Investigation of the properties of aluminum tube used in Thailand Research Reactor TRR-1/M1

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Abstract. Thailand research reactor, TRR-1/M1, operated approximately at 1,200 kWth, which produced maximum neutrons flux of $8 \times 10^{13}$ n/cm$^2$.sec and temperature of ~400°C at hottest spot. This paper presents the material degradation analyses of an aluminum (Al6061) tube used as a pneumatic transferred irradiation tube at position G33 in the TRR-1/M1 reactor core from 1977 to 2005. The analyses consisted of oxide characterization and radiation hardening measurement. The oxide characterization was done using XRD grazing angle technique for phase identification, and SEM for surface morphology and cross-section investigation. The radiation hardening was evaluated through Vicker-hardness measurement. Results showed that oxide on the aluminium tube consisted of three layers; a transition layer, a Al oxide layer of Bayerite (Al(OH)$_3$) or Gibbsite (Al$_2$O$_3$.3H$_2$O), and a thin layer of small grains of Quartz (SiO$_2$). The results revealed that neutron-captured reaction of Al produced Si, which can cause changes in material properties from loss of Al content in bulk material. The hardness test showed that Al tube specimens were softer than control specimens. Overall outcome of the study explained the major degradation mechanisms in the reactor core, which led to suggestions on maintenance and service life time of the materials for safe operation of the reactor.

1. Introduction
Thailand’s research reactor has been in operation since 1962. The reactor was converted from an MTR type to a TRIGA-MARK III type with low-enriched uranium fuels in 1977, called TRR-1/M1. Since the TRR-1/M1 has been in service for over 42 years after the modification, reactor core structural materials would experience aging issues such as corrosion, irradiation embrittlement, wear, fatigue, etc. A set of research works was conducted by Office of Atoms for Peace in collaboration with Thailand Institute of Nuclear Technology. The research has a major goal in evaluating aging degradation effects on the reactor core structural materials. The first work was reported in 2017, which focused on the evaluation of neutron damage rate and its effects on mechanical properties of the reactor in-core components, made from SS304 and Al6061, after 39 years of service [1]. Results revealed that neutron damages could affect mechanical properties of the SS304 clad tremendously, whereas it would have small effects on the Al6061 structural material. The present study focuses on investigations of two major aging mechanisms, namely, corrosion and irradiation hardening on an Al6061 irradiation tube that was dismantled from the TRR-1/M1. Results from this study will fulfil understanding of aging mechanisms in TRR-1/M1.
Aluminum alloys is chosen as structural materials in research reactors because of their good corrosion resistance, low thermal neutron captured cross section, and fair mechanical properties. Several types of research reactor including MTR, TRIGA, and Russian designed reactors uses aluminum alloys for fuel cladding and sometimes for core structure components, i.e., core shroud, thermal column, irradiation tube, and piping, etc. These aluminum alloys include, grades Al1100 (or Al1050), Al6061, PAR-1 (Poland) and SZAV-1 (Russia) [2, 3]. The TRR-1/M1 has most of its structure made of Al6061. Since the alloys were employed in the research reactors under coolant water, they generally undergo aqueous corrosion under temperature ranges from room temperature to approximately 200°C. The corrosion exhibits three major forms including uniform, pitting, and galvanic corrosions. Parameters that affect the corrosion are service temperatures, impurities in water, pH, conductivity, and perhaps radiation. Corrosions in the aluminum alloys had been studied thoroughly. However, effects of radiation on corrosion of the alloys in research reactor have not been reported extensively. Irradiation effects on mechanical behaviour of Aluminum alloy had been reported from many studies. High neutron fluence (energy) was reported to cause loss of ductility and fracture toughness [4].

Objectives of this study are to investigate and understand aging effects of the reactor core structural materials made of Al6061 by focusing on two major degradation mechanisms, namely, corrosion and radiation effects on mechanical properties. The results will describe corrosion products, oxide thickness, and hardness after service for approximately 29 years. Expected outcomes from this study are; to evaluate service lifetime of components made from Al6061 in the research reactor, and to apply information and knowledge from this study in the safety regulations of research reactors.

