MENENS - WP2 Literature Study: Corrosion of Aluminium in Methanol Environment

TNO **innovation for life**

Mobility & Built Environment
www.tno.nl
+31 88 866 20 00

TNO 2024 R10082 – 23 July 2024

MENENS - WP2 Literature Study: Corrosion of Aluminium in Methanol Environment

Author(s)	T.J. Slangen
Classification report	TNO Internal
Title	TNO Internal
Report text	TNO Internal
Number of pages	16 (excl. front and back cover)
Number of appendices	0
Project name	MENENS
Project number	060.48968

Contents

1   Introduction

Within the MENENS project the partners are interested in the corrosion properties of methanol in combination with aluminium tank material. Currently, methanol is considered a viable alternative fuel for ships, particularly with the maritime sector's desire to become more sustainable.

The corrosion effects of methanol on steel tanks is currently researched by TNO in the context of the Green Maritime Methanol (GMM) project. This is important research for the majority of ships, however some ships are also constructed with aluminium and corrosion research in this field is limited. Typically, aluminium AA5083 is used in the naval industry for construction of the skin and the tanks. This type of aluminium has good corrosion resistance to seawater, high strength and excellent weldability.

The corrosion properties of aluminium exposed to methanol have been studied by partners in the MENENS project, but inconclusive evidence was found to establish the safe use of aluminium for methanol storage. Therefore, in this report additional literature has been studied and recommendations are given for follow-up experiments.

The outline of this report is as follows. The first chapter "Tank conditions" shows the limits of the research and the relevant conditions to take into account for the corrosion. The second chapter "Types of corrosion" describes the different relevant corrosion mechanisms and explores the relation with methanol. The third chapter "Methanol additives" dives into the separate corrosion effect of each additive on the aluminium. The next chapter "Methanol exposure tests" shows some results of the research performed by Feadship on the effect of methanol on the corrosion of aluminium. Finally, conclusions and recommendations are given.

1.1   Revision history

Date	Description	Originator	Reviewer	Project Manager	Approver
7 May 2024	Applied feedback	SNT	HDM	HKM	DTS
6 June 2024	Minor typographical errors	SNT	TGL	HKM	DTS

2 Tank conditions

The corrosion of aluminium, used for manufacturing of a methanol storage tank on board of a ship, is of interest. Aluminium could be very useful due to the thick oxide layer that forms which protects the aluminium. Ships are usually manufactured from EN AW 5083 (Euronorm standard) or AA5083 (Aluminium Association system), which is a medium strength alloy with excellent corrosion properties. The properties of this type of alloy are shown in table 2.1.

Table 2.1: Chemical composition of EN AW 5083, considered similar as AA5083, according to EN573-3 (weight %).

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Others total	Aluminium
0.40	0.40	0.10	0.40-1.00	4.00 – 4.90	0.05 – 0.25	0.25	0.15	0.15	Remainder

The environment where the aluminium has to function is fully or partly submerged into methanol or is exposed to nitrogen gas, as the tank will be inerted. Due to the nitrogen generator there could be up to 5 % oxygen present in the nitrogen gas. It is expected that the temperature in the tank ranges from 15 °C to 30 °C.

The IMPCA Methanol Reference Specifications gives general guidelines to specify methanol and how to test for the extra components [1]. Methanol is typically sold under IMPCA Reference Specifications or ASTM grade A or AA. Pure methanol is very hard to produce, which why most producers specify their product according to these specifications. For reference, the sales specification of methanol and bio-methanol produced for ships of OCI-Global has been compared [2]. Both bio and normal methanol comply to the same specifications as given in IMPCA. In table 2.2 the most important contents for corrosion are shown. Since the IMPCA specifications are not a standard, not all (bio)methanol comply to these and different or higher amounts of impurities can be present.

Table 2.2: Most important corrosion specifications of (bio)methanol from OCI-Global.

Purity	Acetone	Water	Ethanol	Chloride as Cl	Sulphur	Acidity as acetic acid	Iron
%WT on dry basis	mg/kg	%W/W	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Min 99.85	max 30	max 0.1	max 50	max 0.5	max 0.5	max 30	max 0.1

3 Types of corrosion

In this chapter a short overview of the corrosion mechanisms are given. For each mechanism the effect of methanol on aluminium is elaborated on.

