NMP3-CT-2003-505953

ASTERIXE

- Development of advanced surface technology for extended resistance in extreme environment -

Instrument: **STREP**
Thematic Priority: **NMP**

36M Publishable activity report (Deliverable 7.6)

Period covered: *from 01/01/2004 to 31/12/2006*
Date of preparation: *02/04/2007*

Start date of project: *01/01/2004* Duration: *36 Months*

Project coordinator name: *Dr. Pierre JULIET*

Project coordinator organisation name: *CEA Commissariat à l'Energie Atomique*

Revision [7]

Document Information

Document Name: 36M Publishable Activity Report - D7.6
ID ASTERIXE_36MPublishableActivityReport_D7 6_CEA_020407_V7.doc
Revision: Version 7
Revision Date: 02/04/2007
Author: Pierre Juliet/CEA
Dissemination level: Public

Diffusion list

Consortium and the EC

Approvals

	Name	Company	Date	Visa
First Author	Jetta Keranen	ALMA	23/03/2007	OK
Coordinator	Pierre Juliet	CEA	02/04/2007	OK
Quality Manager	Jetta Keranen	ALMA	23/03/2007	OK

The report was circulated also to the Steering Committee for validation.

Documents history

Revision	Date	Modification	Author
Version 1	15/12/2006	First draft	Keranen/ALMA
Version 2	28/02/2007	Second draft based on partners texts	Keranen/ALMA
Version 3	13/03/2007	Third draft based on partners texts	Keranen/ALMA
Version 4	19/03/2007	Fourth draft based on partners texts	Keranen/ALMA
Version 5	23/03/2007	Fifth draft based on partners texts	Keranen/ALMA
Version 6	02/04/2007	Sixt draft	Juliet/CEA
Version 7	02/04/2007	Final draft based on partners texts	Keranen/ALMA

Content

ASTERIXE – Development of advanced surface technology for extended resistance in extreme environment (Contract no NMP3-CT-2003-505953)

1. Project execution

Project objectives

ASTERIXE aims to **develop innovative combined surface treatments** to promote a technological breakthrough for high performance in the field of **Environmental Barrier Coatings (EBC's)**. These coatings play a key role in high temperature (>600°C), highly corrosive environments and high mechanical (and cumulative) stress conditions. The goal of the project is to open **new routes of surface engineering** by **combining coating deposition** and **advanced post treatment technologies by pulsed e-beam (PEB)**. The understanding of the phenomena interacting on the coating composition and structure will be developed throughout the project with the creation and optimization of a **model predicting the coating composition and structure after post treatment**.

The corrosion resistant **coatings** will be deposited by a range of **different processes**, **electrochemical, spray** or **vapour deposition**, the process choice being mainly dependent on the elemental composition needed to fulfill the application requirements. The **pulsed e-beam treatment** will be used to give the coating its final structure and morphology. This may for some applications involve **interface melting** promoting coating to base material alloying. As a result, the **coating process** will be **optimized** by using the results of the **predictive model**, and by **testing new combinations** with respect to the chemical composition (new chemical systems, hybrid layers, self-repairing coatings…).

The TBC (Thermal Barrier Coating) will be deposited by EBPVD. This technology allows the development of luminescent phosphorus (Lanthanides) insertion into the YSZ. The project aims to validate both material and diagnosis technology.

Project deliverables include:

- A new concept of interface treatment leading to enhanced coating adhesion strength by simultaneously melting of the coating and the substrate surface
- A new process of extremely fast surface quenching from the melt leading to values of density and toughness of the surface layer close to the theoretical "bulk" values without affecting the substrate material
- A new route to obtain still unavailable chemical compositions by combining multilayer coating and surface alloying
- A new route for a self diagnostic coating or sensor coating designed to allow "in service" temperature measurements

Consortium

Coordinator

Dr Pierre JULIET, juliet@chartreuse.cea.fr, www.prodige.com
Commissariat à l'Energie Atomique – CEA – Grenoble (F)

