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Preparation of Aluminum Oxide Films Under Water Exposure – Preliminary Report on 1100 Series Alloys

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August 2018

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LIST OF ABBREVIATIONS

ASNF	Aluminum-Clad Spent Nuclear Fuel
ATR	Advanced Test Reactor
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
XRD	X-Ray Diffraction

1.0 Summary

This report describes laboratory experiments performed to produce oxyhydroxide (oxide) films on aluminum 1100 series alloy substrates at various water/temperature conditions. The aluminum alloys selected in this program are types used on aluminum-clad research reactor fuel, and the water/temperature conditions are selected to produce film structures that would be prototypic to those formed on the fuel as a result of reactor exposure and post-discharge water and/or dry storage exposure.

The experimental set-up and results to characterize the oxide morphology, thickness, structure, and chemical composition are reported. The results from this work will be compared to oxide characterizations of fuel cladding alloys that have been exposed to actual reactor and post-discharge service conditions. The aim is to develop a laboratory protocol to produce specimens for further studies for response under drying and radiation conditions.

The work in this report is interim results and preliminary information prepared under Task 6, Milestone 6.1 in TTQAP SRNL-RP-2018-00610 as part of the action plan described in Ref. [1]. Additional experimental milestones are in progress and will be reported upon completion.

2.0 Background: Literature data on morphology of aluminum oxides formed in water

Several studies in the literature have investigated the morphology and composition of the oxide layer resulting from water exposure, providing points of comparison for the structures observed in present experiments. Bernard and Randall [2], Vedder and Vermilyea [3], and Alwitt [4] discussed the composition and morphology of hydroxides grown on nominally pure aluminum samples at water temperatures ≤100°C without forced flow. Underhill and Rider [5] and Rider and Arnot [6] considered 2024 and 7075 Al alloys in 40-100°C without forced flow. Vedder and Vermilyea [3] covered a range of pH while the others used distilled water. Pawel et al. [7] and Griess et al. [8] described more limited observations of the composition and appearance of films grown under forced flow with heat flux through the surface.

Underhill and Rider [5] and Rider and Arnot [6] (2000) took SEM images showing the evolution of the oxide surface structure at different stages of short-term (≤2 h) immersion times for Al 2024 and 7075 alloys immersed in 40°C, 50°C, and boiling water without forced flow (Figure 2-1, Figure 2-2, and Figure 2-3). The oxides grown in 40-50°C water (Figure 2-1 and Figure 2-2) appear to start as isolated particles on the surface of the aluminum and then grow into a highly porous, spongelike oxide structure over the first hour of immersion [5]. The hydroxide was identified as pseudoboehmite based on IR spectra [5]. Given the temperature range of 40–50°C, the pseudoboehmite would be expected to age into gibbsite or bayerite for longer immersion times. The oxide thickness, measured by atomic force microscopy after chemically removing a section of the film to expose the bare substrate, increased approximately linearly with sample weight gain per unit surface area with a slope corresponding to 0.52±0.03 cm^3/g [5]. A simple comparison of the apparent film density $1/(0.52\ \text{cm}^3/\text{g}) = 1.92\ \text{g/cm}^3$ with the measured density of pseudoboehmite (2.4 g/cm^3 [2]), gibbsite (2.42 g/cm^3 [9]), or bayerite (2.53 g/cm^3 [9]) suggests a porosity on the order of 20-24%. The oxide grown in boiling water displayed a similar porous, spongelike morphology after 30 s of immersion (Figure 2-3). After 30 minutes of immersion in boiling water, the oxide appeared to form platelets oriented roughly perpendicular to the surface with random orientation about the axis perpendicular to the surface. The edges of the platelets result in a “needle-like” appearance. This structure remained evident through the rest of the images (up to 240 minutes exposure), and the average length and thickness of the platelets appear to increase over time.

Vedder and Vermilyea [3] performed immersion tests in distilled water for thin films (~1 μm) of aluminum evaporated onto glass cover slides with and without anodic Al_2O_3 films, as well as for aluminum foil to corroborate results for the evaporated thin films. They found consistent results between the evaporated films and foil, and also concluded that the oxide morphology grown on preexisting anodic oxide was similar or identical to that grown on fresh aluminum surface. For a film with an anodic oxide immersed in 100°C distilled water for 30 minutes, they observed platelets with their edges oriented towards the water, about 300 Angstroms thick and 1500 Angstroms wide, by using TEM images of a carbon replica cast from the hydroxide-water interface [3]. They stated that the platelets were visible after only 1 minute of immersion in 100°C, and that the exposed surface morphology remained essentially the same for immersion times above 1 minute [3] . For "longer" immersion times, "mounds of platelets" were sometimes observed, which were assumed to result from localized "excessively active areas" [3] . The hydroxide-metal interface after 3 minutes of immersion in boiling water was found to be smooth to a resolution of 300 Angstroms, except along the grain boundaries where the oxide penetrated further into the base metal [3]. Based on infrared spectroscopy, they identified the hydroxide as pseudoboehmite; however, XRD on the same sample was apparently inconclusive [3]. Deuterium exchange was performed to gain insight into the length-scale of the oxide structures. Based on deuteration rates and the diffusion coefficient for deuterium in boehmite, they concluded that most protons (and thus most hydroxy groups) were within 6 Angstroms of the surface, suggesting that the platelets were very thin and surrounded by water-accessible pores [3].

