Neutron Reflectometry Studies of Aluminum - Saline Water Interface Under Hydrostatic Pressure.

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Abstract

The structural stability of Al layers in contact with 3.5 wt.% NaCl water solution was investigated at a temperature of 25°C and hydrostatic pressures from 1 to 600 atm using neutron reflectometry. A pressure-temperature (P-T) Neutron Reflectometry (NR) cell developed at Los Alamos National Laboratory (LANL) was used to understand the behavior of thin (~900Å) aluminum layers in contact with saline liquid. Experimental results suggest that in the preliminary stages of corrosion the influence of pressure accelerates the mechanism of interactions of the oxide film with Cl⁻ and H₂O with lower speed compared to results found in the literature.

Keywords A. aluminum; B. passive films; C. neutron reflectometry; D. solid-liquid interfaces; E. pressure studies of thin metallic films.

Introduction

With an increasing effort to tap into energy (gas hydrates, oil, minerals, *etc.*) and material resources that lie within the deep sea, there is a great need for long-term, low-maintenance infrastructure and equipment that can withstand the harsh deep sea environment. Materials (metals, alloys, composites, *etc.*) operating in the deep sea are exposed to a corrosive environment dictated by several chemical and physical factors including pH, dissolved oxygen (DO) content, chloride ion activity, salinity, ocean currents, temperature, hydrostatic pressure (1 atm for every 10 m in depth), and others. Aluminum and its alloys find widespread use in marine environments for civil and defense transport vessels, shipbuilding components, offshore rigs, drill pipes for deep wells, atmospheric diving suits, and others. There are several reports on corrosion behavior of aluminum and its alloys in artificial/natural sea water in open sea, shallow depth conditions while investigations at high hydrostatic pressures are somewhat limited.

Earlier studies (Beccaria *et al.*) [1-3] on pure aluminum and its alloys exposed long term to natural sea water at various depths observed severe pitting and increased average corrosion rates at lower dissolved oxygen content. However, it has been suggested by Huesler [4] that pitting in aluminum arises from a combination of factors including increased activity of OH^- ions, lower pH, CO_2 content ($\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$), and decreasing dissolved oxygen content. The effect of hydrostatic pressure on these variables is complicated (as reported by Dexter [5]) and it is of interest to isolate pressure effects on the stability and composition of passivating oxide layers of pure aluminum as well as its alloys. The series of studies by Beccaria and co-workers addressed the explicit role of hydrostatic pressure with revealing insights. They surmised that at high pressure, the passivating layer is primarily $\text{AlO}(\text{OH})$ which offers less protection compared to the amorphous $\text{Al}(\text{OH})_3$ layer formed at ambient pressure. Immersion tests of pure aluminum in seawater (pH 8.2, DO ~7 ppm at 20°C) showed that the average corrosion rates increased by

~20% at 300 atm and were accompanied by an increased localized corrosion number and deeper pits. The increased susceptibility to pitting was confirmed by electrochemical tests particularly for longer immersion times (up to 120 h). As anticipated, the behavior of aluminum alloys was influenced by the additives that affect the chemical, physical, and mechanical properties of the passivating layer. [1-12]

For example, higher hydrostatic pressure increased localized corrosion of 6061-T6 alloy while generalized corrosion was inhibited by the formation of an Mg-Al oxide layer. It is evident that the nature of an initially passivating layer and its modifications at higher pressure in the early stages of corrosion plays an important role in determining the susceptibility to localized and general corrosion. *In situ* surface measurements of local breakdown of the passivating layer due to penetration of ions and pitting initiation are necessary. These measurements are particularly challenging, especially at high pressures. Neutron Reflectometry (NR) is a powerful technique that is well suited for investigating surface changes of thin films and can provide insights into interfacial phenomena due to the highly penetrating nature of neutrons. The availability of a newly developed high pressure cell provides an opportunity to perform this advanced surface characterization. Furthermore, exploiting scattering contrast variations of aqueous media using isotopic substitution (H_2O vs. D_2O) in contact with the metal surface represents a unique opportunity to study corrosion behavior. In this work, we present the first NR study of the effect of hydrostatic pressure (up to 600 atm) on the surface oxide (Al_2O_3) stability of sputtered pure Al-films on quartz substrates in contact with a representative salt solution (3.5 wt.% NaCl in D_2O or H_2O) as well as pure D_2O or H_2O . A detailed analysis of the NR spectra reveals that the passivating layer exhibits an overall decrease in scattering length density (*SLD*) with minimal change in thickness. This suggests a changing chemical composition and implies a smaller

