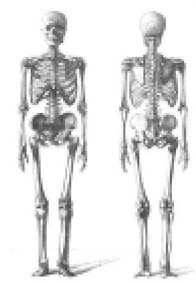
Final publishable summary report - attachment

An executive summary (not exceeding 1 page).

The main aim of the project is to select coating materials and to produce powders using **mechanochemical reactions** by **High Energy Ball Milling** (**HEBM**) and coatings by means of **Cold Gas Spraying** (**CGS**) suitable for 3 different industrial applications, namely:

- ***Aeronautical applications:*** *high temperature resistant and long life load bearings for Aeronautical components working in harsh fretting conditions;*
- ***Mechanical applications: a****brasion and fretting resistant coatings for aluminum alloys employed in automotive industries for the engines manufacturing;*
- ***Biomedical applications:*** *a new class of nanostructured Ti-based coatings for improved performances on osseointegration (due to nanostructure), biocompatibility and high wear resistance.*





The project started with the definition of the final coating properties based on the industrial requirements of end-users and was concentrated on:

- *definition of properties and performances frame for load bearings, mechanical components and biomedical applications;*
- *material systems design based on "product performance/tribological/thermodynamic" integrated approach.*

Aeronautical applications

A customer specifications showed that bearings employed in investigated aeronautical components are submitted to a combination of two (sliding and fretting) wear types (*nickel with intermetalics)*

Coating characteristics:

- dense, thick and nanostructured;
- higher hardness and better friction behavior against temperature;
- elevated temperature corrosion resistant;
- coefficient of friction better than benchmark;

Biomedical applications

Main targeted applications are implant joints with problems due to wear (*titanium reinforced)*

Coating characteristics:

- dense, thick and nanostructured;
- enhanced hardness and wear resistance;
- biocompatibility.

Mechanical applications

Abrasion resistance is the main requirement for this type of application (*FeCu reinforced by Alumina)*

Coating characteristics

- dense, thick and nanostructured;
- high hardness much better than the steel substrate;
- coefficient of friction better than benchmark;
- high repeatability.
  (WC in cobalt matrix)

Coating characteristics

- dense, thick and nanostructured;
- very high hardness.

Main project achievements:

- Reactive powders, suitable for CGS deposition, successfully developed, characterized and validated;
- CGS process properly integrated in the chain manufacturing both for low reactive and highly reactive deposition;
- Nanostructured CerMet coatings deposited via CGS;
- Reliable coatings with superior properties compared with benchmarks;
- Advanced CGS equipment developed for the spraying;

A summary description of project context and objectives (not exceeding 4 pages)

The main aim of the SUPERTSONIC project was to select coating materials and to produce powders using **mechano-chemical reactions** by **High Energy Ball Milling** (**HEBM**) and coatings by means of **Cold Gas Spraying** (**CGS**) suitable for 3 different industrial applications, namely:

Aeronautical applications:
high temperature resistant and long life load bearings for aeronautical components

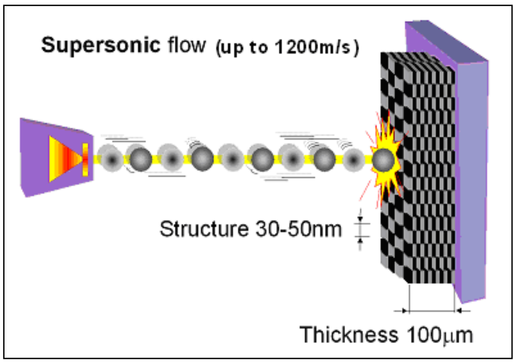
Mechanical applications:
abrasion resistant and fretting resistant coating for aluminum alloys employed

Biomedical applications:
a new class of nanostructured Ti based coatings for improved

working in harsh fretting conditions	*in automotive industries for the engines manufacturing*	*performances on osseointegration (due to nanostructure), biocompatibility and high wear resistance.*

The crucial point was to integrate the production of the appropriate powder with the coating technology. This work was focused on:

- ❖ *investigation and development of mechano-chemical synthesis route by means of HEBM of reactive and non-reactive powder systems that could be suitable for final application;*
- ❖ *development of CGS equipment;*
- ❖ *development of supersonic CGS deposition process for nanostructured systems.*



Scheme of the CGS deposition process of the nanostructured coatina

The reasons of choosing the technology involved in the project were as follows:

High Energy Ball Milling:

- ❖ *solid state reactions can be exploited;*
- ❖ *composition can be tailored on customer's demand;*
- ❖ *ceramic reinforcements added as nano-dispersions.*
- ❖ *possibility to have no equilibrium phase*

Cold Gas Spraying:

- ❖ *solid state process, nanostructure preserved from powder to coating;*
- ❖ *able to deposit temperature sensitive materials (no melting);*
- ❖ *possibility to achieve thick coatings with reduced thermal stresses.*

SUPERSONIC project profited three deposition ways of nanopowders:

1. *Pure kinetic – non reactive powders*
2. *Kinetic and reactive – reactive powders*
3. *Complex – powders including solid lubricants (deposited using single or two phase flow).*

Description of the work performed

The project started with the definition of the final coating properties and materials design based on the industrial requirements of end-users. Development of the HEBM production of suitable powders invented for different applications included:

- ❖ searching for the best combination of process parameters;
- ❖ adaptation the milling and post milling machines to reactive powder;
- ❖ standardization of method to analyze powder for CGS.

Powder quality control involved:

- powder particles shape, size and its distribution,
- reactivity.

The supersonic deposition process (CGS) controlled parameters as following:

- powder feeding rate and nozzle shape (different, depending of deposited material),
- working gas temperature and pressure,
- a stand-off distance.

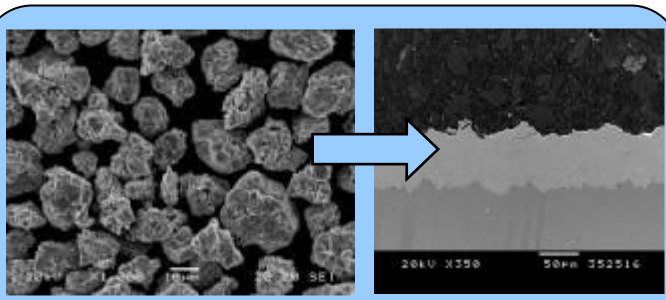
SUPERSONIC designed and developed new and innovative coatings for three applications:

AERONAUTICAL APPLICATIONS

NICKEL-TIN

COATING CHARACTERISTICS:

- **SELF LUBRICANT BEHAVIOR,**
- **DENSE, THICK AND NANOSTRUCTURED;**
- **HIGHER HARDNESS AND BETTER FRICTION BEHAVIOR AGAINST TEMPERATURE;**
- **ELEVATED TEMPERATURE CORROSION RESISTANT;**
- **COEFFICIENT OF FRICTION BETTER THAN BENCHMARK**



Designed Ni-reinforced nanopowder agglomerated in micrometric grains.

Thick and dense Ni-based coating

BIOMEDICAL APPLICATIONS

MAIN TARGETED APPLICATIONS ARE IMPLANT JOINTS WITH PROBLEMS DUE TO WEAR.

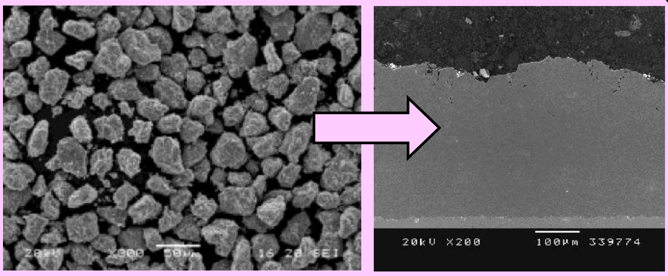
TITANIUM-CERMET

TWO KIND OF POWDERS:

- **NON REACTIVE**
- **REACTIVE**

COATING CHARACTERISTICS:

- **DENSE, THICK AND NANOSTRUCTURED,**
- **ENHANCED HARDNESS AND WEAR RESISTANCE,**
- **BIOCOMPATIBILITY.**



Designed non reactive Ti-CerMet nanopowder agglomerated in micrometric grains.

Thick and dense Ti-reinforced coating

MECHANICAL APPLICATIONS

ABRASION RESISTANCE IS THE MAIN REQUIREMENT FOR THIS TYPE OF APPLICATION.

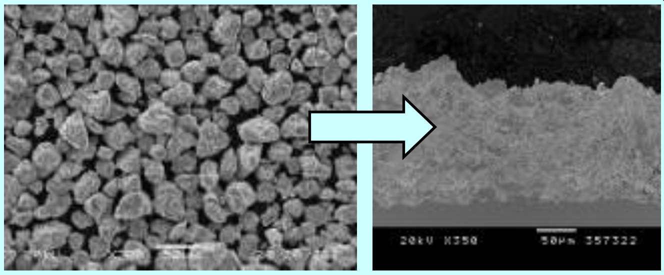
FEALCU REINFORCED BY ALUMINA

TWO KIND OF POWDERS:

- **NON REACTIVE**
- **HIGHLY REACTIVE**

COATING CHARACTERISTICS:

- **DENSE, THICK AND NANOSTRUCTURED,**
- **HIGH HARDNESS MUCH BETTER THAN THE STEEL SUBSTRATE,**
- **COEFFICIENT OF FRICTION BETTER THAN BENCHMARK,**
- **HIGH REPEATABILITY.**



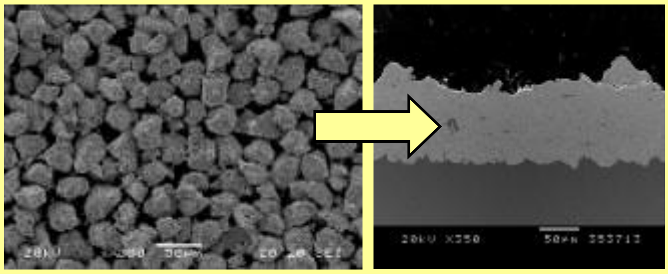
Designed FeCuAl-Al_2O_3 nanopowder agglomerated in micrometric grains.

Thick and dense FeCuAl-Al_2O_3 coating

WC IN COBALT MATRIX

COATING CHARACTERISTICS

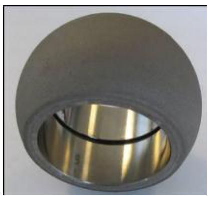
- **DENSE, THICK AND NANOSTRUCTURED,**
- **VERY HIGH HARDNESS,**
- **IMPROVED TRIBOLOGICAL PROPERTIES:**
  WEAR RESISTANCE AND LOW COEFFICIENT OF FRICTION.

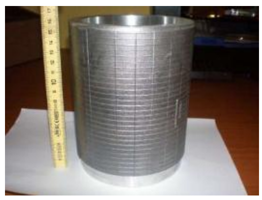


Designed Co-WC nanopowder agglomerated in micrometric grains.

