The intermetallic phases in AA7075-T6, including the nm-scale precipitate MgZnCu and 10-μm size Mg2Si, S-phase, Al7Fe2(CuMn), and Al4(FeMn), (SiCu), were identified and evaluated with respect to chemical composition, structure, and relative nobility. Evaluation of each major intermetallic particle (IMP) after exposure of the alloy to electrolyte allowed assessment of their roles in the localized corrosion. Different corrosion scenarios, including dealloying, trenching, particle etching out/dissolution, localized anodic and cathodic behavior of the IMPS, and corrosion sequences were studied. Combined with previous studies, the results advance the understanding of the electrochemical properties and the associated mechanisms of localized corrosion in aluminum alloys.

Al7Cu2Fe from the surface as the surrounding matrix is corroded, or by the sequential combination of the above two mechanisms due to the polarity switching from anodic to cathodic (e.g. S-phase). Studies have been carried out in recent years trying to correlate pitting to localized corrosion around/in intermetallic particles. It has been reported that the trenching around clusters of particles and particle (e.g. S-phase) dissolution serves as the basis of metastable and stable pit formation. However, the effects of intermetallic particles in the pit or meta-stable pit formation are still not thoroughly understood. The A more recent study suggested that anodic dissolution around isolated particles does not result in stable pit formation. Inconsistency still exists in the interpretation of current transients because of metastable pits, stable pits, or even interactions between pits.

The structure and electrochemical properties of particles and their roles in localized corrosion in Al alloys have been extensively studied using different techniques, including Scanning Kelvin Probe Microscopy (SKPFM), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Transmission Electron Microscopy (TEM), microcell measurements, and more recently atom probe tomography and neutron scattering. The studies have focused on the compositions of IMPS, pitting events, oxygen reduction reaction kinetics, Volta potential evaluation, etc. These studies have provided insight into the mechanisms of localized corrosion in the study of legacy 7075 aluminum alloys. However, there is a need for improved characterization techniques, as well as further data collection and analysis.

In the present work, the microstructure and chemical compositions of IMPS in AA7075-T6 and the localized corrosion associated with them were studied using several of the above-mentioned microscopy and spectroscopy techniques, including TEM, SEM, and EDS. Topography and Volta potential mapping was carried out using SKPFM to determine the relative nobility of each phase type (matrix and various IMPS) in ambient air environment after polishing and after sequential exposure to sodium chloride solution. Post exposure features of IMPS were re-examined using the above-mentioned techniques to determine the specific roles of the IMPS. These combined results allow a better understanding of the electrochemical behavior of IMPS, galvanic coupling between IMPS and the matrix, and preferential attack of active contents in IMPS and the matrix, which may provide feedback for the improved design and application of such alloys.

**Experimental**

Alloy specimens of dimensions 5 mm × 5 mm × 2 mm were cut from AA7075-T6 alloy plates, were successively ground down to 1200-grit with ethanol as lubricant, followed by polishing using 6, 3, 1, and 1/4 μm diamond slurry in ethanol, and finally rinsed with ethanol. Diamond-shaped micro-indenters with diagonal length of ~75 μm were made on the specimen surface to assist the accurate

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The intermetallic phases in Aluminum Alloys and Their Roles in Localized Corrosion

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The 7xxx Al-Zn alloys, such as grade AA7075-T6, are extensively used in aerospace applications because they offer high specific strength and excellent fatigue resistance. 1,2 7xxx alloys are precipitation hardenable through aging as the result of alloying elements that are added to precipitate a variety of fine intermetallic phases, which can act as effective dislocation barriers. However, the segregation of certain elements, development of heterogeneous microstructure on a larger scale, and the formation of relatively large (μm size) intermetallic phases can degrade the corrosion resistance of these alloys. 3

The localized corrosion of Al-Zn alloys in corrosive environments is primarily related to galvanic interactions between the matrix and various intermetallic phases, including various hardening precipitates, dispersoids and constituent particles, among which large (submicron to 10-micron scale) intermetallic particles (IMPS) are of particular importance, as they represent a large volume fraction in the Al alloy matrix. This raises concerns regarding material failure associated with intermetallic phases during service by localized corrosion and stress corrosion cracking or environment-assistant cracking. 4

Many different particles are of interest in AA7075-T6, and the major particles that affect localized corrosion follow different mechanisms, but also share certain similarities. 15-17 The relative nobility of an IMP is closely related to its chemical composition. Cu- and Fe-rich intermetallics are usually more noble (showing high Volta potential) with respect to the matrix. 14 Cu-rich particles promote the water reduction reaction more effectively than the Al matrix surface due to Cu enrichment in the oxide film on the particle surface. 18,19 However, the effects of intermetallic particles in the pit or meta-stable pit formation are still not thoroughly understood.

The A more recent study suggested that anodic dissolution around isolated particles does not result in stable pit formation. Inconsistency still exists in the interpretation of current transients because of metastable pits, stable pits, or even interactions between pits.

The structure and electrochemical properties of particles and their roles in localized corrosion in Al alloys have been extensively studied using different techniques, including Scanning Kelvin Probe Microscopy (SKPFM), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Transmission Electron Microscopy (TEM), microcell measurements, and more recently atom probe tomography and neutron scattering. The studies have focused on the compositions of IMPS, pitting events, oxygen reduction reaction kinetics, Volta potential evaluation, etc. These studies have provided insight into the mechanisms of localized corrosion in the study of legacy 7075 aluminum alloys. However, there is a need for improved characterization techniques, as well as further data collection and analysis.