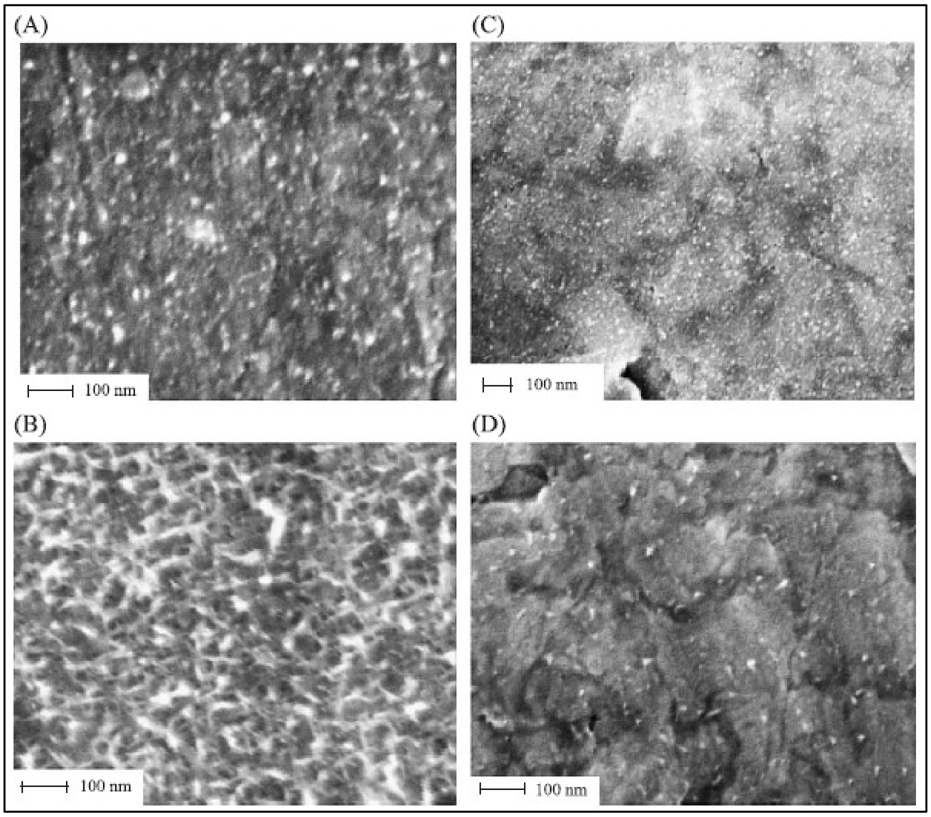


Figure 2-1. SEM images of 2024 (top) and 7075 (bottom) aluminum after immersion in 40°C water for 30 min (left) or 60 min (right). (Fig. 12 of [5])

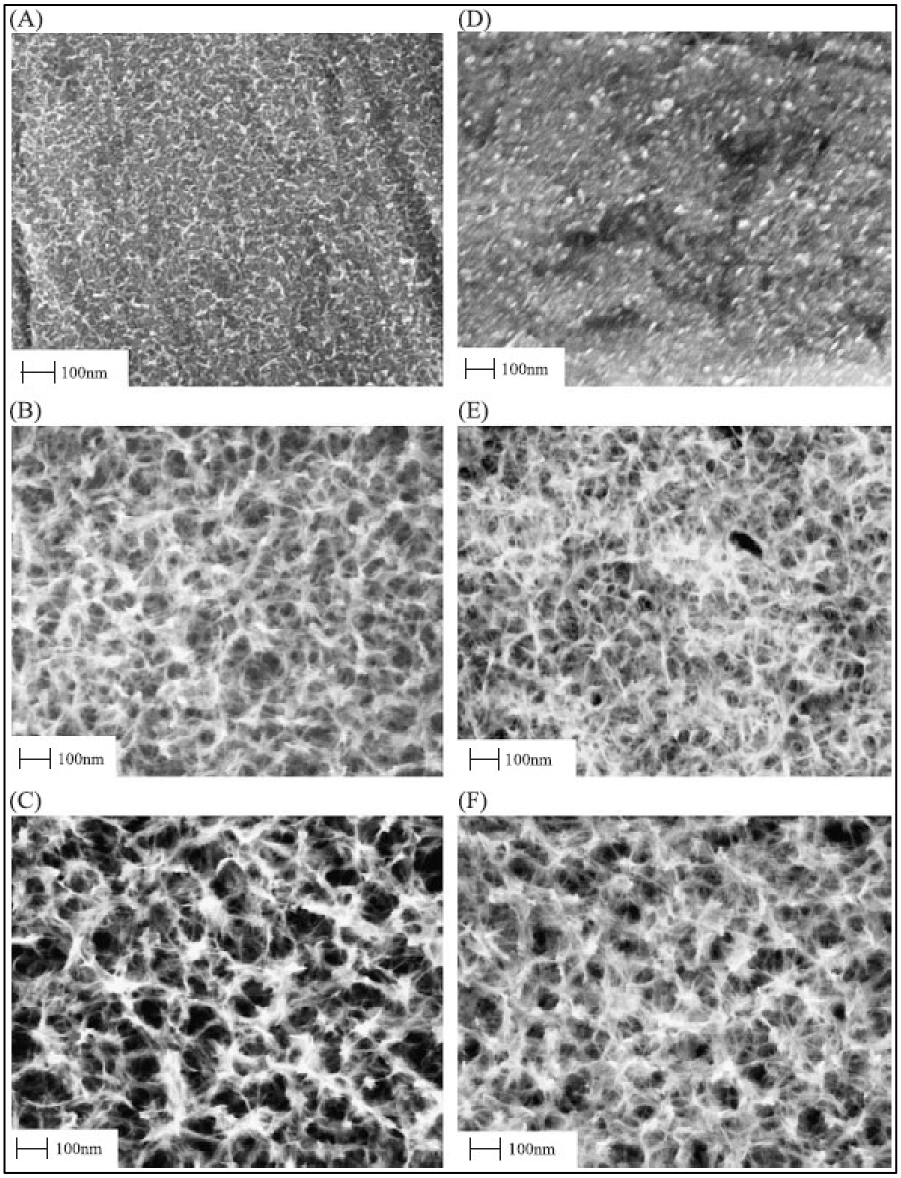
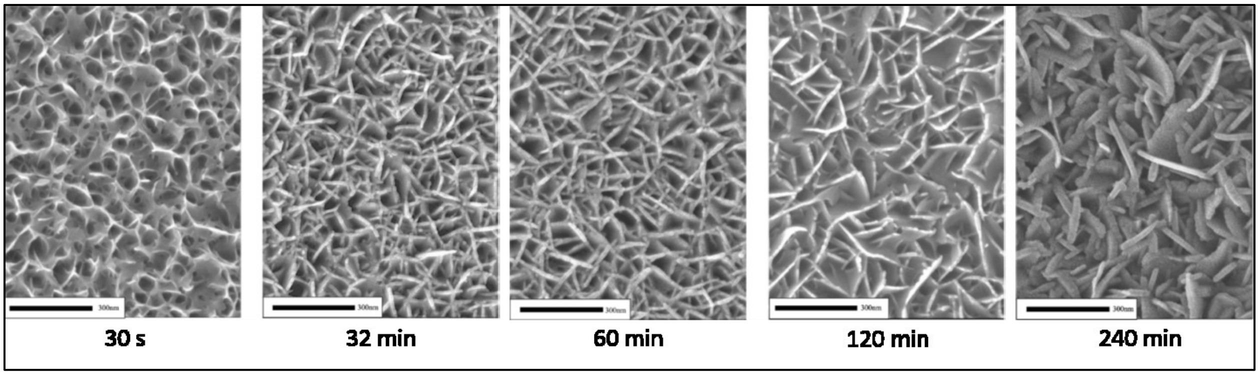


