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TITLE:

Investigating Corrosion at the Metal-Paint Interface Using Time-of-Flight Secondary Ion Mass Spectrometry

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KEYWORDS:
ToF-SIMS, aluminum, metal-paint interface, corrosion, limit of detection (LOD), mass spectra, 2D imaging

SUMMARY:

Time-of-flight secondary ion mass spectrometry is applied to demonstrate the chemical mapping and corrosion morphology at the metal-paint interface of an aluminum alloy after being exposed to a salt solution compared with a specimen exposed to air.

ABSTRACT:

Corrosion developed at the paint and aluminum (Al) metal-paint interface of an aluminum alloy is analyzed using time-of-flight secondary ion mass spectrometry (ToF-SIMS), illustrating that SIMS is a suitable technique to study the chemical distribution at a metal-paint interface. The painted Al alloy coupons are immersed in a salt solution or exposed to air only. SIMS provides chemical mapping and 2D molecular imaging of the interface, allowing direct visualization of the morphology of the corrosion products formed at the metal-paint interface and mapping of the chemical after corrosion occurs. The experimental procedure of this method is presented to provide technical details to facilitate similar research and highlight pitfalls that may be encountered during such experiments.

INTRODUCTION:

Al alloys have wide applications in engineering structures, such as in marine technology or military automotive, attributable to their high strength-to-weight ratio, excellent formability, and resistance to corrosion. However, localized corrosion of Al alloys is still a common phenomenon which affects their long-term reliability, durability, and integrity in various environmental conditions[1]. Paint coating is the most common means to prevent corrosion. Illustration of the corrosion developed at the interface between metal and paint coating can provide insights in determining the appropriate remedy for corrosion prevention.

The corrosion of Al alloys may take place via several different pathways. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) are two commonly applied surface microanalysis techniques in investigating corrosion. XPS can provide elemental mapping but not a holist molecular view of the surface chemical information[2–3], while SEM/EDX provides morphological information and elemental mapping but with relatively low sensitivity.

ToF-SIMS is another surface tool for chemical mapping with high mass accuracy and lateral resolution. It has a low limit of detection (LOD) and is capable of revealing the distribution of the corrosion species formed at the metal-paint interface. Typically, SIMS mass resolution can reach 5,000–15,000, sufficient to differentiate the isobaric ions[4]. With its submicron spatial resolution, ToF-SIMS can chemically image and characterize the metal-paint interface. It provides not only morphological information but also the lateral distribution of molecular corrosion species at the top few nanometers of the surface. ToF-SIMS offers complementary information to XPS and SEM/EDX.

To demonstrate the capability of ToF-SIMS in surface characterization and imaging of the corrosion interface, two painted Al alloy (7075) coupons, one exposed to air only and one to a salt solution, are analyzed (**Figure 1** and **Figure 2**). Understanding the corrosion behavior at the metal-paint interface exposed to the saline condition is critical to understand the performance of the Al alloy in a marine environment, for example. It is known that the formation of $Al(OH)_3$ occurs during Al's exposure to seawater[5], but the study of Al corrosion still lacks comprehensive molecular identification of the corrosion and coating interface. In this study, the fragments of $Al(OH)_3$, including Al oxides (e.g., $Al_3O_5^-$) and oxyhydroxide species (e.g., $Al_3O_6H_2^-$), are observed and identified. The comparisons of SIMS mass spectra (**Figure 3**) and molecular images (**Figure 4**) of the negative ions $Al_3O_5^-$ and $Al_3O_6H_2^-$ provide the molecular evidence of the corrosion products formed at the metal-paint interface of the salt solution-treated Al alloy coupon. SIMS offers the possibility to elucidate the complicated chemistry occurring at the metal-paint interface, which can help shed light on the efficacy of surface treatments in Al alloys. In this detailed protocol, we demonstrate this effective approach in probing the metal-paint interface to help new practitioners in corrosion research using ToF-SIMS.

PROTOCOL:

1. Corrosion sample preparation

1.1. Al sample fixation in resin, and polishing

1.1.1. Mount two Al alloy coupons (1 cm x 1 cm) using epoxy resin in 1.25 inch metallographic sample cups and place the coupons in the fume hood overnight or till the resin is completely cured.

1.1.2. Take out the Al resin cylinders cups from the sample cups. Polish the Al resin cylinders using 240 grit paper with water at a 300 rpm platen/150 rpm in the holder for 1 min.

1.1.3. Polish the Al resin cylinders using the polishing plate with 15 µm, 6 µm, 3 µm, and 1 µm water-based solution for 5 min (each step), sequentially.

1.1.4. Rinse the Al resin cylinders with deionized water (DI) and buff them with cotton.

1.1.5. Rinse the Al resin cylinders again with ethanol and place them in the chemical fume hood till they are dry.

NOTE: Alternatively, the sample can be dried with pressurized air or nitrogen.

1.2. Preparation of the Al corrosion sample

1.2.1. Spray the black paint 2x onto each Al resin cylinder and let them stand in the fume hood for 24 h. The paint is approximately 100 µm thick.

NOTE: The paint is a commercial product with primer mixed in one bottle. It is fast drying and rust preventive.

1.2.2. Engrave four parallel lines (5–6 mm long) straight down on the top of each painted Al resin cylinder using scalpels. Place the lines in the center of the Al alloys.

1.2.3. Immerse one Al resin cylinder into a pH 8.3 salt solution containing NaCl, $MgSO_4$, $MgCl_2$, and KCl, with the scribed surface down. Partially cover the 10 cm x 10 cm Petri dish with its lid.

NOTE: The salt solution is made of 465 mM NaCl, 28 mM $MgSO_4$, 25 mM $MgCl_2$, and 3 mM KCl in 50 mL of DI water, adjusted by 0.1 M NaOH to reach approximately pH 8.3. The solution contains main ions in seawater. The conductivity of the salt solution is approximately 5.5 S/m. The temperature of the solution is 72 °F.

1.2.4. Place the other Al resin cylinder with its scribed surface down in a clean Petri dish and cover it with the lid. Keep both samples in the chemical fume hood for 3 weeks.

1.3. Exposure of the corrosion interface and mounting of the interface in resin

1.3.1. Cut each Al resin cylinder into two halves using a low-speed saw with a diamond blade, perpendicularly to the middle of the marked lines, and trim the excessive resin edge.

1.3.2. Mount all the trimmed Al alloy pieces in a 2 inch sample cup and form an assembly by placing the Al alloy pieces along a circle, with the metal-paint interface facing up. Space out each Al alloy piece.

1.3.3. Repeat steps 1.1.2–1.1.3.

1.3.4. Further polish the metal-paint cross-section in a vibratory polisher affixed to a 2 lbs weight using 0.05 µm of colloidal silica solution on a polishing pad for 4 h.

1.3.5. Repeat steps 1.1.4–1.1.5

NOTE: The fixation and polishing work is important for acquiring sufficient SIMS signals because an unpolished surface will lead to low intensities of secondary ions signals and a poor mass resolution during SIMS analysis.

1.4. Coating of the sample with a sputter coater

1.4.1. Put the polished metal-paint interface assembly in the sputter coater chamber with the interface side up. Close the lid of the sputter coater and start to pump down the chamber.

1.4.2. Follow the regular sputter coater procedure and deposit a 10 nm gold (Au) layer on the metal-paint interface assembly.

NOTE: The purpose of this sample surface treatment is to reduce the charging effect during the SIMS analysis. If the sample is conductive, this step is not necessary.

2. Analysis of the metal-paint corrosion interface using ToF-SIMS

2.1. Loading of the samples in ToF-SIMS

2.1.1. Mount the metal-paint interface assembly containing the salt solution-treated sample and the air-exposed control on the **Topmount** sample holder using screws and clips.

NOTE: The **Topmount** is the name of the sample holder that holds the sample on the top of the sample holder.

2.1.2. Unscrew the locking screw on the load-lock door, and click the button **Stop** on the **Fpanel** window of the ToF-SIMS software graphical user interface (GUI) to vent the load-lock chamber.

2.1.3. Open the load-lock chamber by swinging the sample transfer arm to the right, turn the transfer arm counterclockwise till it attaches to the pin of the **Topmount** sample holder, and then, turn it back.

2.1.4. Swing the transfer arm back to close the door of the load lock and tighten the locking screw on the door to seal the load lock.

2.1.5. Click the button **Start** on the Fpanel window to pump down the load-lock chamber till it reaches ~1.0E-6 mbar or below.

2.1.6. Click the button **Open** on the Fpanel window to open the gate between the main chamber and the load lock.

2.1.7. Push the sample transfer arm attached with the sample holder into the main chamber. Turn the transfer arm counterclockwise till the sample holder is transferred to the sample stage in the main chamber.

2.1.8. Retract the transfer arm all the way back, and click the button **Close** on the Fpanel window to close the gate between the main chamber and the load lock.

2.1.9. Select **Topmount.shi** from the drop-down menu of the pop-up window, select the **Sample Holder**, and click **OK**. The image of the **Topmount** sample holder appears at the right side of the **Navigator** GUI.

2.1.10. Wait until the vacuum level of the main chamber reaches at least 1.0E-8 mbar or below.

2.2. Starting of the liquid metal ion gun (LMIG) and alignment of the ion beam

2.2.1. Check the boxes of the **LIMG**, **Analyzer**, and **Illumination** in the **Power Control** window to power up the liquid metal ion gun (LIMG), analyzer, and light source after the samples are transferred to the main vacuum chamber.

2.2.2. Check the box of **LMIG** shown on the Fpanel window to activate the LMIG setting tab. Click **Start LMIG** from the **Source** subtab under the **LIMG** tab in the **Instrument** Window to activate the LMIG.

2.2.3. Select the predefined file of spectrometry settings in the pop-up window of **Load Settings** and click **Open**.

NOTE: Bi_3^+ is selected as the primary ion beam. The LMIG energy is set to 25 kV. The LIMG chopper width is set to 25 ns. The other settings including emission current 1.0 µA; the heating value is 2.75 A; the suppressor approximately 800–1,000 V; the extractor 10 kV; the lens source 3.3 kV; the cycle time 100 µs; the mass range 1–870 u. The settings may vary depending on the instrument model, the remaining lifetime of the LMIG, and the acquisition requirement for specific samples.

2.2.4. Select **LMIG** in the pop-up window of **Categories** to load, click the **Selected** button, and click **OK**.

NOTE: It takes approximately 5 min to fully start the LIMG.

2.2.5. Select **Positive** from the drop-down menu of the **Instrument Setup** in the Fpanel to determine the ions to be detected.

NOTE: Select **Negative** from the drop-down menu if negative ions are to be measured.

2.2.6. Select the predefined file of the analyzer settings after clicking the button of the **Loading Settings** in the Fpanel to activate the analyzer.

NOTE: The analyzer acceleration is set to 9.5 kV; the analyzer energy is set to 2 kV; the detector is set to 9 kV. The settings of the analyzer may vary due to the configuration of different SIMS models.

2.2.7. Select **Faraday Cup** from the drop-down menu of the **Cursor Position** in the **Navigator** GUI. Click **Go** to move the stage to the Faraday cup.

NOTE: Move the stage to the Faraday cup for the target current measurement.

2.2.8. Select the **Micro** view from the drop-down list of **Video** in the **Navigator** GUI to view the position of the Faraday cup.

2.2.9. Click the center of the Faraday cup under the **Micro** view in the **Navigator** GUI and select **Drive to Marked Position** from the drop-down menu after right-clicking the **SE/SI Primary Gun** window in the **Navigator** GUI.

2.2.10. Select **20 µm x 20 µm** from the drop-down menu of **Specify Raster Field of View** after right-clicking the **SE/SI Primary Gun** window in the **Navigator** GUI.

2.2.11. Click the button **C** from the **Gun** subtab under the **LIMG** tab in the **Instrument** Window to auto-align the ion beam.

2.2.12. Click the **Start** button and check the box of **DC** from the **Pulsing** subtab under the **LMIG** tab to measure the target current.

2.2.13. Click the **X Blanking** from the **Focus** subtab under the LIMG tab and turn the mouse wheel to maximize the target current. Click the **Y Blanking** from the same tab to maximize the target current.