In the present work, the microstructure and chemical compositions of IMPS in AA7075-T6 and the localized corrosion associated with them were studied using several of the above-mentioned microscopy and spectroscopy techniques, including TEM, SEM, and EDS. Topography and Volta potential mapping was carried out using SKPFM to determine the relative nobility of each phase type (matrix and various IMPS) in ambient air environment after polishing and after sequential exposure to sodium chloride solution. Post exposure features of IMPS were re-examined using the above-mentioned techniques to determine the specific roles of the IMPS. These combined results allow a better understanding of the electrochemical behavior of IMPS, galvanic coupling between IMPS and the matrix, and preferential attack of active contents in IMPS and the matrix, which may provide feedback for the improved design and application of such alloys.
In the exposure test, the specimens were immersed into 0.1 M NaCl aqueous solution and periodically removed at 2.5 min, 5 min, 15 min, 30 min, 120 min and 240 min, rinsed with water, naturally air dried in the lab environment, and characterized using microscopic and spectroscopic techniques. Optical micrographs were taken following etching with Keller’s reagent, which is 2 ml HF (48%) + 3 ml HCl + 5 ml HNO₃ + 190 ml H₂O.

Topography and Volta potential mapping of specimens before and after exposure to electrolyte were collected at room temperature (~21°C) in air using SKPFM on a Veeco MultiMode 8 with a Nanoscope V controller. The SKPFM tip was a Bruker OSCM-Pt-R3 coated with platinum on the tip apex. The scan frequency was set at 0.2 Hz with 1024 pixels per scanning line and the scanning of each map takes around 5.5 hr. The measurement was carried out by sequential scans, with the first linescan measuring the topography, followed by a second scan in lift mode at a height of 100 nm measuring the local Volta potential difference between the substrate and the Pt tip. A 2 V bias was applied to the tip to enhance the sensitivity. All images were post-analyzed using the software NanoScope Analysis 1.5.

The microstructure and composition of selected regions were examined by SEM coupled with EDS on a Philips XL-30 Field Emission ESEM and FEI Helios Nanolab Dual Beam Focused Ion Beam (FIB)/SEM. The accelerating voltage ranged between 10–20 kV for SEM imaging, 20 kV for EDS collection, and initially was 30 kV for cross-sectioning of TEM foil and 5 kV for final thinning.

More precise analysis of the composition and structure of particles was carried out using transmission electron microscopy in both TEM and Scanning TEM (STEM) mode on FIB lift out foils, using a JEOL-JEM 2010F TEM equipped with an EDS system. Selected area electron diffraction (SAED) patterns were collected of TEM foils across particles and matrix. The TEM system was also interfaced with a CEOS probe corrector that was used for collecting element maps and high-resolution high-angle annular dark-field (HAADF) images operated in STEM mode.

**Results**

**Examination of bulk surface phenomena.**—The optical micrograph in Figure 1a shows the overall microstructure of the as-polished alloy surface after etching using Keller’s reagent to explore features of IMPs over a relatively large area. The grain boundaries along the elongated grains in the rolling direction were revealed after 15 s etching. Large particles on the scale of a few μm to tens of μm were primarily distributed along the grain boundaries, indicating that the grain boundaries are the preferential formation sites of particles during the casting and thermal mechanical processing. Topography and Volta potential maps were collected in a large-particle-free zone (LPFZ) in an area with dimensions of 75 μm × 75 μm as shown in Figs. 1b and 1c, respectively. The topographic map in Fig. 1b shows a ripple on the surface, which was introduced during the specimen polishing, and some contamination was evident as isolated high features. Other than the bright large particles, the Volta potential map in Fig. 1c also shows numerous sub-μm scale cathodic particles that are extensively distributed through the matrix, a feature that is similar to that observed in AA2024-T3 and AA2060-T8. These particles could initiate galvanic corrosion of the matrix and would eventually be undermined or simply released from the surface, leaving holes in the matrix.

**Identification of large particles.**—S-phase (Al₂CuMg).—A representative large particle in AA7075-T6 was identified, and the secondary electron image, topography, Volta potential, and AFM phase maps are shown in Figs. 3a–3d, respectively. Note the minimum value on the scale bars of the maps is defaulted to zero unless otherwise specified. The elemental analysis of this particle was evaluated by EDS at the pointed marked in Fig. 2a and is tabulated in Table I. The EDS results suggest that this particle was S-phase (Al₂CuMg). The S-phase surface was lower than the surrounding matrix on the topography map (Fig. 2b) because of pre-dissolution that occurred during specimen polishing as described elsewhere. The dissolution of S-phase during polishing was caused by its more active potential relative to the matrix, particularly when the surface oxide layer was being polished away. This occurs even when using ethanol instead of water as a polishing lubricant. As also seen in AA2024-T3 and AA2060-T8, the Volta potential of S-phase on the as-polished surface was higher than the surrounding matrix in Fig. 2c due to surface oxidation when the specimen was exposed to air. Phase imaging in AFM monitors the phase lag between the signal that drives the cantilever to oscillate and the output signal of cantilever oscillation. It is a powerful analysis that is sensitive to surface stiffness/softness and adhesion between the tip and surface, and is useful for the imaging of soft, adhesive, easily damaged, loosely bound, or coated materials. As previously reported in the study of AA2060-T8, lateral inhomogeneities in the surface film can be evaluated by the phase map collected during SKPFM experiments because it differentiates with a clear contrast the intermetallic particle and matrix due to different stiffness of the particle and the matrix, as shown in Fig. 2d.

Mg₃Si.—A second type of large particle is shown in Fig. 3. This large particle was about 10–20 μm in size, anodic to the matrix based on the potential map (60–80 mV less positive than matrix), and part of the particle was lower in height on the topography map due to pre-dissolution that occurred during polishing in ethanol, shown in Figs. 3a and 3b. A foil was lifted out using FIB along the interface of the particle and the matrix at the square region shown in Fig. 3a for precise composition and structural analysis using TEM, and results are given in Figs. 3c–3f. The particle with relatively dark contrast in the HAADF image in Fig. 3c was identified to be Mg₃Si phase (space group Fm-3 m, lattice parameter a = 0.6338 nm) based on the lattice imaging in Fig. 3d and the SAED analysis in Fig. 3e. Mg₃Si is an active phase that often corrodes away upon electrolyte exposure, and may eventually leave a surface cavity. Precipitates with bright contrast in the HAADF image with size of tens of nm can also be seen to have formed both along the

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**Figure 1.** Surface examination of AA7075-T6 after (a) etching with Keller’s reagent for 15 s, (b) topography map and (c) Volta potential map of as-polished surface without Keller’s etching in an area of 75 μm × 75 μm.
Figure 2. Secondary electron image (a), topography (b), Volta potential (c), and phase (d) maps of a representative S-phase particle in AA7075-T6 without electrolyte exposure. Point EDS analysis was carried out at the cross mark in (a). The lower value on the scale bar of maps is defaulted to zero.