Figure 2-2. SEM of 2024 (left) and 7075 (right) aluminum after immersion in 50°C water for 10 min (top row), 30 min (middle row), and 60 min (bottom row). (Fig. 13 from [5])



30 s 32 min 60 min 120 min 240 min

Figure 2-3. SEM images of 2024 aluminum after immersion in boiling water for various amounts of time. (From Figures 1-5 of [6])

3.0 SRNL Oxyhydroxide Growth Experiments

3.1 Experimental setup

Oxyhydroxides were grown on aluminum substrates primarily using a hot wall immersion method in the experimental setup shown in Figure 3-1. This setup heats the water bath through the aluminum sample, providing a heat flux across the sample from one face to the other, and is suitable for replicating conditions in which heat flows in a prescribed direction (e.g. heat transferred to Al fuel cladding in reactor as well as during spent fuel pool storage due to attendant decay heat). The magnitude of the heat flux is not imposed at a set value, but instead varies as needed to maintain the water bath at the specified temperature that is targeted at the reactor pool and cooling pool temperatures. In the hot-wall setup, only one face of the substrate is exposed to the water. Growth tests spanned temperatures from 50°C to 100°C to grow both low and high temperature oxyhydroxides (gibbsite or bayerite and boehmite, respectively).

To assess the effect of the heat flux, an isothermal immersion test was also conducted for some samples. The isothermal test was conducted in parallel with a hot-wall test by fully immersing a second aluminum substrate of the same geometry in the water-bath portion of the hot-wall apparatus. Thus, a pair of samples was exposed to the same water bath conditions, one hot-wall sample with the heat flux through it (with one face exposed to the water) and one isothermal sample with no heat flux through it (exposed to water on all surfaces).

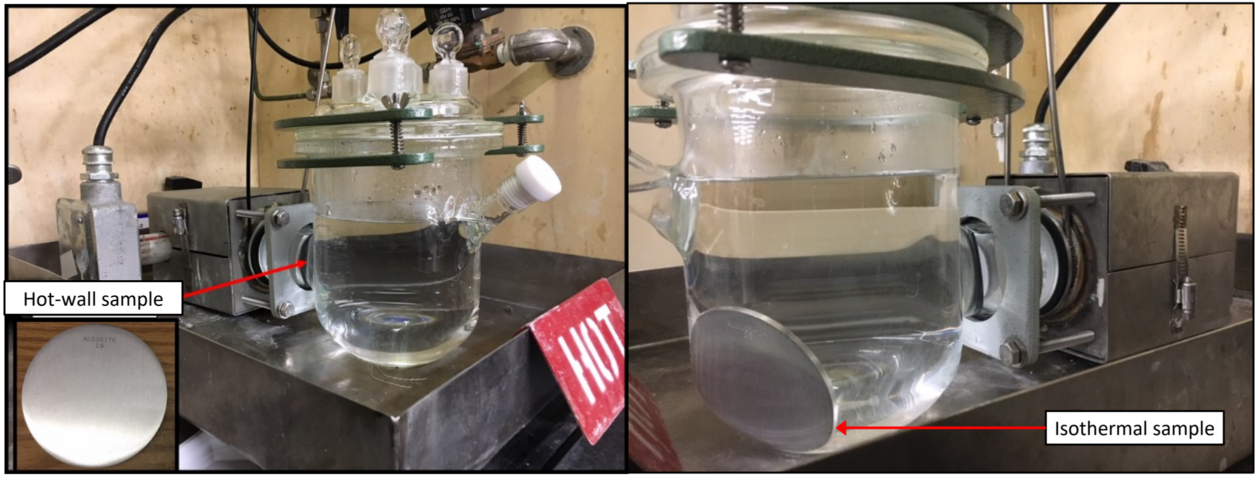


Figure 3-1. Experimental setup for hot wall immersion experiments, showing the locations of (left) the hot-wall samples and (right) the isothermal immersion samples, when applicable.

All tests were conducted by immersion in liquid water at atmospheric pressure. The duration of initial oxyhydroxide tests varied from 7 to 41 days. Following immersion testing by either method, aluminum substrates were removed and sectioned into multiple samples. These samples were used to conduct characterization of the oxyhydroxide layers, including scanning electron microscopy (SEM) and X-ray diffraction (XRD) compositional analysis.

3.2 Results

3.2.1 Hot-wall immersion at 50°C for 29 days

Figure 3-2, Figure 3-3, and Figure 3-4 show results for the oxyhydroxide film resulting from hot-wall immersion in 50°C water for 29 days. The samples were stored in a bag between the end of the immersion test and characterization. XRD indicated that the film was bayerite (Figure 3-2), which is the expected phase for low temperature (less than ~80°C) in neutral water [10]. SEM images of the surface morphology (Figure 3-3) showed a scaly appearance, suggesting that it consisted of platelets of bayerite parallel to the substrate. Images of the oxyhydroxide layer cross-section (Figure 3-4) showed a total film thickness ranging from about 3 to 6 µm. The structure appeared to consist of two, ~2-µm-thick layers of similar coloring separated by a dark line. The outer layer appeared to be divided into segments of a few microns in length in the direction parallel to the substrate, with corresponding waves in the outer profile of the oxyhydroxide film. These segments may correspond to the “scale” structures observed in Figure 3-3.

