ECO-DESIGN ITD

Grant agreement n°270589

Project COPROCLAM

MINUTES OF MEETING

KICK OFF MEETING	
Date of meeting	13 April 2011
Location of meeting	Nancy – CNRS Regional representation
Author	G. HENRION (project coordinator)
Issue date	02 may 2011
Document n°	COPROCLAM_2011_001_MOM_20110413

ATTENDEE LIST

Name	Society/Organization	Remarks & Comments
Myriam ACIMOVIC	CNRS-DR6	Administrative
Philippe COMBES	GIT	
Thierry CZERWIEC	CNRS-IJL	
Teresa DUCHANOY	CNRS-IJL	
Emiliano FORCHIN	Agusta Westland	
Gérard HENRION	CNRS-IJL	Project coordinator
Elodie HERAIL	LTS	
Julien MARTIN	CNRS-IJL	
Johanna MICHIELIN	CNRS-DR6	Administrative
Sophie PETTIER	Eurocopter	
Delphine RENAUX	CNRS-IJL	
Jérôme ROCCHI	LTS	Topic manager
Carlo ZANOTTI	Agusta Westland	

1-Introduction

The meeting was held at CNRS-Nancy (Regional Representation Building) on 13th of April 2011. It started at 10h30. Each attendee introduced him/herself.

1.1 Objective of the meeting

The objectives of the meeting were to:
- remind the aims and organization of the co-proclam project
- talk about technical and administrative aspects
- define the work program for the first months

1.2 Attachments

- 2011-04-13_IJL-kick-off.pdf
- 2011-04-13_LTS-kick-off.pdf
- 2011-04-13_Admin-kick-off.pdf

1.3 Schedule

10h30 – 10h45	Welcome and presentation of participants	
10h45 – 11h15	JTI role and expectations	J. Rocchi (topic manager)
11h15 – 11h45	The Co-ProCLAM project	G. Henrion (coordinator)
11h45 – 12h05	The Co-ProCLAM partners	P. Combes / G. Henrion
12h05 - 12h40	Discussion	
12h40 – 14h00	Lunch break at CNRS staff restaurant	
14h00 – 14h30	Administrative aspects	J. Michielin (CNRS)
14h30 – 15h00	Project organisation	G. Henrion
15h00	End of meeting	

2 Minutes of the meeting

Details on the points that were discussed are reported in the attachments

2.1 Conclusion and decisions

Technical aspects

- regarding **magnesium** alloy samples, Agusta Westland would prefer the study concerns Mg EV21 instead of WE43 ; Eurocopter is still interested in WE43. Both alloys could be studied but this will limit the number of sample of each grade. EV21 will be studied first.

- main objective on Mg samples are: coating thickness 10 to 15 µm ; withstand 100 hrs B117 ; good adherence of resin.

- regarding **aluminium** alloy sample, two different type will be studied : Al 2024 and one among AS7G or AU5NKZ.

- main objectives on Al samples are: coating thickness ≅ 5 µm ; withstand 500 hrs SST.

- sample size for both Al and Mg alloys: must satisfy the requirements for corrosion test, i.e. 150 mm x 100 mm (L x l). Thickness value has less importance (typ. thickness = 5-10 mm).

- samples will be provided by ITDs

- estimation of number of Al samples: ≅ 400 for GIT + 250 for IJL-CNRS.

- estimation of number of Mg sample: to be defined by IJL-CNRS.

- frequency of meetings is fixed (by the DoW) every 6 months. However technical intermediate meetings might be held on request by a partner of an JTI's member

Administrative aspects

- the grant agreement is going to be signed by all parties within a couple of weeks

- the implementation is still not signed and seems to be blocked at one ITD's

2.2 Actions

Action #	who	Description	Due date
1	IJL	define number of Mg sample for each grade	June 2011
2	LTS	provide Al samples to IJL (250) and GIT (400)	July 2011
3	AW	provide to IJL Mg EV21 samples	Sept 2011
4	Eurocopter	provide to IJL Mg WE43 samples	to define
5	IJL	bibliographic report on electrolytes	July 2011
6	IJL	give LTS login and password for the common exchange zone on IJL server	ASAP
7	ITDs	Check about and complete implementation agreement	ASAP

3-Next meeting

Next meeting is planned on the beginning of September 2011 at GIT Toulouse

ECO-DESIGN ITD

Grant agreement n° 270589

Project COPROCLAM

MINUTES OF MEETING

PROJECT MEETING	
Date of meeting	21 June 2011
Location of meeting	Nancy – Toulouse by Webex
Author	Myriam Acimovic
Issue date	24 June 2011
Document n°	COPROCLAM_2011_002_MOM_20110621

ATTENDEE LIST

Name	Society/Organization	Remarks & Comments
Myriam ACIMOVIC	CNRS-DR6	Administrative
Philippe COMBES	GIT	
Gérard HENRION	CNRS-IJL	Project coordinator
Elodie HERAIL	LTS	
Johanna MICHIELIN	CNRS-DR6	Administrative
Nadia Vialas	LTS	Topic manager

1-Introduction

The meeting was requested by topic manager. It was held by Webex on 21st June 2011. It started at 09h15. The objective of the meeting was to review the progress on the project.

Contents of the meeting :

- Presentation by CNRS on the work progress since the starting date of the project
- Presentation by GIT on the work progress since the starting date of the project
- Organisation between GIT-CNRS and between the JTIs members (Liebherr, Agusta, Eurocopter et Turboméca)
- Recruitment
- Quantity of samples needed

2 Minutes of the meeting

Progress of the project :

The bibliographic review (WP2 – CNRS) on the electrolytes is in progress for what concerns Aluminum and, at a lesser extent, for magnesium. Report on the bibliographic review on electrolytes should be available on mid-July.

There has been no test on the effect of electrolyte composition because sample were still not supplied.

Al2024 sample should be delivered soon at:
GIT (400 samples)
CNRS(250 samples)

Some Al2024 samples from a different batch were provided by LTS to CNRS to proceed to some tries
Agusta Westland should provide magnesium samples on end of-August or beginning of September

No information regarding Eurocopter who is in charge of Mg. LTS is going to boost them

Before September choice of electrolyte composition has to be determined in order to allow GIT and CNRS to order the requested compounds and chemicals.

Concerning high frequency processing, M. Beauvir is in charge of processing samples at high frequency. He will then send the processed sample to GIT who will perform the salt spray tests. M. Beauvir will be asked by GIT for coating thickness less than 5 µm (Al) and less than 10 µm (Mg).

GIT needs 3 samples for each conditions: 2 for Salt spray test + 1 for microstructure characterization at CNRS

Recruitment :

GIT : a technician starting on September or October
CNRS : a Post-doc fellow starting on September or October. Offer has been published and several application have already been received

Implementation Agreement :

No progress
Modifications requested by Agusta Westland were not transmitted
Turboméca : there were several exchange between Liebherr and Mr. Julien Gurt Santanach
Eurocopter : Liebherr is going to get in touch with them

3-Next meeting

Next meeting is planned on 8th or 9th September 2011 at GIT Toulouse; Nadia Vialas will arrange the date with all participants

MINUTES OF MEETING

INTERMEDIATE MEETING

Date of meeting	8 September 2011
Location of meeting	CUGNAUX - GIT
Author	Gérard Henrion – Johanna Michielin
Issue date	13 September 2011
Document n°	COPROCLAM_2011_004_MOM_20110908

ATTENDEE LIST

Name	Society/Organization	Remarks & Comments
Philippe COMBES	GIT	
Julien GURT SANTANACH	TURBOMECA	
Gérard HENRION	CNRS-IJL	Project coordinator
Elodie HERAIL	LTS	
Johanna MICHIELIN	CNRS-DR6	Administrative
Sophie PETTIER	Eurocopter	
Nadia VIALAS	LTS	Topic manager

1-Introduction

As planned in Grant Agreement n°270589, the 6 months intermediate meeting of the COPROCLAM project was held in Cugnaux, in GIT premises, on September the 8th 2011.

Contents of the meeting :

- Bibliography report on the electrolyte
- Discussion on the choice of electrolyte composition
- IJL first results on Al 2024 and other grade
- GIT results
- Discussion and work program for the next 6 months
- Administrative aspects
- Recruitments at IJL and GIT
- Next meeting

2 Minutes of the meeting

Bibliography report on the electrolyte:

The goal of this bibliography study was to identify the electrolyte composition used for micro-arc processing aluminium and magnesium alloys, focusing on anti-corrosion efficiency.

G. Henrion presented the results of this bibliography study. The methodology used and the conclusions are exposed in thepdf file attached to this minutes.

Through the presentation, G. Henrion emphasized that the results of the bibliographic review were somehow comforting in the sense that the composition of the electrolytes described in the scientific papers did include most of the time alkaline hydroxide based (composition currently used at IJL and GIT). The concentration is rather low, < 0.1 M/L. It seems though that a high concentration would improve the layer compactness and the corrosion resistance, due to higher electrolyte conductivity.

The additives were rather numerous. Silicate, phosphates or aluminates (SiO_3^{2-}, PO_4^{3-} or AlO_2^- anions) or fluoride (NaF, KF) are often added to the electrolyte. The influence of the concentration of additives is not clearly pointed out. The choice of the additive is important as they can improve the layer growth and the corrosion resistance, fluoride being described as the most efficient to improve corrosion resistance.

Discussion on the choice of electrolyte composition:

G. Henrion suggests to stick with alkaline hydroxides with concentration ranging from 0.01 M to 0.2 M. Additive could be silicate (Na_2Si0_3) and phosphates (Na_3PO_4 or $NaPO_3$, the latter being phosphorous richer. When the goal of realizing thin layers is achieved, addition of some fluorides in the electrolyte will be investigated. GIT suggests that we realize 3 to 4 tests without fluoride. We will then keep the best result in terms of concentration of the electrolyte and then add the fluoride. Note:

there is no difference on the electrolyte composition for treatment on aluminum or on magnesium. The difference will be on the current.

IJL first results on Al 2024 and other grade:

- Effect of electrode gap distance on layer thickness.

We had the distance between electrodes vary. The conclusion is that it does not have any impact on the layer thickness when we use the arc regime. It does have a great influence though when using the soft regime (see figures on slide n°8 of power point presentation).

- Effect of electrode gap distance on thickness homogeneity

The homogeneity varies as well with the distance between electrodes. The smaller the distance is, the more homogeneous the layer (see pictures on slide n°9 of power point presentation).

- Effect of anodic current

We made the intensity of the current vary between 7 and 15 ampere. The experiment was done on a 750 hertz frequency. The surface morphology and roughness varied with an optimum at 10 ampere (see slides 10 to 16).

GIT results:

GIT started the pilot chain and defined the work to be subcontracted to Mr. Beauvir..

Discussion on the work program:

The characterization of layers will be done at IJL on the best samples after GIT made salt spay tests. The tests run at IJL will be SEM, X-ray diffraction, surfometry and hardness measurements

A selection of the samples issued from the sub-contracted part of the work will also be characterized at IJL, in order to estimate the influence of a higher frequency.

We also plan on testing at IJL the effect of using titanium electrodes instead of stainless-steel electrodes. If it makes a difference, GIT might use then as well.

GIT plans on divided the work plan in four phases, the firt one (test preparation) being already done.

- PHASE 2 : October 2011 to March 2012, study on electrolyte on Al 2024 and El21
- PHASE 3 : April 2012 to September 2012 : study on electrical parameters on Al 2024, El21, AS7G06 and WE43

- PHASE 4 : octobre 2012 à mars 2013: tests on clients’ parts.

Administrative aspects:

No progress on the implementation agreement. We are still waiting for the comments of Eurcopter. The comments of Agusta Westland and Turbomeca were not transmited to CNRS either.

Recruitments:

IJL found a Post Doc student to be recruited 10th of October. Her name is Irina SHCHEDRINA. She defended her PhD at Moscow State Institute of Metals and Alloys under the supervision of Pr A.G. Rakoch, on “Properties and growth rate of coatings produced on the Al 2024 alloy while micro-arc oxidation under various modes”. She is thus very qualified for this project.

GIT also recruited a technician who will start on first of October 2011.

Next Meeting:

Next meeting is planned mid of January by phone. The next intermediate meeting will be held in Paris, either in CNRS or in Safran’s premises, mid of March.

ECO-DESIGN ITD

Grant agreement n° 270589

Project COPROCLAM

MINUTES OF MEETING

INTERMEDIATE MEETING

Date of meeting	25 January 2012
Location of meeting	Webex meeting
Author	Gérard Henrion – Johanna Michielin
Issue date	22 February 2012
Document n°	COPROCLAM_2012_006_MOM_20120125

ATTENDEE LIST

Name	Society/Organization	Remarks & Comments
Philippe COMBES	GIT	
Julien GURT SANTANACH	TURBOMECA	
Gérard HENRION	CNRS-IJL	Project coordinator
Elodie HERAIL	LTS	
Johanna MICHIELIN	CNRS-DR6	Administrative
Sophie PETTIER	Eurocopter	
Irina SHCHEDRINA	CNRS-IJL	Post-doc
Nadia VIALAS	LTS	Topic manager

Emiliano FORCHIN is excused to be unavailable to attend the meeting

Contents of the meeting :

- Presentation of last results by IJL
- Presentation of last results by GIT
- Wok program for the next 3 months
- Administrative aspects
- Next meeting

1 - Presentation of last results by IJL:

Since end of Octobre, IJL has recruited a post-doc who is coming from the university Misis (Moscow). She defended her PhD on PEO treatment of aluminium alloys.

G. Henrion presents results concerning the effect of the current pulse frequency and the current pulse anodic amplitude on the growth process and the resulting layers[1].

Effect of the current frequency

Al2214 samples were processed under the following conditions:

- sample sizes = 30 x 50 x 6 mm^3
- electrolyte = KOH + Na_2SiO_3
- electrode gap distance = 28.5 mm
- current waveform parameters chosen for reaching soft regime
- anodic current amplitude = 30 A (75 A/dm^2)
- current frequency range = 100 – 900 Hz

Main results are:

- The higher the current frequency, the faster the transition from arc to soft regime.
- An increase in the current frequency implies :
  - \+ a better homogeneity in thickness over the sample surface (though layer presents strong thickness gradient from the center to the edge due to strong edge effects)
  - \+ a better surface state (lower roughness)
  - \+ a thicker dense layer
  - \- a lower growth rate

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[1] Details of these results are reported in the intermediate report: COPROCLAM_2012_005_Intermediate-report_20120123.pdf

A current frequency in the range 750 – 900 Hz gives the best results. However the current supply cannot deliver current at higher frequency. Tries are going to be performed with a new generator on smaller size samples because of current capabilities of this generator.

Effect of the anodic current amplitude

Al2024 samples were processed under the following conditions:

- sample sizes = 30 x 50 x 2 mm^3
- electrolytes = KOH and KOH+ Na_2SiO_3
- electrode gap distance = 28.5 mm
- current waveform parameters chosen for reaching soft regime
- current frequency = 100 Hz (chosen to allows us to compare with previous experiments that were done with that frequency). Tries have also been performed at 750 Hz
- anodic current amplitude range = 7 – 30 A

Main results are :

- Thickness gradient is still present whatever the current amplitude. Nevertheless, it is less pronounced at low current values, typically lower than 15 A .
- A higher current amplitude (in the range 7 – 15 A) favours :
  - + an improvement of the surface state (lower roughness, Sa = 1 – 2 µm)
  - + a better surface state (lower roughness)
  - + the formation of crystalline alumina (γ Al_2O_3). No α Al_2O_3 was observed. This is likely due to the low intensity of the micro-discharges, and thus a too low local temperature. However, the layer thickness was quite thin (< 10 µm). Consequently, grazing incidence XRD has to be done on these samples to confirm the crystallographic results

- A low current amplitude (in the range 7 – 15 A) favours :
  - + a lower layer thickness (< 10 µm) with rather good homogeneity
  - + a too low current (7 A) results in thin (5µm) layers
  - + nevertheless, these layers (7 A) are stratified which may be detrimental to the corrosion protection

2 - Presentation of last results by GIT:

A technician was appointed since last October. GIT is now in the second phase that concerns the study of the electrolyte composition[2]. It is expected that both GIT and IJL use the same chemicals.

Al2024 samples were processed under the following conditions:

- large size sample
- electrolytes = NaOH+ Na_2SiO_3 (+ KF) (+$Na_4P_2O_7$, 10 H_2O)
- no counter electrodes except the electrolyte tank walls. distance from the electrode = 170 mm
- current frequency = 50 Hz (chosen to allows us to compare with previous experiments that were done with that frequency). Tries have also been performed at 750 Hz
- current parameters and treatment time adjusted to grow 5 µm layers.

Main results are :

- Increasing the Na_2SiO_3 content results in a higher growth rate. Usually the product of the current density times the treatment time is kept constant to keep the layer thickness below 5 µm. Nevertheless, at high Na_2SiO_3 content this cannot be satisfied
- A strong thickness gradient is measured (5 µm in the center, 20 µm at the edge of the sample). It seems that this edge effect is more pronounced as the current increases.
- Whatever the Na_2SiO_3 content, the corrosion resistance is less than 72 h salt spray.
- Adding KF does not change significantly : same current density, similar corrosion results (48 h SP).
- Adding sodium pyrophosphate (in the previous electrolyte) does not change anything.
- Adding finally sodium aluminate: a viscous precipitate forms in the electrolyte; consequently, only 1 try was done. Corrosion results were worst.

3 - Discussion:

It appears that a rather low current amplitude (close to 10 A) and a higher frequency (750-900 Hz) would give the best results in a simple electrolyte.

Using Ti counter electrode has advantage of increasing the electrolyte lifetime by lowering the bath poisoning. However GIT has no possibility to work with an electrolyte tank made of Ti.

Concerning the electrolyte composition, it would be of interest to check what electrolyte elements are inserted in the oxide layer.

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[2] see the GIT's presentation: COPROCLAM_2012_007_GIT_20120125.pdf

4 – Further work:

IJL:

- Study the influence of the current density by changing the sample size instead of the current amplitude
- Start working on Mg El21: electrolyte composition, current parameters
- PEO processing of large size samples (Al2024) for SP tests

GIT:

- Continues on electrolyte composition (Al2024)
- Work on the current parameters with "electronic" generator
- Request J. Beauvir to proceed samples with his new high frequency generator
- test of top coating and painting as requested by AW
- send samples to IJL for characterizations

5 - Miscellaneous:

Mg samples from AW have been received at LTS. LTS sent 50 samples to IJL on 24 January. Samples were sand blasted and Cr-Mn coated. Therefore they need to be surface machined and prepared before processing.
GIT will also receive some Mg samples.

IJL is writing the intermediate report and will send it asap to the partners and JTI members.

The mid-term report (1 year) is intended to be public. It should be written carefully regarding confidential results. It is proposed to submit it to all partners including JTI members for approval prior to transmission to JU.

6 – Administrative aspects:

Signature of the consortium agreement is on the way. Eurocopter and Turbomeca have agreed with the proposal from CNRS.

6 – Next meeting:

Next meeting is planned end of April. This 1st year meeting will be held in Paris. It will be organized by IJL (G. Henrion), probably at CNRS if possible. Otherwise at another place.

ECO-DESIGN ITD

Grant agreement n° 270589

Project COPROCLAM

MINUTES OF MEETING

INTERMEDIATE MEETING	
Date of meeting	24 April 2012
Location of meeting	Paris (FIAP)
Author	Gérard Henrion – Irina Shchedrina
Issue date	29 April 2012
Document n°	COPROCLAM_2012_008_MOM_20120424

ATTENDEE LIST

Name	Society/Organization	Remarks & Comments
Julien GURT SANTANACH	TURBOMECA	
Gérard HENRION	CNRS-IJL	Project coordinator
Elodie HERAIL	LTS	
Sophie PETTIER	Eurocopter	
Irina SHCHEDRINA	CNRS-IJL	Post-doc
Nadia VIALAS	LTS	Topic manager

Unavailable to attend the meeting (excused)
Philippe COMBES (GIT)
Teresa DUCHANOY (IJL-CNRS)
Emiliano FORCHIN (Agusta Westland)
Johanna MICHIELIN (CNRS administrative)
Delphine RENAUX (IJL-CNRS)

Contents of the meeting :

- Progress of the project
- Presentation of last results by IJL
- Wok program for the next 3 months
- Next meeting

1 – Progress of the project

G. Henrion presents a brief review of the different WPs in the project and detail for each WP what was planned to do and what has been done.

