Study of the influence of the initial pH on the aqueous corrosion of an Al-Mg-Si alloy at 70°C

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DE LA RECHERCHE À L'INDUSTRIE

Study of the influence of initial pH on the aqueous corrosion of an Al-Mg-Si alloy at 70°C

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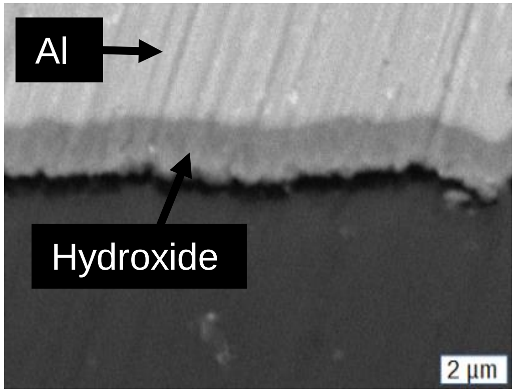
BACKGROUND

Goal of PhD project : understand and predict corrosion of an Al-Mg-Si alloy used in nuclear research reactors

Example of environmental conditions in core :

- Temperature : 70°C
- Pressure : 12 bar
- pH : between 5 and 7
- Water flow rate : 8 m/s

⇒ Harsh environmental conditions = formation of hydroxide layer at surface of aluminium alloy



Hydroxide layer at surface of a Al-Mg-Si alloy

Factors impacting aluminium alloys corrosion :

- Temperature
- Water chemistry → Effect of the pH ?
- Water flow rate
- Pressure

⇒ Study of these impacts in order to minimize aluminium alloys corrosion

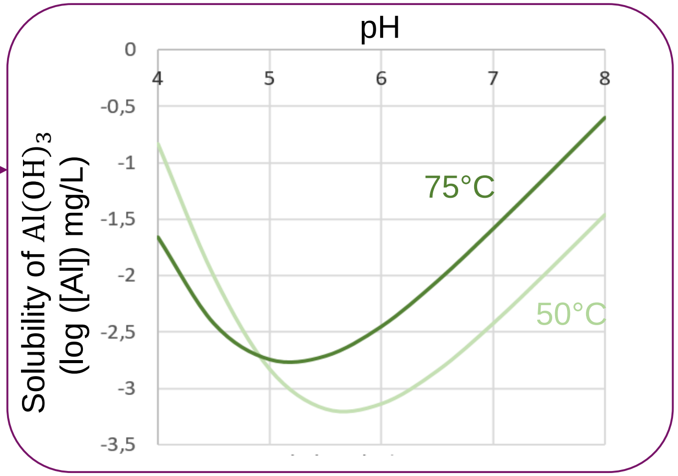
BACKGROUND

Why study the effect of pH ?

⇒ Influence [Al] in solution

⇒ Effect on growth of aluminium hydroxide [1]

⇒ Optimisation of pH in order to limit corrosion of aluminium alloy

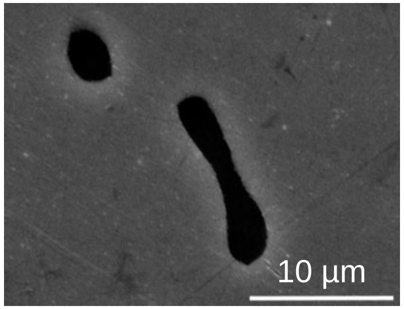


6061-T6 aluminium alloy studied :

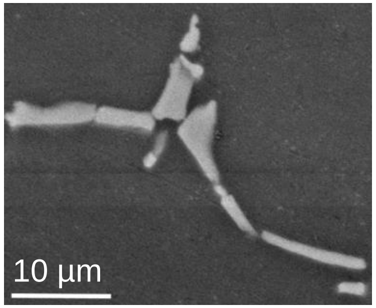
- Chemical composition (wt. %) :

Element	Si	Fe	Cu	Mn	Mg	Cr	Al
Min	0,4	-	0,15	-	0,8	0,04	Balance
Max	0,8	0,7	0,4	0,15	1,2	0,35	

- Two micrometric precipitate families :
  - Mg_2Si particles
  - Iron-rich precipitates



Cross section of Mg_2Si (SEM)



Cross section of IRP (SEM)

EXPERIMENTAL METHODS

Corrosion in autoclaves :

- 316L steel autoclaves, 0,16L, coated in Teflon
- 70°C, 0,5 bar, 33 days
- Three corrosive solutions :
  - pH = 5
  - pH = 6
  - Deionised water

(pH = 5 and pH = 6 → Nitric acid + deionised water)

