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### Approvals

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## Summary of project results

IOLISURF, a 6<sup>th</sup> framework project of the European Union, has been successfully concluded in March 2009. After three years of work, the project generated substantial progress in what is now the frontier of electrodeposition; the use of non aqueous solvents as media for the deposition of aluminium and other metal coatings. IOLISURF partners dedicated most of their efforts to the use of a specific kind of solvents: “ionic liquids” which are organic or inorganic salts which maintain their liquid state at room temperature. With this approach, they developed processes for the electrodeposition of aluminium that was not possible up to now, solving a major stumbling block in the technology of electrodeposition. The partners also developed ionic liquid based deposition processes for silver and chromium, that may improve on the conventional aqueous bath deposition.

Electrodeposition has been one of the first surface technologies ever developed. Already in early 19<sup>th</sup> century, commercial processes for plating substrates with gold, silver, and copper. Over the years, the method has become a sophisticated and versatile way to confer desirable properties to a substrate without the need of using large amounts of expensive materials. Often, electroplating is used for decorative purposes, but a large number of industrial process rely on electroplating for making surfaces that are hard and/or resistant to corrosion.

Yet, despite the variety of the metals and compounds that can be plated by electrodeposition, there remains a problem: not everything can be plated from aqueous solutions. This is a problem well known to chemists: in order to be electrodeposited, the metal ions dissolved in the solution need to capture one or more electrons at the substrate that acts as electrode. In water, there is a competition for these electrons between the metal ions and the naturally occurring hydrogen ions. If hydrogen ions “win”, no metal is deposited and the hydrogen ions are transformed into elemental hydrogen which then bubbles out of the solution. This is what happens for some reactive metals that cannot be electrodeposited in the presence of hydrogen ions.

For the early years of electrodeposition, it has been known that aluminium cannot be deposited from aqueous baths and many attempts have been made to use non aqueous baths to eliminate the hydrogen ions problems. In general, these attempts have not been successful or, if they were, relied on solvents that were not practical for industrial use because of their toxic properties (e.g. toluene). That was a significant technological stumbling block because aluminium plating has major applications as a protective coating.

Such stood the situation until a new class of solvents was developed: ionic liquids. These are ionic salts, that is formed of a positive and a negative ion. We all know examples of this class of compounds: sodium chloride (the common table salt) for instance: in most case we have solid substances. Yet, it is possible to tune the properties of these compounds, using – for instance – large and asymmetric ions, to destabilize the solid phase and make the compound liquid at room temperature. In most cases, this property is obtained using organic ions as cations, whereas anions are often inorganic.

Ionic Liquids are naturally conductive substances. They are also non-toxic, non flammable, have negligible vapor pressure and, in general, are relatively friendly to the environment. So, they can be used as solvents for a variety of applications. With the interest in these substances growing, in the past years their commercial price started to become low enough that an interest in using them as electroplating media started to develop. In particular, they don't contain hydrogen and therefore they have a larger “electrochemical window” in comparison to water. They can be used – in principle - to deposit aluminium and other electropositive metals (e.g. tantalum, titanium, etcetera).

Despite the promise, for many years it was not possible to develop successful methods for the electrodeposition of aluminium from ionic liquids. The deposits were often of poor quality: scarcely adherent to the substrate and dendritic in texture. Good, conformal and compact films remained a challenge. That was the situation until IOLISURF arrived on the scene. By means of a concerted effort, the partners managed to overcome the challenge and to find conditions in which thick and uniform aluminium layers could be reliably deposited on flat metal substrates. This result is of particular importance for several industrial process in which aluminium is used as a protective coating and where, so far, it had to be deposited by expensive and complex methods such as physical vapor deposition or chemical vapor deposition.

