Cathodic Dissolution of Aluminum Alloy AA6061

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Introduction

Aluminum is a common matrix material for low enrichment uranium (LEU) irradiation target. The post-irradiation processing, to isolate and purify the produced ⁹⁹Mo from ²³⁵U fission, should dissolve the AA6061 target matrix. A desirable rapid dissolution of irradiated aluminum target is needed, since the longer the post-processing nuclides production takes place, the lesser availability of ^{99m}Tc radiopharmaceutical would be produced [1].

Aluminum dissolution in alkaline solution occurs chemically, but can also be dissolved when the aluminum is polarized cathodically. This is a phenomenon also referred to as "cathodic corrosion". It was first reported by Caldwell and Albano [2] and further investigated by several researchers [2-9].

In this work, the cathodic dissolution of AA6061 was compared by exposing samples to alkaline solution with and without imposing cathodic potential.

Experimental

Coupons of hot rolled aluminum alloy AA6061 were ground by emery paper with a grid of #180 just to leave deep scratches to trace the dissolution level of the experiments. The samples were duly cleaned soap and water, followed by acetone degreasing and set as cathode in 2.64 cm² bottom opening of a quartz tubular cell. It was used, as electrolyte, an aqueous solution of 0.25 M NaOH with NaCl addition of 1 g/100ml of solution, its pH was 12.3. All experiments were carried out at room temperature. The open potential of this arrangement varied shortly around -1.5 V_{AgCl}. The counter electrode was 304 stainless steel. There were 2 experiments types:

NCP	4 tests	Exposition during 8500 s	No cathodic polarization
DCP	3 tests	Exposition during 1000 s	Direct Cathodic polarization of -2.5 $V_{Ag/AgCl}$

Results and Discussion

The average rate of mass loss was $0.195\pm0.015 \text{ mg/cm}^2\text{s}$ for NCP experiment type and $0.588\pm0.011 \text{ mg/cm}^2$.s for DCP experiments. Significance level of average limits was 95%. So, the direct cathodic polarization with -2.5 V_{AgCl} (DCP) promoted around 3 times more dissolution than a simple exposition of the sample to the electrolyte without any polarization (NCP). Mokkadem *et al.* [9] summarized the electrochemical studies of cathodic polarization with addition of NaCl in alkaline solutions by the following reactions:

$$Al + 4OH^{-} \rightarrow Al(OH)_{4}^{-} + 3e^{-}$$
 (1)

It is well established that this dissolution may happen by the formation of an intermediate hydroxide film. Following the proposal of Moon e Pyun [4], the reaction 1 may be subdivided into others so giving the following reactions:

$$Al + 3OH^{-} \rightarrow Al(OH)_3 + 3e^{-} \qquad (2)$$

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$$
 (3)

Nevertheless, this is a simple model, but in general terms it explains that an excess of hydroxide formed by electrolysis in cathode site leads to chemical dissolution of $Al(OH)_3$ protection film by transforming it into soluble $Al(OH)_4$, which conveys, by no establishment of a hydroxide barrier, to a ready aluminum dissolution by:

$$Al+4H_2O+e^- \rightarrow 2H_2 + Al(OH)_4^- \quad (4)$$

The addition of NaCl helps this formation by increasing $Al(OH)_3$ solubility, since it catalyzes the transformation to the soluble ion $Al(OH)_4^+$ and Cl^- anion is thought to play a role in pit formation and growing [10-12]. The SEM micrographs, showed in Figure 1, are illustrative to help understanding the process of AA6061 dissolution.



Figure 1 – SEM micrographs showing the AA6061 dissolution process: (top-left): original sample; (top-right): NCP experiment ; (bottom-figures): 2 microstructures after DCP experiment. All the magnifications are the same.

As could be seen in the images, the NCP tests promoted dissolution as expected for aluminum alloys immersed in alkaline solutions. The NCP dissolution occurs preferentially at the inclusions sites and at the grain boundaries, since the structural disorder energy at these regions is higher, then susceptible to be corroded.

The grains after NCP have a shallow attack in grain bulk and the dissolution produces fine debris products in the corrosion areas. This debris development did not appear in DCP resulting structure, displaying a general corroded surface much more unblemished. All debris bits were probably consumed quicker for current swapping around the more conductive regions (grain boundaries and inclusions sites). It is noticeable a more profound attack at the grain interior, giving them a concave appearance. It resembles a kind of smoothening consumption of material. An eventual uneven electron flow towards the grain boundaries and inclusion crests prompts H_2 evolution. It is also perceivable, in the DCP images, that pit nucleation is well disseminated all over the polarized surface. And the pits display an intense corrosion role. A model may be idealized having "less alkaline" regions at the structure crests with higher electron flow, which promotes the H_2 evolution. Towards the grain centers, it will be established a "more alkaline" region where Al dissolves preferentially by reaction 1. This electrochemical reasoning may explain why the corrosion rate of AA6061 under cathodic polarization is 3 times higher than the non-polarized dissolution.

Conclusions

Since AA6061could be structural material in irradiation targets, it should be quicker dissolved in post-irradiation processing. The dissolution of AA6061 samples exposed by 0.25 M NaOH with 1 g/100ml NaCl addition could be improved in terms of dissolution rate from $0.195\pm0.009 \text{ mg/cm}^2\text{s}$ to $0.588\pm0.011 \text{ mg/cm}^2\text{s}$ in the same solution just by applying cathodic polarization of $-2.5 \text{ V}_{\text{AgCl}}$ potential. This could be explained by more active H₂ evolution at grain boundary crests and inclusion sites. More alkaline sites at grain interior promotes Al dissolution more effectively, forming a smooth concave appearance of the grains due to the current swapping consuming any eventual surface peaks. This behavior may lead to pit nucleation in several grain sites of the polarized structure, which may become quite corrosive throughout the structure.

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References

- [1] A.M. Saliba-Silva et al., 2011 Int. Nuclear Atlantic Conf. (INAC) ABEN, Belo Horizonte, MG, 2011.
- [2] K. Ogle, M. Serdechnova, M. Mokaddem, P. Volovitch, Electrochimica Acta, 56 (2011) 1711-1718.
- [3] A.R. Despic, J. Radosevic, P. Dabic, M. Kliskic, Electrochimica Acta, 35 (1990) 1743-1746.
- [4] S.M. Moon, S.I. Pyun, Corros Sci, 39 (1997) 399-408.
- [5] T. Ueno, K. Azumi, M. Seo, J Electroanal Chem, 540 (2003) 97-104.
- [6] T. Grigoletto, E. Oliveira, I.G. Gutz, Talanta, 67 (2005) 791-797.
- [7] L. Soler, A.M. Candela, J. Macanás, M. Muñoz, J. Casado, J. Power Sources, 192 (2009) 21-26.
- [8] H.Z. Wang, D.Y.C. Leung, M.K.H. Leung, M. Ni, Ren. and Sustain. Energy Rev., 13 (2009) 845-853.
- [9] M. Mokaddem, P. Volovitch, F. Rechou, R. Oltra, K. Ogle, Electroch. Acta, 55 (2010) 3779-3786.
- [10] L.A. Shalaby, K.M. El Sobki, A.A. Abdul Azim, Corros Sci, 16 (1976) 637-643.
- [11] W.-J. Lee, S.-I. Pyun, Electrochimica Acta, 44 (1999) 4041-4049.
- [12] J. Ren, Y. Zuo, Surface and Coatings Technology, 191 (2005) 311-316.