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Corrosion of Aluminum-based Containers for Neutron Studies with Aqueous Samples under Low Temperatures

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Quasielastic neutron scattering studies frequently employ aluminum (Al) or Al alloys as sample cells. Due to the increasing incident-neutron flux, this research area has experienced continuous expansion; thus, the rate of acquiring data for dilute conditions has increased considerably. One such research topic is water-containing systems. In this study, we investigated the effect of temperature on Al and found that Al corrosion occurs even in a low temperature atmosphere. This was attributed to the different thermal expansion coefficients of Al as a base substrate and Al oxide as a passivating film.

KEYWORDS: Aluminum, corrosion, temperature, thermal expansion coefficient

1. Introduction

BL02 (DNA) in the Materials and Life Science Experimental Facility (MLF), J-PARC, is a near-backscattering ToF neutron spectrometer; it is used to elucidate atomic and molecular dynamics over a wide dynamic range from pico to nanoseconds. Owing to the annual increase in the incident-neutron flux, research area has expanded. Moreover, there has been a significant increase in the rate of acquiring quasielastic neutron scattering (QENS) data, even for dilute solution samples. One such research area is water-containing materials such as protein solutions and polymeric aqueous solutions. In such samples, aluminum (Al) or its alloys are frequently utilized as sample cells because Al exhibits low incoherent scattering, does not have a coherent Bragg peak in the measurable Q -range of standard Si111 analyzer mirrors, as well as good mechanical and machinable properties.

For QENS studies, we often obtain the temperature dependence of the QENS profile of samples and determine physical properties such as activation energy, glass transition temperature, and relaxation time. Moreover, to obtain the energy resolution function, we frequently cool the sample to significantly low temperatures ranging from 10–100 K; at such temperatures, all the dynamics in the system freeze.

After such experiments, during the period of sample storage for radiological cooling, which is typically a few months, it is found that some of the Al cells are broken by the

high pressure of the strong force from the inner side. We investigated the mechanism of such breakage of the Al cell after the QENS experiment.

Most of the Al surface is covered by a natural oxide layer (passivating film). The thickness of the passivating film on the Al surface is 5–10 nm [1]. This film is quickly formed due to the reaction of Al with the water vapor in the air, through the following reaction: $2\text{Al} + 6\text{H}_2\text{O} \rightarrow 2[\text{Al}(\text{OH})_3] + 3\text{H}_2$. Although pure Al reacts with corrosive chemicals, this reaction is typically not well determined and regarded negligible. Subsequently, Al cells with the passivating film are commonly utilized without any treatments.

At high temperatures, liquid or vapor of water can form thick crystallized oxides on the Al surface, such as boehmite, gibbsite, and bayerite. [1]. The boehmite film is known to protect against corrosion [2]. Through the oxidation reaction between aluminum and pure water at temperatures less than 348 K, bayerite ($\alpha\text{-Al}(\text{OH})_3$) is produced, where as a reaction at a temperature exceeding 348 K produces boehmite ($\gamma\text{-AlO}(\text{OH})$) [2]. The thickness of the oxidation layer depends on the surface flatness of the base material, which normally ranges from several tens to several hundreds of nanometers. The surface of the passivating film on Al is not defect-free or robust, thus allowing for additional oxidation under a high-temperature atmosphere with water to enhance the thickness of the oxidation layer.

It is known that Al can be dissociated in water, especially under a low or high pH atmosphere and chloride ion atmosphere [1], which is a type of chemical reaction. This chemical reaction can also be termed as corrosion. The mechanism of this type of corrosion is described in detail in previous literature [1]; hence, it is not discussed extensively in this report. In this study, we focus on the corrosion effect on Al in terms of the oxidation due to water and discuss the effect of temperature on the Al surface.

