

## Publishable Executive Summary

Corrosion protection by nanostructured materials –a big step forward in the industrial usage of these materials – EU project MULTIPROTECT has been successfully finished

The integrated project MULTIPROTECT (advanced environmentally friendly multifunctional corrosion protection by Nanotechnology) was formed by a Europe-wide consortium with the objective to find replacements for hazardous, carcinogenic chromium (VI) based corrosion protection materials. The aim was the development of multifunctional, generally applicable and environmentally-friendly corrosion protection systems on the basis of nanostructured materials with nanoparticles as functional design elements. The combination of the know-how of thirty one partners from thirteen countries from all over Europe and Israel has made this integrated project broad and unique in the expertise of its members bringing together research institutes, universities and industrial end users. With a total budget of 13.7 million euro and a funding of 8.8 million euro, MULTIPROTECT was a medium sized IP in the nanotechnologies, materials and new process section within the 6th Framework program of the European Commission. Coordinated by the Leibniz Institute for New Materials in Saarbruecken, the consortium mainly focused on four different research topics. 1. Nanoparticle design and production to be used in the following 3 objectives, 2. Replacements for hard chromium, 3. Substitutions for chrome conversion coatings by sol-gel based coatings for aluminium alloys, steel and magnesium alloys and 4. Doped, Conductive polymers like polyaniline or polypyrrole for corosions protection coatings. These different fields of work were reflected by the structure of the project in seven workpackages and especially in the sub-structure of the workpackage “development” in eight different sub packages (SP) dealing with the four main research topics assisted by four supporting SPs for detailed investigations on coating properties (tribology and surface properties), health and safety aspects and a modelling of the coating and coating behaviour (Figure 1).

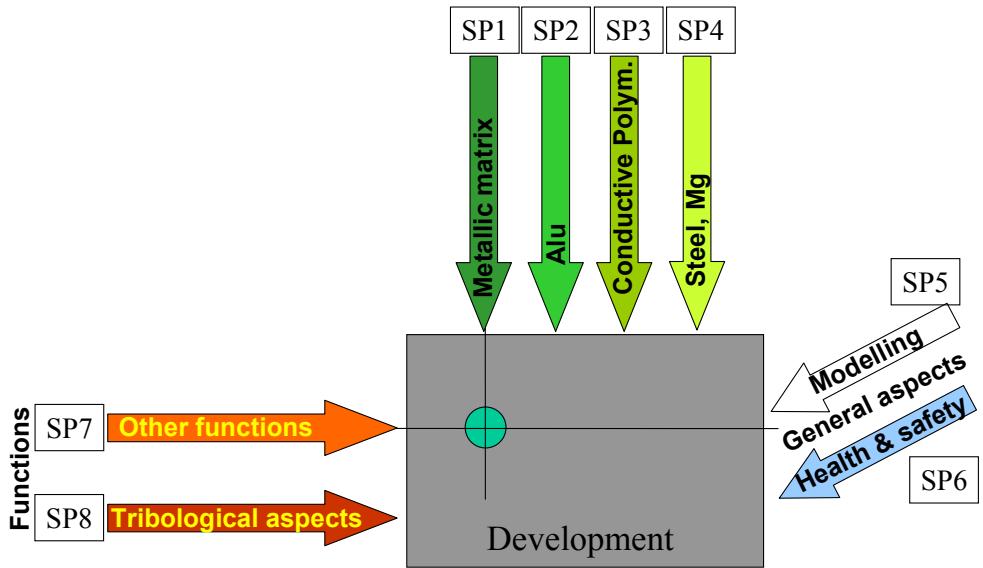


Figure 1: Basic structure of WP3, with a working point highlighted (image courtesy of INM)

Development and results of the project (with focus on the last project year)

**Nanoparticles:** The idea of using nanoparticles as functional design elements was followed during the project period. A water droplet of an inhibitor extract containing chloride ions (electrolyte) is placed on an aluminium plate. Corrosive attack of the electrolyte on the aluminium is checked after fixed times up to three days. A positive effect was recognized for commercial and newly developed nanoparticles and -structures like cerium dioxide, titanium oxide, mixtures of cerium dioxide and titanium dioxide ( $TiO_2$ - $CeO_2$ ), cerium molybdate, spherical particles with different shells, strontium aluminium polyphosphate (SAPP) and layered double hydroxides (Figure 2**Error! Reference source not found.**). These inhibiting materials were incorporated into hybrid inorganic- organic hybrid sol-gel matrices to improve their behaviour in corrosion protection. Especially, amorphous nanoparticles like  $CeO_2$ , mixed particles like  $TiO_2$ - $CeO_2$ , and cerium molybdate but also in-situ formed titanium dioxide showed improved performances and a better behaviour than unfilled coating systems. A patent application on hollow nanospheres was submitted.

To introduce a higher hardness into metallic coatings different types of titanium based hard nano-particles ( $TiC$ ,  $TiN$  and  $TiC/SiC/Si_3N_4$  ( $Ti$ - $Si$ - $C$ - $N$ )) were developed in the project period and used as additive in the electrolyte bath.

In project year three, some of the newly developed nanoparticles like  $TiO_2$ - $CeO_2$  and ( $Ti$ - $Si$ - $C$ - $N$ ) were selected for upscaling. Eight times the normal lab scale amount of particles could be produced after the upscale enough nanoparticles for the demonstrator phase of the pro-

ject. SAPP was made in 5 litre dispersion. At the beginning of the fourth project year coating systems with CeO<sub>2</sub>, TiO<sub>2</sub>-CeO<sub>2</sub>, in-situ formed titanium dioxide and SAPP were selected for the application on demonstrators due to their good corrosion protection abilities.

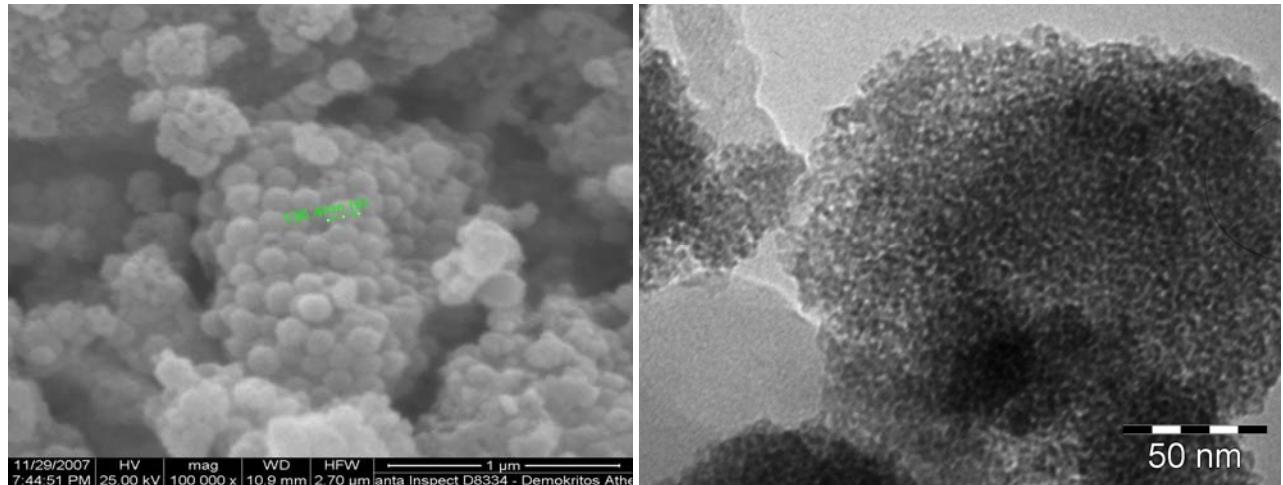


Figure 2: Left: Sub- $\mu$ -containers of CeO<sub>2</sub> were successfully loaded with inhibitor 8-hydroxy-quinoline (image courtesy of NCSR); Right: TEM micrographs for TiO<sub>2</sub>-CeO<sub>2</sub> powders 80:20 thermally treated at 400°C (image courtesy of ICF)

**Hard chromium replacement:** Hard chromium is a commonly used metal coating in different industries in areas with high tribological load. It has a high hardness. However, this coating is deposited from electrolytes containing high concentrations of carcinogenic chromates. Therefore, during the project period nickel and nickel phosphorus coatings, filled with hard nanoparticles (Figure 3), were investigated as substitution for the chromium coating. Hard-Nanoparticles, a combination of Ti, Si, C and N were synthesised and incorporated into the new developed coating matrices. Also alternatives to the electrolyte based Ni and NiP coatings were developed. These were TiCxN1-x ( $0 < x < 1$ ) coatings applied by a sol-gel method on different substrates and also coatings applied by high oxygen velocity fuel technique (HVOF). Except the coatings based on TiCxN1-x, which did not show enough adhesion together with its carrier substance on steel substrates all others were found to be able to replace hard chromium in principle.

