

# Intergranular Corrosion of an Aluminum-Magnesium-Silicon-Copper Alloy

T.D. Burleigh,\* E. Ludwiczak, and R.A. Petri\*\*

## ABSTRACT

The intergranular (intercrystalline) corrosion (IGC) of a heat-treated aluminum (Al)-magnesium (Mg)-silicon (Si)-copper (Cu) alloy was investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM revealed that tall chimneys of corrosion product formed on the surface above the pits during oxygenated salt water immersion. It was postulated that pitting corrosion occurred first and that the corrosion chimneys maintained the acidic, chloride pit environment that subsequently caused IGC (preferential dissolution of the region adjacent to the grain boundaries). TEM foils of the same alloy were immersed in a model pit solution (dilute hydrochloric acid [HCl]) and showed IGC identical to the corrosion attack seen in the bulk samples. Potentiodynamic polarization in the dilute HCl solution verified that pure Al corroded many times faster than the bulk alloy. These results indicated IGC of this alloy occurred because the depleted region adjacent to the grain boundaries corroded rapidly in acidic solutions. The presence of pits with corrosion chimneys, or some type of occluded cells, must have maintained the acidic environment, which caused IGC.

**KEY WORDS:** aluminum alloys, intercrystalline corrosion, intergranular corrosion, pitting corrosion

Submitted for publication March 1994; in revised form, July 1994.

\* Materials Science and Engineering Department, University of Pittsburgh, Pittsburgh, PA, 15261.

\*\* Alcoa Technical Center, 100 Technology Drive, Alcoa Center, PA, 15069 (retired).

(<sup>1</sup>) UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE) and cosponsored by ASTM.

## INTRODUCTION

Salt water exposure can cause intergranular corrosion (IGC) in some aluminum (Al) alloys. Dix explained IGC of Al-copper (Cu) alloys in 1940.<sup>1</sup> During aging at elevated temperatures (200°C), precipitation of discrete particles occurs, with more advanced precipitation at the grain boundaries than in the grain matrix. The grain boundaries are surrounded by narrow zones of Al that etch smoothly. These zones become depleted of alloying elements, and thus become more pure, with a more active corrosion potential (solution potential) in aerated salt water. The dissolution of these purer films occurs rapidly. Thus, corrosion follows these depleted zones along the grain boundaries. This model proposed by Dix<sup>1</sup> has been verified by Kaesche<sup>2</sup> and others.<sup>3</sup>

In some alloy systems, IGC is a result of galvanic corrosion between anodic grain-boundary precipitates and the depleted zones, rather than between the matrix and the depleted zone.<sup>4</sup>

Although results of much research on the different Al alloy systems have been reported, very little research is available on the Al-magnesium (Mg)-silicon (Si)-Cu-manganese (Mn) alloys (6XXX series).

The objective of the present work was to explain IGC of AA 6013-T6 (UNS A96013).<sup>(1)</sup> Partial results of this work have been published previously.<sup>5</sup>

IGC such as occurs in coastal exposures can be duplicated in the laboratory. The ASTM G 110 Standard Practice is an oxygenated salt water

immersion test.<sup>6</sup> After a sample is corroded during the ASTM G 110 test, it is cleaned, metallographically cross-sectioned, and polished to reveal the type of corrosion attack (Figure 1).

## EXPERIMENTAL

The alloy in this study was a heat-treated commercial AA 6013-T6 of composition (wt%): 1.0% Mg-0.7% Si-0.9% Cu-0.3% Mn-0.3% iron (Fe)-balance Al.

Using the ASTM G 110 practice<sup>6</sup> (military specification MIL-H6088D), the samples first were etched for 60 s in a 95°C solution of 5 mL hydrofluoric acid (HF, 48%) and 50 mL nitric acid (HNO<sub>3</sub>, 70%) per liter of deionized water. After etching, the samples were rinsed, cleaned in HNO<sub>3</sub>, rinsed again, and dried. The samples then were immersed for 6 h in a solution of 57 g sodium chloride (NaCl) and 10 mL (30%) hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) per liter of deionized water. Samples for study by scanning electron microscopy (SEM) were not rinsed or cleaned after corroding but were placed immediately in a vacuum desiccator to dry (after the work of Morris, et al.<sup>7</sup>). The dried samples were examined in a JEOL JSM-840A<sup>†</sup> scanning electron microscope (accelerating voltage 10 kV), which was capable of imaging the corrosion product and salt crystals without charging effects.