Contractors

- Forschungszentrum Karlsruhe GmbH – FZK – Eggenstein-Leopoldshafen (D)
- Southside Thermal Sciences Ltd - STS – London (UK)
- Cranfield University – Cranfield (UK)
- Consorzio Interuniversitario Di Scienza e Technologia Dei Materiali – INSTM – Firenze (I)
- Centrum Technologii Cienkowarstwowych SP.zO.O – CTC – Opole (PL)
- Turbocoating – Rubbiano di Solignano (I)
- Fraunhofer Gesellschaft zur Förderung der angewandten Forschung e.V. – Fraunhofer-ILT – München (D)
- European Aeronautic Defence and Space Company – EADS CCR – Suresnes (F)
- KSB Aktiengesellschaft – Pegnitz (D)
- ALMA Consulting Group – Lyon-Nogent sur Marne (F)

Work performed, partners involved

Research activities

WP1: Theoretical requirements of extreme conditions coatings and new measurement methodology

The WP1 aimed to define precisely the extreme service condition envisaged from a diverse range of industrial requirements as well as carry out a theoretical assessment of available, existing coating solutions and an analysis of coating requirements for pulsed electron beam processing. In addition, the application of thermographic phosphor technologies to thermal barrier coating (TBC) systems was studied.

As a result of in Task 1.1 industrial reviews four technological areas, highlighted as extreme, were recommended for study:

1) Conditions involving extreme corrosion processes or extreme oxidation process,
   a) highly corrosive liquids for pumping applications
   b) thermal protection at ultra high temperatures, above 1000ºC.
2) Conditions involving tribo-corrosion,
   a) hydro-abrasive wear, erosion etc
   b) fretting

Having identified the classes of extreme damage to be researched substrate materials were defined that encompass the aerospace industry: aluminium alloys, titanium alloys and steels, the pump industry: steels with various wear resistant coating; and the gas turbine industry: nickel based alloys with corrosion protection coatings or thermal barrier coating systems.

Task 1.2 built on this background to define and develop an innovative combination of coating technologies and surface treatments to provide functionally structured solutions to these extreme service conditions. The goal if this aspect of the study was to investigate the combination of the Pulsed Electron Beam, coupled with more traditional PVD and thermal spray technologies to produce improved functionally gradient surface treatments against severe oxidation, corrosion and tribo-corrosion conditions. Preferred coatings systems were recommended and later investigated.

These included:

1) Advanced lanthanide doped TBC systems, with structural stability up to 1500ºC.

2) New reactive element doped bondcoat systems post processed with PEB for improved surface finish and near surface microstructures.
3) New multi-component, multi-layered metal nitride, metal carbide and diamond like carbon (DLC) coatings for extreme wear applications or as environmental barriers, based on the establishment of controlled nano-structures within the coating system, that can provide functionally gradient properties capable of resisting severe tribo-corrosion conditions.
4) Smart, self sensing coating systems which can provide in-situ diagnostics. This application will focus on sensor TBC systems.

Task 1.3 further extended these definitions by reviewing the feasibility of processing these various coating system surfaces using a pulsed electron beam (PEB). This required a theoretical study of the penetration depths of high energy electrons into a materials surface, using Monte Carlo modeling code. The simulations were performed for two extremes of the materials spectrum, aluminium and tungsten, later titanium as an important aerospace material was also evaluated. For aluminium and titanium it was predicted that consolidation depths of up to or in excess of 10μm could be achieved. For tungsten the coating thickness had to be below 7μm, preferably 4μm and a 120keV beam energy was needed to achieve any consolidation. Later this technology was extended to the surface treatment of MCrAlY high temperature coating systems as reported in Task 4.

The last of the sub-tasks in work package 1, Task 1.4 focused on the design and manufacture of a self diagnostic thermal barrier coating system, from a theoretical perspective. The technology, based on adding thermographic phosphors to the TBC systems was evaluated and suitable phosphor materials reviewed. Three basic approaches were down selected for investigation and all three approaches were studied.