An upscale of two developed lab- scale, nickel-based electrolytes to 200 l bath volume was successful and even the application on demonstrators was successfully undertaken (Figure 4). It turned out that the electrolyte for the deposition of hard nickel doped with c-BN required a 80% lower current density than necessary for EHC

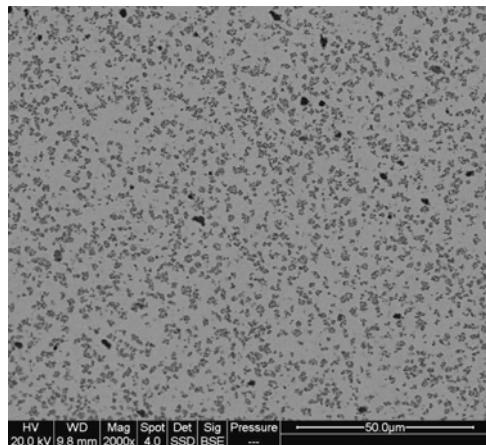


Figure 3: Electrodeposited hard-Nickel Coatings with c-BN Nano-Particles SEM cross section micrograph (image courtesy of IIM)

(electroplated hard chromium), which results in a much lower consumption of electricity, had a higher throwing power than EHC and also a three times higher deposition rate. The coating has lower, but sufficient hardness for industrial use. Also two other systems for hard chrome replacement, one with silicon carbide and another with Ti-Si-C-N nanoparticles, were applied on demonstrators. All the applied systems had quite similar wear resistance as hard chromium coatings and meet the tribological needs of the industry. One coating applied on demonstrators was made by high velocity oxygen fuel spraying (HVOF). This HVOF coating fulfils the industrial requirements SAE AMS 2447 and BOEING BAC 5851.

The machining of the nickel coatings was equal or better than that for EHC. Based on the results of shimmy damper shaft, no risk of leakage was recognized due to the absence of pores/pits and cracks in the coating made from both nickel electrolytes tested. All types of steels tested (including aerospace materials) were easy to coat.

For example, the demonstrator of the Israeli aerospace industry, a piston rod, passed the test procedure of 20.000 cycles without any leakage or damages after visual inspection.

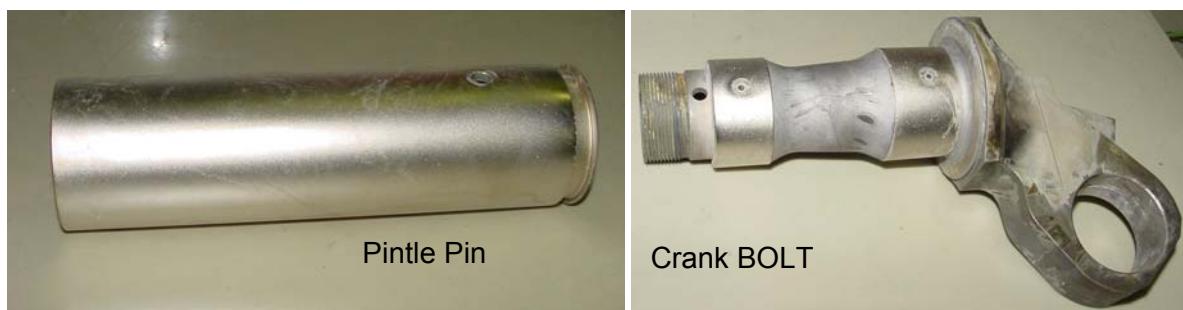


Figure 4: Demonstrators coated with hard nickel coating doped with c-BN nanoparticles (IIM system) (image courtesy of LLI)

Sol-gel coatings for Al: The development of protective coatings for aluminium alloys based on sol-gel processes was another objective of the project. Since 2005, involved partners had developed sol-gel based corrosion protection coatings. These coating materials are based on compositions of different alkoxides, silanes and/or metalorganic compounds and nanoparticles. In project year three, after two years of development and incorporating of different nanoparticles into sol-gel based coating materials six coating systems with good corrosion protection properties and the potential for upscaling were selected for the technology phase. At the beginning of the fourth project year six of the best materials were selected by the industrial partners for application on demonstrator parts.

Two approaches were developed: thick coatings based in epoxy and methacrylate silanes containing nanoparticles and/or inorganic and organic salts acting as inhibitors. These coatings should provide both barrier effect and inhibition effect to the protecting structure. The thickness range goes from 2-3 µm to 50 µm depending on the composition and system. These coatings can be top coated or be used as stand alone system. On the other side, very thin inorganic coatings have been developed to replace conversion coatings. ZrO<sub>2</sub> films and glass-like pure Ce coatings have proved to be an alternative to be applied along with a top-coat.

An upscale of both types of inhibited sol-gel formulations to pilot plant scale was made for all selected systems. It could be shown that the behaviour of the sol-gel lacquer materials is comparable to that of commercial standard coating materials.

The application of the upscaled sol-gel systems on demonstrators by spraying was successfully done without problems (Figure 5). The coated demonstrators were sent back to the providing industrial partner who did their standard performance tests on them. The coatings exhibit active corrosion protection properties, but not the complete performance of chromate-based conversion coatings.

The ZrO<sub>2</sub> thin films work as an adhesion promoter but show limited active protection due to the low inhibitor reservoir, but good adhesion to substrate and paint and good protection against creepage. Pure Ce coatings instead act also as adhesion promoters and present quite good behaviour in Al alloys with excellent performance in Al of series 3000 (Figure 6Figure 7). A new patent application was submitted in this field during the project.



Figure 5: Left: Spray application system at IPA (image courtesy of Fh-IPA); Middle: Skin sheet of aircraft (800 x 600 mm x 3,5 mm, Material 6061, welded stringers, challenge: Homogeneous, uniform coating even on difficult to access areas (lower side of stringer)) (image courtesy of EADS); Right: Sol Gel system used for repair investigation: (image courtesy of EADS)

The thicker coatings have good barrier properties, but with drawbacks in the prevention of creepage. Therefore, a compromise between barrier and active corrosion protection must be found.

It was demonstrated that the repair of sol-gel coatings and even Chromium-Acid-anodized layers (CAA) by the newly developed systems is possible (Figure 5). In these tests sol-gel on sol-gel films perform better than sol-gel on anodised surfaces. By applying the sol-gel films by means of a pneumatic spray gun, an out-of-bath surface treatment for local application was successfully demonstrated (e.g. large integral components, repair etc.



