

# Swedish research on aluminium reactor technology

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### Summary:

A historical survey of the work done in Sweden this subject is given in the first part of the paper.

The second part is elevated to a brief outline of the authors view of the present status of corrosion theories for aluminium in high temperature water. A theory where the crystallization of boehemite from the barrier layer is considered as an important control of the corrosion reaction is presented.

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## LIST OF CONTENTS

	Page
Introduction	3
1. Static	6
2. Existing Theories of Corrosion	8
3. Corrosion Mechanism	9
4. Alloys with Iron and Nickel	<b>12</b>
5. Conclusions	12
References	14

## Swedish Research on Aluminium Reactor Technology.

### Introduction.

Corrosion studies on aluminium alloys for reactor applications have been carried out in Sweden for several years. The first Swedish reactor, R 1, <sup>1)</sup> utilizes aluminium for components such as reactor vessel and canning of fuel elements. The problems with aluminium became more evident when experiments started for a second project, the "Adam" reactor <sup>2)</sup> intended to be built in Västerås by the ASEA company. Although this was a reactor working in the region of 150 °C (heavy water, UO<sub>2</sub>, Al canning) producing heat for central heating, several problems were encountered with aluminium at that time. Some work <sup>3)</sup> had been done in "Reflectal", the 0,5 % Mg aluminium used in the R 1-reactor. The corrosion rate is very low and no problems have been met in the reactor. At temperatures of 100 °C and higher this alloy however has very poor corrosion resistance. Today this is a wellknown fact for all the Al-Mg alloys.

In spring 1958 a first conference was held at Friibergh mansion near Stockholm with the people directly responsible for the aluminium research and development for the Adam project. Participants came from AB Svenska Metallverken, AB Wedaverken, which are manufacturers of aluminium products, from ASEA and from AB Atomenergi.

The purpose of this conference was to discuss the present knowledge of aluminium. Detailed discussions covered topics having an influence on the corrosion behaviour of the alloys such as fabrication methods and metallurgical parameters, mechanical properties, welding techniques etc.

As a result of this conference a program for corrosion testing of several alloys was recommended. The main problem with aluminium alloys is of course their poor corrosion resistance in water at elevated temperatures, and especially in flowing water.

This program was set up to deal with the problems of the Adam reactor and therefore it was concentrated on immediate technical problems in the aluminium technology. A second conference on aluminium problems in reactor technology was held at Friibergh in the autumn of 1958, at which a more fundamental research program on aluminium was outlined and which is now in progress (see below). There were several reasons for shifting over the aluminium research and development work in reactor technology from a broad technical to a more fundamental long range research program. One was that the original Adam reactor project was abandoned for a joint effort on the R 3 reactor (now called the R 3/Adam reactor). Both of these reactor projects were natural uranium-pressurized water reactors. The water temperature differed, however. The Adam reactor was intended only for space heat production with a max. water temperature of 150 - 160 °C, whereas the R 3/Adam reactor is intended for both heat and electric power production, and with a maximum water temperature of 220 - 230 °C. At the water temperature of the former reactor (150 - 160 °C) aluminium was intended to be used both as canning material and for other vital parts. Therefore an extensive aluminium program with a strong technical application was urgently needed. For the present reactor project with its higher water temperature (220 - 230 °C) zircaloy will be used as a canning material. Aluminium has been abandoned, the first reason being its bad corrosion resistance in high temperature water.

A second reason for the shift from aluminium to zircaloy as a canning material is the shift from uranium metal to uranium oxide as the fuel material. It is felt that with the trend towards a high temperature fuel with a high melting point also the canning should be a material not only with good corrosion resistance at the temperature of the coolant, but also with a high temperature strength and a high melting point, and the two lastmentioned properties are not fulfilled by aluminium but by zircaloy.

