blocks were not really short transverse specimens as they were in the control blocks, due to changes in grain shape and orientation resulting from the press forging operation. Thus, any conclusions concerning improvements in inherent stress-corrosion resistance of the press forged blocks are questionable.

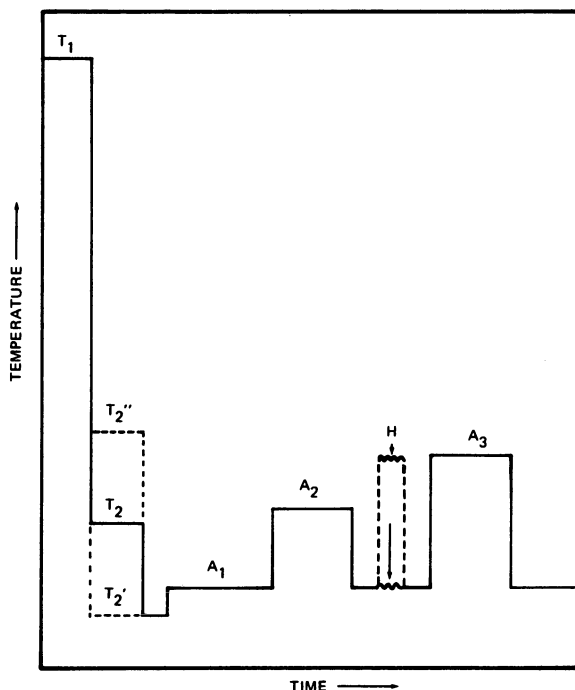


Fig. 128. Thermomechanical treatment scheme for Al-Zn-Mg alloys. T_1 = solution treatment temperature; $T_2'' - T_2'$ = temperature range of quenching medium; A_1 = first stage of aging; A_2 = second stage of aging; H = plastic deformation; A_3 = third stage of aging. (After Conserva *et al.*¹⁸⁹)

New Fabrication Techniques

It is often stated that if end-grain exposure can be avoided, even quite susceptible alloys can be used without undue concern for SCC problems. Unfortunately, it is almost impossible except in the simplest of configurations to produce a forging without any end grain. Furthermore, subsequent machining of the forging generally exposes even more end grain. In an attempt to resolve this problem, a recent study was conducted to minimize end-grain exposure in 7079-T6 in cylindrical landing gear forgings.¹⁹¹ A hollow barrel section was extruded forward or backward such that there was some circumferential grain flow in the barrel wall. Forgings thus produced were significantly more resistant to SCC than the parts produced by the conventional forge, regular cog, and upset cog methods.

However, use of some of the newer high-strength, corrosion-resistant alloys or, in the near future, use of some of the thick-section alloys currently under development will lessen the need for such novel forging techniques, even though such techniques may still be desirable to optimize the grain-flow pattern in some parts.

New Sheet Alloys

Before leaving the subject of new developments, a few words should be said about new developments for sheet applications. The improved exfoliation corrosion resistance of 7075-T76 and 7178-T76 sheet, plate, and extrusions has already been mentioned; in areas where other protective measures have proved inadequate, these T76-temper products can offer improved performance. More recently, new high-strength cladding materials 7011^{192,195-197} and 7008⁴ have been developed for the high-strength 7000-series alloys. The new clad alloys protect the copper-bearing 7000-series electrochemically; in the heat-treated condition, they develop nearly the same mechanical properties as the core alloy, in contrast to the normal 7072 alclad alloy (which does not respond to heat treatment) for these 7000-series materials. This difference results from the increased zinc and magnesium contents in the new clad alloys (Table 1 and Fig. 1). Thus yield strengths for 0.060-in.-thick 7000-series alloys with 7011 and 7008 are 2-4 ksi higher than those for the regular 7072 alclad materials and only 2-3 ksi below those for bare material. Of course, as sheet thickness increases, the difference in strength between bare and clad material decreases. Fatigue strengths of materials clad with 7011 and 7008 are also significantly higher than for materials clad with the lower-strength 7072 alloy (Table 8).

Another new development is the introduction of X7475 alloy sheet (Table 8) in both the high-strength T61 temper and the exfoliation-resistant T761 temper.¹⁹⁸ This alloy is also available with or without the high-strength 7008 cladding. The X7475 alloy is a cleaned-up version of 7075, which has excellent fracture toughness properties comparable to those of 2024-T3, and strength in the T61 and T761 tempers that is only 2-4 ksi below that for the 7075 alloy in the T6 and T76 tempers. X7475-T6 is also nearly identical in strength to 7079-T6 and has a fracture toughness about 20% greater than that for 7079-T6. The high toughness of X7475 results from the reduced iron and silicon contents, which in turn eliminate most of the iron- and silicon-bearing intermetallic particles present in normal material. More effective homogenization and dissolution of copper-bearing

intermetallics during processing is probably also partly responsible for the significantly increased toughness. Toughness values for sheet are shown in Table 8. The limited toughness data for X7475 plate are given in Table 4.

Weldable Alloys

For many welding applications, such as for large storage tanks, structural marine applications, or cryogenic applications, the 5000-series non-heat-treatable alloys such as 5456, 5083, 5086, 5454, and 5052 are often used. Alloys 2014 (Al-Cu-Mg) and 2219 (Al-Cu) have a higher strength-to-density ratio and are therefore often used for aerospace applications (see p. 230). Of the weldable 7000-series alloys, 7039 and 7005 may be considered for structural applications.

In an attempt to provide even higher-strength weldable aluminum alloys with good cryogenic toughness, two additional alloys, 2021 and X7007, have been introduced.¹⁹⁹ The longitudinal and short transverse stress-corrosion resistances of 2021 and X7007 in the unwelded condition are compared with the stress-corrosion resistance of unwelded 2014, 7039, 7005, 6061, and 2219 in Fig. 129. With the exception of the copper-free alloys (7005, 7039, X7007), the data in Fig. 129 were obtained from specimens removed from plate and exposed to a 3.5% NaCl solution by alternate immersion. For the copper-free types, the threshold values for SCC are

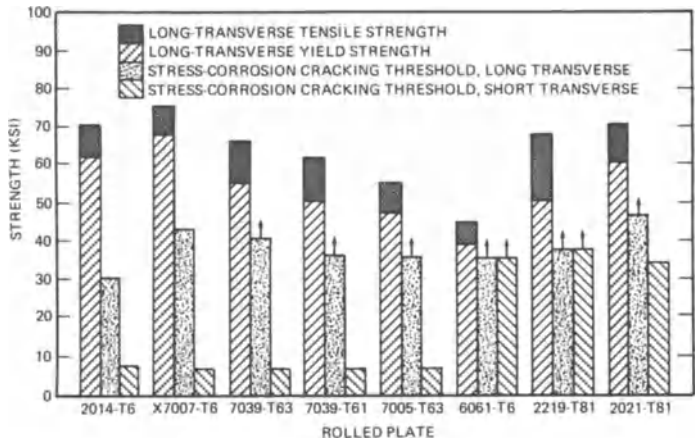


Fig. 129. Stress-corrosion resistance of several weldable high-strength aluminum alloys. Arrows indicate that the specimen did not fail at the highest stress at which it was tested. (After Mayer.¹⁹⁹)

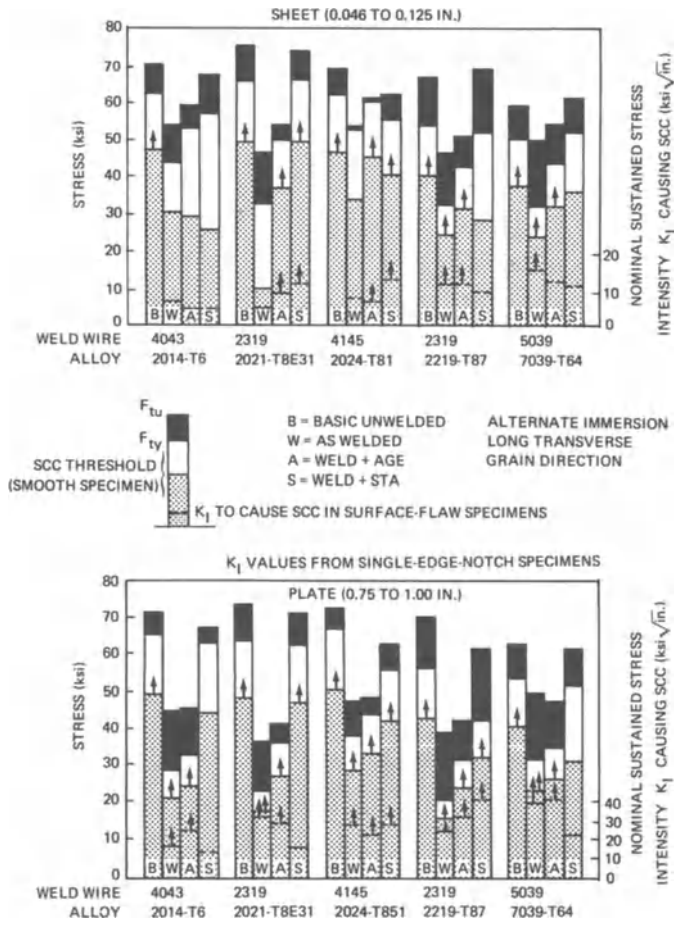


Fig. 130. Mechanical properties and stress-corrosion resistance of sheet and plate weldments of several high-strength aluminum alloys (data from Ref. 200).

based on exposure to an inland industrial atmosphere, which, as previously discussed, provides more reliable information than the alternate-immersion test. Except for 6061-T6, 2219-T81, and 2021-T81, the short transverse stress-corrosion resistance of the alloys shown in Fig. 129 is quite low (7–16 ksi).

In the as-welded condition, the stress-corrosion resistance of many of these alloys is reduced. Stress-corrosion cracks usually develop at the edge of the weld bead if smooth specimens are tested. The reduction of stress-corrosion resistance due to welding is illustrated in Fig. 130. Aging

or resolution treatment and aging after welding often improves resistance to SCC (Fig. 130).

It can be seen from the data in Figs. 129 and 130 that alloys 2021 and X7007 possess attractive strength properties, although the short transverse stress-corrosion resistance of X7007-T6 is quite low. It has been reported that toughness values of repaired welds are much lower for 2021 than for 2219. Since more often than not repair welding is required, this parameter could be of the utmost importance, and a choice among alloys 2021, 2219, or 1044 may well hinge on this factor. Also important, of course, would be the " K_{ISCC} " values for the various alloy-environment combinations, but very little comparative data are available.

DISCUSSION OF STRESS-CORROSION CRACKING IN ALUMINUM ALLOYS

A satisfactory theory of stress-corrosion cracking in high-strength aluminum alloys would have to predict quantitatively and explain from first principles the experimental results presented in the previous sections. Such a theory is not yet available. There are many reasons for the lack of a complete quantitative theoretical treatment of stress-corrosion cracking. Three are mentioned below.

First, quantitative experimental SCC data have only recently become available.^{44,44a,45,67-70,74-76,83,134,166,201-205} Most of the data are presented here for the first time.

Second, theoretical treatments of stress-corrosion cracking attempt to understand the basic mechanisms in atomic dimensions near the crack tip. On this scale, however, observations near the crack tip are extremely difficult, if not impossible. Therefore, the basic assumptions of most theories cannot be verified directly.

Third, the complexity of the subject requires that theoretical treatments take into account mechanical, chemical, and metallurgical aspects. These three aspects are interrelated, as evident from the previous sections of this chapter. Therefore, significant progress toward understanding stress-corrosion cracking is likely to come only from research teams that combine the results of fracture mechanics, chemistry (especially electrochemistry), and metallurgy. Tradition and lack of funds do not favor the formation of such research teams.

Basically, there are two questions a theoretical treatment of stress-corrosion cracking should answer: What causes the crack to grow? What

limits its growth rate? To reduce the energy requirements for crack growth, the environment or its components must react with the metal at or near the crack tip. Depending on the postulated site of the reaction of the damaging species with the stressed metal, the hypotheses proposed for stress-corrosion cracking can be lumped into two groups, as follows.

Damaging Species Reacting at the Crack Tip

The hypothesis that stress-corrosion cracking occurs by stress-activated dissolution^{206–210} belongs to this group, as do those hypotheses that assume that SCC in high-strength aluminum alloys is a kind of intergranular corrosion accelerated either by the opening of the fissure or by rupture of a protective film at the crack front.^{129,211}

Dissolution generally implies the removal of a layer of the solid material along the crack path. Such a layer can be very small; in extreme cases, it is necessary for only a monolayer of the solid on the walls of the crack to react with the environment in the tip zone. Thus there need not be a fundamental difference between the dissolution hypothesis and those hypotheses that assume that adsorption or chemisorption at the crack tip is necessary to rupture the stressed chemical bonds between the atoms of the metal at the crack tip,^{212,213} since adsorption is also the first step for the dissolution process.