Figure 6: Left: ZrO<sub>2</sub> thin films with an epoxy topcoat after 1000 h in SST (Udine); Right: Macroscopic picture of glass-like Ce coating with epoxy based topcoat onto AA2024 after 960 h of Filiform Corrosion Test (ICV). (image courtesy of EADS)

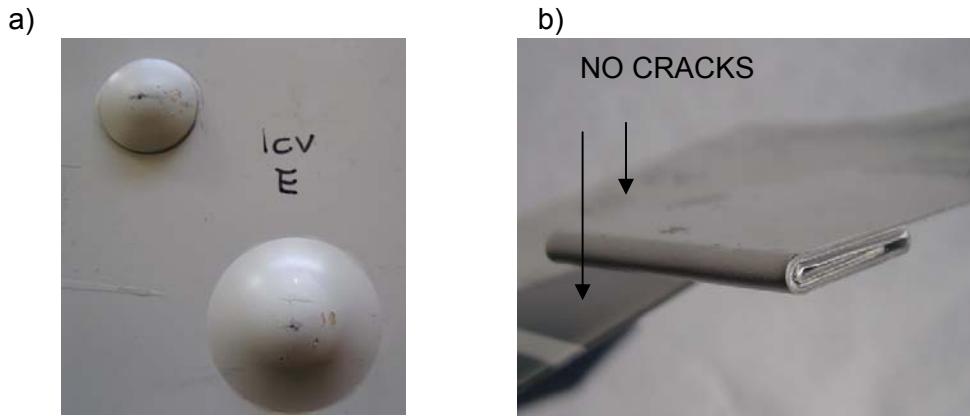


Figure 7: a) Adhesion on embossing and b) Adhesion on T-bend and Cracking on T-bend on AA3105 with a polyester topcoat (ICV) (image courtesy of EADS and PLALAM)

Sol-gel coatings for steel and magnesium: In addition to the protection of aluminium alloys, the corrosion protection of steel and magnesium alloys was an objective of the project.

After four years of development a pre-treatment for AZ31 magnesium alloy with a three layer structure ready for the application on magnesium demonstrators. This corrosion protection system for AZ31 works very well after topcoating. Depending on the quality of the alloy the combined system survived between 500h to 1000h in the neutral salt spray test (SST). Glass-like pure Ce<sub>2</sub>O<sub>3</sub> coatings also provide excellent electrochemical performance to these substrates. After 48 h of immersion in 3.5 wt% NaCl the impedance modulus shows a marked increasing up to values of  $2 \times 10^5 \Omega \text{cm}^2$  after 264 h of immersion, a clear indication of active corrosion protection (Figure 8). The angle phase confirms this active behaviour.

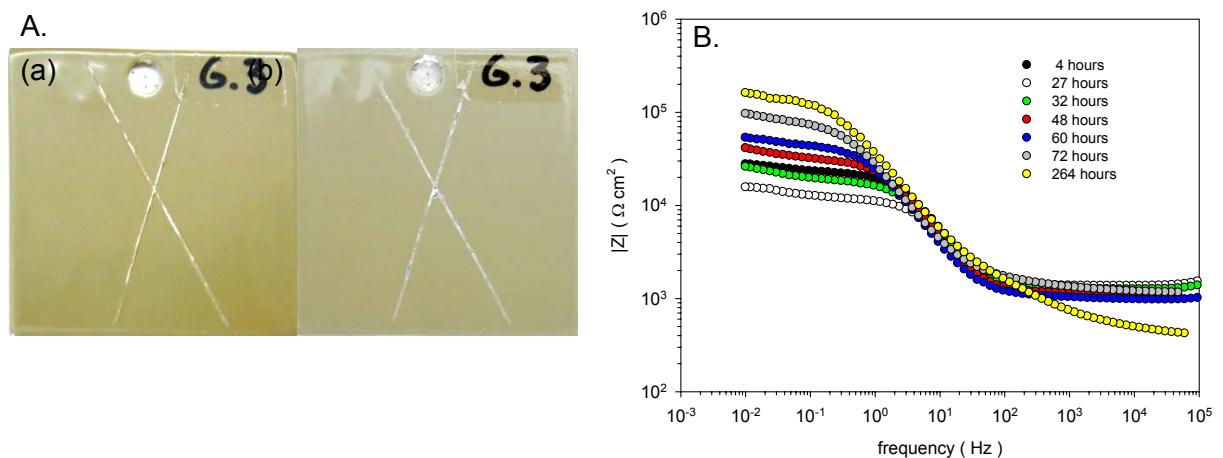


Figure 8: A. SST of AZ31 samples (5x5cm<sup>2</sup>): Specimen pre-treated by three layer coating (TLC) and painted in “Alubin” showed a resistance of more than 1000 hrs (image courtesy of IIM and ALUBIN); B. Bode diagram of the Glass Like- CexOy -Coating with neutral pH on polished AZ-31 (image courtesy of ICV and UNIMAN)

For magnesium ZK10, a one-step manufacturing process of ORMOSIL-Conductive Polymer coatings was successfully developed. The coating exhibited excellent anti-corrosion properties.

A sol-gel based coating for magnetic steel ballasts were developed. Pigments were added to this coating to meet the requirements of the partner and to further increase its barrier properties. The developed coating meets the dielectric requirements for ballasts and exhibits better results in the neutral SST than commercial today-used coatings for these ballasts. Only the low viscosity of the developed coating needs further improvement (Figure 9).



Figure 9: Comparison of a commercial (left) and a MULTIPROTECT coating (right) (INM) on magnetic ballast (Electrostart) after ~120h of neutral salt spray test (image courtesy of INM)

Conductive coatings: A triggered, on-demand release of inhibitor substances was the idea of using conductive coatings for corrosion protection. Conductive coating shall release ions that are part of the conductive coating and incorporated during the coating process by electric energy, when corrosion appears. During the project a new patent application emerge in this area. The realisation of the idea in lab scale was done. Two main systems were developed

during the project period. One, a co-polymeric system based on polyaniline and polypyrrole and another polyaniline system with titanium nanoparticles incorporated. Also sandwich systems with several different coatings were assembled. Good corrosion protection (1000h SST) and adhesion properties of anodic coating containing polyaniline and TiO<sub>2</sub> nanoparticles on AA3105 Al alloy were found. By combining conductive coatings of poly (aniline-co-pyrrole) with sol-gel coatings the performance of conductive coatings could be further improved. The upscaling of the coating bathes were started during the project period but due to unsolved challenges in conserving the bath quality over long time periods the work was stopped.

Modelling: By combining the Nernst equations with the Fick's law of diffusion and other equations a model for the self-healing processes in the coatings was established. To describe the diffusion of inhibitor substance that should appear in the case of corrosion many experiments for leaching out the inhibitor and to investigate local corrosion were done during the project. Finally, in the fourth project year, the model could be used to describe the self-healing processes of coatings measured by SVET technique (Figure 10).

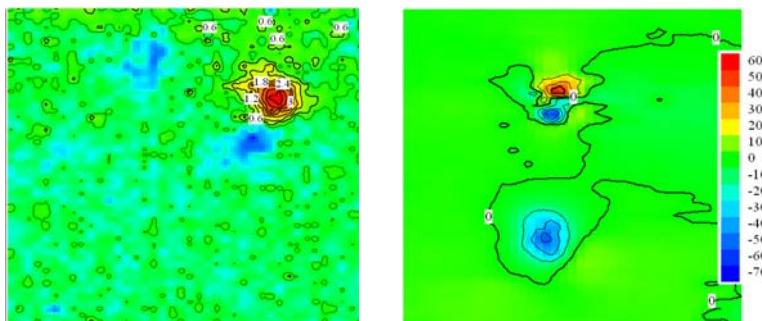


Figure 10: Corrosion current maps (SVET) above the surface AZ31 coated with different sol-gel films obtained after 1 day of immersion. 0.05M NaCl doped with 0.01M 1,2,4-triazole was used as electrolyte (image courtesy of UAveiro)

Simulations of experimental results could be done and could describe the experimental findings (Figure 11)