Foils for transmission electron microscopy (TEM) were thinned mechanically to a thickness of 0.25 mm and then electropolished to perforation using a solution of 25% HNO<sub>3</sub> in methanol maintained at -30°C. The model pit solution was made by adding two drops of concentrated HCl (37%) per liter of deionized water (final pH = 3). The TEM foils were immersed in this HCl solution for a total of 45 s, rinsed with methanol, and dried in air.

Potentiodynamic polarizations were conducted in the same HCl solution (deaerated) at a scan rate of 0.5 mV/s. The surfaces were wet-polished using a 600-grit silicon carbide (SiC) paper prior to the polarizations. The control sample was 99.999% pure Al.

## RESULTS

### *IGC in the ASTM G 110 NaCl-H<sub>2</sub>O<sub>2</sub> Test*

Figure 1 is a metallographic section (photographed with a scanning Auger spectrometer) showing the typical cross-sectional view of IGC seen after the ASTM G 110 test. At the top surface, remnants of pitting corrosion were evident. The

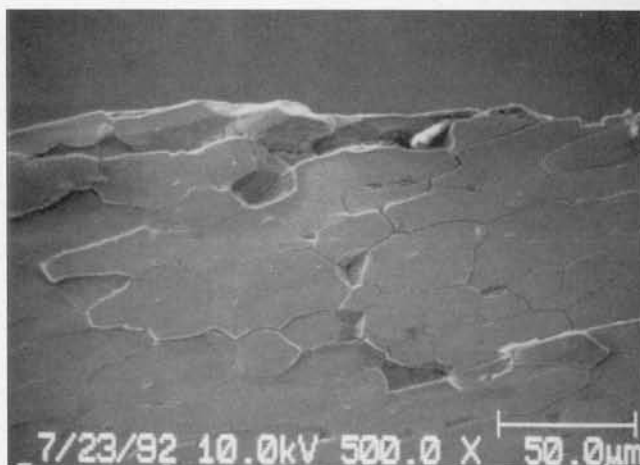


FIGURE 1. Cross-sectional view showing typical IGC (micrograph by scanning Auger spectrometer).

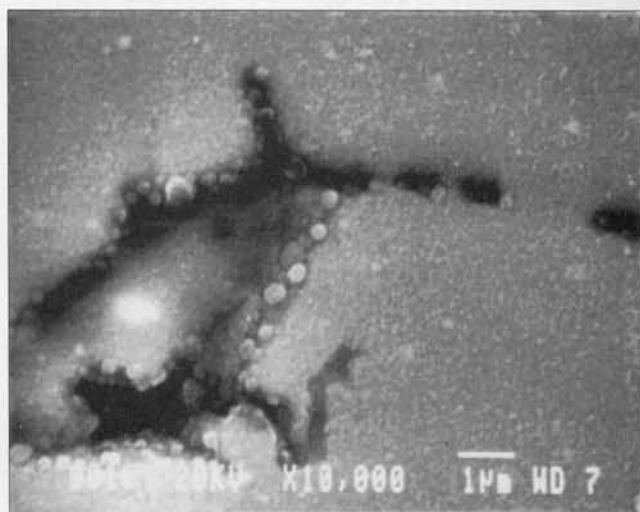
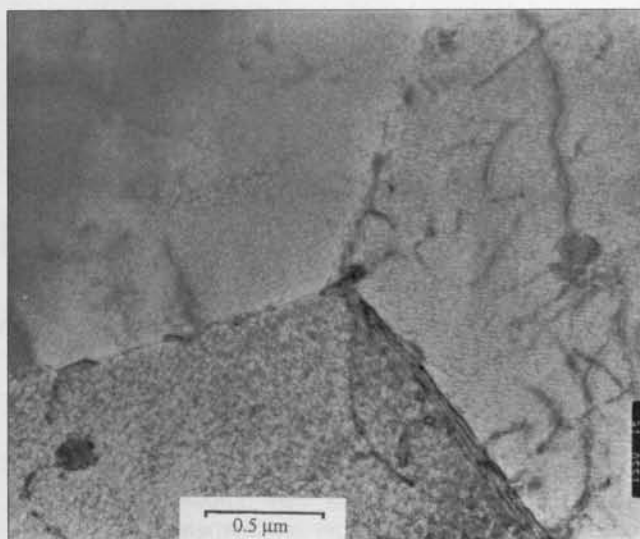


FIGURE 2. Cross-sectional view of IGC made by carbon-coating the polished sample and photographing by SEM. The spheres were identified previously as Al-Mn dispersoids.

center of the micrograph shows grains that were encircled by IGC and which fell out during the cross-sectioning and polishing. Figure 2 shows a SEM closeup of carbon-coated IGC. The width of the IGC was 0.5  $\mu$ m to 1.0  $\mu$ m. The round spheres, remaining within the etched grain boundaries, were identified in previous analyses as Al-Mn dispersoids.