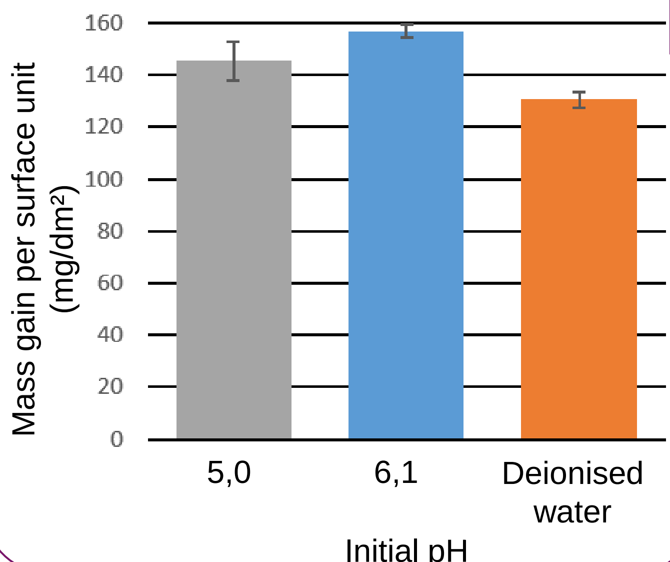
The three autoclaves used

Limit : released Al in solution : $$Al + 3H^{+} \leftrightarrow \frac{3}{2} H_2 + Al^{3+}$$

⇒ pH increases
⇒ But : 65mL of solution = > saturation of Al^{3+}
⇒ Equal final pH (6,7)

OUTLINE OF STUDY

Confirmation of initial pH effect on mass gain of samples :



On what is the effect of initial pH ?

1 Effect on released Al in solution ?

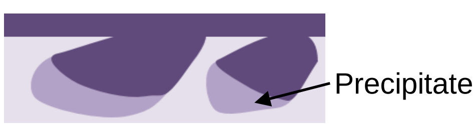
Initial pH	5,0	6,1	Deionised water
Al content (mg/L)	0,2 ±0,04	0,12 ±0,04	0,2 ±0,04
Released Al (mg/dm²)	0,09 ±0,02	0,06 ±0,02	0,09 ±0,02

⇒ **Insignificant effect**

2 Uniform corrosion ?

Uniform corrosion

3 Corrosion of Mg_2Si particles ?



Anodic behaviour of Mg_2Si [2]

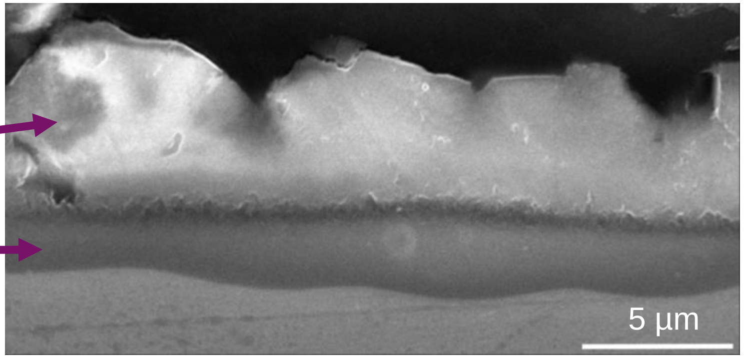
4 Corrosion due to iron-rich precipitates (IRP) ?

Cathodic behaviour of IRP [2]

1. UNIFORM CORROSION (1/2)

Corrosion product at 70°C = two layers of different aluminium hydroxide [1] :

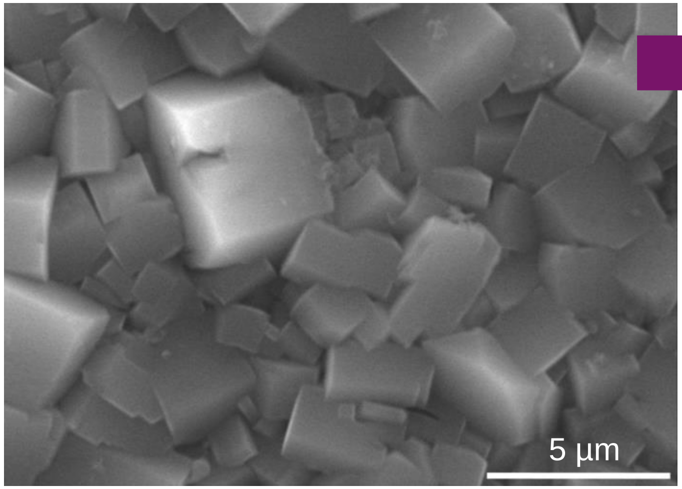
- Bayerite ($\alpha - Al(OH)_3$)
- Pseudo-boehmite (AlOOH)



