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Corrosion Behaviour of Borated Aluminium Used as Neutron Absorber[*]

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ABSTRACT

The electrochemical behaviour of pure and borated aluminium was examined. Measurements were performed in two different electrolytes at 90°C containing different trace-amounts of chloride. For borated aluminium current transients, i.e. metastable depassivation events were found. It is suggested to attribute these transients to less stable passivation layers in comparison to pure aluminium.

INTRODUCTION

For ensuring subcriticality in dual-purpose casks or compact storage racks it is essential to utilise effective neutron absorbers. This becomes more important with increased fuel burn-up and especially as it is desired to store more nuclear fuel assemblies per cask or per given space in the storage pool. Because of the high cross section of ^{10}B for capturing thermal neutrons [1], materials containing Boron such as borated stainless steel or borated aluminium are widely used. In a given cask design weight reduction in combination with better neutron shielding can be reached using ^{10}B enriched borated aluminium.

During loading of casks absorbers will temporarily be in contact with reactor pool water and for wet storage applications this contact is continuous. In both cases corrosion and contact corrosion may occur. Therefore it is important to understand the differences in corrosion behaviour of borated and un-borated absorbers. In the present study corrosion behaviour of aluminium, ^{10}B enriched borated aluminium, stainless steel and zircalloy was examined using different electrochemical methods. Measurements were performed in deionised water with marginal contents of aggressive anions, and in contaminated environment containing 1mg/l chloride at elevated temperature. In this paper the results for borated and un-borated aluminium are presented and discussed. Results for zircalloy and stainless steel will be presented elsewhere.

EXPERIMENTAL

The corrosion studies were performed by electrochemical polarisation measurements. For these a common three-electrode configuration with working electrode, reference electrode and counter electrode connected to a commercially available potentiostat, which was controlled by a PC, was used [2]. The reference electrode was a saturated calomel electrode (SCE), the working electrode was a Teflon standard cell with a 9mm diameter opening and the counter electrode was a glassy carbon electrode.

Samples were prepared from sheet material of pure aluminium (99.9% Al) and aluminium AA1100 (DIN EN AW 1100) with addition of isotopically enriched Boron. The Boron was enriched in its isotope ^{10}B to a level of > 95at% and the Boron content of the alloy was between 4.0 and 4.5at%. Borated samples from two different production-lots (b-Al#1 and b-Al#2) with slightly different Boron contents were examined. Samples were cut in appropriate sizes from the "as received" sheet-material and cleaned in iso-propanol for 5 minutes using an ultrasonic bath just before inserting them into the Teflon standard cell for measurement. No additional sample preparation such as grinding or polishing was performed.

The electrolytes were prepared using 18.1MΩ water (54 nS/cm at 20°C) and NaCl and NaF of supra pure grade. Electrolyte #1 contained 0.15mg/l fluoride and 0.15mg/l chloride. Electrolyte #2 contained the same quantity of fluoride but 1.0mg/l chloride. The low fluoride and chloride contents of electrolyte #1 are already slightly higher than the levels allowed in the primary circuit of German boiling water reactors (BWR). The higher chloride content of about 1ppm in electrolyte #2 was chosen as an example for a contaminated and therefore more aggressive environment.

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[*] **This study is dedicated to Prof. G.K. Wolf on the occasion of his 70th birthday.**

By means of a conventional thermostat the electrolytic cell set-up was kept at 90°C +/-2°C, a temperature approx. 10° above the maximum allowed in the German standard for storage pool water [3] but still relatively easy to handle. The reference electrode was connected via a salt bridge to a Haber-Luggin capillary filled with a polymer membrane, and kept at ambient temperature.

The potentiostatic technique was utilised for the electrochemical measurements, i.e. a constant electrical potential was kept between working and reference electrode over a period of 30 minutes and the current response of the system was recorded. The potential was increased in 10mV steps from -300mV vs. SCE to +400 mV vs. SCE. Prior to starting these measurements the open circuit potential (E_{corr}) was recorded for 30 minutes.