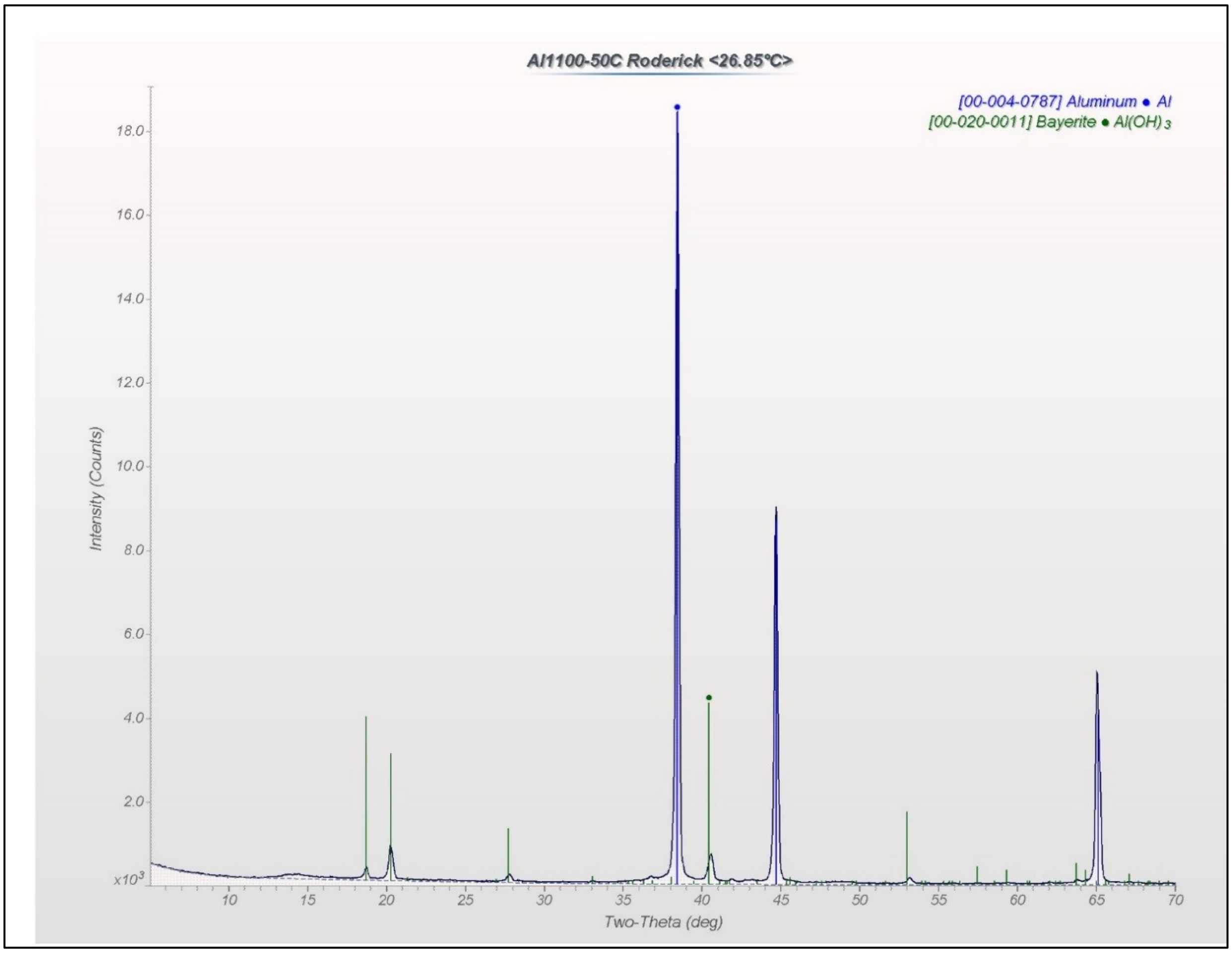


Figure 3-2. XRD spectrum for a hot-wall sample exposed to 50°C water for 29 days, followed by 14 days storage in a bag prior to characterization. The oxyhydroxide layer consists of bayerite, as expected.

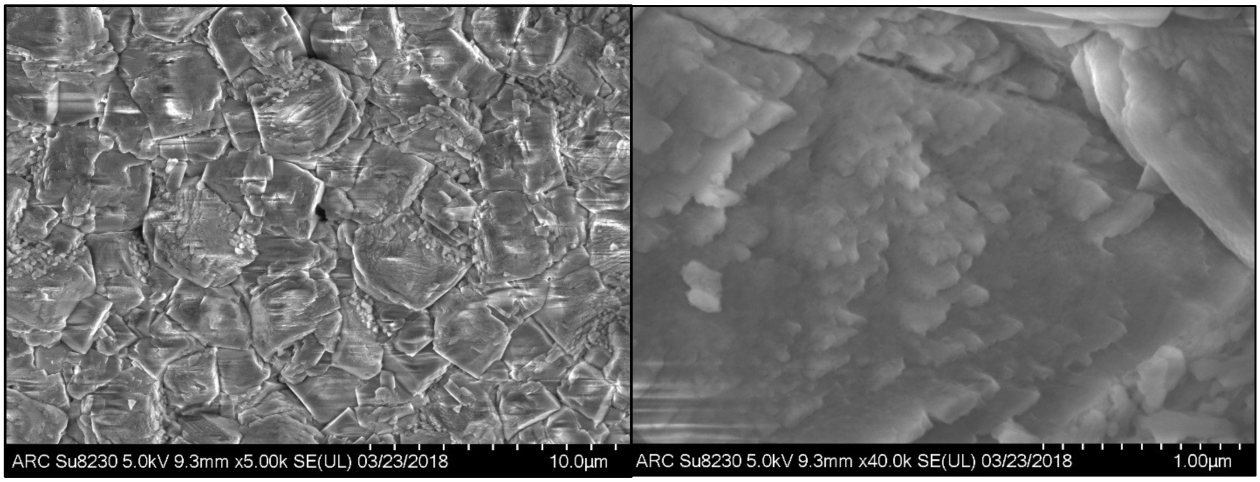
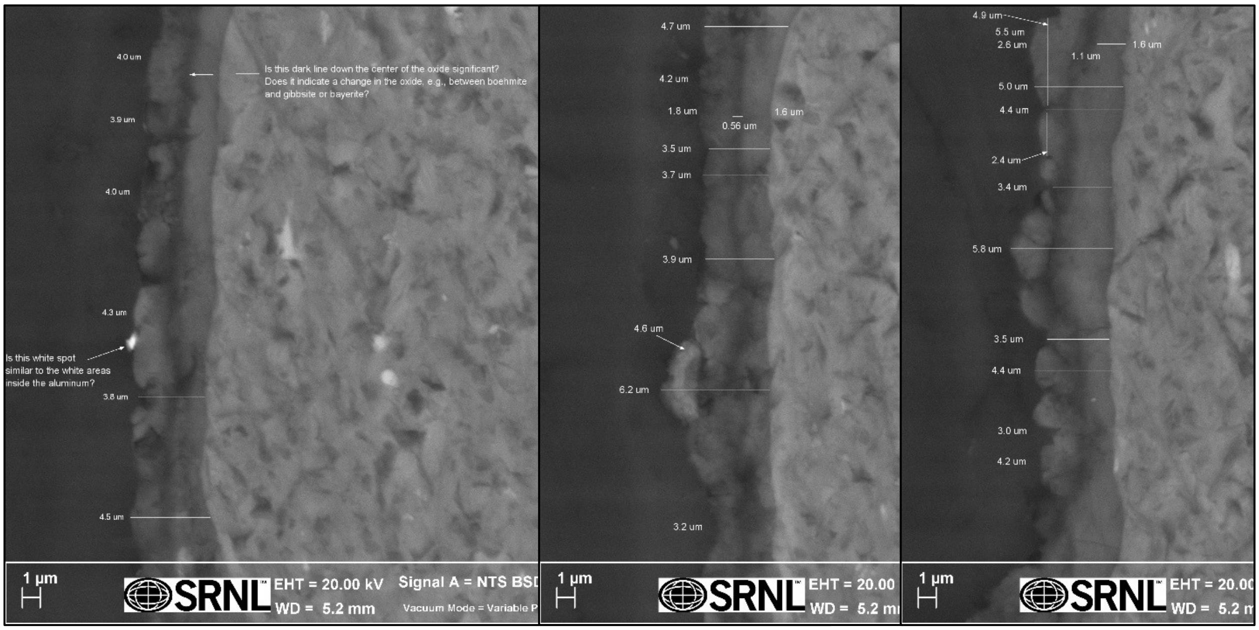