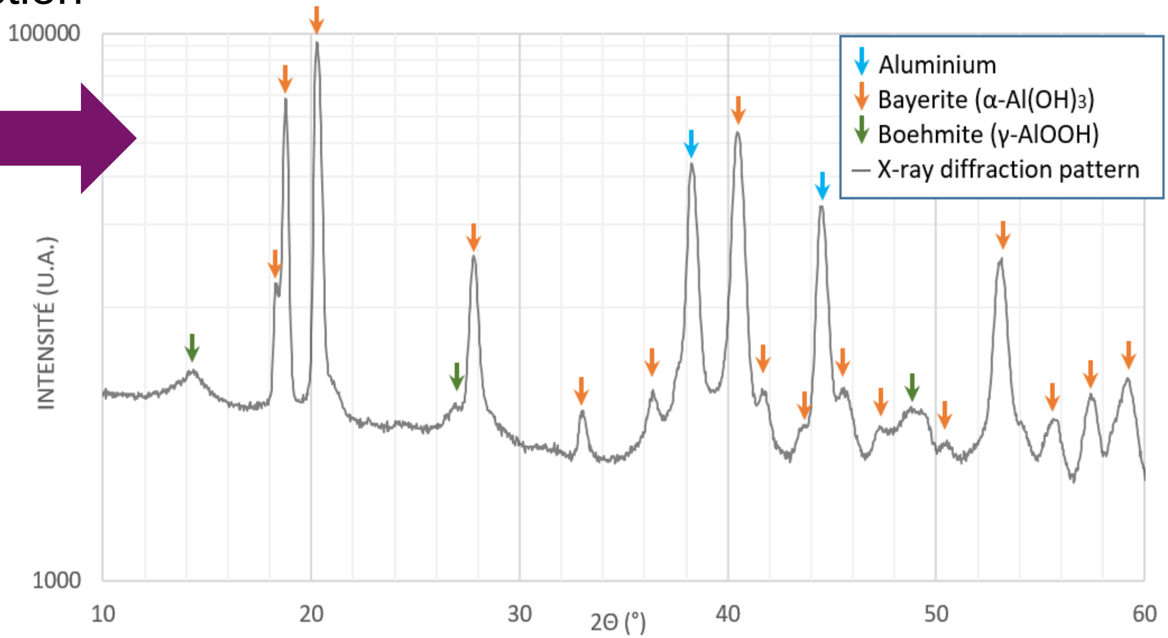
Cross section of aluminium hydroxide (SEM)

Characterizations :

- Grazing incidence X-ray diffraction



Aluminium hydroxide at surface of sample (SEM)

