Executive Summary:

The objective of this research was to develop improved functionality and new coating applications for aluminium anodisation processes in surface engineering. Project Nanocoat has advanced recent innovations towards preparation of ordered nanoporous, nanostructured materials using anodisation methods and applying them to develop commercially relevant novel materials and address the market potential for these improved materials. The nanostructuring process is the growth, during the anodising process, of nanoporous films consisting of well-ordered pores of Anodic Al Oxide in hexagonally close-packed distribution with large aspect ratio. The concept of self-assembly is not yet implemented in actual anodising Al processes due to a number of bottle-necks; project Nanocoat aimed at developing a pilot line equipment and methodologies enabling to overcome them. The objective was to solve actual market needs by achieving the single stage treatment and industrial evaluation of nanostructured aluminium alloys. The overall research methodology of the Nanocoat project followed a progression from detailed laboratory studies through scale-up to applications testing on industrial aluminium grades under industrial relevant conditions, to evaluate their structural and functional characteristics, the reproducibility of the process, and to deliver to end-users suitable test structures as predemonstrators. It was expected that on controlling the formation of the anodised nano-size cell structures on aluminium it is possible to achieve novel performance in terms of adherence, wettability, corrosion and wear, and adsorption/absorption properties. The scope of applications is very large in the field of surface engineering. The specific anodising markets addressed during the project are concerned with improved functionality and new coatings for traditional anodisation processes. In addition, new markets and applications have been assessed, which are based on the enhanced performance of these coatings.

Project Context and Objectives:

Nanomaterials? They measure from 1 to 100 nanometers, are smaller than a virus, but bear huge promises for industry, but also energy, health or multimedia areas.

For more than a decade, nanomaterials have entered our daily life, but here the goal was to know more about some industrial applications: the project results are expected to have a significant impact on the competitiveness and economic performance of the SME participants by expanding existing markets and developing new applications. The project outputs will demonstrate clear market potential and will address specific technology market demands for improved functional anodised aluminium materials derived from nano-structured surface coatings.

Conventional processes for anodised aluminium oxide products are well established across the range of market applications. Standard, long-established manufacturing technologies are in use throughout Europe.

Anodising aluminium is a proven industrial manufacturing technique for improving corrosion resistance, increasing material strength and introducing cosmetic finishes such as metal colouring. Anodic Aluminium Oxide (AAO) industrial products include:

- Decorative or coloured Al surfaces: sealed colourless; electrochemical or chemical colouring
- Anodised base for organic coatings: liquid or powder painting processes
- Corrosion resistance: Hard anodising to produce hard films on Al and its alloys with excellent abrasion & corrosion resistance.
- Adhesive bonding: Porous coatings as primers for surface bonding Al.

The introduction of markedly different technological approaches, which offer significant enhancements in properties and therefore provide differentiation from existing products, will create new market opportunities. The proposers consider that the innovative templated anodisation processes in this research will provide the necessary product differentiation.

The output results will be implemented by the Surface Finishing industry. The impact of the sector is very broad, because of the wide range of products that play a critical role in industries of great strategic importance to the EU. Examples include: civil and military aerospace and maritime, construction, industrial hydraulic applications, automotive, construction, chemicals, food etc.

Companies carrying out these large manufacturing activities in important industry sectors are all customers of the SME manufacturers that form the vast majority of the Surface Finishing/Engineering sector.

Any important impacts on the European surface treatment industry are highly significant to Europe as the sector employs more than 500 000 persons for a total turnover of €40 billion. This industry has over 30,000 SME members in Europe, with the majority employing less than 20 people. The vast majority of these companies are also categorised as SMEs in terms of turnover. The biggest group (53%) has an annual sales volume of between 1 and 5 million Euros.

The industry is broadly distributed across all EU countries. In the vast majority of cases, the types of processes carried out are largely the same wherever they are applied. Typically, SMEs produce components that are sold to end user companies, often very large, who incorporate these components into final products.

The result is that there are no significant geographical barriers. Also, competition between SMEs tends to occur relatively locally, often within single countries, so there are few geographical inter-regional competition issues acting as barriers between SMEs.

This SME intensive industry sector is under increasing competitive pressure from the global market, particularly competition from regions with lower intrinsic costs and less demanding legislative controls. In the context of this highly competitive environment, there is a clear need for new technology to produce higher specification and added value products.

Hence there is a strong need for SMEs in general to create their own intellectual property and develop new products with a clear economic impact leading to increased competitiveness.

S&T Objectives

The overall aim of the proposed research is to develop improved functionality and new coating applications for aluminium anodisation products in surface engineering.

The project will advance recent research innovations in research laboratories at RTD participant ARMINES towards the preparation of ordered nanoporous, nanostructured materials using anodisation methods and applying the methods to develop commercially relevant novel materials.

The proposed research will aim to address the market potential for these new and improved materials.

The expertise and capabilities provided by the project participants will ensure that the following S&T objectives can be realistically achieved and verified within the project timescale:

- Research the techniques for producing nano-structured anodised aluminium materials under industrially relevant conditions
- Develop process protocols including pre-treatments and post-treatments
- Scale-up processes for the treatment of larger areas and adapt processes to treat complex-shapes
- Design and construct an experimental prototype system
- Operate the prototype system over an extended period and address scale-up issues
- Use industrial grade aluminium alloys, in addition to pure aluminium
- Carry out full structural characterisation of materials
- Carry out functional characterisation to evaluate the performance of materials across a range of existing and potential industrial applications
- Consider production issues relating to environmental legislation and apply a simplified Life Cycle Analysis methodology
- Complete a full techno-economic assessment of the project outputs
- Develop a plan for exploitation and dissemination

Project Results:

The anodisation of the aluminium is well known as an industrial process used in many applications in which, subsequently at an electrochemical oxidation by anoding process, it is possible to increase the thickness of the alumina layer naturally present when aluminium is in contact with the oxygen (and water) present in atmosphere.

Objectives of the anodisation processes are essentially devoted to anti-corrosion, decorative, wear resistance purposes. The formation of oxide on the surface of the aluminium protects the metal: the oxide layer, even it is porous, presents a good resistance to the corrosion due to a barrier layer formed at the interface of aluminium metal and oxide layer. The properties of this oxide layer could be improved by controlling the aluminium anodisation process and by using specific parameters.

In particular, important research works have been done since about twenty years to control the layer formation to obtain a special structure which is interesting: the anodic aluminium oxide grown in hexagonal nano-structure, well ordered, if parameters of anodic oxidation are well controlled. This growing is linked also to the nature of the aluminium substrate: pure Al, Al alloys, Al with inclusions...

The goal of the first workpackage (by ARMINES) is to determine and define the parameters of the process for each nature of Al substrate to obtain a regular structure of the anodic aluminium oxide depending on aluminium composition and geometrical form.

In particular:

- To define and select operating parameters to generate porous layers with regular arrangements (nano well-ordered structure) over the widest range of surfaces and substrate
- To define the operating parameters to transfer the results at an industrial level.

1 Anodisation techniques

1.1 Marking and double anodisation

Two methods can be used to initiate the arrangement of the structure: pre-texturing or double anodisation method (see figure 1 in annex I). Both goals are the same: creating a network of nano-cavities on the surface of the substrate which are the “germs” of the nano well-ordered structure.

- The pre-texturing method consists in engraving the surface of the substrate using a gauge to pattern the surface following the wanted structure inscribed in a “negative” form compare to the structure to be obtained. The pattern corresponds to the cell size of the future ordered nanostructure.
- The double anodisation method consists of making a first anodisation to start the ordered structure as the scheme (figure 2 in annex I) shows the principle. This first oxide layer created is completely dissolved in acid solution. The oxide layer is completely removed of the aluminium substrate and lives on the surface marks of the ordered structure. The second anodisation starts from theses marks and grows in a nano well-ordered form.

In the course of the Nanocoat programme, we used only the double anodisation method because it is the method which allows obtaining large nanostructured surface, the pretexturing method is somewhere limited in area and is only used to engrave surfaces equivalent to the surface of the mold.

In the case of double anodisation process, the first anodisation layer (oxide layer) is dissolved in an etching solution of 6% H3PO4 and 1.8% CrO3.

2 Laboratory equipments

Systems used in the laboratory for the first results are presented in the picture (figure 3 in annex I)

The electrolyte is in a double wall glass tank with an approximately volume of 1.5 liter. As the anodisation is an exothermic reaction, the electrolyte has to be cooled to control the temperature of the solution. The coolant is on the external part (blue on the picture): an external cooling system allows regulating the temperature of the cooling liquid at a fixed value which is linked to the wanted temperature of the electrolyte. The nature of the electrolyte studied is variable and described in next paragraph.