NOTE: The target current of the ion beam measured under the mass spectrometry mode should be greater than 14 nA, or greater than 0.5 pA if Bi_3^+ is selected, to achieve the desired intensities of ion signals.

2.2.14. Click the **Stop** button from the **Focus** subtab to stop the measurement of the target current.

2.3. Adjustment of the beam focus at the region of interest

2.3.1. Press the **Z** button on the joystick control panel and push the joystick up to lower down the sample stage till the extractor cone is above the top of the metal-paint interface assembly.

NOTE: It is critical to avoid a collision between the extractor cone and the samples when conducting this step.

2.3.2. Press the **X** and **Y** buttons on the joystick and move the joystick left/right and up/down to bring the interface assembly till it is displayed in the **Macro** view in the **Navigator** GUI.

2.3.3. Switch to **Micro** view in the **Navigator** GUI to locate the region of interest (ROI) of the metal-paint interface.

2.3.4. Set the ROI to **300 µm x 300 µm** after right-clicking the **SE/SI Primary Gun** window to expand the field of the view.

2.3.5. Select the signal type **SI**, raster size **128 x 128 pixel**, and raster type **Random** from the **SE/SI Primary Gun** in the **Navigator** GUI.

2.3.6. Click the black triangle button and the **Adjust SI** button in the **SE/SI Primary Gun** window. The round shape of the secondary ion (SI) image of the ROI will appear in the **SE/SI Primary Gun** window.

2.3.7. Press the **Z** button on the joystick control panel. Move the joystick up or down to bring the round shape of the SI image to the center of the cross-hair in the **SE/SI Primary Gun** window.

NOTE: If the cross-hair is in the middle of the round shape of SI image, it indicates that the image is obtained with good focus.

2.3.8. Uncheck the **Adjust SI** button, and click the square button in the **SE/SI Primary Gun** window to stop the focus adjustment.

2.4. Removal of the surface coating and contamination using the high current mode/DC mode

2.4.1. Select the SE image from the drop-down menu of the **SE/SI Primary Gun** window to observe the DC cleaning progress.

2.4.2. Check the box of DC in the Fpanel and click the black triangle button to start DC cleaning.

NOTE: Keep the DC on for 10 s or till the SE image indicates the gold layer is removed. The duration of the DC cleaning may vary depending on the thickness of the coating.

2.4.3. Click the black square button to stop the DC cleaning when observing the gold coating is removed via the **Micro** view in the **Navigator** GUI.

2.4.4. Switch the SE image to the SI image in the **Navigator** GUI.

NOTE: The reason for using a DC beam is because the DC beam (~14 nA) is powerful enough to remove the Au coating and other surface contamination, while the pulsed beam current (~1 pA) is not adequate.

2.5. Enabling of the surface charge compensation using a flood gun

2.5.1. Check the **Flood Gun** box in the Fpanel to enable the charge compensation.

2.5.2. Click the button **Load Setting File** in the Fpanel. Select the predefined file of flood gun settings after clicking the **Loading Settings** to load the settings of the flood gun.

NOTE: The settings of the flood gun include the following: energy of 20 V, an anode of 300 V, a delay of 2.0 µs, a flood gun filament current of 2.4 A, and a flood gun lead off of 2.0 µs. The settings of the flood gun may vary for different instruments.

2.5.3. Repeat steps 2.3.6–2.3.7 to readjust the focus on the ROI.

NOTE: As soon as the Au coating is removed, the height of the ROI will change. Thus, it is necessary to readjust the focus.

2.5.4. Click the **Reflector** from the **TOF** subtab of the **Analyzer/Main** tab in the **Instrument** Window.

2.5.5. Click the value on the left side of the bar of the **Reflector** to decrease the voltage of the reflector till the round shape of the SI image disappears. Then, increase the reflector voltage by 20 V.

NOTE: This process is done to ensure a flat imaging surface and maximum SI signals. In the negative mode, increase the reflector voltage till the round shape of the SI image disappears and, then, bring it down 20 V.

2.5.6. Repeat step 2.3.8 to stop the focus and reflector voltage adjustment.

2.6. Acquirement of the high-resolution mass spectrum

2.6.1. Click the icons of the **Spectrum** and **Image** in the Fpanel to open the spectrum and images programs.

2.6.2. Display the selected ROI of the metal-paint interface in **Micro** view.

2.6.3. Click the triangle button in the **Navigator** GUI to start a quick scan and a SIMS spectrum will appear in the **Spectrum** program; click the black square to stop the quick scan.

NOTE: The quick scan should only take several scans and usually takes just a few seconds.

2.6.4. Select the **Mass Calibration** from the drop-down list of the **Spectrum** on the toolbar of the **Spectrum** program or simply press **F3** to bring up the mass calibration window after the quick scan is completed.

2.6.5. Select recognized peaks to calibrate the mass spectrum by clicking the corresponding peaks, add the formula in the mass calibration window, and click **OK** to exit the mass calibration window when the peak selection is done.

NOTE: CH_3^+, $C_3H_3^+$, and $AlOH^+$ are selected for calibrating the positive mass spectrum; while OH^- and CN^- and AlO^- are selected for calibrating the negative mass spectrum. The peaks selected for mass calibration may vary for different samples. The deviation of the selected peaks is less than 30 ppm to ensure accurate peak identification.

2.6.6. Add the peaks of interests to the peak list by clicking the peak of the selected ions in the spectrum and clicking the **Add Peak** button on the toolbar.

2.6.7. Click the red triangle button in the Fpanel to open the **Start Measurement** window.

2.6.8. Set the **Raster** type to **Random**, **128 x 128 pixel**, and **1 shot/pixel**, set the **Number of Scans** to 60 scans in the pop-up window, and click **OK** to start the mass spectrum acquisition of the ROI.

NOTE: The mass spectrum acquisition will automatically stop after the desired number of scans are acquired.

2.6.9. Click **Save File** in the Fpanel to save the acquired mass spectrum and name it with a designated file name (e.g., salt solution-treated, air-exposed).

2.6.10. Switch the polarity to **Negative** in the Fpanel and repeat steps 2.5.3–2.6.9 to acquire the negative mass spectrum for the same ROI.

NOTE: SIMS mass spectra of four different ROIs of each sample were acquired for the positive and negative polarities in this study.

2.7. Saving of the analyzed ROI position for additional analysis

2.7.1. Click the **Add** button in the **Navigator** GUI and input the name of the ROI in the pop-up window (e.g., salt solution 1).

2.7.2. Click the **Stage Pos** button and click the **OK** button to save the ROI location.

NOTE: The ROI position is saved for additional SIMS imaging analysis.

2.8. Acquirement of a high-resolution SIMS image

2.8.1. Click the button **Load Setting File** in the Fpanel and select the predefined imaging setting file. Click **Open** to load the imaging settings.

NOTE: The highest lateral resolution or the smallest spot size is optimized in the collimated mode (i.e., the DC mode). In this mode, the smallest aperture in the beamline determines the angle of the aperture. According to the configuration setting of the ToF-SIMS, the highest lateral resolution is when the DC current is approximately 50 pA and the focus can reach around 100 nm. To achieve this resolution, increase the Lens Source while observing the DC current going down, and optimize the X Blanking and Y Blanking till the final DC current reaches 50 pA. The following lists the detailed parameter settings of the imaging mode. Bi_3^+ is selected as the primary ion beam. The LMIG energy is set to 25 kV. The LIMG chopper width is set to 100 ns and the chopper offset is set to 30.9 ns. The other settings include an emission current of 1.0 µA; the heating value is 2.75 A; the suppressor approximately 800–1,000 V; the extractor 10 kV; the lens source 3.5 kV; the cycle time 100 µs; the mass range 1–870 u.

2.8.2. Select **LMIG** in the pop-up **Categories to Load** window.

2.8.3. Repeat steps 2.2.7–2.2.14 to measure the target current and align the ion beam.

NOTE: The desired target current in the imaging mode should be greater than 0.6 nA or approximately 1 pA if Bi_3^+ is selected for measurement.

2.8.4. Select the saved ROI position from the drop-down list of the **Cursor Position** in the **Navigator** GUI. Click **Go**.

NOTE: This step ensures that the mass spectrum and image mapping are acquired from the same ROI.

2.8.5. Repeat steps 2.5.4 and 2.5.5 to adjust the reflector voltage.

2.8.6. Repeat steps 2.6.3–2.6.6 to conduct the mass calibration in the imaging mode.

NOTE: If the software cannot register the selected peaks when doing the mass calibration, check the box **Use Selected Channel** in the **Mass Calibration** window.

2.8.7. Repeat steps 2.6.7 and 2.6.8 to collect the image data.

NOTE: In the imaging mode, set the raster type to **Random**, **256 x 256 pixel**, and **1 shot/pixel**, set the **Number of Scans** to 150 scans, and click **OK** to start the image acquisition of the ROI. The image resolution and scan can be different and they should be determined depending on the sample.

2.9. Retrieval of the sample from the vacuum chamber

2.9.1. Select **Transfer** from the drop-down list of the **Cursor Position** in the **Navigator** GUI and click the **Go** button to bring the sample stage near the gate.

2.9.2. Open the gate by repeating step 2.1.6.

2.9.3. Push the sample transfer arm into the main chamber and turn the arm rod clockwise and forward till it attaches to the pin of the sample holder.

2.9.4. Turn the transfer arm back and retract it all the way.

2.9.5. Close the gate by clicking the button **Close** on the Fpanel and select **No sample holder** in the pop-up **Select Sample Holder** window.

2.9.6. Unscrew the locking screw on the door of the load lock and click the button **Stop** in the Fpanel to vent the load lock.

NOTE: Venting takes approximately 3–5 min.

2.9.7. Swing the transfer arm to the right and turn the transfer arm rod counterclockwise to release the sample holder.

2.9.8. Swing the transfer arm back and tighten the locking screw on the door of the load lock.

2.9.9. Click the **Start** button in the Fpanel to pump down the load lock.

2.9.10. Take off the metal-paint interface resin assembly from the sample holder and place them in a clean Petri dish.

2.10. Turning off the LIMG

2.10.1. Click **Stop LMIG** from the subtab under the LMIG tab in the **Instrument Window**.

2.10.2. Uncheck the boxes of **LMIG** and **Flood Gun** in the Fpanel and uncheck the box of **Illumination** in the **Power** window.

3. Analysis of the ToF-SIMS data

3.1. Export of the SIMS spectrum data

3.1.1. Click **File** on the toolbar of the **Spectrum Program** window and select **Export** from the drop-down list.

3.1.2. Name the spectrum file, save it in the designated folder as a .txt file, and click **OK**.

3.1.3. Type number 10 in the pop-up window to define the binning channel and click **OK**.

NOTE: Binning 10 channels before exporting the mass spectra is a commonly used method for reducing the data size while still keeping the mass resolution and accuracy.

3.1.4. Export the SIMS image data.

3.1.5. Click the **Image Program** icon and double-click the acquired image files to display the SIMS images.

3.1.6. Drag the image of a specific chemical species from the list to the image display window and double-click that image to open the image process window below.

3.1.7. Normalize the image of the selected chemical species to the images of total ions by choosing **Normalize** from the drop-down list of the image process window.

3.1.8. Apply the same color scale to compare the chemical distribution between different samples by adjusting the color scale in the image process window.

NOTE: The raw data of the images can be exported and plotted using other graphical software.

REPRESENTATIVE RESULTS:

Figure 3 presents the comparison of mass spectra between the metal-paint interface treated with salt solution and the interface exposed to air. The mass spectra of the two samples were acquired using a 25 kV Bi_3^+ ion beam scanning in 300 µm x 300 µm ROIs. The mass resolution (m/Δm) of the salt solution-treated sample was approximately 5,600 at the peak of m/z^- 26. The raw data of the mass spectra were exported after binning 10 channels. A graphical software was applied to plot the mass spectra for presentation. It is known that the protective layers containing $Al(OH)_3$ are formed after the Al corrosion starts[6]. The oxide ($Al_3O_5^-$) and oxyhydroxide species ($Al_2O_4H^-$, $Al_2O_5H_3^-$, $Al_3O_6H_2^-$) of $Al(OH)_3$ fragments[7] were observed in the metal-paint interface of the salt solution-exposed Al coupon (**Figure 3a**) and were more prominent when compared to the same peaks in the air-exposed sample (**Figure 3b**). This indicates that the Al coupon exposed to the salt solution had experienced more severe corrosion compared to the air-exposed one. The result is consistent with the known knowledge that solutions containing salts, such as seawater, are chemically aggressive and contribute to the corrosion process of an Al alloy.