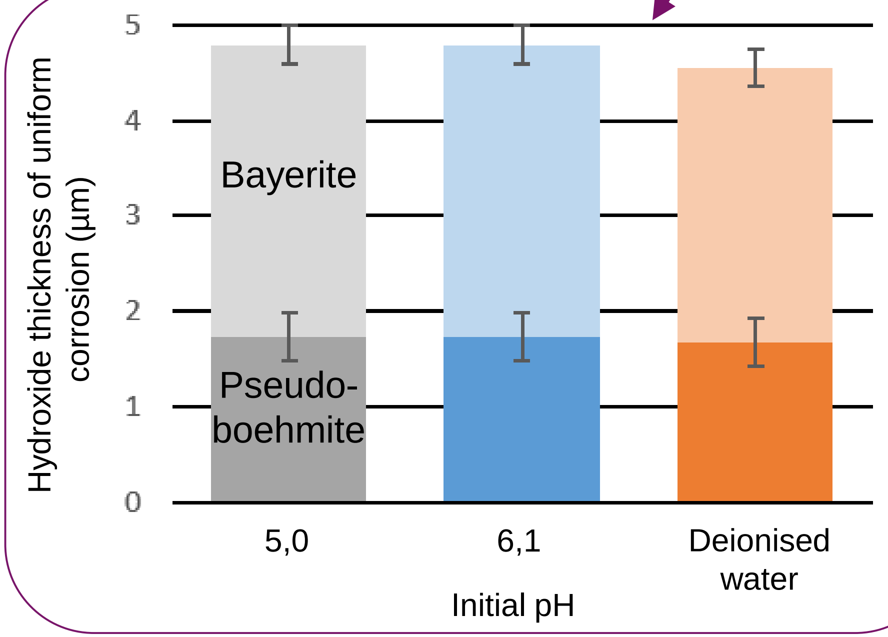


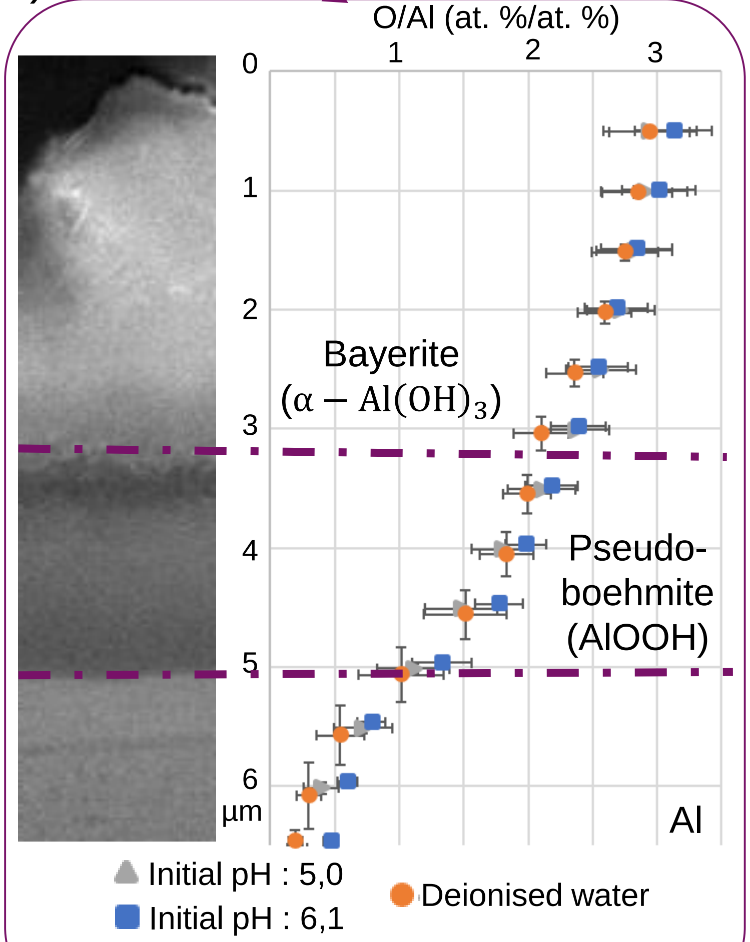
X-ray diffraction pattern of hydroxide layers

1. UNIFORM CORROSION (2/2)

Characterisations :

- Measurement of O/Al ratio depending on depth of hydroxide (by EDS-SEM)
- Measurement of hydroxide thickness (with SEM)





O/Al ratio depending on depth of hydroxide

⇒ No effect of the initial pH on :
- **Cristal size**
- **O/Al ratio**
- **Hydroxide thickness**

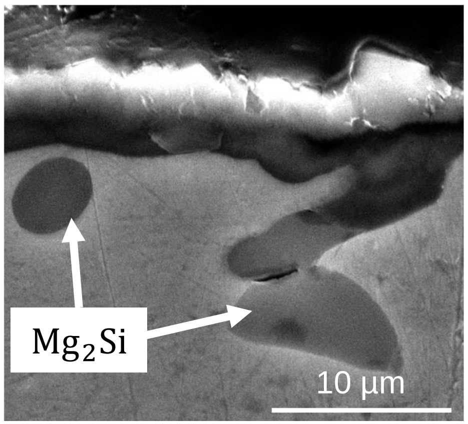
2. CORROSION OF MG_2SI PRECIPITATES

Equation associated to corrosion of Mg_2Si [2] :

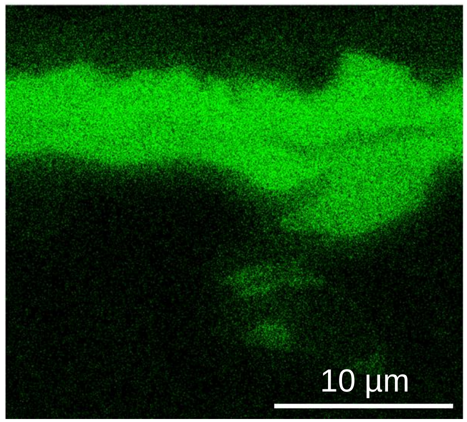
$$Mg_2Si + 2H_2O \rightarrow 2Mg^{2+} + SiO_2 + 4H^+ + 8e^-$$

Characterizations :

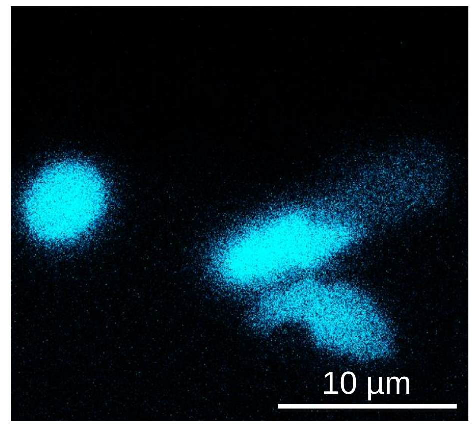
- Maps of chemical elements O, Mg and Si (with EDS-SEM) :



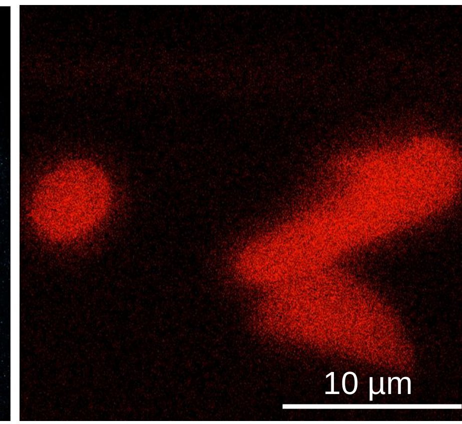
Cross section of Mg_2Si (SEM)



Map of oxygen



Map of magnesium



Map of silicon

- Measurement of the Mg^{2+} content in solution (by ICP-AES) :