IOLISURF has not only developed methods for electroplating metals with aluminium, but also post-treatment methods that improve its properties and permit to use it as high temperature anti-corrosion applications. The project has also developed new methods, still based on ionic liquids, for the electrodeposition of chromium and silver. These metals can be deposited also from aqueous solution, but ionic liquids as solvents allow the deposition of coatings which have different properties than those deposited from conventional bath, also in conditions with less toxicity risks for the operators.

## **Contractors involved**

The IOLISURF consortium included high level research centres, **INSTM**, **IST** and **CRANFIELD** with complementary expertise in the fields of modelling and characterisation of ionic liquids (ILs), electrodeposition from ILs, surface processing and anti-corrosion and high temperature applications.

The ILs were studied, tested, synthesized and provided to the research centres by an industry, **MERCK** and by an SME, **SOLVIONIC**.

In order to validate the generated knowledge for certain applications, **end users** of electrodeposition processes and manufacturer of electroplating treatments (**GALVANICA**, SME), gas turbine (**NP**, IND) and chemical and electrochemical plants (**CABRO**, SME) were also actively involved in the partnership.

A consulting company, **ALMA**, was dedicated to the management of the project.

Full names of **partners** are given below:

Consorzio Interuniversitario Nazionale per la Scienza e la tecnologia dei Materiali, **INSTM** (Italy)

Instituto Superior Tecnico, **IST** (Portugal)

Cranfield University, **CRANFIELD** (United Kingdom)

**MERCK** KgaA, (Germany)

**GALVANICA** PARMENSE di Mauro Fantini (Italy)

**SOLVIONIC** (France)

**CABRO** (Italy)

Nuevo Pignone S.p.A, **NP** (Italy)

**ALMA** Consulting Group SAS (France)

## Scientific approach

To achieve its ambitious objectives, apart the management tasks, the IOLISURF work programme has been split down into 5 work packages:

- 2 work packages are dedicated to **define materials, standards, procedures** and to **synthesize and quality assess** the **ionic liquids** needed for electrodeposition (WP1 and WP2)
- 1 work package (WP3) is dedicated to the development and improvement of **deposition methods**, to understanding the **atomic level processes involved**, and to the definition of the **composition structure and properties of the coatings** deposited
- 1 work package (WP4) is dedicated to the set up of a **small electrodeposition plant** for batch processing, taking into account the need of operating in dry conditions.
- 1 work package (WP5) tests the coatings obtained in relation to **standard industrial requirements**.
- 1 work package (WP6) is dedicated to the **management of knowledge** (intellectual property rights, dissemination activities and exploitation plan).

The objectives of main technical WPs are detailed below:

- WP1 – Preliminary activities and basic specifications
  - To identify the basic specification of the project
  - To identify the relevant ionic liquid needed for the project (preliminary selection)
  - To select the targeted materials and allows selection
- WP2 – Study and synthesis of ionic liquids
  - Develop processes and procedures for the study, synthesis, and characterisation of ionic liquids suitable as electrolytes for the deposition of metals and alloys.
  - Understand the electrochemical behavior and QSAR of ionic liquids.
  - Develop a procedure for the manufacture and the distribution of the ILs between the partnership.
- WP3 - Electrodeposition from ionic liquids
  - Develop processes and procedures for the electrodeposition of selected metals and alloys from ionic liquids as electrolytes
  - Understand the atomic level mechanisms of electrodeposition especially in view of the structure and properties of the IL used
- WP4 - Post-processing and electrodeposition batch processing test device development
  - Develop and optimize methods for the diffusion of deposited layers by thermal and other post-processing methods.
  - Set up a 5 liter test device.
- WP5 - Tests and industrial validation

Test the prepared coatings in industrial parts and conditions “at scale”.

## **Work performed and achievements**

### ***WP0 – Project Management***

#### **1. Project objective**

To ensure an efficient technical, administrative, financial and strategic coordination of the project, in order to reach the goals planned within the Description of Work document.