In conclusion, WP1 successfully achieved all of its aims within planned timescales and established the theoretical basis for the research studies to be undertaken within ASTERIXE on coating systems and surface treatments for extreme service conditions.

WP2: Development of the coupled coating/PEB process for existing coating

No promising results were found after Pulsed Electron Beam post treatment of low melting point PVD coatings. In the same way, there is no interest of a Pulsed Electron Beam post treatment of a high melting point material PVD coating (TiN for example) on a low melting point material substrate (aluminium for example). Concerning titanium deposited on steel, very good results were achieved after Pulsed Electron Beam post treatment. Whatever the process and deposition parameters, it leads to higher hardness, lower friction coefficient and smoother surfaces.

Significant improvements of HVOF (or VPS) as deposited coatings were achieved after Pulsed Electron Beam post treatment. Smoothening and densification of HVOF MCrAlY coatings after the post treatment were observed and, in a general way, there is an improvement of interface bonding of both HVOF and VPS coatings. In the same way, bonding to the substrate can be achieved for coatings deposited by means of thermal evaporation.

Effects of a Pulsed Electron Beam post treatment on simple as deposited coatings depend strongly on the composite film/substrate. In some cases, it has been shown that the quality (smoothening, densification, adhesion improvement…) of this composite can be increased significantly.

WP3: Development of the coupled coating/PEB process for new material coating by surface alloying

Two post treatment methods were explored for their use to create new surface layers; Pulsed electron beams (PEB) and lasers. Lasers were explored to investigate the alloying of AlCr layers deposited by ionic liquids and the re-melting of CrC-NiCr layers sprayed using HVOF technique. Both different tasks could be fulfilled more or less. The alloying operated only at relative high pre-heating temperatures (660°C, the melting temperature of Al) of the sample. Nevertheless, an almost perfect intermixing of coating and substrate could be achieved. The other even more promising result concerns the re-melting of CrC-NiCr coatings. Applying adequate preheating a 25 µm thick layer of this coating could be re-melted und by that densified entirely. Especially the absence of any cracks within this modified layer is very promising. Such laser treated coatings might have a great potential to be used in corrosive seawater environment.
PEB treatment was explored for several different principal architectures, single layers varying in thermo-physical properties like for example melting point, multilayer coatings and single layer multi-element coatings. The alloying of most material combinations worked properly. However, alloying of high melting point materials like W into low melting point materials like Al failed. The idea to overcome such difficulties by introduction of a intermediate layer having medium melting temperature still has to be proven finally. The idea of multilayer coating was explored using AlCr coating with different number of layers. After PEB treatment the starting architecture was not preserved and no influence of the number of layers on the result after PEB treatment could be found. The chosen system AlCr periodically changing, leads in case of thick coatings to highly brittle phases and cracking of such layers after PEB treatment was expected and occurred.
The third point multi-element single layer coating was investigated using a Noricrom target. Beside all difficulties in deposition such layers could be remelted and alloyed to the substrate. The potential of such coating to be used to substitute massive Noricrom parts is one of the most promising outcomes of this WP.

Concerning the study of thermal barrier coating, suitable phosphor compositions were selected from the lanthanide series which posses a high energy band gap and good shielding from the conventional TBC host material – $ZrO_2 8wt\% Y_2O_3$. Sm, Eu, Gd, Tb and Dy all showed promise from this early review. Methods for TBC manufacture based on EB-PVD technology were proposed including an approach to make a temperature, heat flux and erosion damage sensing system embedded in a thermal barrier coating. It was proposed to further research whether such sensors could provide information on the structural integrity and corrosion resistance of the TBC.

In the later stage of the work sensor EBPVD coatings of specific compositions were produced to enable temperature measurements up to 1400°C. This is the first time ever such an approach was taken using EBPVD coatings. Moreover, the phase change occurring during the thermal history can be monitored by suitable spectroscopic techniques.