Initial pH	5,0	6,1	Deionized water
Mg^{2+} content (mg/L)	0,52 ± 0,02	0,53 ± 0,02	0,52 ± 0,02

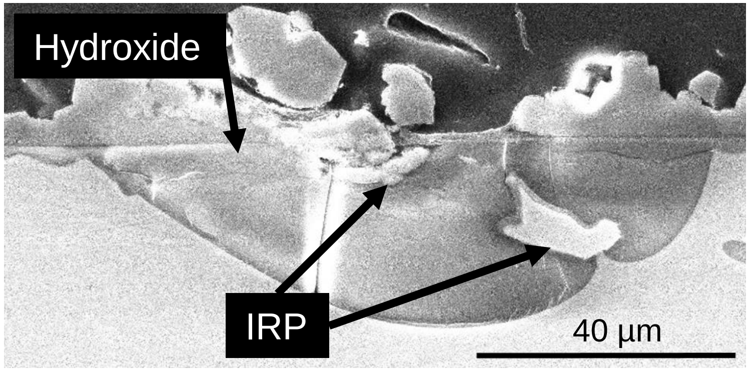
⇒ No effect of the initial pH on Mg^{2+} content in solution

3. CORROSION DUE TO IRON-RICH PRECIPITATES (1/3)

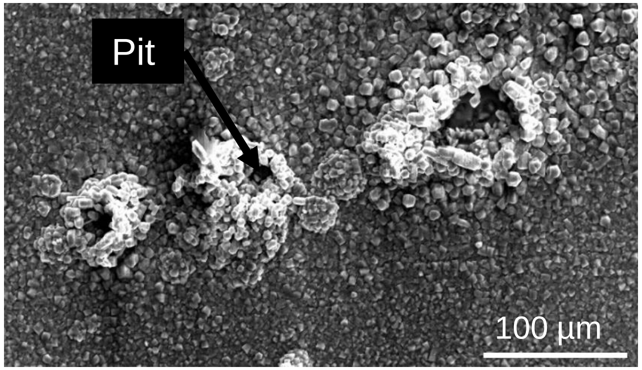
Iron-rich precipitates (IRP) = local cathodes (hydrogen and oxygen reduction)

⇒ IRP accelerate Al oxidation

⇒ Formation of hydroxide pits



Cross section of a pit (SEM)

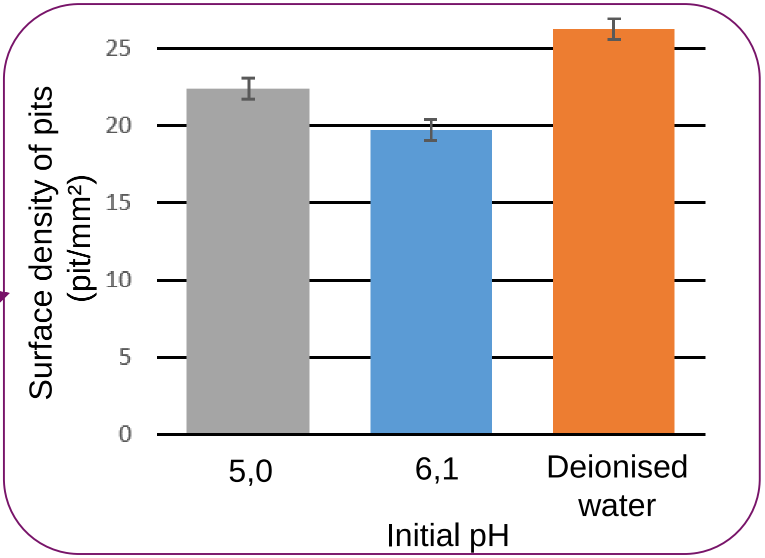


Pits at surface of sample (SEM)

Characterizations : measurement of :

- Surface occupied by pits
- Surface density of pits

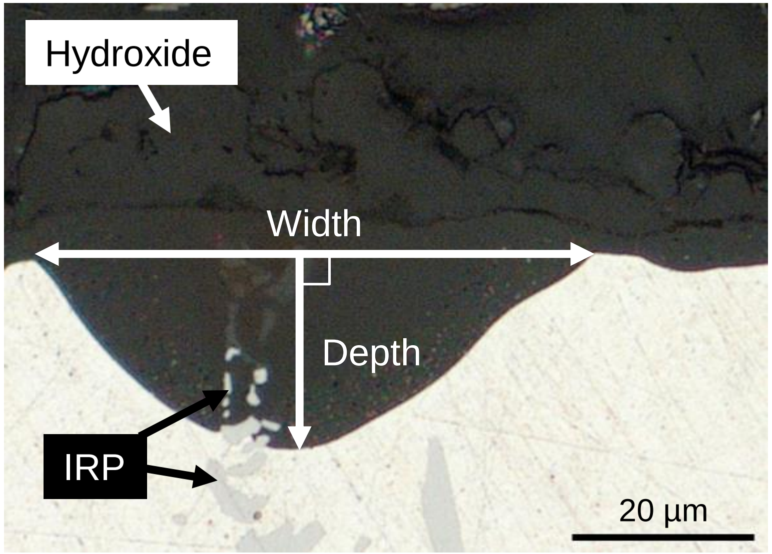
⇒ Effect of initial pH on surface density
But similar occupied surface (14%)