Figure 3-3. SEM images of oxyhydroxide layer surface morphology for a hot-wall sample exposed to 50°C water for 29 days, followed by 16 days storage in a bag prior to imaging, at two different levels of magnification (x5k on left and x40k on right). The morphology has a scaly appearance suggesting platelets of oxyhydroxide parallel to the substrate.


Is this dark line down the center of the oxide significant? Does it indicate a change in the oxide, e.g., between boehmite and gibbsite or bayerite?

Is this white spot similar to the white areas inside the aluminum?

Figure 3-4. SEM images of oxyhydroxide layer cross-sections for a hot-wall sample exposed to 50°C water for 29 days, followed by 29 days stored in a bag prior to imaging. Total oxyhydroxide layer thickness ranges from approximately 3 to 6 µm and appears to consist of two layers separated by a darker line.

3.2.2 Hot-wall immersion at 100°C for 41 days

Figure 3-5, Figure 3-6, and Figure 3-7 show results for the oxyhydroxide film resulting from hot-wall immersion in 100°C water for 41 days. After the end of the immersion test, the samples were stored in room-temperature water for 2 days, then removed and stored in a bag until characterization. XRD indicated that the film was predominantly boehmite (Figure 3-5) with no evidence of trihydroxides. For 100°C, either pseudoboehmite or crystalline boehmite is the expected phase [10]. SEM images of the surface morphology (Figure 3-6) showed a predominantly "needle-like" appearance, which appears to correspond to platelets roughly perpendicular to the substrate and with random rotation, so that the edges of the platelets are seen from this angle. There are also scattered “scale-like” features (Figure 3-6, left) that appear to be overlaid over the “needle-like” morphology. Images of the cross-section (Figure 3-7) showed a total film thickness ranging from about 0.5 to 2 μm. It appeared to be a single-layer film.

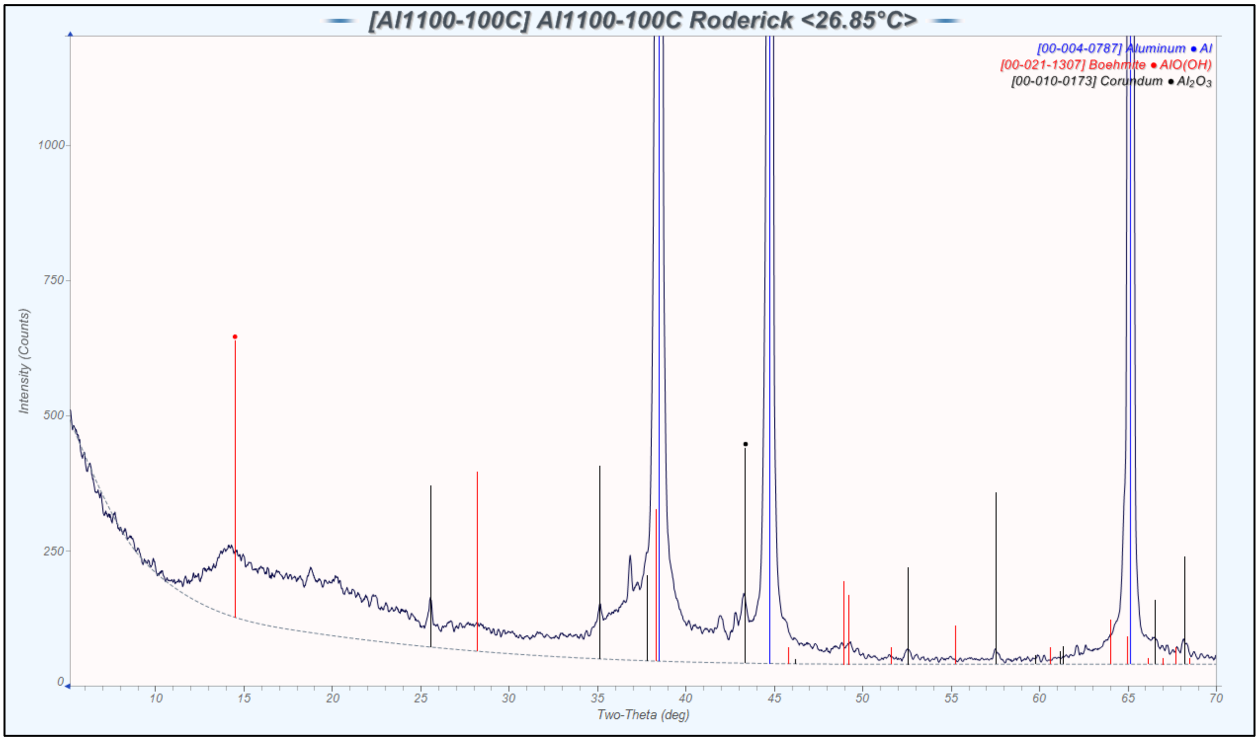


Figure 3-5. XRD spectrum for a hot-wall sample exposed to 100°C water for 41 days, followed by 2 days storage in room-temperature water and 20 days storage in a bag prior to characterization. The oxyhydroxide layer primarily consists of boehmite, with no evidence of trihydroxides.