#### **2. Project achievement**

- creation of a group dynamics for an efficient collaboration between all the partners
- creation of an intranet platform (MYNDSPHERE) to share documents, follow the execution plan, organize meetings
- organisation and follow up of the Steering Committee meetings/audio conferences
- management of the delivery and of the follow-up of scientific, administrative and financial documents, respecting all the deadlines fixed by the European Commission

### ***WP1 – Preliminary Activities***

#### **1. State-of-the art at project start**

Electroplating has been widely used and is readily commercialised to plate more noble metals, e.g. gold, silver, copper, nickel, chromium etc. However, more active metals it is not possible to plate from aqueous solutions because elemental hydrogen is produced rather than plated metal. Thus, for the many years of successful commercial electroplating it was known that aluminium cannot be electrodeposited from aqueous solutions. Alternative process routes have been investigated at a laboratory scale based on non-aqueous solvents, e.g. toluene, or molten salts. Each approach has reached technical barriers to commercialisation. This was the status quo until a new class of solvent was developed – ionic liquids – and this project looks at the potential of using ionic liquids as a solvent to permit active metal electroplating.

#### **2. Project objectives**

- a) Preliminary selection of suitable ionic liquids in function of their physico-chemical properties (conductivity, viscosity, aluminium salt solubility) with the aim to chose the moist suitable for Al-electrodeposition.
- b) Materials and alloy selection, with the aim of down selecting the most promising material systems for research and study in the project work packages WP3-WP5.
- c) Definition of specific coating performance tests that are to be investigated to determine how well the ionic liquid plated coatings perform.

#### **3. Project achievements**

- a) Four types of ILs were individuated including: [EMIM][Al<sub>2</sub>Cl<sub>7</sub>], [BMIM][Al<sub>2</sub>Cl<sub>7</sub>], [BMPL][Al<sub>2</sub>Cl<sub>7</sub>] and [EDMPA][Al<sub>2</sub>Cl<sub>7</sub>].

Furthermore, for each of these ILs, different AlCl<sub>3</sub> molar ratios have been investigated. [EMIM][Al<sub>2</sub>Cl<sub>7</sub>] and [BMIM][Al<sub>2</sub>Cl<sub>7</sub>] resulted the most performing material for Al electrodeposition.

b) It was agreed to research and set-up demonstrator depositions of pure Al onto aluminium alloys like Al-Li and onto non-aluminium materials used for the manufacture of rivets and bolting stock. Both of these examples have large market potentials in the aerospace industry.

A second area was research into chromium (VI) replacement technology, and alternative markets using chromium (III) based ionic liquids. A third theme was the manufacture of aluminium intermetallic alloys, specifically NiAl and (NiPt)Al using Al plating from ionic liquids and post heat treatment. A fourth theme also examined the potential for protecting welded microstructures using aluminium plating from ionic liquids.

c) The third task in WP1 was to identify applications and test regimes for these new ionic applications and test regimes for these new ionic liquid plated coatings. These included:

- Aqueous/galvanic corrosion to be undertaken at IST and ISTM.
- Tribo-corrosion could be investigated at IST should this be necessary.
- Hot corrosion using molten salts can be undertaken at Cranfield.
- Cyclic oxidation of intermetallic alloy coatings at 1100°C would be undertaken at Cranfield.
- Thermal barrier coating manufacture would be undertaken at Cranfield (EB-PVD) and Cabro (plasma spraying).
- Cyclic oxidation of TBC systems will be undertaken at Cranfield.

## ***WP2 – Synthesis and QSAR of new generation and ionic liquids for AL, Cr, alloys deposition***

### **1. State-of-the art at project start**

Prior to this project, aluminium electrodeposition had been demonstrated in chloroaluminate ionic liquids, a class of ionic liquids containing aluminium(III) chloride complexes which are reactive with water and sensitive to oxygen and moisture content. It was unclear if electrodeposition from other, less water reactive and air sensitive materials were possible. Even given the use of these systems, it was unclear if the large-scale production of chloroaluminates could be achieved.

