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**CORROSION OF ALUMINUM ALLOYS IN WATER
AT TEMPERATURES UP TO 100 °C**

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ABSTRACT

An effect of different factors on a water corrosion of aluminum and aluminum alloys at 100 °C has been analyzed on the basis of literature data. A generalized expression has been obtained permitting to evaluate a depth of corrosion in aluminum alloys against a water temperature, a test duration, a water rate and a thermal flux density. By using this expression it is possible to estimate a condition of fuel element claddings after their operation life as well as after a long-term storage in water of a decay pool.

1. Introduction

One of the main factors limiting a life-time of an operation of fuel elements of research reactors is a corrosion rate of fuel claddings and a formation rate of an oxide film.

A corrosion resistance of aluminum and Al alloys depends on many factors: an alloy composition and heat treatment, a temperature of the metal, a water flow velocity and temperature, a thermal flux and irradiation. Numerous data on the corrosion resistance of aluminum alloys obtained mainly in the 60s and 70s of the last century are known. Most of these data are relevant to a temperature range of 230-360 °C. At that time the interest to a high temperature corrosion of aluminum alloys was induced by searching for inexpensive alloys as an alternative to a corrosion resistance of costly zirconium. However, the data available on the Al alloy corrosion at temperatures below 100 °C, which are typical for a fuel operation in research reactors and storage in a decay pool, are rather limited [1-7]. Moreover, the experimental data on the Al alloy corrosion were obtained in the experiments, where, as a rule, each of the above factors was studied separately. Therefore it is impossible to make any recommendations for determining the corrosion rate of the fuel-cladding material for a specified combination of values of these factors proceeding from a variety of the data available.

The author of this work tried to derive a generalized expression for estimating a corrosion behavior of aluminum alloys as a function of a temperature, time, water flow velocity and thermal flux density as well as a thickness of an oxide film formed on the surface of the fuel claddings by the time of a fuel extraction from a reactor.

2. Experimental results

As a rule, a fuel cladding material for research reactors is aluminum of technical purity (designated as 1100, AD1, AMSN-2) or low-alloyed aluminum alloys (designated as 6061 and SAV-1). The corrosion rates of these materials in water of reactor purity have close values, the difference does not exceed 25 %. Since the corrosion rates of Al alloys in pure water were small, practically, there were no tasks to study in details a behavior of Al alloys corrosion at temperatures <100 °C. Therefore the quantity of the available experimental data relevant to this temperature range was small.

A corrosion of Al alloys in water depends on a value of pH. This is because the aluminum hydroxides $\text{Al}(\text{OH})_3$ and AlOOH , which form on the surface of the Al alloys during a water corrosion, have amphoteric properties, i.e. they are well dissolved in both the acidic (at $\text{pH} < 4.5$) and the alkaline (at $\text{pH} > 8.5$) environments. $\text{Al}(\text{OH})_3$ and AlOOH are stable in water within $\text{pH} = 5.0 \div 6.5$ and therefore in this range the Al alloys corrosion resistance is the highest and the corrosion rate practically does not depend on a pH - value. It should be noted that pH of reactor water and pH of decay-pool water become stable exactly in this range of values due to a contact with air, because water there is acidified with carbon and nitric acids. The carbon acid is formed there when CO_2 from the contact air enters the reactor and pool waters. The nitric acid is formed there by a radiolysis of water saturated with nitrogen present in the air.

At temperatures <100 °C a depth of uniform corrosion K of Al alloys follows the parabolic dependence on time τ :

$$K = K_p \cdot \tau^{1/2}. \quad (1)$$

In the coordinate's $K - \tau^{1/2}$ the dependence is linear (Fig. 1).

A usage of parabolic corrosion constant K_p , which is equal to $K \tau^{-1/2}$, permits a comparative analysis of the experimental data obtained by different authors and an estimate of an influence of various factors on the temperature dependence of the Al alloys corrosion rate (Fig.2).