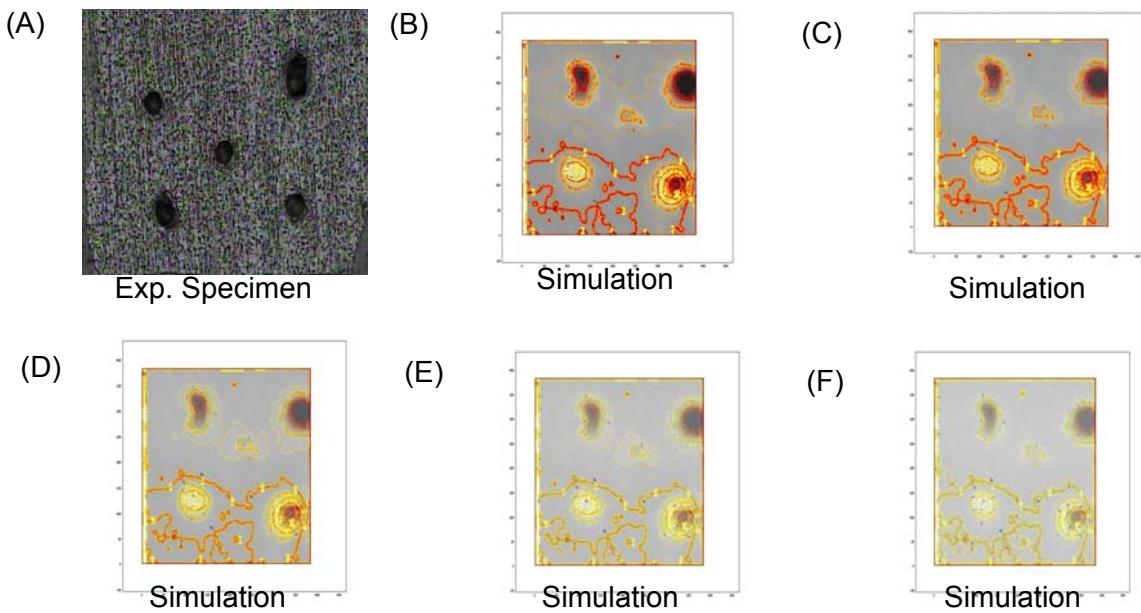


Figure 11: (A) Coated specimen (Al2024) with five micro defects to be exposed to an aggressive electrolyte (NaCl+Water) (image courtesy of UAveiro); Simulation of the MULTI-PROTECT coating self-healing process: (B) Shows the initial time when the interaction of the electrolyte with the metal surface intermetallics initiates the corrosion process in the vicinity of each one of the defects, high variation of chemical potential is noticeable; (D-F) shows the process of inhibitors migration and so a passivation effect of the corrosion process (image courtesy of INM).

To understand the mechanism of self-healing, a special cell for electrochemical noise measurements was designed. With this cell a real time monitoring of the self-healing behaviour of metal surfaces in the neighbourhood of a coating is directly measurable (Figure 12).

A significant decrease of corrosion on metal surfaces in neighbourhood to inhibitor-doped coatings in comparison to those in neighbourhood to non-doped coatings was found. Especially, cerium nitrate provides self-healing.

Also the mechanism of the pitting corrosion of AA2024 alloy was deeper elucidated (Figure 13) during the project. The intermetallics in this alloy play an important role in its corrosion behaviour. In these regions, the oxide layer is thinner and has structural defects that lead to an early attack triggered by chloride ions. In the ongoing process, copper will be enriched leading to an accelerated corrosion of the aluminium alloy by the formation of a galvanic cell in micro scale.

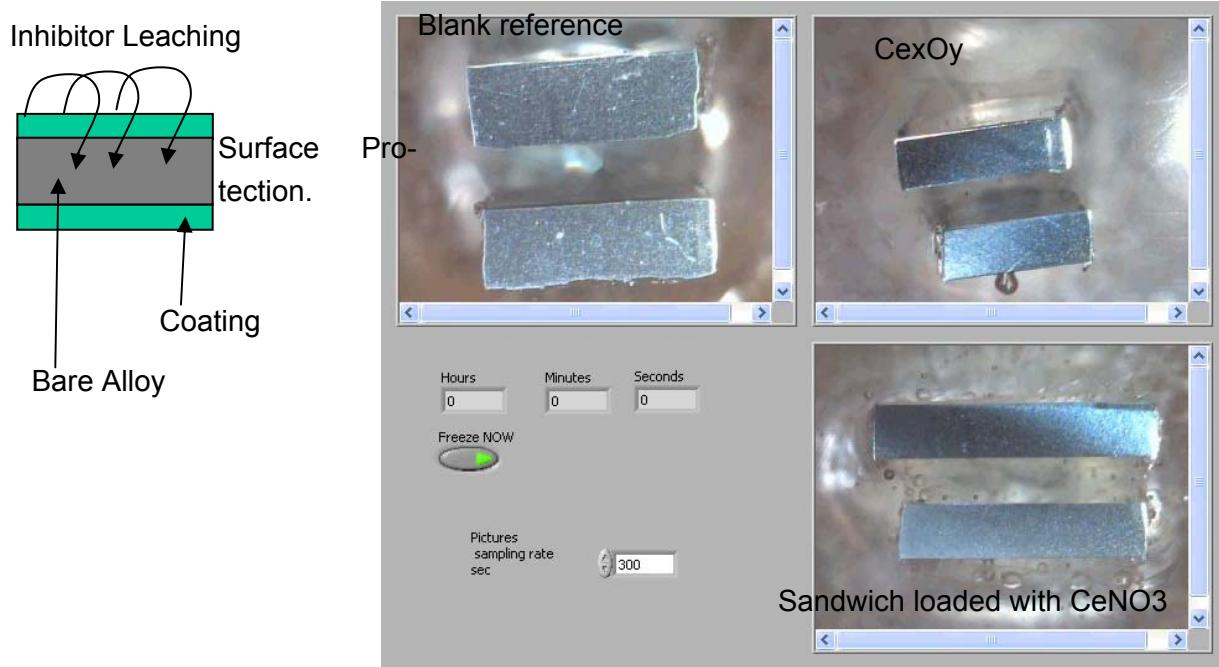


Figure 12: Self healing of coatings: Leaching experiments assisted by real time imaging. → Sandwich loaded with CeNO<sub>3</sub> provides self-healing. (image courtesy of UNIMAN)

The release of inhibitors from the coatings was investigated in leaching experiments. Target of this investigation was the elaboration of experimental data to feed the model with correct border conditions for the simulations of self-healing behaviour. Different release of cerium salts were detected whether a coating was applied on glass or on aluminium specimens. Therefore, diffusion in normal time scales could be proved and also a diffusion of a part of the cerium salt to the aluminium surface is very supposable. Further, the porosity of coatings was measured by ellipsometry to get the pore size distribution and total pore volume. These data were collected to further adjust the model to real conditions.

Health and safety issues of the newly developed protection materials were also investigated during the project by incubation tests in boiling water, artificial sweat and rain water according to the standard ZVO-0101-UV-05. This standard test was originally established to check the release of chromium from chromium conversion coatings.

In the project no release of hazardous material from the developed systems for the protection of aluminium alloys could be detected. Therefore it can be judged that a hazard of these developments to humans or even water organisms is very unlikely.

Beside the scientific results, the project MUTIPROTECT was the starting point of other European projects like NanoTherapy FP7 Ideas and MUST.

