On the Corrosion of Spent Fuel Aluminium Cladding During Wet Storage

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The paper presents the results obtained from the curves curent-potential when Al-Mg_3 samples polarization occurs in solutions that simulate the water from the storage pool. The samples used in research are characteristic for the fuel spent C-36 and EK-10 and also for the storage pool from the Magurele- Romania research reactor deactivation. The study is unique due to the material samples used and due to the fact that the results of electrochemical experiments are correlated to the results from the chemical analysis of water samples from spent fuel storage basins. The paper is in the class of those which serve to the estimation of the dynamics of the degradation of spent fuel cladding during wet storage.

Keywords: aluminium fuel cladding, corrosion

Aluminium and some of its alloys are important materials in more nuclear power or research reactors technology. For example, aluminium alloys are used in nuclear fuel and fuel storage facilities in fuel cladding, fuel matrices, fuel structural components, fuel storage racks, fuel storage canisters, fuel handling devices and fuel storage pool (FSP).

With aluminium clad fuel corrosion issues starting to appear in wet spent fuel storage basins around the world, the International Atomic Energy Agency (IAEA) formulated a corrosion surveillance programme in late 1994. This scientific investigation was implemented in 1996 as part of an IAEA Co-ordinated Research Project (CRP) on Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water [1-3]. A large database on corrosion of aluminium-clad materials has been generated from the CRP and the corrosion surveillance and monitoring programme for aluminium clad production reactor fuel that had already been established at the United States Department of Energy Savannah River Site (SRS) in Aiken, South Carolina [4, 5].

An evaluation of these data indicates that the most important factors contributing to the corrosion of the aluminium are given by: the high water conductivity (over 10 µS/cm); the presence in storage water of one ionic aggressive impurity at unacceptable concentration (Cl^-); the deposition of species particles having normal potential smaller than aluminium (Fe, Ni etc.); the activity of galvanic couples between dissimilar metals (stainless steel–aluminium, aluminium–uranium etc); surface scratches and imperfections in protective oxide coating on cladding;

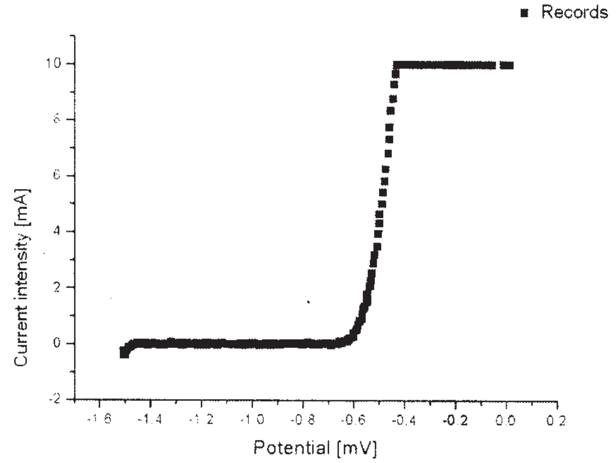

Fig. 1. Current-Potential curve for $AlMg_3$ sample for potential interval from -1.5 to 0.0 V

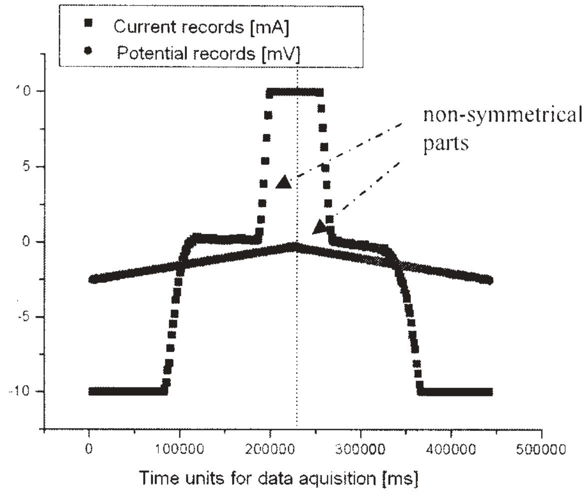

Fig. 2. The curve Current-Potential (black plot) for $AlMg_3$ alloy samples, as a response to the triangular Potential signal (–2.5V; 0.0; –2.5V), (red plot)

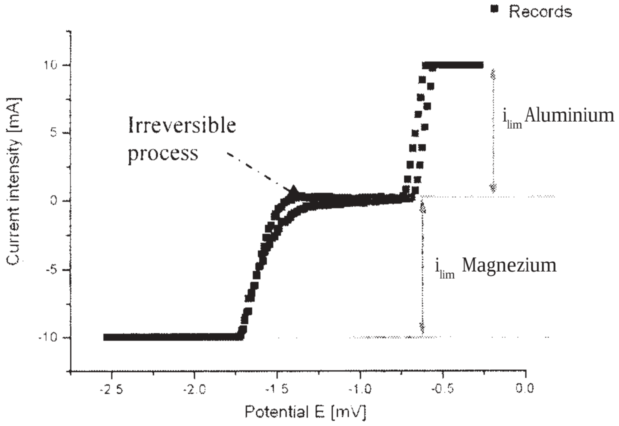

Fig. 3. The graphic Current-Potential for $AlMg_3$ alloy behaviour during variation of electrical potential from –2.5V to 0.0V and from 0.0V to –2.5 V