Figure 3. Examination and identification of a major representative particle Mg2Si in AA7075-T6: (a) topography and (b) Volta potential maps collected using SKPFM; (c) HAADF TEM image of a FIB lift-out in the square region in (a); (d) high resolution HAADF image of Mg2Si particle and matrix; (e) SAED of (d); (f) EDS maps of Al, Cu, Mg, and Zn in the square region in (c). Note the lower end of scale bars in SKPFM maps default to zero.

particle/matrix interface and in the matrix, Fig. 3c. One of these precipitates in the dotted square in Fig. 3c was analyzed using TEM-EDS, which indicated a generic composition of Mg-Zn-Al-Cu, Fig. 3f. The Mg-Zn-Al-Cu precipitate is believed to have nucleated during the cooling process from the solutionizing temperature and is an isomorphous form of the stable phases MgZn2 and MgCuZn.31 A close look into this type of precipitate using high-resolution lattice imaging and diffraction analysis is given in Fig. 4, which reveals that the precipitate is MgCuZn with a lattice parameter of $a = 0.7169$ nm.32

Al7Fe2Cu(Mn).—A third type of large particle was analyzed, and the results are given in Fig. 5. This large particle was also tens of $\mu$m in size, prominently raised above the surface, and possessed a Volta potential of 360–420 mV relative to the neighboring matrix. Precise analysis of chemical composition and structure using TEM/EDS was carried out on a FIB lift-out foil along the interface of the particle/matrix in the square region indicated in Fig. 5b as shown in Figs. 5c–5f. The section showed that this is a composite particle with three different phases having compositions summarized in Table I as determined by EDS. The major component of the large particle, the piece labeled A, was identified to be Al7Fe2Cu(Mn) based on its chemical composition analysis (Table I) and its diffraction pattern along the [110] zone axis (Fig. 5d).32–34 The piece labeled B had a composition of 55.4 Al, 16.3 Cu, 13.2 Zn, 9.5 Ca, and 1.1 Fe (at. %), and the crystal structure was not identified based on the SAED in Fig. 5e. At this point there is no explanation for the presence of Ca in such a compound. The piece labeled C was confirmed to be Mg2Si based on the SAED pattern shown in Fig. 5f. Considering the noble potential of the large particle relative to matrix, the lift-out position of the TEM foil, and the relative size of the three composite pieces, it is more practical to refer to the large particle in Figs. 5a and 5b as a composite Al-Cu-Fe-Mn particle with a major composition of Al7Fe2Cu(Mn) rather than a particle with specific metallurgical structure and chemical composition.

Al15(FeMn)3(SiCu)2.—Analysis of another type of large particle with size of tens of $\mu$m is shown in Fig. 6. As with other large particles, this particle protruded from the surface (Fig. 6a), and had a potential $\sim 300–340$ mV more noble than the matrix (Fig. 6b). The TEM-EDS analysis (Figs. 6c–6e) of the lift-out within the region identified by the dashed square at the interface of the particle and the matrix shown in Fig. 6b revealed a chemical composition of 68.8 Al, 18.9 Fe, 5.3 Si, 2.4 Cu, 2.6 Mn, 1.4 Cr, and 0.6 Zn (see Table I), which indicates that this particle was Al15(FeMn)3(SiCu)2 or Al12Fe3(SiCu).35–39 This type of particle is known to be a minor constituent in AA7075.39 It was also interesting to observe an Mg-Zn-Al-Cu precipitate along the interface of the particle, which was similar to the finding in Figs. 3
Table I. Tabulated chemical compositions (in a.t. %) of all examined particles in this paper based on TEM or SEM EDS. '-' means the counts of the elements were too low to assign existence with confidence.

| Phase assignment | Al | Cu | Fe | Mg | Mn | Si | Zn | Cr | Ca |
|------------------|----|----|----|----|----|----|----|----|----|
| S-phase in Fig. 2 | 49.2 | 24.6 | - | 23.5 | - | - | 2.7 | - | - |
| Mg2Si in Fig. 3 | - | - | - | 61 | - | 39 | - | - | - |
| Al7Fe2Cu(Mn) in Fig. 5d | 72.5 | 5.1 | 19.5 | - | 0.9 | - | 2.0 | - | - |
| Mg2Si in Fig. 5f | - | - | - | 61 | - | 39 | - | - | - |
| Al15Cu2z in Fig. 5e | 55.4 | 16.3 | 1.1 | - | 1.4 | - | 13.2 | 3.2 | 9.5 |
| Al15(FeMn)3(SiCu)2 in Fig. 6 | 68.8 | 2.4 | 18.9 | - | 2.6 | 5.3 | 0.6 | 1.4 | - |
| S-phase in Fig. 7 | 50.3 | 24.3 | - | 22.9 | - | - | 2.5 | - | - |
| Al2Fe2Cu(Mn) in Fig. 10 | 68.2 | 5.1 | 19.3 | - | 4.6 | - | 2.8 | - | - |
| Mg2Si in Fig. 10 | - | - | - | 63 | - | 37 | - | - | - |
| Al15(FeMn)3(SiCu)2 in Fig. 10 | 69.3 | 2.7 | 18.4 | - | 2.8 | 5.1 | 1.7 | - | - |

and 5 that this type of nm-size precipitate was MgCuZn. This type of particle formed in interfacial regions as well as in the matrix where precipitates are of light contrast in Fig. 6c, a similar feature as in Fig. 3.