2. Materials and Methodology

2.1. Aluminum tube

A pneumatic transferred irradiation tube made from aluminum alloy graded Al6061 was loaded in the TRR-1/M1 reactor core during the conversion in 1977. Position of the tube was at G33, figure 1. The tube was dismantled from the reactor in 2005 after serviced for ~29 years. In order to cool down its radiation level, the tube was left in storage for 10 years before performing analyses. Radiation level of the tube was less than 1 μSv/hr. Radiation survey has identified nuclides of Co-60 and Eu-152, which usually found as long half-lived activation products from trace amount of Co, Fe, and Eu due to their high neutron activation cross-section.

![Figure 1. Position of G33 Pneumatic Transferred Irradiation Tube](image-url)
2.2. Sample preparation
The aluminum irradiation tube was cut into 5 parts along the length. Four specimens of 1x1 centimetres were cut from each section by a low speed diamond saw. The specimens from each section were analysed by four techniques described in Section 2.3. Cross section samples were mounted in epoxy resin mixed with conductive filler, then were polished with SiC grinding papers Grits P320, P600, P800, P1200, P2500, and P4000, respectively.

2.3. Analysis
Morphology and composition analyses were conducted with TESCAN Scanning Electron Microscope (SEM) model VEGA3 LM equipped with an Energy Dispersive Spectrometry (EDS) system. SEM images were taken under voltage 20 kV in secondary electron and back-scattered modes. Oxide phase characterized by an X-Ray Diffraction (XRD) of the Bruker XRD model D8 Advance. Grazing angle technique was applied to characterize oxide scale with 3° incident angle in order to limit analysis depth within specimen surface.

2.4. Hardness Test
Investigation of mechanical property changes in the irradiated aluminum tube was done using Vicker Hardness (HV) measurement. The measurement was performed with Wilson Hardness model Tukon 1120/1202 in accordance with ISO6507 [5]. A diamond pyramid with a square base indenter and 1Kgf loading were used for the test with dwelling time set at 10 second. Test specimens were obtained from the middle and from near the end of the tube. Hardness of un-irradiated Al6061 samples was also measured.

3. Results
3.1. Oxide characterization
Oxide characterization consisted of analyses of oxide phases and composition, observation of surface oxide morphology, and measurement of oxide layer thickness. Results will be used to evaluate and understand corrosion behavior of Al6061 in the research reactor core.

Surface oxide

Observation from the SEM showed that surface of the tube covered with oxide scale. Samples from each section of the irradiation tube are similar in nature. There are three distinct features found on the specimen surface.

- General oxide scale: Figure 2 shows general oxide scale, which composed of small granular oxides, and covered most of surface of the specimen. Composition of the oxide consisted of O (~60 wt%), Al (~35 wt%), Si (~5 wt%), and trace elements of Ti, Fe, Mg, and Mn.
- Large oxide grains with light-colour (observed in SEM) that formed on top of oxide scale, figure 3. Composition of oxide consisted of O (~51 wt%), Al (~18 wt%), Si (~26 wt%), and trace elements of Ti, Fe, Mg, and Mn.
- Spallation of the oxide scale exposed alloy substrate underneath the scale, figure 4.
Oxide layer and thickness.

Cross section sample of the tube exhibited three distinct layers of oxides grew on alloy substrate. Figure 5 shows cross section image of oxide layer on the irradiation tube. Alloy substrate is on left-side of the image with smooth and flat edge. Next to the substrate is a dark oxide layer (in SEM image), and a bright oxide layer. Interface of both layers is indistinct. The outermost layer is a small-grain layer that can be observed as the brightest layer on surface.

Thickness of each layer were measured and averaged from five cross section samples of each section of the tube. The thickness of each layer falls into the same trend for all samples. The aluminum oxide layer is thickest among all layers. The transition layer is thinner than the aluminum oxide layer. Thinnest layer is the silicon oxide grain layer, which is easily fall off. Total thickness is approximately 12.98 ± 1.65 μm. Oxide layer thickness is reported in table 1 together with characteristic of three layers.
Composition and phase.

Figure 6 showed composition profile of oxide layers. Each layer exhibited different elements and content. Alloy substrate has major composition of aluminium (>90 wt%). In transition layer, aluminium content decreased from alloy level (>90 wt%) to that of aluminium oxide (<40 wt%). Oxygen gradually increased to that of aluminium oxide level (~65 wt%). Aluminium oxide layer has aluminium ~35 wt% and oxygen ~65 wt% with small amount of silicon. Outermost layer has aluminium ~20 wt%, silicon ~25 wt% and oxygen ~50 wt% with trace elements of iron and chromium.