RESULTS AND DISCUSSION

Aluminium forms a passive oxide film that prevents metal dissolution in neutral media. Because of the high chemical and mechanical stability of this film aluminium is not susceptible to uniform corrosion. However pitting, one form of localised corrosion, is seen in media that contain aggressive anions such as chloride or other halides [4,5]. Pure, unalloyed aluminium is less susceptible to any form of corrosion compared to its alloys or technical aluminium. In general it is suggested that this is due to the stability and homogeneity of the passivating oxide film. Unfortunately fundamental questions about localised corrosion and its initiation are still unanswered. There are a number of theories about the mechanisms but none is commonly accepted or describes all steps of pitting. Generally the interaction between the anions in the electrolyte and the passivating film leads to a local loss of passivity, which results in dissolution of the metal at a high rate. For an overview on this topic see for example G.S. Frankel's recently published review [6].

Electrochemical measurements are one method for investigating the corrosion properties of passive metals. Parameters of interest are the free corrosion potential, E_{corr}, the critical pitting potential, E_{crit}, and corrosion current densities, i_{corr}. Furthermore measurement of electrochemical noise can be used to study localized corrosion [7]. For a given alloy E_{corr}, E_{crit} and i_{corr} are depending on a number of parameters, including but not limited to, pH of the electrolyte, the concentration of ions and oxidising or reducing agents in the electrolyte, temperature, and surface state of the sample. As a general rule: the higher the measured current density, and the smaller the difference between E_{corr} and E_{crit} are, the more susceptible a given alloy is to localised corrosion.

Current Density Measurements

In order to receive current density vs. potential diagrams from the potentiostatic measurements, the mean current density over the complete 30 minutes, i_{mean}, and its standard deviation was calculated from the individual recordings. With the given low ion-concentration in the electrolytes the recorded current densities are low over a wide potential range. This leads to a situation where electronic noise is overlaid on the recorded current. Furthermore one has to take into account that transport phenomena may influence the recorded data more strongly than in electrolytes with higher ion contents. Therefore care has to be taken when interpreting the results and comparing the measured data with existing data for other electrolytes with higher conductivity.

In electrolyte #1 all samples showed a similar behaviour. The recorded mean current densities were very low in the cathodic branch of the curves, in some cases even close to the resolution of the equipment. In the anodic area current densities were higher and there was more pronounced noise. The recorded i_{mean} for pure aluminium and b-Al#1 in electrolyte #2 (Fig. 1) showed, for the major part of the potential range, an ohmic behaviour and the expected diffusion hindering at higher current densities. However, lower current densities for b-Al#1 in comparison to pure aluminium at potentials below approx. $-150mV_{SCE}$ indicated that oxygen reduction is hindered on this surface. A similar behaviour was found for b-Al#2, which also exhibited a generally lower cathodic current density.

As expected both borated aluminium alloys showed higher current densities than the pure aluminium in the anodic branch of the curves (Fig. 1). For b-Al#2 at potentials above $-100mV_{SCE}$ a fast increase in i_{mean} and a number of single current transients was found. One is tempted to conclude that this indicates the onset of stable pitting corrosion. However, the concentration of chloride is very low. Additionally neither pure aluminium nor the other alloy showed any pitting under these conditions. Furthermore the surface obviously repassivated spontaneously at higher potentials where one would never expect such behaviour for stable pitting.

Other authors have shown that the corrosion behaviour of aluminium is influenced by the surface condition, even by the way how samples are ground or polished [8]. For stainless steel Böhni et al [9] showed that initiation of pits preferably starts at inclusions or second phase particles. It is therefore reasonable to assume that inhomogeneities or defects in the passivating layer cause the electrochemical behaviour seen for b-Al #2.

Metastable Depassivation Events

In literature formation of metastable pits, i.e. pits that initiate grow for a short time and then repassivate, are described for the early stages of localised corrosion. When recording potentiostatic current vs. time diagrams these metastable corrosion events can be seen as anodic current transients [10]. It has been reported that such transients occur at potentials far below the critical pitting potential (E_{crit}). For typical metastable pits, the current density rises in an exponential like manner and quickly decreases when the pit is repassivated. However, a different behaviour was found when very small areas of stainless steel were examined [11]. In the latter case the fast rise and subsequent fall of the current was attributed to nucleation of pits caused by rupture of the passivating film, and immediate repassivation without growth. In any case the individual current transients are believed to represent individual corrosion events. Such transients may however overlap to form more pronounced peaks in the current vs. potential diagram.