WP 1 (management, training, coordination) is still ongoing. Intermediate report (6 month) was sent to the partners and JTI members. Since the project started, 5 meetings were held (including 2 webex meetings).
Training of people that were recruited at IJL and GIT have been trained on the MAO facilities but also on the characterization tools (I. Shchedrina: SEM, EDX, 3D profilometry)

WP 2 (study of the electrolyte).
Task 2.1, bibliographic review on electrolytes has been done. Deliverable D1.1 was achieved on July 2011.
Other tasks are stil on going. Task 2.2 (electrolytes for Al2024) was done by GIT and is rather complete. Deliverable D2.2 is close to be completed Study of the electrolytes for processing Mg was started on March (note that Mg-EV21 samples were received on February 2012). Sample characterization and corrosion test have been partly realized. IJL-Nancy systematically carries out SEM and EDX characterization on cross section of the samples. GIT carries out corrosion tests on GIT-processed samples. It is necessary to exchange samples between both partners.

WP3 (process parameters).
As for WP2 studies on the effect of the current parameters (current amplitude, current density, current frequency) on the processing of AL2024 samples have already been performed and allowed the partner to identify some trends which seems to be beneficial to the elaboration of rather homogeneous, compact layers with low porosities. However, it still remains hard to achieve thin covering layers without large porosities. Attempts to draw growth kinetics have been done. Similar study on Mg-EV21 are on the way.

WP4 (study of the discharges)
Characterization of the MDs by means of fast video recording (> 100 000 frames/second) was undertaken which makes It possible to count the discharges onto the surface and follow their evolution over the process time. Two aspects are worth noting: first, MDs only appear during the anodic phase of the current. Second, there exists a delay between the appearance of MDs and the rising edge of the anodic current pulse. This delay is likely related to the layer

electrical properties and thickness. Some attempts to explain this phenomenon are proposed which need confirmation or proof.
Studies regarding Mg processing are scheduled within the next period.

2 - Presentation of last results by IJL:

During the period January to April 2012, IJL-Nancy continued studying the effect of the current density and current frequency on the resulting oxide layers achieved onto Al2024 and Mg-EV21. Detailed results are given in the attachment
The following aspects are pointed out:

regarding Mg EV21

- The bulk material contains large precipitates which are mainly made of Nd. No other expected alloying element (Gd, Zr) have been detected by EDX. The composition of the Mg alloy needs to be more precisely known. AW will be asked on the Mg alloy composition
- Adding phosphate in the electrolyte (mainly made of KOH) improves the process. The more phosphate, the more homogeneous the coating
- Adhesion of the coating is very poor. Is there an effect of the precipitates?
- The coating grows more inside the material than outside
- A rather low current amplitude (typ. 15 A or less) should be favoured

regarding Al2024

The main purpose of this period was to shed light on the influence of the current density on the resulting layers. Current density was already studied by changing the current amplitude while keeping the sample size constant and using flat counter electrodes. Here, the sample size was changed while keeping the current parameters constant. These tries were done using a cylindrical counter electrode which was expected to lower the edge effects. Therefore:

- Current density seems to be the significant parameter (compared with current amplitude)
- Flat counter electrode seems to give better results (in terms of thickness, homogeneity, compactness)
- Adding silicate results in more porous coating ; homogeneity in terms of thickness is better (from centre to edge)
- Growth rate is higher when adding silicate in KOH
- Adhesion of the coating is very poor. Is there an effect of the precipitates?
- It is still hard to achieve thin adhesive homogeneous layer

- Homogeneous, rather thick compact layers may be achieved using rather high current density or using longer process time.

4 – Further work:

On Mg

- Pursue with different electrolytes (More phosphates, higher/lower KOH content, adding fluorides)
- Increase the process time to achieve homogeneous layers
- Process samples at higher current frequency (typ. 750 Hz)

On Al

- Work on the counter electrode shape (wire, rod, other shape).
- Pursue with the characterization of the micro-discharges
- Process large size samples with "optimum" conditions to allow corrosion tests to be performed at GIT facilities
- Investigate the sample properties by means of Electrochemical Impedance Spectroscopy (EIS) at IJL facilities
- SEM characterization of GIT processed samples (not received yet)

5 – Administrative aspects:

The implementation agreement was signed by CNRS, LTS, Eurocopter and Turbomeca. GIT and Agusta Westland are requested to sign it ASAP.

6 – Next meeting:

Next meeting will be a webex meeting on 29 May 2012. Another webex meeting is scheduled on first half of July. Formal meeting is scheduled on October. It is proposed to hold the meeting at Agusta westland in Milano. Topic manager (LTS) is going to discuss such possibility with AW.

7 – Attachment:

Presentation by IJL: Results on Mg EV21 and Al2024

MINUTES OF MEETING

INTERMEDIATE MEETING	
Date of meeting	29 May 2012
Location of meeting	Webex meeting
Author	Gérard Henrion
Issue date	12 July 2012
Document n°	COPROCLAM_2012_010_MOM_20120529

ATTENDEE LIST

Name	Society/Organization	Remarks & Comments
Nathalie APPEL	CNRS-DR6	Administrative
Philippe COMBES	GIT	
Julien GURT SANTANACH	TURBOMECA	
Gérard HENRION	CNRS-IJL	Project coordinator
Sophie PETTIER	Eurocopter	
Aline ROCCHESANI	CNRS-DR6	Administrative
Nadia VIALAS	LTS	Topic manager

Emiliano FORCHIN is excused to be unavailable to attend the meeting

Foreword

This webex meeting was held due to the unavailability of GIT to attend the formal meeting in Paris on April 24th.

Contents of the meeting :

- Presentation of last results by GIT
- Administrative aspects
- Next meeting

1 - Presentation of last results by GIT:

GIT presents the last results that were obtained when processing Al2024 with varying the current frequency, current density and electrolyte composition. Current frequency and current density were investigated in the range 50–900 Hz and 5-30A/dm^2 respectively. Depending on the current amplitude and frequency, the processing time was adjusted so that to get a layer thickness about 5 µm.
Electrolyte containing NaOH, Na_2SiO_3, $NaAlO_2$ and $Na_4P_2O_7$ were tested.
Details of the experimental conditions are given in appendix.

Summary of conclusions :
Electrolytes containing NaOH and Na_2SiO_3 : An increase in the Silicate concentration leads to a more uniform layer with a lighter more homogenous color. It also allows to decrease the current density (at constant processing time) resulting thus in lowering the edge effect. Current frequency does not seem to have any effect on the layer uniformity. Whatever the silicate content corrosion pits appear after 24 hours salt spray test.

Adding KF to the last silicate electrolyte up to 0.015 Mol/L results in a thicker layer (all other parameters kept constant). From first visual observation of the treated samples it appears that electrical parameters do not have significant effect neither on the visual aspect nor on the corrosion resistance (salt spray tests). Corrosion pits appear after 24 hours salt spray test. No effect of the current frequency or density on the corrosion resistance has been observed.

Electrolyte containing $NaAlO_2$ and $Na_4P_2O_7$: hard to use. The layer uniformity and current density change with the current frequency. Corrosion pits appear after 24 hours salt spray test. No effect of the current frequency or density on the corrosion resistance has been observed.

Perspectives :

- Further characterizations at GIT (weight measurement, test of paint adherence)
- Study of the effect of electrolyte temperature and of the cathodic to anodic current ration
- One sample of each processing condition will be send to IJL for deeper characterization (SEM, EDX)
- Conditions will be given to Mr. Beauvir for treatment at high current frequency

- Start processing Mg samples

2 – Forthcoming work IJL :

Analyses of GIT samples. Results will be presented on next webex meeting inJuly.

Contact E. Rocca regarding sealing. However it seems unlikely that sealing will be efficient on PEO layers

Give GIT parameters sets that seems to be the more favorable.

3- Next meeting :

Next meeting will be held through webex on July 11th.

4 – Appendix – GIT slides:

See file COPROCLAM_2012_011_GIT_20120529

MINUTES OF MEETING

INTERMEDIATE MEETING	
Date of meeting	13 July 2012
Location of meeting	Webex meeting
Author	Gérard Henrion
Issue date	16 July 2012
Document n°	COPROCLAM_2012_011_MOM_20120713

ATTENDEE LIST

Name	Society/Organization	Remarks & Comments
Philippe COMBES	GIT	
Julien GURT SANTANACH	TURBOMECA	
Gérard HENRION	CNRS-IJL	Project coordinator
Irina SHCHEDRINA	CNRS-IJL	
Nadia VIALAS	LTS	Topic manager
Emiliano FORCHIN	Agusta Westland	Excused
Sophie PETTIER	Eurocopter	Excused

Contents of the meeting :

- Presentation of last results by IJL
- Presentation of last results by GIT
- Next meeting

1 - Presentation of last results by IJL:

Since the last meeting, IJL has been working on the analyses of samples provided by GIT. These samples were processed using various electrolyte compositions, with different sets of electrical parameters. Typically, base electrolyte consists of 0.01 Mol/L NaOH with addition of Na_2SiO_3, $Na_4P_2O_7$ and $NaAlO_2$. Current density, current frequency and treatment time are investigated in the ranges 2 to 20 A/dm2, 200 to 400 Hz and 10 to 40 minutes respectively. Details of experimental conditions with sample numbering are given in appendix 1.

Main conclusions may be drawn as follows:

- a high current frequency (400 – 900 Hz) gives better results in terms of layer coverage, homogeneity and porosity.
- increasing the silicate content in electrolyte improves the layer homogeneity, adhesion and coverage. It also reduces the porosity and the thickness gradient across the sample.
- addition of potassium fluoride in electrolyte increases the porosity of the coating and adhesion to the substrate. Coating within these conditions are more homogeneous, more compact and more uniform. There is almost no edge effect.
- though it is difficult to use and hard to handle, electrolyte composed of Na4P2O7 and NaAlO2 gives rather good results in terms of coverage and adhesion. However those coatings are very porous and exhibit a strong thickness gradient; Edge effect is also much pronounced. Nevertheless, within similar conditions (electrical parameters), the average layer thickness, as measured on cross section observation, is about twice that get with other electrolyte conditions. It is worth noting that Eddy current measurement results in similar values (even a little bit less for C1 electrolyte compared with other electrolyte compositions). This is likely due to the higher porosity of the coating which induces a underestimated Eddy current thickness value.

Whatever the conditions, the coating seems to detach very easily from the substrate. This may be due to the metallographic preparation, especially embedding. It is suggested to deposit a Ni-based thick layer (> 10µm) (electrochemical deposit) previous to the metallographic preparation to avoid coating removing. NV will give deposit conditions.

Whatever the conditions, corrosion resistance (salt spray test) does not exceed 48 hours (see GIT's presentation)

IJL's presentation is available in file COPROCLAM_2012_013_IJL_20120713.pdf

2 – Presentation of last results by GIT :

Over the last period, GIT investigated the effect of some process parameter as current waveform ($R=I_P/I_N$ = 39-69%) and frequency (100-400 Hz), electrolyte temperature (10 – 23 °C)on the corrosion resistance of processed samples. Electrolyte B6 (NaOH 0.01M, Na_2SiO_3 0.07M, KF 0.02M) was used. coating thickness is about 5 µm.

- whatever the process conditions within this series, the corrosion resistance does not exceed 48 hours salt spray.
- a lower electrolyte temperature (10°C compared with 23°C) results in a slightly thicker coating. Change in electrolyte temperature does not change anything regarding corrosion resistance.
- neither the current frequency nor the cathodic to anodic current ratio (I_P/I_N) does have an influence on the corrosion resistance which does not exceed 48 hours salt spray test
- coating thickness seems to be the main parameter for corrosion protection.

GIT also performed salt spray test on samples provided by IJL. These samples were processed in KOH electrolyte (without any additive). Coating thickness is about 5-7 µm in the center and close to 10µm at the edge. Here also, corrosion pits appear after 24 hours salt spray. More than 10 corrosion pits are visible after 48 hours.

GIT's presentation is available in file COPROCLAM_2012_014_GIT_20120713.pdf

3- Miscellaneous :

It is suggested to make some tries of sealing with some corrosion inhibitor products (Alodine ?); Also hot water sealing could be tested. However, according to E. Rocca, water sealing would not work because of a too strong porosity of the MAO coatings

Complete the bibliography study and look for other electrolyte compositions. search also in the field of anodizing.

4- Next meeting :

Next meeting will be held AW in Italy. date is to be defined with E. Forchin. G. Henrion will get in touch with E. Forchin to organize the next meeting.

5 – Appendix :

Appendix 1 : Process conditions of GIT's samples that were analyzed at IJL (following pages)
Appendix 2 : Slides of IJL : see file COPROCLAM_2012_013_IJL_20120713.pdf
Appendix 3 : Slides of GIT : see file file COPROCLAM_2012_014_GIT_20120713.pdf

Galvanoplastie Industrielle Toulousaine

Réf. : GIT/PC/08/12 | **Date : 16/07/12** | **Page : 1/2**

TRAITEMENTS CERAMIQUE

De : **M. San Miguel / Ph. Combes**

OBJET : **CO PROCLAM : Essais série n°2 (Mai 2012)**

Etude des électrolytes à base de silicate de sodium
Etude des électrolytes à base d’aluminate de sodium

Eprouvettes envoyées à l’Institut Jean Lamour pour caractérisation

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	Electrolytes		pH	Conduc	Référence	Paramètres	Ep (µm)	Aspect visuel	Tenue en brouillard salin (Heures)														
	Concentration massique	Concentration molaire							0	24	48	72	96	120	144	168	192	216	240	264	298	312	336
B3	Hydroxyde de sodium 0,4g/L Silicate de sodium 8.5 g/L	Hydroxyde de sodium 0.01 mol/L Silicate de sodium 0.04 mol/L	12,6	14,5	2024 GIT 364	200 Hz 25 min 4.3 A/dm^2	4,8	Surépaisseur	🟩	🟥	🟥	*Arrêt de l’essai en BS* *≥10 Piqures*											
					2024 GIT 362	400 Hz 25 min 4.3 A/dm^2	5,1	Surépaisseur	🟩	🟥	🟥	*Arrêt de l’essai en BS* *≥10 Piqures*											
					2024 GIT 347	900 Hz 25 min 4 A/dm^2	3,6	Surépaisseur	🟩	🟥	🟥	*Arrêt de l’essai en BS* *≥10 Piqures*											
B4	Hydroxyde de sodium 0,4g/L Silicate de sodium 14.8 g/L	Hydroxyde de sodium 0.01 mol/L Silicate de sodium 0.07 mol/L	12.9	17.9	2024 GIT 386	200 Hz 25 min 3 A/dm^2	4,7	Aspect uniforme	🟩	🟥	🟥	*Arrêt de l’essai en BS* *≥10 Piqures*											
					2024 GIT 387	400 Hz 25 min 3 A/dm^2	4,4	Aspect uniforme	🟩	🟥	🟥	*Arrêt de l’essai en BS* *≥10 Piqures*											
					2024 GIT 395	900 Hz 25 min 4 A/dm^2	4,2	Aspect uniforme	🟩	🟥	🟥	*Arrêt de l’essai en BS* *≥10 Piqures*											

	Electrolytes		pH	Conduc	Référence	Paramètres	Ep (µm)	Aspect visuel	Tenue en brouillard salin (Heures)														
	Concentration massique	Concentration molaire							0	24	48	72	96	120	144	168	192	216	240	264	298	312	336
B5	Hydroxyde de sodium 0,4g/L Silicate de sodium 14.8 g/L Fluorure de potassium 0.28 g/L	Hydroxyde de sodium 0.01 mol/L Silicate de sodium 0.07 mol/L Fluorure de potassium 0.005 mol/L	12.7	21.0	2024 GIT 426	200 Hz 25 min 3 A/dm²	4,5	Aspect uniforme	🟩	🟥	🟥	*Arrêt de l’essai en BS* *≥10 Piqures*											
					2024 GIT 421	400 Hz 40 min 2 A/dm²	4,0	Aspect uniforme	🟩	🟥	🟥	*Arrêt de l’essai en BS* *≥10 Piqures*											
					2024 GIT 424	400 Hz 25 min 3 A/dm²	4.2	Aspect uniforme	🟩	🟥	🟥	*Arrêt de l’essai en BS* *≥10 Piqures*											
					2024 GIT 432	400 Hz 10 min 7,5 A/dm²	4.8	Aspect uniforme	🟩	🟥	🟥	*Arrêt de l’essai en BS* *≥10 Piqures*											
					2024 GIT 415	900 Hz 25 min 4 A/dm²	5.1	Aspect uniforme	🟩	🟥	🟥	*Arrêt de l’essai en BS* *≥10 Piqures*											
B6	Hydroxyde de sodium 0,4g/L Silicate de sodium 14.8 g/L Fluorure de potassium 1.12 g/L	Hydroxyde de sodium 0.01 mol/L Silicate de sodium 0.07 mol/L Fluorure de potassium 0.02 mol/L	12,5	23.01	2024 GIT 450	200 Hz 25 min 3 A/dm²	5,2	Aspect uniforme	🟩	🟥	🟥	*(En cours de réalisation)*											
					2024 GIT 445	400 Hz 40 min 2 A/dm²	4.5	Aspect uniforme	🟩	🟥	🟥	*(En cours de réalisation)*											
					2024 GIT 455	400 Hz 25 min 3 A/dm²	5,2	Aspect uniforme	🟩	🟥	🟥	*(En cours de réalisation)*											
					2024 GIT 458	400 Hz 10 min 7.5 A/dm²	5.5	Aspect uniforme	🟩	🟥	🟥	*(En cours de réalisation)*											
					2024 GIT 441	900 Hz 25 min 4 A/dm²	5.3	Aspect uniforme	🟩	🟥	🟥	*(En cours de réalisation)*											
C1	Pyrophosphate de sodium 3.46 g/L Aluminate de sodium 0.41 g/L	Pyrophosphate de sodium 0.01 mol/L Aluminate de sodium 0.005 mol/L	10.9	10.5	2024 GIT 477	200 Hz 40 min 4.5 A/dm²	4.4	Aspect uniforme	🟩	🟥	🟥	*(En cours de réalisation)*											
					2024 GIT 488	200 Hz 25 min 5.5 A/dm²	4.1	Aspect uniforme	🟩	🟥	🟥	*(En cours de réalisation)*											
					2024 GIT 491	200 Hz 10 min 20 A/dm²	4.6	Aspect uniforme	🟩	🟥	🟥	*(En cours de réalisation)*											
					2024 GIT 481	400 Hz 40 min 4,6 A/dm²	4.6	Aspect uniforme	🟩	🟥	🟥	*(En cours de réalisation)*											

MINUTES OF MEETING

INTERMEDIATE MEETING	
Date of meeting	20 Novembre 2012
Location of meeting	Milano at Agusta Westland
Author	Gérard Henrion
Issue date	06 December 2012
Document n°	COPROCLAM_2012_015_MOM_20121120

ATTENDEE LIST

Name	Society/Organization	Remarks & Comments
Philippe COMBES	GIT	
Julien GURT SANTANACH	TURBOMECA	
Emiliano FORCHIN	AGUSTA WESTLAND	
Gérard HENRION	CNRS-IJL	Project coordinator
Mariella PESETTI	AGUSTA WESTLAND	
Nadia VIALAS	LTS	Topic manager

Unavailable to attend the meeting (excused)
Sophie PETTIER (Eurocopter)
Irina SHCHEDRINA (CNRS-IJL)

Agenda :

- Presentation of last results GIT
- Presentation of last results IJL-CNRS
- Discussion on results
- Lunch break
- Work plan for the next three months
- After the project (03/2012)
- Administrative aspects (if any)
- Next meeting

1 – Presentation of last results by GIT (see attachement)

P. Combes starts his presentation with a reminder of the first three series of tries that were performed on Al 2024. He then presents last results which concern the study of the effect of the coating thickness and the sealing processing on the corrosion resistance. Treatment have been carried out using electrolyte B6 (NaOH + Na_2SiO_3 + KF 0.01+0.07+0.02 M/L). Two sealing procedures were tested ($K_2Cr_2O_7$; Alodine 1200). without sealing, corrosion resistance is 48 h (1st pit) for a layer thickness value of 15 µm. For thinner layers, the corrosion does not exceed 24h (1st pit). Whatever the sample thickness < 15µm) 10 pits corrosion appear after 72 hours. Change in current frequency seems to have no effect.
Measurements of the layer weight have been done according to the NF ISO 2106 : 2011 standard; The layer mass is proportional to its thickness leading to a layer density of 2.3 – 2.7 g/cm^3.
Sealing with potassium dichromate improves the corrosion resistance up to 120 hours (10 pits). Improvement is better when sample were MAO processed with a current frequency of 100 Hz (compared with 750 Hz).
Impregnation with Alodine 1200 gives worst results regarding corrosion (72h) for samples processed at 750 Hz. If the impregnation time exceeds 15 min, the layer is dissolved by Alodine.
Samples processed at a 100 Hz current frequency are much resistant to impregnation (25 min) and exhibit corrosion resistance up to 216 h (10 pits).
During impregnation, the layer shows a better adhesion when achieved at 100 Hz compared with that formed at 750 Hz.