3.1 Uniform corrosion

With aluminium, this type of corrosion is observed only in highly acidic or alkaline media, in which the solubility of the natural protective oxide film is high [3]. The corrosion products are then unable to form a protective layer. This type of corrosion develops as many pits of very small diameter, in the order of a micrometre, and results in a uniform and continuous decrease in thickness over the entire surface.

Methanol is an amphoteric solvent, being both a weak acid and a weak base. Therefore, methanol in water does not/barely alter the pH of water. According to Vargel [3], at room temperature, in pure methanol the decrease in thickness of aluminium in general is below 0.1 mm per year. The results are the same irrespective of whether the samples are completely immersed in methanol, partially immersed or exposed to the methanol vapor.

3.2 Pitting corrosion

Aluminium is prone to pitting corrosion in media with a pH close to neutral. Pitting corrosion occurs when the metal is put into permanent or intermittent contact with aqueous media: water, seawater, rain water, and humidity. Experience shows that when pitting corrosion occurs, it will always develop during the first weeks of exposure [3].

Pitting corrosion can develop in the presence of chlorides. Chloride Cl^- ions are adsorbed on the natural oxide film, followed by the rupture of the film at weak points, with formation of microcracks that are a few nanometres wide. However, most pits will stop after a few days. The accumulation of corrosion products at the top of the pit, forming the dome of a volcano, will progressively block the entry of the pit. This will hinder the exchange of ions, especially when chloride Cl^- ions are involved, which explains why pitting slows down or even stops. This mechanism is illustrated in figure 3.1.
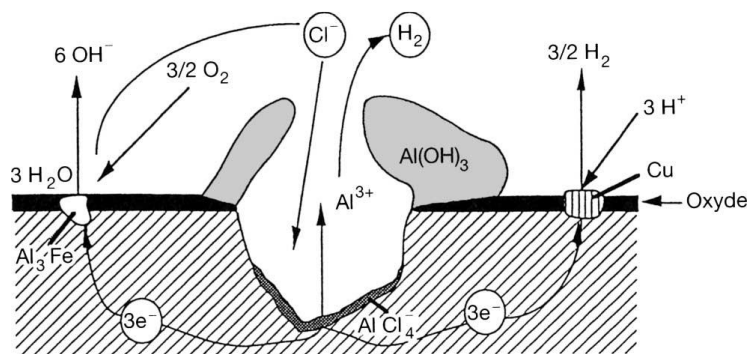

Figure 3.1: Mechanism of pitting corrosion of aluminium [3].

Since the pH will be close to neutral this phenomenon can be of interest. This is confirmed by the Methanol Institute [4] who warn for pitting corrosion due to the chloride in the methanol. Some research has been done by the Naval Surface Warfare Center [5]. They tested different aluminium alloys in pure methanol with 0.5 % water at ambient temperature. The 5052-32 anodized aluminium sheet decreased its corrosion rate from 15.24 micrometre per year (μmpy) after 10 minutes to 3.55 μmpy after 24 hours. This indicates the tendency of this surface toward passivation in the methanol. Generally, aluminium alloys will passivate in pure water. However, if water is not sufficiently present to help stabilize and replenish the oxide layer, passivation may not be maintained even in a relatively nonhostile environment such as methanol. In the presence of 1-20 % water the corrosion rate decreases [6].

A relatively low amount of chloride ions (0.5 mg/kg) in methanol of IMPCA specifications is present, compared to salt water (20.000 mg/kg). A study performed by Vargas & Kannoorpatti on the corrosion of polished AA5083-H321 in seawater found that the corrosion rate, estimated by weight loss, is reduced from 22.0 μmpy in 24 days to 14.0 μmpy in 68 days [7]. It is expected that the pitting corrosion is lower in pure methanol due to less chloride ions in the medium. This hypothesis is confirmed by Feadship who had Fraunhofer perform the research [8].