overall corrosion rate but increased susceptibility to local phenomena like pitting. The changes in chemical composition are likely due to a gradual hydration of the oxide layer, which is susceptible to breakdown due to interactions with Cl^- ions during the continuous exposure of the Al-film to the saline solution. This is in accordance with the study by Beccaria *et al.*.

Material and Methods

Neutron scattering methods are uniquely suited for high-P investigations because neutrons are highly penetrating and are able to “see through” robust high P-T cell walls with relatively low attenuation, enabling the examination of interfacial phenomena occurring on material surfaces at high P-T [13]. With the need for high-P NR capabilities becoming apparent in general, corrosion in extreme conditions is one of the specific scientific problems which requires to be addressed due to its engineering and national security importance. For the pressure studies of Al layers in contact with saline water we used a new NR P-T cell developed at Manuel Lujan Jr. Neutron Scattering Center for the Surface Profile Analysis Reflectometer (SPEAR) [14] which is capable of reaching 200 MPa (~30,000 psi) and 200 °C [14].

In Neutron Reflectometry (NR), a collimated neutron beam is directed at an interface at a glancing angle and the reflectivity (R), defined as the intensity ratio between elastically scattered and incident beam, is measured as a function of momentum transfer vectors $Q_z = 4\pi \sin(\theta) \lambda^{-1}$, *i. e.* $R(Q_z)$. The changes in the $R(Q_z)$ are indicative of the changes to the solid surfaces due to solid-fluid interfacial interactions. Analysis of specular NR (incident angle equals the reflected angle, Q_z perpendicular to surface) provides detailed information about the scattering length density

(*SLD*) distribution as a function of depth. Further details on parameters involved in *SLD* modeling are given in ‘Results & Discussion’.

In particular, for systems involving an aqueous interface, using solutions made of heavy (D_2O) versus light (H_2O) [water](#) allows us to enhance the scattering contrast and to gain additional insights into the chemistry occurring at the interface. It should be noted that scattering of neutrons is highly sensitive to H/D substitution due to the large differences in scattering cross section of different hydrogen isotopes. The capability of performing NR measurements at high P-T is state-of-the-art and available at the Manuel Lujan Jr. Neutron Scattering Center for the Surface Profile Analysis Reflectometer (SPEAR) [12]. The newly designed P-T cell is capable of achieving 200 MPa (~1970 atm) using a hydrostatic pressure media (typically the fluid in contact with the material surface) that can be external heated to 200 °C [12].

The 3.5 wt. % NaCl solution was prepared with both H_2O (ultrapure MilliQ, 18.2 M Ω cm) and D_2O (99.8% D, Acros Inc.) without further purification. Metallic Al thin films (~900 Å thickness) were deposited on 10 mm thick monocrystalline quartz wafers (50.8 mm in diameter) by DC magnetron sputtering under inert conditions (high purity Argon gas). Film contamination was minimized using pre-cleaned (H_2SO_4 - H_2O_2 piranha solution), outgassed quartz wafers inside a sputter chamber with a base pressure of 10^{-6} torr. The sputtered Al films possess uniform thickness and adhere strongly to the quartz wafer without altering substrate properties. When in contact with air the Al layer develops a thin passivation layer of Al_2O_3 . The surface oxide that forms on the aluminum, Al_2O_3 , has a higher scattering length density (*SLD*) than pure Al, providing neutron scattering contrast between the two materials (Al: $2.08 \times 10^{-6} \text{ \AA}^{-2}$; crystalline Al_2O_3 : $5.74 \times 10^{-6} \text{ \AA}^{-2}$). The corresponding change in the distribution of the *SLD* over time at

high P can be probed by NR measurements. Additional information on NR spectral interpretation and the high P-T cell is provided in Supplementary Materials.