Thick and dense Co-WC coating

End-user qualification of coatings on real parts





Aeronautical application
Bearings for engine-to-pylon mounts
Low and high temperature wear tests, thermal shock tests, endurance tests

Biomedical application
Knees implant components
Mechanical testing: adhesion, shear force, abrasion tests.
Biocompatibility: cytotoxicity, endotoxin analysis, bioburden

Mechanical application
Inner cylinder coating on soft aluminum parts
Thermal shock tests
Abrasion resistance tests

Summary

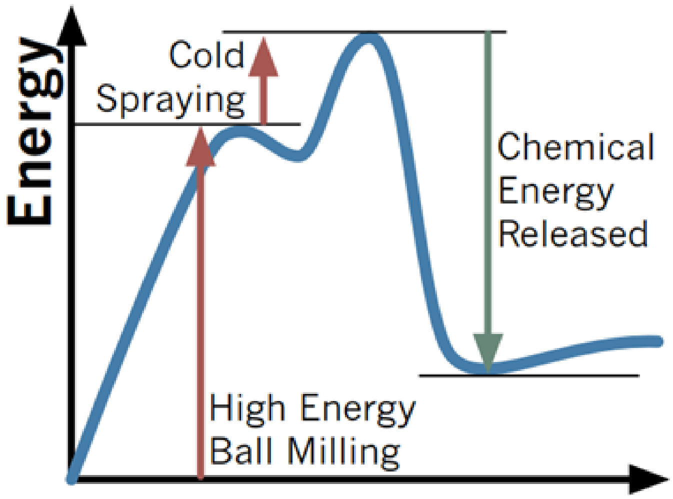
Main achievements of the SUPERSONIC project:

1. Reactive powders, suitable for CGS deposition, successfully developed, characterized and validated;
2. CGS process properly integrated in the chain manufacturing both for low reactive and highly reactive deposition;
3. Nanostructured CerMet coatings deposited via CGS;
4. Reliable coatings with superior properties compared with benchmarks;
5. Advanced CGS equipment developed for the spraying;
6. Validation of materials performed through real applications.

A description of the main S&T results/foregrounds (not exceeding 25 pages)

<u>Design of the materials and reactive principle (KUL)</u>

Supersonic project aimed to create a manufacturing chain, by exploiting HEBM and CGS technology, able to manage powders conceived in such manner to contain incomplete chemical reactions. The reactive deposition allows the formation of hard reinforcement improving the mechanical properties of the coating not accessible with standard powder and CGS process. The impact energy onto the substrate is used to trigger the incomplete reactions delivering the chemical energy stored in the material.



Base-concept of Supersonic project

Design and selection of a limited number of candidates is based on end-users requirements by keeping into consideration that the used materials have to be able to be sprayed via CGS and to create hard CerMet phases embedded in a soft metallic matrix that could withstand high temperature and possess a low coefficient of friction. The proper formation and distribution of intermetallic phases, by reactive milling or by reactive spraying, has a key role in order to achieve dense coatings with the targeted requirements.

Aeronautical case study

Aeronautical components are actually consisting of steel coated with Ag-based materials. the principal aim is to replace Ag coating and to increase life span of bearings used in aeronautical engines.

Criteria for selecting candidate systems:

- Lower coefficient of friction than 0.3;
- Withstand high operating temperatures (160-570ºC);
- Thermal stability/high melting point;
- Should not degrade by reacting with the environment

The selection has been performed on thermodynamic basis and mechanical properties. A class of materials with self-lubricant behaviour at high temperature and enhanced mechanical properties has been created reinforcing Nickel matrix with intermetallic phases developing specific oxide at the targeted working temperature.

The amount of Nickel is maximized to fit the tribological requirements and the amount of intermetallic former is calculated to guarantee both the formation of hard intermetallic phases and the self-lubricant behaviour at high temperature.

Biomedical case study

Biomedical application regards the coating of Titanium joint with biomedical wear resistant materials. The actual materials used are Stellite6 and austenitic stainless steels. The aim is to improve wear resistance of joints with biocompatible CerMet coatings.

Criteria fixed by the end-user for selecting candidate systems are:

- Biocompatible material;
- Abrasion resistant material;
- Osteointegration properties;

- Stress shield phenomena minimized.

A titanium matrix is reinforced with ceramic carbide materials in order to achieve high hardness, compactness and density of coatings deposited. In order to meet the fixed requirements two ways have been explored.
The reactive deposition of Titanium has been proposed in a first step. It allows to achieve, thanks to the reactive stage, a percentage of ceramic reinforcements near to the 100% in the final coating. It has been developed for biomedical applications but it isn't applicable in the particular case considered due to the thermal treatment needed to complete the reaction after the CGS.

Due to the low density achieved and to the not completed intermetallic formation, a second pick has been suggested by producing a low reactive variant of Ti composite via reactive milling. The percentage of ceramic reinforcements is the highest reachable maintaining the consistency and the compactness of powders and coatings. So obtained coatings, if applied on Ti-substrates, have fulfil ISO standard of biocompatibility.

Mechanical case study
In order to improve the abrasion resistance of dump tracks and to substitute 5xxx aluminium alloy series, FAC-Al and WC-Co materials have been proposed.
The criteria followed for selecting the candidate systems are:
- High abrasion resistance;
- Should not degrade by reacting with the environment;
- Low cost;

FAC-Al: Alumina dispersed in a Fe-Cu-Al matrix. The material design was based both on the lubricating effect of soft areas and the good resistance to abrasion of harder areas. Alloying elements as Al decrease the coefficient of friction, while, particles of alumina increase the tribology of coating.
Basing on this concept, two routes with different reactive stage have been performed. In the low reactive variant the 15% of Al_2O_3 is finely dispersed in a Fe-Al-Cu matrix by assuring outstanding behaviour in sliding and fretting conditions similar to WC-Co based CerMet but with tougher metallic structure. While, in the highly reactive variant it is exploited the exothermal reaction between Fe_2O_3 and Aluminium to form hard CerMet phases of Al_2O_3 embedded in a metal matrix. The percentage of hard and soft phases is similar to the low-reactive material but the costs are significantly inferior.

Designed WC-Co material is an agglomerated nanometric Tungsten Carbide in a Cobalt metallic matrix refined by high energy ball milling process. The addition of Al enhances the wear-resistance since Al is an alloying element that increases the cohesion within the coating, form Al_2O_3 and reduce porosities. Thanks to the deposition employed the decarburization of WC is minimized, keeping improved the mechanical and tribological properties. Possibility to achieve high thickness with reduced tensile thermal stresses is possible by using CGS technique.

Powder materials production and safety measurements (MBN-MTS)
MBN had the role to synthetize and manage innovative nanostructured materials conceived in such manner to store residual chemical energy. The adopted manufacturing route consists in the synthesis of nanopowders by high energy ball milling (HEBM): a proprietary technology internally developed

to synthesize, on industrial scale, a wide range of materials by inducing solid state reactions mechanically activated.
A system, or more, of powder materials has been developed for each case study by taking into consideration the initial requirements and the goals of the project.
For the aeronautical case study a class of materials with self-lubricant behaviour at high temperature and enhanced mechanical properties has been created reinforcing Nickel with intermetallic phases. The amount of Nickel has been maximized to fit the tribological requirements and the amount of Tin is calculated to guarantee both the formation of hard intermetallic phases and the self-lubricant behaviour at high temperature.

In the biomedical case study Titanium metal matrix has been reinforced with ceramic biocompatible materials and the optimization of the material has been performed for two different variants. A low reactive variant has been produced by maximising the carbides content and, at the same time, by guarantying the consistency and the compactness of the final powders and coatings. The efforts made to avoid the contamination have allowed the complete biocompatibility, following the ISO standard, of the material.
The highly reactive variant allows to achieve a percentage of hard phases near to the 100% thanks to the carbide formation that occurs during the deposition by CGS. This kind of material isn’t applicable to the specific biomedical case in exam because a thermal treatment is needed to guarantee the complete CerMet formation and to avoid biocompatibility issues, moreover the temperature reached during the reaction is too high and could compromise the integrity of the substrate.

Three material variants have been produced for the mechanical application: one based on the reinforcement of a Cobalt matrix and two based on a Fe-Cu-Al system.
WC-Co powders are conceived as a nanostructured system of tungsten carbides inserted in a metal Cobalt matrix. The calculated percentage of Aluminium added and the deposition method employed ensure a minimized decarburization of the WC, the increased cohesion within the coating and the reduction of the porosities by keeping improved the mechanical and tribological properties also thanks to the Al2O3 formation. Furthermore this powder represents the only chance to spray hard CerMet WC materials by CGS.
The so named FAC-Al represents a system constituted of alumina dispersed in a Fe-Cu-Al matrix. The design of this material is based on a compromise of soft (lubricating effect) and hard (good resistance to abrasion) areas. Alloying elements as Al decrease the coefficient of friction, while, particles of alumina increase the tribology properties of the final coating. Two reactive variant has been produced following the described concept. The low reactive variant is represented by a system formed of 15% of Al2O3 finely dispersed in a 50Fe-10Al-25Cu matrix by assuring an outstanding behaviour in sliding and fretting conditions similar to WC-Co based CerMet but with tougher metallic structure.
FAC-Al highly reactive variant exploits, during the CGS deposition, the exothermal reaction between Fe2O3 and Aluminium to form the hard CerMet phases of Al2O3 embedded in a metal matrix. The percentage of hard and soft phases is similar to the low-reactive material but the costs of the material are significantly inferior.

All the materials produced have been optimized for the CGS deposition in terms of size distribution, morphology and hardness. Aiming the optimization of the materials and of the production process MBN has employed technologies for the recovering of fine/coarse particles and for the rounding of the powders in the desired size. The recovering of the discarded materials allows the diminution of the costs by increasing the yield of the production process. The fine powders have been recovered using a spray dryer apparatus while the coarse particles have been resized via low energy process of ball milling. The particles rounding has been achieved thanks to a centrifugal gas system and the resulting powders highlight a better flowability.

In matter of reactive materials MBN has lavished many efforts in order to guarantee the safety during the production/handling of materials and, moreover, to achieve a reliable and repeatable reactive grade.

The study and design of reactors to treat reactive powders for different material systems (Ni, Ti , Fe, WC based) has been performed allowing the reliability of process in terms of composition and phase distribution.

Aiming the safety during the production the entire apparatus has been revised:

- Protected milling environment: protection against accidental explosions (already available at MBN);
- Sealed milling apparatus: conditions are checked each time;
- Tailored system for the management and the unloading of fine powders via inert carrier gas (fine powders are highly reactive);
- Passivation protocol at the end of milling process;

Aiming the safety after the production and during the handling MBN has taken the following countermeasures:

- Absence of ignition sources in handling environment;
- Personal protective equipment;
- Aerated and protected environment for handling and stocking;
- Packaging in conformance with EU directives;
- MSDS updated with the last standard;

In addition to these arrangements MBN has developed also some internal proofs in order to evaluate the reactivity of the produced materials by revealing the trigger energy and the propagation rate in different activation conditions: mechanical, thermal and electrical.

To protect the acquired foreground MBN has finally applied a patent to the production of such reactive materials.

Optimization of CGS deposition (UB)

In Cold Gas Spraying (CGS) the powder particles (typically 10 to 50 μm) are accelerated to very high velocities (200 to 1000 m.s-1) by a supersonic compressed gas jet at temperatures well below their melting point. The powders, upon impact with the substrate, experience an extreme and rapid plastic deformation which forces contacts at high local pressure permitting to bond together the particles and to form rapidly thick layers of material.

The principal constrains of this technology are the limited range of suitable materials available in the market and the impossibility to spray hard materials like CerMet.

Supersonic project aims to surpass this limits by introducing the innovative concept of the reactive deposition. In the specific case the kinetic energy involved in the process may be used to trigger and to complete the reaction stored within reactive powders allowing the CerMet deposition.

UB contributes to the project by optimizing the deposition via CGS of the innovative nanostructured powders developed. The principal focus was to understand the influence of the spraying process parameters on the reactive coating formation. A proper set of parameters allows to obtain optimized coatings both in terms of properties and in terms of deposition efficiency. To reach a deposition control is important to improve the reliability of the entire manufacturing chain.