When the TEM foils were immersed directly in the ASTM G 110 solution of NaCl-H<sub>2</sub>O<sub>2</sub>, they showed only general attack across the entire foil (Figure 3) and no preferential attack at the grain boundaries. Therefore, the neutral NaCl-H<sub>2</sub>O<sub>2</sub> solution alone did not seem to preferentially attack these grain boundaries. (Hunter, et al., had reported preferential

<sup>†</sup> Trade name.



**FIGURE 3.** TEM foils corroded in the NaCl-H<sub>2</sub>O<sub>2</sub> solution, exhibiting only general attack.

attack of the grain boundaries of Al 2024 [UNS A92024] in a similar solution.<sup>8)</sup>

#### Corrosion Chimneys Viewed by SEM

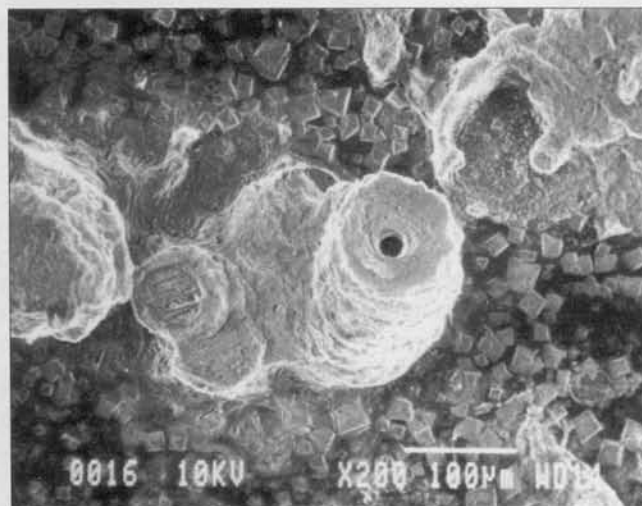
The wet-corroded Al samples were covered with a translucent gelatinous hydroxide film that turned white upon drying. The uncleaned corroded surface was difficult to photograph with an optical microscope because of the large depth of field of the corrosion product. Hübner and Wranglen described a "porous hydroxide diaphragm" over the pit that

prevented mixing of the pit electrolyte and the bulk electrolyte.<sup>9</sup> This current examination with the SEM showed no diaphragms but instead showed corrosion chimneys across the corroded surface (Figures 4[a] and [b]). The chimneys were shaped like volcanoes or pipes with a hole in their center and were very fragile and collapsed when disturbed. These chimneys most likely were formed as hydrogen (H<sub>2</sub>) evolved in the pit and bubbled upward. Beneath each chimney was a pit, as verified by circling several chimneys with a microscope scribe, then cleaning the sample with a chromic acid solution and rephotographing the surface. Chimneys (or tubes) also have been reported on Fe corroding under special conditions.<sup>10</sup>

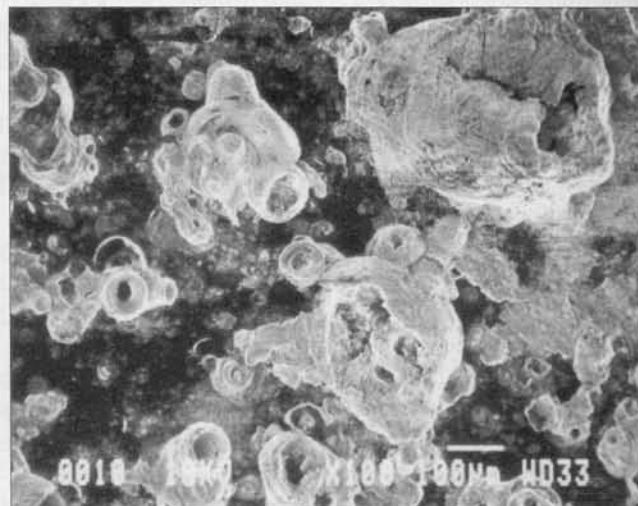
#### TEM Foils Etched in Dilute HCl

When the TEM foils were etched in the NaCl-H<sub>2</sub>O<sub>2</sub> solution and showed no preferential attack of the grain boundaries (Figure 3), it was apparent that oxygenated salt water alone did not cause IGC of AA 6013-T6. Therefore, a dilute HCl solution was used to imitate the pit electrolyte. It was understood that dilute HCl was not the actual pit electrolyte composition, but it appeared to have a similar corroding effect.