Figure 4 depicts 2D molecular images of selected Al species m/z^- 161 $Al_3O_5^-$ and 179 $Al_3O_6H_2^-$

acquired from the metal-paint interface treated with a salt solution (**Figure 4a**) and the interface exposed to air (**Figure 4b**). The depicted ion intensities of m/z$^-$ 161 and 179 were both normalized to the intensities of total ions. The images of the same peak were adjusted to the identical color scale. The images were obtained from 100 scans of 256 x 256 pixels of the 300 µm x 300 µm ROI. The 2D images provide the distribution of the chemical species of the Al corrosion products in two different samples. The peaks m/z$^-$ 161 and 179 were more prevalent in the metal-paint interface treated with the salt solution, displaying stronger intensities than the ones shown in the air-exposed sample. This result agrees with the mass spectra results and further demonstrates ToF-SIMS's analytical capabilities of chemical identification and molecular imaging.

FIGURE LEGENDS:

Figure 1: Photos showing the metal-paint interface preparation process. Figure 1 depicts the metal-paint interface preparation process. After the Al coupons were fixed in the epoxy resin (**a**), they were sprayed with the commercial paint product and set for 24 h till they were completely dry (**b**). Four lines were scribed on the paint on top of the Al coupon cylinders (**c**). The carved Al coupon cylinders were exposed to air or a salt solution for 3 weeks in Petri dishes (**d**). The Al coupon cylinders were cut and trimmed to expose the metal-paint interfaces (**e**) and coated with gold layers prior to ToF-SIMS analysis (**f**).

Figure 2: The schematic of the metal-paint interface analysis by ToF-SIMS and a photo of the IONTOF V instrument. Figure 2 illustrates the analysis process of the metal-paint interface using ToF-SIMS. The metal-paint interface (**a**) was bombarded by a Bi_3^+ primary ion beam and generated the secondary ions, resulting in mass spectra (**b**) and a SIMS image (**c**). The ToF-SIMS V instrument (**d**) used for the metal-paint interface analysis described in this work is displayed.

Figure 3: Comparison of mass spectra of the metal-paint interfaces of Al coupons. The figure shows the spectral difference between the interface treated with a salt solution and the one treated with air.

Figure 4: Molecular images of chemical species at the metal-paint interface of Al coupons. This comparison shows the difference in 2D distribution of species formed in corrosion by salt solution and by air.

DISCUSSION:

ToF-SIMS differentiates the ions according to their time of flight between two scintillators. The topography or sample roughness affects the flight time of the ions from different starting positions, which usually leads to a poor mass resolution with an increased width of peaks. Therefore, it is critical that the ROIs being analyzed are very flat, to ensure good signal collection[8].

Another pitfall to avoid is charging. Since the Al-paint interface was fixed with the insulating resin, charging was expected. Charge accumulates on the sample surface as the ROI is bombarded with the primary ion beam, affecting the kinetic energies of ions that are emitted from the surface.

Charging results in wide peaks and a decreased mass resolution. To avoid the negative influence of this effect, 10 nm of gold was sputtered on the interface surface to form the conductive path prior to SIMS analysis. Other methods can be applied to reduce the charging effect, including applying the flood gun, optimizing the voltage of the reflector, and selecting **Random mode** as the beam raster pattern. The flood gun generates a stable electron current with low energy. It is commonly used for charge compensation during the SIMS analysis[9–11]. In addition, the voltage of the reflector, an ion optic that enhances the mass resolution, needs to be adjusted, depending on the degree of charging. ToF-SIMS software provides an efficient way to optimize the reflector as described in step 2.5.5 of the protocol. The selection of **Random mode** as the beam raster pattern before acquiring SIMS data further reduces the charging effect. This mode mitigates the problem occurring in the row-by-row scanning mode, allowing the accumulated charge more time to dissipate[9,11].

ToF-SIMS can be equipped with multiple ion sources, including—but not limited to—Cs^+, C_{60}^+, and Bi_n^+. Polyatomic ion sources (e.g., Bi_3^+ and C_{60}^+) produce higher yields of secondary ions emitted from the sample surface compared to atomic ion beams (e.g., Cs^+ and Bi_1^+)[12–13]. Furthermore, comparing Bi_3^+ to C_{60}^+, Bi_3^+ is more surface sensitive to low-mass fragments and, thus, has a higher lateral resolution with better images[12]. Therefore, Bi_3^+ was selected as the analysis beam in this work since we focused on the low-mass peaks related to aluminum corrosion species.

ToF-SIMS is a sensitive surface technique that can provide chemical specificity with a high spatial resolution[14]. Other surface tools applied in corrosion studies include XPS and SEM/EDX[2,15–17]. XPS can provide quantitative measurements of the chemical state and electronic state of the elements that exist within a sample but with a higher LOD (0.1%) than SIMS (parts-per-billion–parts-per-million level)[18–19]. SEM/EDX is not as sensitive as ToF-SIMS, although SEM is often used to obtain morphological features of surfaces. In addition, the chemical mapping of SIMS makes it possible to visualize the molecular ion distribution at the corrosion interface, while SEM/EDX only provides the elemental ion mapping. Thus, SIMS's molecular mapping is more informative in investigating the interfacial corrosion process.

This work demonstrates that ToF-SIMS is a powerful tool in deciphering the corrosion speciation at the interface due to its low LOD, high mass resolution, and high spatial resolution. Furthermore, SIMS offers multimodal microanalysis, attributable to its quasi-nondestructive nature. Thus, the same sample can be analyzed by other analytical tools and provide comprehensive information. Ideally, the integration of SIMS, XPS, and SEM can provide more comprehensive insights into corrosion behavior at the metal-paint interface.

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DISCLOSURES:

The authors have nothing to disclose.