It was felt, however, that the research and development work of aluminium should not be abandoned, but shifted to a more fundamental, long range research. Aluminium is a rather wellknown metal and an understanding

of the different properties which have an influence on its corrosion resistance should have a great value not only for aluminium but for metals in general. Aluminium might also be used as a canning in watercooled reactors in the future, if its corrosion properties are increased, especially for moderate water temperature. Its price is comparably low and its technology at least better known than that of zircaloy.

At present our work on aluminium is divided on several hands. Alloys for the experiments are manufactured at Svenska Metallverken in Finspong. Metallographical studies on these alloys are also performed by them. Corrosion testing and welding experiments are performed at ASEA, Västerås. Studies on corrosion kinetics are undertaken by AB Atomenergi in Stockholm. A program performed in Trondheim by professor Winterbottom on the growth and properties on thin oxide films on aluminium studied by polarized light is sponsored by AB Atomenergi and IFA at Kjeller.

The program for research on aluminium today in Sweden will be directed to testing of alloys developed at the different laboratories in the world which are working or have been working on corrosion studies of aluminium. This might seemingly be unnecessary doublework, but our work so far has shown that it is extremely difficult to compare different alloys. The results reported in literature give us no great help, since they contain many contradictory results. Our program includes testing of the well-known alloys like AEREAL 4, M 388, Chalk River 196, some of the Sacalay alloys and some of the russian alloys with high silicon content. No new ideas of our own exist that have made it possible to compose alloys based on other ideas than the above mentioned. The main task at present is to build the equipment and train the personnel necessary for this type of work. Our first work in dynamic conditions were performed at ASEA, Västerås. The loop has caused much trouble itself and has been rebuilt several times. The results of the looptesting so far have shown that especially the welding of aluminium alloys for fuel element canning contains many problems. A second loop is under construction at ASEA and most of our continued studies will be aided by this machine. A rather small

loop with 200 °C maximum temperature is under assembly at AB Atomenergi in Stockholm. Corrosion studies of some of the above mentioned alloys are performed under static conditions at AB Atomenergi. Since the results of static tests seem to be rather erratic when no control of the water chemistry can be maintained, tests under semistatic conditions with better control of the water composition will soon begin. It is our intention at AB Atomenergi to perform some studies using the common methods in electrochemical research. Especially more detailed studies of the components and nature of polarisation on corroding surfaces of aluminium alloys have been planned by the author.

Our discussion on the corrosion of aluminium have to a very great extent been devoted to the mechanism and kinetics of the reactions, since these phenomena are very little understood and many contradictions can be found in literature on aluminium corrosion.

It is of course clear that the problem for aluminium as a reactor material is not only one of that corrosion. The welding problem is extremely important, as well as high temperature strength and several other properties.

I will concentrate the later part of my talk on corrosion and give some common observations on the corrosion mechanism of aluminium together with my own viewpoints on this process.

#### 1. Static.

In water above 100 °C aluminium has shown the following behaviour.

1. The rate of reaction follows a parabolic law for some time.
2. After a certain period the rate of reaction is transformed to linear function with time. The length of this period is a function of alloy and milieu of exposure<sup>4)</sup>.

The following observations concern the adhering corrosion products on the surface of the metal:

One layer of corrosion products is found adjacent to the metal-surface, it is usually called the barrier-layer. The thickness of this layer is considered not to be a function of the time of exposure, but of the temperature. It is usually estimated at a thickness of about 10 Å for each 100 °C. (Thus 100 °C exposures give 10 - 15 Å, 200 °C give 20 - 25 Å, 300 °C give 30 - 35 Å). The layer is characterized as amorphous  $\text{Al}_2\text{O}_3$  with traces of boehemite. Since this layer is very thin, and situated between the metal and the next layer of corrosion-products, studies of the layer have been difficult to perform.

On the outside of the barrier layer a porous layer, sometimes called the bulk layer will be growing. The main content of this layer is boehemite,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . While the thickness of the barrier layer is constant, the bulk layer grows with time of exposure. The layer is in one side forming from the barrier layer, while it is dissolving in the medium of corrosion in its other side.

