

innovaTiAl

Innovative Coatings for Aerospace, Energy and Automotive Industry



Innovative
processes and materials
to synthesize knowledge-based
ultra-performance nanostructured
PVD thin films on gamma titanium aluminides



Addressing Societal and Industrial Needs

Sometimes, technical progress strongly relies on contributions which are completely unexpected at a first glance. For example, people are fascinated by the superb Airbus A380 airplane, particularly due to its gigantic size, its passenger capacity and its comfort. However, taking a closer look, it becomes evident that materials and manufacturing techniques are the real “miracles” that are covered behind this new aircraft. Novel materials, such as composites and new metallic materials, their fabrication technologies and innovative parts production technologies contribute largely to the success of the enormous engineering challenge of a megaliner aircraft.

Fostered by the aerospace industry, a new class of lightweight alloys has been developed over the last two decades which can sustain temperatures beyond 600°C at only half the weight of steel or nickelbase alloys.

These so called gamma titanium aluminides have proven to meet the requirements for automotive combustion engines as well as for aeroengines, and can be used in gas turbines for power generation. In recent years, different components such as turbocharger wheels, valves or compressor and turbine airfoils made out of gamma titanium aluminides have been successfully developed on a small series or demonstrator scale and have shown major performance benefits.

Today, cost issues as well as the unavailability of a processing chain are major hurdles for mass production of parts. Recently though, the European aeroengine industry was strongly spurred to speed up the implementation process of gamma titanium aluminides by global competitors.

For certain applications, the limited immunity of gamma titanium aluminides against oxidation, wear, erosion and particle impact makes their use challenging. Obviously, the full potential of these innovative materials can only be reached if measures are taken to minimize the degradation imposed by these types of attack. The INNOVATIAL project has addressed in particular the need of these materials for coatings that can enhance both their performance and durability in aggressive environments.

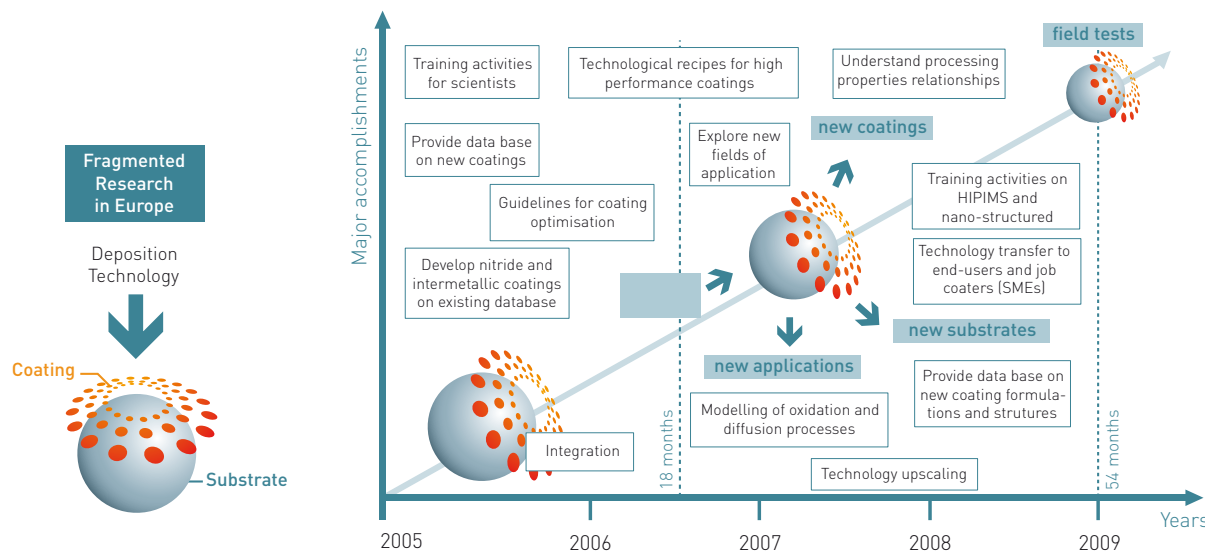
The down-selected coatings developed in the project have proven superior performance relative to any other attempt for protection of titanium aluminides so far, even at the high temperature end at 1000°C. At the same time, the revolutionary novel coating deposition process called HIPIMS (high power impulse magnetron sputtering) is being further developed within the project, enabling fabrication of unique coating architectures and properties.