As mentioned above, all samples exhibited a lot of electronic noise in both types of electrolytes. For b-Al#2 however typical current transients, i.e. electrochemical noise was seen (Fig. 2). In electrolyte #1 these transients appeared at electrode potentials above + 330mV$_{SCE}$ and in electrolyte #2 they were already visible at +100mV$_{SCE}$. In both cases sudden increases of the current density and exponential like decay was observed. Whereas in electrolyte #1 only single transients appeared, in electrolyte #2 multiple transients sometimes overlapped and the number of transients increased with increasing electrode potential (Fig. 2). This behaviour could be expected because of the higher chloride concentration in electrolyte #2. The authors believe that the transients can be associated with local pit nucleation or depassivation events, i.e. a situation where the local anodic reaction of the metal – which results in either thickening of the passive layer or dissolution of the metal – starts, and repassivation without pit growth leads to a fast decrease of the current density back to the passive current level.

It is not completely understood how and where such nucleation or metastable depassivation events take place. One possibility is that AlB$_2$ or AlB$_{12}$ phases, which are both present in the alloy (the latter at low concentrations), act as nucleation sites. Other possible causes include mechanical surface defects or inhomogeneities and inclusions in the alloy. In any case such electrochemical events start at locations where the passivating film is either more conducting or thinner. I. e. one can see the influence of inhomogeneous surface films, which provide protection as long as present but are more easily destabilised than the protective layer on homogeneous surfaces.

SUMMARY AND CONCLUSIONS

Results of electrochemical measurements on pure aluminium and borated aluminium in as-received surface condition in two different electrolytes containing traces of chloride at 90°C were presented. For borated aluminium current transients, which are an indicative for metastable depassivation events, could be seen. Pure aluminium – known for its corrosion resistance – did, as expected, not exhibit such current transients.

The transients and higher current densities for borated aluminium have been attributed to locally thinner and/or less stable passivation layers on the surface. The causes for such inhomogeneous passivation layers could be manifold ranging from pure mechanical surface defects to inclusions in the alloy.

It should be noted that the method deployed in this study has to be regarded as a kind of electrochemical microscopy. The actual loss of material through metastable depassivation or nucleation events especially at potentials below E_{crit}, even over an extended period of time, can be neglected on a macroscopic scale [12].