This equipment is sufficient for small samples but for larger one, the volume of electrolyte has been increase to about 10 litres. The pictures (figure 4 and figure 5 annex I) show the equipment with the cooling system and electrodes.

This configuration with a larger volume allows the possibilities to realize anodisation of larger samples even a higher power is necessary (same voltage but higher intensity), without temperature variations during the anodisation process (increasing temperature by Joules effect).

3 Process to obtain anodic aluminium oxide ordered

3.1 Samples

In a first time, we used only pure aluminium samples from Goodfellow (samples bought to Goodfellow Company), with a purity at 99.999 % (ref: AL0006920) in sheet of 1 mm thick.

To obtain a regular structure, these samples have been polished mechanically with SiC abrasive paper from P640 to P4000. Then the surface is polished with fibre plate and diamond solution from 3µm to 1µm.

3.2 Etching

Before anodising, the aluminium sample is etched by phosphoric acid at 10 % during 30 minutes to remove the native oxide layer.

The roughness of the surface has been monitored and standard results obtained by mechanical profilometry measurements are:

- starting aluminium : Ra = 240 nm – 300 nm Rz = □ 4.3 µm
- after polishing : Ra = 60 nm – 90 nm Rz = □ 1.5 µm

3.3 Anodisation : Influence of the electrolyte

Following our experience and a literature survey, it appears that the nature of the electrolyte is one of the criteria which define the size of the pores.

Literature indicates that 3 different types of electrolytes have been investigated and could be used: sulphuric acid, oxalic acid and phosphoric acid.

Tests with each of recommended electrolyte have been conducted during the first part of the programme.

SEM Observation after the second anodisation are shown in annex I (figure 6)

The structure is ordered and the size of the pores is around 25 nm in diameter. The interpores distance is about 60 nm. Thickness of the oxide layer after 2 hours is approximately 6 µm.

SEM Observation after the second anodisation are presented in annex I (figure 7)

The structure is ordered and the size of the pores is about 35 nm in diameter and about 95 nm for interpores distance. Thickness of the oxide layer after 2 hours is approximately 16 µm.

SEM Observation after the second anodisation are presented in figure 8 (Annex I)

In the case of Phosphoric acid, the structure seems to be less ordered but the pore size is larger: around 120 nm in diameter for pores and around 150 nm for interpores distance. Thickness of the oxide layer after 2 hours is approximately 8 µm.

When phosphoric acid electrolyte is used, it has to be noted that the recommended value for voltage between anode and cathode is around 190 V. But due to our rectifier characteristics, it is impossible to increase the voltage to this high value and the voltage has been limited at about 160 V (maximum of our rectifier).

3.4 Anodisation : Influence of the double anodisation

SEM pictures of the surface of the oxide layer results are presented in figures 9 and 10 (Annex I): they have ben obtained after a single and a double anodisation in an oxalic electrolyte.

After the first anodisation process, the nanoporous structure is created but the pores are not well ordered neither well define (figure 9). The pores seem to be unevenly present on the surface of the structure and the size of the holes and cells are different.

However, after the double anodisation process the pictures (figure 10) showing the surface of the alumina structure, show the interest of the double anodisation on the nano well-ordered structure.

3.5 Anodisation : Shape of the subtract

Usually the sample comes from a sheet of pure aluminium (figure 11). Trying to study influence of the sample geometry, anodisation of a small cylinder (6 mm diameter, lengh 7 cm) of the same aluminium purity (99.999% Al) from Goodfellow Company has been realised. This anodisation process on pure aluminium cylinder has been realised in an oxalic acid solution, using same parameters as for flat samples. The aluminium oxide layer grows with an ordered structure as for flat samples after a double anodisation process.

As presented in pictures 12, annex I (SEM examination at different magnification) formation of a well-ordered structure on surface of cylindrical samples (diameter 6 mm) is not influenced by the shape of the substrate.

3.6 Anodisation : Influence of the purity of the aluminium

Influence of the substrate purity has been studied on Aluminium alloy (AG3-5754) compared to results obtained on pure aluminium. Results of SEM examinations are presented in figure 13 annex I.

Structure on AG3-5754 is more irregular than for pure aluminium sample even an ordered structure appears in the alumina obtained on these alloys: some perturbations are present in the network of the structure. The presence of foreign atoms in the alloys disrupt the formation of alumina column and so the formation of the nano well-ordered structure.

As for alloys, impurities (precipitate) included in the aluminium influence really the arrangement of the structure.

The influence of inclusions in the substrate has already been investigated during the PhD research works of Pascal THOMAS in EMSE Laboratory (2008). Results shown that these impurities give perturbation in the formation of the well-ordered structure: due to the nature of impurities, formation of alumina structure is impeded and so some defaults appears in the ordered structure.

3.7 Anodisation : aluminium alloys

One test has been made with an aluminium alloys (Aluminium series 2XXX) which contains approximately 4% of copper. In this case the well-ordered structure is not present. However an adjustment of parameters could improve the quality of the structure and the determination of well-ordered parameters will be discuss in following paragraphs.

3.8 Anodisation : Influence of the surface preparation

Following our experiments during the WP1, surface preparation is important to obtain well ordered structure.

Surface of samples has to be degreased (acetone + water +ethylic alcohol) and polished before first anodisation.

The necessity of polishing is important as growing of pores occurred perpendicularly to the surface and so if the surface is too rough, pores cannot grow in an ordered manner.

Mechanical polishing and electrochemical polishing have been compared and results appear to be equivalent. This is due to the fact that during the process of double anodisation, the first step (first anodisation) removes the strain-hardened layer created during mechanical polishing. Picture 14 shows results obtained after mechanical polishing and electrolytic polishing (H_3PO_4 - 66%vol. + H_2SO_4 - 33% vol. at 75°C, 150 mA/cm², duration 10 min.). There is no real difference between the two types of preparation.

However, voluntarily, no solution using chloric, or perchloric acid and/or other chemical hazardous components has been tested and used during the programme as industrial applications would be hazardous

3.9 Anodisation : Influence of the temperature

Previous experiments (Cf PhD thesis of P. THOMAS) have evidenced that the optimal temperature to obtain ordered structure is between -3°C and 20°C. When the temperature increases it occurs a degradation of the nanostructure between 30°C and 40°C (for oxalic acid) and at a temperature higher than 40°C the structure is clearly disordered.

During the Nanocoat programme, more experiments have been done to define the exact influence of the temperature, in particular using different solution and substrate composition

3.10 Pores opening

The size of the pores could be enlarged by dissolving a part of the wall of cells. The dissolution of the aluminium oxide is made by etching the sample in phosphoric acid.

SEM examination of nano-structured surface in oxalic acid at different magnification before and after opening pores operation are given in Annex I (figure 15).

3.11 Coloration of the anodic oxide layer

The aluminium anodic layer could be colored by filling porous structure by different solution or by electrolysis. Some tests have been done in cooperation with the Nanocoat Partners ProMet and C-Tech.

4 Anodisation parameters definition

During a meeting of the RTDs performers (Gardanne (France) : November 2011), it appears that some complement of information from Industrial Partner PROMET are important due to the anodisation parameters, more particularly on the electrolyte and on the voltage control.

PROMET makes industrial hard anodisations by using the already defined high concentred electrolyte composed by mixing sulphuric acid (2.2 M) and Oxalic acid (0.2 M) at a temperature of -3 to 0°C.

More, the process itself is slightly different as for industrial reasons (too important intensity at the beginning), voltage of the anodisation process is increased from 0 to approximately 40-50 V in 5 minutes then a stable period is running for 1 hours, anodisation is ending by an increase of the voltage to 60 V. At the laboratory scale, the voltage is increased very rapidly and maintained constant along the anodisation process.

For the final application it will be interesting to know exactly the differences on the final layer.

But as a results of this meeting, it was decided that the anodisation solution which will be used in the future will be the PROMET solution: 220g/L (2.2 M) of H_2SO_4 and 15 g/L (0.2 M) of Oxalic acid $(COOH)_2$.

4.1 Specific electro formulation

As shown in the previous paragraph 4.3, the diameters of the pores depend on the nature of the electrolyte. The table here after summarise the composition of the different electrolyte used during the Nanocoat program.

4.2 Operating protocol

Investigations to define the better condition of anodisation have been made and this protocol will be used for all samples produced in laboratory conditions.