Of the ten Al films sputtered on quartz substrate, two samples (named L1 and L9) which exhibited the smallest roughness and high in-plane homogeneity (best NR spectra in air) were chosen for high pressure measurements with fluid media. The quartz substrates with the Al films were placed inside a ‘standard cell’ for control experiments at 1 atm (D_2O , H_2O , $D_2O+3.5$ wt% of NaCl fluid) and within the high P cell for higher pressure measurements. It is noted that the hydrostatic pressure is generated by using the 3.5 wt. % NaCl solution as the pressure media that is in contact with the Al films. NR spectra were collected for ~3 hours with the same experimental parameters (time of scan, temperature, neutron slit size, *etc.*) and five pressure increments (1, 150, 300, 450 and 600 atm). Small fluctuations in the beam intensity were corrected by the beam monitor reading.

Results and Discussions

NR measurements using the high P-T cell are challenging due to extended alignment and safety protocols. Therefore, several baseline NR spectra were collected for L1 and L9 samples using a standard solid-fluid NR cell to ensure the stability of the Al films when exposed to fluids (H_2O , D_2O , $D_2O+NaCl$) at 1 atm. Representative baseline NR spectra are compiled in the Supplementary Materials (Fig.1S-3S). At 1 atm, the Al film (L9) in contact with pure D_2O or $D_2O+NaCl$ solution did not exhibit any noticeable change confirming a stable Al/ Al_2O_3 layer over the course of 12 hours (Fig. 1S, Supplementary Materials). Similar stability at 1 atm was observed with Al film (L1) in contact with pure H_2O , D_2O and $D_2O+NaCl$ solution (Fig. 2S). This Al-film was subsequent mounted in the high P-T cell in contact with H_2O , and subjected to

300 atm to ensure long term (10 hours) high pressure stability of the Al-film (L1). The high P cell was depressurized and pure H₂O was replaced with H₂O+3.5 wt% NaCl.

The set of NR measurements at various pressure increments to investigate the stability of Al-film (L1) in contact with the saline solution is schematically shown in Fig. 1. A total of 14 NR spectra were collected (~3 hours per spectrum) and the Al-film (L1) was in contact with saline solution for more than 50 hours. In Fig. 2, three representative spectra at 1 atm (t = 0 hours), 300 atm (20 hours), and 600 atm (50 hours) are shown with starting time of data collection given in parenthesis. The NR interference fringes (spacing between two fringes) indicate no significant change in the total thickness accompanied by minimal changes in intensities at low Q_z .

In order to analyze NR spectra, a priori knowledge of the chemical composition (*SLD*) as a function of depth is necessary. The *SLD* profile is modeled as a sequence of slabs (quartz – Al-film – Al₂O₃ – fluid) connected by an interfacial (chemical) roughness parameter. The *SLD* can be calculated according the following equation:

$$SLD = \rho \cdot N_a \cdot \sum b_i / M \quad [E1]$$

where b_i is the coherent scattering length of the i^{th} atom, ρ is density, M is molecular weight and N_A is Avogadro's number. Since the *SLD* is a function of chemical composition and mass density, the *SLD* profile provides direct information about the density. As the first approximation, *SLD* values of the quartz substrate, the Al-film, and the fluid were fixed (quartz: $4.18 \times 10^{-6} \text{\AA}^{-2}$, Al: $2.08 \times 10^{-6} \text{\AA}^{-2}$, H₂O: $-0.56 \times 10^{-6} \text{\AA}^{-2}$) and the following parameters were allowed to vary: (a) thickness of Al and Al₂O₃ layers, (b) *SLD* of Al₂O₃, (c) interfacial roughness. A least squares refinement procedure for the utilized four NR measurements of Al-film (L1) under different contrast and high P conditions: (a) D₂O (1 atm), (b) H₂O (1 atm), (c)