A new electrolyte containing sodium tungstate has been tested. First samples processed with this electrolyte do not exhibit a corrosion resistance greater than 48 hours salt spray. Further tries are still in progress.

Treatments using the high frequency generator (J. Beauvir) are in progress.

2 - Presentation of last results by IJL (see attachement)

IJL presents results on Al2024 alloy processed with various KOH concentrations (2 - 7 g/L ; 0.04 – 0.125 Mol/L) in electrolyte. For low concentrations, the sample is corroded by the electrolyte and there is quite no layer growth. As the KOH concentration is increased, the whole sample surface is covered, and an interface layer appears all along the sample coating interface. For [KOH] > 4g/L, the coating porosity decreases, especially the density of large pores
As previously observed, a strong edge effect is observed which results in a thicker layer at the edge than in the center of the sample.

J. Gurt-Santanach (turboméca) suggests using a Hull cell, which is an electrolyte tank with non-parallel electrodes. This would allow us to "control" the current lines between the two electrodes and get insights into the possible ways to reduce edge effects.

Concerning MAO processing of Mg El21, an electrolyte containing phosphates and fluoride has been investigated. Composition of the electrolyte was $KOH+Na_4P_2O_7+KF$ with concentrations 2+4+8 g/L (0.04+0.015+0.14 Mol/L).
Two current frequencies were tested: 100 Hz and 750 Hz with an anodic current of $20A/dm^2$.
In both cases, the coating is very porous and the change in frequency does not appear to induce significant changes in the coating structure. A lower growth rate is observed at 750 Hz compared with 100 Hz.
It is worth noting that the coating thickness is quite homogeneous all over the sample surface, what has never been observed until now.
Corrosion test have not been done on these sample. However, one large size sample processed with similar conditions has been given AW for testing.

Regarding the preparation of samples before MAO processing.AW recommend to remove the protective treatment of cast samples by using Chromic acid instead of machining or polishing before MAO processing. This is to ensure feasibility and applicability onto real parts.

4 – Further work:

4.1 : GIT

Study on aluminium 2024
Tests with post treatment with chromium III
Do a literature search to find new electrolyte composition
Find new post treatments without chromium

4.2 : IJL

Check all deliverables and advise the project officer if any delay
Send all partners the reference of the epoxy resin use in metallographic preparation of samples

Give AW the process conditions of the large size sample

Study on aluminium 2024
Perform electrochemical measurements onto samples given by GIT (already scheduled)

Study on magnesium EL21
Continue studies on electrolyte with increasing KOH and KF content
Characterization of processed samples (SEM-EDX, DRX)
Micro-discharge studies
Try with Hull cell

5 – Administrative aspects:

The implementation agreement is definitively signed by all partners. Each of them has received an exemplar.

6 – Next meeting:

Next meeting will be a webex meeting on end of January 2013. G. Henrion will arrange a doodle scheduler to choose the date.

The next face to face meeting will be on end of March 2013. It will be the final meeting of this two year project that started on 01 April 2011.

7 – Attachment:

Presentation by GIT: COPROCLAM_2012_16_GIT_Presentation_20121120
Presentation by IJL: COPROCLAM_2012_17_IJL_Presentation_20121120

ECO-DESIGN ITD

Grant agreement n° 270589

Project COPROCLAM

MINUTES OF MEETING

INTERMEDIATE MEETING	
Date of meeting	29 January 2013
Location of meeting	webex meeting
Author	Gérard Henrion
Issue date	03 February 2013
Document n°	COPROCLAM_2013_023_MOM_20130129

ATTENDEE LIST

Name	Society/Organization	Remarks & Comments
Philippe COMBES	GIT	
Emiliano FORCHIN	AGUSTA WESTLAND	
Julien GURT SANTANACH	TURBOMECA	
Gérard HENRION	CNRS-IJL	Project coordinator
Julien MARTIN	CNRS-IJL	
Sophie PETTIER	EUROCOPTER	
Vittorio SELMIN	CLEANSKY	Project officer
Irina SHCHEDRINA	CNRS-IJL	
Delphine VEYS-RENAUX	CNRS-IJL	
Nadia VIALAS	LTS	Topic manager

Agenda

09:30 – 10:00	Results on the discharge characterization	IJL
10:00 – 10:20	Last results on the processing of Mg EV31	IJL
10:20 – 10:40	MAO processing of Al and Mg at low current density in DC mode	IJL
10:40 – 11:10	Last results at GIT	GIT
11:10 – 12:00	Discussion on results	all

1 – Results on the discharge characterization

G. Henrion presents results on the characterization of the micro-discharges using fast video recording and optical emission spectroscopy. These characterizations concern the MD lifetime, their number density and location on the sample surface as well as the delay between the rising edge of the anodic current and the appearance of the micro-discharges. From these measurements, the following main conclusions may be drawn:

- MDs only appear during the anodic part of the current pulses[1].
- The number density of MDs on the sample surface is strongly dependant on the layer thickness. The number of MD decreases according two different mechanisms (not clearly identified yet) as the layer grows.
- Edge effect as usually observed mainly occurs during the first minutes of treatment (typ. < 5min).
- The delay of MD appearance with respect to the rising edge of the anodic current pulse depends on the layer thickness and therefore on the layer breakdown mechanisms which may involve charge accumulation at the electrolyte – layer interface.

Most of the presented measurements have been carried out on Al2214 alloy. Specific comparative measurements have been performed that clearly showed quite no difference between Al2214 and Al2024 alloy.

Nevertheless, it would be of interest to establish relationship between the MDs parameters and the layer properties in terms of microstructure. According to G. Henrion, this could be difficult to establish considering that the MDs characteristics depends more on the layer thickness than on its microstructure.

Similar work on the characterization of MDs when processing Mg EV31 is on the way. Results will be presented on next meeting.

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[1] *Though it seems possible for some MD to appear during the cathodic part, no clear evidence of cathodic MD has already been reported*

2 - MAO processing of Al and Mg at low current density in DC mode

D. Veys-Renaux presents results on electrochemical measurements performed on Mg EV31 samples that were processed containing silicate and silicate+fluoride additives. From electrochemical impedance spectroscopy, it results that fluoride improves the global corrosion resistance by reinforcing both the diffusion resistance and the charge transfer resistance.

Results on MAO processing of Al alloys at low DC current density (typ. 15 mA/cm^2) point out the important role of the intermetallic phases. An inner layer grown by a conventional anodizing process at the metal interface makes the Cu-rich intermetallic phases disappear. On the other hand, Cu nanoparticles appear which can influence the electrical properties of the dielectric layer and hence its growth.

Simultaneously, an improved corrosion resistance is shown which is due to the anodised inner layer. Nevertheless, the Cu-rich phases remain very sensitive to corrosion.

In the case of Mg (AZ91), the process starts by a usual anodizing (as for Al), the resulting layer conditioning the properties regarding corrosion. Additive elements (fluoride, silicate) are integrated in this anodized layer during the first step of the process.

Addition of silicate improves the corrosion resistance as determined by impedance measurements. Regarding the dielectric breakdown (appearance of first micro-discharges), it is shown that the breakdown occurs at a constant value of the layer capacitance whatever the electrolyte composition. This might be related to the thickness of the anodized layer (typ. 50-100 nm).

3 – Last results on the processing of Mg EV31

I. Shchedrina presents results on the processing of MG EV31 alloy using various concentrations of sodium silicate in the electrolyte. The base electrolyte contains 2 g/L KOH (0.036M) with addition of pure sodium silicate in the range 2-8 g/L (0.0164 – 0.0656 M). Main conclusions are as follows:

- Increasing the sodium silicate concentration slightly enhances the coating growth rate.
- Except for the 6 g/L (0.0492M) Na_2SiO_3 concentration, the edge effect remains almost the same. At 6g/L (0.0492M) edge effect is a little less significant
- It appears that the coating becomes less porous as Na_2SiO_3 content increases. Some dense can be observed as Na_2SiO_3 is greater than 3 g/L (0.0246 M). Moreover, no open pore that reaches the metal surface is observed anymore. Nevertheless whatever the silicate content, the coating is very porous.
- In all coatings two layers are found. In some cases, at low silicate content, parts are uncovered as if the coating (flakes) was removed.

- In the case of 6 g/l (0.0492 M) Na_2SiO_3 the coating is less porous and almost all large pores are closed. The coating has more dense areas in comparison with the others coatings.

It seems that the electrolyte KOH (0.036M) + Na_2SiO_3 (0.0492M) gives best results. Corrosion test and electrochemical measurement have to be done on these samples. IJL will proceed with large size samples (9) within these particular conditions and send (deadline on mid-February) samples to AW for sealing with resin and corrosion testing. Meanwhile another similar sample will be processed with electrochemical measurements at IJL.

4 – Last results at GIT

Ph. Combes presents last results achieved at GIT on Al 2024 using sodium tungstate containing electrolytes with various concentrations. The achieved layers are ~5µm thick and appear homogeneous (visual aspect). Whatever the electrolyte, the corrosion resistance does not exceed 72 hours salt spray test. When sealed with alodine 1200, the corrosion resistance gets slightly higher. Corrosion test after sealing without Cr VI (Surtec) are in progress.

When achieving thicker layers, the corrosion resistance is much improved: 144 hours salt spray for a 30µm thick layer (to be compared with 48 hours for a 5 µm thick layer).

A corrosion resistance of 336 hours salt spray was obtained for a 45 µm thick layer achieved in a 1g/L KOH + 15g/L (0.07M) Na_2SiO_3-$5H_2O$[2] electrolyte.

Corrosion test of samples processed by J. Beauvir at high current frequency are in progress. Samples have been treated in electrolyte B6 (0.01M NaOH + 0.07M Na_2SiO_3+0.02M KF). However, the other process conditions are not known yet.

5 – Check on the progress of the project

A review is done of all expected deliverables. A summary is given in the following table.

	Deliverable name	Expected date	Status
1.1	Intermediate report	6	OK
1.2	Mid-term report	12	OK
1.3	Intermediate report	18	OK
1.4	Final report	24	
1.5	Publications of scientific results	24	on going
2.1	Bibliographic report on the electrolyte	3	OK
2.2	Most suitable electrolyte for Al alloys treatment	15	to discuss

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[2] *This composition of silicate (pentahydrate) comes from a previous presentation from Ph. Combes where it was written that the molar weight of sodium silicate was 212.14 g/mol which correspond to* Na_2SiO_3-$5H_2O$.

2.3	Most suitable electrolyte for Mg alloys treatment	21	in progress
3.1	Best parameter set for processing Al alloy samples	21	in progress
3.2	Best parameter set for processing Mg alloy samples	21	in progress
4.1	Fine characterization of the micro-discharges	15	OK for Al remains to do for Mg
4.2	Results on the plasma surface interaction	18	OK for Al remains to do for Mg
4.3	Description of the growth mechanisms	21	in progress
4.4	Samples processed with optimized parameter conditions	21	
5.1	Demonstrator size processing unit	24	
5.2	Layer on Al alloys, compliant with requirements	24	
5.3	Layer on Mg alloys, compliant with requirements	24	

For what concerns WP2 and WP3, trends have been pointed out, especially regarding the role of fluoride and silicate in the electrolyte and the advantage to work with a rather low current density to avoid strong detrimental arcs as well. The beneficial effect of using a high frequency could be confirmed by results from J. Beauvir.

6 – Next meeting

Next meeting will be held in Toulouse at LTS on March, 27th. It will be the final meeting of this two year project that started on 01 April 2011.

Attendees have to confirm their participation to N. Vialas to arrange access to LTS.

7 – Attachments

Following attachments will be up loaded at the project common zone when received:

COPROCLAM_2013_019_IJL_GH_20130129.pdf

COPROCLAM_2013_020_IJL_DVR_20130129.pdf

COPROCLAM_2013_021_IJL_IS_20130129.pdf

COPROCLAM_2013_022_GIT_20130129.pdf

ECO-DESIGN ITD

Grant agreement n° 270589

Project COPROCLAM

MINUTES OF MEETING

INTERMEDIATE MEETING

Date of meeting	27 March 2013
Location of meeting	Toulouse at Liebherr
Author	Gérard Henrion
Issue date	10 May 2013
Document n°	COPROCLAM_2013_027_MOM_20130510

ATTENDEE LIST

Name	Society/Organization	Remarks & Comments
Philippe COMBES	GIT	
Julien GURT SANTANACH	TURBOMECA	
Gérard HENRION	CNRS-IJL	Project coordinator
Elodie HERAIL	LTS	
Irina SHCHEDRINA	CNRS-IJL	
Nadia VIALAS	LTS	Topic manager

Agenda

10:00 – 10:45	Latest results at IJL
10:45 – 11:30	Latest results at GIT
11:30 –13:00	Discussions
13:00 – 14:30	Lunch
14:30 – 15:30	Administrative issues - second reporting period
15:30	End of meeting

1 – Latest Results at IJL

I. Shchedrina presents results on the processing of MG EV31 alloy using an electrolyte made of 2 g/L KOH (0.036M) with addition of sodium phosphate 4 g/L (0.009 M) and amonium fluoride 8 g/L (0.216 M). Main conclusions are as follows:

- Surface of all the coatings looks very smooth with no visible defects
- The edge effect is much less as a consequence of the increase in electrolyte conductivity in comparison with the previous data
- The most porous parts in the coatings are at the edge of the sample probably because of a larger size of discharges there
- Coatings obtained under a lower frequency are less porous; they have less quantity of open pores and their growth rate is higher. On the other hand the edge effect is lower in the case of higher frequency

Sample processed with different silicate content in KOH were sent to GIT who performed corrosion tests. Though samples had very good visual aspect, none of them satisfied the 100 h requirement of corrosion resistance in salt spray, in spite of the fact that all samples have an average thickness of 25 µm, greater than required.

On the other hand, electrochemical measurements performed in a triple electrode electrochemical cell showed that addition of fluoride slightly improve the corrosion resistance though the samples did not pass salt spray tests successfully.

2 – Latest results at GIT

Ph. Combes presents latest tries carried out at GIT. Results on Al 2024 confirm that the layer thickness is a key parameter regarding the corrosion resistance; 45 µm thick layers pass 336 h salt spray test.

Thin MAO layers on Al 2024 were sealed with Surtec 650 (Cr VI free) which improves the corrosion resistance up to 360 hours salt spry for 4 µm thick layers grown in B6 electrolyte ($NaOH/Na_2SiO_3/KF$: 0.01/0.07/0.02 M).

High frequency current (J. Beauvir's current supply) seems to give better results (96 h salt spray) than similar processing at lower frequency.

Tries on Mg EV31 leads to the following conclusions:

- It is quite hard to get homogeneous layer without powder on the surface
- Adding pyrophosphate in the KOH+Na2SiO3 vase electrolyte makes it possible to grow layer with quite no powdery
- 500 Hz current frequency seems to be an optimum value
- Results also confirm that a value of 0.59 for I_p/I_n ratio gives the best results
- Thick layer (20 µm) achieve more than 216 hours salt spray test.
- Corrosion tests on samples provided by IJL (grown in $KOH/Na_4P_2O_7/KF$ 0.01/0.025/0.13 M electrolyte) are in progress

3 – Discussion and further work

Attendees agree to continue tries in order to finish all already started works. This hold especially for what concerns the corrosion tests of high frequency Al2024 processed samples. IJL will also performed microstructural characterization of GIT samples (Al2024 and MGEV31).

Concerning the deliverable of the project, the definition of parameter sets that would result in coating complying with the requirements is not so easy. However, clear trends can be established concerning the current parameters and the electrolyte composition.

D2.2: Most suitable electrolyte for Al 2024 alloys treatment

- Complex electrolyte composition does not improve the coating performances
- The best additive in alkaline base electrolyte regarding corrosion resistance is silicate containing salt. Increasing the silicate content gives better results in terms of corrosion resistance
- Increasing the coating thickness (some tens µm) makes it possible to comply with the requirements regarding corrosion without any further post-treatment
- Thin MAO layers (< 5µm as expected) remain very porous and have poor anti-corrosion properties. Nevertheless, sealing without Cr VI containing compounds has been demonstrated that extend corrosion resistance over 300 h salt spray

D2.3: Most suitable electrolyte for Mg alloys treatment

- Silicate addition improves both coating adhesion and compactness. However a too high silicate concentration in the electrolyte is detrimental to the coating. Thus, the silicate concentration should be less than 0.05 mol/L
- Addition of phosphate improves the coating adhesion and reduces the pulverulence of the coating (fig. 1). It also reduces the edge effect and leads to a more homogeneous coating with quite no thickness variation between the edge and the centre of the sample (table 1)
- Addition of fluoride improve the corrosion resistance according to electrochemical and EIS measurements
- Increasing the coating thickness (some tens µm) makes it possible to comply with the requirements regarding corrosion without any further post-treatment
- Thin MAO layers (< 5µm as expected) remain very porous and have poor anti-corrosion properties. Nevertheless, sealing without Cr VI containing compounds has been demonstrated that extend corrosion resistance over 300 h salt spray.

	Thickness @ edge (µm)	Thickness @ centre (µm)
100 Hz, 10 min	18.2	18.8
750 Hz, 13.33 min	26.6	25.2

Table 1: Thickness variation over the sample surface for two process conditions. Jp=20A/dm^2 ; Electrolyte= KOH/$Na_4P_2O_7$/KF (0.035/0.009/0.14 mol/L)

Figure 1: Top view of Mg EV31 sample processed within phosphate containing electrolyte (right) and without phosphate (left)/ J=20A/dm^2, f = 500 Hz, t=5 min.

D3.1/D3.2: Best parameter set for processing Al and Mg alloy samples

- Within the range of low values (< 50°C), the electrolyte temperature has quite no effect on the layer growth and layer properties.
- The use of a current pulse frequency in the medium range (typ. 500 Hz < F < 1000 Hz) improves the coating quality in terms of porosity and compactness. Regarding

corrosion, best results (though they did not comply with the requirements) were obtained within this frequency range.

- The current density should be adjusted so that strong arcs do no develop at the sample surface. Obviously, micro-discharges are needed for the oxidation process to continue, but a rather low current density (typ. ≤ 20 A/dm2) should be preferred, even if this requires increasing the process time.
- Although it slightly influences the edge effect, the gap distance between the work electrode and the counter electrodes has quite no effect on the coating properties.
- Using titanium counter electrodes preserves the electrolyte of too fast aging, especially in the case of low volume electrolyte tank.

Agusta Westland is still interested in processing real size parts. This must be discussed with GIT in order to check the possibility of such treatment using GIT facilities.

GIT also wants to continue working on Mg EV31. Therefore IJL will send remaining untreated samples to GIT

7 – Attachments

Following attachments will be up loaded at the project common zone when received:

COPROCLAM_2013_024_IS_IJL_20130327.pdf

COPROCLAM_2013_025_GH_IJL_20130327.pdf

COPROCLAM_2013_026_GIT_20130327.pdf

ECO-DESIGN ITD

Grant agreement n° 270589

Project COPROCLAM

FINAL REPORT

Issue Date	May 2013
Authors	Gérard HENRION, Philippe COMBES, Teresa TOLL-DUCHANOY, Irina SHCHEDRINA, Delphine RENAUX
Topic	COrrosion PROtection of Light Alloys by Micro-arc oxidation
Document n°	COPROCLAM_2013_028_Final-report_20130510

ECO-DESIGN ITD

Grant agreement n° 270589

Project COPROCLAM

Final report

Corrosion protective coating on light alloys by micro-arc oxidation

By

Gérard HENRION, Philippe COMBES, Teresa TOLL-DUCHANOY, Irina SHCHEDRINA, Delphine RENAUX

May 2013

Contents

Foreword

Several deliverable expected throughout the project were not delivered and uploaded to the ECAS plateform since many of them were interdependent. Therefore the present report covers all of these deliverables. Simultaneously, parts of this report were extracted in separate files and uploaded as deliverable when possible.

1 - Introduction – Objectives

Over the last two years, we have been working on the micro-arc oxidation (MAO[1]) of Al2024 and Mg EV31 alloys in order to develop the micro-arc coatings that may advantageously replace conventional anodizing and comply with the aeronautical requirements especially in terms of corrosion protection of the processes parts.

Briefly, the main objectives of the work, as described when applying to the call for proposal, may be summarized as follows:

i) Carrying a deep investigation into the influence of the process parameters in order to get a strong knowledge in the mechanisms that govern the micro-arc process; it was thus expected to achieve a control of the layer growth through the management of the process parameters. A particular attention has been paid on the electrolyte composition and electrical parameters.

ii) Defining the best parameters sets that will allow the user to grow oxide layer onto light metallic alloys (Al, Mg) compliant with the industrial requirements.

iii) Implementing a demonstrator PEO unit which will make possible the processing of large size part, typically real industrial parts.

