Gamma-radiation-induced corrosion of aluminum alloy: low dose effect

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Abstract. Gamma-radiation-induced corrosion of aluminium alloy 6061 (AA6061) immersed in demineralized water was studied at radiation dose up to 206 kGy using a Co-60 gamma radiation source. The surface morphology and chemical composition of the oxide produced on the post-irradiated samples were investigated using SEM-EDS. The electrochemical corrosion potentials ($E_{corr}$) of the post-irradiated samples were measured. The corrosion behavior of AA6061 appeared to be dose dependent under the experimental conditions. A dramatic change in surface morphology was observed in the samples exposed to gamma radiation at 206 kGy. At this radiation dose the aluminium oxide scale developed can be clearly seen. The results from electrochemical corrosion tests have shown that the corrosion potentials ($E_{corr}$) can be undoubtedly decreased by gamma irradiation, giving corrosion rate of $7 \times 10^{-4}$ mm/yr.

1. Introduction
Aluminium Alloys (AAs) have been the material of choice for application in water-cooled-and-moderated Research Reactor (RR) systems due to their unique mechanical properties, high corrosion resistance in water and low neutron cross-section. Although AAs are known to develop highly stable aluminium oxides under RR conditions (pH 5.6, T<100°C and atmospheric pressure), corrosion in this group of materials has commonly been observed by the reactor personnel. Corrosion of material in RRs is believed to be mostly attributed to ionizing radiations[1-5]. The information regarding effects of ionizing radiations on nuclear materials is highly required for assessment of operation and maintenance as well as safety margins of nuclear reactors. Ionizing radiation can interact with material via both direct and indirect mechanisms (effects). Direct interactions of ionizing radiation with material can result in lattice vacancies, self-interstitial atoms and transmutation products (radiation damage microstructure), whereas indirect effect which stems from the chemical reactions between the material surface and the radiolytic primary species (($e^-$)$_aq$, $^\bullet OH$, $^\bullet H$, $H_2O_2$, $O_2$, and $^\bullet O_2^-$) can dictate electrochemistry of the solution and may ultimately lead to corrosion of the material[6-12]. As of now, the effects of ionizing radiation on nuclear materials corrosion are still not yet fully understood. Only limited information regarding radiation-induced/accelerated corrosion of AAs is available. Many key aspects of this system have not been investigated, including corrosion kinetics, corrosion products and surface morphology of the irradiated materials. An earlier study on the effects of neutron and gamma radiation on corrosion of AA claimed that neutron and gamma radiation had no different effects on corrosion of these materials. It was also found in this study that pitting corrosion of the AA samples appeared to be in higher density at a greater distance from the radiation source[13]. This conclusion is completely inconsistent with the findings from the recent works which indicated that corrosion of metal alloys such as stainless steel can be considerably induced and accelerated by...
radiation. The studies also demonstrated that exposing to high dose radiation can initiate stress corrosion cracking and intergranular corrosion in AA[14-16].

To develop accurate understanding of the effects of ionizing radiation - gamma radiation on corrosion of AA, an in-depth study of this system under the RR conditions (low dose effects) has been carried out. The results obtained will not only benefit the reactor personnel in evaluating corrosion level of the AA components, but also provide fundamental understanding of surface chemistry of this chemical system.

2. Experimental Section

An AA6061 sheet (Southwest Aluminium, China) was cut into square-shaped samples with dimensions of 1 inch × 1 inch × 2 mm. The samples were later wet polished with abrasive paper up to 1200 grit using a Buehler MetaServ 250 Twin polisher. To remove polishing residues, the samples were subsequently ultrasonic cleaned in acetone, methanol and ethanol, respectively. Prior to experiment, the samples were weighed and their chemical composition was analyzed using an X-ray Fluorescence (XRF) spectrometer (Bruker, S8 TIGER).

A cobalt-60 irradiator (30366 Ci) at the Thailand Institute of Nuclear Technology was used as radiation source throughout the experiment. During gamma irradiation, the samples were completely immersed in demineralized water in a glass container (using suspension glass hooks). Irradiation time and dose were varied with the maximum dose rate of 4.30 kGy/hr. Dosimetry was performed using Harwell Amber Perspex dosimeter. The sample temperature during irradiation was around 32°C.

The post-irradiated samples were weighed, kept in a desiccator and lastly characterized using SEM-EDS (Hitachi SU8020). An Autolab potentiostat, model PGSTAT302N, with a saturated calomel electrode (reference electrode) and a platinum electrode (counter electrode) was employed to determine the corrosion rates of the irradiated surface.

3. Results and Discussion

Dose effect was investigated by irradiating the AA6061 samples for 48 hours at different dose rates (1.08, 2.14 and 4.30 kGy/hr). The SEM micrographs of the unirradiated and post-irradiated samples can be seen in Figure 1.

![Figure 1. SEM micrographs of AA6061 samples after exposing to gamma radiation for 48 hours at different dose rates: a) unirradiated (immersed in demineralized water for 48 hours) b) 1.08 kGy/hr c) 2.14 kGy/hr and d) 4.30 kGy/hr.](image)

It can be clearly seen in Figure 1a. that uneven white spots were developed on the surface of the blank sample which was fully immersed in demineralized water for 48 hours without exposing to radiation. Presumably, the product is alumina Al(OH)₃, a water insoluble product commonly found when Al is oxidized in water[17-18]. Upon irradiation, the growth of the white product, (presumably Al(OH)₃) was obviously noticed as illustrated in Figure 1b, 1c and 1d. Increasing the dose rate increases the density of this corrosion product. As the dose rate changes from 2.15 to 4.30 kGy/hr, the
density rises considerably. There was no correlation between the product size and dose rate under the experimental conditions.