A reaction occurring at a surface may be separated into a sequence of steps, the slowest of which will determine the rate of the overall process (i.e., the crack growth rate). A possible sequence of such steps is: (1) transport of reactants to the surface, (2) adsorption of the reactants, (3) reaction on the surface, (4) desorption of the products, and (5) transport of the liberated products from the surface into the bulk environment. It is difficult to predict theoretically the rate-limiting step, since it depends not only on the particular material–environment combination, but also on the applied crack-tip stress intensity.

Damaging Species Reacting in the Interior of the Metal

Some of the products of a surface reaction can enter the underlying metal. There are hypotheses for stress-corrosion cracking of high-strength aluminum alloys which assume that hydrogen or chloride diffuse to the grain boundaries ahead of the crack and either reduces the activation energy for dissolution or lowers the cohesive strength.^{50,214} Under such conditions, further possible rate-limiting steps must be considered in addition to those previously mentioned. Such steps could be: (1) diffusion of the proton or chloride through the metal, (2) recombination of hydrogen, and (3) reaction

with the stressed metal at the grain boundary. Since generally these hypotheses assume that plastic deformation as well as triaxial stresses aid diffusion and redistribution of the damaging species, a prediction of the rate-limiting step is difficult.²¹⁵

The important questions a theory of stress-corrosion cracking of high-strength aluminum alloys should be able to answer are listed below.

1. Why does the presence of water (or some liquid metals) reduce the energy requirements for crack growth? (This is a problem in thermodynamics and quantum mechanics.)
2. Why has the crack-velocity versus stress-intensity curve the characteristic shape illustrated schematically in Fig. 131? (In reality, the V - K curve can be much more complicated; see Fig. 55.)
3. What is the rate-controlling step in each part of the V - K curve? (This is a problem in chemical kinetics, possibly also influenced by dislocation dynamics.)
4. What are the stresses and strains at or near the crack tip?
5. Why can no other anions except chloride, bromide, and iodide (according to our present knowledge) accelerate stress-corrosion crack growth? (This is primarily an electrochemical problem.)
6. Why is stress-corrosion cracking in high-strength aluminum alloys almost exclusively intergranular?
7. Why are some alloys and tempers more resistant to stress-corrosion crack growth than others? (Answers to the latter two questions have been attempted from both metallurgical and electrochemical points of view.)

None of the above questions has yet been answered satisfactorily by any theory. What little we know quantitatively will be mentioned in the following sections.

With the present state of the art, the most useful approach is to assume a realistic model of the mechanisms of stress-corrosion cracking and to modify it to fit the macroscopic experimental data. It is of little scientific merit to defend an assumed model if quantitative experimental results are at variance with its predictions. It is only through modifications of our working hypotheses that we can hope to develop a realistic model.

The following discussion is broken down into three parts, depending on whether the predominating aspect is mechanical, chemical, or metallurgical. Following roughly the subjects of the preceding sections (effects of stress, effects of environment, and metallurgical aspects), the discussion reflects the fact that we are still far from a quantitative theory that integrates

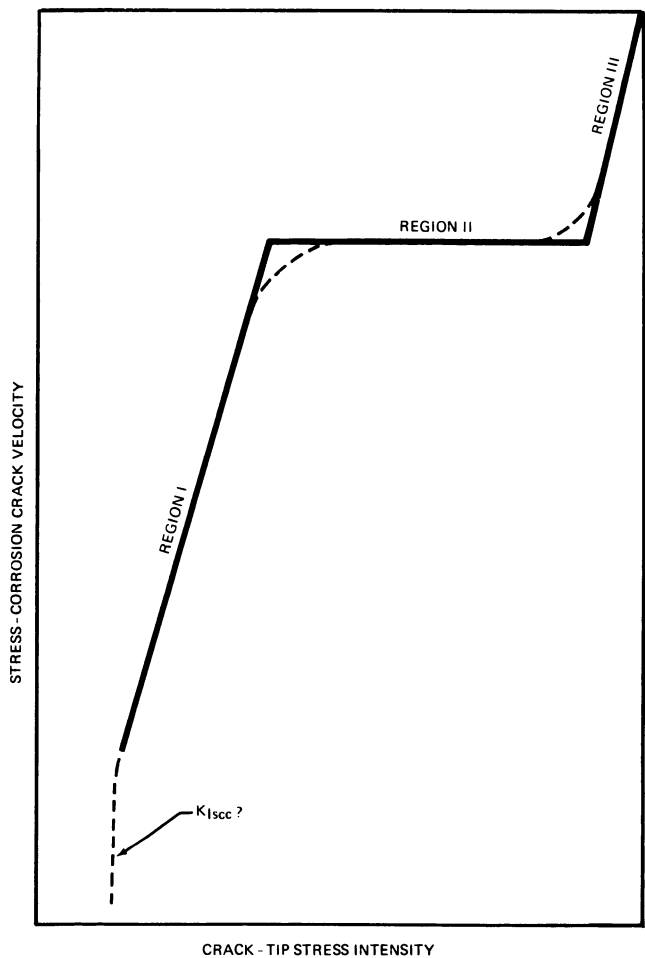


Fig. 131. Various regions of the crack-velocity versus stress-intensity curve.

all three aspects. The discussion emphasizes the *quantitative* aspect of the proposed theories, just as the previous sections emphasized quantitative stress-corrosion data. Of course, acceptable theories must also be in harmony with all qualitative observations.

Effect of Stress on Crack Velocity

The many V - K curves shown in the previous sections amply demonstrate the effect of crack-tip stress intensity on stress-corrosion crack velocity. Figure 131 outlines the various regions of the V - K curve that will

be discussed separately in the following paragraphs. For convenient presentation and discussion, our analysis is restricted to the three most pronounced branches of the V - K curve, called regions I, II, and III, according to previously established terminology.²⁰⁶ Actual test results, however, show that there are also transitions between the regions of the V - K curve.

Stress-Corrosion Crack Growth as an Activated Chemical Process

One of the proposed models of stress-corrosion crack growth is based on the assumption that the crack-tip velocity is controlled by the kinetics of a chemical reaction between the solid and the environment that fills the crack.^{207,208} Since chemical reactions are thermally activated processes, stress corrosion should also be an activated process. In addition, the activation energy for the process is assumed to be stress-sensitive and the reaction would be expected to occur most rapidly where the stress fields are the greatest. Thus, the most rapid reaction between the metal and the environment would be expected at the crack tip. It follows from calculation of the elastic stress field for blunt cracks that for accelerated stress-corrosion cracking to occur, the reaction rate (e.g., dissolution velocity) should be more strongly dependent on stress than a one-half power law.²⁰⁹ Such ideas have been developed into a quantitative theory for stress-corrosion cracking,^{207,208} in which the crack velocity is given by²¹⁰

$$V = V_0 \exp[(-Q + bK_I)/RT] \quad (8)$$

where V is the crack velocity; Q is the apparent activation energy, $Q = E + V_M\gamma/\varrho$; E is the stress-free activation energy; V_M is the molar volume; γ is the fracture surface energy; ϱ is the radius of the crack-tip curvature; $b = 2U/(\pi\varrho)^{1/2}$; U is the activation volume; and K_I is the plane-strain stress intensity. Depending on the values assumed for γ and ϱ , $V_M\gamma/\varrho$ ranges from 10 to 20% of E .

A comparison of Eq. (8) with Eq. (7) and with Fig. 62 shows that the predictions of the theory are in good agreement with the form of the experimental data for crack growth in region I of the V - K curve. The theory predicts a linear relation between the logarithm of the crack velocity and the crack-tip stress intensity. The experimental results for region I stress-corrosion crack growth presented in the section on the effects of environment show indeed that often a straight line in the semilogarithmic V - K plot fits the experimental data best (see Fig. 49, for example).

A modification of the treatment outlined above allowed calculation of the maximum stress dependence of the velocity that could occur in region I

crack growth.²⁰² The result indicated that the maximum slope of the V - K curve in region I is about $2.9 \text{ (ksi in.}^{1/2}\text{)}^{-1}$ if the stresses at the crack tip approach the theoretical limit. Experimentally observed values for the slope of region I in the V - K curves of high-strength aluminum alloys are typically 0.5 – $1.5 \text{ (ksi in.}^{1/2}\text{)}^{-1}$. This suggests that if the analysis²⁰² is correct, extremely high stresses ($\sim E/20$) are reached near the crack tip.

Equation (8) implies that the slope of region I in the V - K curve should decrease as the radius of the crack-tip curvature increases. Thus, the analysis^{207,208,210} would predict a reduced stress dependence of the crack-tip velocity in alloys of reduced yield strength because of the correspondingly enhanced plastic relaxation. Figures 117 and 118 indeed shown an experimental verification of that prediction. If, as some believe,¹⁶⁶ the plastic zone ahead of the crack tip were contained in the precipitation-free zone (PFZ) along grain boundaries in high-strength aluminum alloys, a narrow PFZ should result in a steep region I of the V - K curve. This has been observed.¹⁶⁶ However, it should be recalled that crack-tip plastic zones are usually orders of magnitude larger than the precipitate-free-zone widths. For example, Fig. 106 shows plastic deformation over an area of one to three entire grain diameters.

We have shown that the above model fits some of the experimental SCC data rather well. The model is also compatible with a number of environmental effects and electrochemical hypotheses on stress-corrosion crack growth, which will be discussed later (p. 291), including specifically the hypothesis that dissolution occurs at the crack tip.

Criticisms include the following: The model does not specify just how the stresses at the crack tip enhance the dissolution rate. It is not clear how stresses approaching $E/20$ could be reached near the crack tip, where plastic relaxation certainly occurs. The radius of the crack-tip curvature cannot be measured directly. The fracture surface energy is affected by the plastic deformation generated near the crack tip and cannot be measured directly.

Tensile Ligament Instability

This model for stress-corrosion crack growth is based on the assumption that tiny, free ligaments of the size d_T form from the bulk metal at the tip of a stress-corrosion crack and bridge the crack opening.²¹⁶ It is thought that during crack growth, the ligaments are stretched to the point of tensile instability. In an inert environment, the ligaments would rupture when they reach a critical strain ϵ_c , leading to the failure criterion

$$K_{Ic} = \epsilon_c E (2\pi d_T)^{1/2} \quad (9)$$

The model assumes that an aggressive environment can reduce the strain ϵ_c to cause failure of the ligament by attacking chemically its outer perimeter at a rate V_s . The rate V_s can be thought of as dissolution velocity, although the chemical attack could be any process that reduces the load-bearing capacity of the ligament. The model indicates that the "dissolution velocity" V_s can be as small as 1% of the observed crack velocity in region II of the V - K curve for aluminum alloys, provided Eq. (9) is correct. The model allows no prediction of the stress-corrosion crack-tip velocity as a function of the crack-tip stress intensity.

The threshold stress intensity for SCC is estimated to occur at a K level where the plastic-zone size equals the ligament size d_T . Based on this assumption,

$$K_{\text{ISCC}} = [\sigma_{\text{YS}}/(1 - 2\nu)](2\pi d_T)^{1/2} \quad (10)$$

Unfortunately, d_T cannot be measured independently, and thus the model does not allow a prediction of K_{ISCC} . However, the ligament size d_T can be estimated from Eq. (9) if the plane-strain fracture toughness and the stress-strain curve of the alloy are known. This has been done for alloy 7075-T6, resulting in $d_T = 51 \mu\text{in.}$ and $K_{\text{ISCC}} = 4.5 \text{ ksi in.}^{1/2}$. This compares with the experimental result of 6–7 $\text{ksi in.}^{1/2}$, as discussed earlier.

The model further assumes that the ligaments form around the largest incoherent particles that pervade the material. Thus, in the case of intercrystalline SCC of high-strength aluminum alloys, the spacing d_T of the tensile ligaments should either correspond to the intermetallic particles or to the grain-boundary precipitates (see Figs. 86 and 105). The d_T values are about the size of the intermetallic-particle spacing in commercial high-strength aluminum alloys. Grain-boundary precipitates are separated by a distance that is typically an order of magnitude smaller. Figure 132 shows an electron fractograph of the crack face of a stress-corrosion crack in a high-strength aluminum alloy. Note the intergranular mode of the crack and the intermetallic particles in the grain boundaries. The tensile-ligament-instability model would imply that around each of these particles, a tensile ligament had formed and fractured due to necking and corrosion.