Obviously, objectives (i) and (ii) are closely connected except that whereas objective (i) consider parameters independently, objective (ii) aims at defining the best compromise in between all investigated parameters with respect to their respective influence on the process.

Achievement of these objectives has been checked through the elaboration of oxide layers and analyses of their properties, especially in terms of microstructure and corrosion resistance.

This work was carried out in the framework of the Clean Sky call for proposal JTI-CS-2010-1-ECO-01-003[2] that was launched on 2010. It involved two partners – an industrial one (GIT) and an academic one (IJL-CNRS) – and was organized around 5 work packages as described in the DoW. Besides these two partners, end user companies – Liebherr Aerospace Toulouse SAS (topic manager), Eurocopter, Turbomeca, Agusta Westland– brought a valuable contribution and actively participated to the discussions regarding the progress of the project.

The present report presents the main results and conclusions that where issued over the project duration. In order to make easier reference to the DoW, the next sections will follow the workpackage organization.

We also want to add that we did not consider it useful to recall the context and details of the research program, which have been described previously in the DoW.

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[1] *Since MAO is also known as Plasma Electrolytic Oxidation (PEO) we will use indifferently MAO or PEO acronyms along this report.*

[2] *Title of the CfP : "Development of Chromium free dense and thin micro-arc coatings for corrosion protection of light alloys (Al and Mg)"*

2 - Description of the partner's facilities

2-1: At IJL-CNRS

2-1-1: MAO processing

The processing vessel consists of a PCV electrolysis tank with dimensions 30 x 40 x 30 cm^3. Two opposite sides are equipped with glass windows allowing thus observation and analysis of the micro-discharges by means of emission spectroscopy or fast video imaging. The electrolyte is forced to flow through a cooling device (heat exchanger) in order to keep the electrolyte temperature at a constant value of 30°C.

The Al2024 sample (typ. 30 x 50 x 1 mm^2) or Mg EV31 sample (typ. 30 x 50 x 10 mm^3) is located in the middle of the vessel and connected to the current supply.

Various counter electrodes were used:

- a set of two stainless steel rectangular electrode that face both sides of the sample, with an adjustable position with respect to the sample,
- a similar set of rectangular electrode made of titanium,
- a cylindrical Ti electrode surrounding the sample.

A sketch and pictures of the PEO installation are shown in figure 1 and 2 respectively.

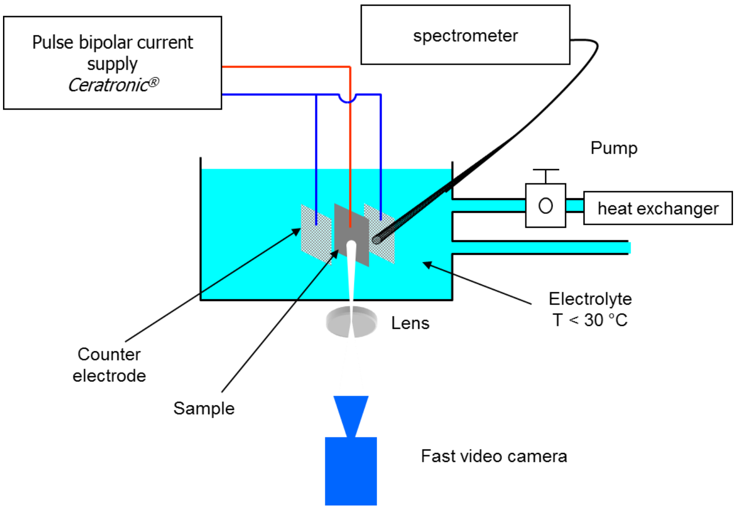

Figure 1: MAO processing unit

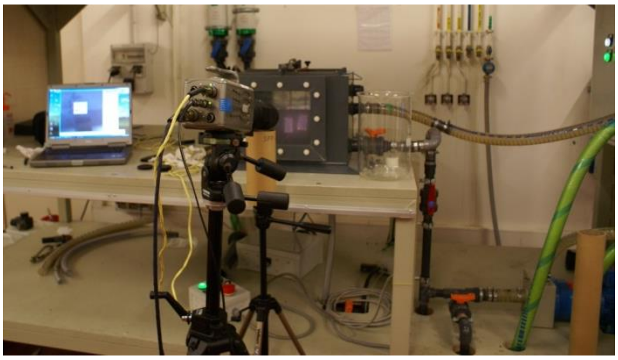

Fig. 2: View of the MAO vessel and the fast video camera installed

Although it is not necessary to perform a surface pre-treatment prior to MAO processing[3], the samples are cleaned with acetone before each treatment to avoid poisoning of the electrolyte bath and to ensure a reproducible initial surface contamination for each sample. Objective of work package 2 was to study the influence of electrolyte composition.

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[3] *G.A. Markov, E.K. Shulepko, O.P. Terleeva, A.I. Slonova, Russ. J. Electrochem. 30 (1994) 18*

The bipolar pulse current generator was supplied by Ceratronic-Recherche[4]. The current waveform may be adjusted by varying the pulse repetition rate (100 Hz $\le F=1/T \le$ 1000 Hz), the current amplitude ($0 \le |I| \le 35$ A) and the duration of each part of the current waveform (1% 1 $\le T_i/T \le$ 99%) (fig.3). It is worth noting that all tries within this project have been performed using current parameters allowing the soft regime[5] to establish.

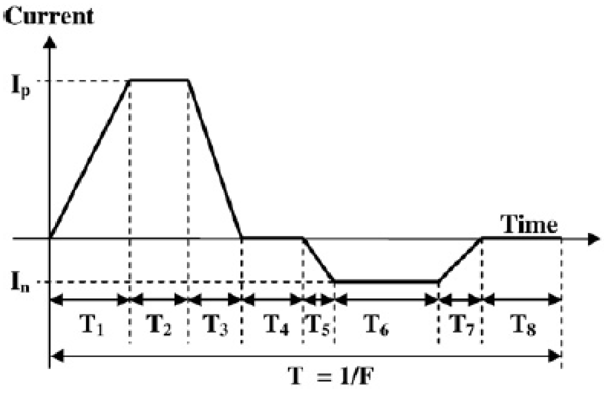

Fig. 3: Typical current waveform with the definition of time and amplitude parameters

2-1-2: Coating analyses

Microstructural analysis of processed samples was carried out by scanning electron microscopy observations on sample top surface and on coating cross sections. The SEM (Phillips XLS 30) was equipped with EDX facility allowing us to perform chemical analysis of the coatings. SEM observations of cross section were also used to determine the coating thickness at different locations of the sample (edge, center) pointing out the thickness heterogeneity of the coating.

Surface topology was investigated by means of SURFASCAN 3S profilometer implemented with « Mountains Map » software to determine surfometric and roughness parameters of the coatings[6].

2-1-3: Micro-discharge investigation

The characterization of the micro-discharges was performed by means of an optical emission spectroscope with a spectral resolution of 0.3 nm. The light emitted by the microarcs is collected by an optical fibre connected to the entrance slit of a monochromator (Jobin Yvon Triax 550) equipped with a CCD detector.

Statistics on the micro-discharges were performed from fast video recording (> 100 000 frame/s) of the plasma events during the PEO process using a Photron Fastcam SA1.1 camera. Home-made software (TRACE[7]) allowed us to determine the number, location on sample and lifetime of the micro-discharges.

2-1-4: Electrochemical measurements

Electrochemical characterizations of processed samples were carried out with a three-electrode cell connected to a Gamry instruments Framework (600 Potentiostat / Frequency Response

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[4] J. Beauvir, Patent WO 01/81658 A1 (2001).

[5] F. Mécuson, PhD thesis, Nancy, (2005) ; F. Jaspard et al. Surf. Coat. Technol. 201 (2007) 207

[6] The results of surfometry have been reported previously (see COPROCLAM_2012_018_intermediate-report_20121231.pdf). Therefore they will not be reported within this report.

[7] TRAcking and Classifying pin-point Events, S. Bardin, PhD thesis, Nancy (2012) ; S. Bardin, et al. Contrib. Plasma Phys. 51 (2011) 246

Analyser) in a reference corrosive solution (D 1384-87 ASTM standard water pH=8.3) whose composition simulates corrosion under atmospheric conditions.

Salt spray tests to evaluate corrosion resistance were carried out at GIT facilities.

2-2: At GIT

2-2-1: MAO processing

The processing vessel consists of a 150 liter tank that make possible to process several sample simultaneously. It is equipped with two stainless steel counter electrode located 17 cm from the samples (fig. 4). The electrolyte temperature is maintained at a constant value (23 °C) by means of a heat exchanger.

Two current supplies are available:

- 50 Hz AC.
- Bipolar current pulses similar to the one used at IJL-CNRS.

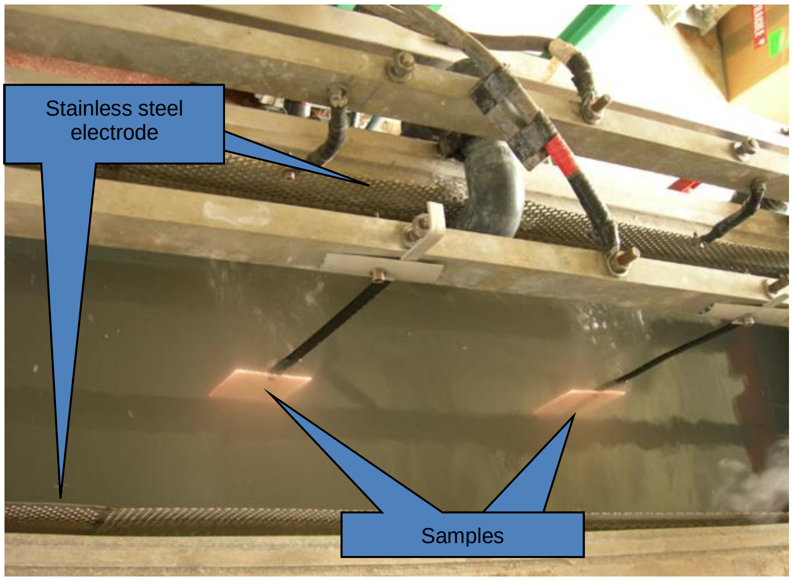

Fig. 4: GIT's PEO facility

2-2-2: Salt spray test

A salt spray facility is available at GIT that allows corrosion test to be performed according to the NF ISO 9227 standard.

2-3: Aluminum and magnesium samples

For the purpose of this project, Al2024 samples were supplied by LTS while Mg EV31 samples were provided by Agusta Westland. The typical composition of both alloys is given in tables 1.

Si	Fe	Cu	Mn	Cr	Zn	Ti	Mg	Al
0.5	0.5	3.8 – 4.9	0.3 – 0.9	0.1	0.25	0.15	1.2 – 1.8	Balance

Table 1a: Chemical composition of Al2024 alloy (wt%, typ.)

Nd	Gd	Ce	RE	Zn	Zr	Mg
2.86	1.38	0.069	0.095	0.25	0.66	Balance

Table 1b: Chemical composition of Mg EV31 alloy (wt% from AW analysis)

3 - Work package 1: Management, coordination, training, dissemination

The objective of WP1 was to guarantee the efficient coordination of the CO-PROCLAM project in order to achieve the objectives fixed in WP 2-5. It included the training of the staff specifically recruited for the project and the dissemination of knowledge (scientific papers, participation at congresses …). The following deliverables were expected:

D1.1: Intermediate report	T0+6
D1.2: Mid-term report	T0+12
D1.3: Intermediate report:	T0+18
D1.4: Final report:	T0+24
D1.5: Publications of scientific results	T0+24

Achievement of WP 1 may be summarized as follows:

3.1 - Staff recruitment and training

As expected a post-doc researcher was appointed at IJL from 24th October 2011 for a first 12 month period as planned initially. The position was extended for 6 months until the end of the project (March 2013).

GIT recruited a technician on 1st October 2012; at the end of the project, GIT decided to maintain him as a permanent staff.

Training with MAO process facilities was done at the partner's facilities by specialized staff. The post-doc researcher was also trained to use SEM, EDX, 3D profilometry, optical microscope and metallographic facilities.

3.2 - Project management, meetings and reports

10 meetings were held, either at one partner place or by webex. The minutes of meeting have been issued after each meeting and given to each partner and to the JTI members (end users) involved in the project. Table 2 summarizes these meetings.

Date	Location	MOM file	Scheduled in DoW	Remarks
2011/04/13	Nancy (CNRS)	COPROCLAM_2011_001_MOM_20110413	No	Kick off meeting
2011/06/21	webex	COPROCLAM_2011_002_MOM_20110621	No	
2011/09/08	Toulouse (GIT)	COPROCLAM_2011_004_MOM_20110908	Yes	intermediate meeting
2012/01/25	webex	COPROCLAM_2012_006_MOM_20120125	No	
2012/04/24	Paris	COPROCLAM_2012_008_MOM_20120424	Yes	mid-term meeting
2012/05/29	webex	COPROCLAM_2012_010_MOM_20120529	No	
2012/07/13	webex	COPROCLAM_2012_012_MOM_20120713	No	
2012/11/20	Milano (AW)	COPROCLAM_2012_015_MOM_20121120	Yes	intermediate meeting
2013/01/29	webex	COPROCLAM_2012_023_MOM_20130129	No	
2013/03/27	Toulouse (LTS)	COPROCLAM_2012_026_MOM_20130327	Yes	End meeting

Table 2: list of meetings held during the project duration

3.3 - Deliverables

WP 1 deliverables consist of reports and publications. Besides scientific communications (see below), the following reports were issued:

D1.1	COPROCLAM_2012_005_Intermediate-report_20120123	6 months: intermediate report
D1.2	COPROCLAM_2012_009_MidTerm-Report_20120525	12 months: mid-term report
D1.3	COPROCLAM_2012_018_Intermediate-report_20121231	18 months: intermediate report
D1.4	COPROCLAM_2012_027_final-report_2010510	24 months: final report

3.3.1 - Dissemination

Regarding communication between partners, a collaborative platform was opened on IJL's file server to improve and facilitate document and/or information transmission. This platform is accessible using login and password to all participants to the project: partner and JTI members.

Several publications have been published or submitted for publication in the framework of the Co-proclam project. Oral and poster communications have been given on occasion of international conferences as well. The corresponding list is given below. These publications and communications constitute deliverable D1.5.

3.3.2 - Publications

Effects of electrical parameters on plasma electrolytic oxidation of aluminium
J. Martin, A. Melhem, I. Shchedrina, T. Duchanoy, A. Nominé, G. Henrion, T. Czerwiec, T. Belmonte
Surf. Coat. Technol. 221 (2013) 70-76

Initial stages of Mg AZ91 micro-arc anodizing: growth mechanisms and effect on the corrosion resistance.
D. Veys-Renaux, E. Rocca, J. Martin, G. Henrion
Electrochimica Acta (submitted).

3.3.3 - Communications

Bipolar current pulse plasma electrolytic oxidation of light alloys : stakes and limits (invited communication).
G. Henrion, C. Rossignol
2nd Int. Conf. Light metal surface finishing, Paris (France), 6-7 Dec. 2011.

Effects of some electrical parameters on the plasma electrolytic oxidation of aluminum (oral communication).
J. Martin, A. Melhem, I. Shchedrina, T. Duchanoy, A. Nominé, G. Henrion, T. Czerwiec, T. Belmonte
26th Int. Conf. on Surface Modification Technologies (SMT 26), Ecully-Lyon (France) 20-22 June 2012.

High-speed video investigation of the plasma electrolytic oxidation process: breakdown and growth mechanisms (oral communication).
G. Henrion, A.Melhem, T. Czerwiec, J.L. Briançon, F. Brochard, T. Belmonte
13 Int. Conf. Plasma Surface Engineering (PSE'2012), Garmisch-Partenkirchen, 10-14 Sept 2012.

Influence of the anodic current pulse density on the oxide layers grown on Al 2024 by the plasma electrolytic oxidation process (poster).
I. Shchedrina, T. Duchanoy, G. Henrion, A. Nominé, J. Martin, T. Czerwiec, A.G. Rakoch, T. Belmonte
13 Int. Conf. Plasma Surface Engineering (PSE'2012), Garmisch-Partenkirchen, 10-14 Sept 2012.

Influence of the current pulse frequency on both the micro-discharges and the processed materials during the plasma electrolytic oxidation of aluminium alloys (poster).
J. Martin, A.Melhem, T. Duchanoy, G. Henrion, T. Czerwiec, A. Nominé, T. Belmonte
13 Int. Conf. Plasma Surface Engineering (PSE'2012), Garmisch-Partenkirchen, 10-14 Sept 2012.

Influence of the electrolyte composition on the oxide layers grown on Mg alloy by the plasma electrolytic oxidation process (accepted as oral).
I. Shchedrina, G. Henrion, J. Martin, D. Veys-Renaux, T. Czerwiec, T. Belmonte
19th Int. Vacuum Congress (IVC 19), Paris (France) Sept. 2013.

4 - Work package 2: *Influence of the electrolyte composition, temperature and ageing on the properties of the MAO ceramic layer grown on Al and Mg alloys*

Five tasks have been assigned WP2. Besides task #1 that consisted of a bibliographic review on the role of electrolyte composition (deliverable D2.1[8]), the four other tasks consisted in finding out the best electrolyte composition for MAO processing Al2024 and Mg EV31. Therefore tasks #2 &

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[8] *COPROCLAM_2011_003_BIBLIO_20110731*

#3 (Al processing and characterization respectively) were done simultaneously as well as tasks #4 & #5 for Mg alloy.

From the bibliographic review (D2.1 available) it resulted that the electrolyte composition should be based on alkaline hydroxide (KOH, NaOH) solutions with addition of some ionic salts. Mostly used additive are silicate, phosphate or fluoride salts. Though a huge variety of additive (including nanoparticles, polymers, etc.) are reported in the scientific literature, no clear evidence has been reported on the effective role of these additives. Therefore, for the present study, we limited the tries to silicate (Na_2SiO_3), phosphate ($Na_4P_2O_7$; $NaPO_3$), aluminate ($NaAlO_2$), tungstate (Na_2WO_4) and fluoride (KF) compounds added to either KOH or NaOH.

A wide range of electrolyte composition was tested with different amount and concentration of alkaline base and additives. A summary of ranges of electrolyte composition is given in table 3.

Compound	KOH	NaOH	Na_2SiO_3	$Na_4P_2O_7$	Na_3PO_4	$NaAlO_2$	KF	NH_4F	Na_2WO_4
concentration (mol/L)	< 3	< 0.01	< 0.2	< 0.02	< 0.16	< 0.02	< 0.02	< 0.22	< 0.02

Table 3: range of concentration of the different chemicals for electrolyte preparation

For each electrolyte condition, a set of samples was processed which made it possible to perform coating analyses and corrosion tests.

From all the tries, the following conclusions may be drawn:

4.1 - Al 2024[9]

- Whatever the electrolyte composition thin MAO layers exhibit a high porosity and contain electrolyte elements. Meanwhile corrosion resistance is rather poor. This is likely due to the low thickness of the layers. Indeed porosities across the layer may act as pitting start points. In fact, it has clearly been shown that increasing the layer thickness up to 45 µm strongly improves the corrosion resistance that can reach 300 hours salt spray test without any corrosion (fig. 5).
- Increasing the silicate content slightly improves the corrosion resistance of the coating on Al.
- Addition of fluoride has no significant effect on the corrosion resistance.
- Cr VI free sealing post-treatment improves the corrosion resistance up to 300 h salt spray of 4 µm thick MAO coatings.