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Figure 1

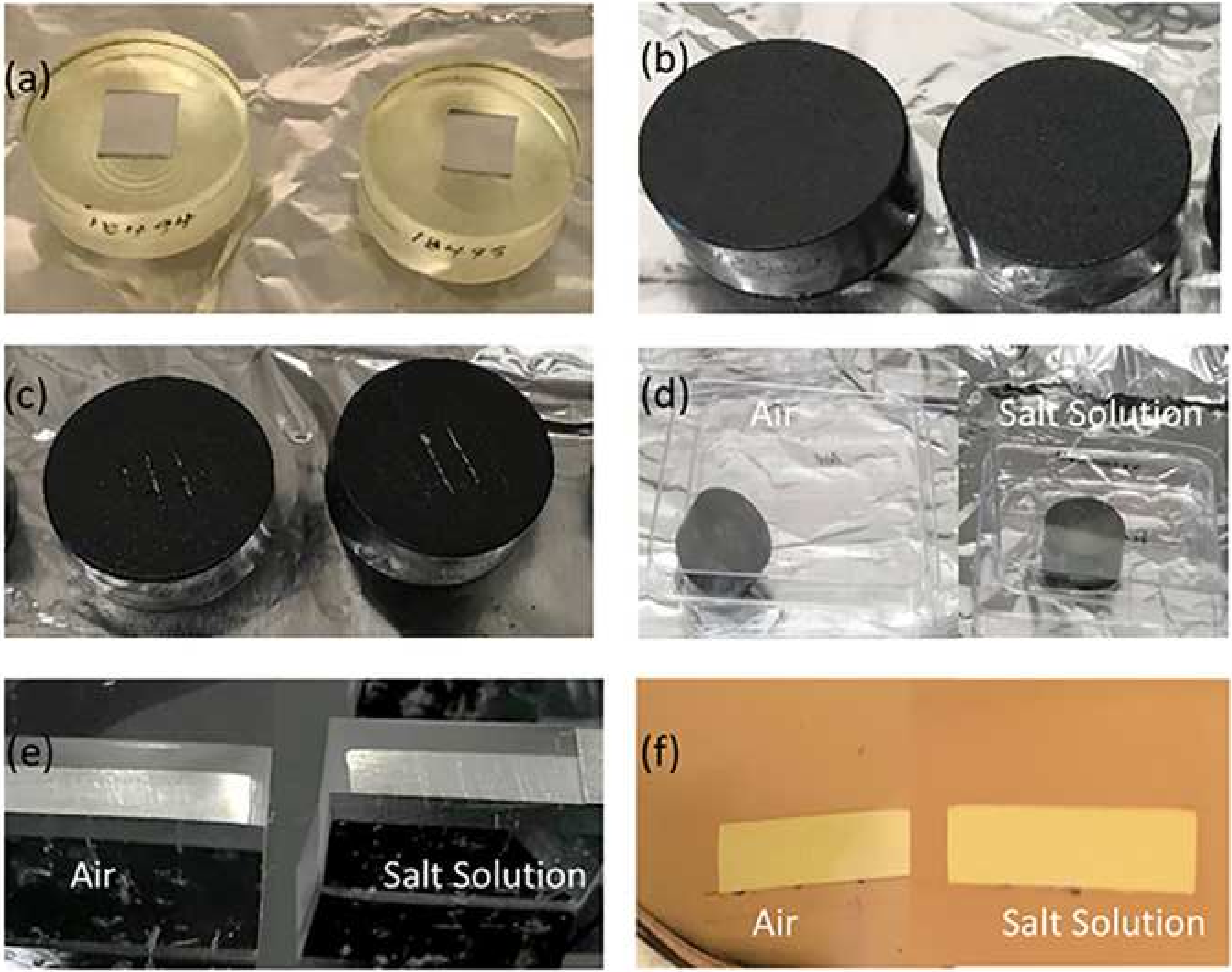
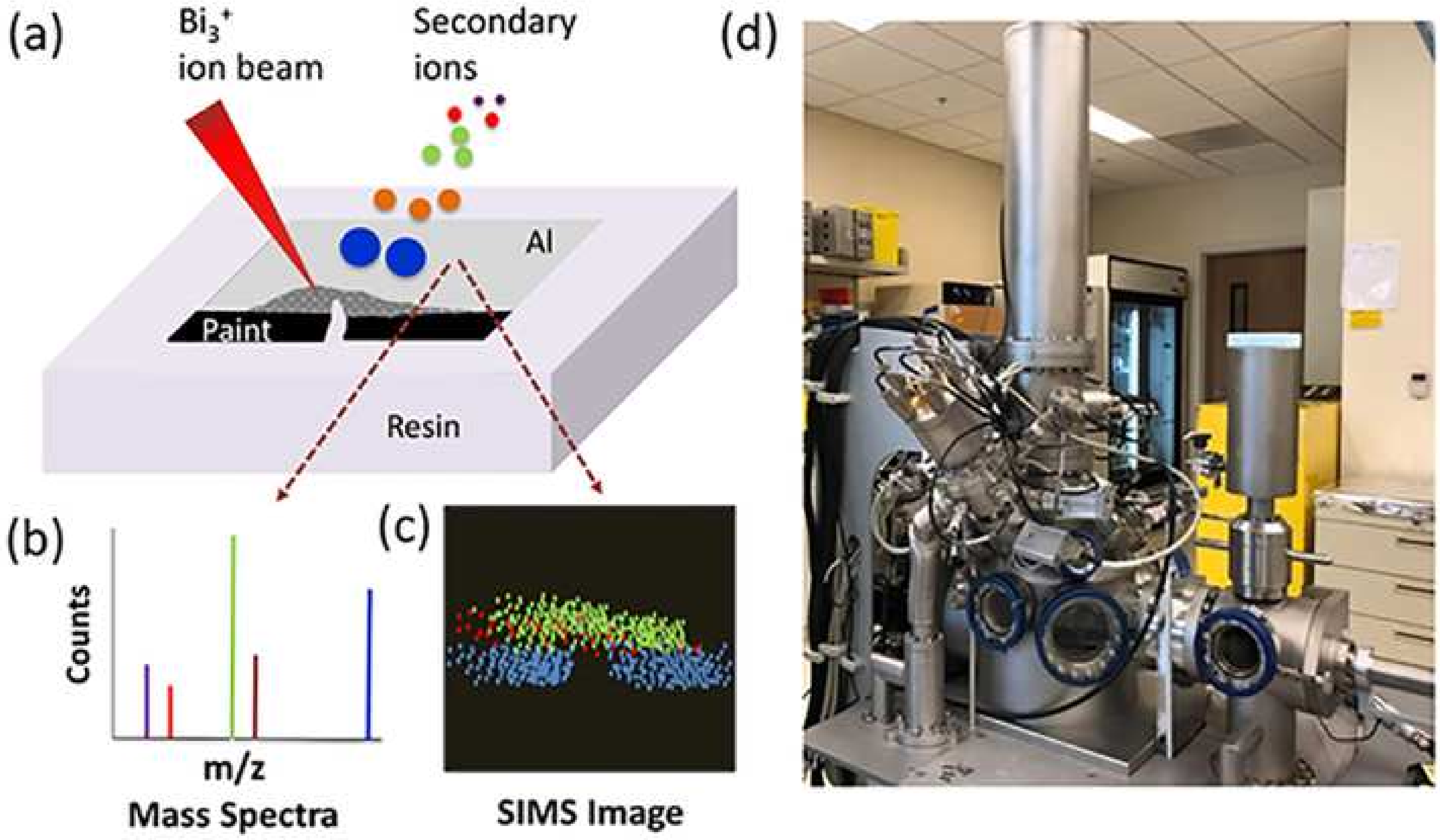
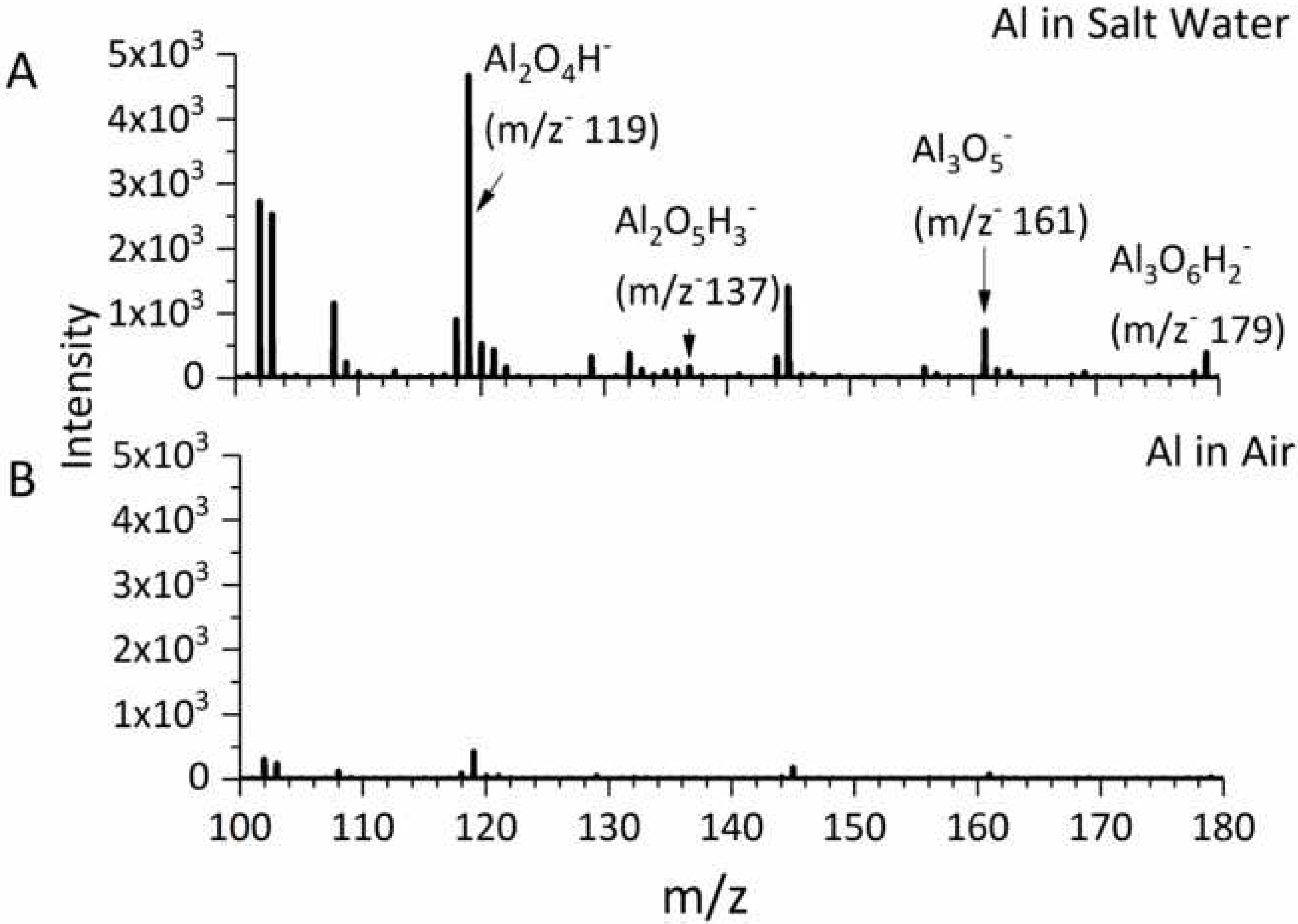
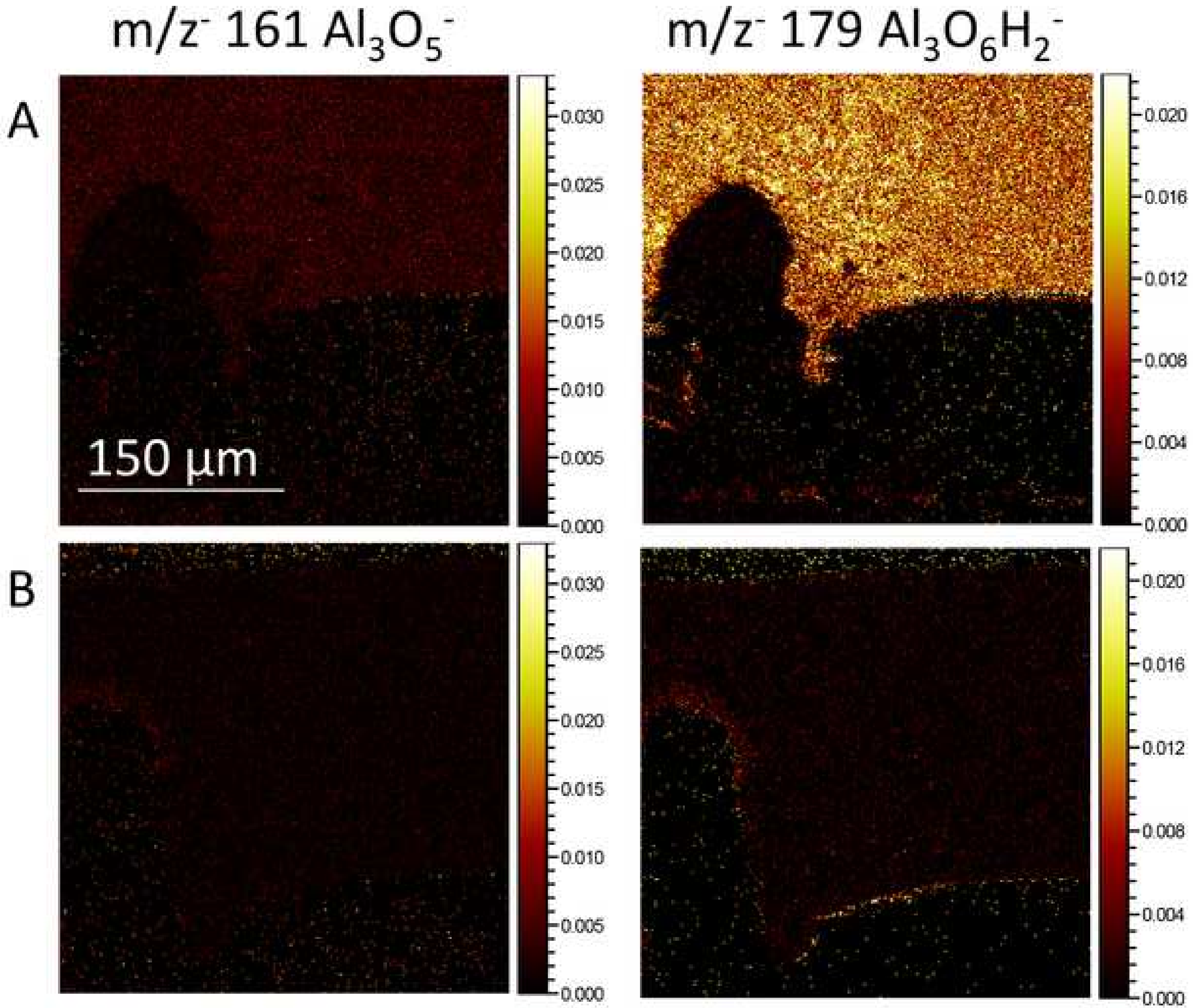

(a)
(b)
(c)
(d)
Air
Salt Solution
(e)
Air
Salt Solution
(f)
Air
Salt Solution

Figure 2


(a)
Bi3+
ion beam
Secondary
ions
Al
Paint
Resin
(b)
Counts
m/z
Mass Spectra
(c)
SIMS Image
(d)


A
Al in Salt Water
$Al_2O_4H^-$
(m/z⁻ 119)
$Al_2O_5H_3^-$
(m/z⁻137)
$Al_3O_5^-$
(m/z⁻ 161)
$Al_3O_6H_2^-$
(m/z⁻ 179)
5x10³
4x10³
3x10³
2x10³
1x10³
0
Intensity
B
Al in Air
5x10³
4x10³
3x10³
2x10³
1x10³
0
100
110
120
130
140
150
160
170
180
m/z


m/z^- 161 $Al_3O_5^-$
m/z^- 179 $Al_3O_6H_2^-$
A
B
150 µm
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0.020
0.016
0.012
0.008
0.004
0.000

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
0.05 µm Colloidal Silica polishing Solution	LECO	812-121-300	Final polishing solution
1 µm polishing solution	Pace Technologies	PC-1001-GLB	Water based polishing solution
15 µm polishing solution	Pace Technologies	PC-1015-GLBR	Water based polishing solution
3 µm polishing solution	Pace Technologies	PC-1003-GLG	Water based polishing solution
6 µm polishing solution	Pace Technologies	PC-1006-GLY	Water based polishing solution
Balance	Mettler Toledo	11106015	It is used for measuring the chemicals.
Epothin 2 epoxy hardener	Buehler	20-3442-064	Used for casting sample mounts
Epothin 2 epoxy resin	Buehler	20-3440-128	Used for casting sample mounts
Fast protein liquid chromatography (FPLC) conductivity sensor	Amersham	AKTA FPLC	Used to measure the conductivity of the salt solution.
Final B pad	Allied	90-150-235	Used for 1 µm and 0.05 µm polishing steps
KCl	Sigma-Aldrich	P9333	Used to make the salt solution.
Low speed saw	Buehler Isomet	11-1280-160	Used to cut the Al coupons that are fixed in the epoxy resin.
$MgCl_2$	Sigma-Aldrich	63042	Used to make the salt solution.
$MgSO_4$	Sigma-Aldrich	M7506	It is used to make the salt solution.
NaCl	Sigma-Aldrich	S7653	It is used to make the salt solution.
NaOH	Sigma-Aldrich	306576	It is used for adjusting pH of the salt solution.
Paint	Rust-Oleum	245217	Universal General Purpose Gloss Black Hammered Spray Paint. It is used to spray on the Al coupons.
Pan-W polishing pad	LECO	809-505	Used for 15, 6, and 3 µm polishing steps
pH meter	Fisher Scientific	13-636-AP72	It is used for measuring the pH of the salt solution.
Pipette	Thermo Fisher	Scientific	Range: 10 to 1,000 µL

Pipette tip 1	Neptune	2112.96.BS	1,000 µL
Pipette tip 2	Rainin	17001865	20 µL
Silicon carbide paper	LECO	810-251-PRM	Grinding paper, 240 grit
Sputter coater	Cressington	108 sputter coater	It is used for coating the sample.
Tegramin-30 Semi-automatic polisher	Struers	6036127	Coarse/fine polishing/grinding
ToF-SIMS	IONTOF GmbH, Münster, Germany	ToF-SIMS V, equipped with Bi liquid metal ion gun and flood gun	It is used to acquire mass spectra and images of a specimen.
Vibromet 2 vibratory polisher	Buehler	67-1635-160	Final polishing step

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February 17, 2019

Review Editor, Dr. Bing Wu
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Response to Reviewers Letter: Revision of 59523_R1.docx

Dear Dr. Wu,

We appreciated your editorial comments. They are very useful for us to improve the manuscript. We have made all suggested revisions to address your comments. Please let us know if there are any further comments or suggestions.