3.3 Transgranular and intergranular corrosion

Transgranular corrosion spreads in all directions and is typically not found in aluminium. Intergranular corrosion propagates at grain boundaries, which is why unlike transgranular corrosion, this form of corrosion consumes only a very small amount of metal and is invisible with the naked eye. This kind of corrosion can form cracks in the material. This type of corrosion is shown in figure 3.2.
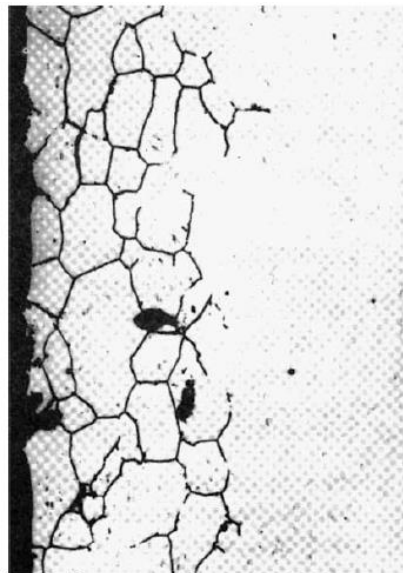

Figure 3.2: Intercrystalline corrosion.

Intercrystalline corrosion is caused by a difference in the electrochemical potentials between the bulk of the grain and the grain boundaries where intermetallic phases precipitate.

Precipitation of an anodic phase occurs in aluminium alloys of the 5000 series with a magnesium content above 3.5 %. Prolonged heating leads to the precipitation of the phase $\beta - Al_3Mg_2$ at grain boundaries. Under appropriate conditions, namely in presence of a corrosive medium, intercrystalline corrosion can occur.

Precipitation of the β-phase is quicker and more intense when
- the magnesium content is high,
- strain hardening is significant, and
- the service temperature is high.

Temperature is not the only parameter which leads to precipitation of the β-phase; this is too often forgotten. Time, i.e. the duration of the exposure to elevated temperature, is also an important parameter, as shown figure 3.3.
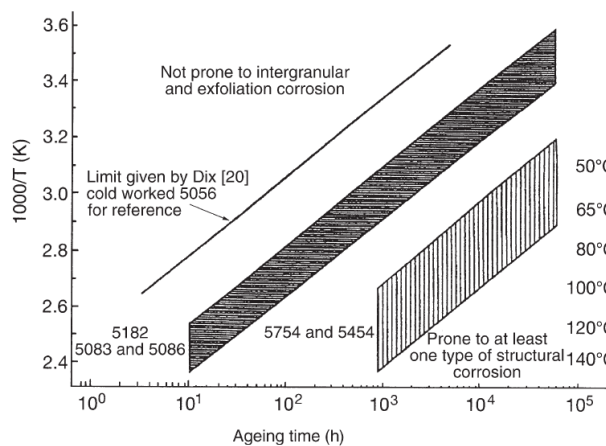

Figure 3.3: Sensitisation of 5000 series alloys. Temperature Time diagram [3].

Sensitisation by precipitation at grain boundaries will not necessarily lead to corrosion. This depends on the environment. As shown by experience, even with heat exchangers operating in seawater at temperatures well above 65 °C. Certain diesel tank trucks have been used for over 20 years, filled each day at 65 °C and then operating for 8–10 h; this amounts to a cumulated holding time at 65–70 °C for more than 50.000 h [3].

Since the 1950s, all these parameters have been studied extensively. Appropriate heat treatment during the manufacturing process may stabilize these alloys, leading to a discontinuous, pearl-chain-like precipitation of the β-phase at grain boundaries. A H116 temper (and its equivalent H321) guarantees that alloys such as 5083, 5086, 5456 are prone neither to intercrystalline nor to exfoliation corrosion. However, if the service conditions are such that the β-phase precipitates at the grain boundaries, these tempering procedures will not prevent corrosion [3].

3.4 Exfoliation corrosion

Exfoliation corrosion is a type of selective corrosion that propagates along a large number of planes running parallel to the direction of rolling or extrusion. Between these planes are very thin sheets of metal that are not attacked, but gradually pushed away by the swelling of corrosion products, peeling off like pages in a book; hence the term "exfoliation corrosion". The metal will swell, which results in the spectacular aspect of this form of corrosion. An example of this type of corrosion is shown in figure 3.4.