Thinned TEM foils were immersed in the dilute HCl solution (two drops HCl per liter of water) and examined. Preferential attack occurred along the grain boundaries (Figures 5 and 6). The grain-boundary precipitates (identified in previous analyses as Al-Cu or Al-Cu-Mg-Si) remained suspended in the corrosion product. A narrow band (0.5 μm total width)

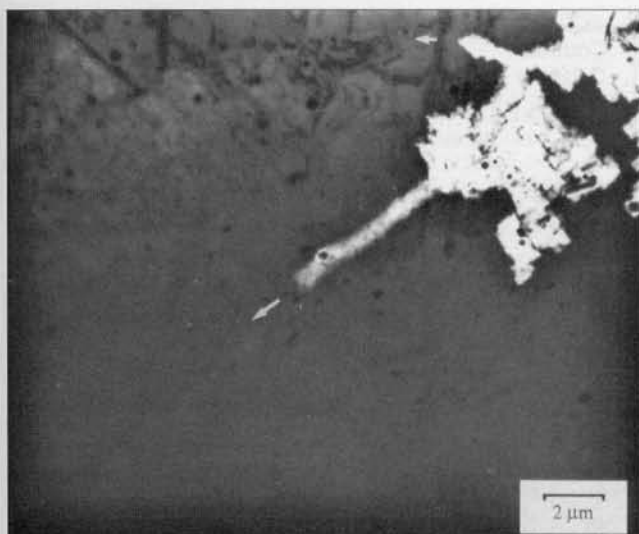


(a)

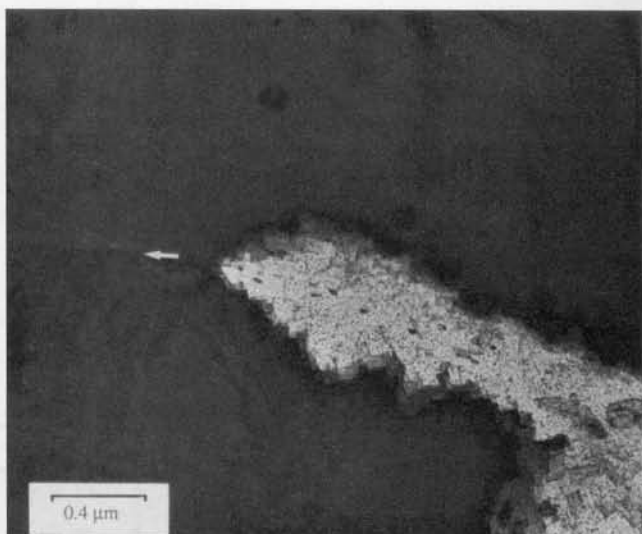


(b)

**FIGURE 4.** SEM micrographs showing the corrosion chimneys that formed over corroding pits during immersion in the NaCl-H<sub>2</sub>O<sub>2</sub> solution. Cubic salt crystals were evident on the surface.



**FIGURE 5.** TEM foil etched in the dilute HCl solution showing preferential dissolution along the grain boundaries (marked with white arrows).



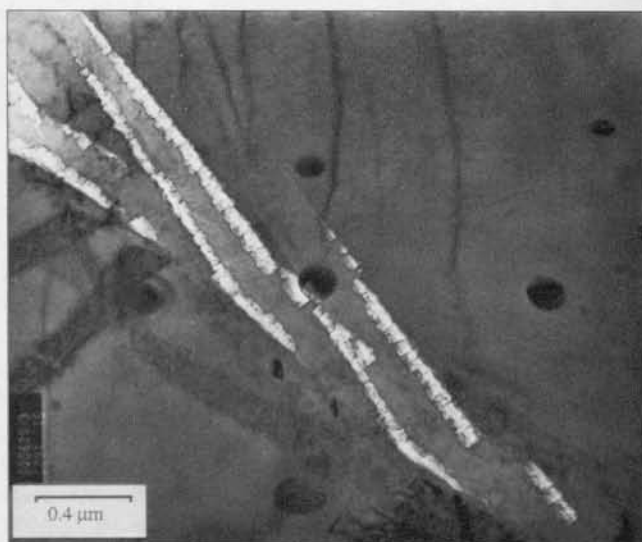
**FIGURE 6.** A higher magnification of the upper grain boundary in Figure 5 showing preferential attack of the area adjacent to the grain boundary. Grain-boundary precipitates were left suspended in the corrosion product.

dissolved preferentially on either side of the grain boundary. The HCl solution also dissolved preferential slip bands (Figure 7). The depleted matrix adjacent to Al-Mn dispersoids also was susceptible to preferential attack (Figure 8).