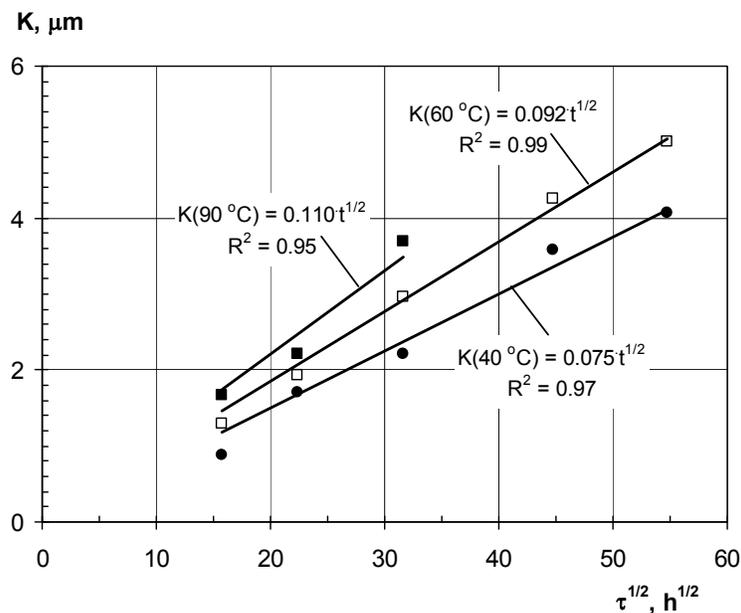


Figure 1: A depth of general corrosion of SAV1 alloy in water against $\tau^{1/2}$. The water is saturated with CO_2 and contains 0.005 mol/l H_2O_2 ; 0.05 mg/kg Cl^- and 0.01 mg/kg Cu [7].

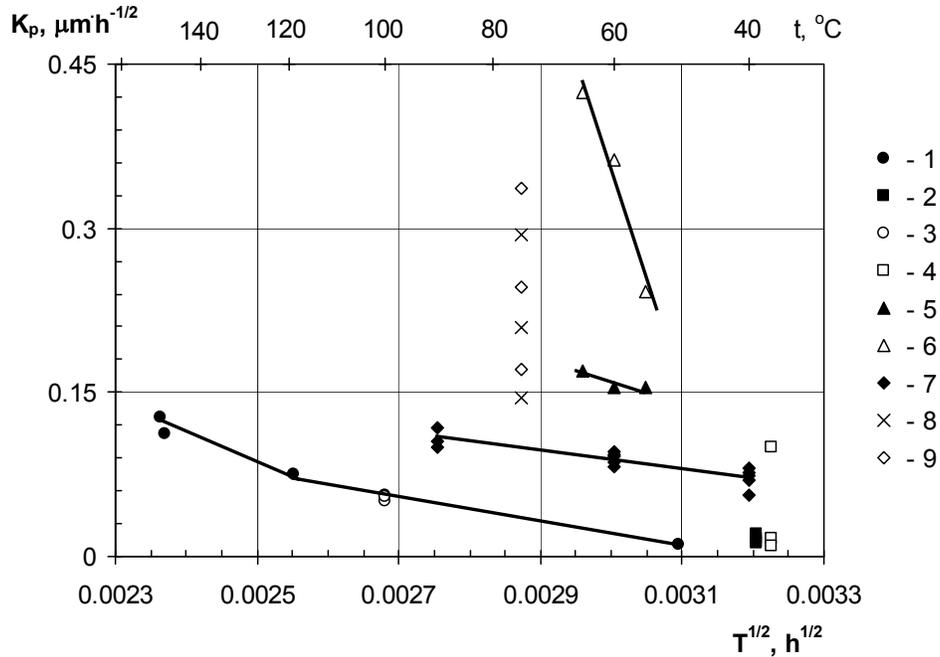


Figure 2: An influence of temperature, water velocity and thermal flux density on a parabolic corrosion constant K_p of Al alloys: 1 - alloy 2S, water pH=7, statics [1]; 2 - alloy 1100, water, statics [2]; 3 - alloy 1100, dynamic tests $V=0.9\pm 2.1$ m/s, [3, 4]; 4 - alloy AD1, in-pile tests, $\Phi = (1.2\div 1.5)\cdot 10^{19}$ n/cm² [5]; 5 - alloy 6061, nonisothermal dynamic tests, $V=3.0$ m/s, $q=1.25$ MW/m² [6]; 6 - alloy 6061, nonisothermal dynamic tests, $V=3.0$ m/s, $q=2.55$ MW/m² [6]; 7 - alloy SAV-1; water saturated with CO₂ of a content 0.005 mol/l H₂O₂, 0.05 mg/kg Cl and 0.01 mg/kg Cu, statics, [7]; 8 - alloy SAV-1, dynamic tests, $V=6.0$ m/s; 9 - alloy AMSN-2, dynamic tests, $V=6.0$ m/s.

The data in Fig. 2 indicates that a change in the parabolic corrosion constant K_p depends on the test conditions and its dependence on temperature is of the Arrhenius-type

$$K_p = K_o \cdot \exp(-Q/RT), \quad (2)$$

and is plotted as a straight line with a different angle of slope in the coordinates $K_p - 1/T$ (Fig. 2).