In addition to the development of protective coatings for titanium aluminides, the INNOVATIAL project has successfully developed coatings for tools suitable to machine difficult to machine aerospace and automotive materials. Performance of the new tool coatings was outstanding even under harsh cutting conditions.

Within 54 months of extensive research and development, the INNOVATIAL consortium has come up with many important successes in the fields of new coatings, nanomaterials, processing technologies and characterization techniques. Some of the coatings developed within the project will be available on the market soon. The novel HIPIMS deposition technique applied to coating manufacture in this project has now made its way into industrial application in various areas of production within and beyond the focus of the INNOVATIAL project. Therefore, this project is a perfect example of European collaborative research and development that strengthens Europe’s leadership in high technology fields to serve society and the environment.

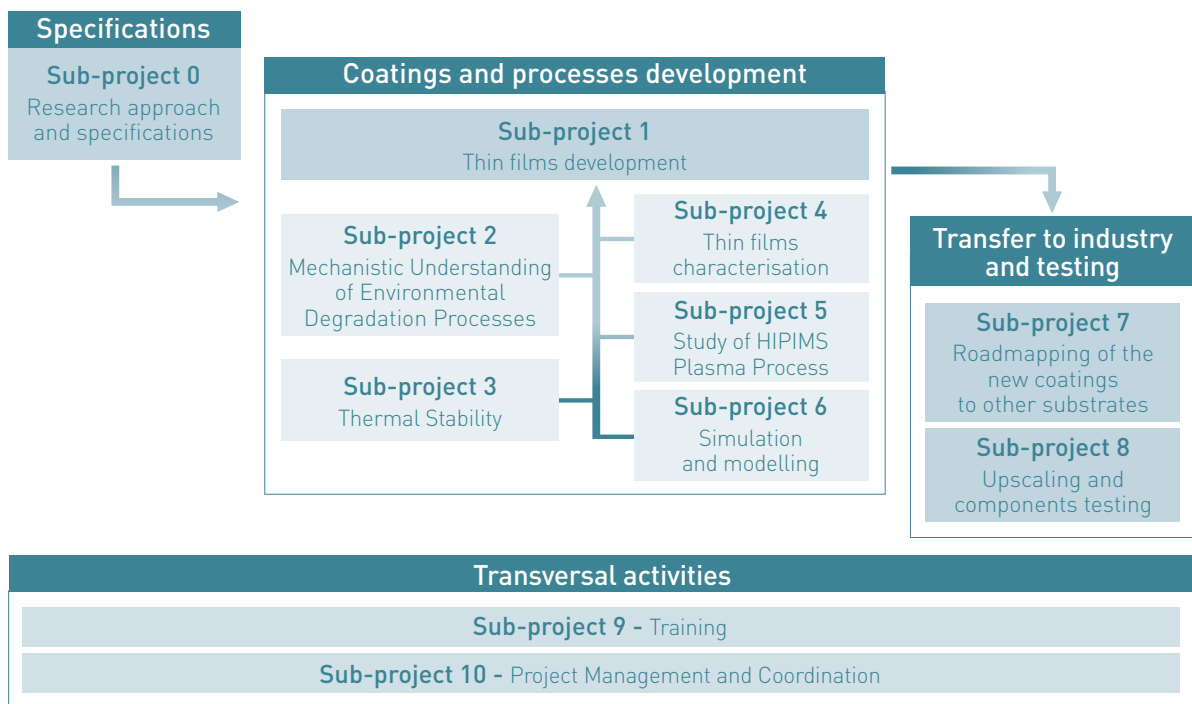
The extraordinary results obtained by INNOVATIAL coatings contribute greatly to the enhancement of Europe’s leadership in the field of innovative light weight materials for a wide range of high tech applications. While aerospace, automotive and energy industries are the pacemakers in this project, it can be expected that other industries will pick up the materials and technologies developed quickly.

Roadmap



Starting from strongly fragmented research in Europe, the INNOVATIAL project succeeded with a strong integration of the major players in the field of coatings development, fabrication, characterization and testing as well as application.