Here is a point-by-point response to each of the editorial comments as requested. The comments are listed first, and our responses follow each comment.

The revised or added text is highlighted in blue font in the manuscript file for your convenience. We believe that the current version, especially the protocol and the figure description are more comprehensive and easier to follow. We look forward to hearing from you about the decision of this paper in the near future.

Sincerely,

Xiao-Ying Yu, Ph.D.
Senior Scientist

Attachment

1. Response to reviewers' comments;
2. Revised manuscript: a copy with highlighted changes and a copy showing no highlights
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Editorial comments:

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

Reply: The manuscript has been thoroughly re-reviewed after the revision to ensure there are no spelling or grammar issues.

2. For each figure, please provide a title and a short description of the figure in Figure Legend. Please bold the title.

Reply: The title of each figure is provided in bold font. A short description of the figure is also added to explain each figure. The following shortened figure captions are used.

Figure 1. Photos showing the metal-paint interface preparation process.

Figure 2. The schematic of the metal-paint interface analysis by ToF-SIMS and a photo of the IONTOF V instrument.

Figure 3. Comparison of mass spectra acquired from the metal-paint interfaces of Al coupons treated in a salt solution and in air.

Figure 4. Molecular images of chemical species at the metal-paint interface of Al coupons treated in salt solution and in air.

3. Please use h, min, s for time units.

Reply: The time units have been replaced by h, min, s accordingly in the manuscript and result files.

4. If button clicks/menu selections are identified (e.g., quotes or cursive text has been used), change them to bold text. Use either | or > between the clicks/selections. Example: click File > Options > Advanced or File | Options | Advanced

Reply: The button clicks or menu selections have been bolded with quotation marks or cursive format removed. The “>” is applied to the sequential operations in the protocol.

5. Please use µm instead of micron in Table of Materials.

Reply: The word “micron” has been replaced by “µm” in the Table of Materials as suggested.

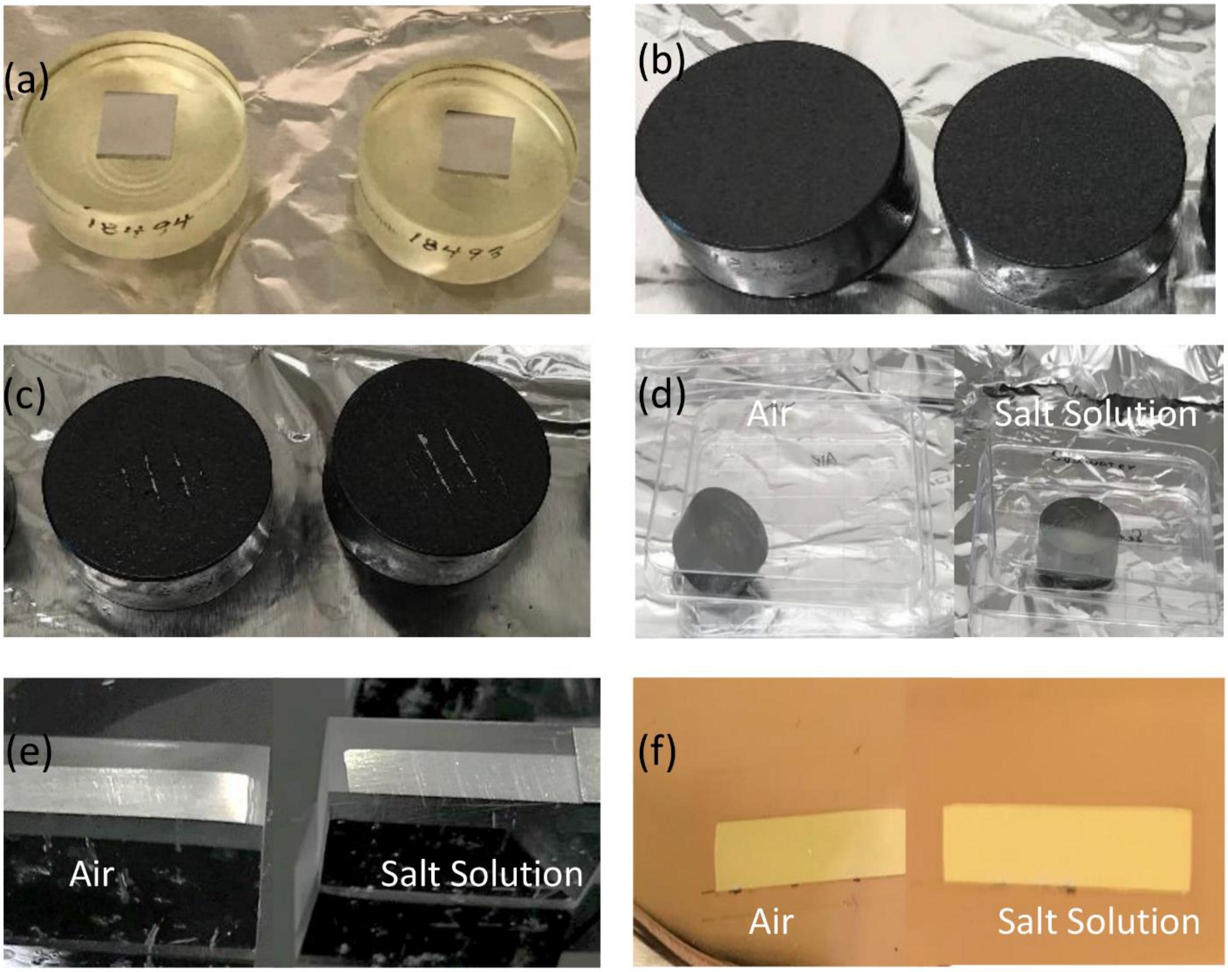

Figure 1. Photos showing the metal-paint interface preparation process.

Figure 1 depicts the metal-paint interface preparation process. After the Al coupons are fixed in the epoxy resin (a), they are sprayed with the commercial paint product and set for 24 h till they are completely dry (b). Four lines are scribed on the paint that is on top of the Al coupons cylinders (c). The carved Al coupon cylinders are exposed to air and salt solution for three weeks in petri dishes, respectively (d). The Al coupon cylinders are cut and trimmed to expose the metal-paint interfaces (e) and coated with gold layers prior to ToF-SIMS analysis (f).

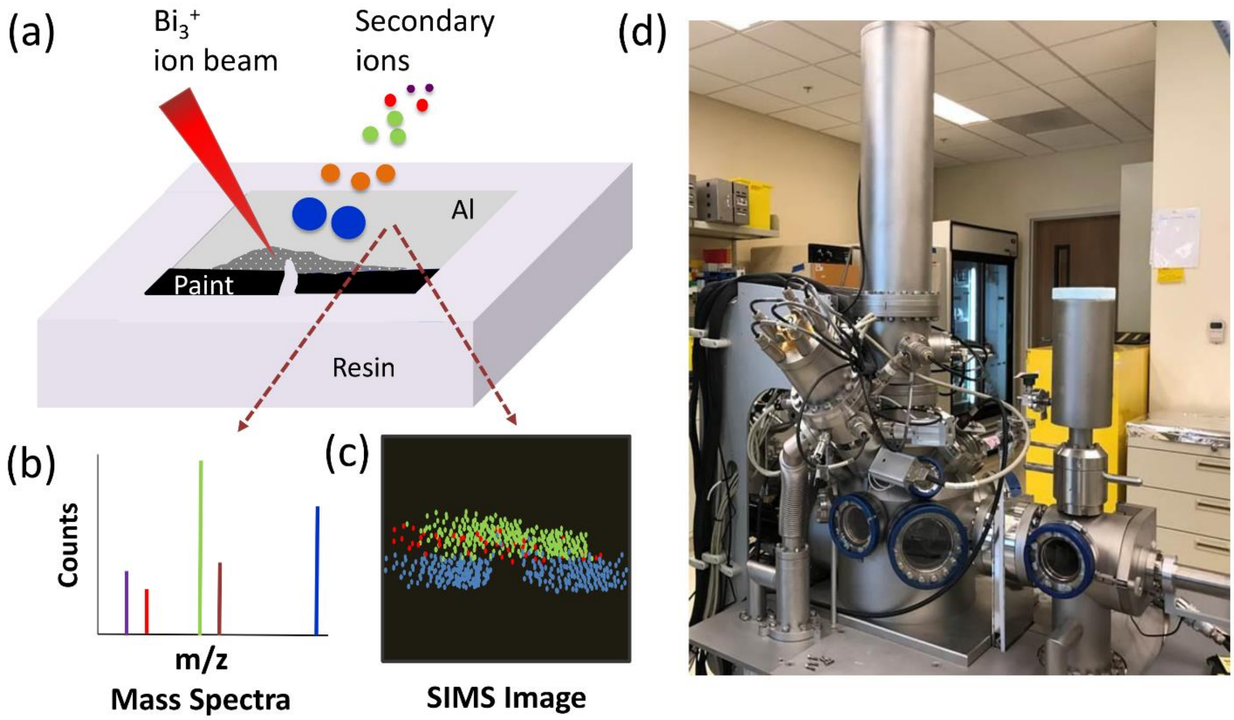

Figure 2. The schematic of the metal-paint interface analysis by ToF-SIMS and a photo of the IONTOF V instrument.

Figure 2 illustrates the analysis process of metal-paint interface using ToF-SIMS. The metal-paint interface (a) is bombarded by Bi_3^+ primary ion beam and generates the secondary ions, resulting in the mass spectra (b) and SIMS image (c). The ToF-SIMS V instrument (d) used for metal-paint interface analysis in this work is displayed.

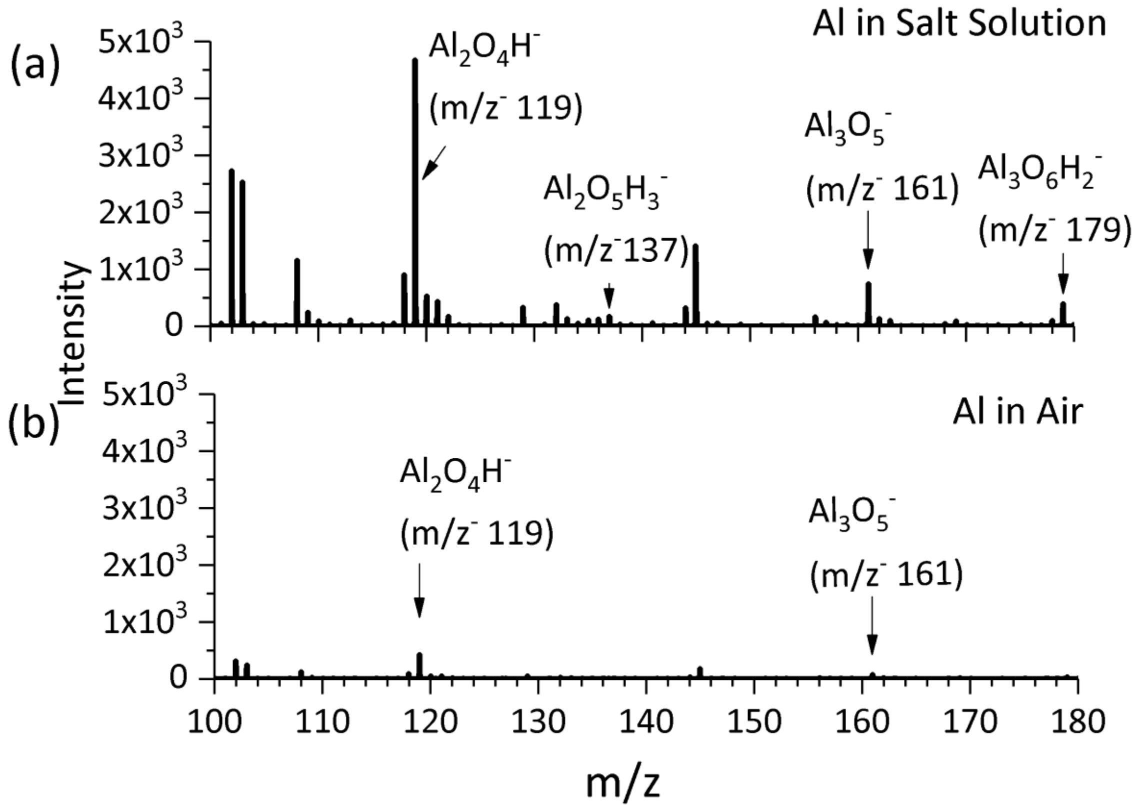

Figure 3. Comparison of mass spectra acquired from the metal-paint interfaces of Al coupons treated in a salt solution and in air.