The tensile-ligament-instability model is based on the assumption that K_{ISCC} is "real and inviolable".²¹⁶ However, as discussed earlier (p. 144), stress-corrosion crack growth in high-strength aluminum alloys extends to very small crack velocities and the existence of a true K_{ISCC} has yet to be demonstrated. According to Eq. (10), K_{ISCC} is determined by metallurgical parameters only and should therefore be independent of the environment. If we may approximate K_{ISCC} by " K_{ISCC} " as defined earlier

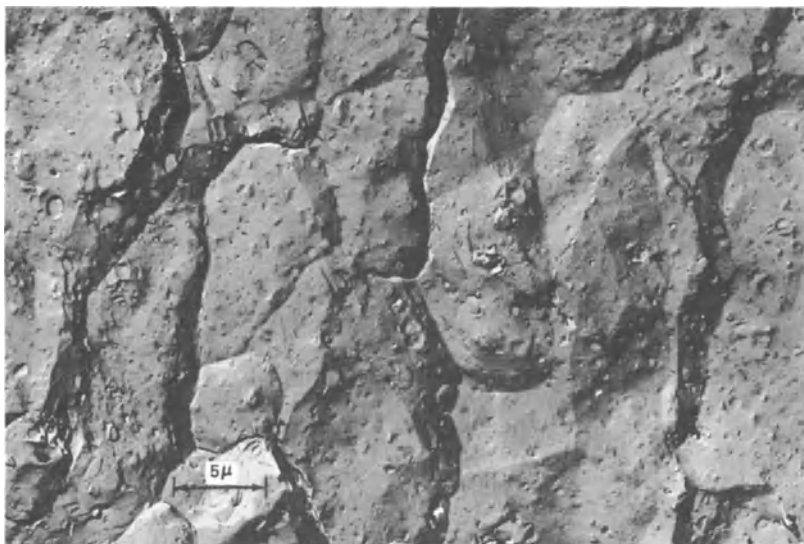


Fig. 132. Electron fractograph of a stress-corrosion crack in a commercial high-strength aluminum alloy.

(p. 145), we can show that the assumed invariance of K_{ISCC} is consistent with some of the data reported in this chapter, but in contrast with other data.

Many variations of the environment affect only the plateau velocity (often changing it by several orders of magnitude) and leave region I of the V - K curve unaffected, as illustrated in Figs. 21, 42, 47–51, 53, 55, 64, 66, 72, and 74. This would be expected from Eq. (10) if K_{ISCC} can be approximated by “ K_{ISCC} .” However, Figs. 59 and 62 show that such a “ K_{ISCC} ” can change greatly with $p\text{H}$ as well as with temperature, implying that either Eq. (10) is wrong (K_{ISCC} not invariant) or the true K_{ISCC} is much smaller than anyone has measured to date for aluminum alloys. There is indeed some evidence for the latter; Table 6 shows extremely small K_{ISCC} values for cracks filled with liquid mercury. Nonetheless, Eqs. (9) and (10) would be of little value since they predict $K_{\text{ISCC}} = 4.5 \text{ ksi in.}^{1/2}$ for alloy 7075-T6, whereas Table 6 gives $K_{\text{LME}} = 0.84 \text{ ksi in.}^{1/2}$ for the same alloy.

Stress-Induced Diffusion and Stress-Corrosion Cracking

Several authors have proposed that SCC may be caused by stress-induced diffusion of hydrogen or chloride in solid solution.^{50,214} The solute atoms are assumed to concentrate at or near the crack tip; e.g., in

regions of highest triaxial stress⁵⁰ or at the elastic-plastic boundary.²¹⁴ It is further assumed that the high concentration of solute atoms near the tip of a crack will enhance the reaction between solute and solvent atoms, and the weak fracture strength of the reaction product may cause sub-critical crack growth.^{214,215} Alternatively, it is postulated that a high concentration of hydrogen at grain boundaries causes a decrease of the activation energy for dissolution of the grain-boundary material.^{50,217} Most of these assumptions are rather vague and speculative, although some audio-radiographic evidence appears to show an increased concentration of damaging species ahead of the crack.

An interesting quantitative treatment of stress-corrosion cracking based on similar ideas has recently been presented.²¹⁵ It is assumed that an elastic hydrostatic tensile stress field exists at the tip of a crack and that this elastic stress field interacts with solute atoms because of the mismatch in solute and solvent atomic sizes. Based on this assumption, a quantitative treatment of the corresponding diffusion problem indicates that the concentration of the solute atoms can increase rapidly near the crack tip. The highly concentrated solute atoms are assumed to react with the bulk material in a first-order reaction, producing a reaction product of very low fracture strength. If the crack growth rate is proportional to the reaction rate, the following equation results²¹⁵:

$$\log(V/C_0) = \gamma + (MK_I/kT\delta_2^{1/2}) \quad (11)$$

where V is the crack-tip velocity, C_0 is the solute concentration on crack surfaces, γ is a constant at a given temperature, M is a parameter that determines the magnitude of the elastic interaction, K_I is a crack-tip stress intensity, δ_2 is a material structural size parameter, K is the Boltzmann constant, and T is absolute temperature.

A comparison of Eq. (11) with Eq. (7) shows that the theory predicts correctly the stress dependence and temperature dependence of the crack velocity in region I of the V - K curve. No quantitative prediction of the absolute value of the velocity is yet possible because of the several adjustable parameters in Eq. (11).

Specific criticisms of this model are: (1) The stress field at the crack tip is treated elastically, and no correction for plastic relaxation at the crack tip is made. (2) It is difficult to assume that solute atoms could be the damaging species for SCC in high-strength aluminum alloys. It was shown earlier (p. 169) that stress corrosion can occur in moist air, and thus chloride seems not to be necessary. On the other hand, aluminum alloys are always

loaded with hydrogen in solution; yet SCC does not occur in inert atmospheres, indicating that hydrogen in solid solution is not sufficient to cause stress-corrosion cracking.

Effects of Environment

The effect of environment on the propagation of stress-corrosion cracks is most conveniently studied (and most accurately measured) in the stress-independent plateau region of the crack-velocity versus stress-intensity curves. For any given alloy, this permits a separation of the environmental effects from the mechanical and metallurgical parameters. Moreover, experimental results have shown that in many (but not all) cases, region II is the only part of the V - K curve that is affected by the environment. Therefore, this discussion is concerned primarily with the effects of environment on the plateau velocity in region II of the V - K curve.

Influence of Water Vapor on Crack Propagation in Gaseous Atmospheres

It was pointed out (p. 163) that dry gases such as argon, hydrogen, oxygen, nitrogen, and air do not support measurable stress-corrosion crack growth. It is the water vapor content of the gases that makes stress-corrosion cracks grow. Region I of the V - K curves seems little affected by the water vapor content of the gases, but the plateau depends linearly on the water vapor pressure. This can be rationalized in the following way.

Starting at the lower end of the V - K curve (see Fig. 42, for example), crack velocity increases with increasing stress intensity, probably following a relation like the one given by Eq. (8). In region I, the crack velocity could be limited by the kinetics of the tip reaction as outlined earlier (p. 286). As the crack velocity increases, it might eventually reach a limit set by the rate at which the damaging species arrives at the crack tip. The rate-limiting step could be either the diffusion of water vapor through the gas that fills the crack or the diffusion of water through an oxide layer covering the crack tip. In either case, we would expect the crack velocity to be strongly dependent on the water vapor concentration in the bulk atmosphere, but nearly independent of the applied crack-tip stress intensity. This is indeed what is observed for the plateau velocity (see Figs. 41 and 42).

A quantitative treatment has been given for a crack with walls parallel almost to the crack tip.²⁰⁶ The crack-tip velocity was assumed to be limited by the diffusion of water through a stagnant layer of nitrogen gas covering

the crack tip. The following result was obtained for the velocity in the plateau region of the V - K curve:

$$V = 0.0275 C_{\text{H}_2\text{O}} D_{\text{H}_2\text{O}} / \delta_1 n \quad (12)$$

where $C_{\text{H}_2\text{O}}$ is the water vapor concentration, $D_{\text{H}_2\text{O}}$ is the diffusivity of water vapor in nitrogen gas, δ_1 is the thickness of the stagnant layer of nitrogen gas covering the crack tip, and n is the number of molecules of water required to arrive at the tip zone to break a single bond and can be related to the number of monolayers formed in the tip zone.

Equation (12) predicts correctly the linear relation between crack propagation rate and water vapor concentration that we found experimentally for a high-strength aluminum alloy (see Fig. 41). The theory does not predict the absolute value of the crack velocity because δ_1 and n are not known and cannot yet be measured independently.

If the crack tip were covered by a layer of corrosion products (oxide, hydroxide), the mechanism of crack propagation would be different since the water vapor would have to diffuse through the layer of corrosion products to reach the crack tip. The mathematical treatment of this situation would yield a result very similar to Eq. (12). The corrosion-layer thickness would be substituted for the gas-diffusion-layer thickness, and the diffusion coefficient for water in the corrosion layer would be substituted for the diffusion coefficient of water vapor in gaseous nitrogen. Since the equation obtained by this substitution would be identical to Eq. (12), either crack growth mechanism would describe the results presented in Fig. 41 with the same degree of satisfaction. The same conclusion may be drawn concerning surface diffusion of water to the crack tip, provided the surface-diffusion coefficient and the surface-diffusion thickness are substituted for the corresponding gas quantities. Consequently, it is not readily apparent which process is actually occurring during SCC of high-strength aluminum alloys in moist, gaseous environments.

It is possible that the tip of a stress-corrosion crack of a high-strength aluminum alloy exposed to moist gases contains a pocket of water rather than being filled with gas, as assumed above. If water were at the crack tip, the proposed gas-diffusion mechanism that led to Eq. (12) would be invalid. Whether or not there is liquid water at the crack tip is difficult to say. A calculation of water condensation in a stress-corrosion crack in glass at room temperature indicated that it is possible for water to condense near the crack tip when the relative humidity is higher than 30%.²⁰⁶ For drier environments, no condensation is predicted.

Our experimental results showing a linear relation between crack velocity and moisture are also an indirect indication that the crack tip was dry. The effect of moisture on crack velocity would be difficult to understand if there were a pocket of liquid water at the crack tip all the time.

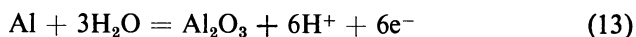
It is important to know whether a stress-corrosion crack tip contains a pocket of liquid water. If it is dry, all theories of stress-corrosion cracking based on the electrochemistry of metal dissolution are invalid, including those that explain the differing susceptibility of various alloys with the difference in electrochemical potential of the precipitates and phases at or near the grain boundary. The mere occurrence of SCC in gaseous atmospheres and the strong dependence of crack velocity on water vapor pressure casts doubt on the hypothesis that SCC is due to chloride diffusing through the metal ahead of the crack tip and weakening the bond between the tip grains.

To summarize, the cause of stress-corrosion cracking in high-strength aluminum alloys in gaseous atmospheres can best be stated with the slogan of a brewery in the Pacific Northwest: *It's the water!*

SCC of Aluminum Alloys in Aqueous Solutions

Stress-Corrosion Cracking in Distilled Water. A change of the environment from gases with 100% relative humidity to immersion in liquid distilled water does not change the V - K curves of high-strength aluminum alloys very much. The only exception is alloy 7079, where such a change of environment increases the plateau velocity by a modest factor of three (compare Figs. 40, 46, and 111). The similar growth rates in liquid water and gases saturated with water vapor indicate that in neither environment is the crack growth limited by the rate that water arrives in the crack-tip zone. There must be a slower rate-controlling step yet to be identified. Diffusion through an oxide layer at the crack tip is one of the possible rate-controlling steps.

Corrosion of Aluminum in Water. When freshly exposed aluminum comes in contact with water, it covers itself with an oxide layer. It has been shown that the essential steps of this reaction are formation of an amorphous layer of Al_2O_3 , dissolution of the oxide, and precipitation of aluminum hydroxide.²¹⁸ The reaction between aluminum and water can be written²¹⁹



During the propagation of stress-corrosion cracks in aluminum alloys immersed in neutral aqueous solutions, a gas can generally be observed

bubbling up from the crack tip. Chemical analysis of the gas has shown it to be H_2 . It is not impossible that part of the hydrogen developed near the crack tip enters the metal, but it must be kept in mind that commercial aluminum alloys already contain quantities of hydrogen.