Project Breakdown



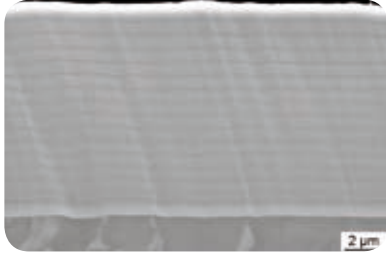
Coatings Development and Fabrication

To meet the challenges of the demanding applications in the INNOVATIAL project several innovative strategies were implemented in the coating development process as well as utilisation of the novel HIPIMS technology. Four different coating strategies were followed to develop coatings to protect γ -TiAl against environmental attack involving nanoscale multilayers, nanocomposites, intermetallic coatings and thermal barrier coatings (TBCs).

| Coating | Deposition technique | Coater | Thickness [μm] | Oxidation performance |
|---|----------------------|--------------|-----------------------------|-----------------------|
| Nanoscale multilayer coatings | | | | |
| TiAlYN/CrN + Al ₂ O ₃ | UBM | HAUZER | 3.5 | 2000h / 750°C |
| CrAlYN/CrN | UBM | SHU | 5 | 2000h / 850°C |
| CrAlYN/CrN | HIPIMS | SHU | 4.5 | 1000h / 900°C |
| CrAlYN/CrN + Al ₂ O ₃ | HIPIMS / UBM | SHU / HAUZER | 5.5 | 2500h / 850°C |
| Nanocomposites | | | | |
| TiAlYN | UBM | MUL | 4 | 1000h / 750°C |
| CrAlYN | UBM | MUL | 4 | 1000h / 900°C |
| Intermetallic layers | | | | |
| Al ₂ Au | UBM | MUL | 4 | 1200h / 850°C |
| Ti-Al-Cr | UBM | DLR | 10 | 1000h / 900°C |
| Ti-Al-Cr-Hf | UBM | DLR | 10 | 1000h / 900°C |
| Ti-Al-Cr-Y | UBM | DLR | 20 | 1000h / 950°C |
| Ti-Al-Cr-Zr-Y | HIPIMS | SHU | 11 | 1000h / 1000°C |
| TBC systems | | | | |
| CrAlYN/CrN + YSZ | HIPIMS / EB-PVD | SHU / DLR | 4.5 / 150 | 1000h / 900°C |
| CrAlYN + YSZ | UBM / EB-PVD | MUL / DLR | 4 / 150 | 1000h / 900°C |
| Ti-Al-Cr + YSZ | UBM / EB-PVD | DLR / DLR | 10 / 150 | 1000h / 900°C |
| Ti-Al-Cr-Y + YSZ | UBM / EB-PVD | DLR / DLR | 20 / 150 | 1000h / 950°C |

Ti-free CrAlYN based nanoscale multilayer coatings were introduced by Sheffield Hallam University (SHU) where Y was used in all critical areas of the coating such as the interface, the base layer and the coating. Various top coats such as CrAlYON (SHU) and Al₂O₃ (Hauzer) were developed for further enhancement of the tribological and high temperature performance of the coating. Due to the HIPIMS etching, CrAlYN/CrN showed excellent adhesion to γ -TiAl and various other substrates like stainless steel and cemented carbide. Unlike many nitride coatings, CrAlYN/CrN reduces its friction coefficient with increasing the temperature and outperforms many intermetallic coatings in aggressive H₂/H₂S/H₂O environment. Most importantly it was demonstrated that HIPIMS deposited CrAlYN based multilayers can preserve the mechanical properties and realise less than 10% fatigue deficit of the base γ -TiAl material.

Ti-55Al-15Cr-0.3Zr intermetallic coatings deposited by standard magnetron sputtering technique produced by the German Aerospace Center (DLR) were further adjusted in chemical composition and densified by HIPIMS/HIPIMS technology at SHU. The approximately 11 μm thick coating exhibited a dense layered structure and established the formation of a thin continuous alumina scale during high temperature exposure in air. The protective scale was still present after dwell time periods at 1000°C exceeding 1000 h, providing effective oxidation protection to γ -TiAl based alloys. The HIPIMS/HIPIMS intermetallic Ti-Al-Cr-Zr-Y layer is also a suitable bondcoat for thermal barrier coatings due to the excellent adherence of zirconia topcoats to alumina scales and represents the most oxidation resistant coating in INNOVATIAL.



Cross section SEM of a γ -TiAl sample coated with HIPIMS intermetallic Ti-Al-Cr-Zr-Y.