## DISCUSSION

IGC was not produced on the TEM foils in the neutral salt water solution, but it was produced in the dilute HCl solution. (The dilute HCl solution was not identical to the pit electrolyte since there were no metal cations, but the HCl appeared to be a good model solution.) Therefore, IG attack appeared to be dependent on the presence of the acidic pit solution. An idealized cross section of a corrosion chimney is shown in Figure 9. The occluded cell beneath the chimney allowed the formation of the acidic, chloride ( $\text{Cl}^-$ ) pit environment, which has been documented by previous researchers (e.g., Holroyd, et al.,<sup>11</sup> and Foley<sup>12</sup>).  $\text{H}_2$  evolution occurred readily in this acidic environment, and as  $\text{H}_2$  bubbles rose upward, they pumped solution from the pit. The corrosion product chimney naturally formed as the aluminum hydroxy chloride compounds ( $\text{AlCl}_x(\text{OH})_{3-x}$ ) were pumped up the chimney and into the bulk neutral solution.<sup>12-13</sup>

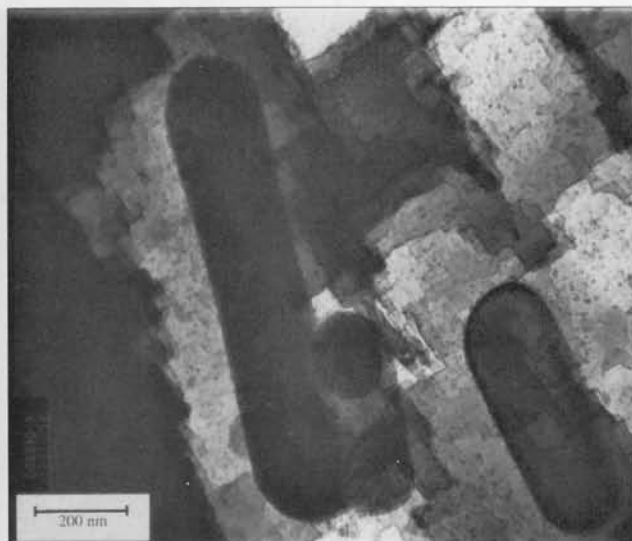
In the neutral solution, the  $\text{AlCl}_x(\text{OH})_{3-x}$  reacted with water to precipitate the  $\text{Al}(\text{OH})_3$  gelatinous hydroxide that formed the chimney. Some of the chlorides were trapped in the corrosion product, and some chlorides were freed to return to the pit to continue the reaction. The acidic,  $\text{Cl}^-$  environment in



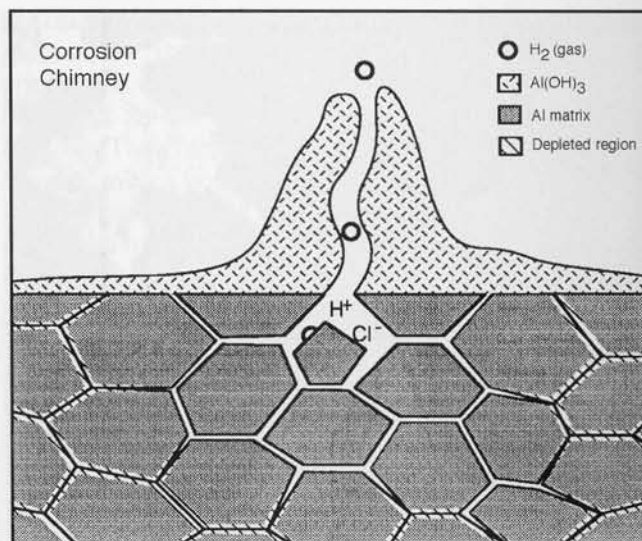
**FIGURE 7.** Preferential slip bands dissolved preferentially in this TEM foil etched in dilute HCl.

the pit preferentially attacked the grain-boundary regions.