To find out the best spraying conditions a number of deposition parameters needs to be considered in each experiment:

- Carrier gas pressure;
- Gas temperature
- Spray distance
- Traverse velocity
- Use of pre-chamber
- Number of layers
- Other hardware set-ups (i.e. adaptation for highly reactive powders)

The process deposition has been tailored for reactive powders and continuously improved on the basis of the tribological and microstructural outcomes of the sprayed coatings. In particular, efforts have been made to understand and develop a consistent approach to deposit different reactive powders on different substrates through an experimental matrix.

UB Research Approach is systematic and consists in the following matrix:

- Designing the deposition parameters to understand their influence on the resulting coating;
- Running cold spraying experiments on different nanostructured reactive powders systems using different substrates;
- Basic characterization of coatings deposited.
- Sending specific samples to partners in order to quantify coatings properties and receive a feedback to finally optimize the coating for the required applications.

The reactivity of some systems during the impact experienced by the powder when arrive to the substrate surface has been studied.

The CGS development and optimization have been validated thanks to the production of real components used in aeronautical, biomedical and mechanical applications. A great amount of samples has been performed for each materials system studied in order to find the correct spraying parameters. The so obtained samples have been tested in the properties required by the end-user and, by the point of view of the final deposition, geometries similar to the demonstrator components have been tried. In particular, efforts were made to understand and develop a consistent approach to deposit different low-reactive powders on different substrates.

<u>Aeronautical case study</u>

The first trials on final components presented a different deposition behaviour in comparison with the samples sprayed for the testing phase. To avoid the detachment of the coating and to improve the adhesion onto Inconel substrates it was decided to increase the active surface before the spraying process with pre-process operation of grit-blasting. This action provides more adherence to the substrate and more cohesion between layers.

<u>Biomedical case study</u>

The coatings obtained with the initial powders showed some detachments, due to the inhomogeneous flowability of the powders, in the outer layers despite the well bonding to the substrate was assured. Thanks to the combined work of MBN-IMPACT this issue was overcame and the optimization of this material has been performed. The so obtained coatings present higher thickness, better density and lower surface roughness. The increasing of carbide content in the powders allows the increment of the hardness from about 350 HV, in the case of the low carbide content, to 650HVN for the high CerMet content. The coating showed enough thickness to be polished, a good distribution of the reinforcements of carbide in the matrix and a well bonding to the substrate (~60 MPa).

In terms of specific requirements for biomedical applications specific tests were carried out. The coatings need to pass some strict controls as shear, bond, specific wear test (Taber test) and in-vitro assays. Once performed the tests, the optimized coating fulfilled and, in some cases, even increased the minimum requirements.

Mechanical case study

FAC-Al is a metal-ceramic nanocomposite that represents an evolution of the already known FAC material consisting in 4 phases: Fe and Cu as metal matrix, Al_2O_3 and intermetallic FeAl as reinforcements.

The CerMet phases are achieved thanks to the exothermic reaction:

$$Fe + Fe_2O_3 + Al + Cu \rightarrow Fe/Al_2O_3/Cu + Fe/Al$$

The reaction can occur partially during the HEBM and be completed during the CGS deposition in the low reactive variant or it can occur completely in the CGS deposition for the highly reactive variant of this material.

FAC-Al low reactive

After the optimization, involving more than 50 process experiments, an homogeneous, thick and dense coating with good phases distribution was achieved fully keeping the nanostructure of initial powders. The hardness obtained for this coating is 650 HV and a good adhesion of ~60 MPa is achieved.

FAC-Al highly reactive

The highly reactive powders require tuned arrangements to the CGS equipment. During the project IMPACT has provided different solutions to improve the CGS standard equipment and to allow the reactive deposition. After the optimization of the spraying parameters it has been possible to produce a well bonded and dense coating. It is important to take into account that reaction took place during the spraying process and brings to the formation of Alumina thanks to the exothermic reaction between hematite and aluminium. This aspect is corroborated after analysing the XRD results where it can be seen the reduction of the hematite phase peak and the formation of aluminium oxide phase. The resultant phases in the coating were analysed by EDS and 5 different zones were found in the coating corresponding to the different phases.

Hardness rises up to 365 HV with an increase in terms of pressure and temperature up to 38-780ºC.

WC-Co-Al

The WC-based cermet is a well-known system for wear resistance applications. The metallic 50µm Co/Al matrix is needed to provide toughness to the composite and to accommodate residual stresses produced during the powder deposition, owing the difference between their thermal expansion coefficients.

The optimized system shows low thickness (usual for high hardness powders), high density, well substrate bonding and hardness of 1100 HV. In terms of abrasive wear resistance a comparative test has been performed with coatings obtained with conventional technologies (HVOF) and it was concluded that coatings obtain by CGS improve these properties, taking into account the differences in metallic matrix content.

Optimization of CGS equipment (IMPACT)

The current equipment is tailored on not reactive powder coming from atomization process and, moreover, it is thought to spray simply geometries. To use agglomerated and reactive particles and to coat complex geometry it is needed a substantial upgrade of the CGS apparatus. One of the major effort of the project was to adapt the Cold Spray apparatus in order to overcome the existent technological limits.

Powder feeding equipment

This component use the “turbulence feeder” principle, it increases the flowability of the materials and allows to spray also not flowing particles. With this tune it is possible to spray a with a good repeatability and reliability a continuous flow of particles material. Those spray results can vary by using other powders than copper, especially using reactive nano-powders. Because of different behaviours of the different powders there has to be a possibility to easily adjust the spray rate and feeding conditions during the process. There must be a possibility for the spray operator to interactively change the feeding conditions and herewith the spray rate.

Nozzle development

Several spray test where performed at UB and Impact, using reactive powders. Finding proper parameters and strategies to spray these types of powders mostly ended up with blocked nozzles. The powder might be reacting in the divergent part of the nozzle and a coating is being built up on the nozzle wall. Similar problems where known by the industry, using nickel-based alloys with cold spray (aeronautical case study).

To improve the processes behaviour it was used a different nozzle material in order to reduce the roughness of the inner wall and to avoid sticking phenomena. The usual material is WC, mainly because of it wear resistance, and it can be substituted with ceramics, such as SiC or SiN to reach surfaces nearly to no roughness finishing.

Powder injection

To avoid the nozzle clogging it was re-looked the way with which the powder is injected in the cold spray gun. With usual geometry of the powder injector it was clear that the powder can touch, during the transportation, the wall of the nozzle very often and the chances that the particles will deposit on the nozzle wall increase. A second problem, thinking of reacting powders could be, that the nano-powders can react in the bow of the injector.

To overcome these issues the idea was to design a part that will force the particles to stay in the centre of the main gas stream preventing that particles can hit the inner surface of the nozzle. The new developed powder injector forces the carrier gas in such manner to build a "gas-cushion" and to smoothly deflect the particles in to the direction of injection, without touching the walls.

Cooling device

Cooling device avoids heating of the powder particles close to the nozzle wall helping to reduce the clogging and to increase the lifetime of the component. Further this sanction helps to avoid thermo-shocks at the ceramic nozzle during the shut-down of the system.

Aiming the improvement of this component, during the project, different cooling devices have been developed exploiting different cooling means (air, water and liquid) and an increased cooling effect has been achieved.

Central powder feeding

Reactive powder might react in the bended tube of the powder injector. To overcome this issue it would be necessary to inject the powder and the carrier gas directly in the centre of the gas stream and in the exact same direction. The central feeding unit developed allows the particle feeding centrally by the forcing performed by the gas carrier that constrains the material inside the flow avoiding the clogging.

Adjustments made to increase the yield of the process

To increase the efficiency of the process in terms of quantity of powder transportable by the gas carrier some adjustable funnels have been developed.

More important, for the injection of close geometries, it has been developed a powder injection system that allows to spray powder with 90° of angle. This device has been developed specifically for the inner cylinder proposed for the mechanical application, it can be used for close geometries with minimum radius near to 100 mm;

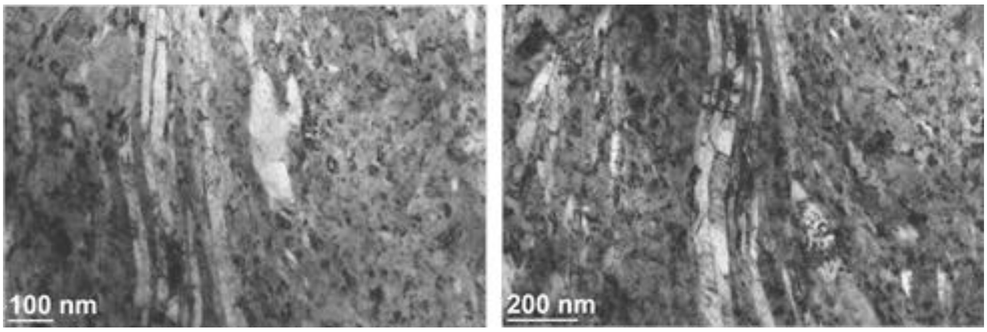
Thanks to this adaptations the reactive deposition has achieved during the project without issues of clogging and with an excellent reliability of the process.

Materials validation – Microstructural evaluations (AGH)

The main investigation effort was directed to find if the composition and nanostructure of the starting powders was transferred to the coatings.
Investigations show that HEBM produces powders characterized by a fine and homogeneous chemical distribution of elements and an "ultrafine" (nanometric) crystalline structure. Powder particles look compact and cross sections revealed a good phase distribution.
CGS technology is used to transfer nano-phased powder onto the substrate in the form of dense coatings with very little or no change of the crystal structure or material properties.
Since CGS of reactive nanopowders is not a conventional industrial coating process, microstructural characterization is essential to get information on process outputs and to allow further process optimizations. Generally, it was found that the supersonic CGS promotes the retention of a nano grain/crystal size of the original powder in the sprayed coatings.

Aeronautical case study

The dense coatings achieved have a limited amount of cracks or flaws either at the substrate interface or between sprayed splats, this indicates that a satisfactory adhesion was achieved too.
TEM analysis show a lamellar microstructure of the coatings probably produced by the kinetic energy achieved during the spraying. The particle impacts generate thin layers or "splats" and these splats subsequently adhere to the substrate surface by mechanical interlocking and localized diffusion forming the particular lamellar structure.