Based on the above description, the following secondary phases were identified: nm-scale intermediate-state precipitate MgZnCu, µm-scale anodic particles Mg2Si and S-phase (Al2CuMg), and 10-µm size cathodic particles Al15Cu2z(CuMn) and Al15(FeMn)3(SiCu)2. The electrochemical properties of MgCuZn precipitate have not been reported yet, but MgCuZn is believed to be more active than the Al matrix free of particles. This is because even the less active MgCuAl is more active than the Al matrix according to previous work. Mg2Si particles are part of a group of intermetallics that just simply corrode away upon electrolyte exposure due to their low corrosion potential relative to matrix. The S-phase particles actually start off cathodic because of the air formed film after fresh polishing, then become anodic and corrode when that film breaks down, finally switching polarity again owing to the Cu-enrichment that accompanies dissolution such that they end up as cathodes capable of driving matrix dissolution.7,47 Al7Fe2Cu(Mn) and Al15(FeMn)3(SiCu)2 particles generally act as cathodic sites right after polishing until the neighboring matrix reached a similar potential difference between the particle and the surrounding matrix.41 A gradient in the phase map in Fig. 7c1 suggests corrosion product such as oxide and/or hydroxide coverage. Within 2.5 min, the corrosion attack primarily focused on the S-phase particle in the examined region through the selective dissolution of Al and Mg. This resulted in a porous and noble surface, which contributed to the cathodic behavior of the S-phase that led to galvanic dissolution of surrounding matrix.

Exposure of particles to electrolyte.—Exposed S-phase (Al2CuMg).—Fig. 7 summarizes the exposure tests of a representative S-phase particle in AA7075-T6 examined in detail using SKPFM before and after exposure to 0.1 M NaCl for times up to 240 min. Because of its pre-dissolution during specimen polishing as previously described, the S-phase was low relative to the surrounding matrix on the topography map (Fig. 7a0) in the as-polished surface. However, this S-phase particle showed a higher potential than the matrix on the potential map Fig. 7b0 due to the surface oxidation, which is similar to the S-phase behavior in AA2024 and AA2060.45,47 Correspondingly, the phase map in Fig. 7c0 suggests that there was a gradient in the surface film.

This specimen was then exposed to 0.1 M NaCl for 2.5, 5, 10, 15, 30, 60, and 120 min at OCP and was periodically removed for SKPFM analysis of the S-phase particle in air. After 2.5 min exposure, the particle/matrix interface was more clearly defined than that of the as-polished surface due to the lowering of the surface of the whole S-phase particle in the topography map Fig. 7a1. The preferential dissolution of Al and Mg in S-phase possibly led to a greater Volta potential difference between the particle and the surrounding matrix in Fig. 7b1. This is consistent with previous studies on S-phase in AA2024-T310 and AA2060-T8.7 It was also reported that nm-sized fragments of copper (typically 10–100 nm) may fall off (due to lack of physical support) from the corroded particle into the solution, oxidize, and then preferentially deposit on the particle remnant and the surrounding matrix.41 A gradient in the phase map of the S-phase particle became more evident in Fig. 7c1 suggesting corrosion product such as oxide and/or hydroxide coverage. Within 2.5 min, the corrosion attack primarily focused on the S-phase particle in the examined region through the selective dissolution of Al and Mg. This resulted in a porous and noble surface, which contributed to the cathodic behavior of the S-phase that led to galvanic dissolution of surrounding matrix.

After 15 min, the contrast at the particle/matrix interface became sharper with the development of a continuous trenching, Fig. 7a2. The bright contrast in the center of the particle in the topography map indicates a non-uniform enrichment of noble composition due to dealloying, which is barely visible in the potential map (Fig. 7b2) but more evident in the phase map (Fig. 7c2). The primary corrosion attack started to shift from S-phase to anodic dissolution of the matrix, causing attack along the particle/matrix interface. As a result, a continuous trench along the interface and a porous matrix structure appeared in Fig. 7a2. The strong galvanic interaction resulted sequentially in an increased rate of cathodic reduction reaction on the particle, local alkalinization, Al oxide destabilization, galvanic corrosion of matrix, and growth of the crevice in width and depth. Electrochemical redeposition of Cu on the porous structure along the crevice might also occur and further act as cathode driving matrix dissolution and propagation.41 The region with increased Volta potential in Fig. 7b2 broadened to the surrounding matrix, which will be shown later to result in Cu enrichment and oxide coverage on this attacked region, which is consistent with previous observations.10 A ring with bright contrast appeared right outside the crevice along the particle/matrix interface probably because of oxide coverage, which may further support galvanic activities.

Figure 4. High resolution examination of MgCuZn precipitate: (a) HAADF of lattice and (b) corresponding SAED.
Figure 5. Examination and identification of a major representative Al-Cu-Fe-Mn particle in AA7075-T6: (a) topography and (b) Volta potential maps collected using SKPFM; (c) HAADF TEM image of a FIB lift-out in the square region in (b); SEAD of (d) region A, (e) region B, and region C in (c); (g) selected EDS maps of the same region in (c). The lower value on the scale bar of the SKPFM maps is defaulted to zero.

Figs. 7a3–7c3 show that the heterogeneous structure within the S-phase particle and the interfacial region were more prominent in the topography, potential, and phase maps after 30 min than after 15 min. The dissolution of the matrix continued as indicated by the further expanded corroded matrix structure. The bright ring right along the porous matrix also propagated toward the matrix and was more prominent than after 15 min, as shown in Fig. 7c3 due to aggressive galvanic dissolution of matrix and the formation of corrosion products. Note that the porous structure expanded farther into the matrix compared to 15 min exposure because the matrix sustained anodic dissolution, which enhanced the ring contrast.

After 120 min exposure to 0.1 M NaCl, the attack along the interface progressed, as the attack widened into a larger trench and the particle appeared to be on its way to being completely corroded based on the increased trench depth and width (Fig. 7a4). Globular-shaped products (Fig. 7a4) with relatively low potential (Fig. 7b4) compared to precipitates.