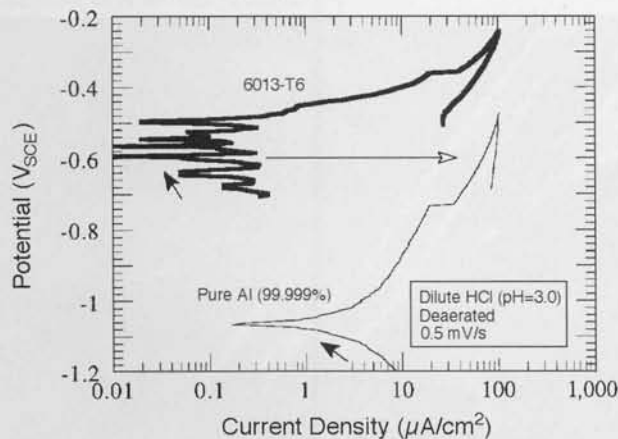
One reason why the grain-boundary regions appeared more susceptible was that they were of purer Al, having been depleted of alloying elements (the grain-boundary precipitates acted as sinks for the alloying additions). Potentiodynamic polarizations are shown in Figure 10 for the bulk alloy vs pure Al in the deaerated HCl test solution. At  $-0.6 V_{\text{SCE}}$  (the corrosion potential for AA 6013-T6), AA 6013-T6



**FIGURE 8.** TEM foil showing preferential attack adjacent to these Al-Mn dispersoids after immersion in the dilute HCl.



**FIGURE 9.** The corrosion chimney formed by  $H_2$  rising out of an active corroding pit. The precipitation of  $Al(OH)_3$  formed the rising chimney.



**FIGURE 10.** Potentiodynamic polarization of pure Al (representing the depleted region adjacent to the grain boundary) and bulk AA 6013-T6 in dilute HCl. At  $-0.6 V_{SCE}$ , the pure Al corroded 500 to 1,000 times faster than the bulk alloy.

corroded at  $0.1 \mu A/cm^2$ , while pure Al corroded at  $50 \mu A/cm^2$  to  $100 \mu A/cm^2$ . The pure Al (representing the depleted region adjacent to the grain boundary) corroded 500 to 1,000 times faster in the dilute HCl than the bulk alloy. Therefore, the depleted regions, which were purer than the bulk alloy, appeared to corrode much more rapidly than the bulk alloy in the acidic,  $Cl^-$  pit environment.

Two points could be concluded:

— Neutral oxygenated salt water alone did not attack the depleted regions along the grain boundaries of this heat-treated Al-Mg-Si-Cu alloy.

The preferential attack of the grain-boundary region occurred instead in the dilute HCl solution. Therefore, if the bulk solution is neutral, then IGC can occur only in occluded cells (corrosion pits), where the local pH can become quite low. It might be reasonable to postulate that if there are no occluded cells (such as crevices or pits), and if the bulk environment is neutral, then IGC should not occur even with the presence of depleted grain boundaries.

—To prevent pitting and subsequent IGC, the formation of occluded cells and corrosion chimneys should be prevented. Frequent cleaning, buffing, and waxing are common maintenance methods that remove the corrosion chimneys and prevent the occluded acidic cells from forming.

## SUMMARY

- ❖ TEM foils of the heat-treated Al-Mg-Si-Cu alloy (UNS A96013) did not exhibit IGC after immersion in neutral oxygenated salt water, but they did exhibit IGC after immersion in a dilute HCl solution.
- ❖ SEM micrographs demonstrated corrosion chimneys over the corrosion pits. The corrosion pits appeared linked to IGC since the pit electrolyte could preferentially corrode the grain boundaries.

## ACKNOWLEDGMENTS

The authors acknowledge the assistance of R. Kilmer, F.S. Bovard, J.I. Petit, and the Alcoa Technical Center.