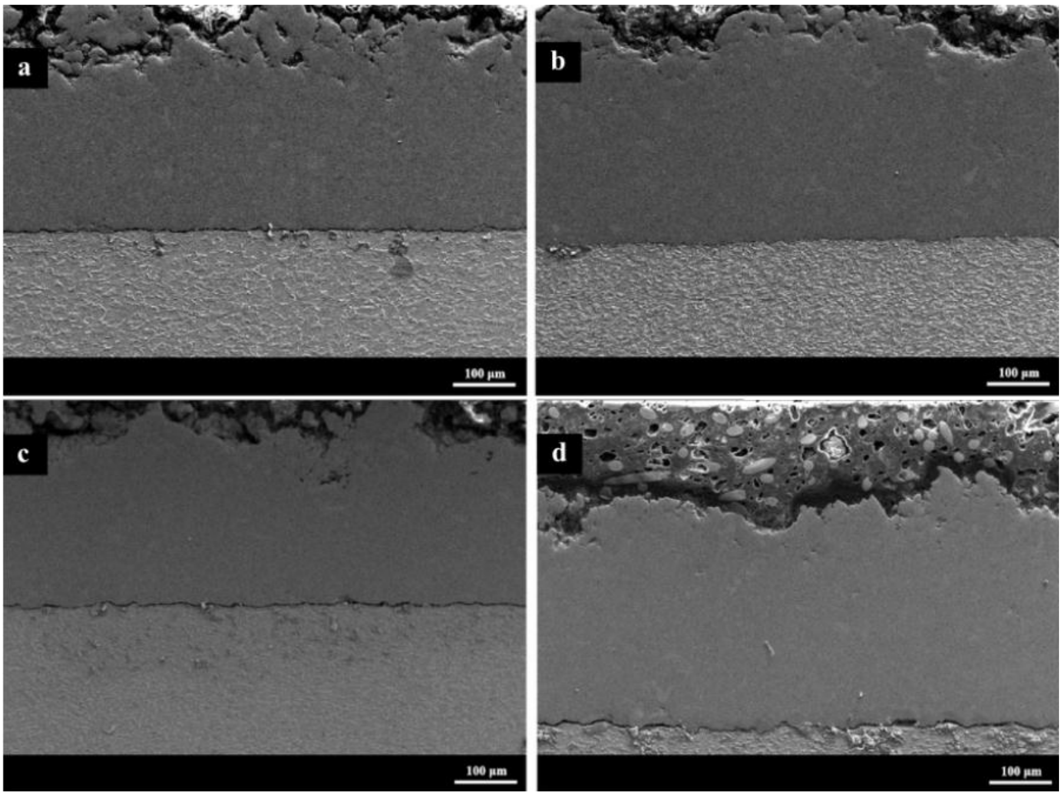


TEM images: Lamellar structure

The overall thickness of analyzed coating is about 100 μm, whereas the individual splats, consisting of homogeneously dispersed and nanostructured Ni-Intermetallic phases, have a thickness less than 100 nm. The XRD pattern reveals the presence of a Ni-intermetallic solid solution, the grain size of the initial powders (20-50 nm) slightly varies by confirming that grain growth phenomena are minimized, and the nanostructure is retained in the coating.
The good adhesion of these coatings could be explained by deformation and grain-refinement of the top part of the substrate, due to high mechanical stresses induced during the impact of the splats onto the substrate.

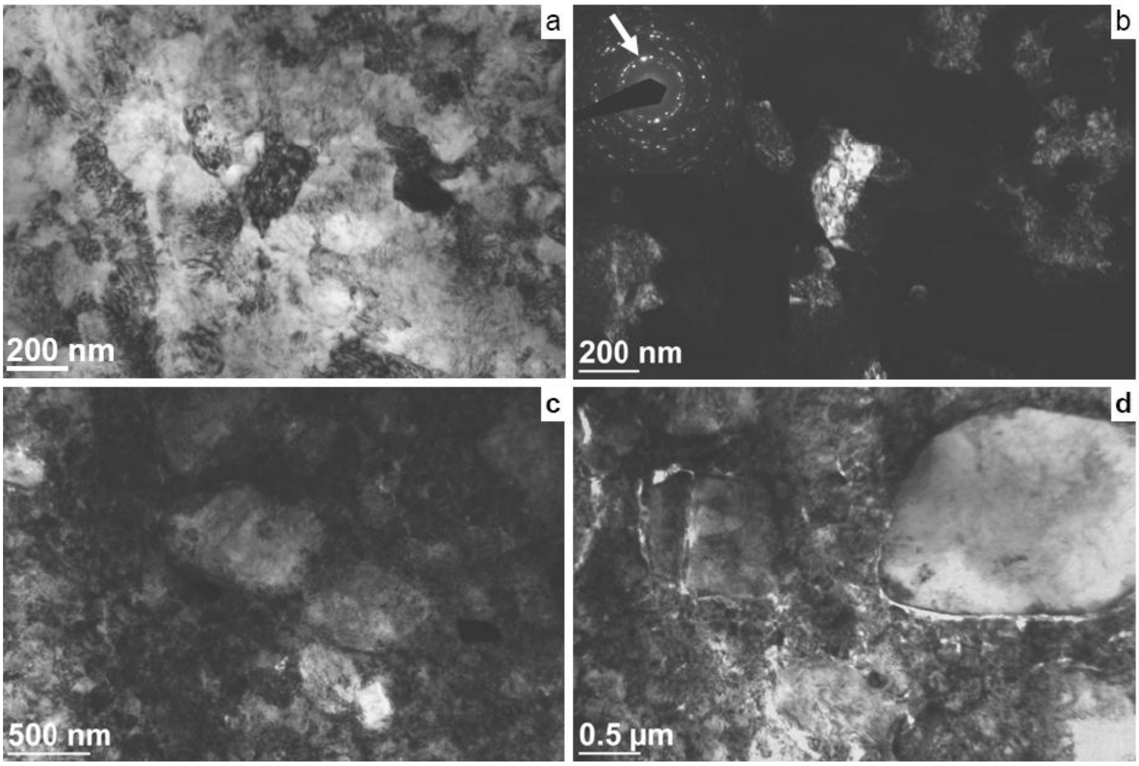
Biomedical case study

First deposited coatings showed poor adhesion, much porosity and not uniform CerMet distribution. The optimized materials, instead, provide homogeneous and dense coatings with strong interface and CerMet reinforcements uniformly distributed in the Ti matrix, as confirmed by STEM/EDS and TEM analysis.



Cross-section of reinforced Titanium coated samples

Since the powder nanostructure is conserved, TEM investigations confirm the nanostructure (grains with nanometer dimensions) of the CGS coatings. The unchanged structure and grain size may positively influence the mechanical properties. The Ti-CerMet coatings are formed by heavily deformed structures with an appropriate balance of hard intermetallic and soft Ti phases.



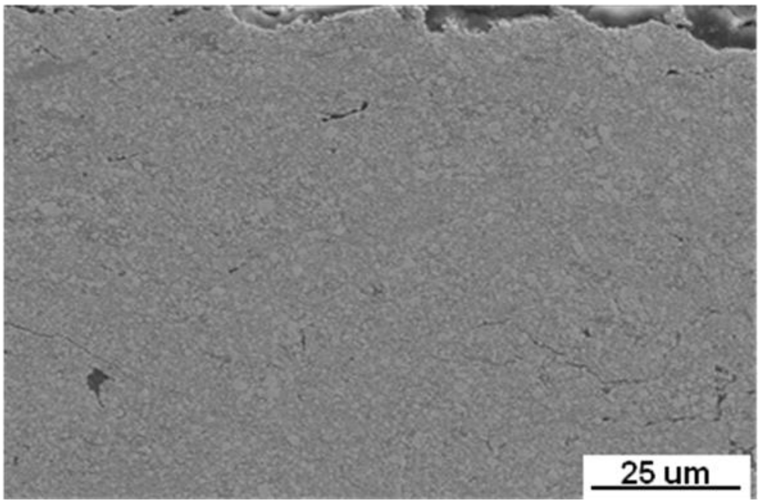
TEM plain view images show microstructure

Thanks to CGS, homogenous coatings of Tiα and CerMet, ranged from 250 μm to 350 μm, are obtained. It was shown that supersonic spraying conditions limit the exposure time of powders to high temperatures, and therefore help in maintaining the nanostructure of the initial powders.

Mechanical application

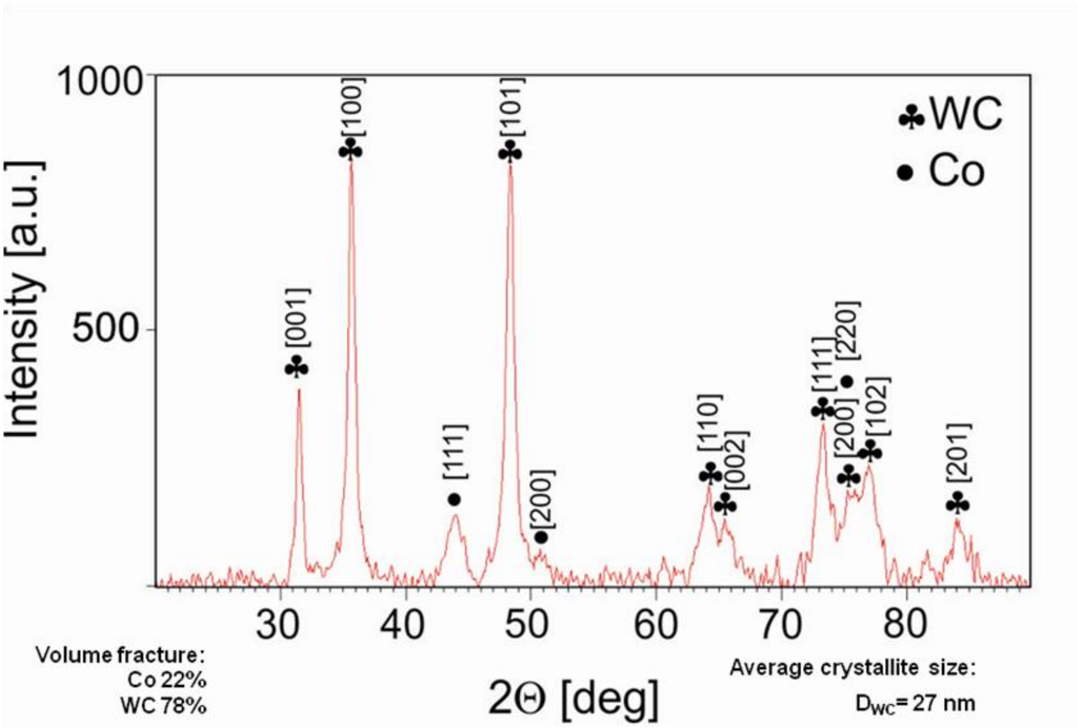
WC-Co-Al

Average crystal size for WC phase, calculated by Williamson-Hall formula, is estimated as 19 nm while in the deposited coatings is about 27 nm. Coatings analyzed are dense and homogeneous, therefore without porosity, with good adhesion to the substrate and uniform thickness of about 180 um.



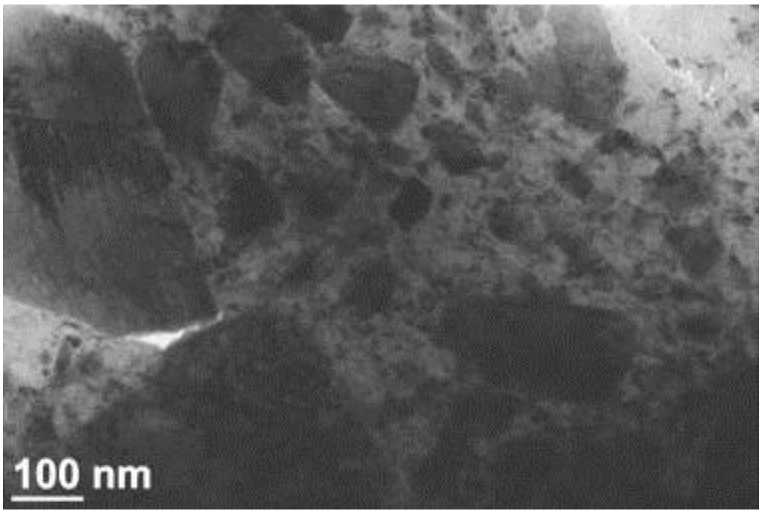
SEM microstructure of the cross-section WC-Co coating

X ray diffraction studies of WC-Co coatings indicate distinguishable WC (about 78%) and Co (about 22%) phases.