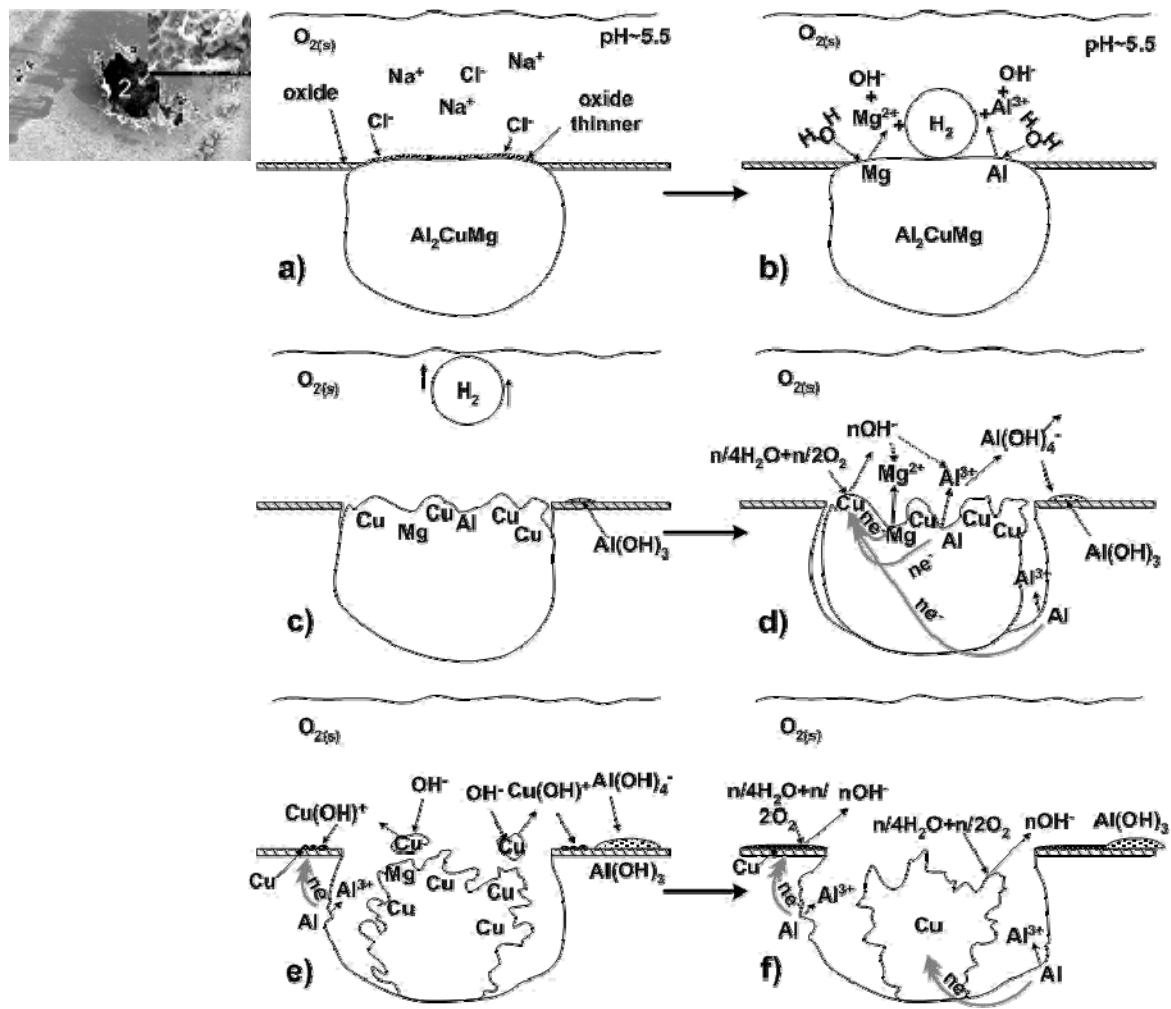


Figure 13: Mechanism of pitting formation on AA2024 (image courtesy of UAveiro)

From the non-academic point of view this project was a real integrated project. Companies were working closely together with academic institutions of European wide level and were strongly influencing the developments.

A web page to inform the public and to manage the project was established. Lot of work was done in the management of the consortium and in the dissemination of results. This was done in publications and also in two information workshops for the industry. 70 people attended the event in Munich and gave positive feedback to this activity. Two newsletters on the results were published and distributed.

## Main achievements of the first project year

During the first project year, the work package two (WP2) "Definition" was finalised and thresholds and benchmarks were established for the development partners. The workpackage three (WP3) "Development" was started and divided into eight subprojects.

In the development of hard chromium replacement coatings a co-deposition of nickel with different carbide nanoparticles shows a significant increase of the coating hardness (from 250 to 450 HV). The hardness increases along with a good dispersion of nanoparticles in the coatings. A good dispersion however, depends on a suitable composition of the electroplating bath and on the modification of the nanoparticle surface. Additionally, TiN coatings deposited on sintered Al<sub>2</sub>O<sub>3</sub> were obtained. These coatings have good adhesion, thicknesses in the range 500-800 nm, nano-hardnesses of 700-900 HV, microhardness of 1600 to 2500 HV and low coefficient of frictions (0.2 to 04).

In the first year, most partial objectives have been reached, in particular, the production of mono and dioxide nanoparticles for inhibiting purposes were done. These new types of redox-nanoparticles were synthesised and examined in droplet tests. First results show a promising self-healing effect of the nanoparticles, which may be compared with that from of Cr<sup>6+</sup> containing coatings. The further work in the first year was directed at incorporating these particles into sol-gel to identify several coating systems that present signals of self-healing behaviour and barrier protection, representing candidates for the replacement of chromium containing coatings on aluminium alloys, steel and magnesium.

Different types of nanocomposites have been synthesised: CeO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and ITO particles of small size and uniform size distribution. In parallel, hollow SiO<sub>2</sub>, TiO<sub>2</sub>, and CeO<sub>2</sub> have also been prepared. Polyaniline (PANI) and poly pyrrole films were grown onto different alloys (2024, 3035, 6082 and 7075) by electropolymerisation. The nanoparticles were incorporated into the conducting polymer matrices as shown by SEM/EDS measurements. PANI provides a more effective layer than PPY on Al-alloys, as proved by SSFCT measurements. PANI was combined with the different nanoparticles given previously. Immersion tests showed (3 days in 3.5% NaCl) that the PANI/TiO<sub>2</sub> system provides the best corrosion protection among other samples tested. It was also found that the presence of CeO<sub>2</sub> prevents polymerisation of aniline or pyrrole on the substrate. However, polymerisation occurred when both of the monomers are used simultaneously in the presence of CeO<sub>2</sub>. Nanoparticles have also been incorporated into hybrid layers coated onto different substrates, including steel. Immersion tests (in a solution of 5% NaCl) for different times revealed that films on steel, AA2024 and AA7075 aluminium alloy substrates have resisted up to 48 h without pit formation.

## Main achievements of the second project year

The main work of the second year in MULTIPROTECT was the further development of corrosion protection systems based on nanotechnology. Further, the work package four (WP4) "Technology" for up-scaling and pre-industrial application has started during this period.

In the reporting period substitutions for hard chromium coatings with hardness of 670 HV and another type with hardness of 750-830 HV based on Ni respective NiP and nanoparticles could be developed. According to these findings, the hardness threshold of 600 HV defined as a minimum requirement for an industrial application could be reached. Systems for up-scaling were chosen.

In the development of corrosion protection coatings for aluminium alloys self-healing within nanoparticle doped chromium-free coatings was demonstrated by means of electrochemical measurements (

Figure 14). Many experiments were performed to further optimise the corrosion protection of those coatings. The influence of adding particle in different amounts to a sol-gel coating is given in Figure 15. In the end coatings with very good barrier functions and very long resistant times in salt spray test were found. A decision on systems for upscaling was done.

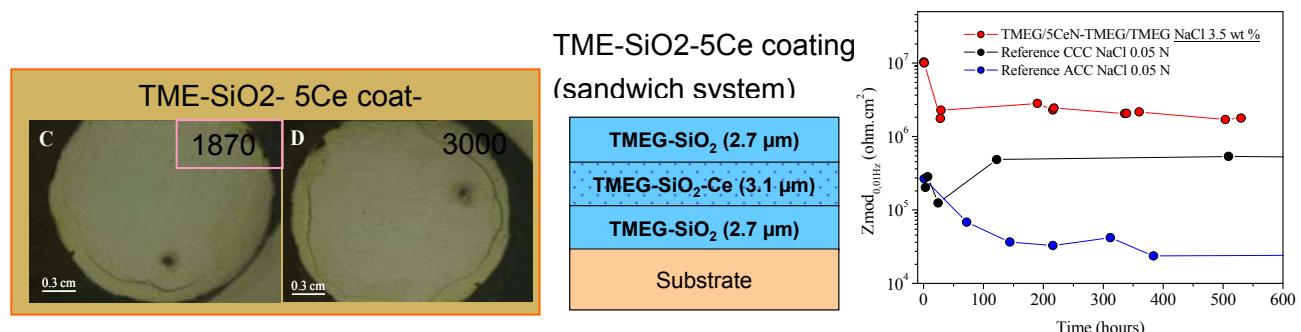


Figure 14: Methacrylate based three layer sol-gel coating with self-healing abilities (image courtesy of ICV)

In the field of conducting polymers on aluminium alloys the resistant times in SST could be increased to 1000h hours (AA3105). A potential self healing by the release of doping agents was seen by electrochemical measurements.

Also on steel and magnesium steps forward could be done. A coated steel specimen survived more than 1000h exposure to SST. Inhibitors for magnesium alloys could be discovered.