The thermodynamic data concerning corrosion of aluminum in water are conveniently displayed in the simplified potential- pH diagram in Fig. 133.²¹⁹ The solid lines separate the field of stability of the various species under equilibrium conditions at 25°C. The equilibrium diagram in Fig. 133 is valid only in the absence of substances with which aluminum can form soluble complexes or insoluble salts. The areas representing the theoretical conditions of corrosion, immunity, and passivation are indicated in Fig. 133. In the presence of sufficiently acid solutions, aluminum decomposes water,

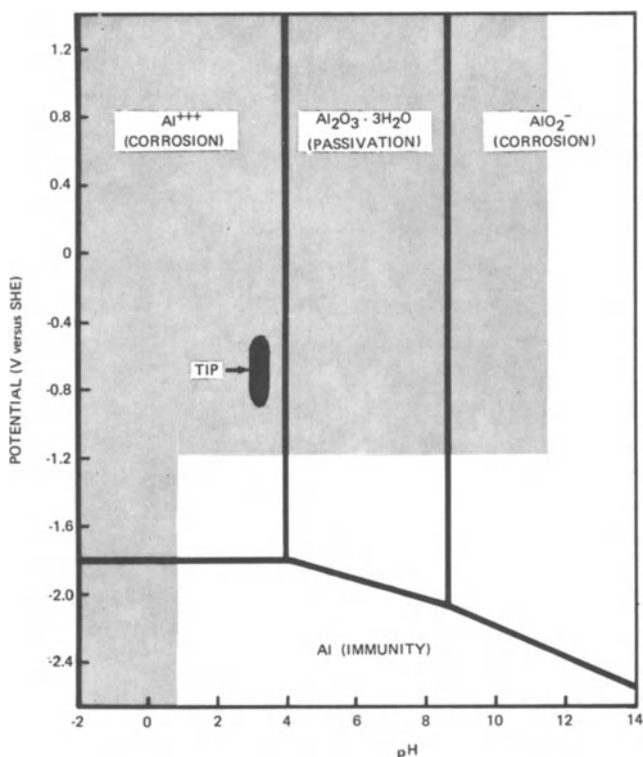
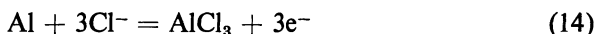


Fig. 133. Simplified potential- pH diagram for the aluminum-water reaction. (After Deltombe *et al.*²¹⁹). Shaded areas show conditions under which chloride, bromide, and iodide accelerate stress-corrosion cracking. (After Speidel.⁴⁴) Black area shows conditions at the tip of such a stress-corrosion crack.

dissolving as trivalent Al^{3+} ions with the evolution of hydrogen. In solutions of pH roughly between 4 and 9, aluminum tends to become covered with a film of oxide, as indicated above. In the presence of sufficiently alkaline solutions, aluminum decomposes water with the evolution of hydrogen, dissolving as aluminate ions AlO_2^- .

Solution Chemistry within Stress-Corrosion Cracks and Corrosion Pits. In the region of passivation (Fig. 133), pitting corrosion of aluminum can occur in the presence of chloride, bromide, and iodide ions at potentials more positive than a certain "pitting potential."^{*} It is significant that these specific pitting agents are also the only anions known to accelerate SCC of aluminum alloys in aqueous solutions, as reported in the section on effects of environment. Titanium alloys show an analogous behavior with respect to pitting and stress-corrosion cracking in aqueous solutions.^{219a} If a corrosion pit, an intergranular corrosion fissure, or a stress-corrosion crack develops, the chemistry within the flaw will change with respect to the bulk solutions, as illustrated schematically in Fig. 134.

Consider a growing corrosion pit or stress-corrosion crack in a high-strength aluminum alloy immersed in a neutral or slightly alkaline chloride (bulk) solution (bromide or iodide may be substituted for chloride with equal results). At the tip of the growing pit or crack, fresh aluminum metal is exposed and supposedly forms Al^{3+} .^{88,221} The current density corresponding to this reaction is known to be several tenths of an amp per cm^2 in the case of pitting,²²¹ but it will be higher in the tip zone of a stress-corrosion crack.¹³⁹ Only part of this current is carried out of the flaw by aluminum ions since the current is distributed according to the mobility of the ions present. There are also chloride ions in the flaw and, if their concentration is high, a significant part of the current is transported by them. This transport is toward the tip of the flaw. If part of the Al^{3+} remains in the tip zone, the solution there will become concentrated and eventually saturated in AlCl_3 . Indeed, there are reasons to suppose that part of the tip zone may be covered by a solid layer of $\text{AlCl}_3 \cdot \text{H}_2\text{O}$.²²¹ However, it is not yet quantitatively known to what extent the formation of oxide according to Eq. (13) and the formation of aluminum chloride according to the following equation compete at or near the crack tip:



* The pitting potential of aluminum in 1 M NaCl solution is -480 mV (SHE) , independent of pH in the interval pH 2–11, but dependent on the chloride concentration.^{220,221}

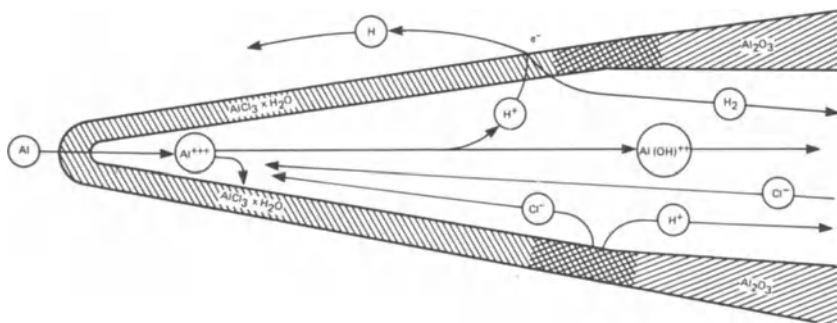
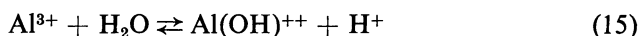


Fig. 134. Summary of proposed reactions near the tip of a stress-corrosion crack in aluminum alloys exposed to aqueous chloride solutions.

The formation of a solid layer of $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ at the crack tip indicated in Fig. 134 is therefore just an assumption.

Considering the solution chemistry in a crack, part of the Al^{3+} ions can be hydrolyzed by the reaction^{88,221}



Therefore, the solution inside the crack is acidified. Part of the H^+ forms H_2 at the crack walls, from where it is observed to emanate. Part of the hydrogen may enter the metal. Consider again the potential- $p\text{H}$ diagram in Fig. 133. It does not take into account the presence of the halide ions in the aqueous solutions, nor the presence of alloying elements in the solid. Thus, some changes are to be expected in a real pitting or SCC situation. More important, the potential- $p\text{H}$ diagram does not reflect the kinetics of the reactions involved. Nevertheless, assuming for the moment that the general form of the diagram may be applicable to the chemistry near a stress-corrosion crack tip, Fig. 133 illustrates that a protective oxide layer should not be stable in acidified solutions of $p\text{H}$ less than 4. Thus, if the solution inside a crack or pit acidifies according to Eq. (15), it would be possible that the oxide layer does not form near the tip, but possibly forms a certain distance away from the tip, as indicated in Fig. 134.

What evidence do we have for the existence of a concentrated, acidified AlCl_3 solution in a stress-corrosion crack?

1. Acidification of the solution inside a crack or pit. Experimental and theoretical results were reported 13 years ago on a study of the solution chemistry in a 0.04-mm-wide crack in an aluminum alloy exposed to a 0.5 M aqueous NaCl solution. Calculations based on Eq. (15) predicted

a pH of 3.5. Direct pH measurements of the electrolyte recovered from the crack yielded pH values of 3.2–3.4.⁸⁸ Similar measurements of the pH in stress-corrosion cracks of a high-strength aluminum alloy have recently confirmed those results, yielding a pH of 3.5 in the crack.⁸⁹ The presence of acidity in flaws and pits has long been known.²²¹

2. Concentration of Al^{3+} in pits and cracks. Studies of pitting corrosion have indicated a high concentration of Al^{3+} near the tip of the pit.^{220,221} Tests of solutions from the interior of stress-corrosion cracks have confirmed the presence of the Al^{3+} ion.⁸⁹

Some implications of the solution chemistry changes inside a crack are illustrated in Fig. 133. The shaded area indicates the wide range of pH and potential for which chloride, bromide, and iodide accelerated stress-corrosion cracks in aqueous solutions. As mentioned above, the pH inside a crack seems to establish itself near 3.2–3.5, as indicated by the black dot (labeled “tip”) in Fig. 133. The potential drop in a stress-corrosion crack has yet to be reliably measured, and thus the potential at the crack tip is not known. The scatter allowed by the size of the black dot includes the mixed potential as well as the open-circuit potential measured with stress-corrosion cracked specimens of high-strength aluminum alloys during crack propagation in an aqueous chloride environment.⁴⁴

Stress-Corrosion Crack Velocity Limited by Mass Transport Kinetics

The mass-transport-kinetics (MTK) model was first developed for SCC of titanium alloys in aqueous chloride, bromide, and iodide solutions²²² and later extended to aluminum alloys.^{202,223} It indicates that the stress-corrosion crack velocity in region II of the V – K curve is limited by the transport of halide ions to the crack tip.

Assume that some active species such as chloride, bromide, or iodide is required at the crack tip for accelerated stress-corrosion crack growth. The current of halide ions to the crack walls is related to the crack velocity by²²²

$$I_- = 2n/Q_x V \quad (16)$$

where I_- is the current per unit thickness specimen, n is the number of monolayers of halide ions adsorbed at the walls, Q_x is the charge density of a monolayer, and V is the crack-tip velocity.

There are reasons to assume that n is higher than 14 for aluminum alloys,²²⁴ and a probable value is $n = 30$.²⁰² The current is related to the

mass transport flux of halide ions into the tip zone by²²³

$$I_- = zFAj \quad (17)$$

where z is the valence, F is Faraday's equivalent, A is the cross section of the crack in the unit thickness specimen, and j is the mass flux.

At the boundary of the tip zone,

$$j_- = -D(dC/dy) - (z/RT)DC(d\phi/dy) \quad (18)$$

where D is the halide-ion diffusivity, C is the halide-ion concentration, y is the distance from the tip of the crack, and ϕ is the potential.

The first term on the right side of Eq. (18) gives the contribution of diffusion to the halide-ion mass flux, while the second term of the sum gives the contribution due to electrolytic migration. Combining Eqs. (16)–(18) gives²²³

$$V = \frac{D[-zFA(dC/dy) - zFA(zF/RT)C(d\phi/dy)]}{2nQ_x} \quad (19)$$

It was shown above that there is probably a saturated aluminum trihalide solution in the stress-corrosion crack. Therefore, the first term in the sum of Eqs. (18) and (19) can be considered negligible, and the migration term becomes dominant.

The MTK model is in good agreement with a substantial number of experimental observations on stress-corrosion crack growth in region II of the V - K curve:

Halide-Ion Concentration. The theory, according to Eq. (19), predicts that the crack velocity should be proportional to the halide-ion concentration. This agrees well with the experimental observations reported in Figs. 52 and 54.

Temperature. The temperature dependence of stress-corrosion crack growth in region II, according to Eq. (19), would be determined mainly by the temperature dependence of the diffusivity D of the halide ions. The activation energy of ~ 4 kcal/mole measured for region II (Fig. 63) is well within the range predictable for the activation of a process limited by ionic mass transport.²²⁵ The very different effect of temperature on the slow crack growth rate reported in Fig. 64 and 65 seems to indicate that for such cases, the transport of halide ions through the liquid is not rate-controlling.

Ionic Species. To explain the fact that chloride, bromide, and iodide accelerate SCC in aluminum alloys is outside the scope of the MTK model.

However, since the crack becomes acidic (as shown earlier), hydrogen ions and Al^{3+} ions partially displace other cations within the crack so that the velocity is independent of those cations reported earlier (p. 177).

Electrochemical Potential. Assuming the crack tip remains at the mixed potential, Eq. (18) predicts a linear relation between crack velocity and applied electrochemical potential. This is consistent with the data reported in Fig. 57, but the scatter in the data is too large to draw final conclusions about the experimentally observed relation between crack velocity and potential.

Viscosity. The diffusivity of halide ions can be expressed by²²²

$$D = D_0\mu_0/\mu \quad (20)$$

where D_0 and μ_0 are constants and μ is the viscosity of the solution.