XRD diffraction pattern of WC-Co coating

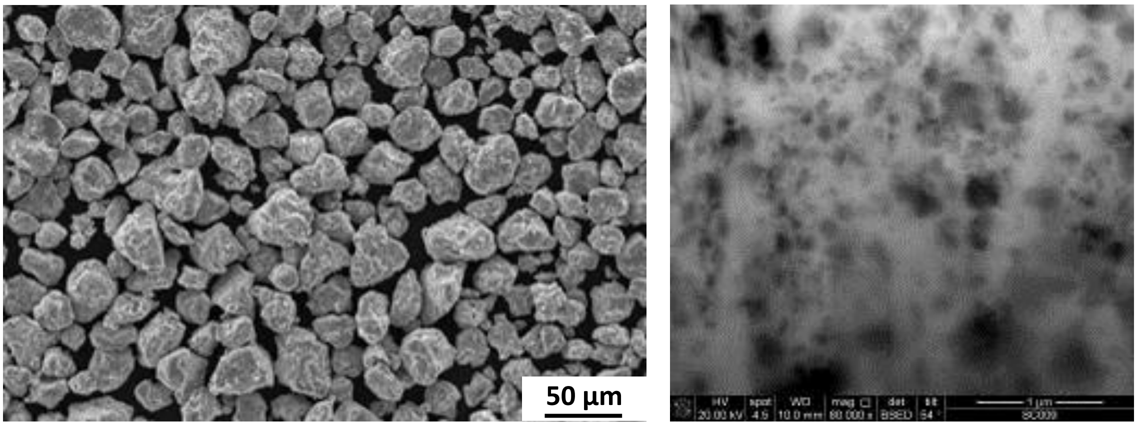
TEM investigations confirm the structure made of small (nanometric size) WC particles embedded in the Co matrix. Such microstructure is favorable because small and hard WC particles assure high hardness and wear resistance of coatings, and relatively soft Co matrix provides high impact strength. Moreover highly refined and distributed carbides particles advantageously influence the mechanical properties.



TEM microstructure of WC-Co coating

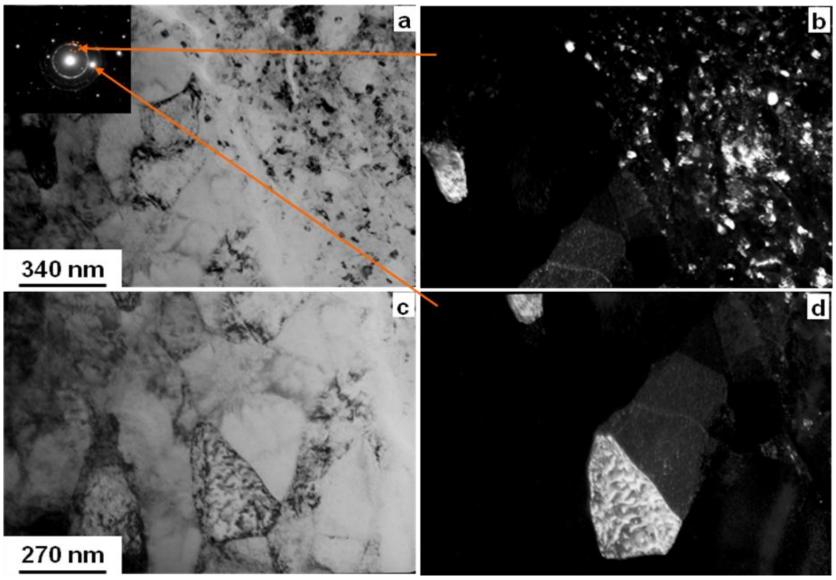
FAC-Al

The SEM investigations, on particle section, show a very fine and uniform nano-particles dispersion with a progressive refinement of constituent phases by increasing milling (from 5 um to ~1 um scale)



SEM and TEM images showing powder structure

TEM images confirm the nano-size of the grains in the supersonic sprayed coatings. FAC-Al coatings have areas with larger grain size (80-300 nm) as well as areas with ultrafine particles. Due to such structure, the CGS coatings exhibited better tribological properties than that of the examined benchmark materials.



TEM bright – (a, c) and dark – (b, d) field plain view images show microstructure of the FAC-Al coatings

HEBM induces the formation of both hard and soft phases due to the high reactivity of the nanostructured feedstock powders.

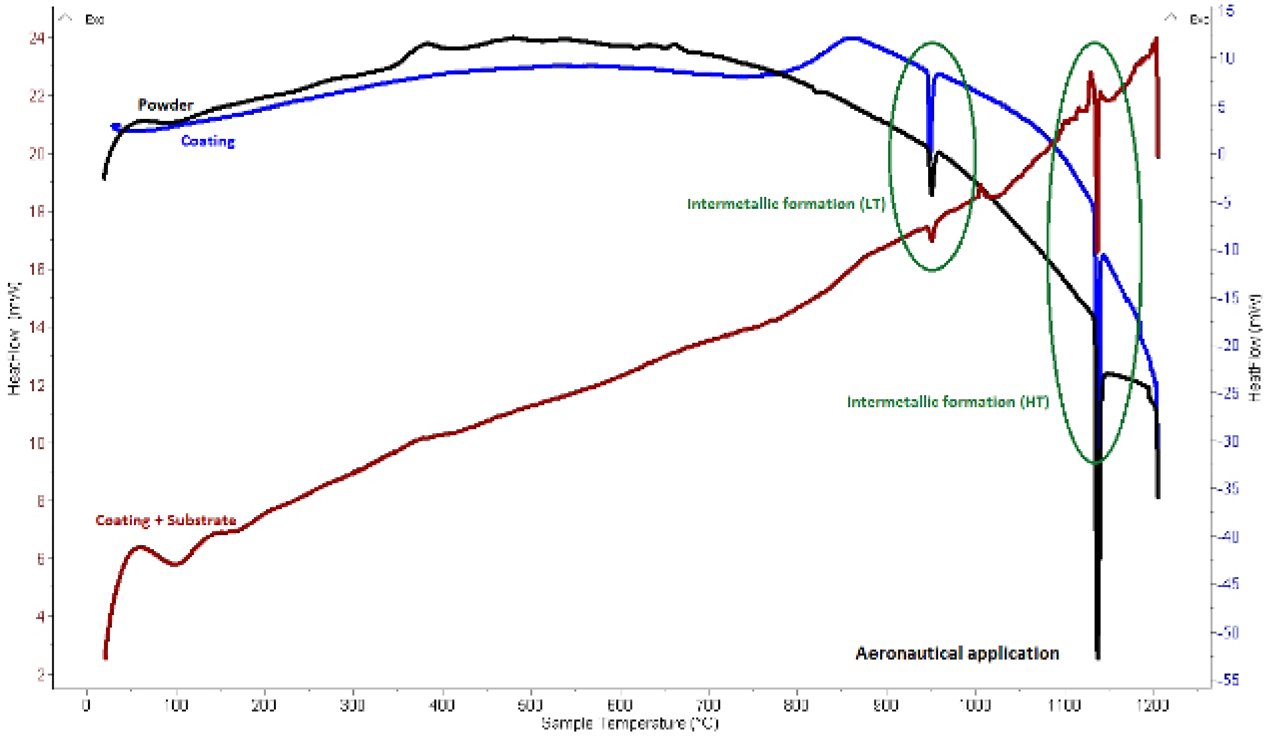
<u>Materials validation – Thermodynamic evaluations (IMNR)</u>

Thermodynamic prediction and analysis have been performed for each Supersonic materials in order to evaluate enthalpy modifications, kinetic parameters and thermal stability of substrate/coating systems. The evaluations of powders reactivity and coatings stability were done by direct measuring and comparing the enthalpy released during heating with the thermodynamic values predicted by using a special Mathcad subroutine.

Aeronautical application

Thermal analysis of reinforced Ni powders present peaks at different temperatures due to the successive formation of different intermetallic compounds (Low Temperature and High Temperature). The energy released represents around 8-10% from the theoretical value. Phase evolution with increasing temperature shows the increase of crystallite sizes from 30 to about 100 nm.

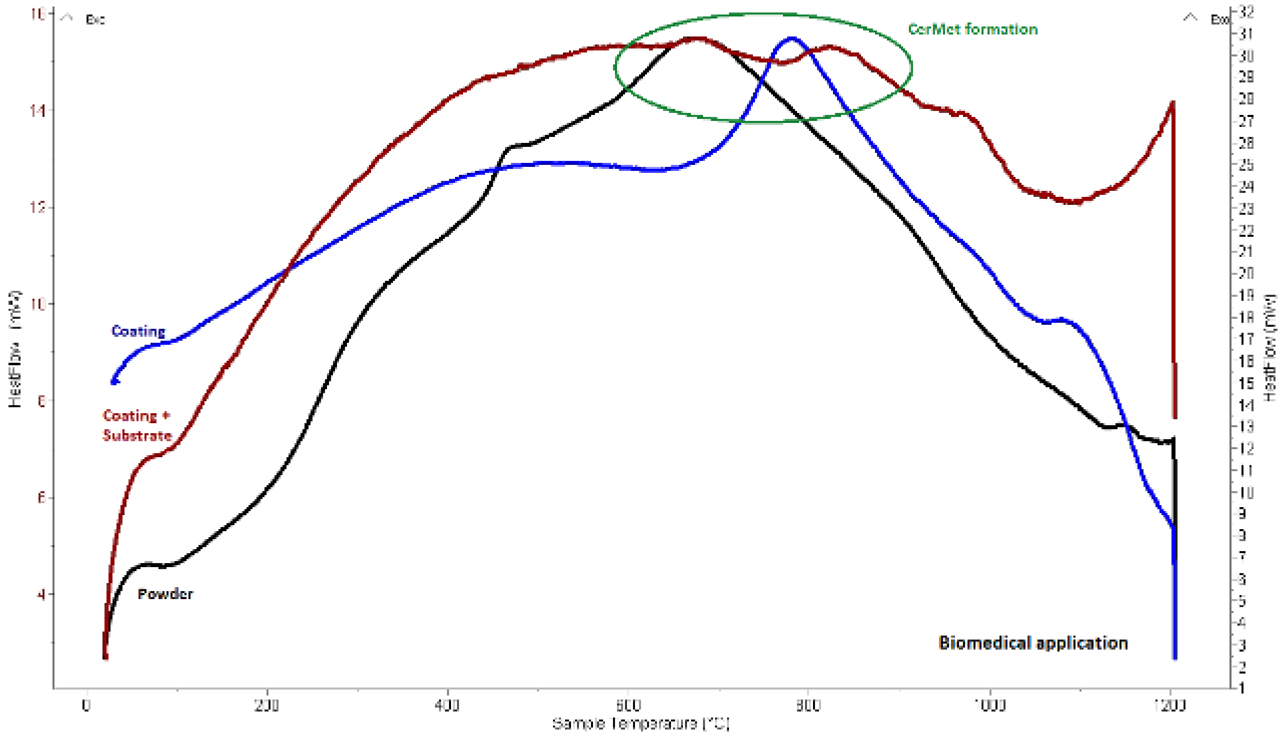
The coatings, both alone and applied to an Inconel substrate, show the consecutive formation intermetallic phases by increasing the temperature, as already highlighted in the powders behavior.