The grazing angle XRD with 3° incident angle characterized oxide scale phases on three samples. Results revealed that major oxide is aluminium oxide in forms of Gibbsite (\(\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}\)) and Bayerite (\(\text{Al(OH)}_3\)). The analysis also showed another type of oxide, which is silicon oxide in forms of Quartz (\(\text{SiO}_2\)) and Cristobalite (\(\text{SiO}_2\)). One of sample showed aluminium silicon oxide of Kaolinite (\(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\)). Note that the diffraction peaks of quartz appeared clearly in a sample that has large area of white particles on surface, figure 7.

Table 1. Summary of characteristic of three oxide layer on an aluminium irradiation tube used in TRR-1/M1 for 29 years.

<table>
<thead>
<tr>
<th>Oxide layer</th>
<th>Morphology</th>
<th>Composition/ Phase</th>
<th>Thickness (Micrometres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition layer</td>
<td>Observed between alloy substrate and Al- oxide as dark area (in SEM)</td>
<td>Al content decreased from alloy level (&gt;90 wt%) to that of Al oxide (&lt;40 wt%). O content gradually increased to that of Al oxide level (~65 wt%)</td>
<td>2.27 ± 0.78</td>
</tr>
<tr>
<td>Aluminium oxide layer</td>
<td>Dense and thick oxide scale</td>
<td>Gibbsite ((\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O})) and Bayerite ((\text{Al(OH)}_3))</td>
<td>9.66 ± 1.15</td>
</tr>
<tr>
<td>Silicon oxide layer</td>
<td>Thin layer of oxide grains on the outermost surface</td>
<td>Quartz ((\text{SiO}_2)), Cristobalite ((\text{SiO}_2)), and Kaolinite ((\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4))</td>
<td>1.05 ± 0.89</td>
</tr>
</tbody>
</table>

3.2. Hardness measurement

The measurement result shows that there is no difference in hardness between the samples from the end and the ones from the middle of the tube. The average hardness of the tube is lower than the hardness of control specimen and the ASM standard [6] values of 107 HV (Converted from Brinell Hardness Value of 95 HB). Table 2 presents results from Vicker Hardness test.
Table 2. Vicker Hardness (HV) test result.

<table>
<thead>
<tr>
<th>Article I.</th>
<th>Specimen from end of the tube</th>
<th>Specimen from middle of the tube</th>
<th>Un-irradiated Al6061 w/T651 tempering</th>
<th>ASM Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average HV</td>
<td>91.07</td>
<td>90.84</td>
<td>118.91</td>
<td>107</td>
</tr>
<tr>
<td>S.D</td>
<td>3.18</td>
<td>2.85</td>
<td>3.30</td>
<td></td>
</tr>
</tbody>
</table>

4. Discussion

Results of oxide characterization and hardness measurement revealed that the Al6061 irradiation tube had aging degradation issues. Corrosion of the aluminum tube exhibited general aqueous solution. However neutron transmutation has influence on oxide formation. In addition,

4.1. Oxidation of Al tube

Oxide characterization revealed that oxide formed on the Al6061 tube consisted of:

- Transition layer where aluminium diffused outward to oxide scale and oxygen diffused inward to substrate.
- Main oxide scale is Gibbsite (Al$_2$O$_3$.3H$_2$O) or Bayerite (Al(OH)$_3$). Both of them are considered as passive oxides. Gibbsite is formed at temperature below 77°C in pH between 5.8 – 9. Bayerite is formed in pH below 5.8. [2] This finding revealed that water chemistry of TRR-1/M1 was properly treated, but sometimes the pH is slightly lower than 5.8. According to Safety Analysis Report (SAR) of the TRR-1/M1, the coolant water must be purified to control conductivity less than 5 μS/cm and pH between 5.0 and 7.5 to minimize oxidation of the components.
- Small oxide grains layer consisted of silicon oxide in forms of Quartz (SiO$_2$) or Cristobalite (SiO$_2$), and aluminum-silicon oxide of Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) at the outermost surface of oxide. Silicon in the oxide grains occurred from neutron-captured reaction of aluminium. There are three consecutive mechanisms in the formation of SiO$_2$: first mechanism is aluminium oxide formation, second is transmutation of aluminium to silicon, and the last one is silicon oxide formation. Sequence and detail information needs to be further studied. In addition, the small SiO$_2$ grains easily spall off. They will increase impurity, radioactivity and conductivity of coolant water.