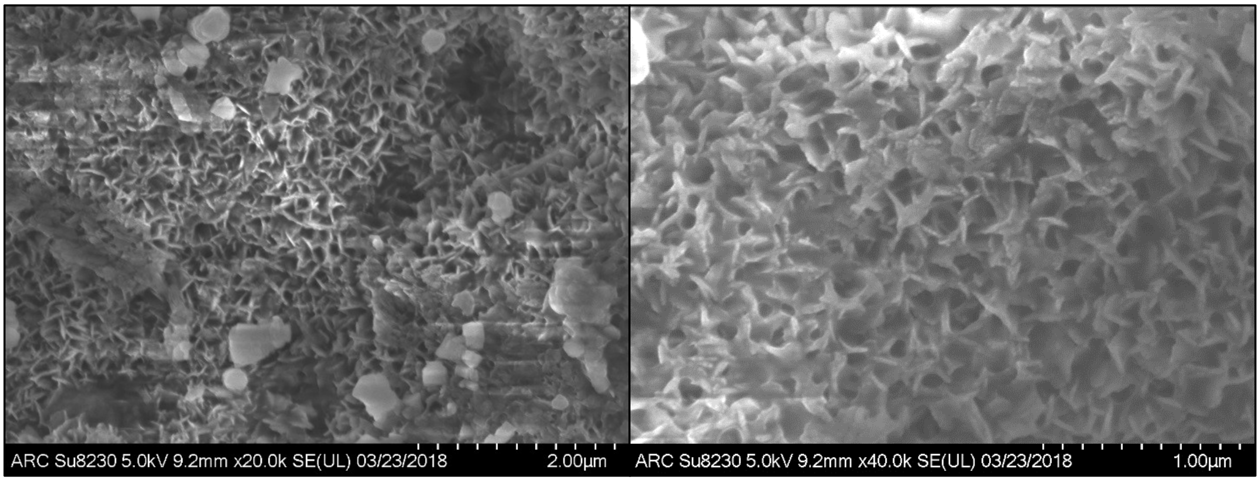


Figure 3-6. SEM images of oxyhydroxide layer surface morphology for a hot-wall sample exposed to 100°C water for 41 days, followed by 2 days storage in room-temperature water and 22 days storage in a bag prior to imaging, at two different levels of magnification (x20k on left and x40k on right). The oxyhydroxide morphology appears to consist mostly of platelets oriented roughly perpendicular to the substrate with random rotation, plus scattered platelets oriented parallel to the substrate.

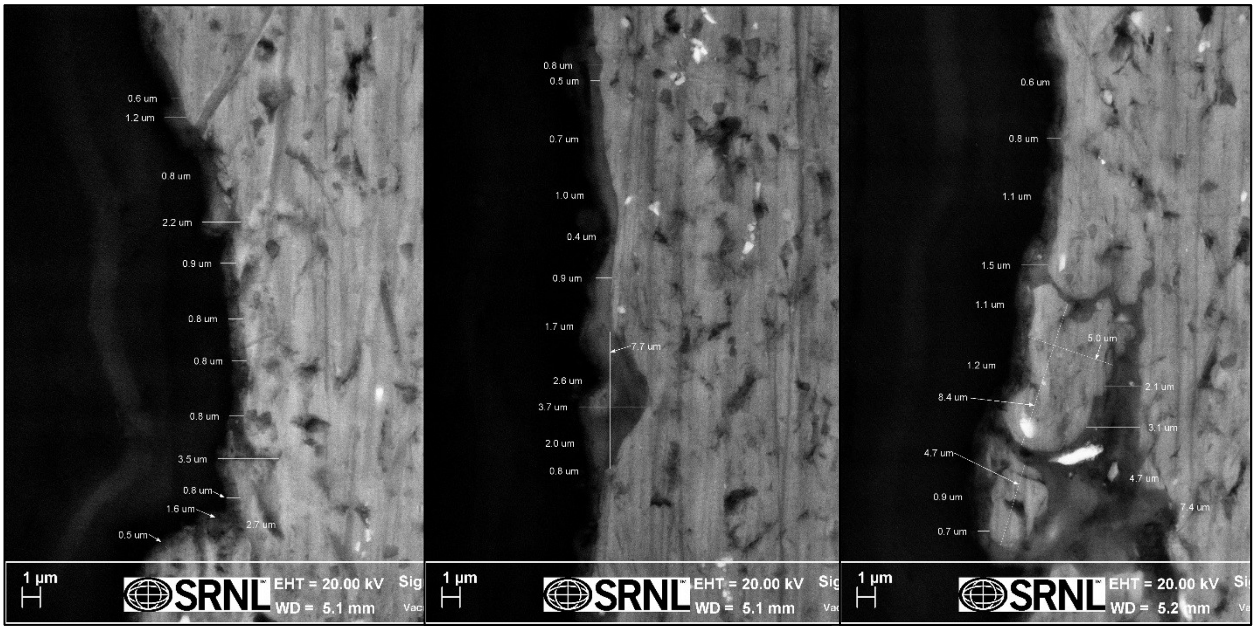


Figure 3-7. SEM images of oxyhydroxide layer cross-sections for a hot-wall sample exposed to 100°C water for 41 days, followed by 2 days stored in room-temperature water, and 28 days stored in a bag prior to imaging. Total oxyhydroxide layer thickness ranges from approximately 0.5 to 2 µm and appears to be a single layer.

3.2.3 Hot-wall versus isothermal immersion comparison at 100°C for 7 days

The results for a head-to-head comparison of hot-wall versus isothermal immersion growth are shown in Figure 3-8 and Figure 3-9. The samples were exposed in the same 100°C water bath for 7 days, with the surface imaged the same day the immersion test was completed. The samples were stored in bags prior to XRD characterization. The oxides observed on the water-exposed surfaces of the two samples were very similar to each other, with no apparent differences attributable to the presence or absence of heat flux through the sample.

XRD indicated that both films consisted of boehmite with no evidence of trihydrates (Figure 3-8), as expected for 100°C exposure. Both samples displayed the “needle-like” surface morphology with similar length scale (~0.25 µm needle length).