H₂O + 3.5 wt. % NaCl (1 atm), (d) H₂O + 3.5 wt. % NaCl (600 atm) after 50 hours, was executed. It is noted that (a) & (b) measurements were carried out using a standard cell while (c) & (d) were carried out in the high P cell. The results of the simultaneous refinement are given in Fig. 3 showing measured data, calculated NR spectra (left panel, offset by a decade), the resulting *SLD* profile (middle panel), and an expanded view (right panel) of the *SLD* profile in the Al/Al₂O₃/H₂O region. From the *SLD* profile, it is evident that the only difference is the change in the *SLD* of Al₂O₃ layer: (a) against D₂O ($3.63 \times 10^{-6} \text{Å}^{-2}$) (b) against H₂O ($3.35 \times 10^{-6} \text{Å}^{-2}$). We can calculate the volume fraction of spaces or porosity (x) accessible to liquid penetration by assuming that the capping Al₂O₃ layer has a dry *SLD* (A). From the following scattering contrast condition equations for D₂O and H₂O measurements, we obtain a porosity of $x = 4\%$ for the Al₂O₃ layer.

$$3.63 \times 10^{-6} \text{Å}^{-2} = x \cdot 6.3 \times 10^{-6} \text{Å}^{-2} + (1-x) \cdot A \quad [\text{E2}]$$

$$3.35 \times 10^{-6} \text{Å}^{-2} = x \cdot (-0.56 \times 10^{-6} \text{Å}^{-2}) + (1-x) \cdot A \quad [\text{E3}]$$

The *SLD*'s of the H₂O and D₂O subphases are $-0.56 \times 10^{-6} \text{Å}^{-2}$ and $6.3 \times 10^{-6} \text{Å}^{-2}$, respectively. The calculated reflectivity spectra (left panel) is obviously not in good agreement with the experimental spectra ($\chi^2 = 19.7$) especially for the D₂O measurement. We attribute this disagreement to differences in cell configuration, spatial variation of measurement areas during transfer from standard to high P cell, and possible purity issues of D₂O.

A second sequence of refinements was carried out using three NR spectra of the Al-film (L1) mounted in the high P cell: (a) H₂O (1 atm), (b) H₂O + 3.5 wt. % NaCl (1 atm), (c) H₂O + 3.5 wt. % NaCl (600 atm) after 50 hours. The *SLD* values of quartz: $4.18 \times 10^{-6} \text{Å}^{-2}$, Al: $2.08 \times 10^{-6} \text{Å}^{-2}$, and H₂O: $-0.56 \times 10^{-6} \text{Å}^{-2}$ were fixed and the following allowed to vary: (a) thickness of Al and

Al₂O₃ layers, (b) *SLD* of Al₂O₃, (c) *SLD* of H₂O+3.5 wt. % NaCl perturbed around $-0.44 \times 10^{-6} \text{Å}^{-2}$, (d) Interfacial roughness. It is noted that the thickness of the Al and Al₂O₃ layers was assumed as a common parameter for all the three NR spectra. This is a valid assumption since the fringe spacing was essentially the same implying no significant change in layer thickness between the measurements. The results are shown in Fig. 4 with fits to NR spectra (left panel, offset by a decade), the resulting *SLD* profile (middle panel), and an expanded view (right panel) of the *SLD* profile in the Al/Al₂O₃/H₂O region. A clear improvement is observed ($\chi^2 = 7$) with the following changes in the *SLD* of the Al₂O₃ layer upon exchange of H₂O ($3.76 \times 10^{-6} \text{Å}^{-2}$) to H₂O+3.5 wt% of NaCl. ($3.87 \times 10^{-6} \text{Å}^{-2}$) and decrease in *SLD* ($2.67 \times 10^{-6} \text{Å}^{-2}$) at higher pressure (600 atm). Fluid exchange at 1 atm has minimal effect on the *SLD* of Al₂O₃, which is within the resolution limits (3%), however, after 50 hours of exposure to saline solution at varying pressures (Fig. 1), the *SLD* decrease is pronounced. We attribute this decrease in *SLD* of Al₂O₃ layer to a combination of factors: (a) pressure-induced penetration of liquid phase (increased Cl⁻ interactions) with the Al₂O₃ layer, (b) chemical reaction to form low *SLD* products such as Al(OH)₃, hexahydrate aluminum chloride ($SLD = 1.9 \times 10^{-6} \text{Å}^{-2}$), and others. It is noted that elemental scattering lengths for Na, Cl, O and H are $3.63 \times 10^{-5} \text{Å}$, $9.58 \times 10^{-5} \text{Å}$, $5.80 \times 10^{-5} \text{Å}$ and $-3.74 \times 10^{-5} \text{Å}$, respectively. Therefore the decrease in the *SLD* of this layer under pressure cannot be explained by simple accumulation of high scattering length atoms like Na, Cl or O on top of the Al₂O₃ layer without forming a new chemical compound. Additionally, the experiments do not show any significant change in the thickness of the Al₂O₃ layer, which would accompany such a build-up.