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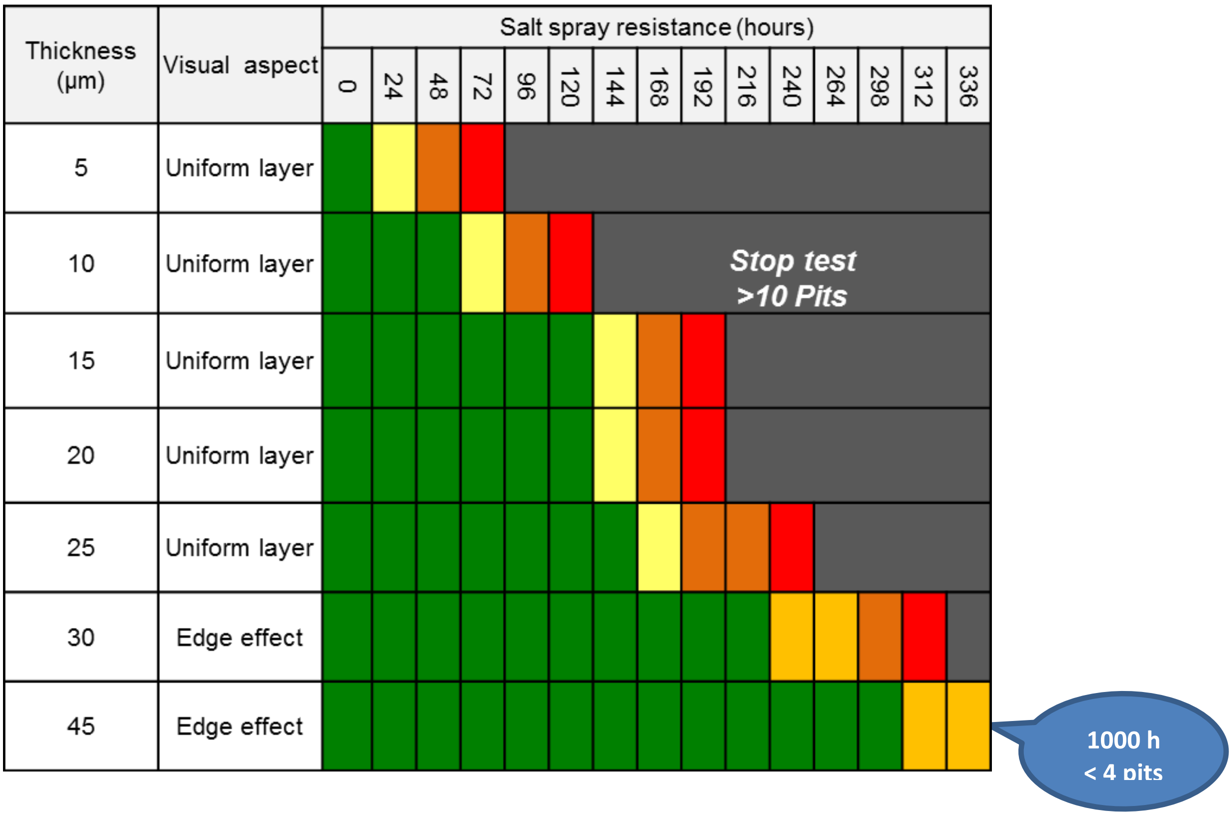
[9] *Detail on the effect of electrolyte composition on the MAO coatings on Al 2024 are reported in document COPROCLAM_2012_018_Intermediate-report_20121231. See also documens COPROCLAM_2012_007_GIT_20120125*

- Electrolyte temperature was found to have no influence on the resulting PEO coatings.
- The use of a small volume of electrolyte results in a more or less fast aging of the bath, depending on the nature of the counter electrodes.



Thickness (µm)	Visual aspect	Salt spray resistance (hours)														
		0	24	48	72	96	120	144	168	192	216	240	264	298	312	336
5	Uniform layer	🟩	🟨	🟧	🟥	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛
10	Uniform layer	🟩	🟩	🟩	🟨	🟧	🟥	⬛ Stop test >10 Pits	⬛	⬛	⬛	⬛	⬛	⬛	⬛	⬛
15	Uniform layer	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟧	🟥	⬛	⬛	⬛	⬛	⬛	⬛
20	Uniform layer	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟧	🟥	⬛	⬛	⬛	⬛	⬛	⬛
25	Uniform layer	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟨	🟧	🟧	🟥	⬛	⬛	⬛	⬛
30	Edge effect	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟡	🟡	🟧	🟥	⬛
45	Edge effect	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟡	🟡

1000 h
< 4 pits

Figure 5: Influence of the layer thickness on the corrosion resistance of MAO processed Al 2024. Electrolyte composition: KOH=0.018mol/L; Na_2SiO_3=0.12 mol/L (GIT)

4.2 - Mg EV31

Magnesium samples were MAO processed using the same chemicals than for aluminum, with a limitation to alkaline hydroxide, silicate, phosphate and fluorides. Unlike aluminum, MAO coating on magnesium EV31 are difficult to grow and always present a high porosity (fig. 6), even for rather thick layers (> 20 µm).

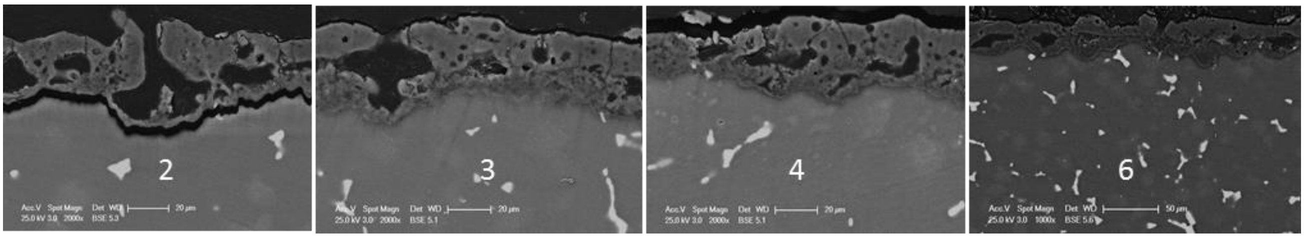


Figure 6: SEM micrograph of cross section of Mg samples after MAO processing in KOH+ x g/L Na_2SiO_3. Values of x are indicated in the figures. (100 Hz, 15 min, 40 A)

On the other hand, addition of silicate in the electrolyte (up to 6 g/L) improve the top surface while an excess in silicate results in detrimental corrosion of the sample (fig. 7).

Figure 7: pictures of Mg samples after MAO processing in KOH+ x g/L Na_2SiO_3. Values of x are indicated in the figures. (100 Hz, 15 min, 40 A)

Regarding the addition of silicate it may be concluded that:

- With the increase in sodium silicate concentration the coating growth rate slightly increases. However, quite no consequence was observed on the edge effect with increasing the silicate content. Among all samples, the one processed with 6 g/L silicate exhibited a slight improvement of the edge effect.
- It seems that the coating becomes less porous with the addition of the Na2SiO3 in the electrolyte – it is possible already to find some dense areas in the electrolyte 3 and especially in 4 and 6 g/l Na_2SiO_3, also there are no anymore open pores that reaches the metal surface, but still in all the cases the coating is very porous.
- In almost all samples, the coating consists of two sub-layers However, in the case of 4 g/l Na_2SiO_3 concentration, the intermediate layer does not completely cover the interface. Therefore if the outer layer flakes off somewhere, there is no protective layer at those places.
- In the case of 6 g/l Na_2SiO_3 the coating is less porous and almost all large pores are closed. The coating has more dense areas in comparison with the others.

Meanwhile, it was shown that addition of fluoride reduces the edge effect that is usually observed. Though this results in better homogeneity in thickness of the layer, fluoride does not significantly improve the coating microstructure.

It is also worth noting that a higher concentration in potassium hydroxide (base electrolyte) improves the coverage rate[10]. Indeed, for [KOH] < 0.035 mol/L, quite no layer is grown on the Mg sample which is corroded by the electrolyte. For [KOH] > 0.035 mol/L there is still no uncoated area at the edge (even inside the empty places and large pores) and for [KOH] > 0.07 mol/L the

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[10] *cf. doc Coproclam_2012_017_IJL_20121120.pdf*

coating porosity decreases, as well as the quantity of large pores, while the quantity of through-pores gets lower.

Regarding corrosion, besides salt spray test, an electrochemical study was carried out on the samples that were expected to have the best coating.

4.2.1 - Electrochemical study of PEO MgEV31 samples

In order to better understand the electrochemical mechanisms involved in the corrosion resistance of anodized pieces, electrochemical measurements were performed on chosen samples. The treatment conditions are gathered in table4. The electric parameters and the time of anodizing were kept constant; only the composition of the electrolytic bath was modified.

Sample #	[KOH] (g/L)	[Na_2SiO_3] (g/L)	[KF] (g/L)	Thickness (µm)
1	2	6	0	24
2	4	4	0	22
3	4	4	8	20

Table 4: List of chosen samples and process conditions (f=100 Hz, J=40 A/dm^2, t=15 min)

The electrochemical behavior of anodized samples was studied in an aerated corrosive solution (D1384-87 ASTM standard water: Na_2SO_4 148 mg.L^{-1}; $NaHCO_3$ 138 mg.L^{-1}; NaCl 165 mg.L^{-1}, noted ASTM water[11]) using a three-electrode setup. This solution was chosen because of its moderate aggressiveness, and the results obtained can be well-correlated with long exposure to atmospheric conditions[12][13]. The samples were mounted horizontally as circular working electrodes (area in contact with the electrolyte: 3 cm^2), facing a Pt-grid used as the counter electrode. The reference electrode was a KCl-saturated calomel electrode (Hg/ Hg_2Cl_2, E=+0.242 V/SHE). All the working electrode potentials are given versus this reference. This device was connected to a PAR Versastat4 potentiostat/frequency response analyzer driven by a computer equipped with a Versastudio software for data acquisition and analysis.

The following electrochemical sequence was applied for each sample:

- Corrosion potential was measured for 5 minutes in order to stabilize the interface.

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[11] *Annual book of ASTM standards, copyright ASTM, Pa 19103 (1986)*
[12] *C.E. Barchiche, E. Rocca, C. Juers, J. Hazan, J. Steinmetz, Electrochim. Acta 53 (2007) 417*
[13] *C.E Barchiche, D. Veys-Renaux, E.Rocca, Surf. Coat. Tech 205 (2011) 4243*

- Electrochemical impedance spectroscopy (EIS) was carried out at the corrosion potential, over the frequency range 10 mHz–300 kHz with an applied AC perturbation potential of 20 mV magnitude.
- Corrosion potential was measured for 2 hours.
- Electrochemical impedance spectroscopy (EIS) was carried out at the corrosion potential, using the same parameters as previously, in order to observe the way of degradation of the samples in the reference corrosive medium.
- Anodic potentiodynamic curve was then recorded with a scan rate of 1 mV s−1 (after about 3h of immersion in the corrosive ASTM water).

The measurements of the corrosion potentials are overlaid in figure 8.

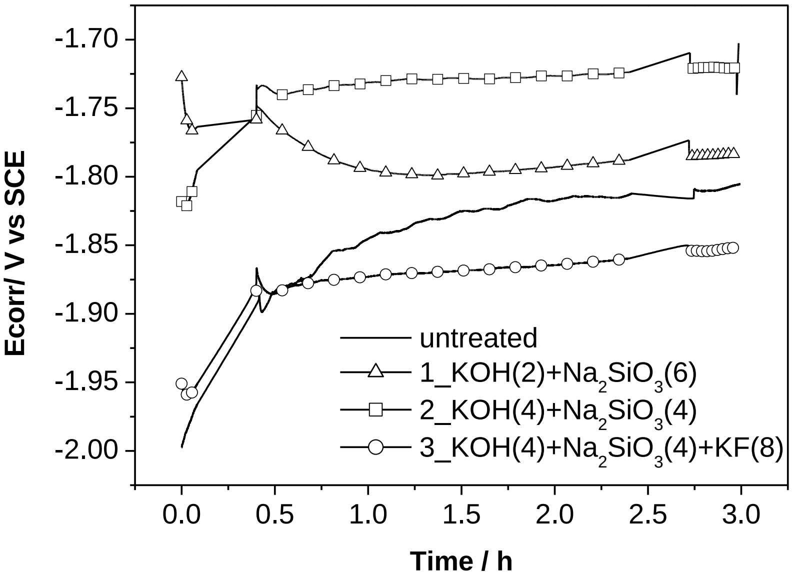

Figure 8: Corrosion potentials measured during the electrochemical sequence in ASTM water.

In all cases, the stability of the electrochemical interface seems to be reached after 1 hour immersion in ASTM water. As already observed in precedent works, the presence of silicates in the electrolytic bath induces a slight ennoblement of the interface[14] , whereas the addition of fluorides leads to lower values of the corrosion potentials, demonstrating an inhibition of the cathodic reaction (water reduction)[11].

The anodic polarization curves, recorded after 3 hours immersion in ASTM water, are displayed in figure 9.

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[14] *Ha Bach, Master thesis, Université Henri Poincaré, Nancy (2007).*

All the treatments reduce the anodic current density on the passivation plateau of about one order of magnitude. However, for samples anodized in electrolytes containing only silicates as additives, this passivation plateau is interrupted at -1.1 V/SCE by the apparition of a pitting phenomenon leading to a brutal increase of the anodic current density. With addition of fluorides to the electrolytic bath, the anodic current density remains low all over the range of anodic potentials, indicating a slightest sensitivity to pitting corrosion.

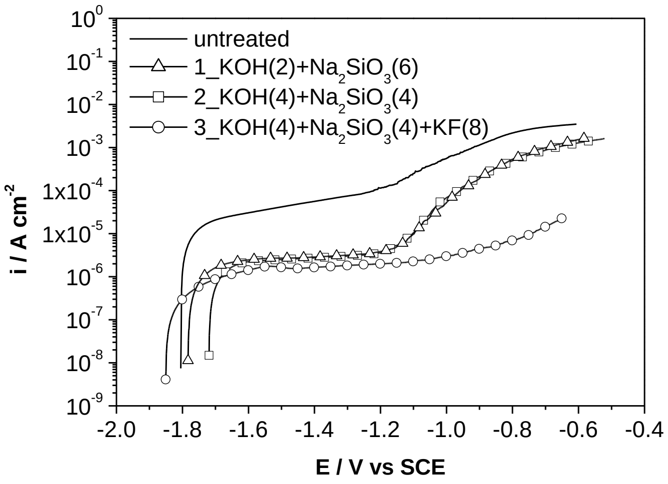

Figure 9: Anodic polarization curves recorded after 3 hours immersion in ASTM water.

Impedance spectra recorded after 5 minutes immersion in ASTM water and after about 2h30 immersion are displayed respectively in figures 10 and 13 in Bode representation.

From a qualitative point of view, the global corrosion resistance of the different materials can be estimated by the extrapolation of the impedance modulus to very low frequencies. All the anodizing treatments bring an improvement of this global corrosion resistance, the best results being obtained by the addition of fluorides in the electrolytic bath. The low global resistance of the untreated sample after 5 minutes immersion in the corrosive media is accompanied by a pitting phenomenon, indicated by the inductive behavior at low frequency corresponding to the adsorption of chemical species.

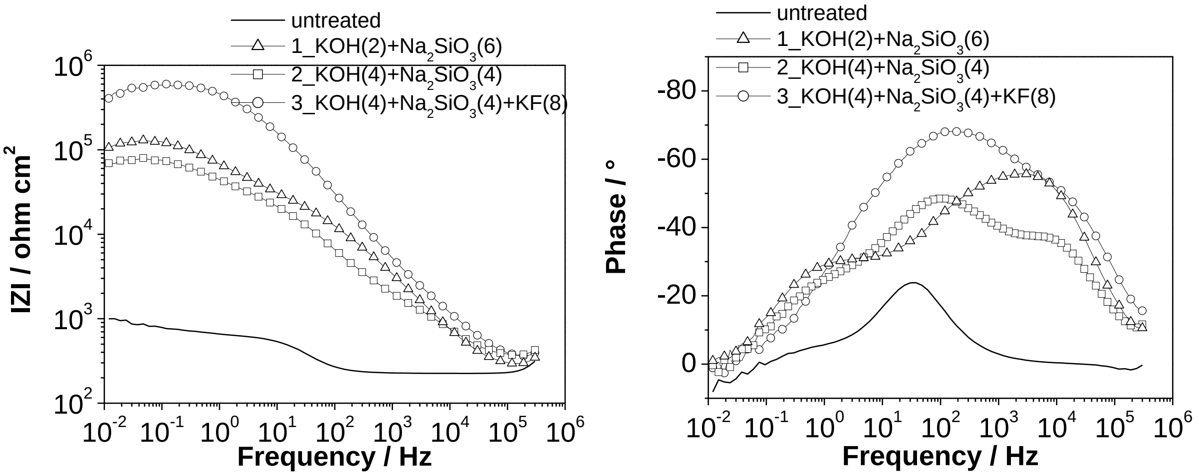

Figure 10: Bode impedance spectra recorded after 5 minutes immersion in ASTM water.

A finer description of the electrochemical processes occurring at the interface of the coated samples can be achieved by a modeling of the spectra all over the frequency range. As it can be clearly observed in the Bode phase diagrams, three different time constants can be distinguished and the equivalent circuit depicted in the figure 11, classically used for an electrode coated by two super-imposed porous layers[15], can be proposed.

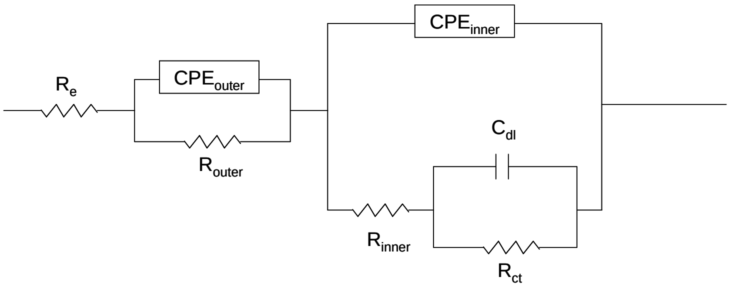

Figure 11: Equivalent circuit proposed for the modeling of the electrochemical interface.

- At high frequency (104 Hz range), the (R_{outer} and C_{outer}) time constant can be associated to the dielectric properties of the outer part of the coating and the electrolyte resistance in the pores. A constant phase elements CPE is introduced to take into account the heterogeneities of this part of the coating.

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[15] *Mark E. Orazem, Bernard Tribollet in “Electrochemical Impedance Spectrocopy”, Edited by John Wiley and Sons (2008), Hoboken New-Jersey, p160.*

- At middle frequency (102-103 Hz range) the (R_{inner} and C_{inner}) time constant can be associated to the dielectric properties of the inner part of the coating and the electrolyte resistance in the pores. A constant phase elements CPE is introduced to take into account the heterogeneities of this part of the coating.
- At low frequencies (1 Hz), the (R_{ct} and C_{dl}) time constant can be assigned to the charge transfer resistance and the double layer capacitance at the metal surface (at the bottom of the pores).

An example of fitting of the EIS spectra by using Boukamp's algorithm implemented in Zsimpwin software[16] is given in figure 12.

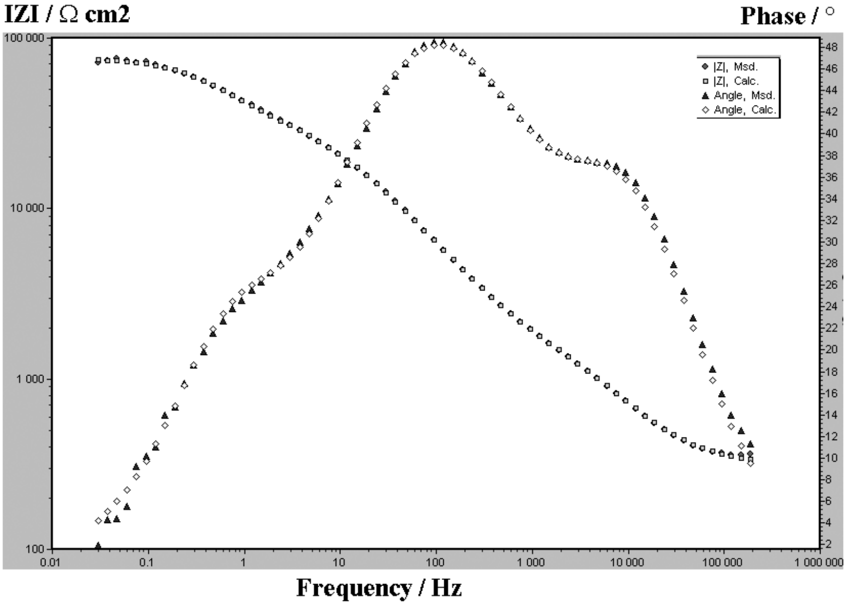

Figure 12: Comparison between experimental and fitted impedance spectra in Bode representation: example of sample 2 (anodized in KOH 4 g L^{-1}+Na2SiO3 4 g L^{-1}) after 5 minutes immersion in ASTM water.

R_e Ω cm^2	CPE_{outer} S s^n cm^{-2}	n	R_{outer} Ω cm^2	CPE_{inner} S s^n cm^{-2}	n	R_{inner} Ω cm^2	C_{dl} F cm^{-2}	R_{ct} Ω cm^2
302	$2.8\ 10^{-7}$	0.86	494	$2.3\ 10^{-6}$	0.66	$4.6\ 10^{4}$	$1.0\ 10^{-5}$	$2.9\ 10^{4}$

Table 5: Electrical parameters corresponding to the refinement of the EIS spectra drawn in the figure 12.