The irradiation time experiment was performed with the dose rate of 4.30 kGy/hr. The effects of radiation on the morphology of AA6061 from this experiment are shown in Figure 2. It is evident that irradiation time has great influence on the density of the corrosion product. There was also no correlation observed between the product size and time. The elemental composition analysis of the irradiated surface by Energy Dispersive X-ray Spectrometer (EDS) revealed that the white product was composed of aluminium, oxygen and carbon (Figure 3.), suggesting the formation of aluminium oxide as expected. Though it is well-known that at room temperature the corrosion product generated from oxidation of Al in water is in the form of amorphous alumina[17,19], there is no information regarding aluminium oxide structure in the system involving radiation reported. This challenging issue is left to be explored in our future work. The carbon component detected is likely to come from contamination during the sample preparation process. In addition, SEM images of the sample cross-section exposed to gamma radiation indicated that pit formation is undetectable at this range of radiation dose. The differences in weights of pre- and post-irradiated samples are not statistically significant, thus indicating no effects on weight loss at the radiation doses studied (see Table 1).

Figure 2. SEM micrographs of AA6061 samples after exposing to gamma radiation at different time (dose rate 4.30 kGy/hr): a) 8 hours b) 24 hours and c) 48 hours.

Figure 3. a) SEM micrograph of AA6061 samples after exposing to gamma radiation for 48 hours at dose rate 4.30 kGy/hr and b) EDS spectrum of the corrosion product indicated in Figure 3a.
Table 1. Weight change of AA6061 samples after immersion/irradiation.

| Immersion/Irradiation Time (hr) | Dose Rate (kGy/hr) | Weight (g) | Weight change (g) |
|---------------------------------|-------------------|------------|-------------------|
|                                 |                   | Pre- | Post-               |
| 8                               | 0                 | 3.0416 | 3.0413 | 0.0003 |
|                                 | 4.30              | 2.9925 | 2.992   | 0.0005 |
| 8                               |                   | 3.0956 | 3.0949 | 0.0007 |
|                                 | 4.30              | 2.8126 | 2.8125 | 0.0001 |
| 24                              | 0                 | 3.0608 | 3.0618 | 0.0007 |
|                                 | 4.30              | 3.0332 | 3.0325 | 0.0007 |
| 24                              |                   | 3.0199 | 3.0197 | 0.0002 |
|                                 | 4.30              | 2.992  | 2.9925 | 0.0005 |
| 48                              | 0                 | 3.1784 | 3.1782 | 0.0002 |
|                                 | 4.30              | 3.1627 | 3.1619 | 0.0008 |
| 48                              |                   | 3.0376 | 3.0371 | 0.0005 |
|                                 | 1.08              | 2.8443 | 2.8437 | 0.0006 |
| 48                              |                   | 2.7154 | 2.7146 | 0.0009 |
|                                 | 2.14              | 2.3393 | 2.3381 | 0.0012 |
| 48                              |                   | 2.8539 | 2.853  | 0.0009 |
|                                 | 4.30              | 2.9875 | 2.9873 | 0.0002 |
|                                 |                   | 3.1071 | 3.1067 | 0.0004 |
|                                 |                   | 3.0416 | 3.0413 | 0.0003 |

The results from the electrochemical measurements of the blank (unirradiated), 16-hour-irradiated and 24-hour-irradiated samples (4.30kGy/hr) in demineralized water are presented in Figure 4. A similar shape of potentiodynamic polarization curves was observed for all 3 samples. The values of corrosion potential ($E_{corr}$) and corrosion current ($I_{corr}$) density obtained, presented in ($E_{corr}$, $I_{corr}$), are (-0.181 V, 7.54 × 10⁻⁸ A/cm²), (-0.284 V, 7.18 × 10⁻⁸ A/cm²) and (-0.494 V, 3.68 × 10⁻¹⁰ A/cm²) for the blank, 16-hour-irradiated and 24-hour-irradiated samples, respectively. Based on this study, it is clear that gamma irradiation can shift $E_{corr}$ of the AA6061 sample to more negative values, thus decreasing corrosion resistance. The $I_{corr}$ density values of the irradiated samples were found to be not systematic. The evidence from $E_{corr}$ measurements confirms that gamma exposure can increase corrosion susceptibility of AAs. The corrosion rate of the irradiated samples given by this electrochemical study is ca. 7 × 10⁻⁴ mm/yr. The calculation of this corrosion rate was based on Faraday’s Law shown in Equation (1)[20]:

$$CR = K_1 \frac{I_{corr}}{\rho} EW$$

Where:
- $CR$ is corrosion rate in mm/yr,
- $K_1$ is a constant equal to 3.27 × 10⁻³ mm-g/µA-cm-yr,
- $\rho$ is density in g/cm³ of the material used in corrosion testing ($\rho_{Al6061} = 2.70$ g/cm³), and
- $EW$ is equivalent weight, mass of the material in g that will be oxidized by the passage of one Faraday of electric charge, ($EW_{Al6061} = 9.01$ g).
Figure 4. Polarization curves for the AA6061 samples obtained in demineralized water.

4. Conclusion
Gamma-radiation-induced corrosion of AAs can be revealed by SEM-EDS in conjunction with an electrochemical technique. Pitting corrosion was not detected under the experimental conditions. It is strongly evident that gamma irradiation can significantly accelerate aluminium oxide formation on AA6061. The density of aluminium oxide was found to increase with irradiation time and dose. The correlation between irradiation dose and $E_{corr}$ was observed. However, $I_{corr}$ is dose insensitive. The corrosion rate extracted from the electrochemical data is approximately $7 \times 10^{-4}$ mm/yr.

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