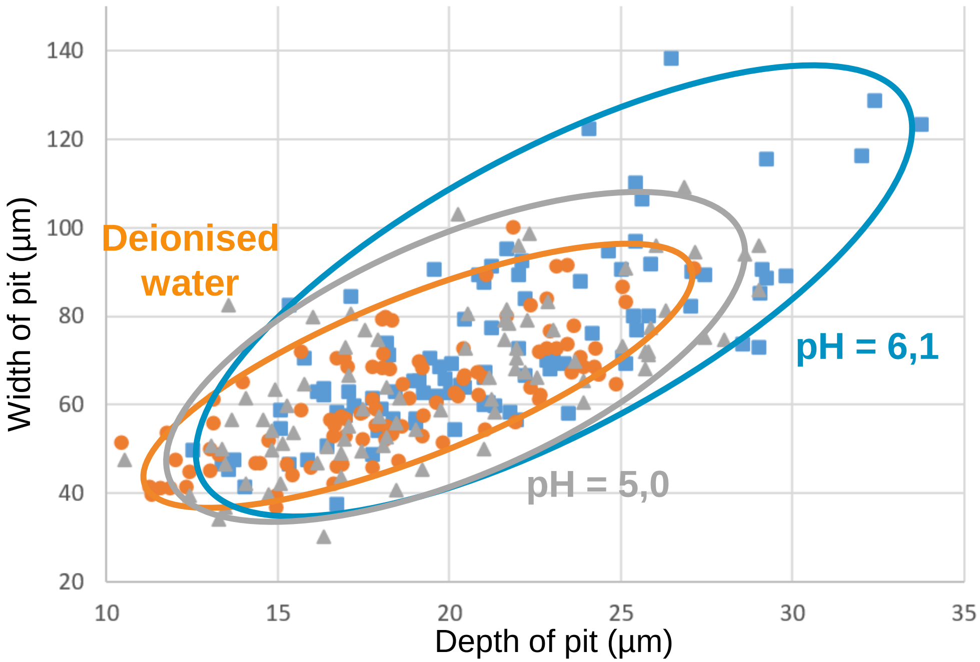
3. CORROSION DUE TO IRON-RICH PRECIPITATES (2/3)

Initial pH=6,1 : less pits per surface unit

⇒ Measurement of width and depth of pit



Cross section of pit (OM)



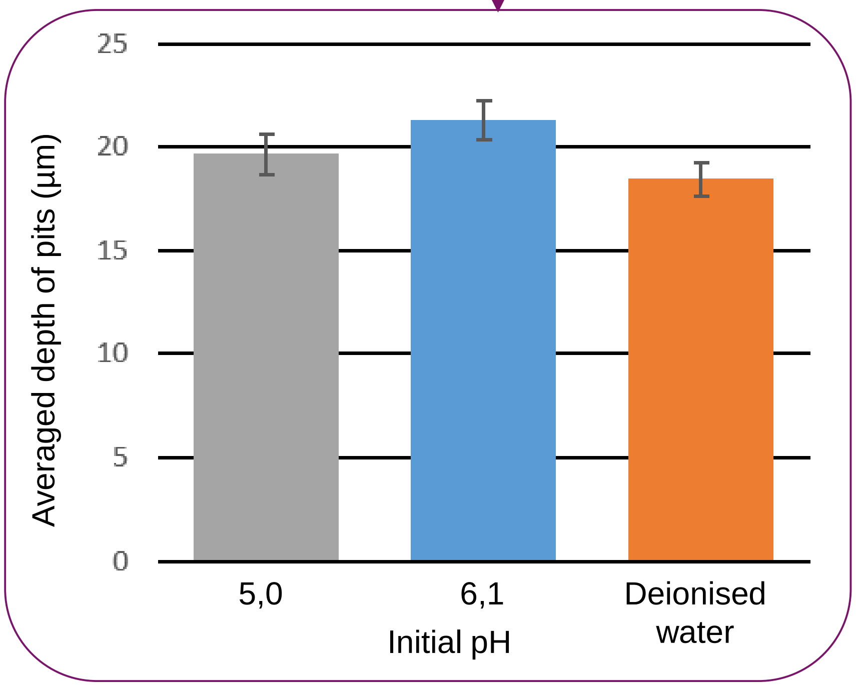
⇒ **Initial pH=6,1 : widest and deepest pits**