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[16] *B.A. Boukamp, Solide State Ionics 20 (1986) 31*

According to these values, the outer part of the coating would be thicker than the inner part (the capacitance being inversely proportional to the thickness). However, due to the large discharge channels in the outer part, its resistance is lower.

The differences between the different samples can be interpreted qualitatively.

The increase in the silicates content in the electrolyte seems to slightly improve the impedance of the outer part of the coating (the shift between curves 1 and 2 occurs in the “high frequency” range) by densification and/or thickening of this layer.

The increase of the global resistance by the addition of fluorides in the anodizing bath seems to be mainly due to the contribution in the low frequency range (and to a lesser extent to the contribution in the middle frequency range). Actually, this effect can be attributed to a best covering rate at the metal/inner layer interface that reduces the active surface of the metal and therefore increases the charge transfer resistance and decreases the double layer capacitance (proportional to the active surface) at the same time.

After 2.5 hours of immersion in the corrosive medium (figure 13), the three contributions to the impedance of the system are more difficult to distinguish (in particular the contributions in low frequency and middle frequency range).

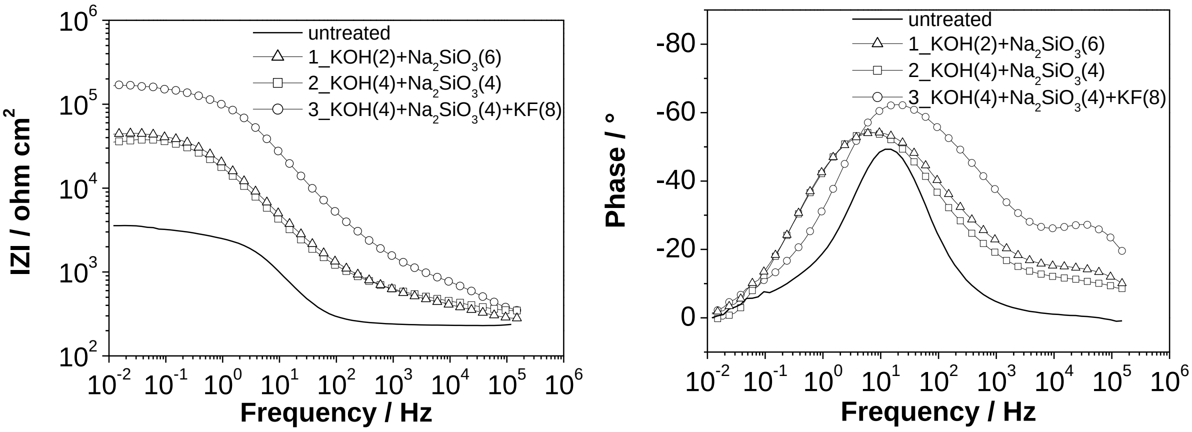

Figure 13: Bode impedance spectra recorded after 2.5 hours immersion in ASTM water.

The global corrosion resistance of the untreated sample is increased. Actually, the surface is passivated and no more pitting occurs at the corrosion potential. This result is consistent with the presence of the passivation plateau on the anodic polarization curve.

The global corrosion resistance of the treated samples is twice lower than initially. This decrease of the protective properties seems to be due to a decrease of the contribution at high frequency (corresponding to the outer part of the coating). After 2.5 hours of immersion, the global resistance of the treated samples is about one order of magnitude higher than the corrosion resistance of the untreated one, consistently with the current density on the passivation plateau that is reduced by about one order of magnitude.

The impedance data obtained on the surfaces coated without fluorides are similar.

The resisting properties of the sample coated in the fluorides containing bath remain the best due to the inner part of the coating that better covers the alloy surface.

From this electrochemical study, it can be concluded that the PEO treatments in the chosen conditions improve the corrosion resistance of the magnesium alloys by the growth of two stacked porous layers.

Even if an increase in the silicates content in the anodizing bath seems to slightly increase the protective properties of the grown layer, this effect is no more visible after 2.5 hours of immersion in the corrosive medium. The best results observed by salt spray tests for samples anodized in the higher silicate-content bath can however not be explained by this electrochemical study since it is often difficult to exactly corroborate results from electrochemical studies carried out in immersion and salt spray tests involving electrochemical phenomena in droplets.

The addition of fluorides in the anodizing bath improves both the global resistance to corrosion (decrease of the global corrosion rate) and the sensitivity to pitting corrosion, thanks to a best covering of the alloy surface.

4.3 - Deliverables

D2.1: Bibliographic report on the electrolyte was issued on July 2011 as document COPROCLAM_2011_003_BIBLIO_20110731.

D2.2: Most suitable electrolyte for Al 2024 alloys treatment

A precise composition of electrolyte suitable to achieve MAO coatings on Al 2024 which comply the requirements was not clearly found out. Nevertheless, trends may be drawn from the achieved results:

- Complex electrolyte composition does not improve the coating performances.
- The best additive in alkaline base electrolyte regarding corrosion resistance is silicate containing salt. Increasing the silicate content gives better results in terms of corrosion resistance.

- Increasing the coating thickness (some tens µm) makes it possible to comply with the requirements regarding corrosion without any further post-treatment.
- Thin MAO layers (< 5µm as expected) remain very porous and have poor anti-corrosion properties. Nevertheless, sealing without Cr VI containing compounds has been demonstrated that extend corrosion resistance over 300 h salt spray.

D2.3: Most suitable electrolyte for Mg alloys treatment

As for Al2024 alloy, no clear definition of the electrolyte composition can be drawn for the PEO processing of Mg EV31 alloy. However, from the performed study, it can be concluded[17]:

- Silicate addition improves both coating adhesion and compactness. However a too high silicate concentration in the electrolyte is detrimental to the coating. Thus, the silicate concentration should be less than 0.05 mol/L.
- Addition of phosphate improves the coating adhesion and reduces the pulverulence of the coating (fig. 14). It also reduces the edge effect and leads to a more homogeneous coating with quite no thickness variation between the edge and the centre of the sample (table 6).
- Addition of fluoride improve the corrosion resistance according to electrochemical and EIS measurements.

	Thickness @ edge (µm)	Thickness @ centre (µm)
100 Hz, 10 min	18.2	18.8
750 Hz, 13.33 min	26.6	25.2

Table 6: Thickness variation over the sample surface for two process conditions. Jp=20A/dm^2 ; Electrolyte= KOH/$Na_4P_2O_7$/KF (0.035/0.009/0.14 mol/L)

Figure 14: Top view of Mg EV31 sample processed within phosphate containing electrolyte (right) and without phosphate (left)/ I=20A/dm^2, f = 500 Hz, t=5 min.

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[17] *see also COPROCLAM_2012_007_GIT_20120125.pdf, COPROCLAM_2012_011_GIT_20120529.pdf; COPROCLAM_2012_024_IJL_20130327.pdf*

5 - Work package 3: *Influence of the processing parameters on the properties of the MAO ceramic layer grown on Al and Mg alloys*

Regarding the effect of the process parameters, investigations were mainly carried out on the effect of the anodic current amplitude (and therefore the corresponding cathodic current amplitude), current frequency and the influence of the gap distance between the electrodes as well, with subsequent characterization of the processed samples. Work was driven according two approaches; one consisted in adjusting the process time to achieve an oxide layer with final known thickness (based on previous studies), while the second consisted in keeping the process time at a constant value so as to allow us study the effect of the process parameters on the growth rate and growth kinetics.

5.1 – Case of Al 2024

In the case of Al 2024, current density, current pulse frequency and electrode gap distance were investigated in the range 12-90 A/dm^2, 100-900 Hz and 8-160 mm respectively.

The effect of current density, current frequency and electrode gap distance on the MAO layers grown on Al has been reported previously[18].

Increasing the frequency favors the layer properties in terms of compactness and porosity) though a strong gradient in thickness still exists from the edge to the center of the sample. However, one can expect that using higher frequency would improve the layer compactness while maintaining a layer thickness compliant with the end-user requirements.

Achieving thin layer needs rather low current amplitude. However, it is not yet clear which of the anodic current amplitude or the anodic current density is the most relevant parameter. Therefore, it is needed to clarify this aspect. Up to now, changes in current density were done by varying the anodic current amplitude while maintaining the sample size constant. Thus it is plan to change the current density by changing the sample size while maintaining the anodic current amplitude at a constant value. This work is on the way.

The effect of the electrode gap distance was also checked. It appears that a large electrode gap improves the growth rate. On the other hand, increasing the electrode gap is detrimental to the thickness homogeneity over the sample surface and a strong thickness gradient occurs from the center to the edge of the sample. This was ascribed to the strong increase in the electric field at the edges of the sample (this phenomenon is well known as edge effect). Consequently, various

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[18] *see COPROCLAM_2012_004_MOM_20110908; COPROCLAM_2012_005_Intermediate-report_20120123; COPROCLAM_2012_014_GIT_20120713.pdf*

size/shape were used as counter-electrodes. A particular cylindrical counter-electrode was tested with the sample located in the middle of the cylinder. Though this configuration seemed to reduce edge effect, the thickness gradient still exists with this configuration.

Regarding the corrosion resistance, study of the influence of process parameters leads to the following conclusions:

- Changing the current frequency (in the range 100-1000 Hz) does not influence the corrosion resistance which remains below 48 hours salt spray.
- Increasing the frequency up to 14 kHz slightly improves the corrosion resistance; 96 h salt spray resistance have been achieved for a coating thickness of 12 µm.
- Though it influences the layer microstructure and compactness, the anodic to cathodic current ratio ($R = I_p / I_n$) has no effect on the corrosion resistance (< 48 h salt spray).
- The value of the anodic current modifies the growth kinetics and the microstructure of the layer whose porosity depends on the current value. However, no influence on the corrosion resistance was noted. Nevertheless, it is more suitable to process with rather low current density to limit large and open porosities.
- A low current density strongly reduces the edge effect and the "burning" of the sample (fig. 15).
- The electrolyte temperature seems to influence neither the coating microstructure nor the corrosion resistance.

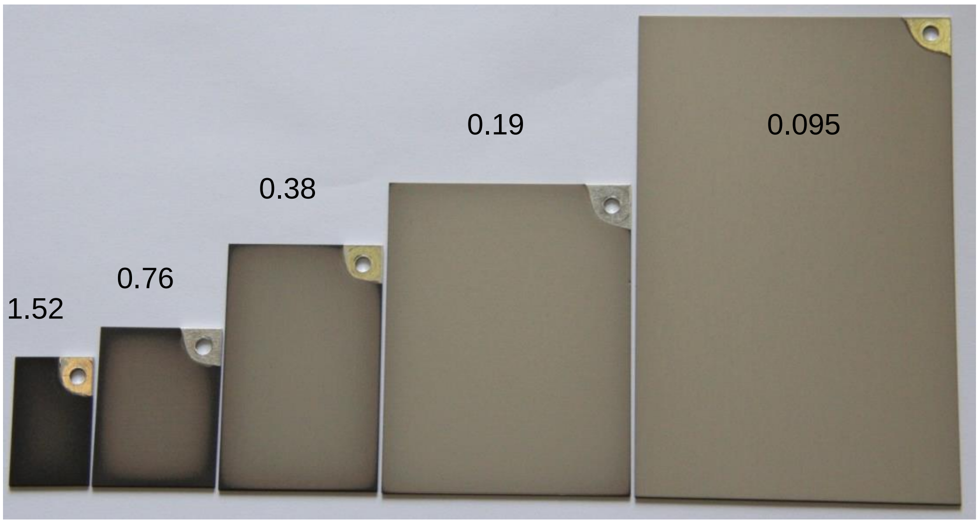

Figure 15: Picture of Al2024 samples after MAO processing with all the same process parameters. Due to the change in sample size, only the current density (indicated in the figure in A/cm^2) changes

5.2 – Case of Mg EV31

Due to the poor adhesion of the coating on Mg EV31 and the difficulty to achieve quite good layers, less tries were performed on Mg regarding the effect of process parameters; most efforts were devoted to the study of electrolyte composition.

However some results may be pointed out:

- As for aluminum, the current density value should be kept rather low (typ. $\leq$ 20 A/dm^2) since magnesium oxide coating is much more sensitive to discharges than aluminum one.
- Increasing the current frequency (some 100s Hz) tends to improve the coating properties, and the corrosion resistance.
- A rather low current frequency (typ. 100 Hz) seems to reduce the porosity of the layer which exhibit less open pores. It also favors the growth rate. On the other hand, edge effect is much more pronounced as compared with higher frequency (typ. 750 Hz).
- The value of the anodic current modifies the growth kinetics and the microstructure of the layer whose porosity depends on the current value. However, no influence on the corrosion resistance was noted. Nevertheless, it is more suitable to process with rather low current density to limit large and open porosities.
- The electrolyte temperature (T < 50°C) seems to influence neither the coating microstructure nor the corrosion resistance.

5.3 – Deliverables

D3.1/D3.2: Best parameter set for processing Al and Mg alloy samples.

Results of investigations lead to similar trends regarding the effect of the process parameter (especially electrical parameters) on the coating grown on both Al2024 and Mg EV31. Therefore, the two expected deliverables can be merged in a single one:

- Within the range of low values (< 50°C), the electrolyte temperature has quite no effect on the layer growth and layer properties. Nevertheless, other studies performed out of the frame of the Coproclam project have shown an increase in the α-Al_2O_3/ γ-Al_2O_3 when strongly increasing the electrolyte temperature (fig.16). Besides the mechanical properties, this change in the crystallographic phase of aluminium oxide might influence also the electrochemical properties.
- The use of a current pulse frequency in the medium range (typ. 500 Hz < F < 1000 Hz) improves the coating quality in terms of porosity and compactness. Regarding corrosion, best results (though they did not comply with the requirements) were obtained within this frequency range.
- The current density should be adjusted so that strong arcs do no develop at the sample surface. Obviously, micro-discharges are needed for the oxidation process to continue, but a rather low current density (typ. $\leq$ 20 A/dm^2) should be preferred, even if this requires increasing the process time.
- Although it slightly influences the edge effect, the gap distance between the work electrode and the counter electrodes has quite no effect on the coating properties.
- Using titanium counter electrodes preserves the electrolyte of too fast aging, especially in the case of low volume electrolyte tank.

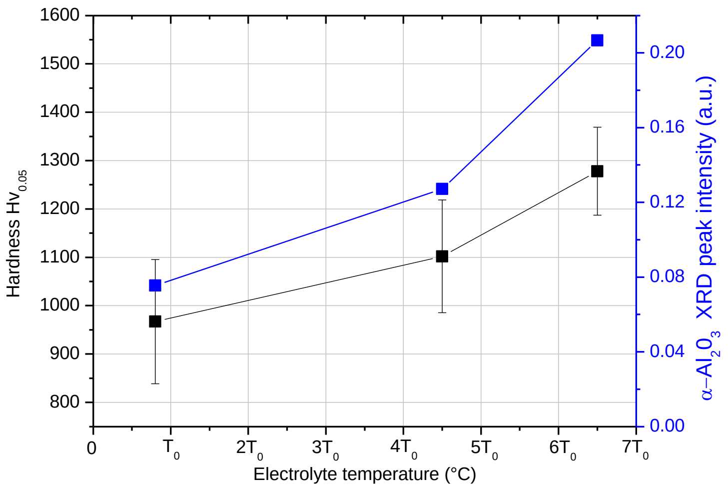

Figure 16: effect of the electrolyte temperature on the α-Al_2O_3 content in the MAO coating grown on aluminium and resulting hardness variation

6 - Work package 4: *Investigation in the physics of the micro-discharges*[19]

The behavior of the micro-discharges was investigated (in the case of Al only) using optical emission spectroscopy and fast video image recording (> 100 000 frames/second). The former allows us to determine the electron temperature and electron density of the plasma discharges while the latter leads us to get insights into the size, location and lifetime of MDs as a function of the process parameters (anodic current density, current frequency, gap distance). The following sections reports on the main results from these investigations.

These studies have started before the start of the Coproclam project and were first carried out on Al 2214 grade alloy. Consequently, most of this study has been continued on Al2214. Therefore one can question about the differences that may exist between Al 2024 and Al 2214 regarding the behavior of micro-discharge when PEO processing. In fact, MDs behavior in non-sensitive to the alloy grade as will be discussed in the following sections (§6.3). This is mainly due to the similarity of both alloys (table 7) which differ mainly by the Mg and Zn contents, and to the fact that micro-discharges are related to the aluminum oxide breakdown, that is quite independent on the alloying elements.

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[19] *see also COPROCLAM_2013_019_IJL_GH_20130129*

	Mg	Cu	Mn	Cr	Si	Zn	Al
A-2024	1,2-1,8	3,8-4,9	0,3-0,9	0,1	0,5		balance
A-2214	0,2 – 0,8	3,9-5,0	0,4-1,2	0,1	0,5 – 1,2	0,25	balance

Table 7: Elemental composition (wt%) of Al2024 and Al2214 aluminum alloys

6.1 – Micro-discharges characteristics (Al2214)

Using fast video recording of the plasma events allows us to get insights into the micro-discharge characteristics such as brightness, lifetime, number density on the surface, size, location on the sample surface and delay with respect to the current pulses.

A commonly admitted characteristic of PEO process is that micro-discharges only occur during the anodic half period of the current pulses which we have proven by simultaneously recording the light emitted by the MDs and the current waveform.

Whatever the process conditions the number of micro-discharges that develop on the surface decreases as the process goes on. This comes from an increase in the layer thickness with the process time (fig. 17). Indeed, as the coating gets thicker, the breakdown of the dielectric layer requires higher current; consequently there are less electrical charges to ignite new micro-discharges whose number decreases. On the other hand the current flowing in a single micro-discharge gets higher too. It is worth noting that the number density of MDs decreases according to two different mechanisms which are not well understood yet.

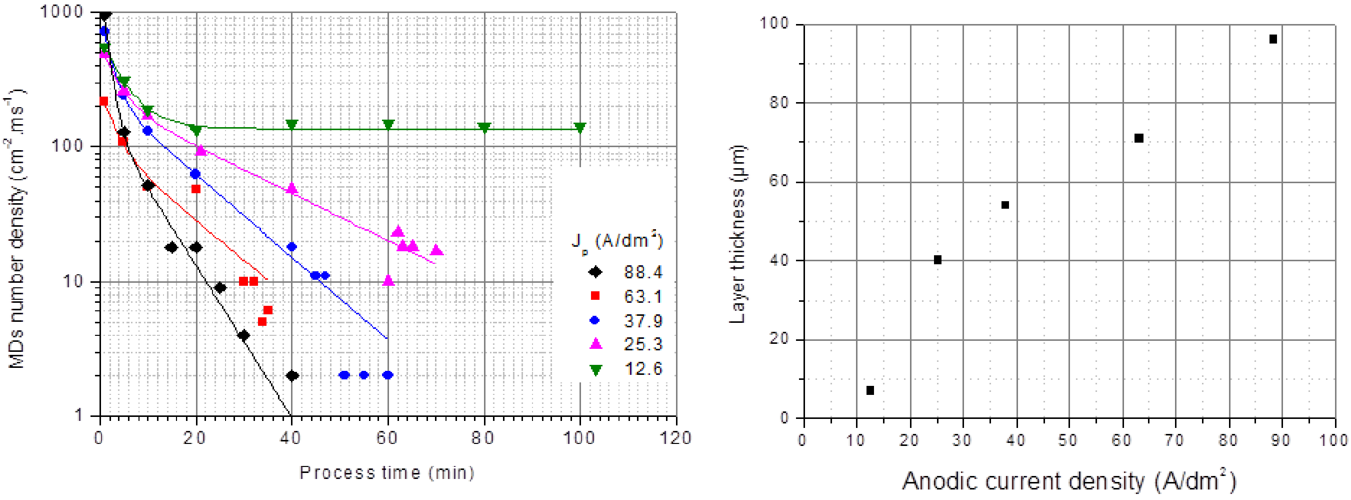

Figure 17: Variation of the number density of MDs with the process time (left) and thickness of a 40 min growth layer on Al2214 sample (right).

Besides the MD number density, the investigation of the location of MDs on the sample surface during the process time have been directly related to the edge effect and to the thickness gradient between the edge and the center of the sample. In fact, figure 18 clearly shows that most of the MDs are located at the outer border of the sample, which has consequences on the layer thickness homogeneity.