Typical DSC diagram of Ni-intermetallic coatings on Inconel substrate

Biomedical application

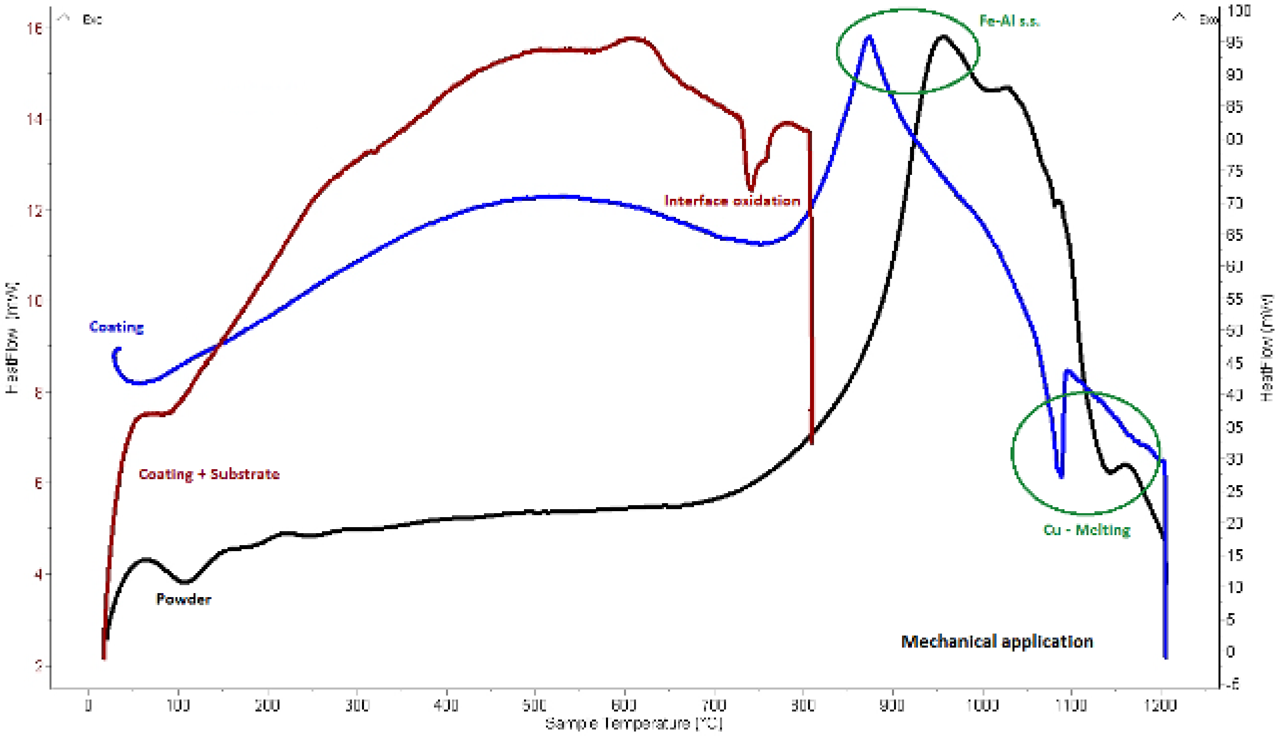
Thermal analysis of reactive Ti powders show a released energy around 8.5% from the maximum theoretical value. The activation energy of the solid state reaction was estimated to 140.6 kJ/mol by Kissinger method. Ti-CerMet coatings on Ti substrate have a good thermal stability. The limiting operating temperature, around 780-823°C, corresponds to the residual CerMet formation, observed in both powders, coatings and coated substrates. In the optimal deposition conditions the mean crystallite sizes increase from 14 to 22 nm.



Typical DSC diagram of Ti-TiC coatings on Ti substrate

Mechanical application

Thermal analysis of FAC-Al powders show an high reactivity with heat energy content depending on the HEBM parameters while the analysis on coatings show the interface oxidation around 870^{0}C that is also the upper limit of operating temperature. An increase of mean crystallite sizes from 48 to 67 nm was observed in the optimal coating conditions, the formation of Fe-Al solid solutions reduce the grain growth.



The energy released is around 11% from the maximum theoretical value. The activation energy of 17.5 kJ/mole calculated using Avrami-Erofeev method.

The experimental results and developed models strongly support the initial assumption that supersonic deposition of reactive nanostructured powders allow to obtain new coating systems with controlled phase composition and crystallite sizes in the nano-metric range having enhanced structural properties.

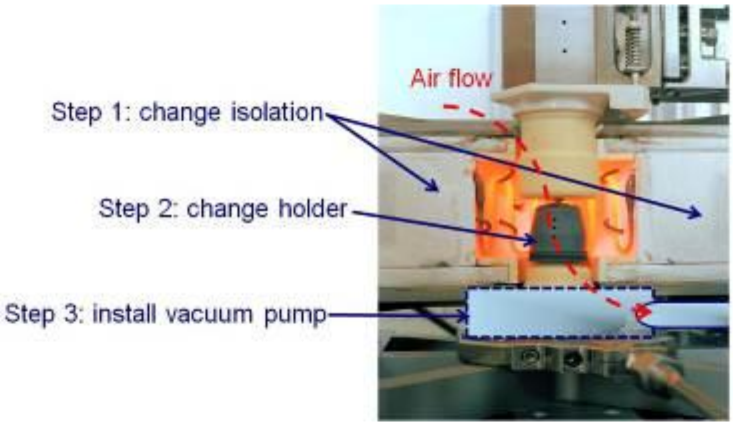
Materials validation – Tribological evaluations (KUL)

The evaluation of the frictional and wear characteristics of the supersonic sprayed coating has been performed in order to establish a structure-property relationship for the achieved materials. Benchmark materials are evaluated to rank the produced supersonic coatings and to indicate the advantages and drawbacks of applying such coatings.

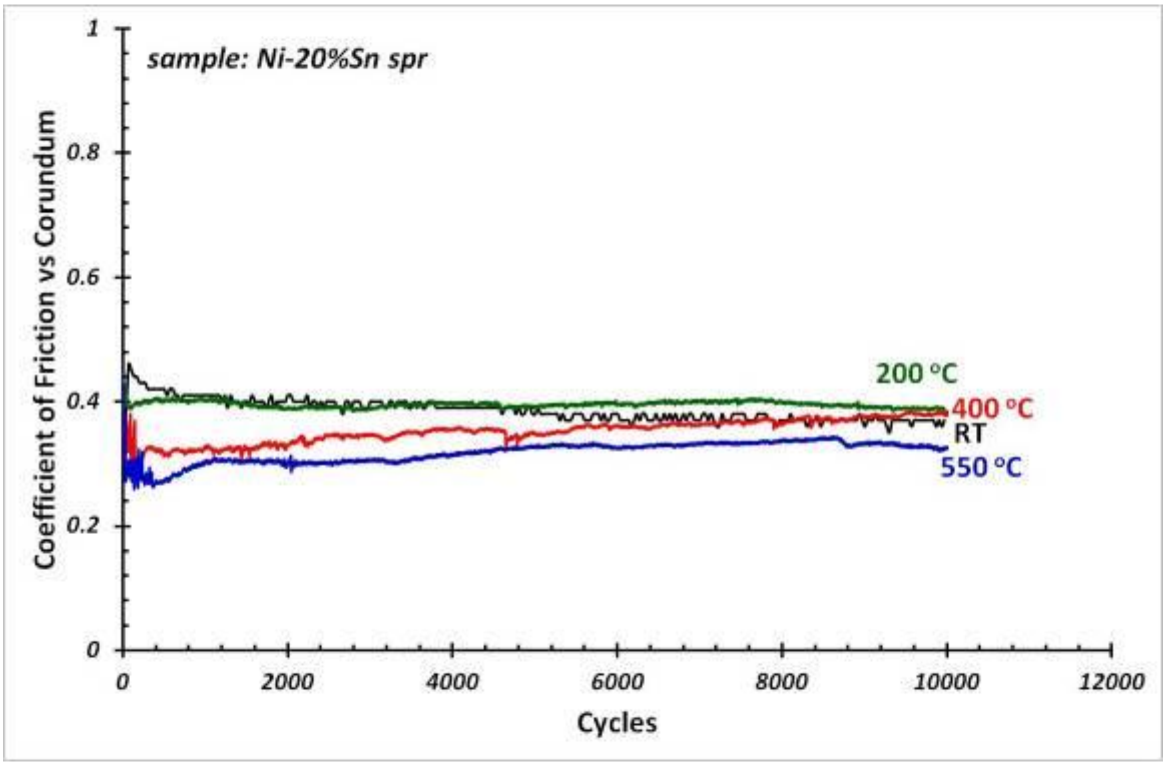
A methodology has been developed to investigate the material behaviour in experimental conditions similar to the actual working ones. In this perspective, important information on the functionality of the coatings can be drawn, whereas the obtained data will provide feedback and know-how on how to further optimize these materials.

Aeronautical application

The evolution of tribological properties has been studied both at room (RT) and high (HT) temperatures. The material behaviour was evaluated in a temperature range of 25ºC up to 550ºC thanks to a tailored apparatus properly modified to be able to work at these temperatures.

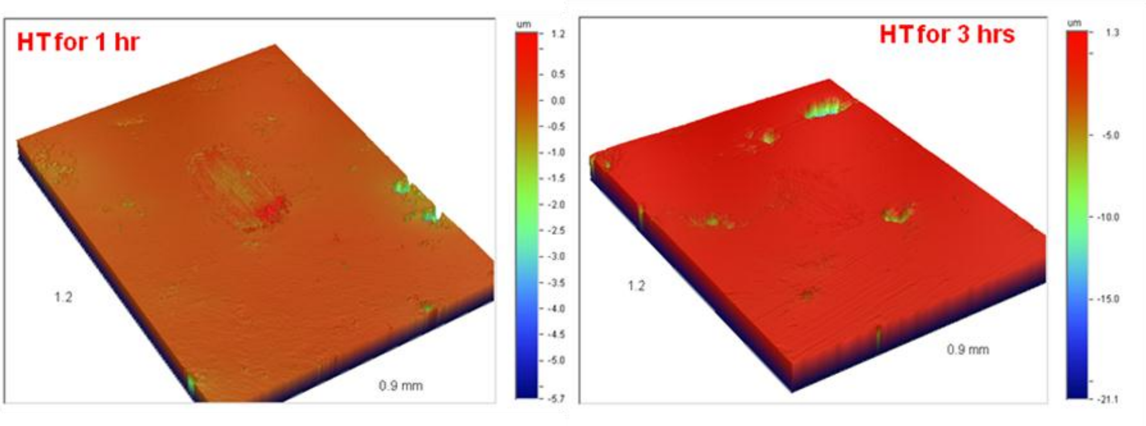


Ni-based coating show an improved tribological behavior by combining a low coefficient of friction (COF) and a decreased wear depth. The frictional behavior of sprayed Ni-Sn coatings is not affected by test temperature (up to 550ºC), while the wear depth increases with the heat increasing. Frictional properties are not affected by the test temperature due to the formation of an homogenous and compact oxide tribo-layer at the contacting surface.



Effect of test temperature on frictional properties

In addition, surface topography analysis indicate that the structural changes do not significantly affect the wear behavior of supersonic sprayed coatings.