Electrodeposition of chromium from non-aqueous systems had also not been demonstrated, with the exception from the chloroaluminate systems mentioned above. All successful attempts to electrodeposit chromium from ionic liquid media had been carried out using hydrates of chromium(III) salts, which face the same challenges as aqueous based systems.

As ionic liquids are relatively new materials, there were no general models for predicting the transport properties of these materials. Standard engineering tools such as COSMO-RS simply have no capacity for dealing with solutions composed of anionic and cationic components. Selecting which pair of anionic and cationic components would give the optimised viscosity, density, specific conductivity, metal complexation, etc. was strictly a matter of intuition and systematic measurement of physical properties.

### **2. Project objective**

The goals of WP2 were threefold. The first was to develop processes and procedures for the study, synthesis, and characterisation of ILs suitable as electrolytes for the deposition of metals and alloys. The second was to understand the electrochemical behaviour and QSPR of ILs. The third was to develop procedures for the manufacture and the distribution of the ILs between the partnership.

### **3. Project achievement**

In the area of aluminium electrodeposition, a rigorous attempt was made at the beginning of the project to develop non-chloroaluminate ionic liquids for the electrodeposition of aluminium, thus avoiding the water- and air-sensitive nature of the chloroaluminates. As these attempts were proving futile, it was therefore decided to focus attention on optimising the conditions with which the chloroaluminates were produced, minimising their exposure to moisture during their production and handling. During the course of this project, the partners were provided with ca. 20 kg of chloroaluminate ionic liquids. Simultaneously, although driven by a different end user, Merck produced and delivered multi-tonnes of a chloroaluminate product, thus demonstrating the feasibility of large scale production of these materials.

Materials for chromium electrodeposition was approached in two manners. The first approach was the use of aqueous chromium(III) salts dissolved in non-chloroaluminate ionic liquids. A combination of chromium trichloride hexahydrate in 1-butyl-3-methylimidazolium tetrafluoroborate proved the most successful for the production black chrom deposits (see below). An alternative non-aqueous system was also developed, overcoming the reported difficulty of dissolving chromium(III) salts in non-chloroaluminate ionic liquids. Conversion of anhydrous chromium trichloride to an organic hexachlorochromate complex provided a readily soluble precursor for dissolution in a much broader range of ionic liquids ever before achieved. Electrodeposition of chromium from these solutions was demonstrated, but time did not allow for development of an industrially relevant electroplating system. Patent applications on the use of hydrated chromium(III) salts for the preparation of black chrom and on the preparation of anhydrous hexachlorochromate ionic liquid solutions have been filed with the European patent office.

In order to provide the basis data set for QSAR modelling of the physical properties of ionic liquids, a series of measurements of the density, viscosity and conductivity of a range of ionic liquids was carried out. The model which was derived from an analysis of these measurements was tested and the results published in Physical Organic Chemistry. Further measurements of the effect of neutral co-solvents on the physical properties were also generated, although time did not allow for their use in generating a model for this behaviour.

## ***WP3 – Electrodeposition from ionic liquids***

### **1. State-of-the art at project start**

At the start of the research work, electrodeposition from ionic liquids was a process described in the scientific literature but which was not reported to be industrially utilized. In most cases, the coatings obtained were described as dendritic and scarcely adherent to the substrates.

## **2. Project objective**

The objective of the IOLISURF project was a decisive advance in the quality of the coatings obtainable from ionic liquids, with a specific aim towards diffuse aluminium coatings for high temperature protection of superalloys. Other applications were also examined, such as decorative coatings and black coatings for applications in the solar or heat exchanging industry

## **3. Project achievement**

The project attained nearly all its original objectives, in particular we developed a new process for the electrodeposition of aluminium that produces coatings which are compact and adherent. Other processes for the electrodeposition of black chromium and other materials have also been developed.