Equation (20), combined with Eq. (19), gives²²³

$$V = \frac{D_0\mu_0[-zFA(dC/dy) - zAF(zF/RT)C(d\phi/dy)]}{\mu 2nQ_x} \quad (21)$$

According to Eq. (21), the MTK model predicts that the stress-corrosion crack velocity should vary inversely with viscosity. This is indeed what has been found experimentally (see Fig. 67).

Metallurgical Aspects

In this section, we would have liked to present those theories that predict quantitatively the stress-corrosion performance of high-strength aluminum alloys, based solely on the microstructure and composition of the alloy. There is no such theory; indeed, there is not even a single successful attempt to relate the stress-corrosion V - K curve and the microstructure of aluminum alloys on a quantitative basis. This is all the more deplorable since hundreds of papers have been written on the relationship between microstructure and stress-corrosion cracking of aluminum alloys. Even the single most important metallurgical treatment to improve stress-corrosion resistance—the overaging of precipitation-hardened alloys—has not yet been analyzed quantitatively.

Qualitative hypotheses on the relationship between microstructure and stress-corrosion resistance are still highly controversial. They have been reviewed adequately,²²⁶ allowing the present section to be brief. Progress in understanding the metallurgical aspects of stress-corrosion cracking of

high-strength aluminum alloys will come when hypotheses and tests they are supposed to explain are made quantitative, and assumptions upon which the hypotheses are based can be checked independently.

Alloy Composition

Stress-corrosion cracking has been observed in aluminum-rich alloys of the following systems^{51,227}:

Al-Ag	Al-Cu-Mg	(2000)
Al-Cu	Al-Mg-Si	(6000)
Al-Mg	Al-Mg-Zn	(7000)
Al-Zn	Al-Zn-Mg-Cu	(7000)

Although no systematic quantitative work on the effect of alloy composition has been done, the following rules seem to be valid for stress-corrosion cracking in aqueous solutions:

1. Pure aluminum is not susceptible to SCC.
2. For any given alloy system, susceptibility to SCC increases with the amount of alloying additions that can be put in supersaturated solid solution.
3. Stress-corrosion resistance of the ternary and higher-order alloys listed above is influenced not only by the sum of the amounts of alloying additions, but also by their ratios.²²⁸
4. Small additions (several tenths of a percent) of Cr, Mn, Zr, Ti, V, Ni, and Li to the high-purity binary, ternary, and quaternary alloys mentioned above can reduce the susceptibility of wrought products in the longitudinal and long transverse directions.^{228,229}

Precipitation Hardening

According to the experimental data reported in the section on metallurgical aspects, the effect of precipitation hardening on resistance to stress-corrosion cracking seems to follow these rules: (1) The initial stages of precipitation hardening decrease the resistance to SCC.¹⁴⁴ (2) Precipitation hardening beyond peak hardness (overaging) can increase the resistance to SCC.¹⁴⁴ Figure 113 (qualitatively) and 114 and 117 (quantitatively) illustrate these observations. Since precipitation hardening is of the utmost importance for high-strength aluminum alloys, studies on the effect of metallurgical parameters on SCC have often attempted to explain these two rules. The following hypotheses are among those discussed presently.

Precipitate-Free Zones. It is well established that preferential precipitation during aging of Al–Zn–Mg alloys can lead to the formation of a precipitate-free zone (PFZ) at grain boundaries.²³⁰ Wide PFZ's are easily observed in ternary alloys. Figure 135 shows an example of a grain-boundary triple point with associated precipitation-free zones.⁴⁴ In commercial high-strength aluminum alloys, PFZ's are much smaller and often are not observed at all. Therefore, most studies on the relationship between PFZ width and stress-corrosion resistance have concentrated on high-purity, ternary Al–Zn–Mg alloys of academic interest. Three schools of thought have developed, each contradicting the others: (1) Reducing the PFZ width will *increase* resistance to SCC.²³¹ (2) Reducing the PFZ width will *decrease* resistance to SCC.²³² (3) PFZ width is of minor or no importance to SCC resistance.^{144,233} Those who believe that PFZ's are important in the resistance to SCC assume this is so because preferential deformation

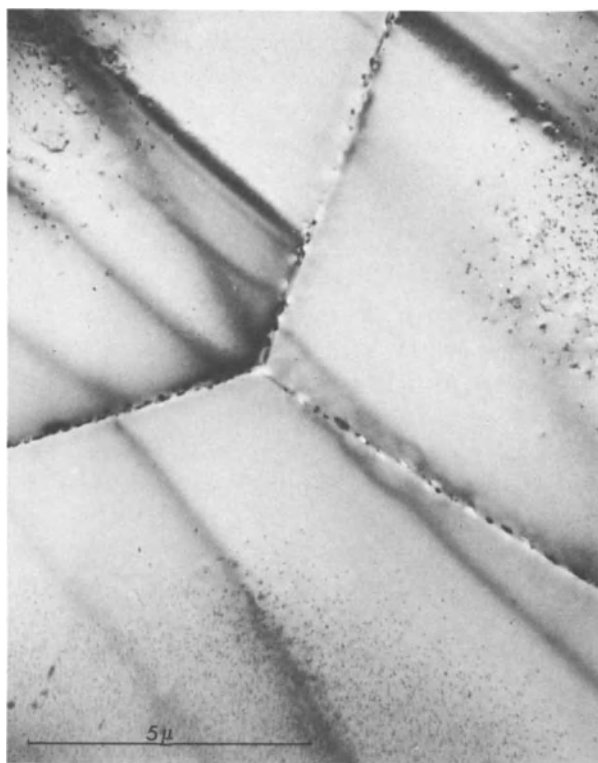


Fig. 135. Precipitation-free zones at grain boundaries of a high-purity Al–Mg–Zn alloy.

in the PFZ leads to preferential dissolution and thus to intercrystalline SCC.^{163,232}

At this time, neither the PFZ hypothesis nor the experiments supporting or contradicting it are on a quantitative basis, and thus the hypothesis is open to speculation and criticism.

Interaction of Dislocations with Precipitates and SCC. This hypothesis proposes that the effect of precipitation hardening on the resistance to SCC is due to the interaction of dislocations with those precipitates that cause the hardening.^{144,234–237} High-strength aluminum alloys exhibit characteristic dislocation arrangements after deformation. In material of low resistance to SCC, straight, narrow bands of high-dislocation density extend across the grains. The dislocations in the bands are piled up against the grain boundaries. In materials aged to a reduced susceptibility, the slip bands contain dislocations of irregular curvature and many dislocation loops. It is thought that different dislocation–particle interactions cause the differences in slip mode, and it is concluded that resistance to SCC in high-strength aluminum alloys is reduced by precipitates that are sheared by plastic deformation. Particles bypassed by moving dislocations are thought to result in improved stress-corrosion resistance.¹⁴⁴ According to the dislocation–particle interaction hypothesis, overaging reduces stress-corrosion susceptibility because the volume fraction of particles that can be sheared decreases.¹⁴⁴

The hypothesis that dislocation–particle interaction affects the resistance to stress-corrosion cracking in high-strength aluminum alloys predicts specifically that¹⁴⁴ (1) matrix precipitates (i.e., GP zones) and not grain-boundary precipitates or the PFZ control resistance to SCC, and (2) susceptibility to stress-corrosion cracking in aqueous chloride solution increases with the volume fraction of the GP zones. Results of recent experimental investigations are in full agreement with these predictions.^{233,238,239}

The dislocation–particle interaction hypothesis is at present being transformed into a quantitative SCC theory.^{44,239} Until a quantitative comparison of theory and experiment is presented, the assumptions and predictions remain open to questioning, as do the other hypotheses mentioned.

SCC Due to an Anodic Path along Grain Boundaries

Nearly three decades ago, a “generalized theory of stress-corrosion cracking” was given^{129,137} that describes the mechanism of stress-corrosion cracking of aluminum alloys as follows: Corrosion occurs along localized paths, producing fissures; components of tensile stress normal to the path

then create a stress concentration at the base of the localized fissures. In aluminum alloys, such pre-existent anodic paths are thought to be due to the difference in electrochemical potentials between grain-boundary precipitates or grain-boundary margins and the grain interior.⁵¹ The role of stress in stress-corrosion crack growth is thought to be the opening of the fissures, thus exposing fresh, unprotected metal to corrosion attack. It is assumed that in this way, corrosion along the grain boundary is accelerated because freshly exposed metal is more anodic. This theory is still widely accepted, especially in the aluminum industry, because it is consistent with many experimental observations concerning the effect of heat treatment on resistance to SCC, as pointed out in the section on metallurgical aspects and alloy development.^{51,85}

These ideas have never been transformed into a quantitative theory that would allow the prediction of stress-corrosion crack velocity as a function of crack-tip stress intensity and metallurgical and environmental parameters. In particular, the role of stress is defined rather vaguely and, indeed, the whole “generalized theory of stress-corrosion cracking” is a misnomer. It should read “generalized theory of intergranular corrosion,” since it describes that phenomenon rather well, based on the potential differences of various constituents and zones along grain boundaries in aluminum alloys.⁵¹ It predicts the selective dissolution of anodic regions in or adjacent to grain boundaries in aluminum alloys. The model fails to explain even qualitatively why some alloys are susceptible to intergranular corrosion but not to SCC and, conversely, why some alloys are susceptible to SCC but not intergranular corrosion when unstressed, as would be expected for a process based on simple electrochemical differences. Such qualitative arguments are substantiated by the observations compiled in Table 14. It is obvious that intergranular corrosion is neither necessary nor sufficient for stress-corrosion cracking to occur. This indicates also that selective dissolution of anodic regions in or adjacent to grain boundaries in aluminum alloys is neither necessary nor sufficient for stress-corrosion cracking to occur. It has been noted that the addition to sodium chloride solutions of compounds that cause severe intergranular corrosion has no more effect on the time to failure of a particular high-strength aluminum alloy than the addition of inhibitors, and thus there is a fundamental difference between stress-corrosion cracking and intercrystalline corrosion.²⁴⁰

Nevertheless, susceptibility to stress-corrosion cracking and intercrystalline corrosion often do go hand in hand. The anodic-path hypothesis has the merit of being among the first to attempt a correlation between

Table 14. Relationships Between Intergranular and Stress-Corrosion Cracking in Some High-Strength Aluminum Alloys

Intergranular corrosion and stress-corrosion cracking			No intergranular corrosion and no stress-corrosion cracking			No intergranular corrosion but stress-corrosion cracking			Intergranular corrosion but no stress-corrosion cracking		
Alloy	Environment	Ref.	Alloy	Environment	Ref.	Alloy	Environment	Ref.	Alloy	Environment	Ref.
7075-T651	{ NaCl-AlCl ₃ solution acidified with HCl }	51	7075-T73 7075-O 2024-T3 quenched at rates > 3000°F/sec	{ Chloride solutions }	51	7039-T64	{ Boiling 6% NaCl solution }	241	6061-T6	{ Alternate immersion in 3.5% NaCl solution }	51
7178-T651 7075-T651 7079-T651	{ Acidified aqueous iodide solutions }	44		{ Chloride solutions }	92	7075-T651	{ Hexene Engine oil Flight fuel Air, 2% RH }	44	Al-Mg-Si alloys	{ Chloride solutions }	51,56, 57,58
2024-T351 6070-T6 6066-T6 and slowly quenched 6061-T4	{ Alternate immersion in 3.5% NaCl solution }	51				7079-T651 7039-T64 7039-T61	{ Air, 50% RH }	44	2024-T6 2024-T8	{ Chloride solutions }	51
						7075-T6 & 2024-T3 re-heat-treated & rapidly quenched	{ Chloride solutions }	51			

microstructure and stress-corrosion experience. This hypothesis has been used to explain the superior stress-corrosion resistance of the overaged alloy 7075 in the T73 temper compared to the T6 temper.⁶²

Initiation of Stress-Corrosion Cracks in High-Strength Aluminum Alloys

Stress-corrosion cracks initiate within less than 5 min from purely mechanical precracks when highly stressed SCC-susceptible aluminum alloys are immersed in neutral aqueous sodium chloride solutions at room temperature.⁴⁴ In the same alloy-environment combination, reinitiation of stress-corrosion cracks that were arrested by cathodic protection can occur within 5 sec after the electrochemical potential is brought back to a value between the rest potential and the pitting potential.⁴⁴ Results of systematic studies on this effect now under way may show whether diffusion of damaging species through the metal ahead of the crack tip can be part of the mechanism of stress-corrosion cracking in high-strength aluminum alloys.