Figure 3 presents the comparison of mass spectra between the metal-paint interface soaked in a salt solution and the interface exposed to air. The mass spectra of the two samples are acquired using 25 kV Bi_3^+ ion beam scanned in 300 µm x 300 µm ROIs. The mass resolution (m/Δm) of salt solution treated sample is approximately 5600 at peak of m/z^- 26. The raw data of the mass spectra are exported after binning 10 channels. A graphical software is applied to plot the mass spectra for presentation. It is known that the protective layers containing $Al(OH)_3$ are formed after the Al corrosion starts[6]. The oxide ($Al_3O_5^-$) and oxyhydroxide species ($Al_2O_4H^-$, $Al_2O_5H_3^-$, $Al_3O_6H_2^-$) of $Al(OH)_3$ fragments [7] are observed in the metal-paint interface of salt solution exposed Al coupon (Figure 3a) and are more prominent comparing to the same peaks in air-exposed sample (Figure 3b). It indicates that the Al coupon exposed in the salt solution has experienced more severe corrosion comparing to the air-exposed one. The result is consistent with the known knowledge that the solution containing the salts, such as seawater, is chemically aggressive and contributes to the corrosion process of Al alloy.

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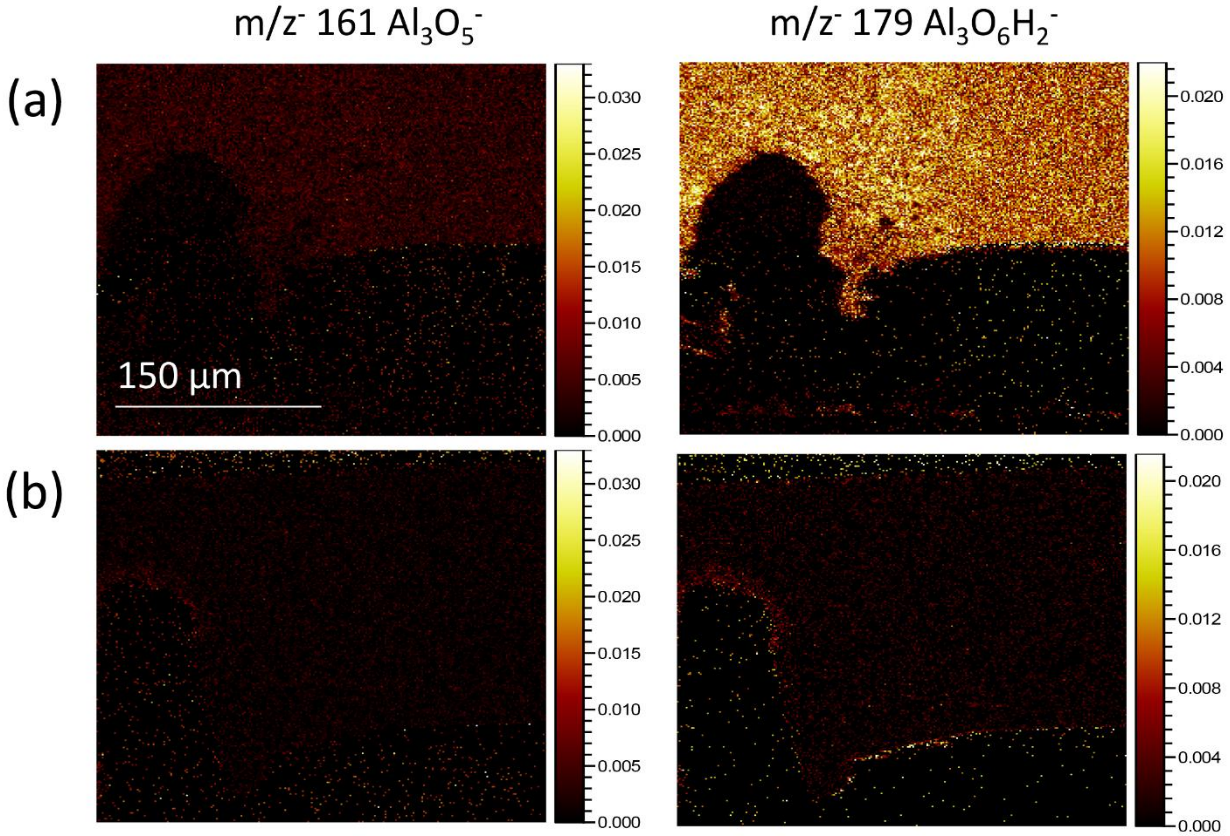

Figure 4. Molecular images of chemical species at the metal-paint interface of Al coupons treated in salt solution and in air.

Figure 4 depicts the 2 dimensional (2D) molecular images of selected Al species m/z^- 161 $Al_3O_5^-$ and 179 $Al_3O_6H_2^-$ acquired from the metal-paint interface treated with salt solution (Figure 4a) and the interface exposed to air (Figure 4b). The depicted ion intensities of m/z^- 161 and 179 are normalized to the intensities of total ions, respectively. The images of the same peak are adjusted to the identical color scale. The images are obtained from 100 scans of 256 x 256 pixels of the 300 × 300 µm ROI. The 2D images provide the distribution of the chemical species of the Al corrosion products in two different samples. The peaks m/z^- 161 and 179 are more prevalent in the metal-paint interface treated with salt solution by displaying stronger intensities than the ones shown in the air-exposed sample. This result agrees with the mass spectra results and further demonstrates ToF-SIMS's analytical capabilities of chemical identification and molecular imaging.

TITLE:

Investigating corrosion at the metal-paint interface using ToF-SIMS

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KEYWORDS:

ToF-SIMS, aluminum, metal-paint interface, corrosion, limit of detection (LOD), mass spectra, 2D imaging

SHORT ABSTRACT:

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was applied to demonstrate the chemical mapping and corrosion morphology at the metal-paint interface of an aluminum alloy after being exposed in a salt solution compared with the specimen exposed in air.

LONG ABSTRACT:

Corrosion developed at the paint and aluminum (Al) metal-paint interface was analyzed using time-of-flight secondary ion mass spectrometry (ToF-SIMS), illustrating that SIMS was a suitable technique to study the chemical distribution at metal-paint interface. The painted Al alloy coupons were immersed in a salt solution and exposed to the air only, respectively. SIMS provided chemical mapping and 2D molecular imaging of the interface, allowing direct visualization of the morphology of the corrosion products formed at the metal-paint interface and mapping of chemical after corrosion occurred. The experimental procedure of this method was presented to provide technical details to facilitate similar research and highlight pitfalls that one may encounter during such experiments.

INTRODUCTION:

Aluminum (Al) alloys have wide applications in engineering structures, such as in marine technology or military automotive, attributable to their high strength-to-weight ratio, excellent formability, and resistance to corrosion. However, localized corrosion of Al alloys is still a common phenomenon which affects their long-term reliability, durability and integrity in various environmental conditions[1]. Paint coating is the most common means for corrosion prevention. Illustration of the corrosion developed at the interface between metal and paint coating can provide insights in determining the appropriate remedy for corrosion prevention.

The corrosion of Al alloys may take place via several different pathways. X-ray photoelectron spectroscopy (XPS) and scanning electron microscope/energy-dispersive X-ray spectroscopy (SEM/EDX) are two commonly applied surface microanalysis techniques in investigating corrosion. XPS can provide elemental mapping but lacks of holist molecular view of the surface chemical information[2-3]. While SEM/EDX provides morphological information and elemental mapping but with relatively low sensitivity.

Time-of-flight secondary mass spectrometry (ToF-SIMS) is another surface tool for chemical mapping with high mass accuracy and lateral resolution. It has low limit of detection (LOD) and capable of revealing the distribution of the corrosion species formed at the metal-paint interface. Typically, SIMS mass resolution can reach 5,000-15,000, sufficient to differentiate the isobaric ions[4]. With its submicron spatial resolution, ToF-SIMS can chemically image and characterize the metal-paint interface. It provides not only morphological information but also the lateral distribution of molecular corrosion species at the top few nanometers of the surface. ToF-SIMS offers complementary information to XPS and SEM/EDX.

To demonstrate the capability of ToF-SIMS in surface characterization and imaging of the corrosion interface, two painted Al alloy (7075) coupons exposed to air only and salt solution, respectively, were analyzed (Figures 1 and 2). Understanding the corrosion behavior at the metal-paint interface exposed to saline condition is critical to understand the performance of the Al alloy in marine environment, for example. It is known that the formation of $Al(OH)_3$ occurs during the Al's exposure to seawater[5], but the study of Al corrosion still lacks comprehensive molecular identification of the corrosion and coating interface. In this study, the fragments of $Al(OH)_3$ including Al oxides (e.g. $Al_3O_5^-$) and oxyhydroxide species (e.g. $Al_3O_6H_2^-$) were observed and identified. The comparisons of SIMS mass spectra (Figure 3) and molecular images (Figure 4) of the negative ions $Al_3O_5^-$ and $Al_3O_6H_2^-$ provided the molecular evidence of the corrosion products formed at the metal-paint interface of the salt solution treated Al alloy coupon. SIMS offers the possibility to elucidate the complicated chemistry occurring at the metal-paint interface, which can help shed light on the efficacy of surface treatments in Al alloys. In this detailed protocol, we demonstrated this effective approach in probing the metal-paint interface to help new practitioners in corrosion research using ToF-SIMS.

PROTOCOL:

1. Corrosion Sample Preparation

1.1. Al Sample fixation in resin and polishing

1.1.1. Mount two Al alloy coupons (1 cm × 1 cm) using epoxy resin in 1.25” metallographic sample cups and place the coupons in the fume hood overnight or till the resin is completely cured.

1.1.2. Take out the Al resin cylinders cups from the sample cups. Polish the Al resin cylinders using 240 grit paper with water at 300 rpm platen/150 rpm in the holder for 1 min.

1.1.3. Polish the Al resin cylinders using the polishing plate with 15 µm, 6 µm, 3 µm, and 1 µm water-based solution for 5 min (each step), sequentially.

1.1.4. Rinse the Al resin cylinders with deionized water (DI) and buff them with cotton.

1.1.5. Rinse the Al resin cylinders again with ethanol and place them in the chemical fume hood till they are dry.

Note: Alternatively, the sample can be dried with pressurized air or nitrogen.

1.2. Prepare Al corrosion sample

1.2.1. Spray the black paint onto each Al resin cylinder twice and let them stand in the fume hood for 24 h. The paint is approximately 100 µm thick.

Note: The paint is a commercial product with primer mixed in one bottle. It is fast drying and rust preventive.

1.2.2. Engrave four parallel lines (5-6 mm long) straight down on the top of each painted Al resin cylinder using scalpels. The lines are in the center of the Al alloys.

1.2.3. Immerse one Al resin cylinder into pH 8.3 salt solution containing NaCl, $MgSO_4$, $MgCl_2$ and KCl with the scribed surface down. Partially cover the 10 × 10 cm^2 petri dish with its lid.