The corrosion rate of Al alloys is essentially influenced by a water flow speed V and a thermal flux density q . The corrosion rate increases by a factor of 5 to 10 with these influences.

The water velocity effects the Al corrosion because the process of corrosion on aluminum and Al alloys proceeds along with the simultaneous formation and dissolution of the oxide film in water; and the Al portion migrating to the water depends on test conditions. Thus, this portion is of the order 10 % under static conditions (in an autoclave). In the dynamic conditions it increases with a water coolant velocity and makes ~30 to 50 %. When some critical value of the water velocity is exceeded, an erosive wear of the oxide film can occur to increase the Al portion migrating into water to 80-95%. In accordance with the heat-mass exchange theory [8] the increase in the corrosion rate with the water velocity is attributed to a decreasing thickness of a diffusion layer near the surface of aluminum. It resulted in the acceleration of both the delivery of an oxidant to and the removal of dissolved elements of Al corrosion products from the surface of aluminum. According to the heat-mass exchange theory [8] the limiting diffusion current of corrosion I (all other conditions being equal) is directly

proportional to Reynolds number (or a water velocity as a first approximation) to the power m and Schmidt number to the power k :

$$I \sim A \cdot Re^m \cdot Sc^k. \quad (3)$$

The constants m and k in expression (3) depend on hydrodynamic characteristics of a water flow, i.e. at a streamline flow $m=k=0.33$ and at a turbulent one $m=0.58$ and $k=0.33$.

In the research reactors employing the fuel elements the thermal fluxes of an order $1 \cdot 10^6$ W/m² are developed. The accelerating effect of the thermal flux density on the Al corrosion rate is due to the formation of the oxide films, which are quite thick, on the surface of aluminum; the thermal conductivity of the films is almost by a factor of 40 to 50 less than that of Al, e.g. ($\lambda(\text{Al}(\text{OH})_3)=1.90 \div 2.25$ W/(m·K) [9, 10] and $\lambda(\text{Al})=90$ W/(m·K) [11]). Finally, a temperature of operating fuel claddings is several tens of degrees higher than a water temperature. Thus, the thermal flux effect on the Al corrosion rate, probably, can be taken into account with an allowance in a temperature factor in equation (2)

$$K_p = K_o \cdot \exp\{-Q/R(T+\alpha q)\}. \quad (4)$$

By combining (1), (3) and (4) and taking account that $Re \sim V$, a generalized expression can be written for a depth of aluminum corrosion as

$$K = K_o \cdot \tau^n \cdot (V/V_o)^m \cdot \exp\{-Q/R(T+\alpha q)\}, \quad (5)$$

where the effect of a temperature, time, water velocity and thermal flux density is taken into account. The value V_o in eq. (5) is the water flow velocity due to a water convection in the static autoclave tests. According to [11] the value V_o is set equal to 0.13 m/s for a temperature range 20 to 100 °C.

Representing equation (5) in the form

$$\ln(K) = \ln(K_o) + n \ln(\tau) + m \ln(V/V_o) - Q/R(T+\alpha q), \quad (6)$$

and applying the least square method to it, the values of the constants in (5) can be obtained.

Thus, by a mathematical treatment of all the data in Fig. 2 (the data from [7] are excluded as water constant is different there) the expression for determining the depth of Al alloys corrosion is obtained:

$$K = 26,31 \cdot \tau^{0,5} \cdot (V/V_o)^{0,48} \cdot \exp\{-4700/R(T+\alpha q)\}, \quad (7)$$

with the terms in the units as follows: K , μm ; V , m/s; τ , h; $\alpha = 23.9 \cdot q^{-0.1} \cdot \exp(1 \cdot 10^{-3} T)$ as obtained from a comparison of autoclave and dynamic tests.

Judging by Fisher criterion, expression (7) describes adequately the corrosion process in aluminum, the constants constituting it are of statistical significance and the correlation factor is equal to 0.93. The comparison of the estimated values of the corrosion depth with the experimental ones (Fig. 3) shows a satisfactory agreement between them.

However, the calculation values are lower than the experimental ones for the more aggressive composition of water [7] saturated with CO₂ and electrolytic gas, this water contains 0.005 mol/l H₂O₂, 0.05 mg/kg Cl⁻ (in the form of FeCl₃) and 0.01 mg/kg Cu (in the form of CuCl₂). Its acceleration factor, as opposed to that of pure water, strongly depends on temperature and weakly depends on time $f = 36.98 \cdot t^{-0.69} \cdot \tau^{0.08}$.