2. Materials and methods

Aluminum foil sheet with a thickness of 12 μm was purchased from Mitsubishi Aluminum Co., Ltd. Its purity was determined to be 99.4–100%, using energy dispersive X-ray spectrometry (EDX). Al films with thicker oxidation layers were prepared by placing in a hot, pure water (363 K) bath for 1 h to produce boehmite on the aluminum surface, based on the method reported in literature [2]. Calcium chloride (CaCl_2) was purchased from FUJIFILM Wako Pure Chemical and used as a corrosion solution with a concentration of 0.25 mol/L.

Scanning electron microscopy (SEM) images were obtained using S-4800 (Hitachi, Japan) at room temperature (rt). Further, scanning probe microscopy (SPM) (NanoScope V Dimension Icon (Bruker)) was used to determine the surface roughness after corrosion at rt. After corrosion, the samples were cleaned with pure water several times and completely dried; thereafter, data (scan area: $3\text{ }\mu\text{m} \times 3\text{ }\mu\text{m}$) were obtained in the contact tapping mode using Si-cantilevers in air at rt. In this study, the roughness, R_A , was calculated using the arithmetic mean deviation of the assessed profile.

The QENS experiments were performed using the BL02, J-PARC MLF [3] with a resolution of 3.2 μeV at rt. The profiles of the sample containers composed of A1070 (engineering-grade pure Al) and boehmite coated A1070 were compared. The Al content of A1070 is 99.7 wt%.

3. Results & discussion

We examined the temperature dependence of the surface damage of the passivating film of Al under a dry state. Dry Al and boehmite coated Al foils, treated at 77 K (liquid nitrogen), 194 K (dry ice), 253 K (freezer), 298 K (rt), and 363 K (hot bath control without water contact) for at least 3 h, were prepared, and their surface morphologies were observed using the SEM images at rt. The images revealed that the Al surface had no evident cracks/pits at 298 K, whereas the other samples that were treated at different temperatures developed cracks/pits (black regions in the left panels of Fig. 1); the damage that appeared at 363 K was the highest among all the samples. The thermal expansion coefficients of Al and Al oxide are $\sim 23 \times 10^{-6} \text{ K}^{-1}$ [4] and $\sim 7 \times 10^{-6} \text{ K}^{-1}$ [5], respectively. A crack could be generated at the interface between the base Al body and the Al oxide film because the difference in their thermal coefficients exceeds a factor of three. In this dry system, the destruction of the passivating film was confirmed. However, in the experiment conducted in air at rt, the crack must be immediately covered by a newly produced passivating film due to the moisture in air. Further, a passivating film can be easily destroyed in a defect or weak region. On the contrary, in the case of the boehmite coated Al surface, no evident cracks/pits were observed in the SEM image at 77–363 K (right panels in Fig. 1), and temperature dependence of surface roughness was not observed. Although a thicker oxide layer of boehmite, which has a unique crystal structure, may release stress caused by temperature change from the interface, no relevant information could be obtained from the SEM images.

Subsequently, we determined the effect of temperature on corrosion using a corrosive aqueous solution— CaCl_2 . CaCl_2 was selected for the following reasons: inexpensive, good water solubility, and non-hazardous material. In this solution, water and chloride ions undergo a chemical reaction against the Al substrate [1]. As observed, the passivating film on the Al base material can be destroyed by changing the temperature. Thereafter, the fresh surface emerging due to this destruction can easily react with water or chloride ions, thereby promoting additional oxidation or pitting corrosion.

The boehmite coated Al foils and Al foils were immersed in the CaCl_2 solution and sealed. The samples were stored at 77 K (liquid nitrogen), 194 K (dry ice), 253 K (freezer), 298 K (rt), and 363 K (hot bath) for at least 3 h, and then returned to room temperature. The salt solutions frozen at the low temperature were completely dissolved at room temperature. When pitting corrosion occurs, the surface roughness, R_A , increases. The R_A