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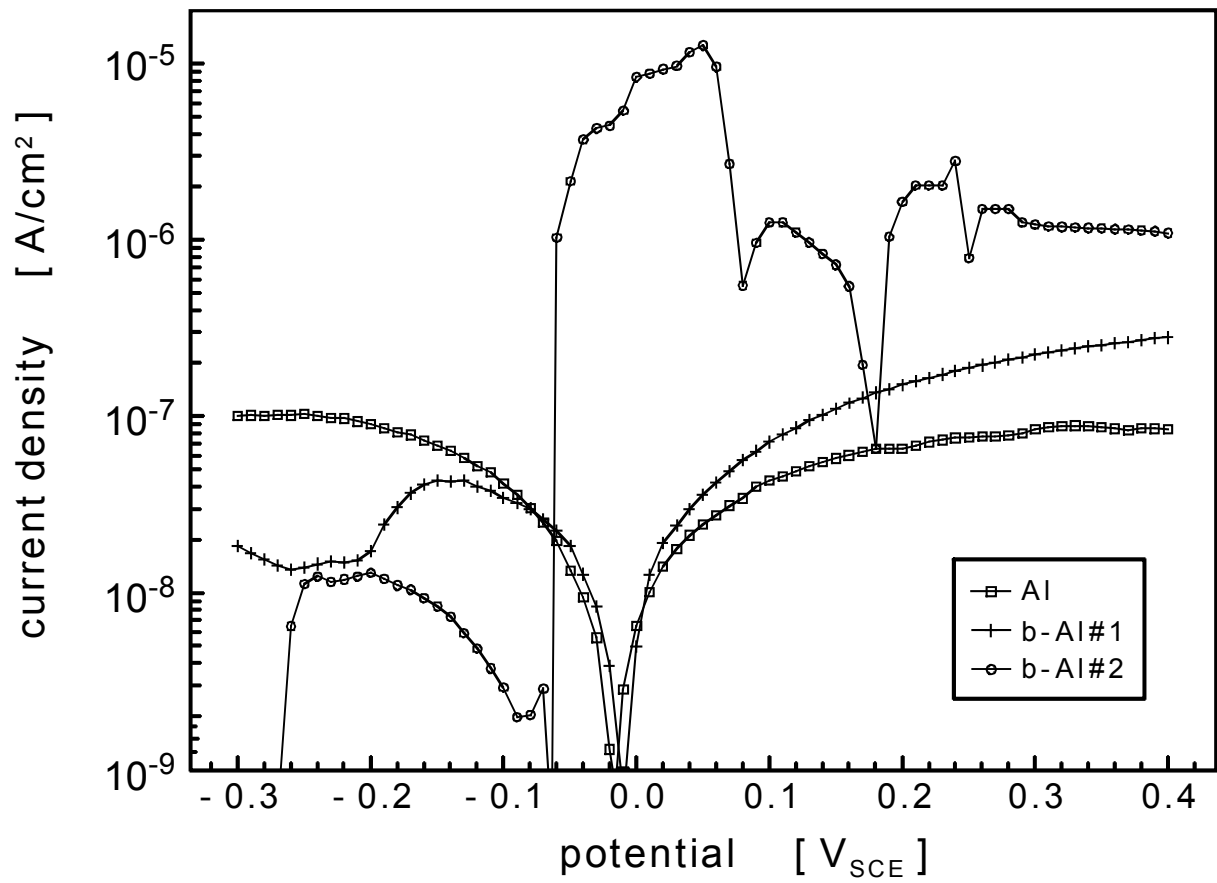
Fig. 1 Semilogarithmic current density vs. electrode potential plot; measurement points represent steady state current densities under potentiostatic conditions in electrolyte #2.
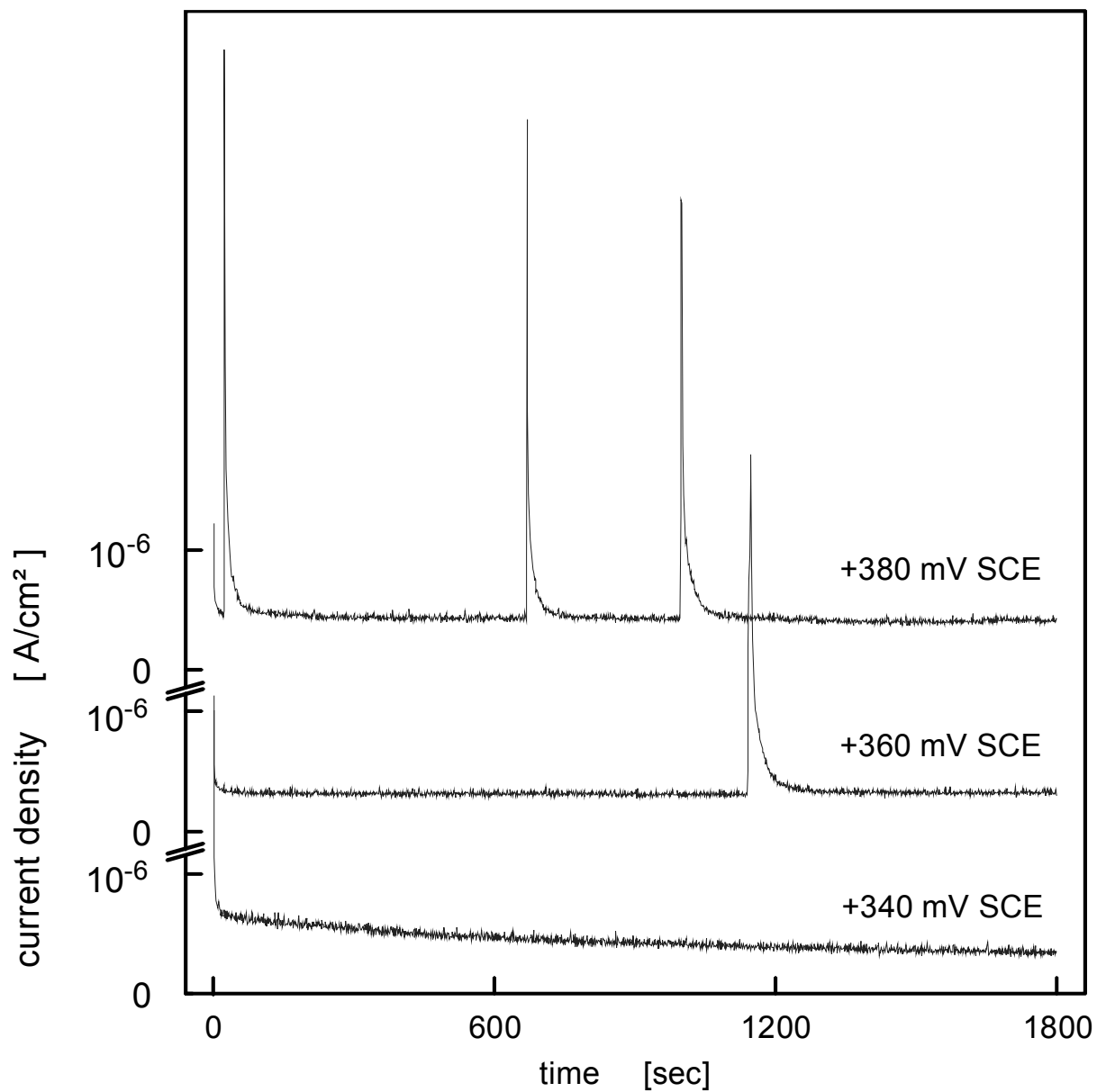
Fig. 2 Current transients recorded for b-Al#2 in electrolyte #2 at different electrode potentials.