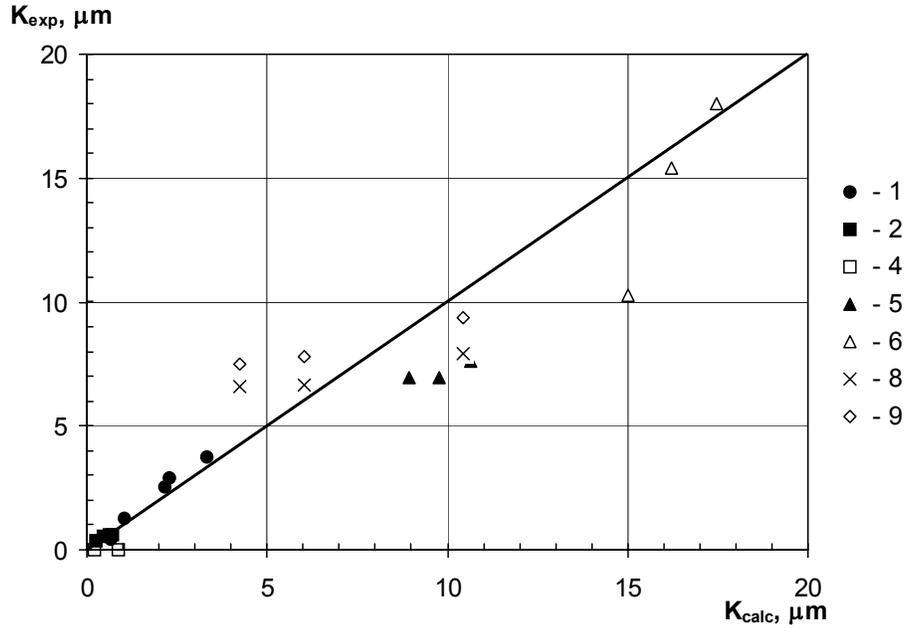


Figure 3: A comparison of experimental K_{exp} and calculation K_{calc} values of corrosion depth in aluminum alloys

Besides the uniform corrosion, the Al alloys are subjected to pitting corrosion, especially when water contains chlorine ions and copper. Thus, the depth of the pitting corrosion reached 50 μm in the fuel claddings after 5 years of operation in the IRT-2000 reactor. According to the data in [13] the kinetics of the pitting corrosion of Al follows a cubic dependence. Thus, neglecting an incubation period (by assuming that pitting corrosion starts to develop immediately after an immersion of the alloy into water) one can obtain the dependence for the pitting corrosion kinetics, for 40 °C it takes on the form

$$K_{pit}(\mu\text{m}) = 1.47 \cdot \tau^{0.33}. \quad (8)$$

The data on the effect of a neutron flux on the Al alloy corrosion are scarce and sometimes they are contradicting. Some data show that irradiation accelerates the Al corrosion rate, other data say that it does not effect it or the effect is positive. In spite of contradictions in the experimental results a majority of the researchers are of the opinion that irradiation decreases the corrosion rate of Al and Al alloys rather than increases it.

3. Estimation of the thickness of oxide film on “KM004”fuel element

In order to check expression (7) for applicability the experimental fuel elements with dispersion uranium–molybdenum fuel were used, the fuel elements were included into the fuel element assembly “KM004” and tested in the IVV-2M reactor [13]. For the estimation of the thickness of the oxide film formed on a fuel element surface the data on the power of the fuel element of the first type size (Fig. 4) and the data on a water temperature at the input and output of the fuel assembly in each cycle of in-pile tests (Fig. 5) were used.

The thickness of the oxide film δ was estimated with the assumptions that the film is formed as bayerite $\text{Al}(\text{OH})_3$ and the value of an Al corrosion products release into water is equal to 40 %. The estimation was made using the recalculated coefficient

$$\alpha = (A_{\text{Al}} + 3A_{\text{O}} + 3A_{\text{H}}) \cdot \rho_{\text{Al}} / A_{\text{Al}} \cdot \rho_{\text{Al}(\text{OH})_3} = 2.59,$$

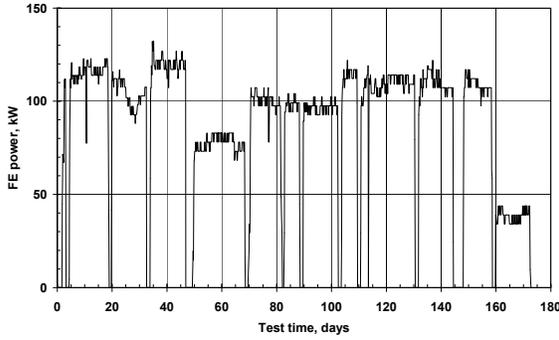


Figure 4: Changes in power of fuel element in fuel assembly “KM004” during in-pile tests