WP4: Characterise at the lab scale the coating functional properties

The characterization at the lab scale of the coating systems obtained by the consortium produced many interesting results which were crucial for the project development. It allowed a continous feedback among the characterization, deposition and post treatment phases allowing the optimization of the processes. Further, the quality of the characterization work produced was excellent covering several topics for the dissemination of the technical and

scientific work in referred journals. A precise determination of the coatings' properties has been fully achieved in agreement with original objectives.
The efficiency of the PEB treatment provided by FZK on the coatings deposited by Turbo has been demonstrated as it was found that the lifetime of the HVOF MCrAlY's bond coats dramatically increases. It was clearly demonstrated by the cyclic oxidation tests performed by Cranfield as stated in the table following reported:

	Test 1	Test 2	Test 3
HVOF	471	215	545
HVOF + PEB	921	778	Not failed*
VPS	323	98	159-180
VPS + PEB	261	98	213
LVPS	110	102	196
PtAl	210	313	148

It appears that the PEB treatment of the HVOF bondcoats significantly improves the cyclic oxidation life of the coatings. This is not the case of those prepared by VPS. It was also demonstrated that HVOF bond coats show significantly better performance than any other state of the art technology.
Fretting wear tests were run at EADS in order to determine the wear resistance properties of different coatings deposited on two types of titanium substrates. The results obtained for PVD tungsten coating deposited on Ti 10 2 3 and Ti-6Al-4V indicate an impact of the substrate on the wear and friction behaviour of the coating, in favour to TA6V substrate. It was demonstrated that good results were obtained with the W coating deposited at the CEA and EB post treated by FZK. The electrochemical measurements realised on aluminium and chromium coatings allowed to conclude that the coatings presenting AlCr based materials can be considered as an inadequate solution to avoid corrosion, even if multinanolayers have been obtained. Although, it can be noticed, that the sacrificial behaviour of coatings demonstrates their interest as a cadmium alternative only if it is possible to modify the surface morphology by increasing the coating density. It was what EADS expected with the post electron beam treatment, but, the coatings post treated showed a poor porosity too and a non sacrificial behaviour due to the modification of the surface composition.
A very low level of intensity between the two electrodes (steel + coating and aluminium 2024T3) is very interesting in each case to prevent galvanic corrosion. This study shows that each coating density is too low and also can not play a role in a protection against corrosion. These measurements allowed us to demonstrate that the post electron beam treatment realised in this program, is too hard and modify the material composition instead.
The SIMS characterization which has been used for the determination of alloying and diffusion processes has been performed on various substrates. The evidence of interdiffusion process in a heat treated aluminum electrodeposited coating on a nickel substrate has been found. Such aspect was crucial indicating the possibility to expand the use of the aluminium electrodeposition to the production of coatings for high temperature. The topic is still subject of reaserch in the context of a further EU funded project "Iolisurf" which is entirely dedicated to this topic and that was started on the basis of the results obtained in ASTERIXE.
Further, standard and sensor EBPVD coating systems were tested on a thermal gradient test rig and have shown similar durability. The test was performed in a 'realistic' condition showing high surface temperatures achieved by heating with an oxygen–gas flame and 'cool' substrates (achieved by cooling with air). This caused temperature gradients of between 200-300 °C.

WP5: Concept of an industrial equipment capable to integrate both processes

The original aim to design an integrated facility that means a facility combining the coating and the PEB process in one process chamber was given up, due to the uncontrollable interference of the magnetic fields of the coating and the PEB facility.

Two configurations, a batch and a roll to roll equipment concept are possible. Both require, due to the above mentioned problems by the magnetic fields, two individual process chambers with a transfer chamber in between these two chambers. In the case of roll to roll equipment the main problem will be to evaluate and adjust the efficiency and the time needed for the coating process and the PEB treatment.

Finally a stand alone PEB facility for the treatment especially of HVOF sprayed MCrAlY due to the extremely positive obtained with such treated coatings was designed. The integration into the production process was positive evaluated. The design of the new facility is that flexible that it can be adapted via any kind of transfer system to other coating processes and devices. Even for a roll to roll equipment the electronic part, cathode, accelerator, marx and control unit can be used without any major changes.