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a poor water circulation in the pool. These factors, operating both independently and synergistically, may cause corrosion of the aluminium. The single most important key to prevent corrosion consists, respect to the storage basin, in maintaining of good water chemistry. As example we show that water conductivity near 1 μS/cm generally ensures that aggressive impurity ions, such as chlorides, are in the ppb range. When chemistry is maintained in this regime, corrosion of aluminium alloys is minimized [6].

The aim of this paper is to present the results obtained through electrochemical methods on the stability behaviour of $AlMg_3$ alloy samples, which is the same material used for nuclear aluminium cladding for EK-10 and C-36 nuclear fuel elements, and to correlate those results with the water sample analysis from spent fuel storage at the Magurele site in Romania. In this way the corrosion of the spent fuel aluminium cladding in those specific wet storage conditions could be estimated. Consequently, it is possible to propose adequate measures for diminishing the corrosion phenomena, so the integrity of the cladding could be maintained until the spent fuel becomes ready for reprocessing.

Experimental part

Several samples of $AlMg_3$ alloy were used for analysis through the potentiometric method [7]. The electrochemical system was composed of an electrochemical cell, in which the working electrode was the $AlMg_3$ cylindrical sample; the auxiliary electrode was a Pt grid; and the reference electrode was the saturated calomel electrode. Several cylindrical samples were made from $AlMg_3$ alloy. One of those was kept as the control sample. To obtain an exact surface for the working electrode, the lateral surface of the cylindrical $AlMg_3$ samples was isolated through a Teflon wrapper. A solution of NaCl 0.5 M was used as the electrolyte. The response from the system was recorded as a function of time in relation to the electrical current (i) resulting from the electrochemical process that took place in the system. Initially a variable potential was applied from –1.5V to 0.0V; thereafter the domain was extended from –2.5V to 0.0V due to the inflexion observed at –1.5V (fig. 1). A potentiometer was used to apply a triangular potential signal (fig. 2). The response from the system was recorded as a function of time in relation to the current (i) resulting from the electrochemical process that took place in the system. In the graphic were observed two thresholds: one is the diffusion current dissolving Mg; the higher limit corresponds to the diffusion current dissolving Al (fig. 3).

Represented in the same figure, the results obtained for a variance of the potential from –2.5V to 0.0V and from 0.0V back to –2.5V indicate that the graphs are not identical, which means that the dissolving process of the $AlMg_3$ alloy through an electrochemical process is an irreversible process (fig.3).

Very similarly curves have been obtained working with the water samples from the storage basins located in the storage site Magurele- Romania. The dissolving of Mg appears very clearly and this fact indicates that in the chemical analysis of the water from storage basins an unacceptable Mg ions concentration must be observed.

It is important to show here that the intensity of the irreversible process characterizing the Mg dissolving in the cases when the liquid are water samples from Magurele storage basins is small by comparison to those reported with figures 2 and 3. So, the Mg dissolving has identified by means of curves current - potential in looping technique. It is expected that Mg^{+2} in water samples from storage basins to be present.

Water samples analysis results

The data obtained from the electrochemical study of AlMg3 alloy corrosion behaviour were evaluated together with the analysis of the water samples taken from the spent fuel storage (SFS) away from reactor (AFR), from basins 2 and 4 at Magurele site, and from the distilled water tank (reservoir 3) which supplies the water for the spent fuel storage replenishment.

Table 1

RESULTS OF THE WATER SAMPLES ANALYSIS

Parameter	Measurement Units	Water Sample Basin 2	Water Sample Basin 4	Distillate water (reservoir 3)	Admissible limits
pH	$-lg[H^+]$	4.41	4.25	5.97	5.5-6
Conductivity	μS/cm	25.6	29.9	25.1	2-3
Mg	mg/L	0.57	0.51	0.047	
Na	mg/L	0.47	0.49	0.37	
K	mg/L	12.2	0.63	0.07	
Fe	mg/L	0	0.033	0	
Al	mg/L	0	0	0	
Cu	mg/L	0	0	0	
Cl-	mg/L	2.13	4.32	2.69	0.02
SO42-	mg/L	0.37	2.58	1.13	
NO3-	mg/L	0	0	0.13	
NO2-	mg/L	12,2	10.3	8.3	

Table 2

DATA CONCERNING AL CLADDING CORROSION AS FUNCTION OF THE WATER COMPOSITION [8]