### ***WP4 – Post-processing and electrodeposition batch processing test device development***

#### **1. State-of-the art at project start**

Before IOLISURF, two different commercially accepted process routes were utilised to form bond coats as part of a thermal barrier coating system for high temperature applications: these were custom MCrAlY alloys deposited by plasma spraying and NiAl/(NiPt)Al bondcoats manufactured using CVD aluminising. Electroplating of aluminium and post processing of the electroplated coating to form an oxidation resistant bond had not been previously researched.

#### **2. Project objective**

- a) To determine whether aluminium electroplated from ionic liquids could be utilised to form adherent bondcoats as part of a TBC system for high temperature applications. A secondary aim was to assess the performance of this new coating against the classical CVD aluminised design.
- b) To determine if the electroplating process of aluminium from ionic liquids could be scaled up for industrialisation.
- c) To determine whether aluminium could be plated onto AlLi alloys therefore providing corrosion resistance to this class of alloy.

#### **3. Project achievement**

- a) Able to deposited dense, compact and adherent aluminium coatings from ionic liquids on nickel based superalloys, steels and aluminium alloys.
- b) Able to post heat treat the aluminium to form desirable nickel aluminide intermetallics as high temperature environmental protection coatings and bondcoats for TBCs. Two different processing routes are to be patented.

- c) Semi-industrial 5L tank has been designed, fabricated and commissioned. It is currently being used within an industrial environment.
- d) Able to plate relatively large components (300x300mm) with a good quality adherent coatings.
- e) Successfully coated ALi alloys with Al. Huge potential for aerospace design

#### **WP5– Tests and industrial validation**

##### **1. State-of-the art at project start**

Environmental protection coatings and bondcoats produced using CVD and plasma spraying have been used within industry since the 1970's. Within the laboratory these coatings have been tested using cyclic oxidation, isothermal oxidation trials and high temperature corrosive environments. The performance of these CVD deposited aluminides and their mode of failure is well understood.

##### **2. Project objective**

- a) To determine whether the bondcoats produced within WP4 could be a viable alternative to those produced using traditional techniques.
- b) To determine whether a ceramic topcoat coating could be applied to the bond coat to make a desirable high temperature thermal barrier coating system.
- c) To determine whether turbine blades could be electroplated with aluminium

##### **3. Project achievement**

- a) New bondcoats based on nickel aluminide intermetallic have been produced from electroplated aluminium using a number of novel heat treatment regimes. Two different processing routes based on ionic liquid plated Al have been shown to produce coatings which are microstructurally and mechanically similar to those produced using traditional CVD techniques.
- b) A ceramic thermal barrier coating (8% Yttria stabilised Zirconia) has been successfully applied to bondcoats produced from ionic liquids, demonstrating the feasibility of this technique to manufacture bondcoats at potentially lower cost than the classical high temperature CVD routes.
- c) Turbine blades have been successfully electroplated with aluminium and heat treated to form a nickel aluminide bondcoat on turbine hardware with acceptable composition control and coating uniformity.

#### **WP6–Knowledge management**

##### **1. Project objective**

- management of knowledge and intellectual property
- establishment of exploitation and dissemination strategies.

##### **2. Project achievement**

A public web site was created: [www.iolisurf.eu](http://www.iolisurf.eu)

A brochure was printed and distributed to the main conferences/congresses of the field  
An exploitation seminar was organised.

16 publications acknowledge the IOLISURF project.

Some exploitable results have also been identified among which are the electrodeposition of aluminium on steel and on nickel alloys, and on lithium-aluminium alloys; the electrodeposition of black chromium on copper for solar heat absorption applications; the development of new chromium(III) complexes suitable for non-aqueous electrochemical systems; a QSAR-based method for the prediction of transport properties of ionic liquids; and prototype systems for the lab-scale electroplating of aluminium from chloroaluminate ionic liquids.