As mentioned earlier, after a certain period the time dependency of the reaction changes from a parabolic to a linear rate. Observations that this transformation is combined with the disappearing of the barrier layer have been claimed<sup>5)</sup>. At this transformation the metal will be attacked intergranularly with blistering as the first evidence, later with more serious deterioration in the grain-boundaries.

The following practical viewpoints have been governing the work published so far on aluminium in different countries:

1. The general rate of corrosion is up to 30 times greater in flowing water with a velocity of 6 m/sek than in static water. Experiments have been conducted with the addition of phosphates, silica and with presaturation of the water with dissolution products of aluminium. Some results have been achieved, but the general rate of corrosion is still too high.

2. Intergranular attack must be avoided. By alloying with nickel and iron as has been done in Argonne and Harwell<sup>6,7)</sup>, the period before intergranular attack has been extended and the working temperature of the alloys have been elevated. The rate of general attack is, however, very little affected in these alloys.

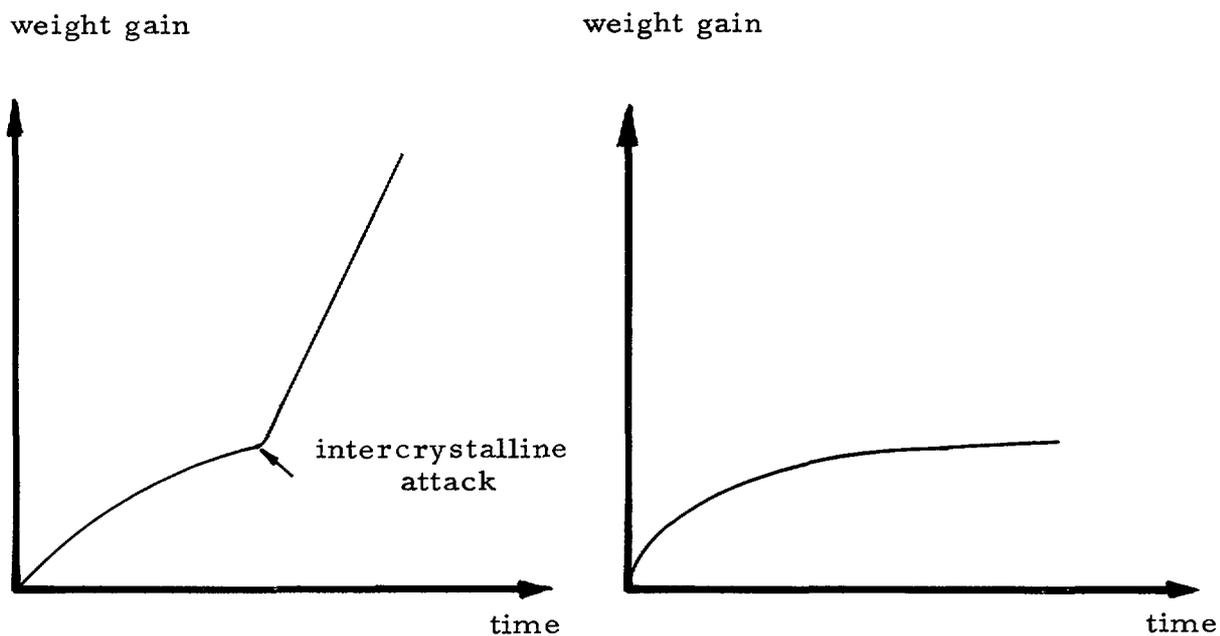
## 2. Existing Theories of Corrosion.