In the work package "Technology" the first pre-industrial spray tests of one of the developed coating systems was successfully done. The coating system could be up-scaled and spray-

ing of this system could be done by an industrial robot on different sorts of substrates. The results were very promising.

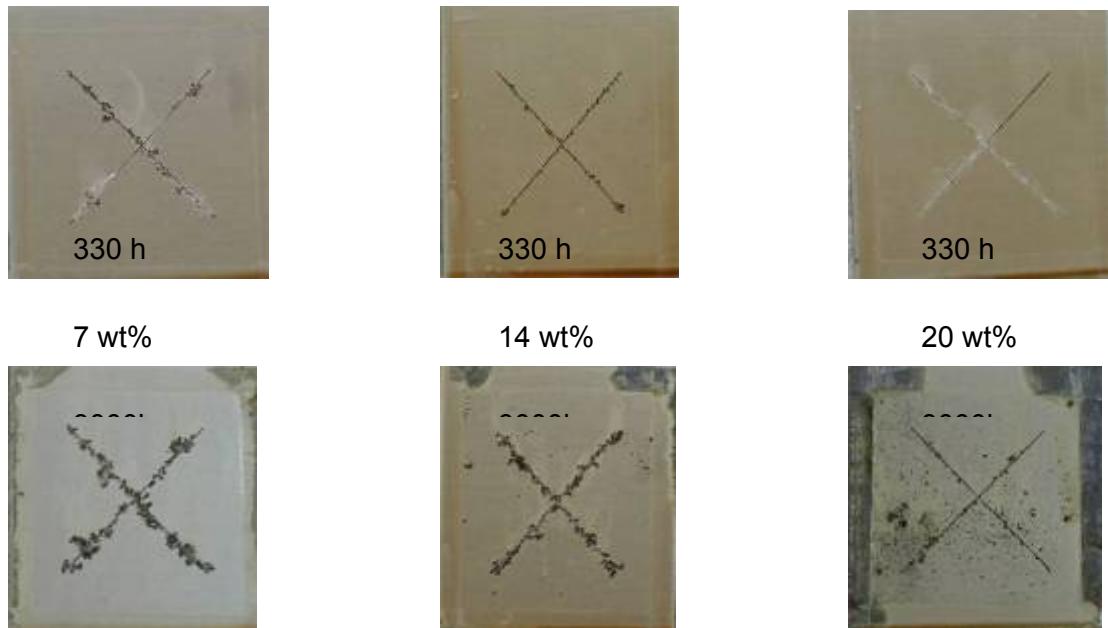


Figure 15: Epoxy based sol-gel lacquer with Cerium dioxide nanoparticles (7, 14, 20 wt%) after neutral salt spray test on aluminium alloy 2024: barrier - creepage behaviour depending on nanoparticle load of the coating (image courtesy of INM).

During the project year workshops on electrochemical techniques (Vincenza, Italy) and nanoparticle synthesis and use in coatings (Szczecin, Poland) were organized for MULTIPROTECT partners.

For dissemination and exploitation purposes the consortium has made 24 publications. Several industries were contacted and informed upon MULTIPROTECT and its targets and achievements.

## Main achievements of the third project year

During project year three, the MULTIPROTECT consortium made a big step forward to the industrial applicability of the developed coating systems. Beside further optimisation of developed systems the technology phase was continued and three different protection materials (sol-gel based lacquers, protection systems based on conductive polymers and substitutions for hard chromium coatings) were transferred to the industrial partners for preindustrial testing. The most promising sol-gel base lacquer systems are now available in amounts of 2 to 5 L and were successfully tested for usability in industrial environments. All systems show good results and no hindrance for an industrial usage. Reproducible syntheses of chromium(VI)-free hard coatings could be established and an up-scaling of the coating bath could be realised. The coatings show good distribution of the particles and high hardness.

The demonstration phase was also started during the third project year. The industrial partners (from aircraft, automotive and construction industry) defined their demonstrators for the application of the developed coating materials and started with the first application tests of the new systems.

In parallel, the coating systems were checked for the release of hazardous materials to the environment. No release of toxic substances could be detected so far.

The mathematical computer model of corrosion processes and self healing could be further developed. Comparison and fitting to experimental data were done in order to allow the description of the movement of inhibitors integrated in the coating.

Two internal training workshops were organised for the participants of the consortium and successfully implemented in Saarbruecken and San Sebastian. The organisation of the first dissemination workshop in Rome in May 2008 was started.

## The consortium

The MULTIPROTECT consortium was formed by 31 partners from all over Europe and Israel, not only by corrosion experts but also by experts for the synthesis and application of coatings. These experts were coming from the field of metal coatings and also from sol-gel science. This combination made the consortium unique and effective in the expertise of its members. Coordinated by the Leibniz- Institute for New Materials (Saarbruecken, Germany) (INM) the consortium was formed by partners from academia, research institutes and companies and industrial partners.

Partners in 2009 in alphabetical order:

Austrian Research Centers GmbH-ARC (Vienna, Austria) (SEI),  
Bühler AG (Uzwil, Switzerland) (BUH),  
Centro Sviluppo Materiali S.p.A. (Rome, Italy) (CSM),  
Consejo Superior de Investigaciones Científicas (Madrid, Spain) (ICV),  
CRN-CASTI, Centro per L'assistenza Scientifica e Tecnologica alle Imprese (L'Aquila, Italy) (CASTI),  
Cromosphere (Dueville, Italy) (CROMOSPHER),  
EADS Deutschland GmbH, Innovation Works, (Munich, Germany) (EADS),  
Elastotec (Thale, Germany) (ELAS),  
Electrostart (Sofia, Bulgaria) (ELSTART),  
European Research and Project Office GmbH (Saarbruecken, Germany) (EURICE),  
FIAT / Società Consortile per Azioni (Orbassano, Italy) (CRF),  
Forschungsinstitut für Edelmetalle und Metallchemie (Schwaebisch Gmuend, Germany) (FEM),  
Hellenic Aerospace Industry S.A. (Scjimatari, Greece) (HAI),  
INASMET (San Sebastián, Spain) (INASMET),  
Institute of Physical Chemistry I.G. Murgulescu Romanian Academy (Bucarest, Romania) (ICF),  
Instituto de Soldadura e Qualidade (Porto Salvo, Portugal) (ISQ),  
Liebherr-Aerospace Lindenberg (Lindenberg, Germany) (LLI),  
National Center for Scientific Research "Demokritos" (Athens, Greece) (NCSR),  
Netherlands Organisation for Applied Scientific Research (Eindhoven, The Netherlands) (TNO),  
Plalam SpA, Lamiera Prelaccata e Plastificata (Ascoli Piceno, Italy) (PLALAM),  
PROFACTOR (Austria, Steyer) (PROFACT),  
Servo Hydraulic Lod / Israel Aircraft Industry Ltd. (Tel Aviv, Israel) (SHL-IAI),  
SHL-Alubin Group (Kiryat Bialik, Israel) (ALUBIN),  
Technical University of Szczecin (Szczecin, Poland) (TUS),  
Technion-Israel Institute of Technology (Haifa, Israel) (IIM),  
The Fraunhofer Gesellschaft IPA, (Stuttgart, Germany) (IPA),  
Universidade de Aveiro (Aveiro, Portugal) (UAveiro),  
University of Chemical Technology and Metallurgy (Sofia, Bulgaria) (UCTM),  
University of Manchester, Institute of Science and Technology (Manchester, United Kingdom) (UNIMAN),  
University of Udine (Udine, Italy) (Udine),

Typoplast (Bulgaria/Switzerland) (TYPO) and GENTA (T.T. Ferioli & Gianotti SpA, Italy) were former partners and have left the project before its finalisation for different reasons.

The management of the project was handled in close cooperation by INM and EURICE. A web page (Multiprotect.org) was set up by EURICE to inform the public on the project and its achievements and to simplify management tasks. Important consortium issues were discussed and suggestions for the general assembly were worked out in the project coordination committee (PCC) formed by the workpackage leaders INM, IPA, IIM, EADS, UDINE and CASTI. Several training workshops, staff exchanges and visits were organized on a European level to increase the success of the process of integration and the impact of the project. In Rome and in Munich two external events were organized to inform the public on the project and its achievements.