Note: The salt solution is made of 465 mM NaCl, 28 mM $MgSO_4$, 25 mM $MgCl_2$, and 3 mM KCl in 50 mL DI water adjusted by 0.1 M NaOH to reach approximate pH 8.3. The solution contains main ions in seawater. The conductivity of the salt solution is approximately 5.5 S/m. The temperature of the solution is 72 °F.

1.2.4. Place the other Al resin cylinder with scribed surface down in a clean petri dish and cover it with its lid. Keep both samples in the chemical fume hood for three weeks.

1.3. Expose the Corrosion Interface and Mount the Interface in Resin

1.3.1. Cut each Al resin cylinder into two halves using low speed saw with a diamond blade, perpendicularly to the middle of the marked lines, and trim the excessive resin edge.

1.3.2. Mount all the trimmed Al alloy pieces in a 2” sample cup and form an assembly by placing the Al alloy pieces along a circle, with the metal-paint interface facing up. Space out each Al alloy piece.

1.3.3. Repeat steps 1.1.2-1.1.3.

1.3.4. Further polish the metal-paint cross-section in a vibratory polisher affixed to a 2 lbs. weight using 0.05 µm colloidal silica solution on a polishing pad for 4 h.

1.3.5. Repeat steps 1.1.4-1.1.5

Note: The fixation and polishing work is important for acquiring sufficient SIMS signals, because unpolished surface will lead to low intensities of secondary ions signals and poor mass resolution during SIMS analysis.

1.4. Coat the Sample with Sputter Coater

1.4.1. Put the polished metal-paint interface assembly in the sputter coater chamber with the interface side up. Close the lid of the sputter coater and start to pump down the chamber.

1.4.2. Follow the regular sputter coater procedure and deposit a 10 nm gold layer on the metal-paint interface assembly.

Note: The purpose of this sample surface treatment is to reduce the charging effect during SIMS analysis. If the sample is conductive, this step is not necessary.

2. Analyze the Metal-Paint Corrosion Interface Using ToF-SIMS

2.1. Load Samples in ToF-SIMS

2.1.1. Mount the metal-paint interface assembly containing salt solution treated sample and air-exposed control on the **Topmount** sample holder using screws and clips.

Note: The **Topmount** is the name of the sample holder that holds the sample on the top of the sample holder.

2.1.2. Unscrew the locking screw on the loadlock door > click the button **Stop** on the Fpanel window of ToF-SIMS software graphical user interface (GUI) to vent the loadlock chamber.

2.1.3. Open the loadlock chamber by swinging the sample transfer arm to the right > turn the transfer arm counterclockwise till it attaches the pin of the **Topmount** sample holder and then turn it back.

2.1.4. Swing the transfer arm back to close the door of the loadlock and tighten the locking screw on the door to seal the loadlock.

2.1.5. Click the button **Start** on the Fpanel window to pump down the loadlock chamber till it reaches ~1.0E-6 mbar or below.

2.1.6. Click the button **Open** on the Fpanel window to open the gate between the main chamber and loadlock.

2.1.7. Push the sample transfer arm attached with sample holder into main chamber > turn the transfer arm counterclockwise till the sample holder is transferred onto the sample stage in the main chamber.

2.1.8. Retract the transfer arm all the way back > click the button **Close** on the Fpanel window to close the gate between the main chamber and the loadlock.

2.1.9. Select **Topmount.shi** from the drop down menu of the pop-up window > **select the Sample Holder** > click **Ok**. The image of **Topmount** sample holder appears at the right side of the **Navigator** GUI.

2.1.10. Wait until the vacuum level of the main chamber reaches at least 1.0E-8 mbar or below.

2.2. Start the Liquid Metal Ion Gun (LMIG) and Align the Ion Beam

2.2.1. Check the boxes of the **LIMG**, **Analyzer**, and **Illumination** in the **Power Control** window to power up the LIMG, analyzer and light source after the samples are transferred into the main vacuum chamber.

2.2.2. Check the box of **LMIG** shown on the Fpanel window to activate the LMIG setting tab > Click **Start LMIG** from the **Source** subtab under the **LIMG** tab in the **Instrument Window** to activate the LMIG.

2.2.3. Select the predefined file of spectrometry settings in the pop-up window of **Load Settings** > click **Open**.

Note: Bi_3^+ is selected as the primary ion beam. The LMIG energy is set to 25 kV. The LIMG chopper width is set to 25 ns. The other settings including emission current 1.0 □A; the heating value is 2.75 A; the suppressor approximately 800-1000 V; the extractor 10 kV; the lens source 3.3 kV; the cycle time 100 µs and the mass range 1-870 u.

Note: The settings may vary depending on the instrument model, remaining lifetime of LMIG and the acquisition requirement for specific samples.

2.2.4. Select **LMIG** in the pop-up window of **Categories** to load > click **Selected** button > click **OK**.

Note: It takes approximately 5 min to fully start the LIMG.

2.2.5. Select **Positive** from the drop down menu of **Instrument Setup** in Fpanel to determine the ions to be detected.

Note: Select **Negative** from the drop down if negative ions are to be measured.

2.2.6. Select the predefined file of the analyzer settings after clicking the button of **Loading Settings** in the Fpanel to activate analyzer.

Note: The analyzer acceleration is set to 9.5 kV; the analyzer energy is set to 2 kV; the detector is set to 9 kV. The settings of the analyzer may vary due to the configuration of different SIMS models.

2.2.7. Select **Faraday Cup** from the drop down menu of the **Cursor Position** in the **Navigator** GUI > Click **Go** to move the stage to the Faraday cup.

Note: Move the stage to Faraday cup for target current measurement.

2.2.8. Select **Micro** view from the drop down list of **Video** in the **Navigator** GUI to view the position of the Faraday cup.

2.2.9. Click the center of the Faraday cup under the **Micro** view in the **Navigator** GUI > select **Drive to Marked Position** from the drop down menu after right clicking the **SE/SI Primary Gun** window in the **Navigator** GUI.

2.2.10. Select **20 µm × 20 µm** from the drop down menu of **Specify Raster Field of View** after right clicking the **SE/SI Primary Gun** window in the **Navigator** GUI.

2.2.11. Click the button **C** from the **Gun** subtab under **LIMG** tab in the Instrument Window to auto align the ion beam.

2.2.12. Click **Start** button and check the box of **DC** from the **Pulsing** subtab under **LMIG** tab to measure the target current.

2.2.13. Click the **X Blanking** from the **Focus** subtab under LIMG tab and turn the mouse wheel to maximize the target current > click the **Y Blanking** from the same tab to maximize the target current.

Note: The target current of the ion beam measured under the mass spectrometry mode should be greater than 14 nA or greater than 0.5 pA if Bi_3^+ is selected to achieve desired intensities of ion signals.

2.2.14. Click the **Stop** button from the **Focus** subtab to stop the measurement of the target current.

2.3. Adjust the Beam Focus at the Region of Interest (ROI)

2.3.1. Press **Z** button on the joystick control panel > push the joystick up to lower down the sample stage till the extractor cone is above the top of the metal-paint interface assembly.

Note: It is critical to avoid the collision between the extractor cone and samples when conducting this step.

2.3.2. Press **X** and **Y** buttons on the joystick > move joystick left/right and up/down to bring the interface assembly till it displays in the **Macro** view in the **Navigator** GUI.

2.3.3. Switch to **Micro** view in the **Navigator** GUI to locate the region of interest (ROI) of metal-paint interface.

2.3.4. Select ROI to **300 µm × 300 µm** after right clicking the **SE/SI Primary Gun** window to expand the field of the view.

2.3.5. Select the signal type **SI**, raster size **128 × 128 pixel** and raster type **Random** from the **SE/SI Primary Gun** in **Navigator** GUI.

2.3.6. Click the black triangle button and the **Adjust SI** button in the **SE/SI Primary Gun** window. The round shape of secondary ion (SI) image of the ROI will appear in the **SE/SI Primary Gun** window.

2.3.7. Press **Z** button on the joystick control panel > move the joystick up or down to bring the round shape of SI image to the center of the cross hair in the **SE/SI Primary Gun** window.

Note: If the cross hair is in the middle of the round shape of SI image, it indicates that the image is obtained with good focus.

2.3.8. Uncheck the **Adjust SI** button > click the square button in the **SE/SI Primary Gun** window to stop the focus adjustment.

2.4. Remove the Surface Coating and Contamination Using the High Current Mode/DC mode

2.4.1. Select the SE image from the drop down menu of **SE/SI Primary Gun** window to observe the DC cleaning progress.

2.4.2. Check the box of DC in the Fpanel > click the black triangle button to start DC cleaning.

Note: Keep the DC on for 10 s or till the SE image indicates the gold layer is removed. The duration of DC cleaning may vary depending on the thickness of the coating.

2.4.3. Click the black square button to stop the DC cleaning when the gold coating is removed under the observation via **Micro** view in the **Navigator** GUI.

2.4.4. Switch SE image to SI image in the **Navigator** GUI.

Note: The reason of using DC beam is because the DC beam (~14 nA) is powerful enough to remove the Au coating and other surface contamination, while the pulsed beam current (~1 pA) is not adequate.

2.5. Enable Surface Charge Compensation Using Flood Gun

2.5.1. Check the **Flood Gun** box in the Fpanel to enable the charge compensation.

2.5.2. Click the button **Load Setting File** in Fpanel > select predefined file of flood gun settings after clicking the **Loading Settings** to load the settings of the flood gun.

Note: The settings of flood gun include the following: energy 20 V, anode 300 V, delay 2.0 µs, flood gun filament current 2.4 A, and flood gun lead off 2.0 µs. The settings of flood gun may vary for different instrument.

2.5.3. Repeat steps 2.3.6-2.3.7 to re-adjust the focus on the ROI.

Note: As soon as the Au coating is removed, the height of ROI will change. Thus, it is necessary to re-adjust the focus.

2.5.4. Click the **Reflector** from the **TOF** subtab of **Analyzer/Main** tab in the Instrument Window.

2.5.5. Click the value on the left side of the bar of **Reflector** to decrease the voltage of the reflector till the round shape of SI image disappears. Then increase the reflector voltage by 20 V.

Note: This process is done to ensure a flat imaging surface and maximize SI signals. In the negative mode, increase the reflector voltage till the round shape of SI image disappears and then bring it down 20 V.

2.5.6. Repeat the step 2.3.8 to stop the focus and reflector voltage adjustment.

2.6. Acquire High Resolution Mass Spectrum

2.6.1. Click the icons of the **Spectrum** and **Image** in Fpanel to open the spectrum and images programs.

2.6.2. Display the selected ROI of the metal-paint interface in **Micro** view.

2.6.3. Click the triangle button ▶ in **Navigator** GUI to start a quick scan and a SIMS spectrum will appear in the **Spectrum** program > click the black square to stop the quick scan.

Note: The quick scan should only take several scans, usually takes a few seconds.

2.6.4. Select the **Mass Calibration** from the drop down list of the **Spectrum** on the tool bar of the **Spectrum** program or simply press **F3** to bring up the mass calibration window after quick scan is completed.

2.6.5. Select recognized peaks to calibrate the mass spectrum by clicking the corresponding peaks > add the formula in the mass calibration window > click **OK** to exit the mass calibration window when peak selection is done.

Note: CH_3^+, $C_3H_3^+$, and $AlOH^+$ are selected for calibrating positive mass spectrum; while OH^- and CN^- and AlO^- are selected for calibrating the negative mass spectrum.

Note: The peaks selected for mass calibration may vary for different samples. The deviation of the selected peaks is less than 30 ppm to ensure the accurate peak identification.

2.6.6. Add the peaks of interests to the peak list by clicking the peak of the selected ions in the spectrum and clicking **Add Peak** button on the tool bar.

2.6.7. Click the red triangle button ▶ in Fpanel to open the **Start Measurement** window.

2.6.8. Set Raster type to **Random**, **128 × 128 pixel**, **1 shot/pixel** > set the **Number of Scans** to 60 scans in the pop-up window > click **OK** to start the mass spectrum acquisition of the ROI.

Note: The mass spectrum acquisition will automatically stop after the desired number of scans are acquired.