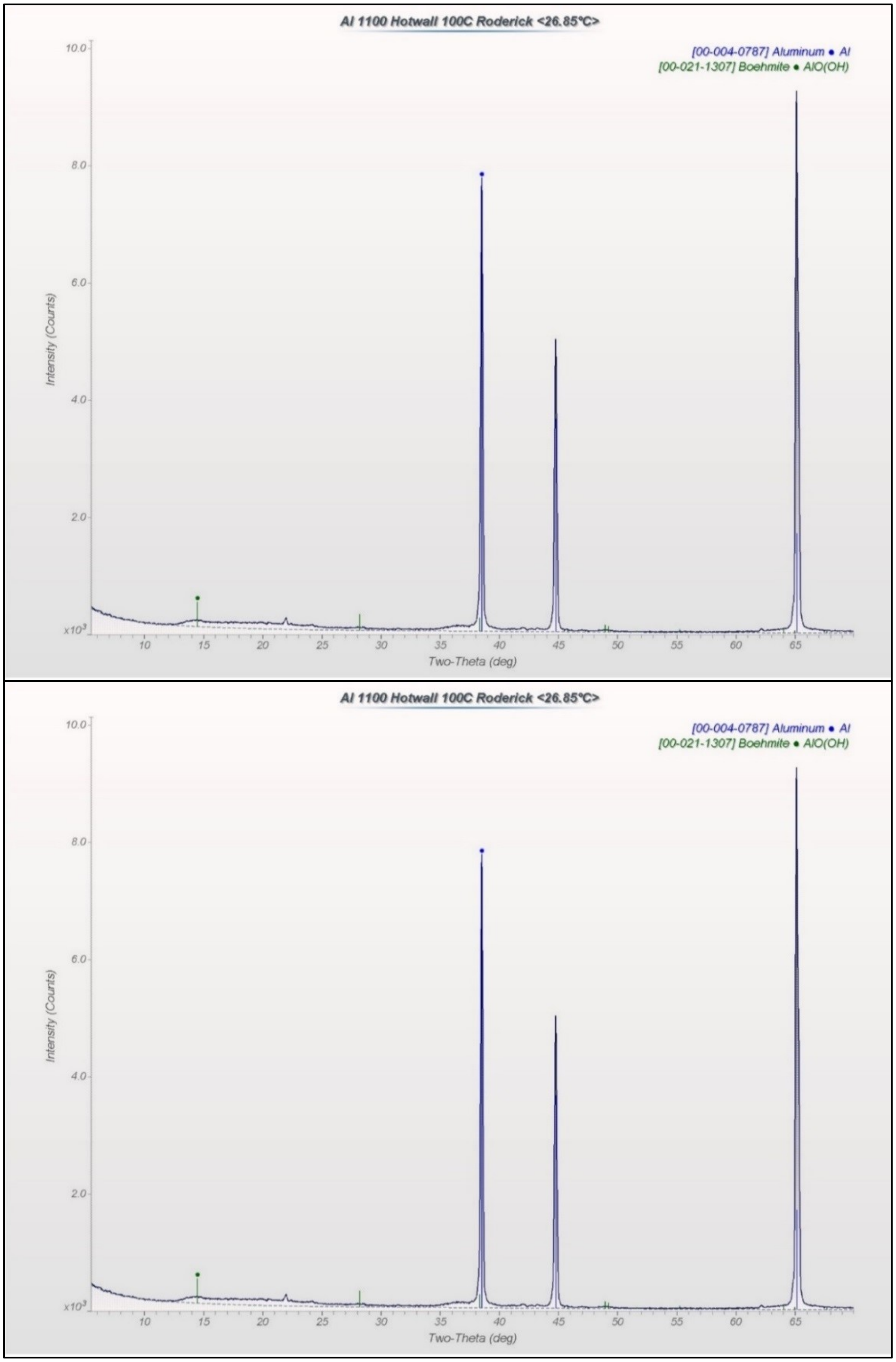
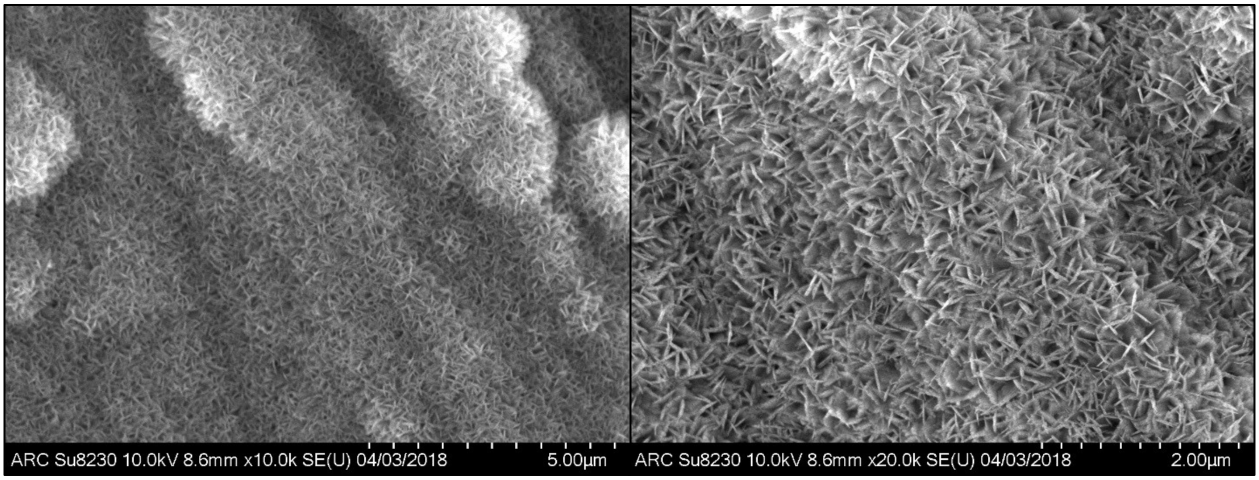


Figure 3-8. XRD spectrum for (top) a hot-wall immersion sample and (bottom) an isothermal immersion sample, both exposed to 100°C water for 7 days, followed by 12 days storage in a bag prior to XRD characterization. The oxyhydroxide layer on both consists of boehmite, with no evidence of trihydroxides.

Hot-wall sample



Isothermal sample

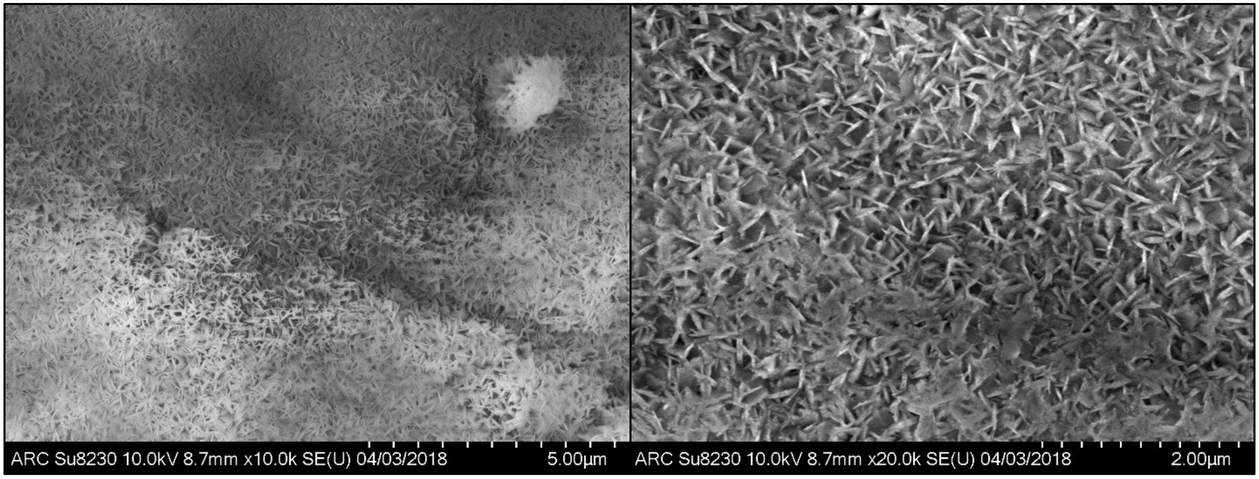


Figure 3-9. SEM images at two magnifications of oxyhydroxide layer surface morphology for (top) a hot-wall sample and (bottom) an isothermal sample exposed to 100°C water for 7 days, imaged on the same day the test ended. The morphology appears to be the same for both hot-wall and isothermal growth and to consist platelets oriented roughly perpendicular to the substrate with random rotation.