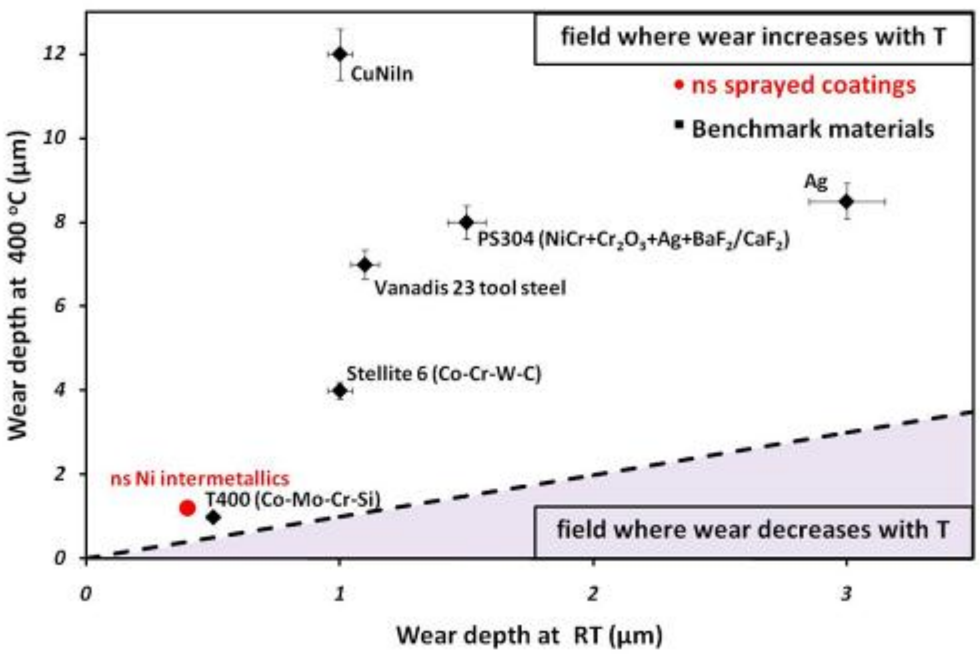


Surface topography of heat treated Ni-Sn coatings after sliding at room temperature

The increasing of test temperature leads to the formation a thicker oxide tribo-layer, localized ruptures of this film leads to the formation of deeper wear grooves and subsequently higher wear depths. Moreover, the degradation of the wear resistance properties occurs both in the sprayed and benchmark materials due to a softening of the materials caused by the grain growth and higher dislocation mobility occurring at higher temperatures. However, the small deviation from the ideal properties indicates a poor influence of test temperature on the tribological properties.

Analysis performed by comparing supersonic and benchmark materials valid the utilization of Ni-based coating for the prototype phase:

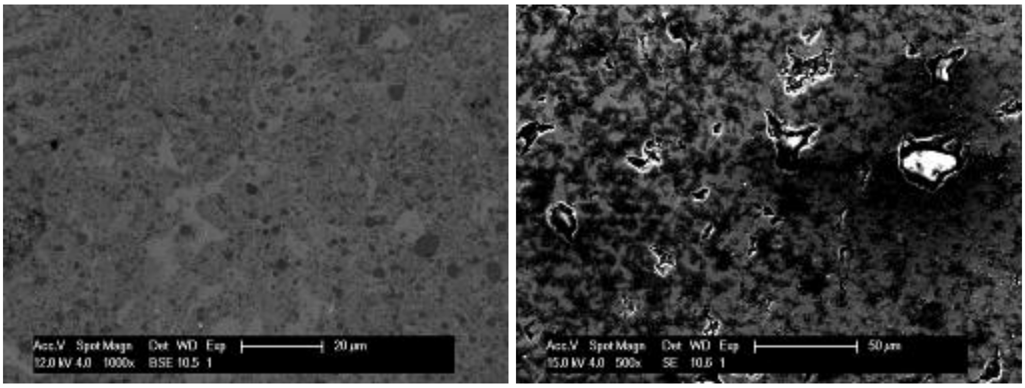
- Cu based benchmark materials are not appropriate for high temperature applications;
- The wear behavior of PS304, Stellite 6, T400 and T800 tribo-alloys is affected by the formation of an oxide tribo-film and debris at the contacting interface;
- Sprayed Supersonic coatings combine a relatively low coefficient of friction with a good wear resistance. The good wear characteristics are maintained even on increasing the test temperature up to 400°C;



(c)

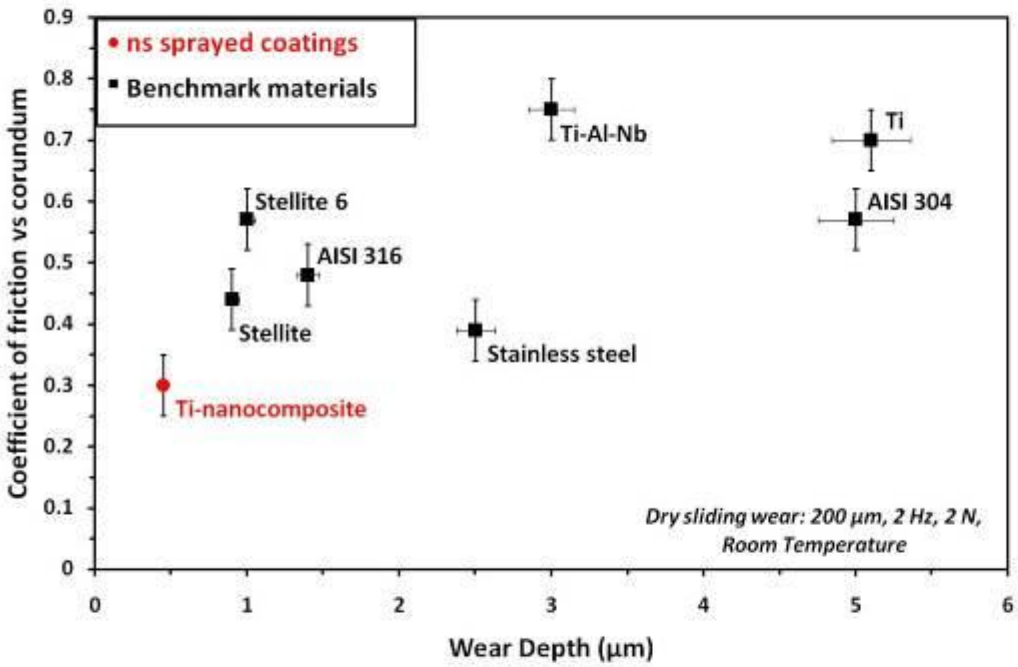
Biomedical application

The evaluations of corrosive-wear behaviour were performed at FALEX in collaboration with KUL. Metallographic investigations of Titanium CerMet coatings, before and after corrosive wear test, show structures highly wear resistant with a minimized loss of material.

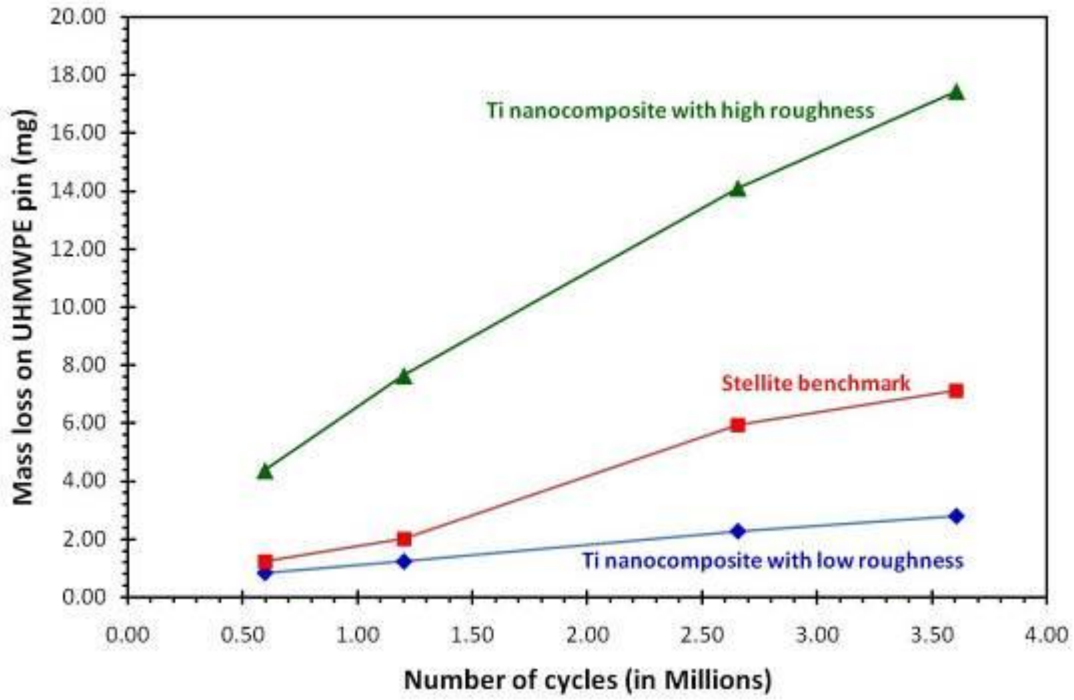


Supersonic coating as-sprayed and after corrosive wear experiments

The major issue concerning this material is the quality of the surface finishing process. The presence of pores on the surface can, in harsh abrasion conditions, decrease the lifetime of the components.
A proper finishing allows to obtain low porosity and roughness by improving the targeted properties. Ti-CerMet coating result better, in terms of COF and wear depth, in comparison to benchmark materials proposed.



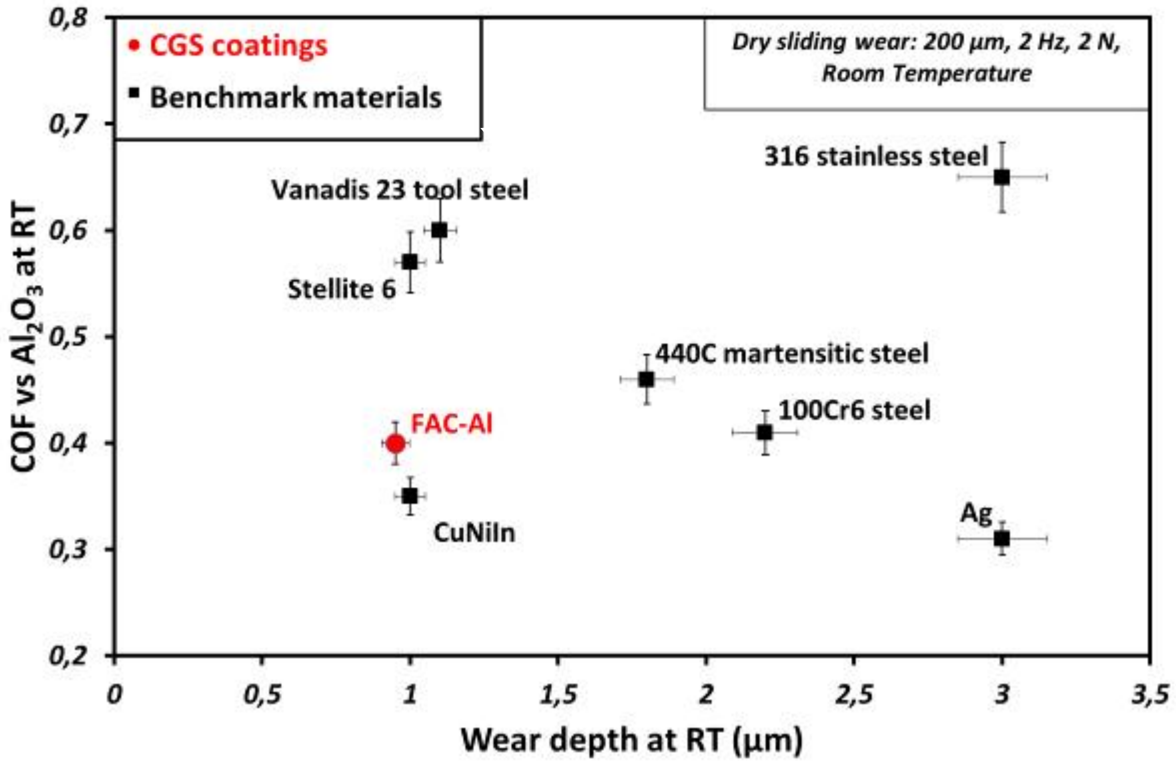
Comparison with benchmark at RT



50-station machine – Comparison between different surfaces finishing

Mechanical application

Tribological behaviour of FAC-Al has been tested by friction and wear measurements via reciprocating sliding experiments. The supersonic nanostructured CerMet have improved wear characteristics and COF compared to some commercial alloyed steels. This can be attributed to the synergetic effects between the alloying elements, the nanostructuring and the formation of an oxide based tribo-layer.