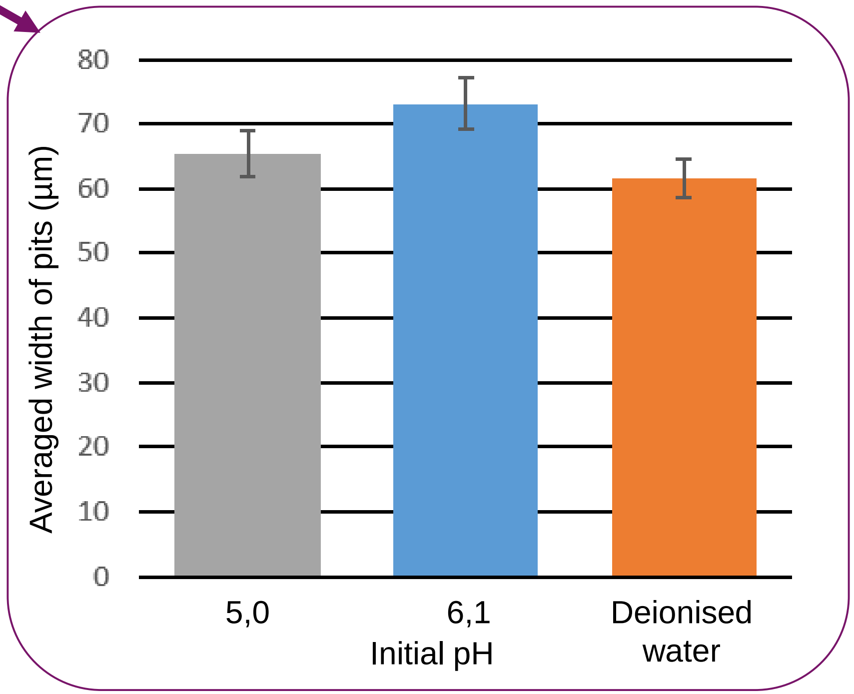
3. CORROSION DU TO IRON-RICH PRECIPITATES (IRP) (3/3)

Initial pH=6,1 : less pits per surface unit

⇒ Measurement of width and depth of pit

⇒ pH=6,1 : averaged depth and width of pits = most important





⇒ **Effect of initial pH on pit :**
Most oxidised Al at initial pH=6,1

CONCLUSIONS

Corrosion tests with three initial pH on 6061-T6 aluminium alloy :

- 5,0
- 6,1
- Deionised water

(5,0 and 6,1 → Nitric acid + deionised water)

⇒ Limit : equal final pH (6,7)

No effect of initial pH on :

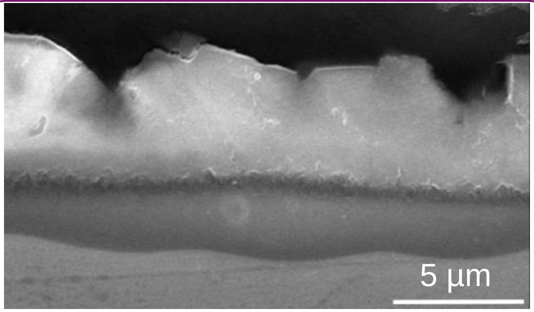
- Uniform corrosion
- Corrosion of Mg_2Si precipitates

Effect of initial pH on galvanic corrosion between iron-rich precipitates (IRP) and Al :

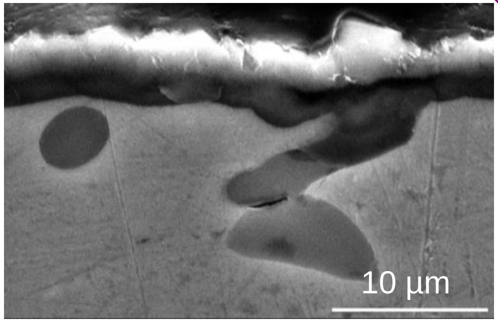
=> At initial pH =6,1, most oxidised Al, widest and deepest pits of hydroxide

Further studies : study of the beginning of the galvanic corrosion IRP/Al

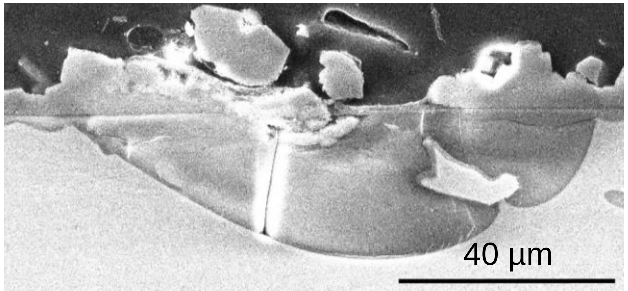
⇒ Short time of corrosion (1-3-7-10d.)