Stress-corrosion crack initiation from smooth specimens has been the subject of several recent studies, with controversial results. One extreme is represented by the observation that "the initiation stage may take months or years while the propagation stage occurs in a matter of minutes or

hours.”⁵⁰ The other extreme is the observation of a stress-corrosion crack in a smooth specimen of alloy 7075-T651 exposed only 30 sec to an aqueous chloride solution of $pH = 0.9$.⁹¹ A similar controversy exists about the site of crack initiation. While some authors^{241a} maintain that “up to 95% of the life of a specimen is taken up by the formation and growth of corrosion pits to a certain degree of acuity from which true stress corrosion cracks emanate,” others⁶² report that “corrosion pits had no effect on crack initiation.”

A likely explanation for the discrepancy of the results of various studies is to assume that stress-corrosion crack nucleation is different in different high-strength aluminum alloys. For example, it has been clearly shown that constituent particles were preferred sites for the initiation of short transverse stress-corrosion cracks in alloy 7039-T64,²⁴¹ while it seems probable that crack initiation in alloys 2219 and 7075 is not influenced by constituent particles.⁶² The surface treatment of smooth SCC specimens also plays a role in the time to failure. A surface layer deformed by machining must be penetrated by corrosion before true stress-corrosion cracks can start.²⁴²

PREVENTING SCC FAILURES IN AEROSPACE AND OTHER STRUCTURES

Attempts to eliminate stress-corrosion cracking problems with high-strength aluminum alloys have not been completely successful. For example, numerous stress-corrosion failures have occurred in the Saturn V launch vehicle, primarily on parts made from 7075-T6, 7079-T6, and 2024-T4.²⁴³ Nor has the Apollo lunar landing module been free from stress-corrosion cracking.^{243,244} While these particular problems have been alleviated by switching to stress-corrosion-resistant alloys and tempers or by changing processing procedures to minimize residual and fit-up stresses, etc., questions may still be asked: Why? Why so many? Why so many in this late stage of our technological advancement?

Some have suggested that the overriding fact about stress-corrosion cracking is a lack of awareness of existing data.²⁴⁵ Hopefully, this trend will be reversed as builders of aerospace and hydrospace equipment shift more design emphasis to materials selection. To help achieve this goal, this paper has attempted to put into perspective the mechanical, fracture, fatigue, and stress-corrosion properties of the more common alloys; the newly introduced alloys such as 7175-T736, 7049-T73, and X7475-T761 and -T61, and some of the developmental alloys yet to be offered com-

mercially. In this manner, those involved in recommending materials to the designer can be made more aware of the changes coming in the area of aluminum alloy development. Thus they can be better prepared to make materials recommendations in the coming years.

Materials Selection

High-Strength Alloys for Hand- and Die-Forging Use

While it is sometimes possible to locate the parting plane of die forgings in an area that will minimize short transverse stresses, it is often difficult or impossible in complex forgings to predict the exact nature of the grain flow at each specific area. Thus, end grains may be exposed after machining, especially on heavily machined parts. For this reason and because of the possible presence of residual surface tensile stresses acting normal to local grain flow and the presence, unintentional though it may be, of fit-up or assembly stresses, alloy 7079-T6 should not be used where stress-corrosion problems must be avoided. This same recommendation also applies to hand forgings. The low survival rates of 7079-T6 industrial-atmosphere stress-corrosion specimens stressed to only 15% of the yield strength (Fig. 45), the rapid stress-corrosion crack growth rates possible in 7079-T6 (Figs. 110 and 111), and actual service experience dictate that this recommendation be made. The recommendation should be even more emphatic in view of the recent development of stress-corrosion-resistant alloys such as 7049-T73, 7175-T736, and 7075-T736, which have strength properties equal to or greater than those for the 7079-T6 alloy (Table 4). Alloy 7075-T73, despite its slightly lower strength properties, can also be justified as a replacement for 7079-T6.

This single recommendation to avoid use of 7079-T6 could save millions of dollars yearly by minimizing downtime necessary to replace cracked parts. The increased reliability and reduced maintenance costs should also be obvious.

While 7075-T6 forgings have shown better service performance than 7079-T6, they, too, are highly susceptible under short transverse stresses; it is recommended that for most applications, 7075-T73, 7175-T736, 7049-T73, or 7075-T736 be considered as replacements for 7075-T6.

For the 2000-series alloys, the artificially aged T6 and T8 tempers provide a higher degree of resistance to SCC than the naturally aged T3 and T4 tempers. Note, however, that alloy 2014, even in the artificially aged T6 temper, is highly susceptible to SCC in the short transverse direc-

tion. In certain applications where parts may be fatigue critical, 2014-T6 forgings are often used successfully despite this short transverse stress-corrosion susceptibility.

For lower-strength application, 6061-T6 has excellent resistance to stress-corrosion cracking.

Alloys for Sheet and Plate Applications

Material selections for sheet and plate applications are often dictated by such factors as fatigue life and fracture toughness rather than stress- or exfoliation-corrosion resistance. However, if service performance has shown that protective measures against exfoliation corrosion of the 7000-series alloys have been inadequate, the newer T76 tempers for 7178 and 7075 and the T761 temper for the newer X7475 alloy can be used. For applications where regular alclad 7000-series alloys have been used, strength and possibly fatigue-life improvements can be obtained by use of the higher-strength 7011 and 7008 clad materials. In addition, significant gains in fracture toughness can be achieved by use of bare or 7008 alclad X7475 alloy.

In fatigue-critical applications or where high toughness is required, 2000-series alloys such as 2024-T3 and 2014-T3 are often used. For most applications, these alloys are used in the alclad condition to protect against general and exfoliation corrosion. It should be recalled that the resistance to stress corrosion and exfoliation corrosion of 2024-T3 decreases rapidly during the first stages of any reheating (Figs. 96, 97, 99, and 113) until a minimum resistance is obtained. Additional heating then increases the resistance. Thus, care must be exercised to ensure that exposure times to elevated temperatures during service or fabrication are below those levels that would sensitize the 2024-T3 to intergranular attack. Too slow a cooling rate during quenching can also sensitize 2024-T3 material to exfoliation and stress-corrosion cracking (Figs. 92–94). Since cooling rates are a direct function of thickness, it is recommended that 2024 products thicker than about 0.25 in. should be used only in the artificially aged tempers (T6X, T8X),¹¹⁶ unless of course protective measures have proven to be adequate in protecting against exfoliation and stress corrosion in parts fabricated from thicker sections.

For marine applications, alloys such as 5052, 5454, 5086, 5083, and 5456 are used. Low-magnesium-content alloys such as 5454 (2.75% Mg) can be used where service temperatures may be expected to exceed 150°F.²⁴⁶ Since extended heating of wrought Al–Mg alloys with magnesium content

in excess of about 3% results in susceptibility to SCC (Figs. 77–80), special sheet tempers designated H343 and H323 were developed to provide good resistance to SCC at ambient temperatures of about 150°F or below for alloys such as 5456 (5.25% Mg) and 5083 (4.45% Mg).²⁴⁶ The even newer H116 and H117 tempers for 5086 and 5456 alloys should be considered if service conditions indicate that the H321 temper may not provide adequate resistance to exfoliation.

Alloys for High-Strength Extrusion Applications

The same general comments made for sheet and plate apply to extrusions. Exfoliation-resistant T76 tempers are also available for 7075 and 7178 extrusions, and these alloy–temper combinations have the additional benefit of improved SCC resistance (Figs. 114–116). Probably the most common problem results when thick extrusions are heavily machined, thus exposing essentially transverse grain structure. This problem can be particularly acute if interference-fit fasteners or stresses from assembly mismatch or joggling are present in the region of transverse-grain structure.

One potential method of minimizing the amount of machining for certain applications is the use of stepped extrusions. Use of these products can provide for thick sections only in the areas where they are needed.

This resume on some of the recommended uses of aluminum alloys, especially some of the newer ones, has purposely been brief and anyone involved in aluminum-alloy selection should consult the various alloy producers.

Proper Design, Fabrication, Assembly, and Finishing Practice

Extensive coverage of the many facets of design, fabrication, and assembly practices that must be closely controlled to avoid SCC problems in high-strength aluminum alloys is beyond the scope of this chapter. If stress-corrosion-resistant tempers cannot be used, certain precautions should be taken to avoid service failures due to SCC. Some of the more common rules are discussed below.⁵⁵

1. Avoid, where possible, the machining of thin sections from thick sections, since the grain structure in the machined part may be adversely oriented with respect to locked-in assembly or quenching stresses (see Fig. 8).
2. When deep hole or pocket machining in thick, non-stress-relieved material is required, rough machine as extensively and as close to finish

dimensions as practicable prior to heat treatment. Even if final machining removes the residual surface compressive layer, the removal of less material after heat treatment exposes lower internal tensile stresses.

3. Avoid deep, blind bores, since an inadequate quench in such areas can lead to high inside-diameter surface tensile stresses.

4. In hand forgings, rings, and many die forgings, minimize residual quenching stresses by using stress-relieved (T652) material, especially when a part is to be machined all over. In die forgings that are not machined all over, caution is required because the T652 compressive treatment tends to produce residual tension stresses of a few thousand psi on the surface of the part.

5. Bending, joggling, roll forming, and twisting can result in residual surface tension stresses that, if combined with adverse grain structure, can lead to stress-corrosion problems. Perform these operations on susceptible material when it is in the freshly quenched ($-W$) temper or possibly hot. Hot-forming of certain 5000-series alloys in the annealed condition is recommended to minimize the effect of cold work as well as lower the residual stresses.

6. Swaging and shape-drawing at room temperature are capable of inducing residual surface tensile stresses in the transverse direction on the formed parts. If feasible with susceptible heat-treatable alloys, form the parts in the O-temper and then heat treat. Alloys 2020, 2024, and 2219 may be swaged in the solution-heat-treated condition and then aged to minimize SCC; however, this procedure is not recommended for 2014 and the 7000-series alloys aged to the T6 temper.

7. Interference-fit bushings and pins can cause stress corrosion. This problem is particularly severe where holes to be bushed are located on the parting plane of die forgings, and this practice should be avoided. Minimize stresses by controlling the interference fit that is permitted. When tolerances required are too tight, make the bushing very thin in comparison to the wall around it so that a larger part of the necessary deformation takes place in the bushing.

8. Eliminate moisture traps. This also applies to faying surfaces, particularly if one of the materials is an absorbent. If one of the materials is a dissimilar metal, galvanic corrosion may occur and accelerate any possible SCC hazard that already exists.

9. Use shims to compensate for assembly mismatch.

10. In complex parts of new design where residual stresses could cause SCC, subject the finish machined part to a stress-corrosion test.

Surface Treatments

The safest way to prevent SCC service failures with high-strength aluminum alloys is to use SCC-resistant alloys and tempers. Where this approach is not possible because of other requirements of the material, adequate protective measures must be taken if alloys and tempers that are susceptible to SCC are used. Such protective measures include treatments of the metal surface, notably shot peening and coating. Obviously, evaluation of the effectiveness of surface treatments as SCC preventatives can be made with smooth specimens only; this is one situation where precracked specimens are of no use. However, this situation will be reversed if and when self-healing coatings and inhibitors are studied.

Shot Peening

One of the most effective SCC preventatives for high-strength aluminum alloys is surface working by shot peening, particularly when used in combination with protective coatings. This procedure can be used as a “fix” in troubleshooting or can be incorporated into the original design of a vehicle.²⁴⁷

Shot peening differs from most protective measures because it changes the surface of the metal instead of merely coating it. Hammering of the shot plastically deforms the surface metal and obliterates the grain structure, resulting in a thin surface layer of metal being placed in compression. Shot peening is effective, therefore, only if: (1) all exposed surfaces are thoroughly worked (saturated) to an adequate intensity, and (2) the resultant compressively stressed layer is not penetrated by either mechanical damage or corrosion.

Usually the cold-worked layer is thick enough to tolerate minor surface scratches. The layer can be penetrated readily, however, by the pitting attack that occurs on high-copper-content aluminum alloys in corrosive environments. Thus, it could be expected that the effectiveness of peening would be related not only to the adequacy of peening, but also to the environment and the resistance to corrosion of the given alloy in that environment. Therefore, shot peening is of no appreciable benefit to stressed specimens of 2014-T651 (low resistance to corrosion) in the 3.5% NaCl alternate-immersion test, where pitting rapidly penetrates the cold-worked layer. However, peening considerably extends the time to failure of stressed specimens of 7079-T651 (comparatively high resistance to pitting). A four-year exposure to a seacoast environment, which is considerably less corrosive than the alternate-immersion environment, showed that peening does improve the performance of 2014-T651 and can prevent failure of 7079-T651.