In addition to the constitution of oxide scale, evidence showed the spallation of oxide. Spallation of aluminium oxide is usually found when oxide scale grew thick. Stress in oxide scale may arise from thermal stress during the reactor operation and cooling down, or mechanical stress from vibration or water circulation. The stress caused oxide scale to spall off after exposure in water for over 42 years. Results form the oxide spallation can cause substrate exposed to water, thus the oxidation rate of aluminium increases. In addition, oxide spalled into water can increase impurities, conductivity and pH of coolant water.

4.2. Effects of neutron transmutation

For structural materials in nuclear reactors, nuclear reactions always occur with composition elements of the material. The results found that neutron transmutation by neutron capture reactions also play important role on chemical and physical properties of the materials, i.e., the SiO$_2$ formation. Aluminium
in Al6061 has relatively high neutron captured cross section. Major nuclear reactions of aluminium for both thermal and fast neutrons are described below.

For thermal neutrons, major nuclear reaction is neutron captured produces gamma reaction \((n,\gamma)\) with cross section of 0.233 barns. Final products of this reaction is \(^{28}\text{Si}\).

\[
^{27}\text{Al} (n,\gamma)^{28}\text{Al}, \quad ^{28}\text{Al} \rightarrow ^{28}\text{Si} + \beta \quad (1)
\]

For fast neutrons, major nuclear reactions are neutron captured produces alpha \((n,\alpha)\) with cross section of 0.125 barns, and neutron captured produces proton \((n,p)\) with cross section of 0.073 barns. (Note that the cross sections are for 14 MeV neutrons.)

\[
^{27}\text{Al} (n,\alpha)^{24}\text{Na}, \quad ^{24}\text{Na} \rightarrow ^{24}\text{Mg} + \beta \quad (2)
\]
\[
^{27}\text{Al} (n,p)^{27}\text{Mg}, \quad ^{27}\text{Mg} \rightarrow ^{27}\text{Al} + \beta \quad (3)
\]

Analysis results clearly showed that silicon was found as \(\text{SiO}_2\) on surface of oxide, and precipitations of \(\text{Si}\) in substrate. Magnesium was found only small amount. This finding revealed that the dominate nuclear reaction is equation (1), which occurred by thermal neutrons and produced silicon. The Si product reacted with water resulted in \(\text{SiO}_2\) formation. However, effect of the quartz formation on the oxidation rate is still unclear, but their spallation can increase impurity in coolant water.

4.3. Effects of neutron on hardness

Thus far, radiation hardening effect is not presented in the aluminum tube. As reported in [7], irradiation of up to 5 displacement per atom (dpa) resulted in only 4-5% reduction in ductility and fracture toughness, whilst an estimation of displacement of Al6061 after 39 years of service in TRR-1/M1 provided in the earlier work [1] is on the order of 4 dpa. Therefore, it is hypothesized that the amount of neutron irradiation is not high enough to induce enough transmutation to cause hardening. The test result, on the contrary, shows decreasing of hardness in the aluminum tube after long service years. This is likely to be caused by tempering effect after long service years, as suggested in literatures [8,9] that reduction of yield strength and hardness of Al6061-T6 occurs under long period of aging at the temperature of approximately 170 to 220 °C.

In addition to the quartz formation, it is observed that Si precipitates formed in the alloy substrate. This probably is also the cause of change in mechanical properties from loss of Al content in bulk material. It is, therefore, implied that the effects of transmutation and tempering overruled those of radiation hardening (at present neutron fluence). Results of hardness test are inconclusive, and require further study.

4.4. Aging mechanism and service lifetime

The results demonstrated that the Al tube used in the TRR-1/M1 experienced aging mechanisms, especially oxidation and transmutation. Service lifetime of the Al tube should be limited by spallation of oxide scale when the scale becomes too thick. In addition the Al tube should be changed after usage in a certain neutron fluence to avoid degradation in mechanical property.

5. Conclusion

This study on investigation of properties of Al tube used in TRR-1/M1 for approximately 29 years demonstrated methodologies to evaluate aging effects of reactor core structural materials. The study focused on two major aging mechanisms, namely, corrosion and irradiation hardening. Results showed that oxidation is major aging mechanisms for Al6061. Radiation hardening did not show significant effects on alloy hardness. Meanwhile, transmutation played an important role on the formation of oxide (quartz), and probably on the mechanical property. Future study should be conducted to fully understand the neutron damage on mechanical properties.
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