Cross section of aluminium hydroxide of uniform corrosion (SEM)



Cross section of Mg_2Si (SEM)



Cross section of pit (SEM)

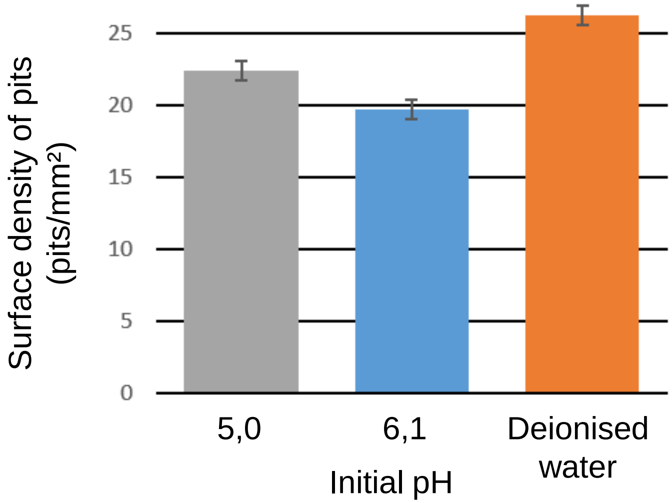
Thank you for your attention

[1] M. Wintergerst, ‘Etude des mécanismes et des cinétiques de corrosion aqueuse de l’alliage d’aluminium AlFeNi utilisé comme gainage du combustible nucléaire de réacteurs expérimentaux.’, Thèse de doctorat, Université Paris XI, U.F.R Scientifique d’orsay, Saclay, 2010.
[2] M. A. Pech-Canul, R. Giridharagopal, M. I. Pech-Canul, and E. E. Coral-Escobar, ‘Corrosion Characteristics of an Al-1.78%Si-13.29%Mg Alloy in Chloride Solutions’, presented at the ICAA13: 13th International Conference on Aluminum Alloys (eds H. Weiland, A. D. Rollett and W. A. Cassada), 2012.

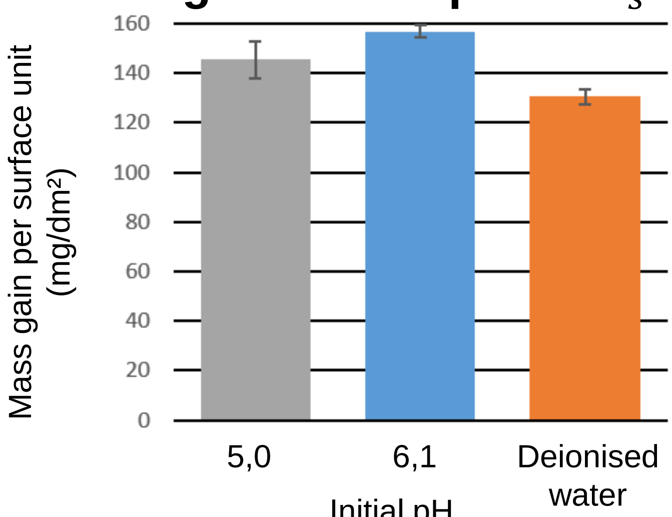
3. CORROSION DUE TO IRON-RICH PRECIPITATES (2/4)

Effect of initial pH on :

- **Surface density of pits** N_{pits}

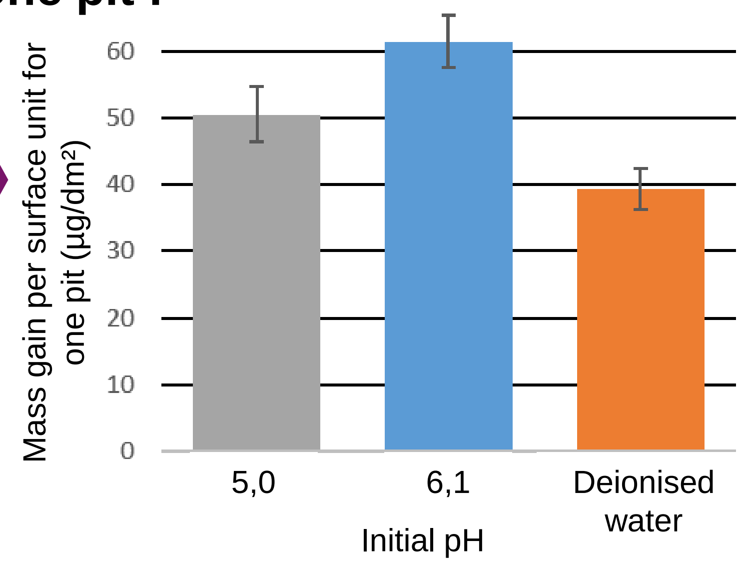


- **Mass gain of samples** Δm_s



$\Delta m_{pits} = f(N_{pits}, \Delta m_s)$

=> Mass gain per surface unit for one pit :



$\Rightarrow$ Initial pH=6,1 : most mass gain by pit

$\Rightarrow$ Most oxidised Al at initial pH=6,1

$$\Delta m_{pits} = \frac{1}{N_{pits} S_{pits}} \left[\Delta m_s - \left(E_{Al(OH)3} d_{Al(OH)3} \frac{M_{3OH}}{M_{Al(OH)3}} + E_{AlOOH} d_{AlOOH} \frac{M_{OOH}}{M_{AlOOH}} \right) * (1 - x) \right]$$