Draley claims that alloying with nickel and iron creates small cathodes of a second phase  $\text{FeNiAl}_9$ . This phase has to be finely divided and evenly distributed in the structure. The beneficency of this distribution has been verified in many laboratories. It is supposed by Draley that these small cathodes are centers for the evolution of hydrogen and thus prohibit or diminish diffusion of atomic hydrogen into the metal structure. These not so easily dissolved particles that will be included in the film of corrosion products will also raise the electron-conductivity of the film. This improved conductivity will simplify the discharge of protons on the active cathodes and thus hydrogen will be evolved further away from the surface of the corroding metal. High contents of hydrogen have been found deep in corroding aluminium. This is hydrogen liberated by the reaction. As a second evidence Draley has shown that making aluminium cathodic in an electric circuit by applying outer electromotive force, the metal is protected against intergranular attack. If the polarity is reversed, the intercrystalline attack is accelerated.

A theory where the intergranular attack is caused not by the formation of hydrogen pressure, but by mechanical cracking has been suggested by others. Most clearly this theory has been stated by Tragert. The volume of boehemite is about twice that of the corroded aluminium. Great compression stresses will be built into the boehemite layer on the aluminium surface due to its unidirectional expansion. Thus cracks easily occur, especially above grainboundaries. The intercrystalline attack is explained by Tragert as a result of the expanding forces of corrosion products formed in the grain boundaries.

By experiments in dynamic conditions some different observations from those from the static experiments have been made.

The rate of attack follows the parabolic law for some time and then transfers to a linear rate tangentially.



### 3. Corrosion Mechanism.

The following reasoning is made by me to simplify the discussion of the kinetics of the corrosion reaction somewhat.

The mechanism of reaction is divided in three parts.

1. Oxidation of metal and formation of barrier layer.  
Metal - Barrier layer
2. Chrystallization of bulk layer from barrier layer.  
Barrier layer - Bulk layer.
3. Dissolution of bulk layer in the corrosion medium.  
Bulk layer - Dissolved aluminiumoxides.

The thickness of the bulk layer has been suggested as the rate determining factor. Diffusion of  $O^{--}$  or  $OH^-$  through the layer has been supposed to be rate determining<sup>9)</sup>. Since the bulk layer grows parabolically in analogy with the rate of reaction, this explanation is easily arrived at.

More thorough discussions of the three reactions mentioned before, however, show that the explanation must be more complicated.

#### Reaction I.

The reaction has been theoretically studied by Mott<sup>10)</sup>. Correspondence between theory and experimental experience is good in the case of oxidation of aluminium in air. Probably the same reasoning can be applied to the formation of barrier layers in water. Thus it is supposed that the field strength is controlling the diffusion of  $Al^{+++}$  ions through the layer, and that the diffusion is the rate determining factor.

The barrier layer is called thus because it serves as an electric barrier. By anodizing in an electrolyte that does not dissolve the layer, no appreciable current flows until a certain potential is applied. The thickness of the oxide layer by anodized aluminium is thus governed by the applied potential. Hass<sup>11)</sup> has made comparisons between thickness determined with the polarized light technique and the applied potentials. He has stated a thickness of 14 Å for the layer per volt of applied potential. His measurements correspond well with the above mentioned theory by Mott.

When the metal corrodes in water, the field strength over the oxide layer will be governed by the corrosion potential. Too little is known, however, today about the corrosion potential of aluminium. Very few electrochemical experiments have been reported, and therefore it is impossible to speculate further into this mechanism.

#### Reaction II.

Crystallization of barrier layer to boehemite means that it will not

reach the final thickness as governed by the fieldstrength. As the boehemite layer increases in thickness its central portions will be well crystallized. This will mean that the water contained in the layer will have a tendency to be restricted to the crystal-water. (Papers that have been published so far on the nature of the layers have mostly dealt with electron optical or X-ray studies. Thus experimental procedure has removed most of the free water content unfortunately). In my opinion as a consequence of the growth of the boehemite layer part of it will serve as an electric barrier.