Figure 6. Examination and identification of a major representative Al$_{15}$(FeMn)$_3$(SiCu)$_2$ particle in AA7075-T6: (a) topography and (b) Volta potential maps collected using SKPFM; (c) HAADF TEM image of a FIB lift-out in the square region in (b); (d) bright field image; (e) EDS maps of Al, Cu, Mg, Mn, Fe, Si, and Zn. The lower value on the scale bar of maps is defaulted to zero.
to the particle appeared. The bright ring structure in Fig. 7c4 was evident in the phase map and matched well with the expanded porous matrix topography and high potential region.

After 240 min of exposure, the trench increased in depth as reflected by the depth scale bar in Fig. 7a5. The potential difference over the mapped surface area reached as low as 24 mV in Fig. 7b5. The globular-shaped products became more evident and attached to the particle residual based on the phase map in Fig. 7c5, but the ring structure was still dense and it expanded toward the matrix.

As support to the SKPFM results in Fig. 7, SEM and optical microscopy examination of the S-phase particle prior to and after exposure to 0.1 M NaCl for 240 min are given in Fig. 8. The S-phase with intact particle/matrix interface prior to exposure is shown in Fig. 8a, whereas the particle was severely attacked after 240 min with an oxide ring next to it as revealed in the optical image in Fig. 8b. The suggested porous structure on top of the particle as well as in the matrix along the interface was confirmed in the SEM image shown in Fig. 8c. This was a result of Al and Mg dealloying in the particle and galvanic corrosion of matrix. The EDS maps in Fig. 8d provide more information regarding the elemental distributions after corrosion attack. After long-term exposure, S-phase was significantly attacked but still not completely corroded based on the remaining Al and Mg in the maps, because the exposure time was not long enough to corrode the whole particle. Cu residual was confirmed because of its distribution over a larger area with brighter contrast in the particle. Besides, Cu was also detected with slightly higher counts at the interfacial region, possibly suggesting Cu deposition in Mg-depleted zone layer and that Mg maintained the potential below the critical potential for Zn dissolution thereby inhibiting Zn dissolution. There is a possibility of the formation of Mg-depleted Zn/Zn oxide film at the particle/matrix interface since Zn is a major alloying element in AA7075-T6. Based on the above description, it can be concluded that Al oxide destabilization and dealloying of Al and Mg occurred in the S-phase particle to leave a Cu remnant, probably with additional Cu deposition as revealed by the Cu ring in EDS map. However, galvanic corrosion and oxidation accompanied by Cu deposition were dominant in the interfacial region.

Fig. 8 shows the time evolution of the topography profiles and Volta potential profiles across the S-phase particle along the white arrow (Fig. 7a0) and black arrow (Fig. 7b0), respectively. For better visualization of the topography evolution of the particle relative to the matrix, the height profiles in Fig. 9a (and hereafter) were adjusted so that the two ends of the height profiles representing the matrix around the particles were set (close) to zero height. Within the first 5 min, the height of particle decreased faster than the matrix. However, at longer times the attack was focused at the surrounding matrix as indicated by the formation and growth in both depth and width of the trench around the particle. The potential of both the S-phase particle and the matrix increased with exposure time until there was nearly no contrast after 240 min exposure due to possible preferential dissolution of active elements in the particle and matrix oxidation as well as Cu enrichment along the particle/matrix interface. The variations of Volta potential difference and height of the particle relative to the matrix over the exposure time exhibit trends similar to those reported for S-phase in AA2024 and AA2060-T8. At the early stages of exposure (normally < 5 min), the particle was more noble but more recessed relative to the matrix as the attack was focused on the particle. Beyond 5 min, the corrosion attack primarily occurred on the matrix along the interface as both the Volta potential and topography of the surrounding matrix changed toward the values of the particle. The surrounding matrix was further attacked at 240 min, with the potential hardly distinguishable from the particle. The Volta potential scale bars representing the variation of the entire scanned surface in Fig. 7b5 also reflect the feature of the decreasing potential difference as a function of time. However, the range of the scale bar representing potential variation over the entire scanned surface in Fig. 7b5 is only 24 mV, which could not be very well distinguished from the profile in Fig. 9b considering the Volta potential range in the Y axis.
Exposed Al$_7$Fe$_2$Cu(Mn), Mg$_2$Si, and Al$_{15}$(FeMn)$_3$(SiCu)$_2$.—Three types of 10-μm scale particles labeled 1, 2, and 3 prior to electrolyte exposure are shown in Fig. 10. According to the tabulated chemical compositions in Table I, these three particles are 1) Al$_7$Fe$_2$Cu(Mn), 2) Mg$_2$Si, and 3) Al$_{15}$(FeMn)$_3$(SiCu)$_2$, respectively. These chemical compositions are based on EDS analyses performed at the squares in Fig. 10a, and they agree well with the earlier TEM characterization of the same types of particles. Notably, the Al$_7$Fe$_2$Cu(Mn) particle and the Al$_{15}$(FeMn)$_3$(SiCu)$_2$ particle stuck out from the surface (Fig. 10b) due to relatively high hardness and noble Volta potential (Fig. 10c), whereas the Mg$_2$Si particles were relatively low on the surface and certain particles were even depressed from the surface. The Volta potential values relative to matrix were measured to be +280 to +320 mV for Al$_7$Fe$_2$Cu(Mn), −80 to −100 mV for Mg$_2$Si, and +200 to +240 mV for Al$_{15}$(FeMn)$_3$(SiCu)$_2$. Several clusters of Al$_7$Fe$_2$Cu(Mn) particles were identified on both maps and may indicate the breakup of a large particle during cold rolling. Therefore, it is reasonable that the Al$_7$Fe$_2$Cu(Mn) particles were heterogeneous in chemistry and structure and existed in clusters. The same clustering was observed for Mg$_2$Si. However, the Al$_{15}$(FeMn)$_3$(SiCu)$_2$ phase was an isolated particle. Note that the examined region in Fig. 10 was randomly captured along a grain boundary area and was therefore representative of the bulk surface property. Additional regions of similar size were also examined and they all revealed that Al$_7$Fe$_2$Cu(Mn) and Mg$_2$Si particles were clustered with a much larger number density than Al$_{15}$(FeMn)$_3$(SiCu)$_2$ particles, and they are believed to be the major constituent particles on the tens of μm scale in AA7075-T6.