2.6.9. Click **Save File** in the Fpanel to save the acquired mass spectrum and name it with designated file name, e.g., salt solution treated, air-exposed.

2.6.10. Switch the polarity to **Negative** in Fpanel and repeat steps 2.5.3-2.6.9 to acquire the negative mass spectrum for the same ROI.

Note: SIMS mass spectra of four different ROIs of each sample were acquired for the positive and negative polarities in this study.

2.7. Save the Analyzed ROI Position for Additional Analysis

2.7.1. Click the **Add** button in **Navigator** GUI > input the name of the ROI in the pop-up window, e.g., salt solution 1.

2.7.2. Click **Stage Pos** button > click **OK** button to save the ROI location.

Note: The ROI position is saved for additional SIMS imaging analysis.

2.8. Acquire High Resolution SIMS image

2.8.1. Click the button **Load Setting File** in Fpanel > select the predefined imaging setting file > click **Open** to load the imaging settings.

Note: The highest lateral resolution or the smallest spot size is optimized in the collimated mode, i.e., DC mode. In this mode, the smallest aperture in the beamline determines the angle of the aperture. According to the configuration setting of the ToF-SIMS, the highest lateral resolution is when the DC current is approx. 50 pA and the focus can reach around 100 nm. To achieve this resolution, increase Lens Source while observing the DC current going down, and optimize the X Blanking and Y Blanking, till the final DC current reaches 50 pA.

Note: The following lists the detailed parameter settings of the imaging mode. Bi_3^+ is selected as the primary ion beam. The LMIG energy is set to 25 kV. The LIMG chopper width is set to 100 ns and chopper offset is set to 30.9 ns. The other settings including emission current 1.0 �A; the heating value is 2.75 A; the suppressor approximately 800-1000 V; the extractor 10 kV; the lens source 3.5 kV; the cycle time 100 µs and the mass range 1-870 u.

2.8.2. Select **LMIG** in the pop-up **Categories to Load** window.

2.8.3. Repeat the steps 2.2.7-2.2.14 to measure the target current and align the ion beam.

Note: the desired target current in imaging mode should be greater than 0.6 nA or approximately 1 pA if $Bi_3^+$is selected for measurement

2.8.4. Select the saved ROI position from the drop down list of **Cursor Position** in **Navigator** GUI > click **Go**.

Note: This step ensures that the mass spectrum and image mapping are acquired from the same ROI.

2.8.5. Repeat steps 2.5.4 -2.5.5 to adjust reflector voltage.

2.8.6. Repeat steps 2.6.3 -2.6.6 to conduct the mass calibration in the imaging mode.

Note: If the software cannot register the selected peaks when doing the mass calibration, check the box **Use Selected Channel** in **Mass Calibration** window.

2.8.7. Repeat steps 2.6.7-2.6.8 to collect the image data.

Note: In imaging mode, set raster type to **Random**, **256 × 256 pixel**, **1 shot/pixel >** set the **Number of Scans** to 150 scans > click **OK** to start the image acquisition of ROI. The image resolution and scan can be different and they should be determined depending on the sample.

2.9. Retrieve the sample from the Vacuum Chamber

2.9.1. Select **Transfer** from the drop down list of the **Cursor Position** in the **Navigator** GUI > click **Go** button to bring the sample stage near the gate.

2.9.2. Open the gate by repeat the step 2.1.6.

2.9.3. Push the sample transfer arm into the main chamber > turn the arm rod clockwise and forward till it attaches the pin of the sample holder.

2.9.4. Turn the transfer arm back and retract it all the way back.

2.9.5. Close the gate by clicking the button **Close** on the Fpanel > select **No sample holder** in the pop-up **Select Sample Holder** window.

2.9.6. Unscrew the locking screw on the door of the loadlock > click the button **Stop** in Fpanel to vent the loadlock.

Note: Venting takes approximately 3-5 min.

2.9.7. Swing the transfer arm to the right > turn the transfer arm rod counterclockwise to release the sample holder.

2.9.8. Swing the transfer arm back > tighten the locking screw on the door of the loadlock.

2.9.9. Click **Start** button in Fpanel to pump down the loadlock.

2.9.10. Take off the metal-paint interface resin assembly from the sample holder and place them in the clean petri dish.

2.10. Turn off LIMG

2.10.1. Click **Stop LMIG** from subtab under LMIG tab in **Instrument Window**.

2.10.2. Uncheck the boxes of **LMIG** and **Flood Gun** in Fpanel > uncheck the box of **Illumination** in the **Power** window.

3. Analyze ToF-SIMS Data

3.1. Export SIMS Spectrum Data

3.1.1. Click the **File** on the tool bar of the **Spectrum Program** window > select the **Export** from the drop down list.

3.1.2. Name the spectrum file and save it in the designated folder as .txt file > click **OK**.

3.1.3. Type number 10 in the pop-up window to define the binning channel > click **Ok**.

Note: Binning 10 channels before exporting the mass spectra is commonly used method for reducing the data size while still keeping the mass resolution and accuracy.

3.1.4. **Export SIMS Image Data**

3.1.5. Click the **Image Program** icon > double click the acquired image files to display the SIMS images.

3.1.6. Drag the image of a specific chemical species from the list to the image display window > double click that image to open the image process window below.

3.1.7. Normalize the image of the selected chemical species to the images of total ions by choosing **Normalize** from the drop down list of the image process window.

3.1.8. Apply the same color scale to compare the chemical distribution between different samples by adjusting the color scale in the image process window.

Note: The raw data of images can be exported and plotted using other graphical software.

REPRESENTATIVE RESULTS

Figure 1 depicts the metal-paint interface preparation process. After the Al coupons are fixed in the epoxy resin (a), they are sprayed with the commercial paint product and set for 24 h till they are completely dry (b). Four lines are scribed on the paint that is on top of the Al coupons cylinders (c). The carved Al coupons cylinders are exposed to air and salt solution for three weeks in petri dishes, respectively (d). The Al coupon cylinders are cut and trimmed to expose the metal-paint interfaces (e) and coated with gold layers prior to ToF-SIMS analysis (f).

Figure 2 illustrates the analysis process of metal-paint interface using ToF-SIMS. The metal-paint interface (a) is bombarded by Bi_3^+ primary ion beam and generates the secondary ions, resulting in the mass spectra (b) and SIMS image (c). The ToF-SIMS V instrument (d) used for metal-paint interface analysis in this work is displayed.

Figure 3 presents the comparison of mass spectra between the metal-paint interfaces treated with salt solution and interface exposed to air. The mass spectra of the two samples are acquired using 25 kV Bi_3^+ ion beam scanned in 300 µm x 300 µm ROIs. The mass resolution (m/Δm) of salt solution treated sample is approximately 5600 at peak of m/z$^-$ 26. The raw data of the mass spectra are exported after binning 10 channels. A graphical software is applied to plot the mass spectra for presentation. It is known that the protective layers containing $Al(OH)_3$ are formed after the Al corrosion starts[6]. The oxide ($Al_3O_5^-$) and oxyhydroxide species ($Al_2O_4H^-$, $Al_2O_5H_3^-$, $Al_3O_6H_2^-$) of $Al(OH)_3$ fragments [7] are observed in the metal-paint interface of salt solution exposed Al coupon (Figure 3a) and are more prominent comparing to the same peaks in air-exposed sample (Figure 3b). It indicates that the Al coupon exposed in the salt solution has experienced more severe corrosion comparing to the air-exposed one. The result is consistent with the known knowledge that the solution containing the salts, such as seawater, is chemically aggressive and contributes to the corrosion process of Al alloy.

Figure 4 depicts two dimensional (2D) molecular images of selected Al species m/z$^-$ 161 $Al_3O_5^-$ and 179 $Al_3O_6H_2^-$ acquired from the metal-paint interface treated with a salt solution (Figure 4a) and the interface exposed to air (Figure 4b). The depicted ion intensities of m/z$^-$ 161 and 179 are normalized to the intensities of total ions, respectively. The images of the same peak are adjusted to the identical color scale. The images are obtained from 100 scans of 256 x 256 pixels of the 300 × 300 µm ROI. The 2D images provide the distribution of the chemical species of the Al corrosion products in two different samples. The peaks m/z$^-$ 161 and 179 are more prevalent in the metal-paint interface treated with salt solution by displaying stronger intensities than the ones shown in the air-exposed sample. This result agrees with the mass spectra results and further demonstrates ToF-SIMS's analytical capabilities of chemical identification and molecular imaging.

FIGURE & TABLE LEGENDS:

Figure 1. Photos showing the metal-paint interface preparation process.

Figure 2. The schematic of the metal-paint interface analysis by ToF-SIMS and a photo of the IONTOF V instrument.

Figure 3. Comparison of mass spectra acquired from the metal-paint interfaces of Al coupons treated in a salt solution and in air.

Figure 4. Molecular images of chemical species at the metal-paint interface of Al coupons treated in salt solution and in air.

DISCUSSION:

ToF-SIMS differentiates the ions according to their time of flight between two scintillators. The topography or sample roughness affects the flight time of ions from different starting positions, which usually leads to poor mass resolution with increased width of peaks. Therefore, it is critical that the ROIs being analyzed is very flat to ensure good signal collection[8].

Another pitfall to avoid is charging. Since the Al-paint interface was fixed with the insulating resin, charging was expected. Charge accumulates on the sample surface as the ROI is bombarded with the primary ion beam, affecting the kinetic energies of ions that emitted from the surface. Charging results in wide peaks and decreased mass resolution. To avoid the negative influence of this effect, 10 nm gold was sputtered on the interface surface to form the conductive path prior to SIMS analysis. Other methods can be applied to reduce the charging effect include applying the flood gun, optimizing the voltage of the reflector, and selecting Random mode as the beam raster pattern. The flood gun generates a stable electron current with low energy. It is commonly used for charge compensation during the SIMS analysis.[9-11] In addition, the voltage of the reflector, an ion optic that enhances the mass resolution, needs to be adjusted depending on the degree of charging. ToF-SIMS software provides an efficient way to optimize the reflector as described in step 2.5.5. The selection of Random mode as the beam raster pattern before acquiring SIMS data further reduces the charging effect. This mode mitigates the problem occurs in the row-by-row scanning mode, allowing the accumulated charge having more time to dissipate[9, 11].

ToF-SIMS can be equipped with multiple ion sources, including but not limited to Cs^+, C_{60}^+, Bi_n^+. Polyatomic ion sources (e.g. Bi_3^+, C_{60}^+) produce higher yields of secondary ions emitted from the sample surface compared to atomic ion beams (e.g. Cs^+, Bi_1^+) [12-13]. Furthermore, comparing Bi_3^+ to C_{60}^+, Bi_3^+ is more surface sensitive to low mass fragments and thus has higher lateral resolution with better images[12]. Therefore, Bi_3^+ was selected as the analysis beam in this work since we focused on the low mass peaks related to the aluminum corrosion species.

ToF-SIMS is a sensitive surface technique that can provide chemical specificity with high spatial resolution[14]. Other surface tools applied in corrosion study include XPS and SEM/EDX[2, 15-17]. XPS can provide quantitative measurements of the chemical state and electronic state of the elements that exist within a sample but with a higher LOD (0.1 %) than SIMS (ppb-ppm level)[18-19]. Another surface analysis tool commonly applies for corrosion research is SEM/EDX. However, SEM/EDX is not as sensitive as ToF-SIMS, SEM is often used to obtain the surface morphological features. In addition, the chemical mapping of SIMS gives visualization of the molecular ion distribution at the corrosion interface; while SEM/EDX only provides the elemental ions mapping. SIMS's molecular mapping is more informative in investigating the interfacial corrosion process.

This work demonstrates that ToF-SIMS is a powerful tool in deciphering the corrosion speciation at the interface due to its low LOD, high mass resolution, and high spatial resolution. Furthermore, SIMS offers multimodal microanalysis, attributable to its quasi non-destructive nature. Thus, the same sample can be analyzed by other analytical tools and provide comprehensive information. Ideally, the integration of SIMS, XPS and SEM can provide more comprehensive insights of the corrosion behavior at the metal-paint interface.

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DISCLOSURES:

The authors have nothing to disclose.

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