Management and use and dissemination activities

WP6: Knowledge dissemination and exploitation of the results

The main objectives of the work packages were i. the organisation of the knowledge management and strategies (including continous benchmarking) and ii. the dissemination of project results to the scientific community and to a wider range of potential users. The public results of the plan for using and disseminating the knowledge are attached at the end of the report.

WP7: Management of the project

The work package included the carrying out the technical, administrative, financial and strategic coordination of the project and the animation of the consortium:

- Building up the ASTERIXE communication platform "PRODIGE" with administrative, financial, technical, communication and archive sections,
- Producing and updating the Project Quality Assurance Plan detailing, for example, practices and advancements of the project; periodical follow-up of the Project Quality Indicators,
- Collection and submission of activity, management and financial reports on due dates,
- Organisation of the periodic project meetings,
- Creation of the project brochure for external diffusion,
- Management of contract and Consortium Agreement amendments, …

The completion of the management tasks in WP6 and 7 strongly depended on the efficiency and reactivity of the consortium and also a good communication between partners. A well-scheduled and quality methods according to standard and efficient procedures and followed by all partners, made easier the full accomplishment of these activities.

End results achieved

Increasing the working temperature of turbines is of key importance in both energy production and aeronautic fields and ASTERIXE provides definitive breakthrough concerning the TBC systems including bond coat and oxide layer.

- Concerning the bond coat, the PEB process allows a coating densification providing a factor 2 life time improvement. Moreover, the surface alloying with Zr could increase also the corrosion resistance.

- Concerning the YSZ layers, lanthanides insertion allows on line temperature monitoring up to 1400°C instead of 800°C initially planned. Moreover, the temperature stability of the YSZ is increased by this dopant insertion.

These very promising results concern both bond coat and YSZ layers and open the way for a new generation Thermal Barrier Coating system of advanced functionality.

To propose these technologies to the aeronautic and terrestrial turbines market, the following development have to be carried out:

- Qualification of a spectroscopic "field detection" system.
- Implementation of the dopant insertion in the atmospheric plasma spray technology.
- Industrial development of large size PEB facilities.