After 30 min exposure to 0.1 M NaCl, there was no evident trench development around the Al$_7$Fe$_2$Cu(Mn) particle, but corrosion attack such as small pits appeared in and around the particle in Fig. 11a as compared to the as-polished surface in Fig. 10. These attacks, probably preferential dissolution of Al, as reported for similar particles in AA2060-T8, occurred at the boundaries of heterogeneous domains in the particle where the Volta potential was slightly low. As a result of that, the potential of the particle in Fig. 11b increased by about 700 mV whereas the matrix surface oxidation was not as severe as that occurred in the particle, which means the primary attack in this time period focused on the particle by preferential dissolution of active elements.

After 60 min, trenching was more evident in and around the particle in Fig. 11a. Correspondingly, the bright region with high potential map expanded toward the matrix region in Fig. 11b, indicating the...
transition of the primary corrosion attack from the particle to the matrix. The particle being cathodic drove the galvanic dissolution of the anodic matrix, primarily the dissolution of active alloying elements, leading to the emergence of the attacked matrix.

At 240 min, the attack at the particle/matrix interface was advanced with the growth in width and depth surrounding the entire particle as well between the domain boundaries in the heterogeneous particle, as shown in Fig. 11a3. The matrix surrounding the particle was clearly distinguished after further galvanic corrosion of the matrix. The potential was high, suggesting oxide coverage and potential Cu enrichment there. The potential of the surrounding matrix increased as observed from the bright contrast in Fig. 11b3, probably because of the dissolution, oxidation, and Cu enrichment, just as was observed for S-phase particle, which led to a decreased potential difference of only about 200 mV between the particle and the matrix. However, the particle still protruded from the surface and the crevice development around the particle was not severe enough to release it. This noble particle may have eventually been undermined given enough exposure time, based on the previous studies on Al-Cu-Fe-Mn particles in AA2024-T34,5 and AA2060-T8.7

The surface topography of the Al7Fe2Cu(Mn) particle after exposure to 0.1 M NaCl for 240 min was also reexamined using optical microscopy and SEM, as shown in Fig. 12. An oxide ring was observed along the porous matrix structure in Fig. 12a, exactly the same feature as observed for the S-phase particle after electrolyte exposure. The porous matrix structure in the SEM image (Fig. 12b) was in good agreement with that observed in the SKPFM topography map. The difference of the porous structure between the S-phase and the Al7Fe2Cu(Mn) particles should be noted: the porous structure in the Al7Fe2Cu(Mn) particle was not as developed as that in the S-phase because S-phase experienced significant dealloying by having high content of Mg and Al. However, the Al7Fe2Cu(Mn) was always more noble than the matrix and only limited dealloying occurred within the studied time scale.

The topography profiles and Volta potential profiles across the Al7Fe2Cu(Mn) particle along the white and black arrows in Fig. 11a1 and 11b1 respectively after various periods of electrolyte exposure are given in Fig. 13. The potential and potential difference change for both the particle and the surrounding matrix generally followed a similar trend as observed for the S-phase particle. The potentials of both

Figure 10. Examination and identification of large particles 1) Al7Fe2Cu(Mn), 2) Mg2Si, and 3) Al15(FeMn)3(SiCu)2 without nobility switching in AA7075-T6 prior to electrolyte exposure: (a) secondary electron image; (b) topography and (c) Volta potential maps. The lower value on the scale bar of maps is defaulted to zero.

Figure 11. SKPFM examination a Al7Fe2Cu(Mn) particle in AA7075-T6 in Fig. 10 after electrolyte exposure to 0.1 M NaCl for: 30 min (a1, b1), 60 min (a2, b2), and 240 min (a3, b3). White and black arrows represent line scan profiles of topography and Volta potential across the particle. The in-set topography map in a1 represents the as-polished surface. The lower value on the scale bar of maps is defaulted to zero.

Figure 12. Reexamination of the Al7Fe2Cu(Mn) particle in Fig. 10 after 240-min exposure to 0.1 M NaCl solution: (a) optical image showing three-ring structure; (b) secondary electron image.
the particle and the matrix increased with increasing exposure time due to the preferential dissolution of active elements in particles and matrix oxidation as well as Cu enrichment along the particle/matrix interface. The variations of the height difference and Volta potential difference of the particle relative to the matrix over the exposure time also exhibited similar features as a Al-Cu-Fe-Mn particle reported in AA2060-T8. At the early stages of exposure (< 60 min), the particle became more noble and decreased in height relative to the matrix as the attack was focused on the particle by dealloying. After 60 min, the corrosion attack primarily occurred in the matrix along the interface as both the potential and topography of the surrounding matrix moved toward the values of the particle because of surface oxidation and oxide coverage. The surrounding matrix was further attacked at 240 min, with the potential difference less than about 200 mV, but the particle still stuck out from surface with reduced height.

The region of Mg$_2$Si and Al$_{15}$(FeMn)$_3$(SiCu)$_2$ particles in Fig. 10 after electrolyte exposure was reexamined using SKPFM, as shown in Fig. 14. After 30 min exposure, the anodic particle Mg$_2$Si corroded as indicated by the decreased height in the topography map (Fig. 14a1) and increased Volta potential (Fig. 14b1), so that it switched nobility relative to the as-polished surface. Both the surface and the edge of the Al$_{15}$(FeMn)$_3$(SiCu)$_2$ particle were intact without clear corrosion attack.