## REFERENCES

1. E.H. Dix, *Trans. AIME* 137 (1940): p. 11-40.
2. H. Kaesche, "Pitting Corrosion of Aluminum and Intergranular Corrosion of Aluminum Alloys," in *Localized Corrosion*, eds. B.F. Brown, J. Kruger, R.W. Staehle (Houston, TX: NACE, 1974), p. 516.
3. E.H. Hollingsworth, H.Y. Hunsicker, "Corrosion of Aluminum and Aluminum Alloys," in *Metals Handbook*, 9th ed., Vol. 13 (Metals Park, OH: ASM, 1987), p. 583-609.
4. J.E. Hatch, ed., *Aluminum - Properties and Physical Metallurgy* (Metals Park, OH: ASM, 1984), p. 242-319.
5. T.D. Burleigh, "Microscopic Investigation of the Intergranular Corrosion of Alloy 6013-T6," *Proc. 3rd Int. Conf. Aluminum Alloys*, Vol. 2 (Trondheim, Norway: NTH & SINTEL, 1992), p. 435-440.
6. ASTM G 110, "Standard Practice for Evaluating Intergranular Corrosion Resistance of Heat-Treatable Aluminum Alloys by Immersion in Sodium Chloride + Hydrogen Peroxide Solution," 1993 Annual Book of ASTM Standards, Vol. 3.02, *Wear and Erosion; Metal Corrosion* (Philadelphia, PA: ASTM, 1993), p. 471-472.
7. J.W. Morris, T.M. Devine, C.S. Kumai, *CAM Research Notes* 3, 3 (Oct. 1990).
8. M.S. Hunter, G.R. Frank, D.L. Robinson, "Mechanism of Corrosion of 2024 Alloy as Revealed by Electron Microscopy," *Proc. 2nd Int. Cong. Metallic Corrosion* (Houston, TX: NACE, 1963), p. 102.
9. W. Hubner, G. Wranglen, "Studies on the Mechanism of the Pitting Corrosion of Aluminum," in *Current Corrosion Research in Scandinavia*, ed. J. Larin-kari (Helsinki, Finland: Sanoma Osakeyhtio, 1964), p. 6,069.
10. O.L. Riggs, J.D. Sudbury, M. Hutchinson, *Corrosion* 16, 6 (1960): p. 94-98.
11. N.J.H. Holroyd, G.M. Scamans, R. Hermann, *Corrosion Chemistry within Pits, Crevices, and Cracks* (London, England: HMSO, 1987), p. 495.
12. R.T. Foley, *Corrosion* 42, 5 (1986): p. 277-288.
13. K.P. Wong, R.C. Alkire, *J. Electrochem. Soc.* 137, 10 (1990): p. 3,010.

## NACE CAMPBELL AND WHITNEY AWARD RECIPIENTS TO BE FETED AT CORROSION/95

NACE International presents awards at its annual CORROSION conference to honor members for service and commitment to the Association. Among the honorees at CORROSION/95, March 26 to 31 in Orlando, Florida, will be the recipients of the W.R. Whitney Award and A.B. Campbell Award.

### Whitney Award

The W.R. Whitney Award recognizes individuals who have made national or international contributions leading to a better understanding of corrosion science through education or work.



F. Peter Ford (General Electric, Schenectady, New York) is being recognized this year for his

quantified development of the slip dissolution mechanism of environment-sensitive cracking in a form that allows the predictive solving of

engineering problems. Ford's elucidation of metal cracking has been applied to the solution of such problems in the electric power and other industries. Ford's interests include other material-environment relations, among them cladding for nuclear fuel, resolution of corrosion problems in chemical plants, and development of specialty coatings for nuclear reactors and gas or steam turbines subject to environmental or thermal degradation.

Ford earned his Ph.D. in corrosion science from Cambridge University (United Kingdom). He has had more than 65 papers published and holds two patents. Ford is chairman of the NACE Research Committee and is active in Association technical committees.

### Campbell Award

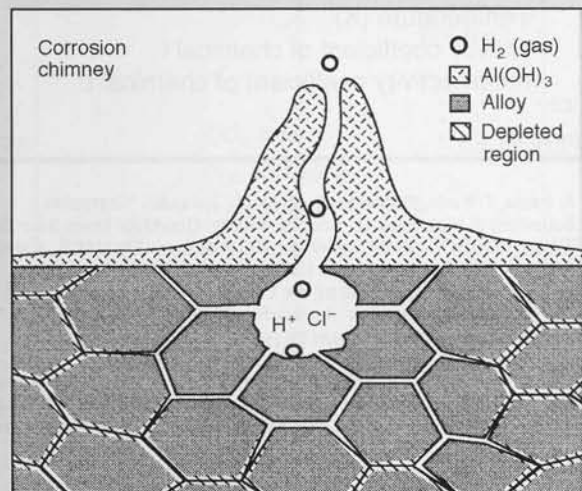
The A.B. Campbell Award recognizes the author of the most outstanding manuscript published in *CORROSION* or *Materials Performance* magazine by an author 35 years old or younger during the previous year.



Bob Prescott (Pulp and Paper Research Institute of Canada, Vancouver, British Columbia)

is being presented the award this year for his paper "A Study of the Growth of  $\alpha$ - $\text{Al}_2\text{O}_3$  Scales Using High-Resolution Imaging Secondary Ion Mass Spectroscopy," which appeared in the January 1994 issue of *CORROSION*, page 62. Prescott earned his Ph.D. in high-temperature corrosion from the University of Manchester Institute of Science and Technology (United Kingdom).