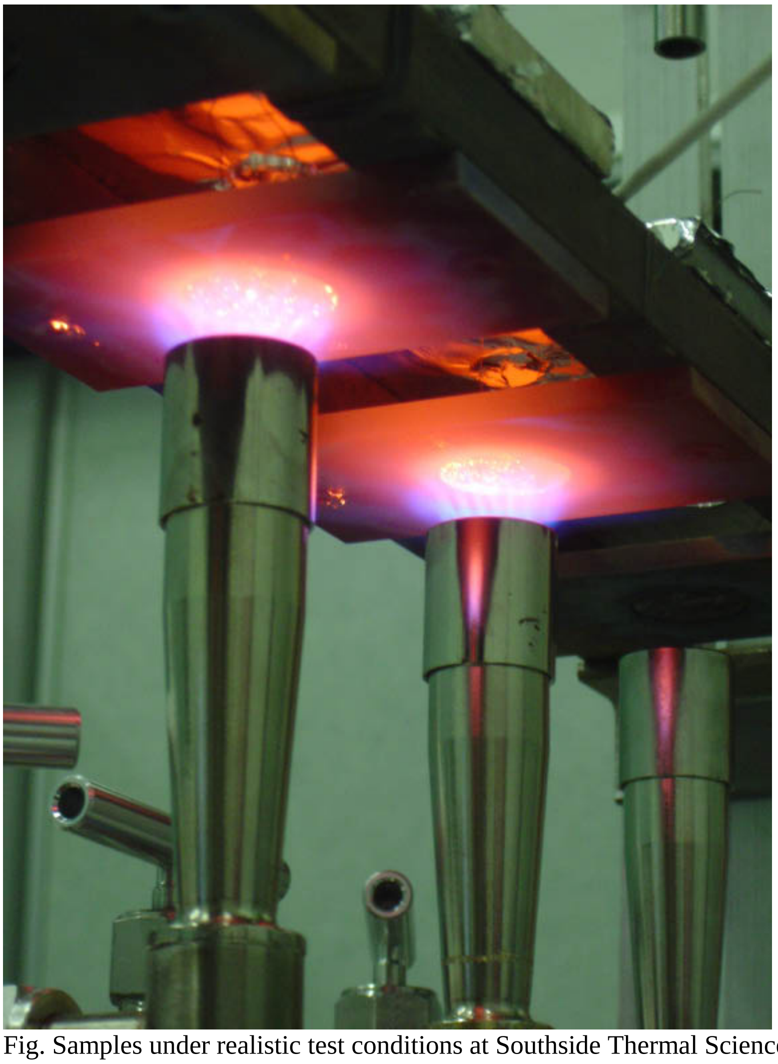

Fig. Samples under realistic test conditions at Southside Thermal Sciences, London.

2. Dissemination and use

The below table gives some details on the already publishable results and non-confidential knowledge available from the project. For any inquiries (like for publications), please contact:

Dr Pierre JULIET, juliet@chartreuse.cea.fr
Commissariat à l'Energie Atomique – CEA – Grenoble (F)

Main publishable results identified and their status

Result no	Description of knowledge	Functionnality, main advantages	Innovation, application	Stage of development	Possible market applications or further actions needed/offered
R1	**New coating by coupling deposition technologies and PEB :**				
	1.1 Architectures to alloy a high melting point material to a low melting material	Specific architecture how to combine materials with very different melting points that allows their post treatment by PEB facilities.	Introduction of intermediate layer that allows the successful remelting of High melting point materials on low melting point materials Abrasive coatings on substrates of light element	S&T knowledge, lab result	Sector: Coating Further research or development Type of exploitation: Direct by consultancy; Indirect by licences, subcontracting
	1.3 New original composition by combining multilayering to PEB	PEB treatment can be easily used on coated substrates in order to enhance significantly adhesion as well as roughness. The main result concerns the choice of the composite to be treated by electrons beam. Thus, the melting point of the coating has to be relatively closed to the	PEB treatments can be performed successfully on coatings deposited by means of different PVD technologies (magnetron sputtering, cathodic arc evaporation and Electron Beam Evaporation) with various parameters. PVD and PEB treatments coupling process could be used for mechanical applications. Moreover, coatings obtained by vacuum processes are always "porous"; Corrosion resistance of these deposits should be	S&T knowledge, guidelines, methodologies, development phase – laboratory tested, prototype available for demonstration	Sectors: Aerospace, Gas Turbines, Industrial Turbines, Diesel Engines, Hard coatings for cutting and forming tools, anti-corrosion coatings

Result no	Description of knowledge	Functionnality, main advantages	Innovation, application	Stage of development	Possible market applications or further actions needed/offered
		melting point of the substrates.	enhanced by increasing the barrier properties.	– field tested	
	1.5 PEB post treatment of bondcoats	Increase of density, grain refinement, change of oxidation kinetic, inrcreases durability of TBC's	Volumetric remelting by Pulsed electron beam of pre-deposited coatings and by rapid cooling achievement of fine grained, homogenous pore free surface layer Turbine blades in stationary gas turbines	S&T knowledge, lab result	Sector: Coating Further research or development, licence agreement, private- public partnership, information exchange, available for consultancy
R2	**New coating by coupling ILS and laser post-treatment**				
	2 New coating by coupling ILS and laser post-treatment	Protection of base materials from hot and wet corrosion. Cheap way to the deposition on metallic aluminum coatings	New route for making alloy coatings starting from liquid phase electrodeposition plus laser post treatment The coating systems are intended for corrosion protection applications	Idem	Sector: Coating Further research or development Type of exploitation: Licences, subcontracting