- Samples (2 x 6 cm) are taken from pure aluminium plate (Goodfellow supplier).
- Surface preparation is rtealized by polishing the sample with different paper of SiC and Diamond solutions to obtain mirror surface without scratch.
- Before anodisation, the sample is degreased with acetone and etched in a H_3PO_4 (10%) solution at room temperature during 30 minutes.
- The voltage is progressively increased to the value wanted without limitation of current.

- The time of the first anodisation has been fixed at 3 hours to be sure that the structure is well ordered.

- After the first anodisation, the sample is rinsed and the oxide layer is dissolved in a solution of 6% H_3PO_4 and 1.8% CrO_3 during 2 hours to remove completely the oxide.

- The sample is then rinsed again and dried: so it is ready for the second anodisation.

- The second anodisation is made using the same protocol for electrolytical parameters.

- The duration of the anodisation process is defined in accordance with the oxide thickness intended.

4.3 Industrial application

Tries for application of the Laboratory parameters to industrial hard anodisation have been made in the PROMET premises. During common tests made in May 2012, double anodisation process has been tested in an industrial environment on pure aluminium sheets (A5 format).

1 – The first sample (S1) has been hanged on a titanium jig (PROMET system) for the first anodization procedure:

- Surface preparation: etching in soda solution, acid etching in proprietary (PROMET)solution - Rinsing after each operation.

- Anodization in a tank (1000L) solution (- 3°C): 220 g/L H_2SO_4 – 15 g/L Oxalic acid at 20 V during about 40 min. (ramp of current) – 2 to 3 A/dm²

- Coloration in mineral black solution (commercial)

- Result: coloration of S1 seems to be “pale” on about half of the surface due to an insufficient thickness of the alumina layer

2 – Definition of the operating procedure:

- Dissolution of the first anodization for the first sample S1□second anodization of first sample S1

- In the same time and operation, first (and single one) anodization for the second sample (S2) same conditions as previously except: duration 100 min. voltage is increasing from 20 V to 40V progressively

- Coloration of the two samples (single – S2 and double anodization S1) in mineral black solution
- Sealing in a proprietary solution (boiling aqueous solution with acetate salts)

Results and report made during these tests are presented in the D6.2 deliverable.

Following some difficulties in the realisation of the anodisation in PROMET company (essentially due to the new formulation of the electrolyte: mixed of sulphuric and oxalic acid), tests in the same condition (using the industrial bath) have been made in Laboratory of EMSE/ARMINES.

Conditions and parameters of the tests are given in the following table.

Examination of structure and results obtained on double anodisation are presented in annex I, figure 16.

These different results demonstrate that it is possible to obtain a well-ordered structure on pure aluminium with an industrial electrolyte. Tests to improve the process using sulfo-oxalic acid have been realised. Results rae presented in the following paragraph.

5 Improvement of the anodisation parameters

After definition of the electrolyte composition, the others parameters having an influence on the anodisation process have been investigated.

5.1 Improvement of the anodisation parameters using industrial solution (Sulfo-Oxalic acid) (Pure aluminium)

As a general point-of-view, during the first anodisation, the internal evolution of the structure becomes homogeneous after a lap of time (not necessary well-ordered). So by examination of the structure obtained after a first anodisation it is possible to define if the “stable” structure obtains with the parameters used during the anodisation procedure allows the formation of a nano well-ordered structure.

By examination of the remaining structure obtained on the aluminiuum substrate after dissolution of first alumina layer it is possible to know the conditions for obtaining the best well-ordered structure. The following schema indicates the procedure the first anodisation

If general conditions are correct and well defined the structure obtained at the end of the first anodisation would be well-ordered. The second anodisation following the structure “printed” by the first anodisation, will induce a well-ordered structure. This method allows determining the parameters of anodisation.

The protocol we used to characterize the anodisation parameters is:

- Polish the aluminium
- Make a first anodisation
- Dissolve the aluminium anodized layer
- Examination of the surface by SEM

5.2 - Determination of the better potential on pure aluminium

Following first experiments, it appears that the most important parameter is the voltage between aluminium (working electrode/anode) and counter electrode (cathode). However we have studied also the influence of temperature.

- Influence of voltage

The pictures 16 (Annex I) show results on the aluminium surface (temperature -3°C) after the dissolution of alumina layer obtained by varying the potential: 15V, 20V, 25V, 30V, 35V, 40V, 45V.

Following these results, the best potential is assumed to be 35 to 45 V, but due to the joules effect and cost reason, the potential used will be 35 to 40 V.

This method of “ordered-potential” determination will be used in the future for industrial aluminium alloys.

Same experiments have been used for the determination of the best temperature. As a result, the best temperature has been defined to be -3°C to 0°C.

5.3 Influence of the temperature of the electrolyte

SEM Observation of the surface after one anodisation and dissolution of the alumina layer are presented in figure 17 (annex I).

The samples made a 20°C shows a nano structure but not a nano well-ordered structure compare with samples made a 0°C.

5.4 Determination of the better potential on aluminium alloys 6082

As previously indicated, observation is made on the surface after dissolution of the alumina layer.

SEM Observation of the surface after one anodisation is presented in figure 18 (Annex I). A high potential is also requested to obtain an ordered structure. This conclusion has been verified by realization of double anodisation on Aluminium alloy (6082).

The structure appears nano well-ordered, even if it is less ordered than on pure aluminium.

5.5 Determination of the better potential on aluminium alloys 2024

SEM Observation of the surface after single anodisation and dissolution of the alumina layer are presented in figure 19 (Annex I). During these experiments on 2024, a nanostructured alumina layer has been obtained but it is not well-ordered as for pure aluminium or 6082 alloy.

5.6 Ordered structure on other aluminium alloys (6060 and 5005)

These tests have been made on parts from SOBINCO company which is in contact with a partner of Nanocoat programme the Falex Tribology NV Company. Information on this SOBINCO Company will be provided by Falex Tribology.

1 – Tests in EMSE/ARMINES laboratory

The company SOBINCO is interested by realisation of well-ordered nanostructure on aluminium alloy parts. The interest for this company is to increase the wear and corrosion resistance of parts used in building in particular for decorative application.

For testing the process, SOBINCO company has sent to some partners (C-Tech and FALEX) some parts.

The parts received are part of door: handle part (alloy 5005), door hinge (alloy 6060)

The elemental composition of the aluminium alloys used is different from the alloys tested previously. Composition is given in the following table:

The objective is to obtain a nano well-ordered nanostructure on the industrial samples received. SOBINCO has not been able to give us samples without anodisation process. So the first operation has been to dissolve the alumina layers on the samples before testing our anodisation process. This dissolution has been made by the method currently used, using a mixed of Phosphoric and Chromic (CrVI) acid.

The operating procedure for testing double anodisation process is the following:

- Dissolution of the industrial (Sobinco) alumina layer in $H_3PO_4 + CrO_3$:

o 3 hours at 55°C

- First anodisation in H_2SO_4 (220 g/l) + $(COOH)_2$ (11 g/l) at 40 Volts
- Dissolution of the layer in $H_3PO_4 + CrO_3$ at 55°C
- Second anodisation in H_2SO_4 (220 g/l) + $(COOH)_2$ (11 g/l) at 40 Volts
- Colouring: using C-Tech method

SEM observation of the surface and of the section of the parts obtained on the SOBINCO samples is given in the following pictures.

During this study, by using 40V as potential difference between parts and cathode, it appears that the rate of formation of the alumina layer is greatly improved. This rate of formation is about 7 to 10 µm/min instead of 0.5 to 1 µm/min in the best case for industrial process.

This rate of formation has been verified by PROMET in his jobshop: confirmation of the improvement of the rate of formation using a higher voltage than classical process. This increase in rate of formation was anticipated but the high deposition rate value is interesting for industrial application.

Due to the high voltage inducing high current intensity particularly at the beginning of the anodisation process, the number of parts treated in one operation (on one jig) is reduced. But as the rate of formation of alumina layer is greatly improve (x7 or x10), it is certainly possible to treat more parts during the same time used for previous treatment at lower voltage.

Tests are in progress to complete and to certify these results.

As conclusion, by using a double anodisation, it is possible to create a well-ordered structure on industrial part (and alloys).

The impurities of the alloys have a large influence on the arrangement. This difference in composition explains why the structure of the alloy 5005 is better ordered than the alloy 6060.

2 – Tests in PROMET Lab and workshop on Door parts from SOBINCO

Following experiments and results obtained in EMSE/ARMINES laboratory, PROMET has tested the process on door hinge (6060).