Finally, we performed refinements of just the five NR spectra (1, 150, 300, 450, and 600 atm), marked by * in Fig. 1, of Al-film (L1) in contact with the saline solution in the HP cell. Those

steps were measured under the exact same experimental conditions, except pressure. For all the measurements small but systematic changes in the intensities of the interference fringes, especially at low Q_z values, are observed as function of increasing pressure (Fig. 5). We performed the data refinement using two approaches. First, we refined the data sets separately with the following common constraints: (a) Constant SLD 's values for quartz substrate ($4.18 \times 10^{-6} \text{ \AA}^{-2}$), Al-film ($2.08 \times 10^{-6} \text{ \AA}^{-2}$), and saline subphase ($-0.44 \times 10^{-6} \text{ \AA}^{-2}$), (b) Fixed roughness parameters (best average values from prior refinements) of the quartz-Al (5 Å), Al-Al₂O₃ (10 Å) and Al₂O₃-subphase (10 Å) interfaces, and (c) Al-film thickness was not allowed to increase with pressure while Al₂O₃ not allowed to decrease with pressure. The results of the refinement are given in Fig. 6 (cf. Table 1). In the second approach, all the five data sets were simultaneously refined with fixed SLD values of the quartz substrate, the saline subphase and the Al layer together with the roughness of quartz-Al interface to the values described above. The results from this refinement are shown in Fig. 4S (cf. Table 2). Independent of the approach (separate vs. simultaneous fit) the described above extensive analysis of the five pressure data sets indicates systematic decrease of the SLD of the Al₂O₃ layer together with a small increase of its thickness upon increase in the pressure. The gradient of these changes is the highest between 150 and 300 atm. The decrease in SLD of the passivating layer is consistent with previous refinements (Fig. 4) due to the factors discussed earlier. It is noted that the SLD of Al₂O₃ layer did not change appreciably in earlier measurements (see. Fig. 3S) when the Al-film was in contact with pure H₂O (up to 300 atm). It can therefore be inferred that the hydration of Al₂O₃ layers is accelerated by a combination of interactions with Cl⁻ ions (increased activity) and high P.