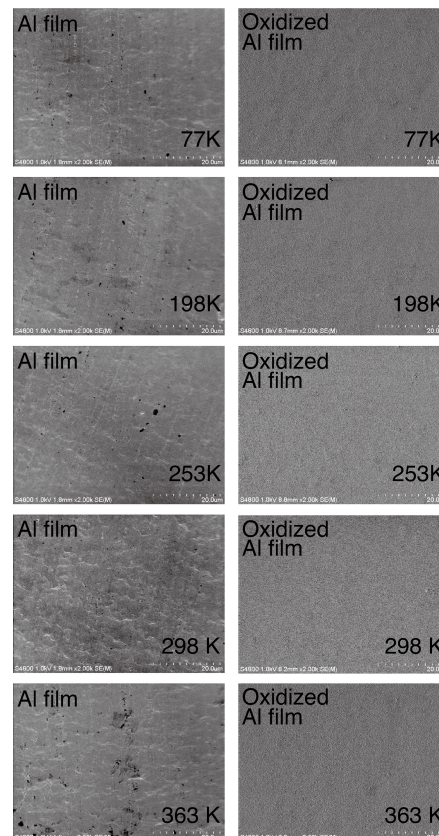


Fig. 1. SEM surface images. Left panels: Al films with respect to the subjected temperatures. Right panels: boehmite coating Al films with respect to the subjected temperatures.

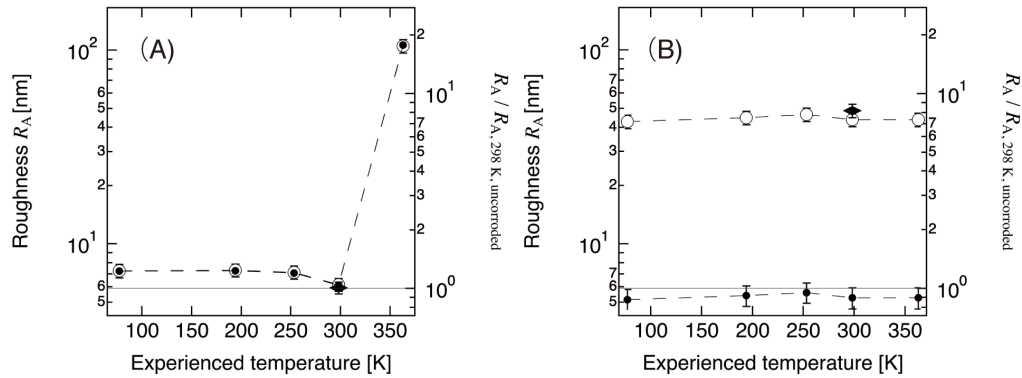


Fig. 2. Roughness, R_A , dependence with respect to the subjected temperature of (A) Al foil and (B) boehmite coated Al foil determined using SPM (left axis). Open circles indicate roughness; diamonds have the roughness of an uncorroded surface (left axis). Closed circles indicate the ratio with respect to the uncorroded surface (right axis).

of the samples was determined using SPM images at rt in air.

Figure 2 illustrates the R_A of the Al foils and the boehmite-coated Al foils with respect to the temperature they were subjected to. In the case of Al foils, we surprisingly found that the roughness of the surface was larger both below and above rt than that of the Al foil treated at rt, whose value was significantly larger than that of the original uncorroded Al foil at rt. Since the increase in roughness can be regarded as an indicator of the promotion of surface corrosion, it must be noted that corrosion can be promoted not only by the Al substrate in a high-temperature atmosphere but also by that in a low-temperature atmosphere (Fig. 2A). The increase in roughness of the Al foil subjected to 363 K might cause a synergistic effect on both the production of the oxide layer on the Al surface and the destruction of the passivating film due to the difference in the thermal expansion coefficient. Although the effect of low temperature is miniscule, the synergy of other factors can promote corrosion or oxidation. Moreover, chemical reactions not only break sealed cells but also change the condition of the sample.

No evident trend was observed in the boehmite coated Al foils at 77–363 K (Fig. 2B). The roughness of the Al foil is higher than that of the boehmite coated Al foil at 363 K, indicating that boehmite is a potential corrosion inhibitor which could be confirmed [2].