Parts anodisation has been realized by manual and automatic system (drived by PC system) and characterization of the results have been made by SEM examination after dissolution.

Results show that it is possible to realize well-ordered alumina structure in Industrial Partner who confirms also that the rate of formation is higher than expected.

6 Titanium anodisation

By using the same parameters defined for the anodisation of the aluminium, sample of titanium have been treated. An oxide layer has been formed on the surface of the titanium but without a real ordered structure.

A porous structure is visible (figure 20) but it has not been possible to create a well-ordered structure.

At the end of Nanocoat programme, an interesting paper has been found following our bibliography survey “Electrolyte Influence on the Anodic Synthesis of TiO2 Nanotube Arrays” Ref: Journal of Non-crystalline Solids 354 (2008) p.5233-5235 Author: V. Vega & al.

The electrolyte solutions which have been tested by the authors contain Hydrofluoric acid Due to the lack of time, experiments and tests have been not continued on Titanium alloys.

7 Microhardness and Scratch test

Evaluation of the microhardness of the alumina layers has been made by Vickers indentation method.

Results of indentation are shown in the following table, picture of indentation an alumina structure is presented in Annex I, figure 21

8 Conclusions

The double anodisation creates the ordered structure and the alumina well-ordered structure depends on a specific voltage.

During the nanocoat programme, following industrial proposal, the tested solution selected and used has been H_2SO_4 (220 g/l) + $(COOH)_2$ (11 g/l) (PROMET formulation), and it has been possible to obtain a well-ordered structure on pure aluminium and some aluminium alloys, except for Alloy 2XXX series certainly due to the high concentration of copper in this kind of alloys. The oxidation potential of copper appears to be the reason of the lack of success for this kind of alloys. These series of aluminium are well known to have a special comportment in anodisation processes.

Following the demand of Falex Tribology NV company, some parts from a Belgium company specialized in the furniture of aluminium parts (domestics) (SOBINCO) have been tested: it has been possible to realize well-ordered alumina structure on these kind of industrial alloys and industrial parts.

The method developed during the programe has been tested by Industrial Partners (PROMET) and results obtained at Laboratory scale have been reproduced in industrial environment.

Results are innovative as to our knowledge it is the first time that well-ordered alumina structure have been realized on aluminium alloys (5XXX and 6XXX series).

Black coloration (without opening pores) appears uniform and attractive after the double anodisation.

Microhardness of the alumina layer remains constant after simple or double anodisation: formation of pores through the alumina layer do not modified the penetration of the indenter.

Results obtained by nanoscratch tests are non consistant and the method has to be re-considered as it gives too macroscopic results in front of the nanostructure

Workpackages 2 and 3 (C-Tech)

Key Work Packages that have been instrumental in testing the industrial viability of the new process were WP2 (Laboratory scale process design & development) and WP3 (Process scale-up), which were intended to be part of a 3-step scale-up progression from the original RTD studies through to the industrial SME production lines.

RTD work that demonstrated the concept of nano-structured anodised aluminium oxide coatings and inspired the present work, focused on the ability to achieve the structures at the laboratory scale, using equipment not optimised for the industrial environment. C-Tech therefore set about constructing a system designed to emulate a realistic and flexible but reduced version of the industrial anodising lines used by the SME manufacturing partners Promet and Ashton & Moore, complete with all of the equipment necessary for pre- and post-processing parts to be anodised. The stage allowed the process to be studied in a realistic environment while not encroaching on the day to day operation of the full-scale anodising lines. Without the construction and operation of the pilot system, the study would not have been possible.

Initially this progression was intended to be done with an initial scale-up from the lab-scale of the anodising tank to a lab-scale version of the full anodising line, followed by a larger, optimised pilot scale system. At the outset however, it was clear that in order to recreate the industrial process at the first scale-up stage, the balance of plant necessary to achieve practical targets (e.g. process heating and cooling, agitation) constituted a key part of the process, and that equipment size was not necessarily as important. It was therefore deemed more practical and efficient to amalgamate the laboratory and pilot systems, and concentrate efforts into constructing a high-quality transferrable system in two intermediary steps from lab-to-pilot-to-production.

In general, the S&T aims from WP2 were designed to develop a series of protocols for the process that would be key to the successful transfer of IP and achieve high quality nanostructured anodised oxide coatings at the industrial scale. However, careful consideration of all process steps was necessary in order to assess the viability of operating the process at this industrial scale, and included:

- Surface preparation, including cleaning and chemical etching for different applications
- Anodising, including all electrical and physical operating conditions necessary to achieve the desired results (e.g. current, voltage, temperature, electrolyte composition, agitation requirements
- All ancillary and downstream processing stages, including rinsing, sealing and colouring for different applications

Accordingly, for WP3, the S&T aims were designed to achieve the necessary scale-up towards an industrial level, with a detailed analysis of the anodising process and all of the necessary ancillary equipment that are normally associated with the anodising step, including:

- Pre- and post-treatment tanks for cleaning, etching, sealing and colouring
- Rinse tanks, individual to each step in the process to avoid cross-contamination
- Anodising tank, complete with ancillary cooling and agitation systems, and power electronics and control system

In detail, the results in accordance with the S&T objectives have included:

- Develop process protocols including pre- and post-treatments

The starting points for the development of process protocols have been two-fold:

o Standard anodising processes. Ashton & Moore and Promet supplied key information about their existing anodising processes, the process steps and their operating conditions, the materials and equipment involved, and product applications and their individual tribological requirements. Falex Tribology also provided important information about the tribological tests that the materials must undergo in order to quantify the performance and compare directly with conventional anodising.

o C-Tech has actively researched anodising, both from an industrial perspective and academic studies. Current practices in all aspects of industrial anodising, including the different alloys involved, has been reviewed through standard literature:

☐ Sheasby & Pinner, “The Surface Treatment and Finishing of Aluminium and its Alloys”, ASM International and Finishing Publications Ltd., 2001 (6th Ed.)

☐ Canning, The Canning Handbook – Surface Finishing Technology, W. Canning plc, 1982 (23rd Ed.)

☐ Metals Handbook, Vol. 2, ASM International, 1990 (10th Ed.)

As a result of this background research, C-Tech drew up a preliminary flow sheet showing each individual step of a proposed prototype, in which the Nanocoat process was to be scaled up and tested in a fully industrialised environment. Many aspects of the Nanocoat process were found to be identical to those found in current industrial anodising plant, including the pre- and post- anodising treatment steps. However, these steps needed to be included in the prototype system to keep the process comparable. The preliminary flowsheet was reviewed by all partners before the construction process.

A final process flowsheet was produced at the end of the project, following lengthy operation of the prototype, including some retrofitting and optimisation of the equipment and the operating conditions. This iterative process involved providing anodised samples to KUL and Falex for characterisation, and comparison with conventionally anodised samples. A final set of conditions has been presented in the final flowsheet, in the Deliverable report D3.2 – Operating Procedures and Final Process Flow Sheet.

- Design and construct an experimental prototype system

The initial strategy for the scale-up process was to produce a small lab-scale system where initial samples would be anodised to compare the results with initial work carried out at Armines and to address possible scale-up issues for a larger prototype system. However, during the early investigations of how the laboratory and prototype systems would be constructed, it was clear that the minimum practical size of anodising tank for a meaningful laboratory study would be large enough to be considered a prototype. Smaller systems of just a few litres would be difficult to practically agitate using the planned system, and to control at a steady state, and there would be few differences from the system operated by Armines. Also, scaling up twice from a small prototype to a larger one, and then to industrial scale would serve little purpose, as the same scaling issues would need to be considered twice. For these reasons, a single lab/prototype system was built to develop the process before transferring to an SME on-site demonstration.

The prototype system, contains all necessary equipment to prepare and anodise small industrial scale parts up to around 20 x 20 x 10cm, from the initial cleaning and etching stages through to colouring and sealing.

- Operate the prototype system over an extended period and address scale-up issues

The prototype system was operated over an extended period, looking at critical operating parameters such as anodising power, temperature and time, heat and mass transfer by agitation, removal of heat from the system, and practical issues of anodising twice with an intermediary stripping process.

The traditional method of agitation is by bubbling air through the tank. This has the effect of moving hot electrolyte away from the components, replacing it with cooler liquid from the bulk of the tank. It also helps to disperse gas and replace ions lost in the oxidation process. The Nanocoat process however, uses voltages and currents much higher than normally used, producing more heat and affecting the ability to anodise and reducing product quality. The effect of increasing agitation by higher air flow through the liquid would have negative effects, by increasing evaporative losses and acid spray from the tank, and energy losses from additional throughput.