This corrosion may be intercrystalline in 2000 and 5000 alloys exhibiting a long-grained structure parallel to the direction of transformation (see above).
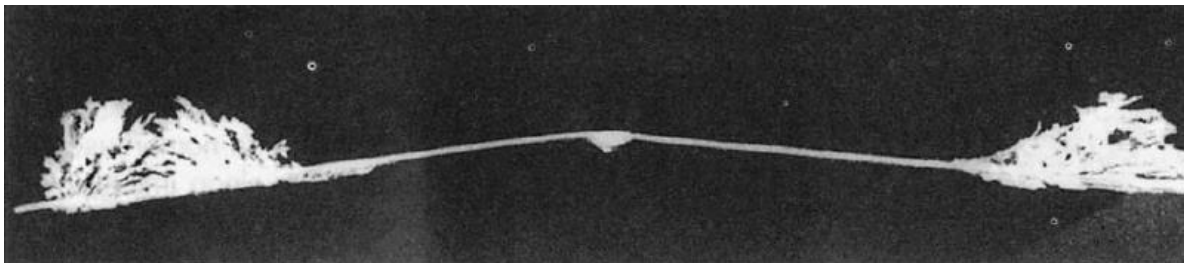

Figure 3.4: Exfoliation corrosion [3].

3.5 Stress corrosion cracking

It is known that the Al-Mg 5000 alloys are susceptible to stress corrosion cracking (SCC) if the Mg content is slightly above (~3 wt%) the room-temperature solubility limit (1.9 wt%) and if a substantial amount of the β-phase, Mg_2Al_3, has precipitated on the grain boundaries, see section 3.3. The solubility of magnesium in aluminium can be seen in figure 3.5. The β-phase precipitation is stimulated by cold work, and to a greater extent by exposure to elevated temperatures (e.g., that result from welding or warm-forming). Typically, susceptibility increases with the continuity of the β-phase layer. Mg_2Al_3 is strongly anodic with respect to the Al-Mg solid-solution matrix and dissolves rapidly in saline environments. Hence, the mechanism of SCC in Al-Mg alloys generally has been considered to proceed by dissolution of the β-phase.
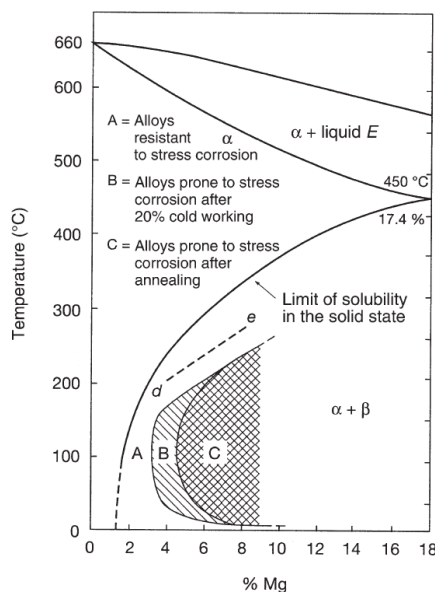

Figure 3.5: Solubility of magnesium in aluminium.

Propagation of stress corrosion cracks always proceeds along grain boundaries. It has been documented that SCC in Al-Mg alloys is also related to hydrogen embrittlement [9].

According to Vargel, stress corrosion of alloys of the 2000 and 5000 series develops only in media containing high amounts of chloride, but not in water having only a low chloride level, or in a humid atmosphere [3].

3.6 Crevice corrosion

Crevice corrosion is a localized corrosion in recesses: overlapping zones for riveting, bolting or welding, zones under joints, and under various deposits (sand, slag, precipitates, etc.). These zones, also called crevices, are very tiny and difficult to access for the aqueous liquid that is covering the rest of the readily accessible surfaces. This type of corrosion is also known as deposit attack.

As soon as an electrochemical reaction occurs in this confined volume, the composition of the contained liquid will change. As a consequence, the dissolution potential becomes more electronegative, and the surface in the recess becomes anodic with respect to the rest of the structure. In the crevice, aluminium is oxidized according to the reaction:

$$Al \rightarrow Al^{3+} + 3e^-$$

<div align="right">Equation 3.1</div>

whereas at the rim of the crevice, oxygen is reduced:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

<div align="right">Equation 3.2</div>

While the metal in the recess is being corroded, oxygen dissolved in the liquid will be consumed. Since the local geometry limits diffusion, the recess will be depleted in oxygen, with an excess of Al^{3+} ions. This leads to an inflow of Cl^- chloride ions. Aluminium chloride will hydrolyse according to the following equation:

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3H^+ + 3Cl^-$$

<div align="right">Equation 3.3</div>
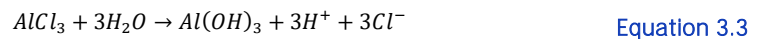
Because of the crevice's small volume, its medium will very quickly become acidic, with a pH value of 2–3. The mechanism is shown in figure 3.6. Unlike certain alloys such as stainless steel, aluminium exhibits a rather low susceptibility to crevice corrosion. When a bolted or riveted assembly that has been exposed to a liquid such as seawater for a long period is dismantled, it appears that crevices are usually sealed by corrosion products of aluminium. This is certainly one of the reasons why aluminium has a rather low susceptibility to crevice corrosion.
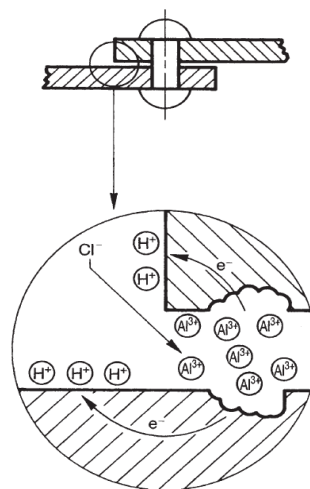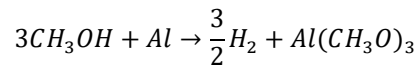

Figure 3.6: Crevice corrosion [3].

3.7 Alcoholate corrosion

At high temperatures, i.e. close to the boiling point of alcohols and phenols, and in a totally dehydrated environment, the OH group can react with aluminium according to the reaction:

$$3CH_3OH + Al \rightarrow \frac{3}{2}H_2 + Al(CH_3O)_3$$

These reactions take place because alcohol (or phenol) dehydrates the protective natural oxide film and modifies its structure. Moreover, since the resulting alcoholate (or the phenolate) is soluble in this medium, aluminium is no longer protected and will, therefore, be continuously attacked. The attack will proceed as pitting.

Experience shows that the addition of a small amount of water, 0.05–0.1 %, depending on the nature of the alcohol or phenol, will completely inhibit the attack of aluminium by phenols, alcohols or mixtures thereof at the boiling point. These traces of water are sufficient to form the natural oxide layer [3].

3.8 Galvanic corrosion

As pure aluminium is highly anodic it will corrode in favour of every metal that is more cathodic. This of course, is only possible in a conductive solution. The electrical conductance of methanol with respectively 0 and 5 % water content is 0.6 and 1.8 $\mu S/cm$ [10]. For a current density of 0.1 $\mu A/cm$, the potential drop will be in the range of 0.17 – 0.06 V/cm, which is very high compared to the galvanic potential which will be in the order of 0.5 to 1 V.

Thus, galvanic corrosion will not spread far. For comparison, seawater has an electrical conductance of 50000 $\mu S/cm$, with a current density of 0.1 $\mu A/cm$, the potential drop will be 0.02 $\mu V/cm$. The Naval Surface Warfare Center has also tested the galvanic corrosion rate with steel to aluminium in methanol. They found no significant corrosion rate [5].

A downside of such high resistance is that any cathodic protection is not feasible as the protection is lost over a short distance. Lunde & Nyborg explained that the protection with a cathode is in the order of 10 – 20 cm for ammonia, which has a conductance of 5 to 10 times higher than methanol [11].

4 Methanol additives

The action of methanol at room temperature mainly depends on its additives or impurities. As an example, the presence of up to 1 % formic acid leads to a superficial attack on the order of 30 μm per year [3].

Considering the chemical composition of methanol according to the IMPCA specifications there could be acetone, water, ethanol, chloride, sulphur, acetic acid and iron present. Water and chloride were already discussed in the previous chapters. The effect of the other additives are elaborated further in the next subchapters.

4.1 Acetone (CH_3COCH_3)

Acetone is the only ketone which is miscible in water. Since the carbonyl group is located inside a carbon chain of variable length, ketones are not very reactive. They are stable products and individually have no action on aluminium [3].

4.2 Ethanol (C_2H_5OH)

In contact with ethanol, pure or in solution, the behaviour of aluminium is very similar to that observed with methanol; it is even generally less susceptible, all the other parameters (concentration, temperature, etc.) being identical [3].

4.3 Sulphur (S)

Sulphur was found to have little to no effects on the corrosion of aluminium. Unlike other common metals, aluminium does not react with sulphur to yield sulphides, even at high temperatures. Aluminium is thus inert in contact with sulphur over a wide range of temperatures, whether solid or liquid (melting point 119 °C) [3]. This is confirmed by Brossia who conducted experiments with AA5052 [12]. AA5052 is chemically very similar to AA5083, where the main differences is a slight decrease in Magnesium and Manganese compared to AA5083.