After 240 min exposure, the Mg$_2$Si particle further corroded and depressed from the surface, where a terrace clearly emerged along the particle/matrix interface in Fig. 14a2. The particle completely reversed potential from being anodic to being cathodic to the neighboring matrix in Fig. 14b2 due to oxidation. As can be confirmed from the post-exposure SEM image in Fig. 15a, the Mg$_2$Si particle was corroded severely so that cracks even appeared in and along the particle. The degradation process for the Mg$_2$Si particle is very
straightforward and it is believed that this particle would continue to corrode until complete removal without causing severe damage to the matrix. There was still no obvious corrosion attack to both the Al15(FeMn)3(SiCu)2 particle and the peripheral matrix (Fig. 14a3 and 14b3), but more localized corrosion sites as well as the initiation of trench in the circled regions at the interface were evident, which was confirmed in the SEM reexamination in Fig. 15b. The slight galvanic corrosion damage between the cathodic particle and the active matrix can probably be explained by their similar corrosion potential. It was reported that AA7075 matrix and a model Al-Fe-Si phase exhibited very similar corrosion potentials. However, the Volta potential of the entire region still increased with increasing exposure time, indicating sustained oxidation of the entire surface. It could be inferred that, as the exposure time increases, more corrosion attack along the interface would occur and may lead to the similar attacked structure as that observed around Al15-2Fe-Cu(Mn) particle.

The topography profiles and Volta potential profiles across the Mg2Si particle and the Al15(FeMn)3(SiCu)2 particle as a function of electrolyte exposure time are given in Fig. 16. The height difference of between Mg2Si particle and matrix increased with exposure time and the particle height decreased after exposure due to its anodic dissolution, Fig. 16a. During the first 30 min, there was also an increase in potential difference between the Mg2Si particle and the matrix in Fig. 16b, even though the matrix potential also increased because of surface oxidation. Between 30–240 min, both the potential of the particle and the matrix continued to increase but the potential difference neared zero. This is in line with the Volta potential evolution of S-phase and Al-Cu-Fe-Mn particles. Regarding the profiles in Figs. 16c and 16d for the Al15(FeMn)3(SiCu)2 particle, there was no large change in both the height difference and the Volta potential difference between this particle and its surrounding matrix. However, the Volta potential of the particle and matrix increased as the exposure time was prolonged, notably with a sharp increase during the first 30 min due
Figure 17. EDS maps showing the element distribution in the region shown in Fig. 10 before (a) and after exposed to 0.1 M NaCl for 240 min (b). Mn maps were not shown here due to weak contrast.

to the rapid oxidation of the freshly polished surface. The sharp peaks in topography profiles and their corresponding valleys of low Volta potential indicated the attachment of corrosion product or contamination to the surface with a relatively low potential as demonstrated by the curvature in the potential. The initiation of a crevice described earlier was not observed in this specific profile. Other than that, the oxidation over this profile could be interpreted as uniform oxidation of the particle surface. Although the potential difference between the particle and the matrix was basically maintained in a range of 200–240 mV, it still exhibited a slight increase in the first 60 min and then decreased gently during limited exposure time. The evolution of Volta potential difference appears to be similar to other particles like S-phase, Al7Fe2Cu(Mn) and Mg2Si after sufficiently long term exposure.

The elemental distribution by EDS mapping in the region in Fig. 10 prior to and after exposure to 0.1 M NaCl for 240 min is shown in Fig. 17. The EDS maps of the three particles Al7Fe2Cu(Mn), Mg2Si, and Al15(FeMn)3(SiCu)2 are shown in Fig. 17a before exposure. There is no clear evidence of preferential oxidation, because O was uniformly distributed in the entire region. After 240 min of exposure, Al and Mg were selectively corroded from the particles, Cu, Fe, and Si remained in the particles, and an increased distribution of O was observed on the particles and the matrix surrounding them. The area of Cu and Fe distribution was slightly expanded beyond the particles due to their deposition along the particle/matrix interfacial region as described earlier. EDS mapping was carried out only at the beginning and the end and not between the sequential exposures to avoid carbon contamination.

Additional exposed particle: Al3Fe(Ni).—One additional particle, which was Al3Fe(Ni) based on the SEM-EDS analysis, was also examined after 240 min exposure for comparison with the above particles to determine similarities and differences, Fig. 18. An evident trench and porous matrix structure after galvanic attack was observed in the topography map due to galvanic dissolution of the matrix, preferentially the dissolution of active elements. Correspondingly, the Volta potential of the particle, the trench and the matrix all increased. All these features are very similar to Al-Cu-Fe-Mn particles and therefore could be treated as the same group of particles. However, slight differences can be noticed. The particle surface was still very clean and smooth after exposure and rarely had pitting or trench attack. The corrosion attack at the interface was slightly worse than that in the Al7Fe2Cu(Mn) particle, as indicated by the large trench, because the
The four major particles, S-phase, Al7Fe2Cu(Mn), Mg2Si, and Al15(FeMn)3(SiCu)2, share similarities but also behaved slightly differently upon electrolyte exposure. The mechanisms controlling the phenomena associated with each particle can be revealed to construct the localized corrosion progression map shown in Fig. 19. Fig. 19 generally describes the Volta potential evolution and the associated level of localized corrosion damage as a function of exposure time in the electrolyte. The reactivity (or nobility) of the materials is correlated to their Volta potential values and thus is added to the progression map in Fig. 19. At the early stage of electrolyte exposure, the corrosion attack occurred in the form of dealloying in the particle, and the Volta potential values followed the order of Matrix < S-phase < Al15(FeMn)3(SiCu)2 < Al7Fe2Cu(Mn). As the immersion time increased, trenching initiated in the peripheral matrix, indicating the transition of major corrosion attack to the matrix because of the preferential dissolution of active elements in the particles. The preferential dissolution of active elements was faster than in the matrix due to high driving force associated with the higher composition of noble element in the particles. During this process, these particles became more noble than they had been, so that the driving force from the net cathode effect of the particles accelerated the galvanic dissolution of the surrounding matrix on the micron scale. As the exposure time increased, the corrosion attack was dominated by the galvanic dissolution of the matrix, even though the preferential dissolution of active elements in the particles continued. Particularly S-phase, being rich in Cu, experienced potential reversal. At the long-term exposure, the particles would be either corroded or released from the surface.