In the even less corrosive inland industrial environment, stressed specimens of both alloys can survive for several years without failure. These effects are illustrated in Fig. 136. Short transverse 7075-T6 tensile specimens stressed to 75% of their yield strength and exposed to the mildly corrosive industrial environment at New Kensington fail in less than six months, whereas shot-peened specimens last longer than 17 years.²⁴⁹

The reason why shot peening can delay or prevent SCC is twofold. First, cold working of the surface develops high compressive surface stresses in a layer several hundredths of an inch deep. Second, the plastic deformation of the surface layer distorts and bends the grain boundaries, thereby impeding the initiation of intergranular corrosion and intergranular stress-corrosion cracks.^{249,251} If pitting corrosion penetrates the cold-worked surface layer, the beneficial effect of shot peening is lost.

The necessity of achieving thorough saturation of the cold-worked surface cannot be emphasized too strongly. Instances where peening was not effective in service applications have often been attributed to critical areas not being worked or worked only superficially.

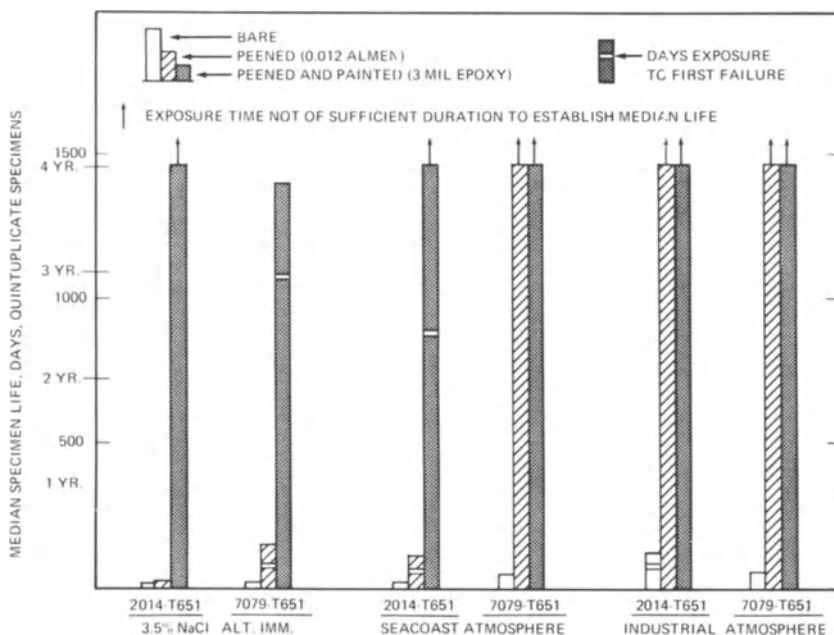


Fig. 136. Comparison of the effect of alloy and environment on the protection against SCC afforded by peening and peening plus painting on specimens stressed in the short transverse direction to 75% of their yield strength (after Lifka and Sprowls²⁴⁸).

Painting and Coating

Paint systems, in general, are effective measures against surface corrosion. However, a significant disadvantage of paint systems in protecting against SCC is that they provide only a barrier layer to exclude the environment. Paint coatings lose much of their effectiveness if mechanical damage occurs (Fig. 137). In this regard, an inadvertent holiday in the coating or a slight scratch may be all that is required to destroy the protective ability of the coating. In service applications, the stress contributing to SCC may be introduced after protective coatings have been applied. Although organic films have excellent flexibility, microcrazing can occur if the metal is deformed appreciably. It is prudent, whenever practicable, and particularly when severe attack is expected, to provide paint protection to shot-peened parts to prevent rapid penetration of the cold-worked surface layer. The excellent protection afforded by the combination of peening and painting is illustrated in Fig. 137.

Water-Displacing Corrosion Preventatives

In many cases, stress corrosion cracks initiate at bushing, bearing, or fastener holes where no real primer or paint protection is available because of the close tolerance or interference fit of the bushing, bearing, or fastener (see Figs. 2 and 138). Such areas are doubly prone to SCC since the machining of a bushing hole, for example, often exposes the locked-in residual tensile stresses from the quenching operation; and if end-grain material is exposed at the hole circumference, SCC problems are very likely. The problem is even more likely if interference fit bushings are installed, since they increase the sustained tensile stress.

Since paints are so easily damaged and because they often cannot be applied where they are needed most, development of improved paints may not be the best approach for developing improved stress-corrosion-inhibitive coatings for alloys like 7079-T6 and 7075-T6. What is needed for these alloys is a coating which can penetrate to the potential initiation site and either displace or prevent entry of water or inhibit the aluminum–water reaction.

Some commercial water-displacing corrosion-preventative oils which are able to penetrate tight joints have recently been tested to measure their ability to decrease the velocity of growing stress-corrosion cracks (Fig. 139). This is in contrast to other inhibitor studies, where the ability to prevent general corrosion has been emphasized.^{250,250a,250b} In saturated NaCl solution, the corrosion preventative decreases the plateau velocity by

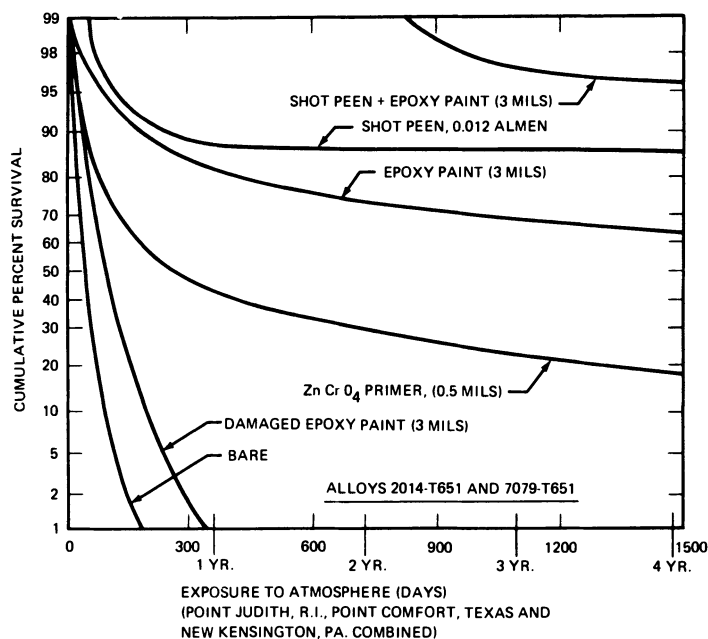


Fig. 137. Relative protection against SCC of various protective systems on 2014-T651 and 7079-T651 short transverse specimens stressed to 75% of their yield strength (after Lifka and Sprowls^{248,249}).

a factor of 1000 as long as it keeps the NaCl solution off the crack tip. In laboratory air ($\sim 40\%$ R.H., 70°F), the plateau velocity is decreased by a factor of two or three. Stress-corrosion crack velocities in specimens coated with these corrosion preventatives and exposed to laboratory air are about the same as in similar specimens immersed in flight fuels, oils, and hydraulic fluids (compare Figs. 139 and 72).

Until the stress-corrosion-resistant tempers of the high-strength aluminum alloys are used exclusively in new designs, these corrosion-preventative oils may find increasing use in protecting critical, stress-corrosion-prone components of aircraft and missile systems already in service.

Galvanic Protection

Since it is impossible to maintain the integrity of coatings in service, sacrificial aluminum anodes or protective claddings are sometimes used to supplement the primary protection provided by the coating. For example, the deep-diving submersible *Aluminaut* uses aluminum anodes to supple-

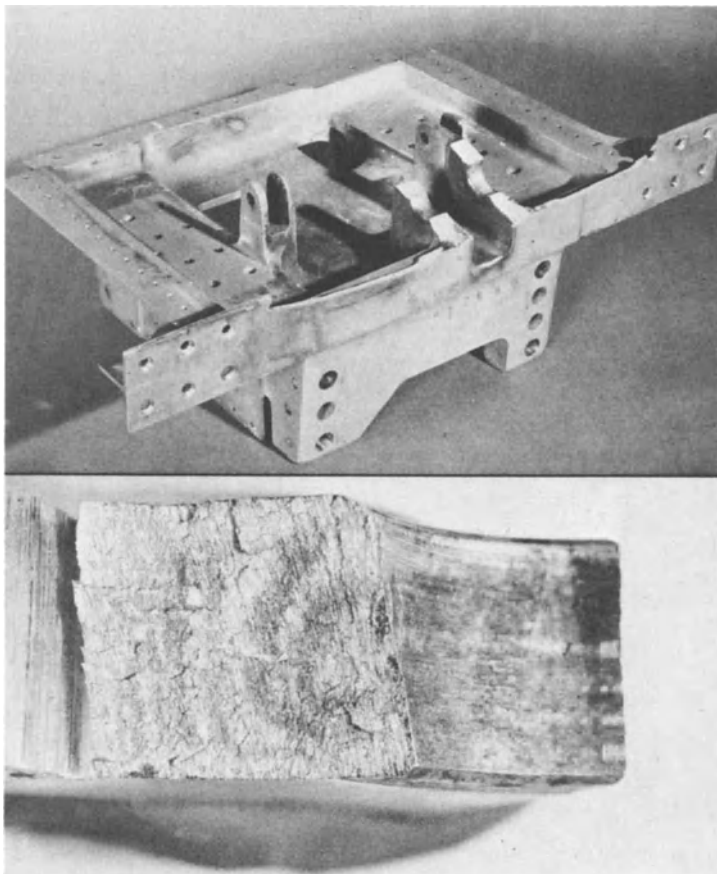


Fig. 138. Stress-corrosion crack emanating from the center of a bushed hole in a 7079-T6 die forging.

ment the protection of the pressure hull offered by several layers of polyurethane coating.⁸⁵

To be highly effective, galvanic coatings must be sufficiently anodic to provide adequate electrochemical protection. The effect of this increasing anodic relationship on the degree of protection for a zinc electroplate and zinc-rich paint on four aluminum alloys is shown in Fig. 140. However, standard solution potential measurements provide only a limited basis for predicting the feasibility of electrochemically protecting any given alloy by a galvanic coating. The actual degree of electrochemical protection depends on both the electrolyte to which the system is exposed and the cathodic area exposed.

The effectiveness of the various galvanic coatings on 2014-T651 and 7079-T651 is compared with some other protective treatments in Fig. 141 and 142. Specimens metallized with the 7072 alloy performed quite well, although some failures did occur in some metallized 7079-T651 specimens. The poorer performance of the metallized 7079-T651 specimens has been rationalized on the basis of the smaller difference in solution potential between the 7079-T651 and the 7072 alloys (Table 15).

While galvanic coatings have the important advantage over other protective measures in that the degree of protection is less affected by mechanical damage or holidays in the coating, there is a limit to the size of the void that can be electrochemically protected. It has been shown that

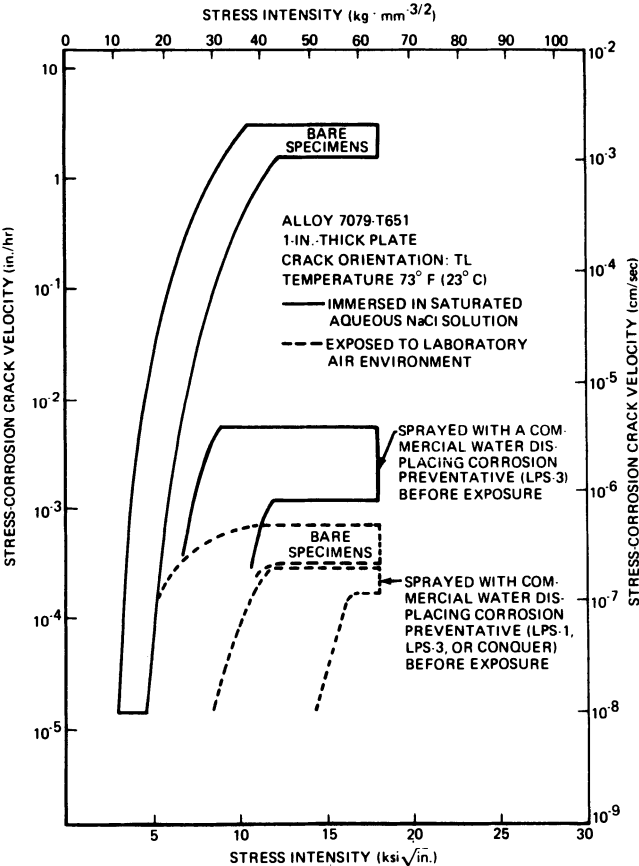


Fig. 139. Effect of some commercial water-displacing corrosion preventatives on the velocity of stress-corrosion cracks in 7079-T651 double cantilever beam specimens.