A more efficient method of agitation was tested using eduction, where fluid is pumped around an external circuit and back in through the eductors, shown in Figure 2, which are strategically placed within the tank. Since the electrolyte is circulated through an external heat exchanger to cool, the eduction system could be incorporated into this circuit. The eductors improve efficiency, since only one fifth of the fluid directed towards the components needs to be pumped around the circuit. The remainder is drawn from the tank through the sides of the eductor and out with the pumped fluid.

Computational Fluid Dynamics (CFD) was used to model the circulation system to find the best configuration of flowrate, number and position of eductors.

As the optimisation process drove the move to more aggressive electrical conditions (40V; 860 mAcm-2), anodisation of larger parts became impossible due to the limitations of C-Tech’s rectifier. This prompted the construction of an in-house custom-built system capable of operating at much higher currents. However, further issues arose when attempting to achieve 40V from the start, which resulted in a runaway current and again limited by the power supply.

A control system was added to allow accurate ramped or stepped control of the voltage. This allowed an initial period at slightly lowered voltage to promote the anodisation process, before climbing to the desired set-point of 40V.

Typical conditions for the optimised anodisation follow:

☐ Anodisation 1: Initial Voltage – 25V; Ramp to 40V over 60s; Hold at 40V for 2min

☐ Anodisation 2: Initial Voltage – 32V; Ramp to 40V over 18s; Hold at 40V for 2min

This produced a coating of 34µm (±2µm).

- Use industrial grade aluminium alloys, in addition to pure aluminium

Initial operation of the prototype system involved anodising pure aluminium to emulate preliminary work performed at Armines and compare the resulting coatings. Subsequent operations involved anodising different alloy more appropriate to industrial applications. 2000 series (high copper content) proved particularly difficult to anodise, producing little or no coating, and so efforts were concentrated on 5000 and 6000 series, common industrial grades.

- Scale-up processes for the treatment of larger areas and adapt processes to treat complex shapes

A number of measures were taken to attract a supplier or end user of aluminium products, including advertising on a number of relevant “Linkedin” message boards, and on the project web-site, to provide parts for industrial studies.

Sobinco, a Belgian aluminium door and window frame manufacturer, provided the project with various components, including a handles, a cover plates, and hinge parts, to the project, which have been anodised and characterised, both tribologically by Falex, and using standard salt spray testing by KUL. The parts were made from 5000 and 6000 series alloys and had requirements of wear resistance (hinge), corrosion resistance (external handles and covers), and colour retention (handles and covers).

Further scale-up has been achieved by Promet, who has carried out the process on their industrial anodising line.

- Consider production issues relating to environmental legislation and apply a simplified Life Cycle Analysis Methodology

A Streamlined Life Cycle Analysis was carried out, and is available as a Deliverable report D5.3.

- Complete a full techno-economic assessment of the project outputs

Contribution to a full techno-economic assessment was done, comparing energy consumption of the Nanocoat process with a conventional process.

In addition to the S&T results, a list of possible applications follows. Taking into account the additional energy requirements and capital expenditure for larger components, the process would be limited to niche or high performance applications where cost is not a consideration. Examples may include:

- Optical applications
- Space applications
- Small aerospace components
- Specialised automotive components
- High value consumer products

Workpackage 6 by KU LEUVEN: FUNCTIONAL AND STRUCTURAL CHARACTERIZATION OF ANODIZED MATERIALS

1. Objectives of KUL Work Package

The main objective of the KUL Work Package was to characterize the colored anodized aluminium oxide (AAO) samples delivered by C-Tech and ProMet. In particular, the following four sub-objectives were identified, namely:

1.1. To investigate the morphological surface structure of the AAO samples. A special attention was given to the detection of the presence of nanostructured, perfectly ordered pores.

1.2. To determine the layer thickness of the AAO samples obtained by making cross-sectional views.

1.3. To investigate the friction and wear behavior at macro-loads of the AAO samples.

1.4. To investigate qualitatively the corrosion resistance of the AAO samples after a 1000 hours acetic acid salt spray (AASS) test.

Attempts have been made to correlate these characteristics to the anodizing parameters employed.

2. Samples investigated and selected testing procedure

AAO samples were grown onto flat substrates made of four different Al grades, namely grade 1050 (C-Tech), grade 6082 (C-Tech), grade 5754 (C-Tech), and grade 2017 (ProMet). These samples were investigated for their morphological surface structure, layer thickness, wear behavior, and corrosion resistance.

In addition, AAO samples were grown onto flat substrates made of Al grade 5754 (C-Tech), and onto Sobinco door hinges and door covers, made of Al grade 6060 (C-Tech) and grade 5005 (C-Tech) respectively. These samples were investigated for their corrosion resistance. A reference door hinge and door cover anodized by Sobinco were included for comparison.

The AAO samples were produced under different anodizing conditions in order to achieve a nanostructured surface morphology with a perfectly ordered pore distribution.

Prior to characterization and testing, the as-delivered AAO samples were ultrasonically cleaned in acetone for 15 minutes, rinsed with ethanol, and dried in a vacuum chamber for 30 minutes at 3.4 mbar. In order to make the AAO samples conductive for SEM investigation, an Au layer was sputtered for 1 minute.

2.1 Morphological surface structure

The morphological surface structure was investigated using a SEM-EDX XL 30 FEG (FEI) at a beam voltage of 10 kV and a working distance of approximately 10 mm.

2.2 Layer thickness

Three different methods have been employed to obtain cross sectional views and hence determine the AAO layer thickness, namely:

1st method: Mechanical deformation approach

It consists in clamping the flat coupons between jaws and on screwing inducing a progressive bending of the samples till 180° is reached or till breaking of the sample.

The tests were done at room temperature and schematically represented in Figures 1a and 1b. The AAO layer thickness was then determined using SEM.

2nd method: Metallographic approach

This method is based on classic metallographic procedure to obtain cross sectional views. It may be helpful in order to confirm the data obtained by the 1° method and to detect very thin top layers, or ductile ones.

It consists of the following steps:

- Sample on its side embedded in resin,
- Followed by mechanical grinding (22 - 14 -7 µm), mechanical polishing (Nap, 3-1 µm), and
- A final oxide diamond polishing (ODP, SiO, 0.1 µm).

The AAO layer thickness was then determined using optical microscopy.

3rd method: Ion beam milling approach

This method is based on the ion milling in a SEM-FIB equipment leading to a cross section in a small area without any mechanical interaction as is the case in the 1st and 2nd method.

2.3 Friction and wear behaviour

Reciprocating sliding wear tests at macro-loads were performed in Fretting II equipment, illustrated in Figure 2. The contact configuration was a ball-on-flat with an $Al_2 O_3$ ball as counterbody, shown in Figure 3. The selected test parameters are listed in Table 1. After the sliding tests, the worn samples were ultrasonically cleaned in acetone for 15 minutes and rinsed in ethanol in order to remove the debris. The morphology and chemical composition of the wear track was investigated using SEM and EDX respectively.

2.4 Corrosion resistance

The AASS test chamber was prepared according to the ISO 3769-1976 standard. The test temperature inside the chamber was 34 - 35°C. The pH of the acetic acid solution was 2.9 - 3.0. Samples were placed inside the chamber at an inclination angle of 15°. The set-up of the salt spray chamber is shown Figure 4. Samples were rinsed with warm water and dried prior to visual inspection.

3. Collaborative work

☐ Flat coupons, Sobinco door hinges, and Sobinco door covers with different Al grades were anodized by C-Tech and ProMet. Details on those samples were provided in Section 2.

☐ Discussions among the industrial partners and RTD perfomers allowed to improve the anodizing conditions in view of obtaining a nanostructured AAO surface morphology. Anodizing parameters which had a significant effect of the final surface morphology and corrosion resistance include the imposed voltage, stripping step, pore opening step, sealing step, and dwell time.

☐ Progress reports regarding the outcome of the characterization and test results were sent out by KUL.

4. Main achievements

4.1 Morphological surface structure, layer thickness, friction and wear behaviour

☐ An overview of the morphological surface structure, layer thickness, friction and wear behavior of AAO grown onto Al 1050, 6082, and 2018 is given in Table 2.