On super purity aluminium Videm<sup>12)</sup> has reported that the barrier potentials have not increased during exposure in autoclaves. On the contrary he has shown that it fairly diminished and stabilizes at a value that is less than what has been claimed in literature. This might indicate that the reactions 2 and 3 are dominating by the corrosion of super purity aluminium. As a result of the purity of the metal, the potential over the barrier layer will be low. The thin barrier layer and the porous dissolving boehemite layer will give poor protection for the metal.

A possible mechanism for the intergranular corrosion observed with many aluminium alloys will be considered next.

The decreasing rate of reaction will have its immediate effect on reaction 1. It is not necessary that the barrier layer consists of only the layer formed by reaction. It is quite possible that the crystallization of the boehemite layer will have a tendency to lower its content of free water and that the boehemite will serve as a barrier to some extent too. If the dissolution of boehemite (reaction 3) is slow, the boehemite thickness increases. Thus the boehemite layer will have a tendency to crystallize, while the amorphous layer next to the metal will be slowly consumed by this process. At the same time mechanical stress in the layer may easily cause cracking. Cracks occurring in the boehemite layer may penetrate to the metal surface. If the barrier layer is weakened by transformation to boehemite, these cracks will give a very

high rate of attack and of evolution of hydrogen. This reaction will be rapid and formation of protective films may not occur.

If reaction 3 is fast enough to prohibit growth of the boehemite layer it would be expected that the risk of intergranular attack is diminished. However the general attack on the metal would be rapid.

By exposing samples in a loop this phenomenon might occur. There is some experimental evidence for this.

#### 4. Alloys with Iron and Nickel.

In these alloys the initial corrosion rate will be high. The potential of corrosion elevated by the cathodic elements will give a thicker amorphous barrier layer. The layers of corrosion products will contain particles of the second phase. This will be benevolent since with eventual cracking of the films, the hydrogen evolution will be concentrated to the second phase cathodes. The corrosion films may even be denser by their inclusions of these particles.

#### 5. Conclusions.

The corrosion of aluminium in water is divided in three primary reactions: formation of the barrier layer, formation of the bulk layer and the dissolution of the bulk layer in the corrosive medium.

Oxidation of the metal occurs in the first reaction. The reaction is electrochemical and governed by the fieldstrength over the barrierlayer.

The second reaction is the hydration of the oxides and the crystallization of boehemite. In normal cases this is the rate determining reaction.

The third reaction is the dissolution of the boehemite layer.

Intergranular attack and rapid deterioration of aluminium alloys would occur in water if the metal is not passivated by oxides. Aluminium alloys always have a protective oxide film developed in air at their fabrication.

When the boehemite layer crystallizes (reaction 2) it can consume part or all of the barrier layer. Stresses developed in the boehemite layer when it crystallizes can easily cause cracking. If the barrier layer is thin or nonexistent the metal will come in direct contact with water in these cracks without any protection from oxide films. The reaction will be very rapid and the fast, heavy evolution will make the formation of protective oxides difficult or impossible.

Alloying with nickel and iron gives higher electrochemical difference of potential (increased fieldstrength over the barrier layer); and thus a thicker barrier. It will also give a boehemite layer that can stand more mechanical stress without cracking due to the inclusion of second phase particles. These alloys thus demonstrate better resistance to intercrystalline corrosion, their general rate of corrosion is only little affected however, especially in flowing water.

## References.

- 1) Eklund  
Cosmos 32, 1954.
- 2) Wivstad and Mileikowsky  
Second Geneva Conference 136.
- 3) Pergelius, Trägårdh  
Teknisk Vetenskaplig Forskning 29, 1958:1.
- 4, 5) HW 51849.
- 6) Draley and Ruther  
Corrosion 12, 1956, 480.
- 7) Huddle and Wilkins  
AERE, Rep. M/R 1669 A.
- 8) CRMET - 700.
- 9) Dillon  
Corrosion 15, 1959, p. 29.
- 10) Mott  
Trans Faraday soc. 43, 1947, p. 249.
- 11) Hass  
J. Opt. Soc. Amer. 39, 1949, p. 532.
- 12) Videm  
Private communication.

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