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The successful application of protective coating systems to allow for the large scale industrial use of γ -TiAl based alloys as light weight components in high temperature applications such as turbine blades or valves heavily depends on the understanding of the relevant physical and

chemical processes occurring during service, as well as the interrelation-ship between environment, protective coating and substrate. Laboratory-scale research at Montan Universität Leoben (MUL) proposed CrAlYN coatings with 1 and 4 at.% of yttrium being oxidation resistant and showing low interdiffusion.

Based on a combination of experimental and computational materials science, employing density functional theory, it is clarified that Cr, Al, and Y share and fully occupy metal sub-lattice sites of a face centered cubic structure. The calculations furthermore proposed the stability range and development of the elastic constants with the chemical composition of the cubic structure, assisting the coating development.

In the INNOVATIAL project a successful development has taken place of PVD technology in general and specifically HIPIMS technology.

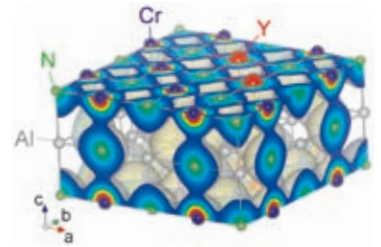
The development made fully automatic process cycles integrating HIPIMS available on the machine installed at SHU. Part of this task was to find a solution for the bias peak current problem, which has lead to a patent application for a special bias power supply or addition of a module to an existing bias power supply. The addition utilizes a very fast arc suppression unit, able to stabilize the bias voltage. This solution is patent pending (patent nr. GB 2437080A).

Within the framework of the INNOVATIAL project, Hauzer has introduced HIPIMS technology in house and is actively marketing this technology since a few years. Together with SHU has Hauzer developed the coating TiAlCrYN/CrN with an Al_2O_3 top coating. The Al_2O_3 top coating was initially produced with pulsed-DC magnetron technology, but this has the disadvantage of a limitation to the coating thickness.

Hauzer worked on the development with dual magnetron technology which enabled thicker coatings, but could also give better coating properties. With this technology it became also possible to improve the properties of the Al_2O_3 top coatings (harder and denser coatings). For this dual magnetron sputtering solution a patent application has been filed.

Using HIPIMS technology enables to perform metal ion etching with rare earth elements: the HIPIMS discharge is particularly suitable to be used for etching of rare metal earth ions. This allows producing hard protective coatings on a conductive substrate that is used at high temperatures. The solution is patent pending (GB0713671.6, EP 08012598.2). Examples for applications are coated tool or components.

In parallel a wide range of aluminide coatings deposited by CVD and pack aluminizing have been studied and developed by Turbocoating on different substrates for application on gas turbine components.



Face centered cubic structure of CrAlYN including the electron density distribution.

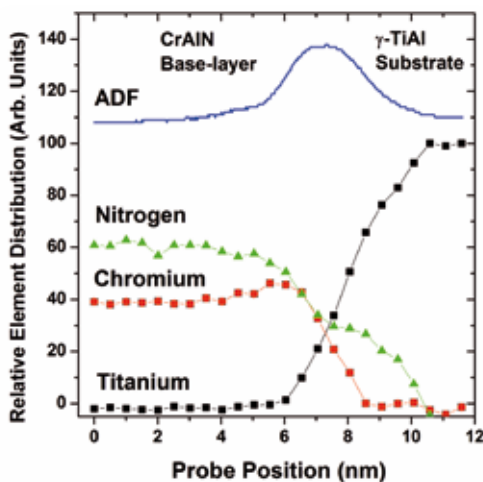


View through a viewport on the plasma of an active HIPIMS cathode (HAUZER).

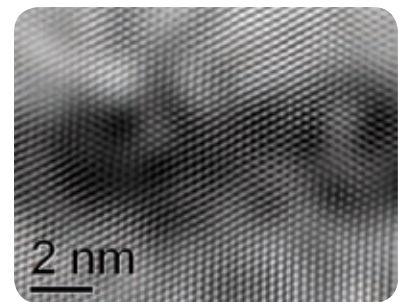
Coatings characterization, testing and modelling

In addition to coatings development and fabrication a major emphasis was placed on the characterization and testing of the coatings developed within the INNOVATIAL project.