☐ An overview of the AAO surface morphologies achieved on Al grade 6082 after single step and double step anodizing is given in Table 3. It is shown that a nanostructured morphology with a perfectly ordered pore distribution is obtained on Al grade 6082, under double step anodizing without a pore opening nor a sealing step and in absence of a dye. Instead, a phosphate-like visual appearance is observed. Introduction of a sealing step under the same anodizing conditions results in the evolution of a nanostructured, perfectly ordered pore distribution to a partially ordered pore distribution. In addition, a decrease in layer thickness and increase in running-in period is noticed.

☐ An overview of the structural and tribological features achieved on a nanostructured morphology with a perfectly ordered pore distribution is shown in Table 4. At low magnification, pitting phenomena and grain boundary effects induced by the anodizing process are revealed. At high magnification, pore sizes ranging from 20 to 23 nm are observed. A coefficient of friction around 0.7 is recorded after 1,000 sliding cycles, resulting in wear track depth of approximately 0.9 □m.

□ An overview of the wear track depth versus the AAO thickness for Al 1050; 6082, and 2015 is shown in Figure 5. The broadest range of AAO layer thicknesses is achieved on Al 1050. Wear through is observed on Al 1050 and 6082. No direct correlation between AAO layer thickness and wear depth is found.

□ An overview of the effect of anodizing parameters on the morphological surface structure, layer thickness, friction and wear behavior of AAO samples grown onto Al 1050 and 6082 are shown in Table 5 and 6 respectively. For both Al grades, the anodizing time, pore opening step, and sealing step during double step anodizing have an effect on the structural and tribological features. In contrast, during single step anodizing, the aforementioned parameters do not seem to induce a significant change.

□ A comparison of the AAO surface morphology obtained after a ramp-up voltage process with and without dwell time is shown in Table 7. The imposition of a dwell time seems to result in a less pronounced pitting corrosion.

4.2 Corrosion resistance

□ Reference door hinges and covers treated by Sobinco have a superior corrosion resistance as compared to the door hinges and covers treated by C-Tech and ProMet. These reference samples only show a small amount of white rust spots and slight discoloration on both the front and at its edges. This is illustrated in Table 8, in which the reference door hinge and cover treated by Sobinco are compared to a door hinge anodized by C-Tech after 1000 hours AASS test.

□ A qualitative ranking of the AAO samples after 1000 hours AASS test has been made based on the amount of white rust spots. It is shown that the samples can be classified in three groups, namely lowest, intermediate, and highest amount of white rust spots.

Preliminary results indicate that the lowest amount of white rust spots is observed under the following conditions:

- single anodized stripped samples seem to exhibit a better corrosion resistance as compared to single anodized unstripped samples under the same anodizing conditions for Al 1050,

- double anodizing on stripped samples results in an improved corrosion resistance as compared to single anodizing on stripped samples for Al 1050, 5754, and 6082,

- imposition of two minutes dwell time on single anodized unstripped samples result in an improved corrosion resistance as compared to the same samples without dwell time for Al 1050, as illustrated in Table 9.

☐ Imposition of dwell time seems to have different effects depending on the anodizing conditions and Al grade used. Two minutes dwell time imposed on:

- double anodized stripped samples results in an inferior corrosion resistance, whereas on single anodized unstripped samples an improved corrosion resistance is observed for Al 1050,

- double anodized stripped samples does not seem to affect the corrosion resistance for Al 5754.

☐ In general, AAO grown onto Al 1050 and 5754 seems to exhibit a better corrosion resistance than onto Al 6082.

5. Work in progress

AASS tests on door hinges and door covers anodized by ProMet and C-Tech have been in progress even after the project officially ended. These tests have terminated on January 14, 2013.

6. Conclusions

6.1 Morphological surface structure, layer thickness, friction and wear behaviour

☐ The majority of AAO samples produced under various anodizing conditions exhibit a nanostructured morphology with only a partially or no ordered pore distribution. In addition, cracks and surface pits are often observed. The broadest range of AAO layer thicknesses is achieved on Al 1050.

☐ The coefficient of friction ranges from 0.6 to 0.9 after 500 sliding cycles on all Al grades. Lower wear resistance on Al 1050 is observed. No direct correlation between AAO layer thickness and wear depth is found.

☐ Only one nanostructured morphology with a perfectly ordered pore distribution (range of pore sizes : 20 – 23 nm) has been obtained on Al grade 6082. This particular morphology with a phosphate-like appearance is produced under double step anodizing without a pore opening nor a sealing step and in absence of a dye. However, surface pitting phenomena and grain boundary effects induced by the anodizing process are revealed. A coefficient of friction around 0.7 is recorded after 1,000 sliding cycles, resulting in a wear track depth of approximately 0.9 □m.

□ No general correlation of structural features to synthesis parameters has been found due to too wide variation of anodizing parameters used. However, preliminary results show that:

- the introduction of a sealing step under the anodizing conditions mentioned in the previous paragraph, results in the evolution of a nanostructured, perfectly ordered pore distribution to a partially ordered pore distribution, a decrease in layer thickness, and an increase in running-in period on Al 6082,

- the imposition of a dwell time during a ramp-up voltage process results in a less pronounced pitting corrosion on Al 1050,

- the anodizing time, pore opening step, and sealing step during double step anodizing have an effect on the structural and tribological features. In contrast, during single step anodizing, the aforementioned parameters do not seem to induce a significant change for both Al 1050 and 6082.

6.2 Corrosion resistance

□ Reference Sobinco door hinges and covers have a superior corrosion resistance as compared to the door hinges and covers anodized by C-Tech and ProMet.

□ A qualitative ranking of the AAO samples after 1000 hours AASS tests has been made based on the amount of white rust spots. No general correlation of corrosion resistance to synthesis parameters has been found due to too wide variation of anodizing parameters used. However, preliminary results indicate that an improved corrosion resistance is achieved by:

- Stripping of single anodized samples on Al 1050

- Double anodizing of stripped samples on Al 1050, 5754, and 6082

- Imposition of dwell time on single anodized unstripped samples on Al 1050

Imposition of dwell time seems to have different effects on the corrosion resistance depending on the Al grade and anodizing conditions employed. On Al 1050, the dwell time improves or deteriorates the corrosion resistance depending on the anodizing conditions. In contrast, on Al 5754 the dwell time does not seem to affect the corrosion resistance.

- In general, AAO grown onto Al 1050 and 5754 seems to exhibit a better corrosion resistance than onto Al 6082.

Potential Impact:

Expected impacts at the European and/or international level

The technology studied during the 2 years in the Nanocoat project has clear market potential and will have a strong impact on the economic prospects the participants via two routes):

- The SME participants will use the technology directly in their own manufacturing operations and/or directly in the services they provide.
- The SME participants will market the technology through process licensing to other manufacturing organisations (via product type, market area, geographical region)

In the latter case, this will lead to improved industrial competitiveness and improved employment across the EU. The surface finishing sector is widely distributed and approximately €30 billion (30 x 109) of finished value product is dependent upon its capabilities. In Germany, there are about 2,100 businesses in the surface finishing industry with about 56,000 employees and a total market volume of €4 billion (4 x 109). The total size of the market in France has been estimated as €6 billion. The added value of the sector is much higher, because metal finishing accounts for only 5% of the total value of the product. Therefore the estimated total added value in Germany, for example, is €80 billion (4% gross domestic product of Germany).

Anodised Aluminium products are established in the following industrial application areas:

- Anodising has been used in building construction for more than 60 years. Anodising gives the safest and hardest architectural finish currently available. Anodised aluminium is easy to clean and requires little maintenance.
- Coating is the process of covering the aluminium surface with a suitable film (layer) made of organic compounds, typically powder or wet paint. Many aluminium components may be painted for various reasons, starting with decoration up to protection against specific environmental influences.
- Decorative finishes are available through metallic finishes and a wide variety of colours. Anodising offers a large increasing number of gloss and colour alternatives and minimises or eliminates colour variations. Unlike other finishes, anodising allows the aluminium to maintain its metallic appearance.
- Adhesive Bonding was developed by the aerospace industry. It produces a porous oxide that is used mainly as a pretreatment for preparing adhesively bonding aluminium

structures in the aerospace industry and to some extent in automotive. The anodised coating is used as an adhesive bonding primer coat on aircraft and aerospace alloy sheets. This is an excellent surface for the epoxy adhesive and also improves corrosion resistance.

The specific anodising markets to be addressed during the project are concerned with improved functionality for traditional anodisation processes and new coatings.

Improved functionality of existing coatings will be explored in the following large market areas: Corrosion & abrasion resistance, Adhesive bonding, Anodised base for organic coatings/painting, Coloured architectural finishes.