REFERENCES

1. G. Erdtmann, *Neutron Activation Tables*, Verlag Chemie, Weinheim, 22 (1976)

2. W. Ensinger, *Protection against aqueous corrosion by ion implantation and ion beam assisted deposition*, in: Y. Pauleau, P.B. Barna (eds.), "Protective Coatings and Thin Films: Synthesis, Characterization and Applications", Kluwer Academic Publishers, Dordrecht, 585 (1997)

3. Sicherheitstechnische Regel des KTA, Regel KTA 3303, Fassung Juni 1990, *Wärmeabfuhrsysteme für Brennelementlagerbecken von Kernkraftwerken mit Leichtwasserreaktoren*, www.kta-gs.de

4. Z. Szklarska-Smialowska, *Pitting Corrosion of Metals*, National Association of Corrosion Engineers, Houston (1986)

5. Z. Szklarska-Smialowska, *Pitting corrosion of aluminum*, Corrosion Science 41 (9), 1743-1767 (1999)

6. G. S. Frankel, *Localized corrosion of metals; a review of the rate-controlling factors in initiation and growth*, in "Passivity of Metals and Semiconductors", M. B. Ives, J. L. Luo, and J. R. Rodda (eds.), The Electrochemical Society Proceedings Volume 99-42, 445 (2001)

7. K. Hladky and J. L. Dawson, *The measurement of localized corrosion using electochemical noise*, Corros. Sci. 21, 317-322 (1981)

8. P. Schmutz and G. S. Frankel, *Influence of dichromate ions on corrosion of pure aluminum and AA2024-T3 in NaCl solution studied by AFM scratching*, J. Electrochem. Soc. 146, 4461-4472 (1999)

9. H. Boehni, T. Suter, A. Schreyer, *Micro- and nanotechnologies to study localized corrosion*, Electrochimica Acta 40 (10), 1361-1368 (1995)

10. O. Lensch, B. Enders, J. Knecht, W. Ensinger, *Examination of the metastable and stable pitting corrosion behaviour of aluminum modified with carbon by ion beam techniques*, Nucl. Instr. Meth. Phys. Res. B175-177, 683-687 (2001)

11. S.P. Mattin, G.T. Burstein, *Detailed resolution of microscopic depassivation events on stainless steel in chloride solution leading to pitting*, Phil Mag. Lett. 76 (5), 341-347 (1997)

12. J. Kruger, *Possible processes and mechanisms that could lead to uniform or localized corrosion of canister alloys over very long times*, in: "Proceedings From an International Workshop on Long-Term Extrapolation of Passive Behaviour", A.A. Sagüés and C.A.W. DiBella (eds.), U.S. Nuclear Waste Technical Review Board, Arlington, December 2001 (www.nwtrb.gov), 21-24 (2001)