4.4 Acetic acid (CH_3COOH)

Like alcohols, they may react violently with aluminium at high temperatures in totally dehydrated media, especially at the boiling point (56 °C). The OH group can react with aluminium as follows:

$$3CH_3COOH + Al \rightarrow \frac{3}{2}H_2 + Al(CH_3COO)_3$$
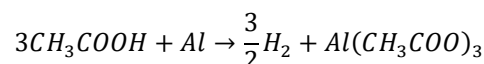
This reaction takes place because the acid dehydrates the natural oxide film and alters its structure. Moreover, since the resulting salt $Al(CH_3COO)_3$ is soluble in the medium, aluminium is no longer protected and will be continuously attacked. This attack often takes place as pitting.

Experience shows that the addition of a small amount of water, between 0.05 and 0.1 %, depending on the nature of the acid, totally prevents the attack of aluminium by boiling organic acids or mixtures thereof [3].

5 Methanol exposure tests

Exposure test were conducted by Fraunhofer in commission by Feadship. Specimens of aluminium alloy EN AW 5083 H111 and steel specimens were immersed in methanol with different added water contents ranging from 0 vol. %, 0.2 vol. %, 0.4 vol. % and 0.6 vol. %. The aluminium surface of samples were scratched and grinded, to locally and globally destroy the natural oxide layer before immersion in the medium. The samples were immersed for 70 days at 40 °C and for 30 days at 60 °C. The maximum corrosion rate found for aluminium at 40 °C is 0.59 μmpy and 60 °C is 0.89 μmpy, which is both very low. This corrosion rate was determined by measuring the mass removed per surface area. According to Fraunhofer no visual signs of corrosion were observed on the specimens [8].
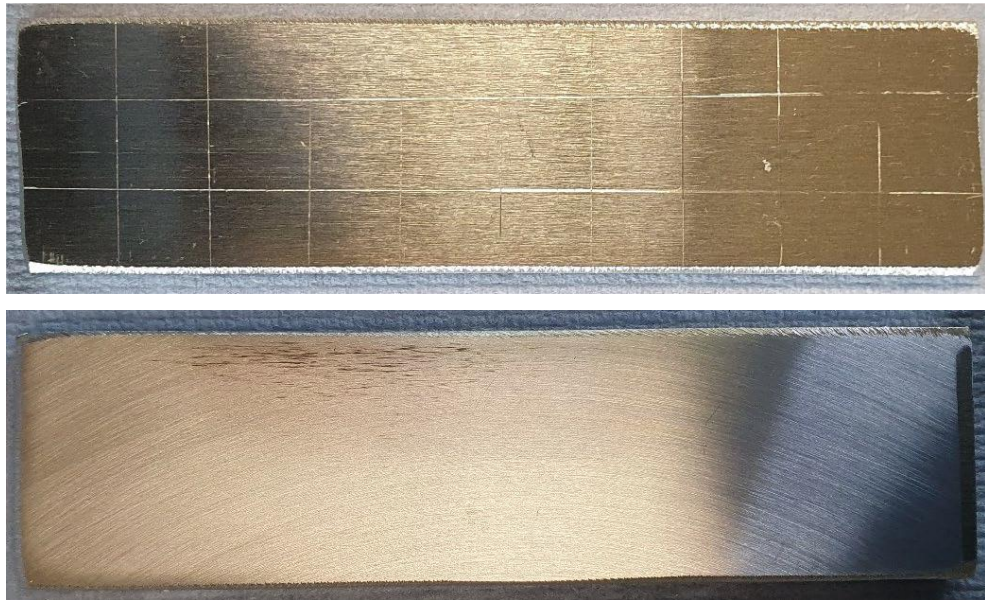

Figure 5.1: Top: Scratched aluminium specimen, bottom: grinded aluminium specimen [10].