The statistics for the market size for existing industrial applications are available from the Association for European Surface Treatment on Aluminium (ESTAL):

- Anodised Al: 279 million m2 or 828 thousand tonnes
- Anodised & Coated Al: 441 million m2 or 1.22 million tones

The construction industry accounts for 59% of anodised products and 78% of anodised & coated products. Other applications are: automotive & transportation; aerospace; industrial products; electronic equipment; furniture; household appliances & decorative design; sports & leisure; packaging. ESTAL represents 452 plants with 15,000 employees in SME manufacturers.

Within the surface treatment industry as a whole, the conversion of aluminium represents about 15 % of the market including around 10 % for anodisation alone i.e. 4 billion Euros. The European aluminium surface treatment market grew by 25% between 2000 and 2005.

New application markets will be assessed, which are based on the enhanced performance of nanostructured coatings. As conventional materials are reaching the limits or their performance and industrial components are subjected to increasing demands in terms of mechanical performance (speeds, loads, temperatures), many industrial manufacturers are facing difficulties taking the 'next technological step'. There are many difficulties to overcome to solve the limitations of current systems.

Surface treatments that can be easily and economically produced by electrochemical techniques (aluminium anodisation) will have an advantage over vapour deposited coatings for many industrial sectors. Price, size and robustness of the production process are key elements to reach an economically viable product. Some examples of new market applications are given:

- Improved lubricity.
- Anti fretting
- Tribocorrosion surfaces
- A specific application is the improvement of emissivity of black anodisation layers obtained by absorption of Ni and/or Cobalt sulphides for Space applications

Time to Market and Economic Justification

As regards the improvement of the industrial performance of traditional anodised products, the initial market introduction by partners in this consortium is a very good prospect within 2 years. Within 5 years following the end of the project, a modestly estimated penetration of approximately 10 % of the anodisation market could be realised, with an expected turnover for European industry of €80 million. This potential market clearly justifies the EC grant of €1.144 million and would clearly make a significant impact in terms of economic growth and employment.

The SME participants will own the marketing rights and royalty payments on the potential market would certainly justify the overall project cost and the individual inputs.

A central result will be to acquire the know-how to scale up the anodisation of nano-sized cell structures from a lab scale into a pilot line. Up scaling involves a modelling and design of electrochemical reactor technology in 50 litre baths. The main technical challenges are the achievement of uniformity and control of the nano-features. The transfer from laboratory scale activities to larger scale processes of interest to industry will result in the availability of test samples from pilot scale production lines which will be unique in Europe.

Cost Acceptance

A general barrier to the implementation of new technologies in SME dominated industry sectors is the level of capital investment necessary for establishing new operational plant and infrastructure. No significant capital investment expenditure is required for the introduction of the process innovations planned as outputs from this research project. Standard processing plant currently used in the surface finishing industry can be readily adapted to the new processes and this is a major objective of the research work planned in NANOCOAT. The capital expenditure costs of anodisation-based methods are very low relative to many alternative methods for producing nanomaterials, and for producing vapour deposited coatings.

Legislation & Regulation

The surface finishing industry relies heavily on a multitude of chemical processes, many of which are toxic and capable of causing significant damage to the environment. The implementation of environmental legislation will continue at an accelerating rate. During Task 5.1 existing legislation will be reviewed and potential future legislation affecting aluminium anodisation processes and the production of nanomaterials will be assessed in terms of the implications for the market potential of products, as well as process operational requirements.

The project outputs are expected to be achieved with minimal use of hazardous chemicals, and certainly to avoid the use of toxic materials such as chromic acid.

Since December 2008, Nanomaterials have been addressed within REACH, and have been the subject of discussions and further studies and deeper analysis.

Nanomaterials come under the REACH regulations and any nanomaterial classified as a new material needs to be subjected to a dedicated registration and specific risk assessment procedure. For substances already on the market in bulk form and produced or imported at the nanoscale , if properties or uses of the substance in the nanoform differ from those in the bulk form, specific information on these properties and uses have to be updated in what is known as a registration dossier, including specific information on any hazardous properties, a safety assessment and risk management measures. In addition, any nanomaterials that fulfil the criteria for classification as being hazardous have to be classified and labelled.

Organisations that undertake anodising operations and that are planning to implement the new Nanocoat technology have an obligation to comply with the existing relevant legislation and to carry out their business in as environmentally sound a manner as possible. This should involve a commitment to promoting and maintaining an environmental policy and ensuring that the impact of any processes used on the environment is as low a level as is practically and economically feasible.

In recent years there have been growing concerns raised about the potential environmental and health and safety impacts of nanomaterials and this has led to increasing calls for legislation to be put in place around the use of such materials. Most of this concern and legislation is related to the fact that, because of their small size, nanomaterials behave significantly differently to their larger sized analogues. In the case of the Nanocoat technology, no discrete nanoparticles are produced but rather a nano-surface morphology of alumina is produced. This means that there should be less concern than for the nano-powder analogues. The only real issue would be if there was a need to use some specific new chemical additive in the Nanocoat process chemistry, as there could be implications under the REACh Regulations and need for registration of the named chemical for the specific application. Otherwise it seems that the main legislative demands on the Nanocoat technology would essentially be the same as those that apply for conventional aluminium anodising. However, it should be noted that the legislation, both European and global, is continually evolving, particularly in the context of nanomaterials and it will be important to continue to monitor the legislative situation for changes that could include the Nanocoat technology.

Potential impact from further research

Most background knowhow for this technique uses aluminium to produce Anodic Aluminium Oxide (AAO). In the future, the research could be extended to other lightweight metals such as titanium, tantalum, zinc, magnesium and niobium.

In addition to surface finishing applications, higher added value anodised aluminium oxide nano-products are expected in electronics in the medium term (e.g. nanopositioning, nanowires) following further research. Although future nanotechnology markets will be highly competitive, the very large current research markets and the future manufacturing markets will ensure that innovative, cost-effective manufacturing processes can supply these growing market needs.

Nanotechnology is a highly skilled, highly technical sector with the result that a very high proportion of manufacturing capacity should be based in the EU, with as many as 500,000 personnel in the EU working in nano-manufacturing. Consequently, businesses are being established throughout the EU specifically to manufacture a wide range of nanomaterials and existing companies are setting up their own nano-manufacturing facilities. Assuming an estimated 25 to 50 workers per nano-manufacturing facility, this equates to 10,000-20,000 manufacturing sites in the EU by 2015, and 40,000-80,000 sites worldwide.

Economic assessment:

The following assessment is based on a comparison of existing anodising processes and the proposed double anodisation.

Clearly, the differences in the process are restricted to the actual anodising and in the additional stripping and pore opening steps in the “Nanocoat” process.

As a basis, we must consider the anodisation of a single component, or ‘jig’ containing the same components having the same surface area and profile. Therefore, consider the samples processed in the Nanocoat prototype rig, having a surface area of 64cm2, to be anodised conventionally, and using the Nanocoat process. Conventional anodising achieves a coating of up to a maximum of 25µm, whereas hard anodising can produce coatings between around 13 to 150µm using sulphuric baths chilled to 0°C. The Nanocoat project has produced coatings comparable to hard anodising, and a comparison will be drawn between the three processes.

Conventional Anodising

Depending on the alloy grade and final application, the anodising process operates generally between 12 and 25V, or higher for more specialist applications. A basic process however, of 16V will be considered, producing around 1µm every 2.5 minutes at a rate of 150Am-2. The process normally operates at room temperature. A maximum coating thickness of around 35µm can be achieved before the layer becomes too resistive for the current to penetrate.

Hard Anodising

For applications that require particularly good abrasion resistance, hard anodising can achieve coatings thicker than 250µm. As with conventional anodising however, there are many processes that are used by different companies to achieve the resulting coatings, ranging from 15-120V; 150-1000Am-2. One of the best known processes is the M.H.C. process developed by the Glenn L. Martin Co. The process uses a 15% sulphuric acid electrolyte operated at 200-250Am-2 and 0°C. To maintain this current, the voltage rises from 30 to 60V for film thicknesses up to 150µm. 34µm can be achieved within 60 minutes at an average of 40V.

Nanocoat Anodising

The parameters used in the Nanocoat project have been optimised over time, with the resulting process operating at 40V and 0°C in both anodising steps, with average currents in the region of 55A (860Am-2) during the first anodisation and 27A (422Am-2) during the second. Coatings of 34µm were achieved within 2.5 minutes. Additional energy is lost from the stripping and pore opening steps, although the latter has been found to be unnecessary, and even detrimental if colour retention is required. This step will therefore be ignored.