As noted earlier, the decrease in *SLD* can be explained only by assuming partial hydration of the Al_2O_3 layer, ($\text{Al}(\text{OH})_3$ has an *SLD* of $1.81 \times 10^{-6} \text{\AA}^{-2}$ ($\rho = 2.42 \text{ g/cm}^3$)), along with formation of mixed aluminum oxychlorides. In fact, the common aluminum chloride hexahydrate, $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$ is a possibility considering its low *SLD* ($0.78 \times 10^{-6} \text{\AA}^{-2}$). However, this is not expected to be a dominant effect, considering that the average *SLD* was considerably higher (End pressure: $2.3 \times 10^{-6} \text{\AA}^{-2} / 2.1 \times 10^{-6} \text{\AA}^{-2}$). In contrast, the presence of anhydrous aluminum chloride (AlCl_3 , $\rho = 2.48 \text{ g/cm}^3$) can be eliminated considering its high *SLD* ($3.6 \times 10^{-6} \text{\AA}^{-2}$). The role of Cl^- ions (increased ionic activity at high pressure) was discussed by Beccaria *et al.* who postulated an increased penetration of Cl^- into the defects in the hydrated Al_2O_3 layer and formation of mixed aluminum oxychlorides as well as other products. However, we note that our calculated porosity from the scattering contrast conditions was only 4 % and likely due to a greater homogeneity and integrity of the sputtered Al-film used in our measurements. We also note that in this study, the Al-film was in contact with the saline solution for 50 hours in contrast to the earlier study where Al-films were exposed to natural sea water for up to 120 hours. The absence of significant changes to the passivating layer thickness suggests a lower corrosion rate compared to earlier reports. However, the changes to the chemical composition (*via SLD* decrease) are in agreement with observations of increased susceptibility to local pitting.

Conclusions

The performed NR experiments of Al/ Al_2O_3 layers in contact with $\text{H}_2\text{O} + 3.5 \text{ wt\% NaCl}$ show virtually no corrosion of the aluminum layers at 600 atm after 50hrs and no change in the aluminum layer thickness for the investigated sample.

The observed decrease in the *SLD* of the starting Al_2O_3 passivation layer cannot be explained by interactions with highly scattering Na, Cl, and O ions forming a new chemical compound.

However, this decrease is consistent with formation of stable Al-Cl-H₂O (or Al-O-Cl-H₂O) complexes or hydration of Al₂O₃ to Al(OH)₃. The experimental results suggest that in the preliminary stages of corrosion (50 hours) the influence of hydrostatic pressure accelerates the mechanism of interactions of the oxide film with Cl⁻ ions and H₂O. The speed of corrosion registered is lower in comparison with Beccaria *et al* experiments and suggests much slower kinetics for the reactions involved, even if we consider that their experiments lasted more than 120 hours. We attribute those changes to chemical composition and also the increased susceptibility to pitting.

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Captions

Fig. 1. Pressure vs. time sequence of NR experiments measured using the L1 sample. Sample was measured in high P/T cell in contact with 3.5 wt% of NaCl in H₂O. Data collection of each NR experiment took approximately 3 hours. Arrows indicate starts of each NR scan.

Fig. 2. Three NR scans of the sample L1 in contact with H₂O+3.5 wt% of NaCl measured using the HP/T cell in three different pressures over the time span of 50 hours. Red curve (open circles) shows the experiment at t (time) = zero at the pressure of 1 atm, the blue curve (open squares) is the measurement at the pressure of 300 atm measured at time $t=20$ hours, and the green curve (full circles) is the measurement at 600 atm obtained after 50 hours. Only small changes in the intensities of the interference fringes at low Q_z values are observed. No change in the spacings of the NR interferences indicate no changes in the total thickness of the investigated layers.

Fig. 3. Left panel: Four NR measurements of L1 sample at different pressures and different scattering conditions. Black curve: measurements in contact with D₂O performed in the ‘standard cell’ at 1 atm pressure; red curve: the measurement in contact with pure H₂O performed in the ‘standard cell’ at 1 atm pressure; green: measurement in contact with H₂O+3.5 wt% of NaCl performed in the HP/T cell at 0 pressure; blue: the final measurement (after 50 hours) performed at pressure at 600 atm in contact with H₂O+3.5 wt% of NaCl. Solid curves are the SLD profiles (shown in the middle and right panel) obtained by fitting the four data sets simultaneously.

SLD's of the quartz substrate and the Al layer had been fixed to the known, calculated values and only the SLD of the subphase, Al_2O_3 layer varied during the fitting procedure. Right panel: Enlarged *SLD* distribution in the Al/ Al_2O_3 /liquid region of L1 sample from middle panel showing changes in the SLD of the layer at different contrasts and pressure conditions. NR data and the fits are shifted by a decade along y-axis for clarity.