6 Conclusions

The effects of corrosion on aluminium are mainly determined by the additives in the methanol. Pure methanol will only have a corrosion effect on aluminium at elevated temperatures where alcoholate corrosion can occur. In non-pure methanol the critical additives expected per IMPCA specification are water and chloride as Cl^-. Increasing the water concentration to at least 0.1 % will prevent alcoholate corrosion. Increasing the concentration further will inhibit pitting corrosion due to the oxide layer being able to passivate the aluminium. The chloride concentration will be the main corrosion susceptibility factor. The chloride ions can react with the aluminium oxide layer and initiate pitting and crevice corrosion. The accumulation of corrosion products at the top of the pit, will progressively block the entry of the pit. This ensures that no deep holes will form in the plate material. It is also expected that crevice corrosion will halt itself due to the build-up of corrosion products.

Comparing the results of corrosion of AA5083-H321 in salt water, which has a substantial higher chloride ion concentration, with methanol and the results of the test of Feadship, it is expected that the mass loss as a result of pitting corrosion remains below the 22.0 μmpy found in the salt water experiment and is closer to the 0.59 μmpy found by Fraunhofer, even at slightly elevated temperatures.

Due to elevated temperatures or simply enough time, the aluminium alloy can become sensitized. This can lead to intergranular corrosion together with stress corrosion cracking. Care should be taken with the choice of temper as this can already sensitize the material before usage. No specific literature about AA5083 and SCC has been found, but according to one source SCC will only take place if the medium contains enough chloride.

6.1 Recommendations

To keep the passive layer of the aluminium intact, a water content of at least 0.1 wt%, which is the upper bound for water content according to the IMPCA specification, should be provided to the methanol. Without this water, the aluminium will be susceptible to pitting, alcoholate corrosion and the corrosion due to acidity acid. Water is needed to create and preserve the strong and protective corrosion layer, specific for aluminium.

It is not expected that trans/inter granular corrosion, exfoliation or stress corrosion cracking will occur on bulk of the tank due to the relatively non-hostile environment and the slow β-Mg$_2$Al$_3$ diffusion at low temperatures. A H116/H321 tempering procedure can stabilize the alloys, preventing sensitization.

However, locally, welding can temporary increase the diffusion, which can sensitize the material. It is therefore recommended, to validate whether inter granular stress corrosion cracking can occur in methanol. This may include exposure tests for alloys with various heat treatments.

7   References

[1]   IMPCA, "Methanol," 27 11 2023. [Online]. Available: https://www.impca.eu/IMPCA.

[2]   OCI-Global, "oci-global.com," 27 11 2023. [Online]. Available: https://documentation.oci-global.com/?_sft_products=bio-methanol,methanol-methanol.

[3]   C. Vargel, Corrosion of Aluminium, Amsterdam: Elsevier, 2004.

[4]   M. Institute, "Compatibility of Metals & Alloys in Neat Methanol Service," 28 11 2023. [Online].

[5]   W. Ferrando, "Corrosion/deterioration of fuel tank materials wetted in methanolic electrolytes," Naval Surface Warfare Center, Dahlgren, 1987.

[6]   V. I. Vigdorovich, "The Corrosion of metals in alcohols and water-alcohol solutions".

[7]   M. Vargas and K. Kannoorpatti, "Corrosion of marine grade aluminium alloys in tropical natural seawater," *Annual Conference of the Australasian Corrosion Association 2013: Corrosion and Prevention 2013,* pp. 266-275, 2013.

[8]   Kaufmann, Dr.-Ing. Heinz;Axel Kansy, M.Sc., "Evaluation of the corrosive effects of different media (methanol, diesel) on aluminum and steel specimens at elevated temperatures," Feadship (Only MENENS and GMM partners), 2022.

[9]   K. Hirayama, H. Toda, D. Fu, R Masunaga, K. S. H Su, A. Takeuchi and M. Uesugi, "Damage micromechanisms of stress corrosion cracking in Al-Mg alloy with high magnesium content," *Corrosion Science,* 2021.

[10] C. Chou and A. Tyto, "TNO methanol corrosion test - 1st report (Only available to GMM partners)," Corrosion, Moerkapelle, 2023.

[11] L. Lunde and R. Nyborg, "Stress corrosion cracking of carbon steel storage tanks for anhydrous ammonia," The fertiliser society, Peterborough, 1991.

[12] C. Brossia, "Corrosion of Iron and Aluminum in Methanol Solutions," in *Corrosion95* .

8 Signature

TNO ❭ Mobility & Built Environment ❭ Delft, 23 July 2024

T.J. Slangen   M. Hagenbeek
Author   Project Manager

R.C. Dragt
Research Manager
Naval & Offshore Structures

TNO innovation
for life