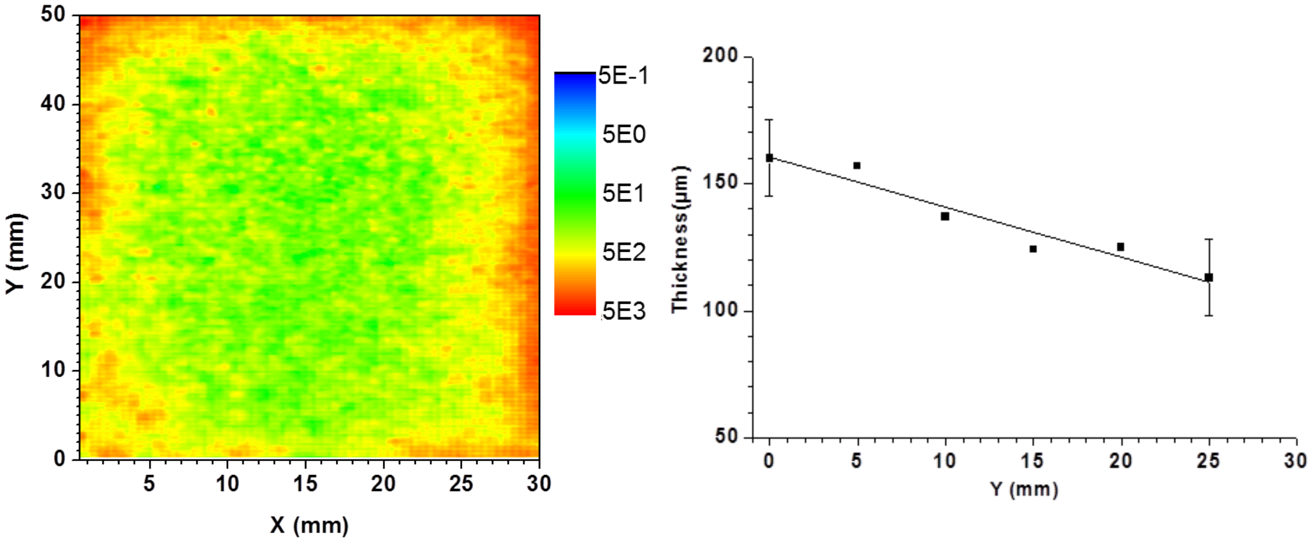

Figure 18: Plot of the surface distribution of discharge events summed over 20 min processing. Note the colored log scale. Process time=25 min; anodic current=25 A (left) and thickness of a 40 min growth layer on Al2214 sample (right).

A more detailed study pointed out that this edge effect only occurs during the first minutes of treatment. Indeed, by considering identical areas of the outer and inner part of the sample, and by looking at the micro-discharges location during one period of the current, it came that after 5 minutes processing, there are as many MDs on the edge as on the center (fig. 19).

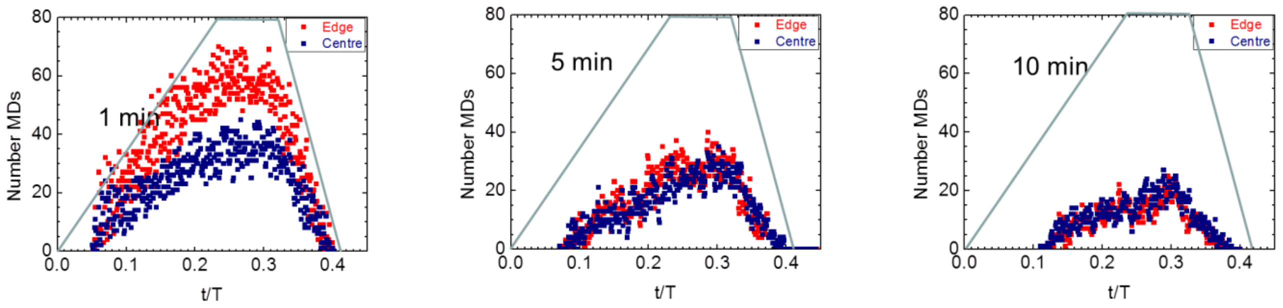

Figure 19: Variation of the number of MDs at different times of the MAO process of Al2214 alloy. J_p=75 A/dm^2; F=100 Hz. Sample size=30 x 50 mm^2. Outer (red) and inner (blue) parts have same area. The blue line represents the theoretical anodic current waveform.

As a consequence, it comes that the edge effect which is detrimental to the coating homogeneity mainly occurs during the first minutes of process. Therefore, it might be of interest in managing the beginning of the MAO process to control this phenomenon. Moreover, this result might be related to the change in the decrease mechanisms observed on the MDs number density.

Another important aspect of MDs characteristics that can influence the oxidation process concerns the micro-discharge lifetime. Indeed, huge charge quantities flow through long live MDs and create large and open porosities. Measurements of the MDs lifetime distribution show that this parameter also depends on the layer thickness and that the thicker the oxide layer, the more numerous the long live MDs (fig. 20). It is likely that this variation is related to the breakdown mechanisms.

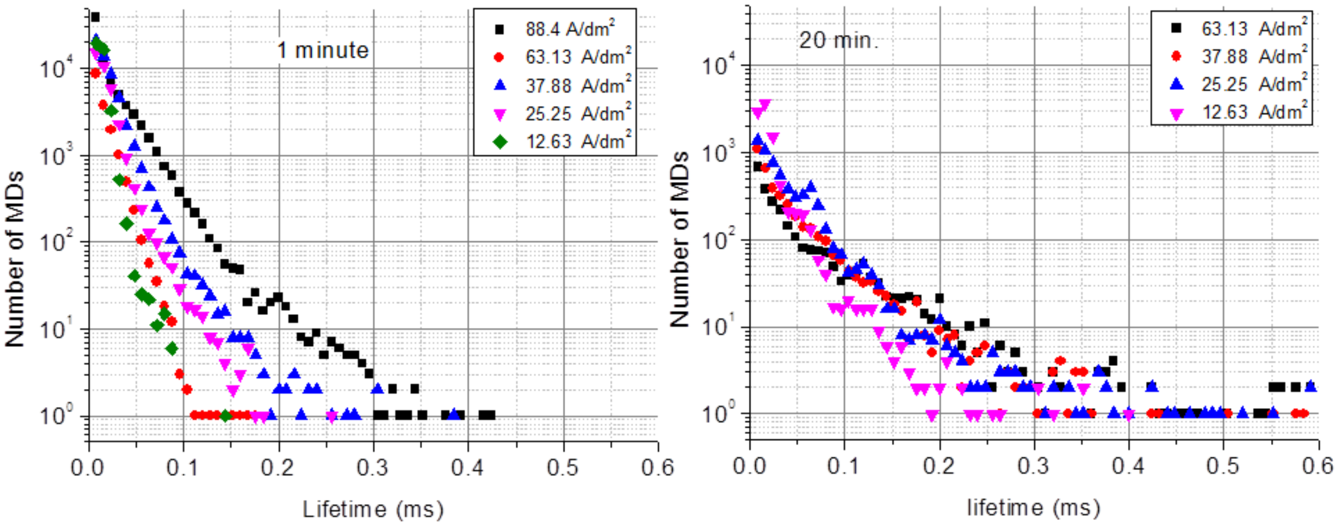

Figure 20: Variation of the MDs lifetime distribution at 1 minute (left) and 20 minutes (right) process time for different current density.Al2214, F=100 Hz

6.2 – Micro-discharges events with respect to the current pulses (Al2214)

A particular aspect of micro-discharge event was pointed out. This is the delay between the rising edge of the anodic current pulse and the appearance of the micro discharges; some kind of breakdown delay which increases as the PEO progresses (as the layer gets thicker). An illustration of this delay is given in figure 21. As for the other MDs parameters, the delay seems to depends on the layer thickness since it increases with the process time (fig. 22).

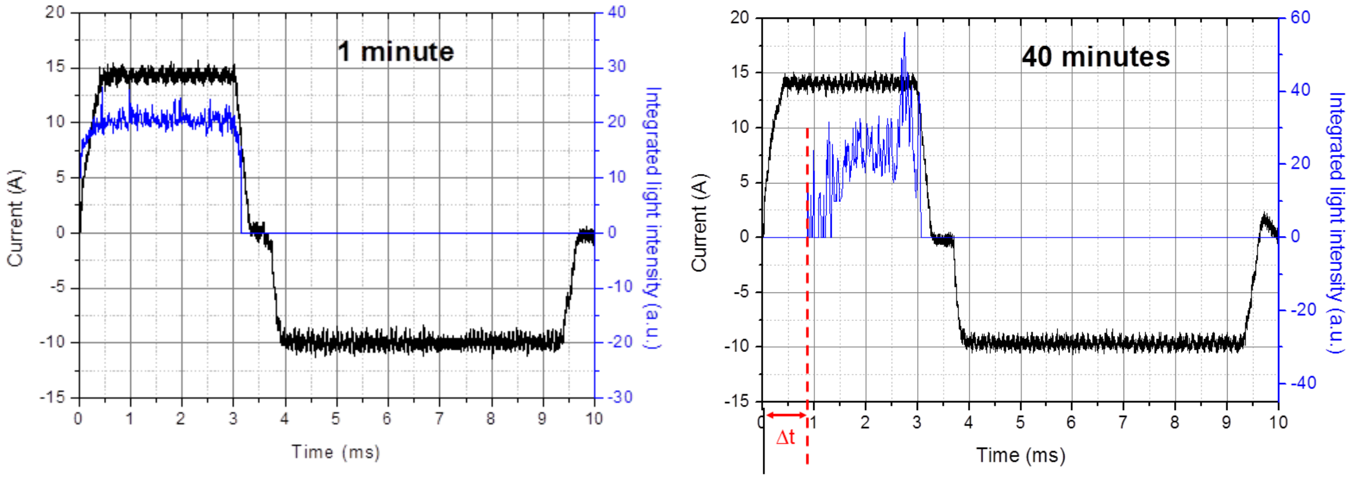

Figure 21: Evidence of the delay between the rising edge of the current (black curve) and the light emission (blue curve). The delay may reach about 1 ms at long process time while it is zero at the beginning of the process. Note also that there is no light emission during the cathodic half period of the current

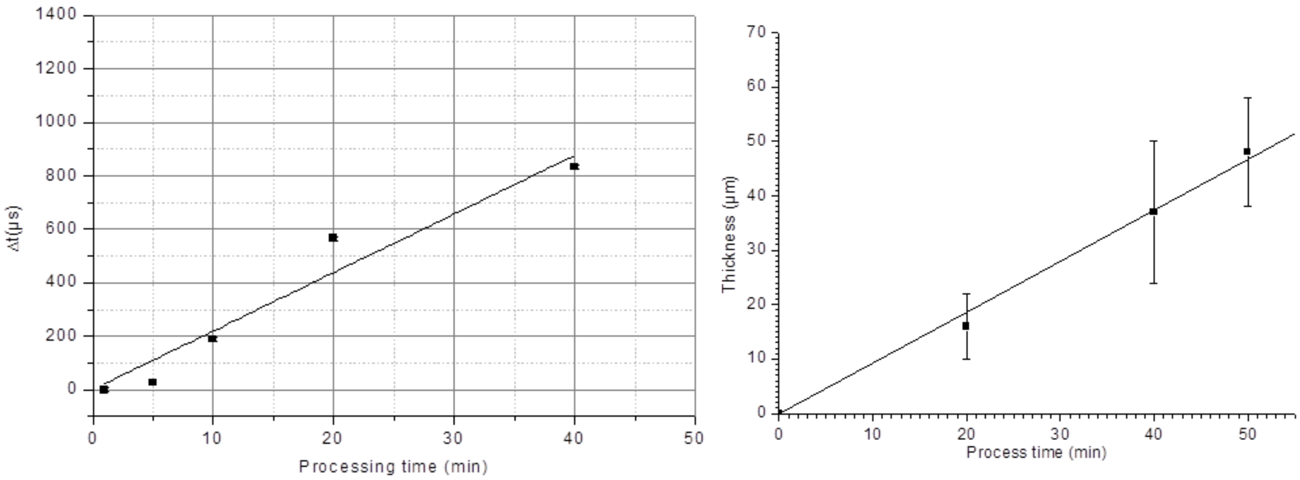

Figure 22: Variation of the breakdown delay (left) and of the layer thickness (right) with the processing time.

As the delay seems to depend on the layer thickness, one would also expect it to depend on the current density which would confirm that it is related to the breakdown mechanisms. This dependence is illustrated in figure 23 which points out that the higher the current density, the faster the delay growth.

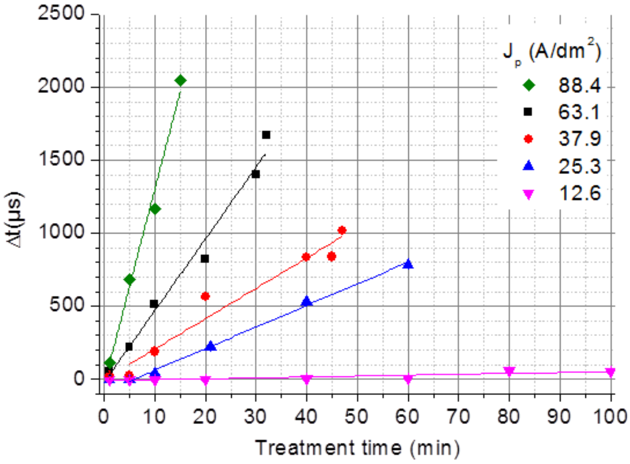

Figure 23: Variation of the breakdown delay with the process time for different process conditions. Al2214, F=100 Hz. See also fig. 17 to compare with the layer thickness

6.3 –Al2214 vs Al2024

In order to validate these results in the case of Al2024 aluminum alloy grade, comparative measurements were performed on both alloys. Results concerning voltage amplitude, and MDs characteristics (breakdown delay, light emission, surface density, surface location, lifetime and size) are reported in figures 24 to 31. For all these measurements, the process conditions were set as follows:

Current frequency:	F = 100 Hz
Anodic current amplitude	I_p = 15 A
Anodic current density	J_p = 38 A/dm^2
Anodic to cathodic current ratio	R = I_p/I_n = 0.59
Charge quantity ratio	r=Q_p/Q_n = 0.89
Electrolyte composition	KOH = 0.018 M / Na_2SiO_3 = 0.013 M
Processing time	t = 40 min
Acquisition rate	125000 frames/second

It clearly appears that there is quite no difference in the behavior of micro-discharge in both cases.