C.N	Basin water composition and exposure time						Al 1000 corrosion		Al 8010 corrosion	
	Cl^- (mg/l)	NO_3^- (mg/l)	SO_4^{-2} (mg/l)	pH	λ (μS/cm)	τ (days)	Pit depth (μ m)	Pits density (Pits/cm^2)	Pit depth (μ m)	Pits density (Pits/cm^2)
1	8	20	15	7.5	175	45	50.4	0.125	1250	0.01
2	8	20	15	7.5	175	75	652	0.125	1180	0.01
3	8	20	15	7.5	175	182	1325	0.125	1090	0.01
4	8	20	15	7.5	175	365	2540	0.125	1310	0.01
5	<0.1	<0.1	<0.1	7.3	2.5	1091	No Pitting		No Pitting	
6	0.2	1.5	0.5	7.4	<5	480	No Pitting		No Pitting	

Table 3

THE COMPUTED VALUES OF PITTING RATE INDEX (I_{pr}) RESPECT TO DATA FROM TABLE 1 AND 2

Water sample	$c_{SO_4^{-2}}$ mg/l	c_{Cl^-} mg/l	pH	λ (µS/cm)	$c_{Cu^{+2}}$ mg/l	i_{pr} (weeks)
Table 2	35	8	7.5	175	<0.01	1.67
Table 1 (B2)	0.37	2.13	4.41	25.6	0.57	5.87
Table 1 (B4)	2.28	4.32	4.25	29.9	0.51	2.77
Table 1 (D.W)	1.13	2.69	5.97	25.1	0.047	7.10
i_{pr} is defined as the number of weeks needed to obtain a maximum pit depth of 1 mm						

The laboratory methods used to analyze the water sample parameters were (1) atomic absorption in flame to identify the presence of metals, and (2) column chromatography (liquid chromatography) to identify the presence of anions in water. Also the *p*H and conductivity of water samples were measured. The results obtained from water sample analyses are summarized in table 1.

As it is expected, in the water samples from basins has been identified Mg^{+2} having very high concentration respect to the distillate water used for replenishment. The Mg^{+2} can not appear in the basins by other ways (as example from the air system used for heat removal) out of corrosion of the fuel cladding.

Results and discussions

The cladding corrosion process is coupled with other two normal processes taking placed in the storage basins; first is the radiolysis process and the second is the mass and heat transfer between the liquid from basins and the surrounding flowing air [6]. These processes can accelerate the corrosion processes especially when the basins water parameters are over the admissible limits (see last column of the table 1). Looking to our reported data we can conclude that the Mg dissolved activates the corrosion by changing cladding material surface and by increasing water conductivity. Table 2 shows the effect of high water conductivity on the corrosion of two Al alloys (Al 1000, Al 8010).

Looking to our data and to data from table 2 and go over the differences between the corrosion of Al 1000 and Al 8010 alloys, which are the consequence of different composition, we can accept that the water composition related to our data is dangerous for $AlMg_3$ cladding; a pitting corrosion can appear as a consequence of water conductivity (λ) and more probably because of an unacceptable *p*H. Pathak and Godard's [9] empirical relationship (1.1) established for predicting the corrosion of aluminium in natural fresh waters, was used to obtain corrosion results for data reported in tables 1 and 2. In table 3 the computation of i_{pr} with respect to basin 2, basin 4 and distilled water reservoir consider the equivalence between Cu^{+2} and Mg^{+2}.

$$\log i_{pr} = 3.5 - 0.28\log(c_{SO_4^{-2}}) - 0.18\log(c_{Cl^-}) - 0.2\log[10^2(pH-7)^2] - 0.42\log(3\,10^3\lambda) - 0.064\log(10^3 c_{Cu^{+2}}) \qquad 1.1$$

It is important to show that the dangerous effect of chloride is augmented by the radiolysis processes which take place in the storage basin whereas the interaction between the radiolysis generated OH, H radicals and Cl^-, H^+ and Al_2O_3 create a stable concentration of active $ClOH^-$ species given by the relation 1.2 [10].

$$-d(c_{ClOH^-})/dt = 1.32\,10^{10}c_{Cl^-}c_{H^+} + 9\,10^4 c_{Cl^-} \quad (1.2)$$

The presence in the water of the radiolysis generated O_2 near to $ClOH^-$ creates a situation when a metal (aluminiun cladding alloy) can be pitted by a rapid dissolution in the pit, while oxygen reduction takes place. The rapid dissolution within the pits tends to produce an excess charge in this area and results in the migration of chloride ions into the pit to maintain neutrality. Thus, there is a high concentration of metal chloride and of hydrogen ions in the pit. As a result, the pits become more acidic, reaching low *p*H levels. This process stimulates metal dissolution.

Conclusions

The electrochemical investigation of AlMg3 corrosion by means of curves Current-Potential has identified an irreversible process characterizing the Mg dissolution.

The special chemical analysis of the water samples from the storage basins from Magurele – Romania shows the presence of Mg^{+2}ions in their composition.

The pitting corrosion computation respect to index show that water from the storage basins from Magurele Romania site present an important corrosion capacity.

The dangerous comportment of Cl^- ion from the basins water is explained by mean of their interaction with the water radiolysis radicals.

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