S-phase in nature is active to Al matrix but the oxide film formed in air after polishing causes it to be cathodic to the matrix for a freshly-prepared specimen. At the early stage of exposure, the particle became less noble and more recessed relative to the matrix as dealloying of Al and Mg continued on the particle, leaving Cu remnant and a porous structure, and an oxide covered the matrix. In the intermediate stage, the major corrosion attack transitioned from the particle to the surrounding matrix and focused on the galvanic dissolution of the surrounding matrix. Notably, S-phase/Cu remnant behaved as cathode even more effective in driving matrix dissolution because Cu remnant was more noble than other particles.

The Al7Fe2Cu(Mn) particle was always cathodic to the matrix, but the corrosion attack initially focused on the particle, not the matrix, because of the dealloying of active Al in the particle and the low potential domain boundaries in the heterogeneous structured particle. However, as the exposure time increased, the primary corrosion attack was dominated by the galvanic dissolution of the surrounding matrix driven by the noble particle. Considering that this particle is slightly more noble than the Al15(FeMn)3(SiCu)2 particle, it is added to the upper part of Fig. 19 indicating higher nobility. Note that the Al7Fe(Ni) particle behaved similarly to Al-Cu-Fe-Mn particles, and therefore they can be categorized into one group of particles that contain Al, Cu, and/or Fe and/or Mn, such as Al13Cu, Al13Fe, Al6Mn(Fe), Al2Cu2Fe, and Al20Mn8Cu2, etc.5,8,15,23,39,43-47

The corrosion attack associated with the Al15(FeMn)3(SiCu)2 particle upon electrolyte exposure was kinetically slower than that of S-phase and Al-Cu-Fe-Mn particles most probably because it contains the semi-metal element Si that is poor in conductivity, which could effectively compromise the reactivity relative to the matrix. This result in less corrosion damage to the matrix. However, attack in the form of localized corrosion occurred in the particle over prolonged exposure time, and it is believed that this type of particle would behave similarly to Al-Cu-Fe-Mn particles during long-term electrolyte exposure. Therefore, this particle is added below the Al7Fe2Cu(Mn) particle in Fig. 18 and may represent a group of Si-containing cathodic particles such as Al13FeSi, Al13FeSi, Al13(FeMn)Si, Al3MnSi, Al(Mn,Fe)Si etc.25,35-38,48 which are more commonly populated in 6xxx aluminum alloys.

Even though the corrosion attack kinetics of cathodic particles and peripheral matrix vary for different particles depending on the relative nobility, chemical composition and exposure time, the corrosion attack associated with each particle followed a similar process over sufficiently long-term electrolyte exposure: preferential dissolution of active elements in the particles, primary corrosion transition to particle/matrix interface, trenching initiation, continuous trenching development, and particle dissolution or release. Beyond this, the relative Volta potential, reactivity, and the associated corrosion damage upon electrolyte exposure of each type of the particles in Fig. 19 can be extended to represent a group of similar particles as mentioned above, and furthermore, the entire hierarchy of localized corrosion progression map could be transferred to other aluminum alloys containing the same/similar intermetallic phases.

Conclusions

1) Intermetallic particles were primarily found along the grain boundaries. Numerous cathodic particles in sub-μm scale were homogeneously distributed through the matrix in freshly polished condition.

2) The intermetallic phases include nm-scale precipitate MgCuZn, anodic particles Mg8Si, S-phase particle, and cathodic particles Al13Fe2Cu(Mn) and Al15(FeMn)3(SiCu)2 with 10-μm size. Their ranking from high to low with respect to Volta potential of the as-polished surfaces follows the order of Al13Fe2Cu(Mn), Al15(FeMn)3(SiCu)2, S-phase, matrix, and Mg8Si.

3) Al7Fe2Cu(Mn) and Mg2Si particles have a much larger number density than Al15(FeMn)3(SiCu)2 particles and S-phase, and are believed to be the major constituent particles of 10-μm scale in AA7075-T6. MgCuZn particles were distributed in the matrix as...
well as along particle/matrix interface, and were believed to affect the electrochemical behavior of the adjacent large particles.

4) Lateral inhomogeneities in the surface film of intermetallic particles were revealed by the SKPFM phase maps.

5) The S-phase particle was initially noble to the matrix because of oxidation in air. At the early stage of exposure, the corrosion process focused on the particle through dealloying of Al and Mg, leaving Cu remnant. In the intermediate stage, the corrosion attack transitioned to galvanic dissolution of the surrounding matrix, and both the potential and topography difference between the surrounding matrix and the particle decreased with increased exposure time.

6) Al15(FeMn)2(SiCu)2 particles exhibited responses to electrolyte exposure similar to S-phase but with a difference in reaction kinetics and reactivity to the matrix. After long term exposure, the S-phase particle was on its way to be completely corroded with a large surrounding trench, trenches developed around Al15(FeCu)(Mn), and trench barely initiated around Al15(FeMn)2(SiCu)2. The corrosion attack associated with particles, however, followed a similar process within sufficiently long-term electrolyte exposure: preferential dissolution of active elements in particles, primary corrosion transition to particle/matrix interface, trenching initiation, continuous trenching, and particle dissolution or release.

7) Mg2Si corroded because of dealloying of Mg, leaving a Si remnant that was not found to act as a cathode driving anodic dissolution of matrix. The Volta potential profile exhibited a feature similar to the above particles: the Volta potential difference between particle and matrix first experienced a sharp increase due to the primary localized dissolution in the particles, then the difference decreased because of corrosion attack transition to surrounding matrix, and finally the gradient was eliminated between the matrix and particles.

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