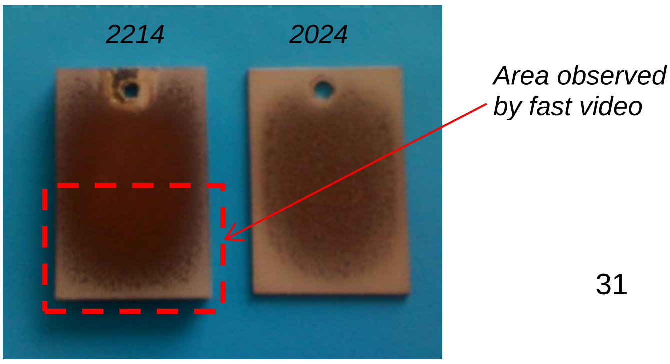

Figure 24: Picture of two samples and identification of the investigation zone

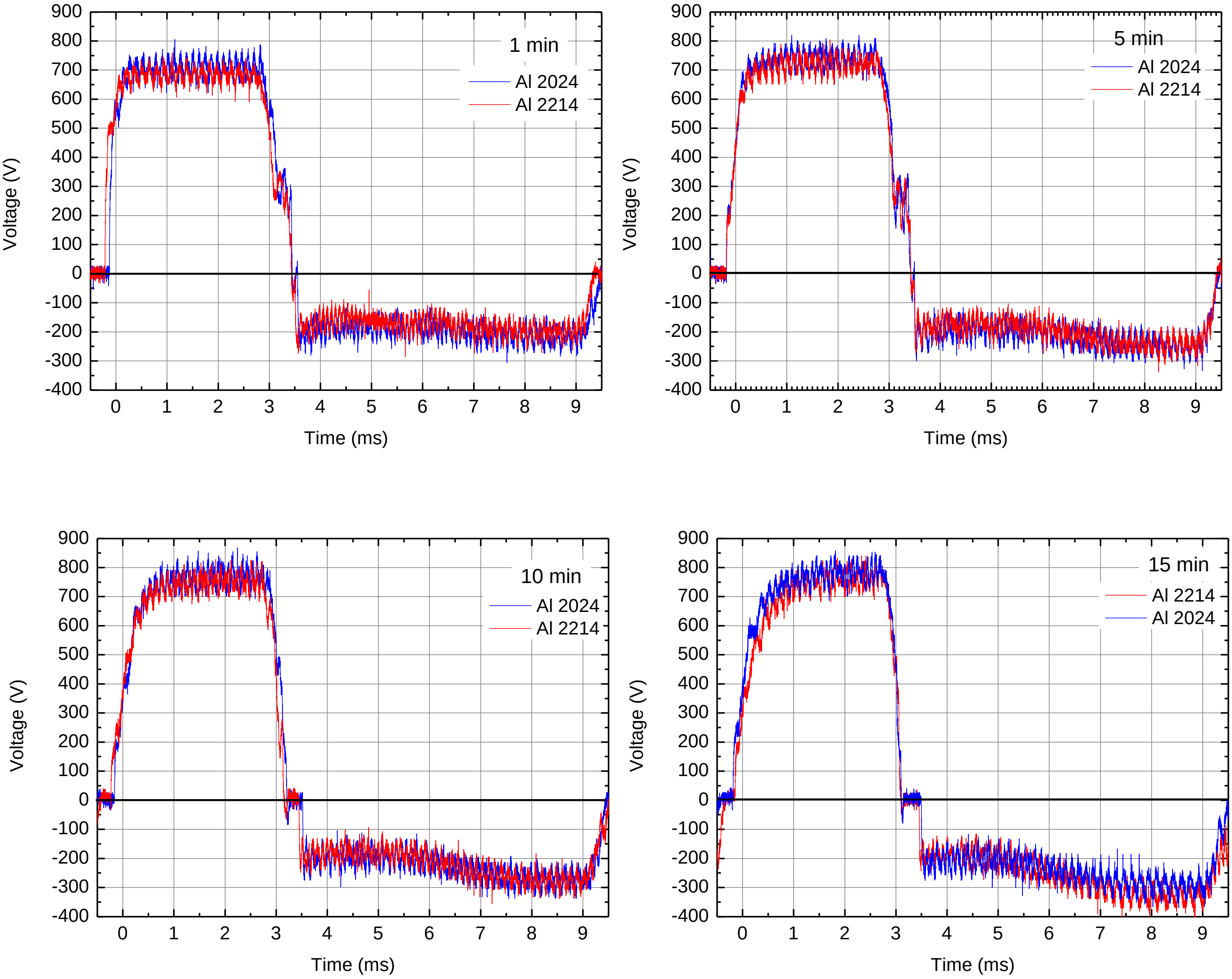

Figure 25: Variation of the resulting voltage at different process times

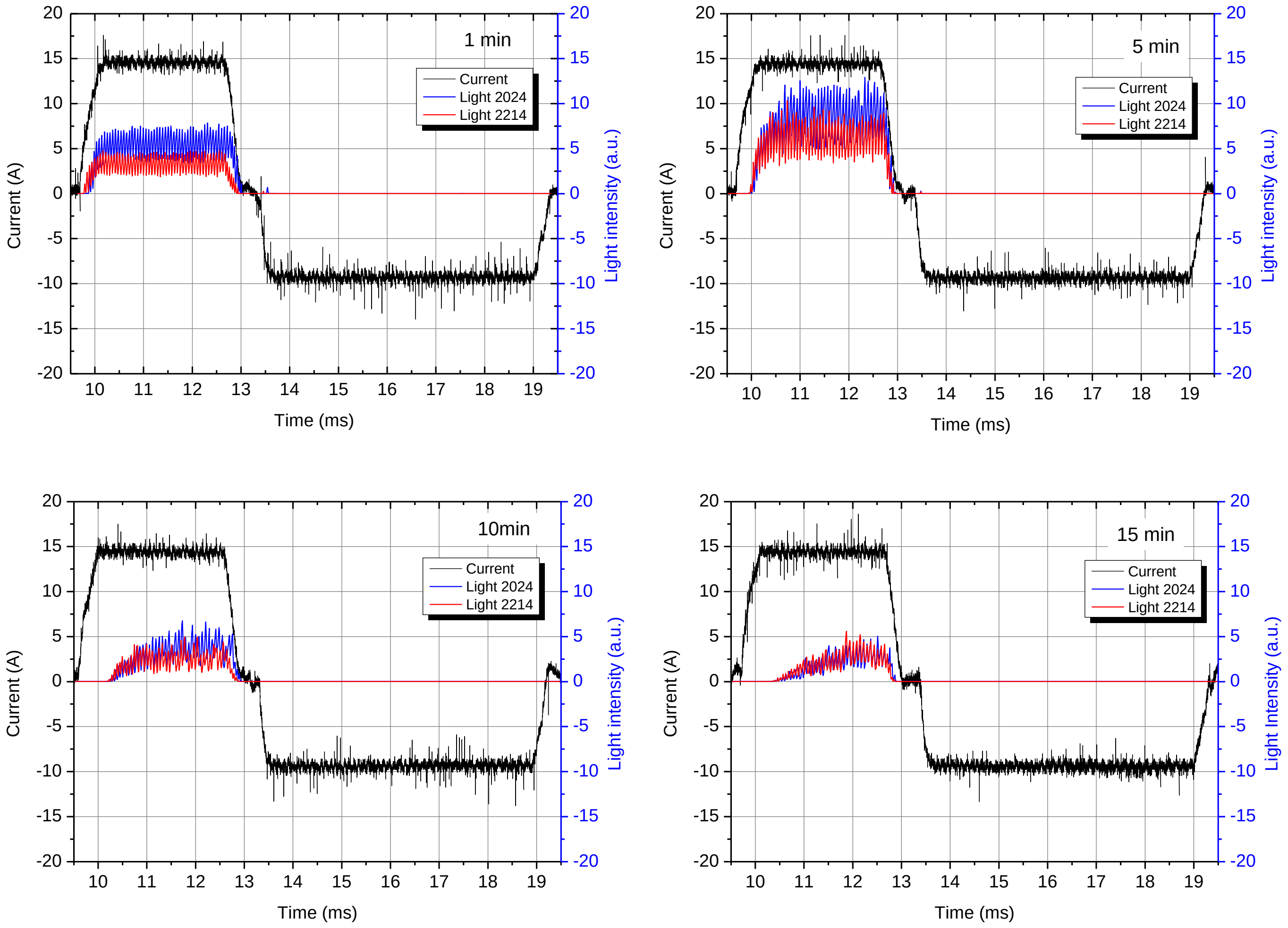

Figure 26: Variation of the MDs light emission with respect to the current pulse

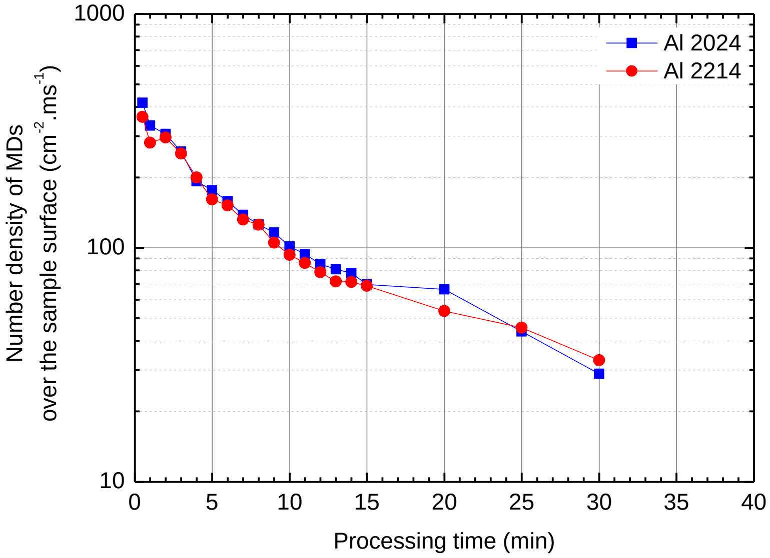

Figure 27: Variation of the number density of MDs over the sample surface with the process time

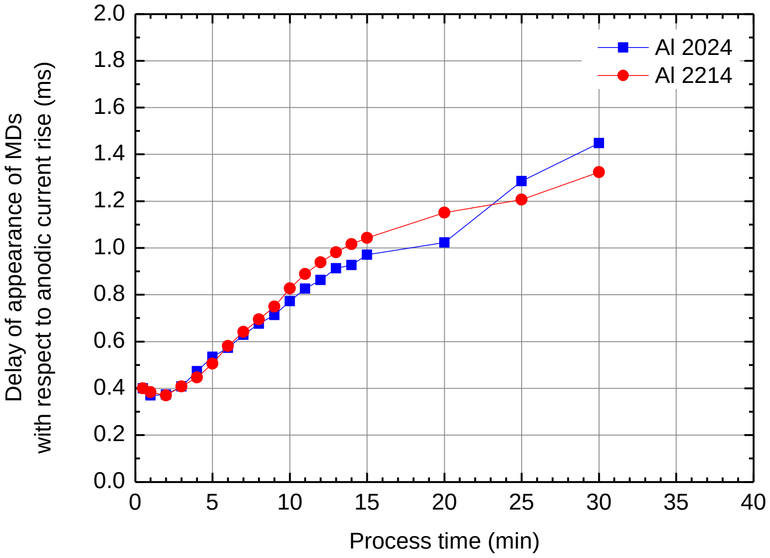

Figure 28: Variation of the breakdown delay with the process time

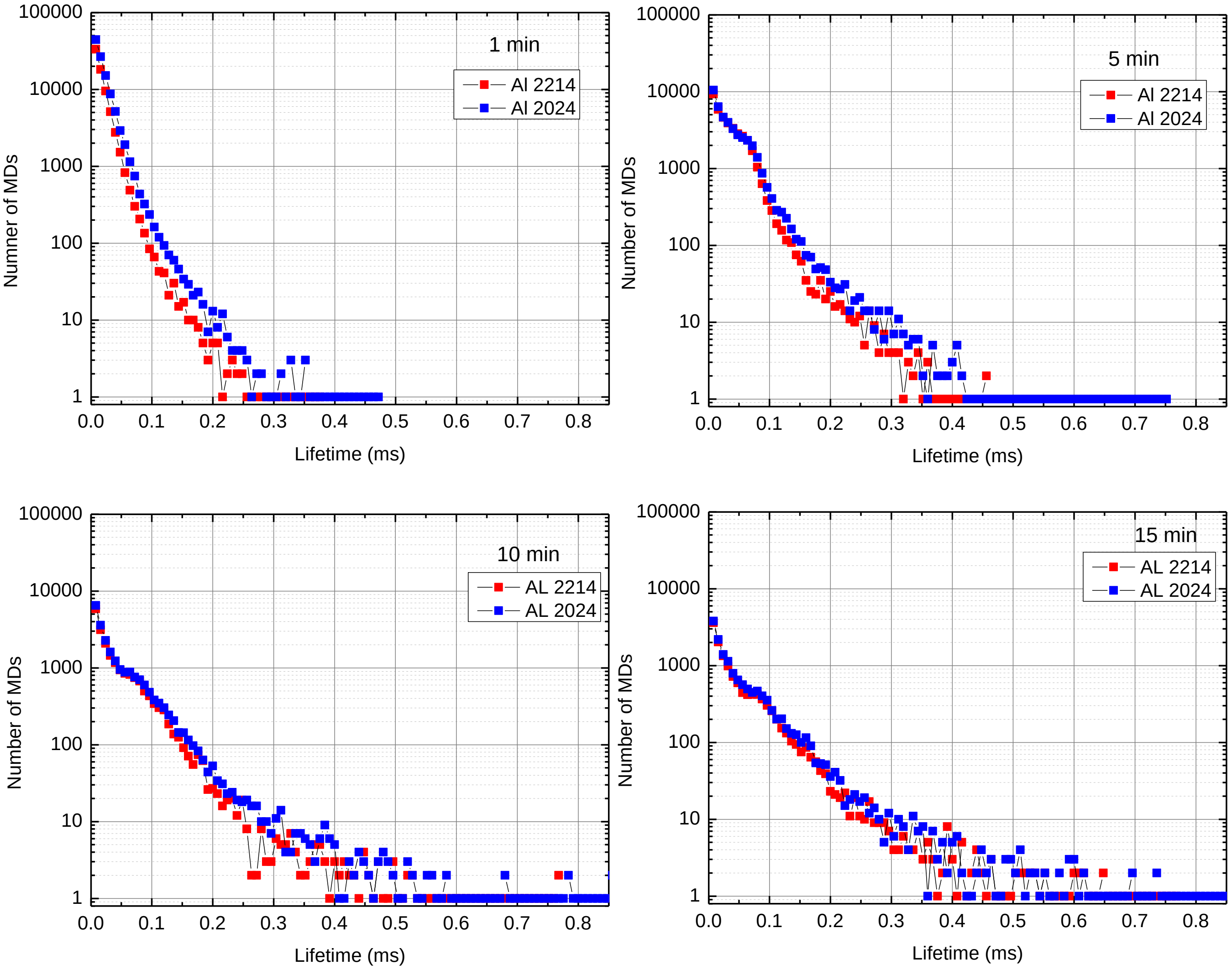

Figure 29: Variation of the MD lifetime distribution at different process times

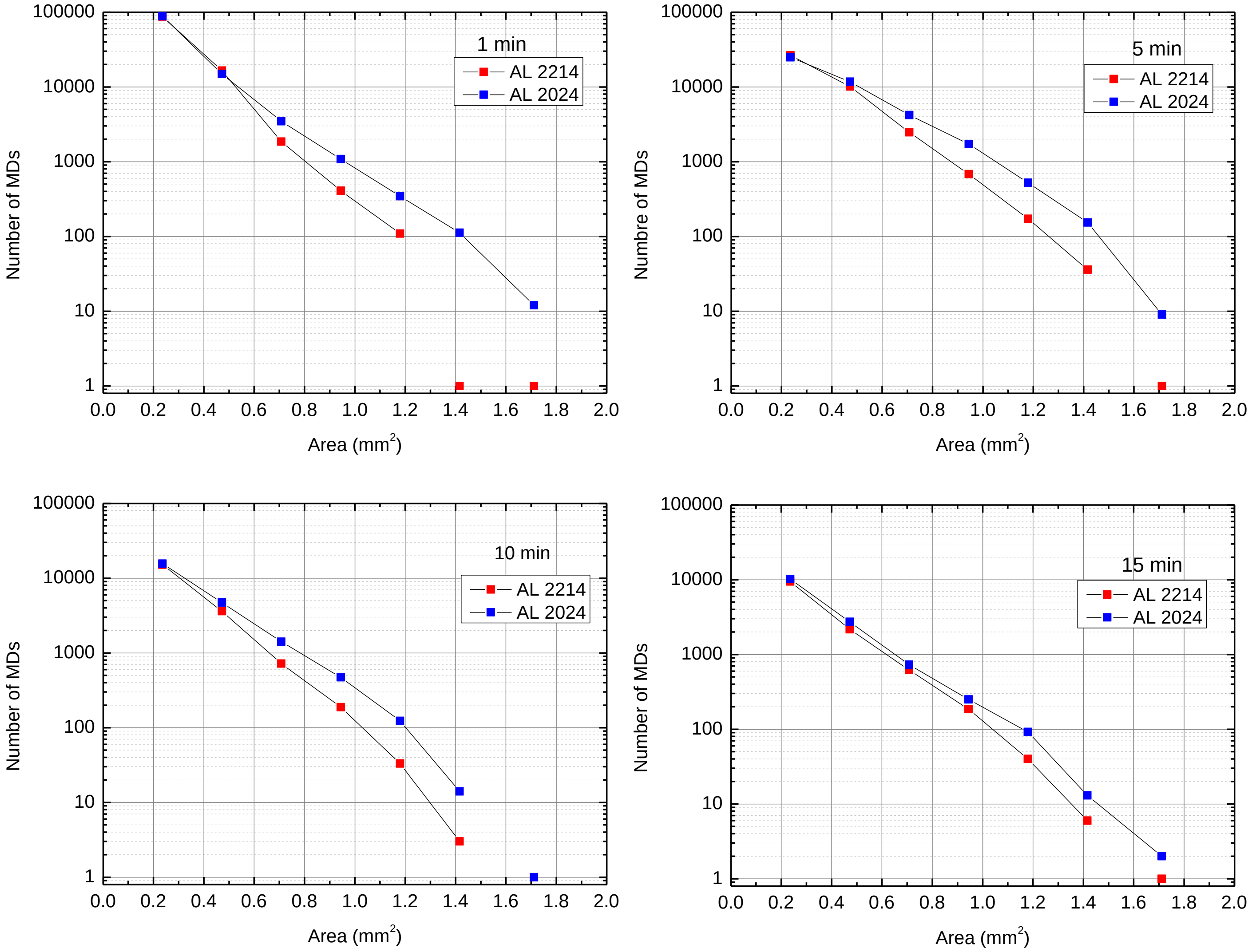

Figure 30: Variation of the MD size distribution at different process times

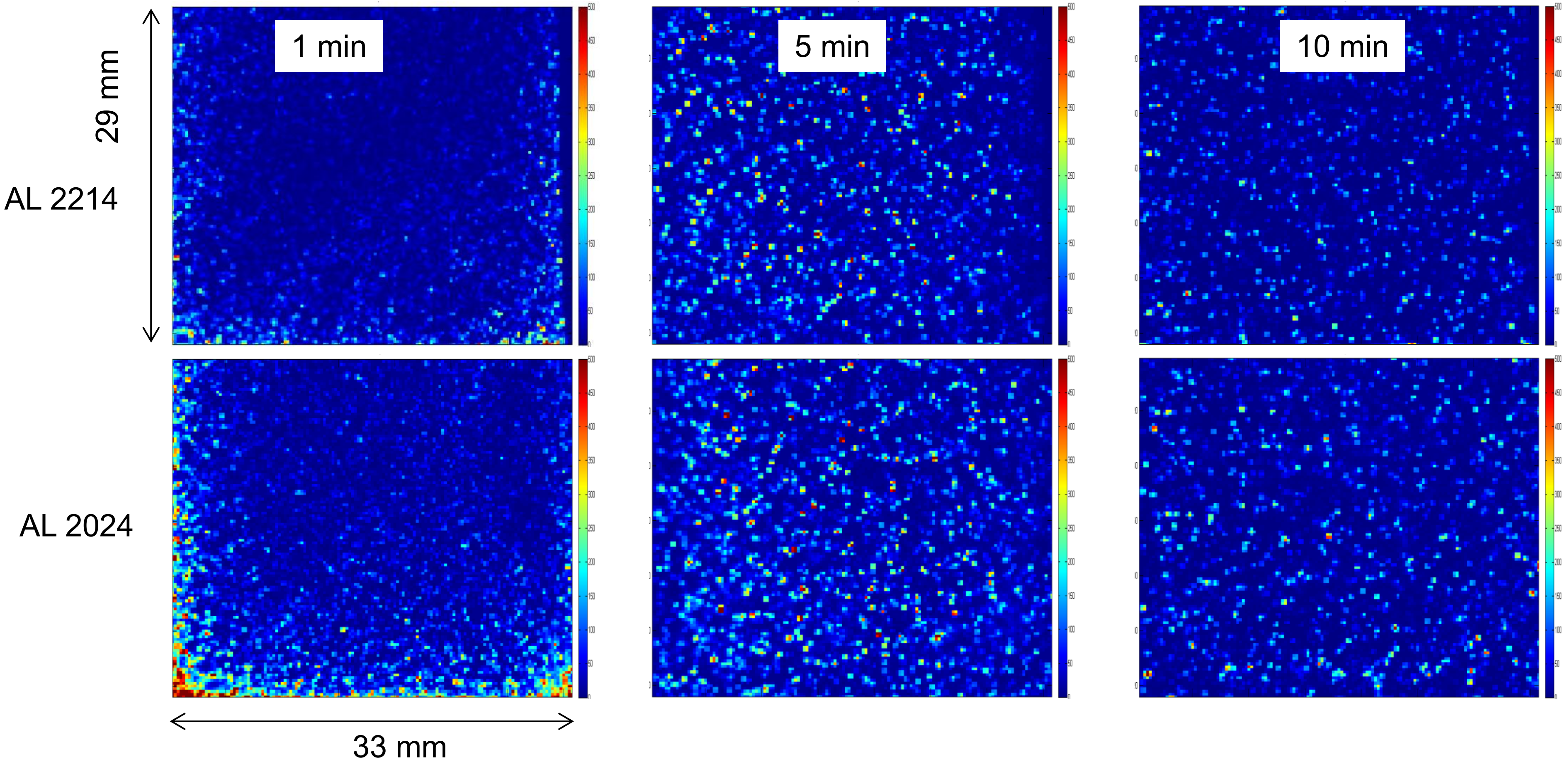

Figure 31: MDs space distribution over the sample

6.3 – Breakdown and growth mechanisms

From these results, some growth mechanisms have been proposed.

First, as the sample is immersed in the electrolyte and the current start to flow, an oxide layer starts to grow as a conventional anodizing process. As the dielectric layer is thick enough, only few current continues to flow through porosities and defect while a quantity of charge accumulates at the electrolyte layer interface. As a consequence, the electric field across the oxide layer increases up to reach the breakdown field. Hence the dielectric layer breaks down thus resulting in micro discharges which permit the accumulated charge to be released through the discharge channels. Meanwhile the oxidation process can continue inside the discharge channel. As all accumulated charges have been driven in the discharge, the process repeats for another sequence of charge accumulation and so on.

6.4 – Deliverables

Regarding this work package, the following deliverables were expected:

D4.1: Fine characterization of the micro-discharges.
D4.2: Results on the plasma surface interaction.
D4.3: Description of the growth mechanisms.
D4.4: Samples processed with optimized parameter conditions.

It is obvious that sections 6.1 to 6.3 above correspond to deliverable D4.1 to D4.3. Breakdown mechanisms are related to the plasma surface interaction (D4.2). However data from emission spectroscopy and fast video recording of the MDs are still under analysis to improve our understanding of the mutual effect of the discharge and of the material. Indeed, some very recent results within specific conditions showed that it is possible to ignite MDs during the cathodic half-period of the current while no MDs appear during the anodic one. As a consequence of that observation which has never been reported, new breakdown mechanisms and a new plasma-surface interaction are under investigation.

However, the study of micro-discharge characteristics did not allow us to establish direct relationships between MD parameters and coating properties. Consequently, D4.4 could not be achieved except within the PEO parameter sets as defined in WP2 (§4) and WP3 (§5).

7 - Work package 5: *Up scaling and technology transfer*

No processing of real part as schedule in the DoW has been processed until now. Indeed, most efforts have been devoted to establish process conditions that would be suitable to reach the requirements in terms of corrosion resistance. As no significant results were achieved yet regarding corrosion resistance, we felt that the treatment of actual parts was premature. However, as some end users are still interested in processing actual parts, this task is scheduled to be done at GIT facilities within the near future. It is thus expected to MAO process Mg EV31 part typical of transmission case castings. This would be performed provided the part sizes are compatible with the MAO vessel dimensions.

8 - Conclusion

The objectives of this project were to find out the most influent parameters on the plasma electrolytic oxidation process applied to Al2024 and Mg EV31 alloys and to define suitable conditions to improve the MAO layer properties in terms of corrosion protection of these alloys.

Investigations were focused on the electrical parameters (current waveform, current density) the geometry (position of the electrodes relative to each other) and electrolyte composition. Investigation of the behaviour of the micro-discharges were also undertaken to both improve our knowledge of the MAO process and to get a better understanding of the plasma surface interaction in this particular condition.

Regarding electrolyte composition, it was established that only silicate (for Al), phosphate and fluoride (for Mg) additives in potassium or sodium hydroxide have an influence on the properties of the resulting MAO coating. On the other hand, to complicated (containing too many or complex additives electrolytes do not change significantly the resulting layers. Nevertheless, none of the achieved coatings passed the requirement in terms of corrosion resistance without sealing post-treatment.

For what concerns the electrical parameters, it was chosen to work within the "soft" regime that was established prior to the beginning of the coproclam project. The particularity of this regime consists in choosing a current waveform with a positive to negative charge quantity ratio less than one. While satisfying this regime, the current frequency and current amplitude (anodic and cathodic) were the main current parameters that were investigated. As reported above, a medium the current density (< 20 $A.dm^2$) appeared as the most suitable range to grow MAO coating while limiting the detrimental effect of arcing. Meanwhile, increasing the current frequency (up to 500 – 700 Hz) also resulted in better results. A few tries (subcontract) with a high frequency generator were performed which did not really showed significant changes in the MAO coating.

A common aspect to all investigation concerns the layer thickness and thickness homogeneity. Indeed, whatever the process conditions, a huge edge effect was evidenced with thickness gradient that could be as large as 50% between the edge and the centre of the sample. It was also evidenced that it would be difficult to achieve a good corrosion protection with MAO coating with only few micron thickness as requested since too much pores remains in the thin coatings due to MDs impacts. Cr VI free sealing (on Al) was successfully achieved on thin layers.

Finally, the physics of MDs was investigated in the case of Al alloy. Though these investigations helped us to describe and understand the MDs behaviour and the breakdown mechanisms as well, no clear conclusion on the relationships between MDs parameters and coating properties could be drawn. Recent experimental data (out of the coproclam project) open now new way of investigation which is expected to shed light on the effective role of the cathodic half-period of the current on the growth mechanisms. Such investigations are on the way.