INNOVATIAL coatings have one thing in common: they have ultra-fine scale structures and the bonding of the coating with the substrate depends strongly on the structure of the interface between coating and substrate. To understand the relationship between the microstructure, the processing and the properties, we have had to apply the very latest atomic resolution electron microscopy. In particular, we have used spherical aberration corrected transmission electron microscopy to determine structure and chemical bonding using electron beams that are smaller than the atoms we examine! Thus, remarkable details of the interface between the HIPIMS γ -TiAl treated substrate and the CrAlN base layer for a CrAlN/CrN coating could be visualized. The HIPIMS treatment has promoted a thin (2-3nm) depth of Cr ion implantation (compared to 5-8nm for a Cr ion arc discharge (-1200V bias)), and excellent atomic bonding, as shown by the clear atomic image.

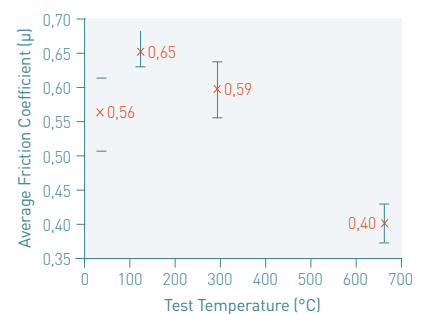


Ultra-high resolution characterisation of the interface between CrAlN/CrN coating, the CrAlN base layer and the γ -TiAl substrate grown using HIPIMS technology, all viewed in cross-section. High resolution atomic image across the image showing the intimate atomic bonding at the interface (right). Atomic resolution chemical composition across the interface (left).



The INNOVATIAL coatings were extensively tested under various conditions such as oxidation hot corrosion and wear. Quite obviously, the different coatings behaved differently under certain testing conditions. Therefore, a major conclusion is that the coatings developed offer not a "one-fits-all" solution but have to be carefully selected according to the service conditions exposed.

It is well known that hard PVD coatings offer greatly improved wear resistance compared to conventional materials. However, one key objective is to develop coatings that offer both high wear resistance and also low friction. This can be achieved at low temperature through coatings such as DLC. However, it is a completely different issue at high temperature, where friction typically increases as temperature increases. Moreover, high temperature wear requires that the structure of the coating does not degrade during prolonged exposure. The newly developed CrAlN/CrN coating using HIPIMS technology offers, for the first time, both high wear resistance and low friction coefficient at high temperature, coupled with excellent coating thermal stability.



Wear behaviour of CrAlN/CrN as a function of temperature; note the remarkably low friction at 630 $^{\circ}$ C

The friction coefficient shows a remarkable reduction at high temperature. The wear resistance of the coating clearly depends on the manufacturing process, with the HIPIMS/HIPIMS technology producing up to a 15 fold reduction in wear rate.

Due to the great importance of high temperature capability of the coatings, interdiffusion between the coatings and the substrate was studied experimentally and by modeling. The Generalized Darked Method as well as the Genetic Algorithm Method were used in order to model the complex multi-component systems. Using these two methods, interdiffusion between TiAlCrY and CrAl-2%YN coatings and a γ -TiAl alloy was successfully modeled. The Genetic Algorithm method was used to optimize the diffusion coefficients in multi-component systems. The optimized diffusion coefficients were then used to compute composition profiles.

Applications

INNOVATIAL coatings were applied to various components such as engine valves, gasifier components, aeroengine airfoils, gas turbine buckets, rollers and dies. The components were supplied by the partners Nuovo Pignone, Ansaldo, MTU Aeroengines, Wolframcarb, Osvat and Fiat.

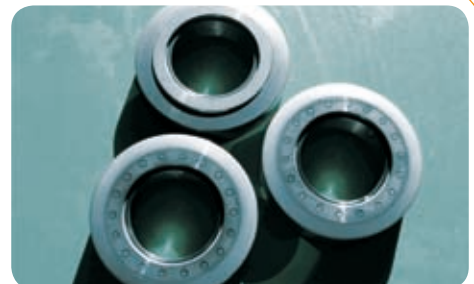
MTU Aero Engines considers the use of INNOVATIAL coatings in a new aero engine concept.



Nuovo Pignone gas turbine buckets (left) and Ansaldo γ -TiAl sections of the syngas exhaust pipe (right) coated with CrAlYN/CrN using HIPIMS technology at SHU.



Osvat engine valves coated with Hauzer DLC H3 coatings (left) and Wolframcarb rolling dies coated with HIPIMS CrAlN/CrN by SHU (right).



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