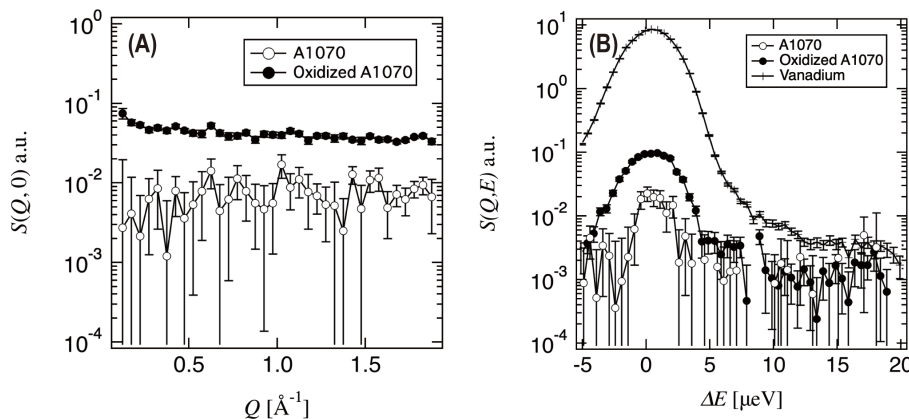


Fig. 3. (A) $S(Q, 0)$ of A1070 cells and oxidized (boehmite-coated) A1070. (B) $S(Q, E)$ of A1070 cell, oxidized A1070 cell, and vanadium (resolution) under $-5 < E [\mu\text{eV}] < 20$ which profiles were plotted an average at $0.125 < Q [\text{\AA}^{-1}] < 1.875$

Further, there was a decrease in the roughness after the corrosion process, in the case of the boehmite coated Al foils; this trend is in contrast with that of Al foils. We consider that corrosion induces leveling of the rough boehmite surface.

The scattering profiles were obtained using sample cells (empty cell) composed of A1070 and oxidized (boehmite coated) A1070 cells; Fig. 3a presents the $S(Q, 0)$ of the cells, and Fig. 3b depicts the $S(Q, E)$ of the cells and vanadium as a resolution function at $0.125 < Q [\text{\AA}^{-1}] < 1.875$ under $-5 < E [\mu\text{eV}] < 20$. Although boehmite ($\gamma\text{-AlO}(\text{OH})$) has a smaller hydrogen content than other structures, such as bayerite ($\alpha\text{-Al}(\text{OH})_3$) and gibbsite ($\gamma\text{-Al}(\text{OH})_3$), large incoherent scattering caused by hydrogen is observed compared to an un-coated Al container with a considerably thin natural oxide layer. The curve shape of resolution (vanadium) in the energy range of -4 to $4 \mu\text{eV}$ was mostly identical to that of the oxidized A1070. Scattering intensities under the other energy range were in the background level ($\sim 3 \times 10^{-3}$). This suggests that the hydrogen atoms in boehmite are tightly bonded and do not significantly affect the QENS analysis. Furthermore, the boehmite-coated Al with high roughness can contain large quantities of water, which could cause incoherent scattering. Although these factors are disadvantageous, oxidation coating is beneficial for corrosion resistance as well as temperature resistance.

4. Summary

In this study, we analyzed the effect of temperature on the Al surface using an aqueous solution sample. Because the thermal expansion coefficients of the Al base material and Al oxide passivating film are different, the passivating film on Al can be destroyed by changing the temperature, which can promote corrosion or oxidation at $77\text{--}253 \text{ K}$. The aqueous corrosive solution is frozen below rt ; however, corrosion occurs when the solution is dissolved above its melting point. Finally, it was found that the effect of temperature can be reduced by coating boehmite on the Al substrate.

When an Al cell for aqueous samples is utilized, we recommend verifying the reactivity through temperature dependence, including low temperatures. If there is an increase in surface roughness, the Al cell without any treatment is not recommended. Nevertheless, when the Al cell is required, increasing the flatness of the surface of the inner wall of the Al cell and coating a thick oxide layer of boehmite could be beneficial, even if the scattering contribution from this cell was higher than that of the A1070 cell. Other candidate cell materials, such as niobium and molybdenum, should be considered, although these can be slightly expensive.

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