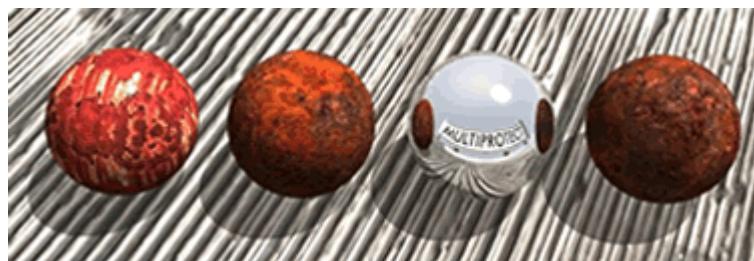
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Logo und Web page: <http://www.multiprotect.org>



## References

- D. Ondratschek (IPA), Neue multifunktionale Nanobeschichtungen - Produktionsgerechte Beschichtungsprozesse entwickeln - New multifunctional nano-coatings - Development of production-oriented coating processes., besser lackieren! N r. 20, 1. (Dezember 2006)
- K.A.Yasakau, M.L. Zheludkevich, S.V. Lamaka, M.G.S. Ferreira (Aveiro), Mechanism of corrosion inhibition of AA2024 by rare-earth compounds, Journal of Physical Chemistry B, 110 (2006) 5515 -5528.
- A. Biedunkiewicz, N. Gordon, J. Straszko, S. Tamir, M. Wysiecki (TUS, IIM), Non-isothermal oxidation of nano-TiC(in polish: Nieizotermiczne utlenianie Nano-TiC), Materials Engineering (in polish: Inzynieria Materialowa), 3(151),(2006), 335-337 (in polish)
- A. Biedunkiewicz, N. Gordon, J. Straszko, S. Tamir (TUS, IIM), Kinetics of thermal oxidation of titanium carbide and its carbon nano-composites in dry air atmosphere Journal of Thermal Analysis and Calorimetry 88 (2007) 717-722
- S. V. Lamaka, M.L. Zheludkevich, K. A. Yasakau, M.G.S. Ferreira (AVEIRO), New high effective organic corrosioninhibitors for aluminium alloy 2024, Electrochimica Acta, 52 (2007) 7231-7247.
- D. Ondratschek (IPA), Multifunktionale, korrosionsschützende Nanoschichten - Multifunctional, anticorrosive nano-coatings, Journal für Oberflächentechnik JOT, 47 (2007) 24
- F.Andreatta, P.Aldighieri, L.Paussa, R.Di Maggio, S.Rossi, L.Fedrizzi (UDINE), Electrochemical behaviour of ZrO<sub>2</sub> pre-treatments on AA6060 alloy., Electrochimica Acta 52 (2007) 7545-7555.
- M.Zaharescu, L.Todan, L.Predoana, C.Andronescu, V.Teodorescu, C.Vasiliu, V.Purcar (ICF), Monocomponent and binary Oxides in the V<sub>2</sub>O<sub>5</sub>-CeO<sub>2</sub> System, Proc.10th Ecers.Conf, Göller Verlag, Baden-Baden, Eds. J.G.Heinrich and C.Aneziris (2007)
- D. Ondratschek (IPA), Hoher Korrosionsschutz mit Nanobeschichtungen -Hohe Schicht-beständigkeit mit Sol-Gel-Systemen - High corrosion protection with nano-coatings -High coating stability with sol-gel-systems, besser lackieren! Nr. 10, (1. Juni 2007)

M.Zaharescu, V.S.Teodorescu, A.Barău, C.Andronescu, N.Preda, F.Papa (ICF), TiO<sub>2</sub>-CeO<sub>2</sub> nanometric powders preped by sol-gel method, Proc.10th Ecers.Conf, Göller Verlag, Baden-Baden, Eds. J.G.Heinrich and C. Aneziris, (2007), p. 1839-1841

M. Wittmar (INM), "Multiprotect": Gemeinsam gegen den Rost, besser lackieren! No. 7 (2007)

M. Wittmar (INM), Europa forscht gemeinsam nach umweltfreundlichem Korrosionsschutz, besser lackieren! No.21, (2007) page 12

Dieter Ondratschek (IPA)

Sicheres Beschichten - Herausforderungen durch neue Materialien im Griff - Coating safely - Challenges by new coating materials under control  
besser lackieren! Nr. 1, (18. Januar 2008)

F. Andreatta, L. Paussa, P. Aldighieri, L. Fedrizzi (UDINE)

Pre-trattamento sol-gel a base ZrO<sub>2</sub> su lega di alluminio AA2024  
Pitture e vernici, 1 (2008) 27-32

O.Zubillaga, F.J.Cano, I.Azkarate, I.S.Molchan, G.E.Thompson, A.M. Cabral, P.J.Morais (I-NASMET, ISQ, UNIMAN), Corrosion performance of anodic films containing polyaniline and TiO<sub>2</sub> nanoparticles on AA3105 aluminium alloy, Surface and Coatings Technology 202 (2008), 5936-5942

Kartsonakis, I., Daniilidis, I., Kordas, G. (NCSR), Encapsulation of the corrosion inhibitor 8-hydroxyquinoline into ceria nanocontainers, Journal of Sol-Gel Science and Technology, 48(1-2) (2008), 24-31

S.K. Poznyak, M.L. Zheludkevich, D. Raps, F. Gammel, K.A. Yasakau, M.G.S. Ferreira (AVEIRO, EADS), Preparation and corrosion protective properties of nanostructured titania-containing hybrid sol-gel coatings on AA2024, Progress in Organic Coatings 62 (2008), pp. 226-235

K.A. Yasakau, M.L. Zheludkevich, O.V. Karavai, M.G.S. Ferreira (AVEIRO), Influence of inhibitor addition on the corrosion protection performance of sol-gel coatings on AA2024, Progress in Organic Coatings 63 (2008) 352-361

A. Biedunkiewicz, N.Guskos, T-. Bodziony, M. Maryniak, J.Typek (TUS), Paramagnetic centers in nanocrystalline TiC/C., Journal of Alloys and Compounds 455 (2008) p. 52-54

S. V. Lamaka, M.L. Zheludkevich, M.F. Montemor, A.F. Galio, C. Trindade, L.F. Dick, M.G.S. Ferreira (AVEIRO), Novel hybrid sol-gel coatings for corrosion protection of AZ31 alloy, *Electrochimica Acta* 53 (2008) 4773-4783

S. Kozhukharov, G. Tsaneva, V. Kozhukharov, J. Gerwann, M. Schem, T. Schmidt, M. Veith (UCTM, INM, EADS), Corrosion protection properties of composite hybrid coatings with involved nanoparticles of zirconia and ceria, *Journal of Univ. of Chem. Techn. Met.* 43 (2008) 73-80 ([http://www.uctm.edu/journal/j2008-1/11\\_Kojukharov\\_73-80.pdf](http://www.uctm.edu/journal/j2008-1/11_Kojukharov_73-80.pdf))

G. Tsaneva, V. Kozhukharov, S. Kozhukharov, M. Ivanova, J. Gerwann, M. Schem, T. Schmidt (UCTM, INM), Functional nanocomposite coatings for corrosion protection of aluminum alloy and steel, *Journal of the Univ. of Chem. Techn. Met.* 43 (2008) 231-238 ([http://www.uctm.edu/journal/j2008-2/9\\_Kojukharov\\_231.pdf](http://www.uctm.edu/journal/j2008-2/9_Kojukharov_231.pdf))

D. Ondratschek (IPA), Nanoschichten sicher auftragen - Applying nano coats safely, *Journal für Oberflächentechnik JOT* 48, (2008), 28-31

S. Kozhukharov, G. Tsaneva, V. Kozhukharov, J. Gerwann, M. Schem, T. Schmidt, M. Veith (UCTM, INM), Corrosion protective behaviour of nanocomposite hybrid coatings, *Bulgarian Chemistry and Industry* 79 (2008) 78-84

V. Kozhukharov, S. Kozhukharov, G. Tsaneva, J. Gerwann, M. Schem, T. Schmidt, M. Veith, (UCTM, INM), Investigations on the corrosion protection ability of nanocomposite hybrid coatings, *Bulgarian Chemical Communications* 40 (2008) 310-318

V. Kozhukharov (UCTM), Nanoscience and Nanotechnology: world-wide status and strategy, *Annual Journal Russe University* 47 (2008) 19 – 28 (in Bulgarian)

A. Strzelczak, G. Mozdzen, J. Lelatko, A. Biedunkiewicz (TUS, SEI), Non-isothermal oxidation of ceramic nanocomposites using the example of Ti-Si-C-N powder: Kinetic analysis method, *Acta Materialia* 56 (2008) 3132-3145

J. Straszko, A. Biedunkiewicz and A. Strzelczak, (TUS), Application of artificial neural networks in oxidation kinetic analysis of nanocomposites, *Polish Journal of Chemical Technology* 10(3) (2008) 21-28

K.A. Yasakau, M.L. Zheludkevich, M.G.S. Ferreira (AVEIRO), Lanthanide salts as corrosion inhibitors for AA5083. Mechanism and efficiency of corrosion inhibition, *The Journal of Electrochemical Society*, 155 (2008) C169-C177.