Prescott's specialties include erosion corrosion in coal gasification systems, oxidation of alumina-forming systems, vapor deposition of protective coatings, and corrosion in power boilers and black liquor recovery boilers. Prescott has more than 20 publications to his credit, predominantly on corrosion in chlorine-containing atmospheres and the growth of oxide scales.



In the January 1995 issue of *CORROSION* (Vol. 51, No. 1, pp. 50-55), the paper "Intergranular Corrosion of an Aluminum-Magnesium-Silicon-Copper Alloy," by T.D. Burleigh, E. Ludwiczak, and R.A. Petri, contained an incomplete figure. A revised version of Figure 9, depicting the corrosion pit as postulated to initiate intergranular corrosion, is shown above.

# MP

MATERIALS  
PERFORMANCE

## In the March issue:

A New Chemical Test Method for Plastics and Elastomers

— John E. Niesse

An Ultrasensitive Fouling Monitoring System for Cooling Towers

— Y. Nohata and H. Taguchi

Water- and Soil-Side Corrosion of Copper Water Service Lines

— A. Cohen and A.J. Brock

**NACE**  
INTERNATIONAL

To subscribe, contact NACE Membership Services Department  
P.O. Box 218340 • Houston, TX 77218-8340  
Call 713/492-0535, ext 81, or FAX 713/579-6694

*CORROSION* is a technical research journal devoted to furthering the knowledge of corrosion science and engineering. Within that context, *CORROSION* accepts notices of calls for papers and upcoming research grants, meetings, symposia, and conferences. All pertinent information, including the date, time, location, and sponsor of an event should be sent as far in advance as possible to: Ira D. Perry, Managing Editor, *CORROSION*, P.O. Box 218340, Houston, TX 77218-8340. Notices which are not accompanied by the contributor's name, daytime telephone number, and complete address will not be considered for publication.

### 1995

**March 13-15 — Research Triangle Institute and EPA 2nd Biennial Conference, Low- and No-VOC Coating Technologies — Durham, NC;** Contact Mary Moore, RTI, P.O. Box 12194, Research Triangle Park, NC, 27709-2194; 919/541-7448.

**\* March 26-31 — CORROSION/95 — Orlando, FL;** Contact NACE, P.O. Box 218340, Houston, TX, 77218-8340; 713/492-0535; telex 792310 NACEHOU; fax 713/492-8254.

**\* April 19 — NACE Wilmington Section 20th Delaware Corrosion Seminar — Wilmington, DE;** Contact Ronald D. Crooks, 7 Ridon Drive, Hockessin, DE, 19707; 302/239-6563.

**May 1-4 — Offshore Technology Conference — Houston, TX;** Contact OTC, P.O. Box 833868, Richardson, TX, 75083-3868; 214/952-9494; fax 214/952-9435; telex 163245 SPEUT.

**May 2-4 — 29th Annual Western States Corrosion Conference — Pomona, CA;** Contact Nick McLachlan, 310/532-9524.

**May 7-12 — 3rd International Symposium on Electrochemical Impedance Spectroscopy — Ysermonde, Nieuwpoort, Belgium;** Contact J. Vereecken, Vrije Universiteit Brussel, Dept. Metallurgy, Pleinlann 2, B-1050 Brussels, Belgium; 32-2-6413254; fax 32-2-6413200.

**\* May 8-10 — 1995 International Conference on Microbially Influenced Corrosion (cosponsored by NACE and the American Welding Society) — New Orleans, LA;** Contact Patricia Irving, 800/443-9353; fax 305/443-6445.

**May 15-16 — Symposium on Tools for Corrosion Intelligence — Denver, CO;** Contact Dorothy Savini, Symposia Operations, ASTM, 1916 Race Street, Philadelphia, PA, 19103-1187; 215/299-2617.

**May 15-17 — Life Prediction of Corrodible Structures — Sapporo, Japan;** Contact T. Shibata, Osaka University, Dept. of Materials Science, 2-1 Yamadaoka, Suita, Osaka, 565 Japan; 81-6-877-5111; fax 81-6-876-4729.

**May 16-19 — 8th International Symposium on Corrosion in the Pulp & Paper Industry — Stockholm, Sweden;** Contact Gösta Svendenius, Swedish Corrosion Institute, Roslagsvagen 101, hus 25, S-104 05 Stockholm, Sweden; 46-8790-9806.

**\* May 23-25 — NACE Europe/Middle East Region Corrosion Conference — Grado, Italy;** Contact NACE Italia Secretariat, c/o OMECO, Via Della Taccona, 26, I-20052 Monzas, Italy; 39-39-748983; fax 39-39-736433.

\* Sponsored by NACE International.