A summary of the process conditions are shown in Table 1, with a worked example of calculations shown in Appendix A.

Results

When compared directly in a process to produce a 34µm coating, which was the average thickness over 12 samples (±2µm) coated using the Nanocoat technique, it is estimated that conventional anodising would consume 24.5 MJm-2 of energy, hard anodising (M.H.C. process) 63.4 MJm-2, and the Nanocoat process 154.5 MJm-2. The increase in energy therefore needs to be justified in performance and lifetime of the anodised parts.

The time taken to anodise is vastly improved over conventional and hard anodising, but this is offset by the additional stripping process. So although just 5 minutes are required for the actual anodisation, the figure is increased to around 38 minutes when the stripping and rinsing steps are included. This is still however, an improvement over conventional and hard anodising, which would take 85 and 60 minutes respectively.

Capital costs on top of existing processes will involve additional tankage for the stripping process, complete with heating requirements and consumables in the form of acid electrolyte. However, the largest capital cost will come from the rectification, since the current density required is 57 times higher than conventional anodising, and 39 times higher than hard anodising. A balance therefore needs to be struck between capital outlay and the number or size of parts that can be anodised in any one batch. This will then impact on the process time. For instance, if the operator had access to a rectifier capable of anodising only a quarter of the surface area using the Nanocoat process, than if the process was to be carried out using conventional or hard anodising, the overall anodising time would increase four-fold, which in turn would be around 1.8 and 2.5 times more than conventional and hard anodising respectively.

The project has generated after only 24 months a limited number of significant data on process costs vs conventional costs - on the basis of the limited knowledge we have at the moment the process actually looks more expensive than conventional and further work should be interesting to envisage, in the form of a follow-up project or a Nanocoat II, to demonstrate enhancements in performance.

Dissemination actions

Promotion actions

1. Visual supports

The visibility of the project, its objectives, partnership, and EU funding can be efficiently announced or reminded through the following actions which have been undertaken:

- Wikipedia: an attempt to present the project has been made but unfortunately the moderators of the Wikipedia website have rejected any kind of advertising of a research project.
- Twitter: this new mode has been used especially with the Midest twitter which announced both in 2011 and 2012 the Nanocoat project meeting and presentation during the exhibition week; also the coordinator’s twitter account has been created in the same purpose.
- Video clip: a presentation on screen, in both English and French versions, has been recorded and presented at several occasions, either alone or within a PowerPoint presentation at several conferences. The clip had a banner showing partners and European Commission and REA agency logos.
- TV interview: at the Final meeting date, a TV interview made directly on stage with the public audience and recorded during the Midest exhibition has enabled the Coordinator to recall the EU funded research scheme and to remind several recent projects including Nanocoat.
- Posters and flyers have been created to be accompanying all presentations or attendance at conferences, workshops, exhibitions, either alongside the presentation or at the poster sessions.

2. Workshops

KUL Workshop

An academic audience was attending this 2-day workshop organized by KU Leuven in the University premises, together with a project meeting.

A presentation by David Hall and Ivan Bujinsters was made at this occasion, followed by open discussion during the break of the workshop.

SEA Workshop

A multi-project workshop was organized by the British SEA, the plating association, grouping industrial attendees as well as academic ones; several projects were presented and discussed, including Nanocoat, for which the presence of the Coordinator IPM², of Ctech Innvation, of Env Aqua Ltd and Ashton & Moore brought sufficient matter for discussions and comments. (see below)

3. Professional associations

Professional associations meetings: CETS (European Committee of Surface Treatment, UITS (French Association of Surface treatment industries, SEA (British plating association), SIRRIS, CETIM, DGO, Aluminium associations… are all different means of disseminating towards the specific sector's industrial members.

As an example: SEA (Birmingham – UK surface treatment association) 2012 workshop:

(…) David Hall from C-Tech Innovation then presented details of a 'Research for SMEs' project called Nanocoat (see www.nanocoat-project.eu), which had a focus on new aluminium anodisation techniques. The aim was to produce uniform nanostructured anodised aluminium oxide coatings and to develop improved functionality and new coating applications for products in surface engineering. David then gave an overview of the Nanocoat process, which actually had two anodising steps, and he described the scale-up activities that C-Tech had undertaken. Eductors were employed to provide energy efficient agitation and heat removal from the process tank and computational fluid dynamics (CFD) was used to help with the equipment design and educator location. Testing had been performed on samples prepared using the Nanocoat process and improvements achieved in a number of key mechanical properties. Structural analysis had shown that the Nanocoat process gave uniform nanostructural coatings. Industrial applications were being tested and a life cycle assessment was being undertaken.(…)

4. Gadget

It had been discussed at the beginning of the project the best way to sensibilize the audience in order to show in a very attractive manner a special part, with a size and a function that can be familiar to anyone, and if possible related to a real-life application.

After some attempts and some internal discussions, the choice of a Nanocoat keyring, which can be coated with the Nanocoat Process has been selected at the majority of the RTD and SME partners attending the RTD meeting on the topic.

A marking showing the project's name will be engraved on the flat keyring, together with a reference to the REA funding scheme.

This keyring is expected to be produced in a sufficient quantity to be comfortably distributed to the interested and serious stakeholders, either at exhibitions such as Midest, or especially at the EU organized Innovation Convention, if the Nanocoat project is selected to participated, next spring in Brussels.

5. Exhibitions:

This label includes all presentations made to dedicated audience, attendance to workshops, attendance to exhibitions on a partner's stand, poster sessions, and conferences:

They have started soon after the project had been officially launched (kick off meeting took place in January 2011) and range over the whole 24-months duration:

EDNANO 8; 17/03/2011; Milan, Italy

This Nanocoat presentation introduced the project at an international conference, held every 18 months and dedicated to nanomaterials. The coordinator was invited there to attend also the next one in order to give all outputs interesting the audience; he was also invited to attend the next Interfinish conference

MIDEST 2011; 15/11/2011 ; Villepinte, France

A Nanocoat Poster dissemination action, with attendance and explanation of the project's whereabouts has been organised on the stand of one of the partners, PROMET, who shared with the coordinator, the explanation and discussions on the stand with relevant stakeholders.

Environord 2012 ; 12/06/2012 ; Lille, France

This annual Northern France event dedicated to innovations was attended and a Poster dissemination action and flyers distribution was made on the organizers' stand.

Industrial Technologies 2012; 19/06/2012; Aarhus, Denmark

Poster dissemination was organized by RTD provider KU Leuven who attended this workshop (Professor Jean Pierre Celis), together with a project's presentation.

KUL workshop on nanostructured surfaces; 27/06/2012; Leuven, Belgium

KUL hosted on 27-28th June 2012 the NANOCOAT plenary meeting in Leuven, together with a special Surface Treatment, Materials and characterization workshop, attended by several guests and by Nanocoat partners, and where a presentation has been performed by David Hall (CTech)

SEA Dissemination Seminar; 29/06/2012; Birmingham, United Kingdom

The British SEA has organized a one-day dissemination seminar on 29th June 2012, in Birmingham, where Nanocoat project was presented and which was attended by CTECH, iPM², ENVAQUA, ASHTON & MOORE on behalf of Nanocoat partnership.

MIDEST 2012; 06/11/2012; Villepinte, France

The Final meeting was held inside the MIDEST exhibition in Paris- Villepinte (6th-9th November 2012) and a cocktail offered by the French plating association (UITS) has grouped all NANOCOAT partners, the industrial plating field representatives as well as the selected Press Journalists; in parallel, PROMET stand was exhibiting NANOCOAT video, as well as flyers and poster, and Pascal Negre, IPM² and Coordinator was interviewed on the MIDEST

TV where he presented the collaborative Research in general and FP7 projects as NANOCOAT in particular.

EDNANO 9; 08/11/2012; Porto; Portugal

As planned early 2011 during the EDNANO 8 where NANOCOAT was presented, the coordinator presented the main project's results during EDNANO 9 on 8th-10th November 2012 in Porto, Portugal. Attendance included several industry and university stakeholders interested by the outcome and by a participation in a possible follow-up of Nanocoat.

Interfinish 2012; 15/11/2012; Milan, Italy

NANOCOAT results have been presented also at the most important conference Interfinish on 14th-16th November 2012 in Milan, Italy where IPM² and ARMINES represented the partners; Flyers were distributed and questions on the topic came from the audience and where answered by Patrick Benaben and Pascal Négré.

List of Websites:

www.nanocoat-project.eu