A.F. Galio , S.V. Lamaka, M.L. Zheludkevich, L.F. Dick, I.L. Müller, M.G.S. Ferreira (AVEIRO), Evaluation of Corrosion Protection of Sol-Gel Coatings on AZ31B Magnesium Alloy, Materials Science Forum. 587-588 (2008) 390-394

Kartsonakis, P. Liatsi, I. Daniilidis, G. Kordas (NCSR), Synthesis, characterization, and anti-bacterial action of hollow ceria nanospheres with/without a conductive polymer coating, Journal of the American Ceramic Society 91 (2008) 372-378.

I.A. Kartsonakis, P. Liatsi, I. Daniilidis, D. Bouzarelu, G. Kordas (NCSR), Synthesis, Characterization and Antibacterial action of Hollow Titania Spheres, Journal of Physics and Chemistry of Solids 69(10) (2008) 214-221.

G. Pappas, P. Liatsi, I. Kartsonakis, I. Daniilidis, G. Kordas (NCSR), Synthesis and characterisation of new SiO<sub>2</sub>-CaO hollow nanospheres by sol-gel method: bioactivity of the new system, Journal of non crystalline solids 354 (2008) 755.

N. C. Rosero-Navarro, S. A. Pellice, A. Durán, M. Aparicio (ICV), Effects of Ce- containing sol-gel coatings reinforced with SiO<sub>2</sub> nanoparticles on the protection of AA2024, Corrosion Science, 50 (2008) 1283-1291.

N. Guskos, E. A. Anagnostakis, G. Zolnierkiewicz, J. Typek, V. Likodimos, A. Guskos, A. Biedunkiewicz (TUS), Magnetic agglomerates in the ternary nanomaterial system Ti-Si-C, Elektronika (Polish journal) 5 (2008) 18

A. Biedunkiewicz, N. Guskos, E. A. Anagnostakis, K. A. Karkas, A. Guskos, P. Figiel (TUS), Magnetic and transport properties of nanocrystalline titanium carbide in carbon matrix, NATO Science for Peace and Security Series-B: Physics and Biophysics, Electron Transport in Systems, Ed. Springer (2008) p. 315-327, Book chapter

Christos Tapeinos, Ioannis Kartsonakis, Penelope Liatsi, Ioannis Daniilidis, G. Kordas (NCSR), Synthesis and Characterization of Hollow Magnetic Spheres, Journal of American Ceramic Society 91(4) (2008), 1052-1056

Paussa L., Andreatta F., Aldighieri P., Fedrizzi L., Di Maggio R., Rossi S. (UDINE), Rivestimenti a base ZrO<sub>2</sub> su lega di alluminio AA6060. Trattamenti e Finiture, 48(5), (2008), 44-52.

O. Zubillaga, F.J. Cano, I. Azkarate, I.S. Molchan, G.E. Thompson, P. Skeldon (INASMET, UNIMAN), Anodic films containing polyaniline and nanoparticles for corrosion protection of 2024T3 aluminium alloy, Surface and Coatings Technology 203 (2009), 1494-1501

S. Kozhukharov (UCTM), Relationship between the conditions of preparation by sol gel route and the properties of the obtained products, Journal University Chem. Techn. Met. 44(2) (2009) 143 – 150. ([http://www.uctm.edu/bg/j2009-2/6\\_Kojukharov\\_143-150.pdf](http://www.uctm.edu/bg/j2009-2/6_Kojukharov_143-150.pdf))

N.Guskos, J.Typek, T.Bodziony, G.Zolnierkiewicz, M.Maryniak, A. Biedunkiewicz (TUS) Ageing effect in nanocrystalline TiCx/C studied by EPR, Journal of Alloys and Compounds 470 (2009) 51-54

Urszula Gabriel, Figiel Paweł, Anna Biedunkiewicz (TUS), Effect of heat treatment on Ti(C,N)-SiC-Si3N4-C ceramic nanocomposites, Solid State Phenomena 151 (2009) 227-233

Dieter Ondratschek (IPA), Beschichtungen mit Nanomaterialien - Coatings with nano materials, Journal für Oberflächentechnik JOT 49 (2009) 18-319

M. Wittmar, M. Veith (INM), Small is beautiful - for longer, European Coatings Journal, (04/2009), H1571, 100-105

M. Schem, T. Schmidt, J. Gerwann, M. Wittmar, M. Veith, G.E. Thompson, I.S. Molchan, T. Hashimoto, P. Skeldon, A.R. Phani, S. Santucci and M.L. Zheludkevich (INM, UNIMAN, CASTI, AVEIRO), CeO<sub>2</sub>-filled sol-gel coatings for corrosion protection of AA2024-T3 aluminum alloy, Corrosion Science 51 (2009) 2304-2315

M.Zaharescu, L.Predoana, A.Barau, D.Raps, F.Gammel, N.C.Rosero-Navaro, Y.Castro, A.Duran, M.Aparicio (ICF, ICV, EADS), SiO<sub>2</sub> based hybrid inorganic-organic films doped with TiO<sub>2</sub>-CeO<sub>2</sub> nanoparticoles for corrosion protection of AA2024 and Mg-AZ31B alloys, Corrosion Science 51(9) (2009) 1994-2005

M.Zaharescu, A.Wittmar, V.Teodorescu, C.Andronescu, M.Wittmar, M.Veith (ICF, INM), TiO<sub>2</sub>-CeO<sub>2</sub> nanometric powders prepared by sol-gel method, Z. Anorg. Allg. Chem. (2009), DOI: 10.1002/zaac.200900186, in press

D. Raps, T. Hack, J. Wehr, M.L. Zheludkevich, A.C. Bastos, M.G.S. Ferreira, O. Nuyken, (EADS, AVEIRO) Electrochemical study of inhibitor-containing organic–inorganic hybrid coatings on AA2024, Corrosion Science 51(5) (2009) 1012-1021

N.C. Rosero-Navarro, S.A. Pellice 1, Y. Castro, M. Aparicio, A. Durán, (ICV) Improved corrosion resistance of AA2024 alloys through hybrid organic–inorganic sol–gel coatings produced from sols with controlled polymerisation. Surface & Coatings Technology 203 (2009) 1897–1903

L. Paussa, N.C. Rosero-Navarro, F.Andreatta, Y. Castro, A. Duran, M.Aparicio, L. Fedrizzi (Udine, ICV). Inhibition effect of cerium in hybrid sol-gel films on aluminium alloy AA2024. Surface and Interface analysis (2009) (in press)

L. Fedrizzi (Editor), Self-Healing Properties of New Surface Treatments (European Federation of Corrosion), Maney Publishing, (15. November 2009), ISBN-10: 1906540365, Book with several contribution of the MULTIPROTECT consortium (8 of 16)

J. Cano, O. Zubillaga, G. Imbuluzqueta, P. I. Azcarate (INASMET) Hexavalent chromium free anodization with conducting polymers and nanoparticles, WO002009098326A1, (Publication: 13.08.2009)

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