3.3 Discussion

Two distinctly different surface morphologies were observed in SRNL samples. Some samples displayed a "needle-like" oxide appearance, which appeared to consist of the edges of oxide platelets oriented roughly perpendicular to the substrate. Other oxides displayed a scaly or "block-like" oxide appearance, which appeared to consist of either block-shaped oxide particles or platelets oriented parallel to the metal surface. A sample of 1100 exposed at 50°C and then stored in air of unknown/uncontrolled humidity (placed in a bag following removal from the immersion test) displays a "scale-like" appearance with no needle-like structures evident. A distinct needle-like appearance was evident (1) over the whole surface of one hot-wall and one isothermal sample exposed at 100°C and imaged almost immediately after exposure and (2) over most of the surface of two samples of different alloys (1100 and 6061 [11]) exposed in the hot-wall apparatus at 100°C and imaged following storage in room-temperature water and subsequent bagged storage (isolated scale-like structures also appeared). A sample of 6061 [11], which was exposed at 50°C and stored in dry air (in a bag inside a desiccator) until SEM characterization, shows evidence of needle-like structures, which appear much less distinct than in samples imaged directly after exposure or after storage in water. Finally, an Advanced Test Reactor (ATR) pre-filmed sample (clad with Al-6061) has a scale-like appearance (Figure 3-10).

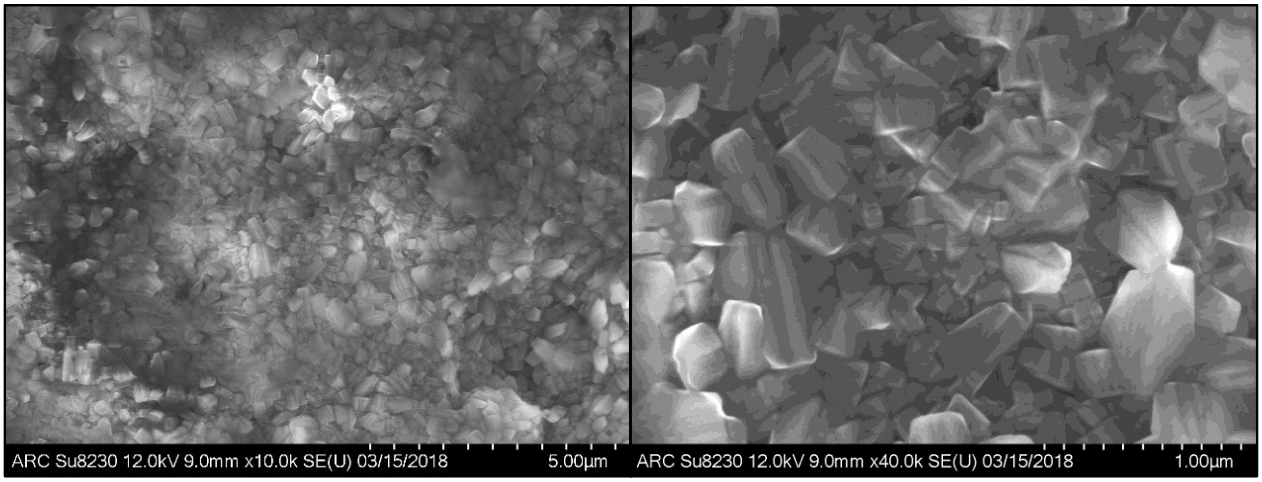


Figure 3-10. SEM images of as-received ATR "dummy" plate at two magnifications (x10k on left and x40k on right). The protective oxide on ATR fuel is obtained through an 18-hour autoclave treatment at 185°C.

The reason for the different surface morphologies is not yet clear. Images from the literature for oxyhydroxide films grown in liquid water for temperatures in the range 40–100°C have shown porous sponge-like or needle-like surface morphologies [5, 6] . No sources reporting the blocky or scaly appearance for aqueous oxyhydroxide formation have yet been identified. However, a previous study [12] observed distinct blocky oxyhydroxide structures for films grown at high temperature in humid air, in an autoclave under 100% relative humidity and 200°C.

The two-layer structure apparent in the cross-section of the 50°C sample, combined with the distinct difference between its scaly surface morphology and the sponge-like or needle-like morphologies observed in the literature for 40–50°C [5, 6] and in current results at 100°C, suggest the possibility that additional film growth may have occurred during bagged storage, i.e., air of unknown humidity. Boehmite is known to be more protective against further corrosion than trihydroxide films [10], so the 50°C sample with a bayerite film would be expected to be more susceptible to further corrosion during storage than the 100°C samples featuring boehmite films. Future testing will more tightly control post-immersion storage conditions and characterization schedules to identify the impact of different storage conditions (dry air, humid air, and room-temperature water) and determine how best to preserve samples for further testing.

4.0 Planned Path Forward

- Additional testing on 1100 series Al is planned to validate and confirm current oxyhydroxide growth process, including additional 50°C tests to clarify whether the morphology observed in the present results is typical or anomalous. In future tests, the post-immersion storage conditions will be tightly controlled to ensure that the as-grown oxyhydroxide is not compromised or degraded during storage.
- An additional growth test will be performed at a temperature near the transition between bayerite/gibbsite and boehmite (~80°C).
- A scaled up hot-wall immersion system has been developed to accommodate larger Al substrates. Oxyhydroxides grown on these larger substrates, including 1100 and 6061, will be used in experimental testing campaigns within other tasks of the action plan [1] on dry storage of Al-clad spent nuclear fuel.

- Ultimately, oxyhydroxides sampled from an RU-1 fuel plate will be compared to oxyhydroxides grown using hot-wall immersion in an effort to validate the representativeness of prepared surrogates.

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