Fig. 4. Left panel: Three NR measurements of L1 sample at different pressures and different scattering conditions. Black curve: measurements in contact with H_2O performed in the HP/T cell at 1 atm pressure; blue: measurement in contact with $\text{H}_2\text{O}+3.5$ wt% of NaCl performed in the HP/T cell at 1 atm pressure; red: the final measurement (after 50 hours) performed at pressure at 600 atm in contact with $\text{H}_2\text{O}+3.5$ wt% of NaCl. Solid curves are the *SLD* profiles (shown in the middle and right panel) obtained by fitting the three data sets simultaneously.

SLD's of the quartz substrate and the Al layer had been fixed to the known, calculated values and only the *SLD* of the subphase, Al_2O_3 layer and roughness parameters varied during the fitting procedure. Right panel: Magnified *SLD* distribution in the Al/ Al_2O_3 /liquid region of L1 sample from middle panel showing changes in the *SLD* of the layer at different contrasts and pressure conditions. NR data and the fits are off-set by a decade along y-axis for clarity.

Fig. 5. NR scans of the sample L1 in contact with $\text{H}_2\text{O}+3.5$ wt% of NaCl measured in the HP/T cell at 1 (black), 150 (red), 300 (green), 450 (blue) and 600 (cyan) atm, respectively. The measurements were performed exactly in the same experimental conditions over the time span of 50 hours. Small -but systematic -changes in the intensities of the interference fringes especially at

low Q_z values are observed as function of increasing pressure. No change in the spacings of the NR interferences indicate no significant changes in the total thickness of the investigated layers.

Fig. 6. Left panel: Five NR measurements of L1 sample measured at 25°C in the HP/T cell in contact with H₂O+3.5 wt% of NaCl at different pressures. Black, red, green, blue and cyan curves correspond to measurements performed at 1, 150, 300, 450, 600 atm, respectively. Solid curves are the fits corresponding to the *SLD* profiles shown in the middle and right panel. Right panel: Magnified *SLD* distribution of the Al/Al₂O₃/liquid subphase region of L1 sample middle panel showing changes in the *SLD* of the layer at different pressure conditions.

The fits were obtained by fitting the five data sets separately with the constraints described in the text. NR data and the fits are off-set by a decade along y-axis for clarity.

Pressure (atm.)	Thickness of Al Layer (Å) (+/- 1.0)	Thickness of Al ₂ O ₃ Layer (Å) (+/- 1.0)	SLD of Al ₂ O ₃ Layer (· 10 ⁻⁶ Å ⁻²) (+/- 0.2)	χ^2
0	925.2	77.6	3.1	2.3
150	925.2	80.7	3.0	3.5
300	925.2	80.7	2.7	7.9
450	925.2	85.0	2.4	10.7
600	924.7	85.0	2.3	15.1

Table 1. The numerical results obtained from the separate fitting of the five pressure data sets.

Pressure (atm.)	Thickness of Al Layer (Å) (+/- 1.0)	Thickness of Al ₂ O ₃ Layer (Å) (+/- 1.0)	SLD of Al ₂ O ₃ Layer (· 10 ⁻⁶ Å ⁻²) (+/- 0.2)	Al-Al ₂ O ₃ roughness (Å) (+/- 0.2)	Al ₂ O ₃ -subph. roughness (Å) (+/- 0.2)
0	936	55.8	2.9	6.4	5.2

150	933	57.6	3.0	8.1	3.7
300	930	69.9	2.5	3.1	4.4
450	931	71.1	2.3	4.0	4.3
600	933	70.1	2.1	8.0	6.6

Table 2. The numerical results obtained from the simultaneous fitting of the five pressure data sets. The χ^2 of the simultaneous fit was 16.2.

Figure 1

Figure 2

Figure 3

Figure 3 left big

Figure 3 middle panel big

Figure 3 right panel big

Figure 4

Figure 4 left panel big

Figure 4 middle panel big

Figure 4 right panel big

Figure 5

Figure 6

Figure 6 left big panel

Figure 6 middle big panel

Figure 6 right big panel