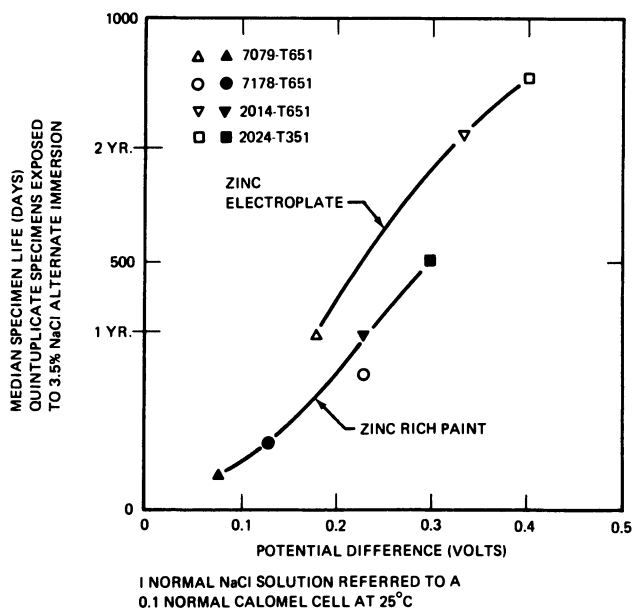


Fig. 140. Effect of increasing potential difference between the substrate metal and the galvanic coating on the degree of protection against SCC of short transverse specimens stressed to 75% of their yield strength (after Lifka and Sprowls²⁴⁸).

a void as narrow as 0.0625 in. can seriously impair the effectiveness of a 7072 metallized coating.²⁵² Some of the drawbacks of 7072 metallized coatings are that they have a rough finish; they are difficult to apply to close tolerances; they sometimes spall when formed, drilled, or counter-sunk; and they can bridge base metal cracks and thus interfere with crack or defect inspection. Also, their porous nature precludes die-penetrant inspection.

Zinc-plated specimens do not perform as well as metallized specimens in the alternate-immersion environment, due to the relatively rapid consumption of the zinc (Figs. 141 and 142). In atmospheric tests, overall performance of the zinc-plated specimens is more favorable, with failures confined to 7079-T651. The effectiveness of zinc electroplate can be improved through use of paint top coats to reduce rapid consumption of the zinc.²⁵² While zinc-electroplate coatings are smooth and relatively non-porous, zinc imparts a greater weight penalty than aluminum metallized coatings.

Zinc-rich epoxy paint systems can be applied with normal paint procedures. Because the zinc must be in intimate contact with the substrate

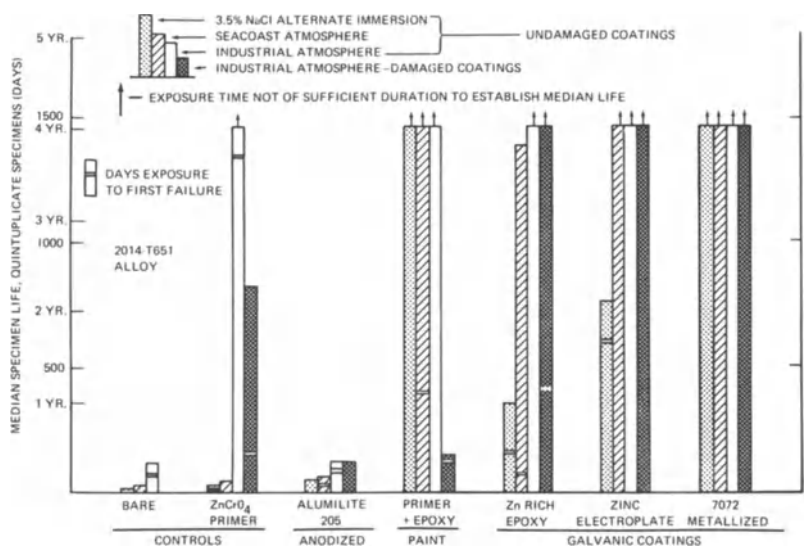


Fig. 141. Comparison of the degree of protection of various systems against SCC of short transverse 2014-T651 specimens stressed to 75% of their yield strength (after Lifka and Sprowls²⁴⁸).

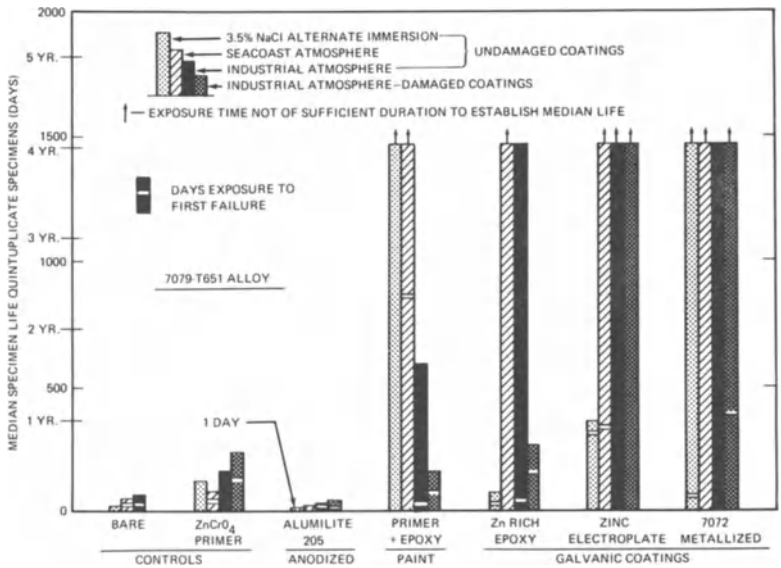


Fig. 142. Comparison of the degree of protection of various systems against SCC of short transverse 7079-T651 specimens stressed to 75% of their yield strength (after Lifka and Sprowls²⁴⁸).

Table 15. Solution Potentials of Some Commercial Aluminum Alloys

Alloy-temper	Solution potential (mV)
2024-T351	-700
2014-T651	-790
7178-T651	-830
7079-T651	-865
7072	-940

Data from reference 248

Average steady value in NaCl-H₂O₂ solution, referred to 0.1N calomel cell at 25°C

metal to provide electrochemical protection, the chromate conversion coating and primer pretreatments cannot be used; thus, adhesion is less for the zinc paint systems than for the other epoxy systems. Zinc-rich paint systems provide appreciable protection, however, except in the severe alternate-immersion environment and when intentionally damaged. (Figs. 141 and 142).

Pure aluminum coatings deposited by such methods as ion vapor deposition or vacuum deposition also provide good protection to 7075-T6 aluminum if the coating is around 1 mil thick and if the coating is protected against pitting attack by a supplementary chromate treatment.

Magnesium pigment added to a proprietary, air-curing, inorganic binder has also proved to be effective in minimizing SCC of 7075-T6.^{251a} Magnesium pigment added to an epoxy primer has also given good results.^{251b}

While some of these shot-peening and coating treatments can do an effective job of delaying SCC, none is a substitute for the selection of a stress-corrosion-resistant alloy. A possible sequence of events leading to failure of a fully protected part is illustrated in Fig. 143. Mechanical damage can cause the loss of the protection afforded by the anodized layer, the primer, and the top coat, thus allowing the environment to reach the shot-peened layer. Under suitable conditions, pitting corrosion can then penetrate the shot-peened layer, leading to SCC if the material is susceptible and if tensile stresses are present. It should be noted that current Air Force specifications require that primary structural aluminum forgings and extrusions used in corrosive environments be subjected to a 2000-hr alternate-immersion test in their bare, final-machined condition to ensure the absence of high residual surface tensile stresses.^{252a} The best way to avoid the problems associated with passing this test is to use SCC-resistant materials.

Protective Treatments for Preventing Exfoliation Corrosion and Faying-Surface Corrosion

Exfoliation corrosion usually starts at fastener holes because the holes are drilled after the protective anodizing and conversion coatings are applied. Under service conditions, electrolytes are present in the form of rain condensation, paint strippers, brighteners, seawater, etc. Corrosion usually originates in the countersink areas because that is where initial penetration by the electrolyte occurs. Exfoliation and general corrosion also often start at faying surfaces where electrolytes penetrate the space between riveted, bonded, or bolted overlapping panels. This type of corrosion can be particularly severe if absorbent materials are located between the faying surfaces. Severe corrosion of this type can cause a loss of structural strength.

Typical methods of combating exfoliation corrosion involve wet installation of rivets treated with polysulfide sealing compound or zinc chromate primer. However, recent tests²⁵³ on 7075-T6 and 7178-T6 have indicated that neither of these materials provides complete protection against exfoliation corrosion, because moisture from sustained high-humidity test conditions eventually penetrated to the inside surface of fastener holes, where corrosion occurred. The moisture was not merely seeping between the sealants and the sides of the fastener holes, but was permeating the sealants.

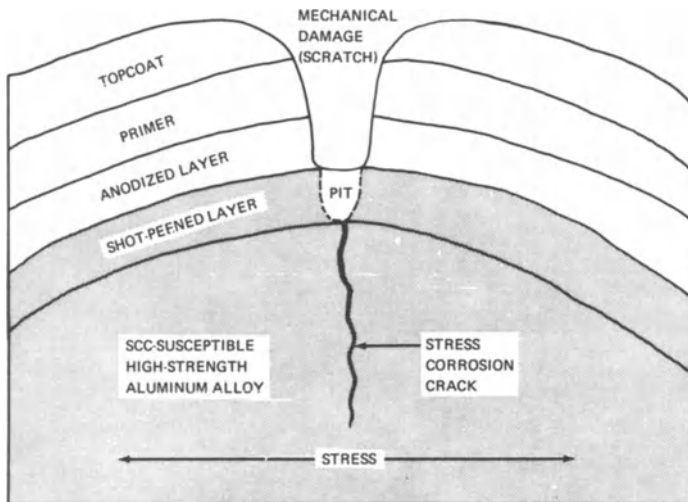


Fig. 143. Schematic representation of a stress-corrosion failure resulting from the local breakdown of several protective systems.

This weakness of the elastomers can be eliminated by incorporating a water-soluble chromate inhibitor into the elastomer.²⁵³ This inhibitor dissolves in any moisture penetrating the sealant/metal interface and converts it into a protective solution. The validity of this concept has been proven by simulated service tests and field tests, and inhibitive sealants are now being used on a number of commercial and military aircraft.²⁵³ Inhibitive compounds are now being produced for brush application, for spraying, for fillet work, and for faying surfaces. A special formulation with aluminum pigment is available for use as a top coating. It should be kept in mind that presently used inhibitors inhibit only general corrosion, but do not inhibit the growth of stress-corrosion cracks.

By reducing the viscosity of the inhibitive sealants, a successful coating system has also developed from these materials; it is now being used on aircraft surfaces, in the rework and refinishing of dry bays, and in the internal spaces of aircraft wings that are not filled with fuel.²⁵³ Depletion of the soluble chromate ions from the elastomer coating is prevented by overcoating with an aluminized elastomeric antileaching top coat.

Proper Storage

Stress-corrosion cracks in susceptible high-strength aluminum alloys such as 7079-T6 and 7075-T6 are often found in parts that have been sitting on the shelf awaiting installation. Residual surface tensile stresses exposed by machining or resulting from straightening or forming operations, combined with a transverse grain structure and the water vapor normally present in the air, are all that are required.

Besides in-service cracking, many parts fail in structures even before the structure has performed its intended mission. For example, some swaged 7075-T6 support struts for the lunar module were found to contain stress-corrosion cracks. Such problems are of great importance, especially since storage times may greatly exceed original plans due to funding cutbacks, etc. In this regard, the data presented in Figs. 40–42 may be very useful. These data suggest that if relative humidities in storage areas are maintained below about 2%, stress-corrosion cracks could not grow faster than about 10^{-8} cm/sec, even if cracklike flaws were already present and loaded to high K_I levels. If relative humidity cannot be maintained at such low levels, then application of some of the water-displacing corrosion preventatives discussed earlier may be helpful in preventing stress-corrosion cracking.

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