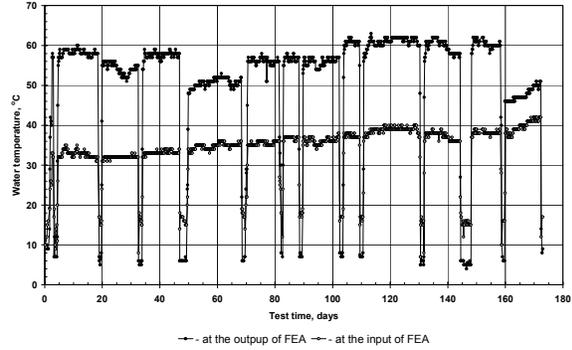


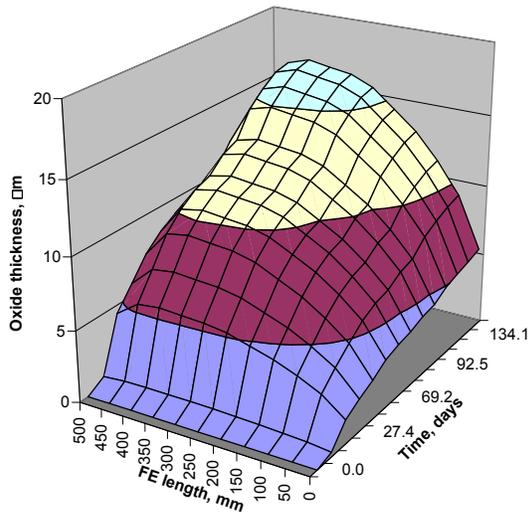
Figure 5: Changes in temperature at the input and output of fuel assembly “KM004” during in-pile tests

where A_{Al} , A_O , A_H are the atomic masses of the aluminum proper, oxygen and hydrogen, respectively, and ρ_{Al} and $\rho_{Al(OH)_3}$ are the densities of aluminum and bayerite, respectively.

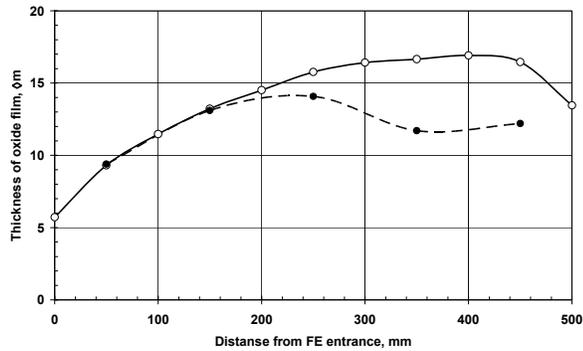
With the account of the above, the expression for determining the oxide film thickness takes on a form

$$\delta = 0.6 \cdot \alpha \cdot K = 40.91 \cdot \tau^{0.5} \cdot (V/V_0)^{0.48} \cdot \exp\{-4700/R(T + \alpha q)\}. \quad (9)$$

The dependencies of the changes in the oxide film thickness along the height of the active layer of the fuel element are shown in Fig. 6 for the oxide films formed on the layer’s surface during the tests (Fig. 6a) and for those matured by the end of the in-pile tests (Fig. 6b).



a



b

Figure 6: Changes in the oxide film thickness along the height of the fuel element during the tests (a) and in the calculation (solid line) and experimental (dash line) values of the thickness of the oxide film formed by the end of the tests (b)

According to the data in Fig. 6 the calculation gives a good fit to the experimental values on the thickness of the oxide films formed in the areas located in the upper half of the fuel element. However, a difference between these values is noticed in the areas starting from the center and proceeding to the output of the fuel assembly, the experimental values are lower than the calculation ones by ~35-42 % there. This difference is due to the spalling of the external layers of the oxide films, which has resulted from the destructive testing used in post-irradiation investigations.

4. Conclusion

The literature data on the corrosion rate of aluminum alloys were analyzed. The expression was obtained for the determination of the corrosion depth and thickness of the oxide film as a function of time, a water coolant velocity and temperature, a thermal flux density. The calculation values of the thickness of the oxide film on the fuel element of the assembly "KM004" tested in the IVV-2M reactor were compared with the values measured in the experiments. The comparison proved a satisfactory fit of the calculation to the experimental data.

5. References

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