FAC-Al CerMet have improved sliding wear resistance when compared to most commercial alloyed steels. However, under abrasive conditions intense sticking phenomena can occur if an appropriate surface finishing is not achieved.

Development of Aeronautical components (SKF)

SKF Aerospace aimed to develop a customised coating, with high wear resistance and low friction, addressed to HT aeronautical bearings. For this specific application the bearings will work at operating temperature of about 570°C in a swivel and vibrational system in which the sliding friction conditions are promoted.

The behaviour of prototype bearings, under sliding wear resistance conditions, can be evaluated thanks to a swivelling endurance test developed properly for the case in exam. The fretting wear resistance has been estimated at tribological level by KUL, the Ni-based material is the best material if compared with current benchmarks.

The promising outcomes have pushed SKF to re-adapted the design of bearings and the whole structure built around it in order to allow the coating with the Ni-based material and the post-operations process of grinding and finishing, necessary for the final application.

Properties of the selected coatings are very different from those used in SKF up to now. For this reason the grinding operations have, also, been reviewed in order to be adapted to these new material. Grinding is an abrasive machining process where a rotating abrasive wheel is used to attain a desired surface roughness with very accurate dimensions and shape. Wheel is dressed according to final surface geometry requirement. About 150μm, from 300 of the starting coatings, are removed during the grinding operation, in order to obtain:

- Required spherical diameter;
- Required surface roughness (Ra 0.2);
- Dense coating with homogeneous properties;

To this aim, several tests have been performed on a prototype inner rings manufactured for the pre-qualification of the bearings. These prototype inner rings also enable to evaluate the SUPERSONIC coatings compatibility with of other process such as:

- Dye penetrant inspection;
- Surface preparation for dry film lubricant application;
- Adhesion of dry film lubricant;
- Spark (erosion) cutting;

The performed spraying of components has allowed to evaluate the costs of the whole production process of a bearing and the final impact on the component price. Keeping in consideration the gas consumption, the efficiency of the process and the time needed to spray each part, the final price for the coated piece is estimated in 136€.

This calculation was made on first prototype trials and keeping in mind that the efficiency of the deposition can be increased with the optimization of the process, the final components, sprayed with Supersonic coatings and technologies, will have a competitive cost on the market.

Development of Biomedical components ALH)

Alhenia aimed to study and introduce innovative biomedical coatings with enhanced properties finalized to the prosthesis manufacturing. In order to evaluate the improvements achieved, a test campaign has been performed by analysing tribological behaviour, wear properties, machinability of coatings and biocompatibility of materials once sprayed.

Mechanical tests performed on coating trials show that the coating reduces the wear of the polymer, used as counterface in the final application, in a long term biomaterials wear test experiment. The

weight loss of the counterface material (UHMWPE) strongly depends on the surface roughness of the final coating. The surface finishing plays a vital role on the wear resistance of the tribo-system, as two-body and three body abrasion phenomena can occur. By examining the wear track after biomaterials wear for the low and high roughness Ti-CerMet, it was found that no significant wear was observed on the surface of the low roughness coatings, whereas wearing off the counterface and "entrapment" of debris particles within the pores (pluck outs) of the high roughness Ti-Cermet coating was evident. In comparison with benchmark materials the Supersonic coatings have shown their superiority in terms of tribological behaviour.
The coating microstructure shows a quite homogeneous layer with a good distribution of the CerMet. The low porosity, under 2%, allows to execute an accurate polishing once the component is sprayed. Moreover the coating achieves bond strength superior to 50Mpa and hardness around 640 HV by indicating remaining CerMet content in the coating.
Biocompatibility of coatings have been tested by Alhenia and the materials result in agreement with the ISO standard:

- Cytotoxicity: < 30% and in agree with ISO 17025, ISO 10993-1,-5,-12;
- Endotoxin: < 20 endotoxin unit/device and in agree with Directive 93/42/EEC, 907385/EEC and DIN EN ISO/IEC 17025:2005;
- BioBurden: < 50 Aerobic mesophilic germs per fitting and in agree with ISO 11737-1;

The obtained results have justified the utilization of this material for the next step of validation that is the coating of components.

Sprayed and polished coatings have been tested following the Standard EN ISO 3274, EN ISO 4287 and EN ISO 4288. The roughness Ra and Rz vary within a restricted range of values with a good repeatability. The so obtained components can be considered as a good starting point for the utilization of the HEBM and CGS technologies in the biomedical industries.

The costs evaluation of the whole production process for the considered biomedical component has been performed. Keeping in consideration the gas consumption, the efficiency of the process and the short time needed to spray each part (less than 5 minutes), the final industrial cost for coating the component is estimated 80€ competitive with other benchmark deposition processes.

The improved properties provide a high added value of these kind of implants. Moreover the final biomedical component coated with nanostructure Ti is considered attractive from an esthetical point of view allowing to place the final implants in a premium user market. For this premium market niche the final selling price of the implant can even be increased becoming also a preferential product choice for Alhenia.

Technological transfer on mechanical applications based on comparison with benchmark materials (FAL)

The main aim was to study how to significantly reduce fretting, abrasive damage in mechanical components and costs by maintaining the original design with the addition of a surface layer with enhanced properties. This means that the coating should not only exhibit superior wear resistance against industrial benchmarks but also have good performance/cost ratio.

The deposited coatings on Aluminium and steel substrates were subjected to industrially relevant tribological tests. Two phenomenon of wear are interesting namely fretting wear and abrasive wear.
The industrial tribological tests are well practised in the industry and generating sufficient data in this direction will be helpful in creating confidence for the coatings.

Fretting is a wear process that occurs at the contact area between two materials under load subjected to minute relative motion by vibration or some other force. During operation, the cyclic stresses and inertia of the system may cause cyclic shear stresses and possible slip, leading to the phenomenon of "fretting". Over a period of time, the fretting can lead to the formation of wear particles under gross slip conditions, or to the formation of fatigue cracks under partial slip conditions.

The industrial standards chosen for this screening criterion are:

ASTM D7217 – Determining extreme pressure properties of solid bonded films using a High frequency linear oscillation test machine.

ASTM D5707 – Measuring friction and wear properties under linear oscillating conditions.

ASTM G204 - 10 Standard test method for damage to contacting solid surfaces under fretting conditions.

The abrasion wear resistance can be divided into two body and three body type. In the two body abrasion a hard counterface scratches or ploughs the softer surface whereas in 3-body there are hard particles trapped in the contact will in-turn damage the two surfaces.

Falex has evaluated both the abrasion scenarios on the coatings by using the appropriate standard.

Two body abrasion study: ASTM G133 - Standard Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear. FAC-Al coatings reveal that same coefficient of friction on different samples which confirms a good inter-sample reproducibility and control of spraying parameters.

ASTM G65, also known as 'dry sand abrasion test', is a very well-known industrial method for qualifying coatings for abrasion resistance. In this test, a static load is applied by a rotating rubber wheel in the presence of a sand curtain. The flowing sand particles cause abrasion of the coating. The wear loss is measured as mass loss before and after the test duration.

The best FAC-Al coatings did not survive this test. The coating was worn through and the mass loss on the coating was 0.2124 g which is equivalent to 4.25 x 10-4 g/cycle. For this reason FAC-Al coatings were discarded for abrasion applications.

The next generation of coatings designed for abrasion resistance are the WC based CerMet. Contrary to FAC-Al, WC based coatings showed excellent wear resistance. The repeatability of the tests was also excellent. Compared to the currently used Al alloy, this coating showed 7 times improvement in wear resistance.

Since in mechanical application it is important the durability of the components, the reliability analysis of the coatings was studied using 50 station pin-on-disk tester. A number of samples can be run simultaneously in order to evaluate wear loss under abrasion conditions. The obtained data can then be used for statistical analysis in order to derive reliability information. FAC-Al and WC-Co-Al were evaluated to study the effect of surface finish on abrasion. Depending on the kind of surface finish there was difference in the abrasion wear damage. This again confirms that a good surface finish is essential for repeatable and superior abrasion resistance.

With the progress of the supersonic project and improving of consortium's know-how, coatings having better tribological properties and wear resistance were obtained. Optimized FAC-Al CerMet coatings exhibited a similar wear resistance to the state-of-the-art Diamond Like Carbon (DLC) coatings. Their improved wear behaviour was attributed to the appropriate balance between hard and soft phases and to nanostructuring of the material. The integration HEBM-CGS has been performed for the materials analysed and, moreover, a customized instrumentation has been developed to coat inner geometries like as engine cylinders.

Supersonic WC-Co-Al CerMet has a higher wear resistance than the HVOF sprayed benchmarks. It is believed that due to the higher kinetic energy of supersonic sprayed technique, more dense and cohesive coatings were obtained. However, the higher the cohesion among the splats of the coating, the better the resistance of the coating to wear. WC-Co-Al CerMet have a lower sliding wear resistance than FAC-Al, whereas for gross sliding conditions (ASTM G65) the results are vice versa.

Eco Design software (contribution asked to GRA)

Coatings serve to protect the value of a material and product, and are typically used to mitigate damage due to a harsh service environment or wear. Coatings can also improve the eco-footprint of a product both by prolonging the life of the material such that product replacement can be delayed or eliminated and also by enabling lower impact substrates to be used in environments for which they would not otherwise have adequate durability. Eco data for coatings is not readily available, and as such requires additional effort to account for during the design phase, typically requiring expert advice. Granta Design collected technical and eco data for substrate-coating systems in the Supersonic project, and integrated this data with accessible materials selection and eco analysis tools in a CAD environment to provide designers (without eco-expertise) with a single user-interface for coating decision-making.

The Eco Audit™ tool supported by the Supersonic project enables the following capabilities during design:

Browse and search materials—browse and query a material database to find the materials and combinations of substrates and coatings or finishing processes (painting, electroplating, powder coating)

Assign materials—assign materials to parts in the CAD model. Key materials properties are applied to the parts for use in further analysis tools, such as stress analysis.

Run eco impact and business risk analyses—estimate key environmental and cost indicators: calculate energy and CO_2 for the full product lifecycle (includes transport and use phases in addition to raw materials, manufacture, and end-of-life), water usage, estimated raw materials cost, RoHS (Restriction on Hazardous Substances), food compliance, indicate critical materials and restricted substances, and end-of-life behavior.

Explore alternatives—set a baseline and see the impact of changes in the materials choice via an interactive eco impact dashboard. You can understand the environmental impact of decisions and make alternative materials selections that better meet regulatory and environmental objectives, without compromising cost or performance.

Generate reports—record your decisions and support communication.

The impacts of Granta's contributions to the Supersonic project include:

1. Capability to perform virtual design of coating
2. Coating selection in CAD
3. Ecological impact of new coating technique and case study materials understood

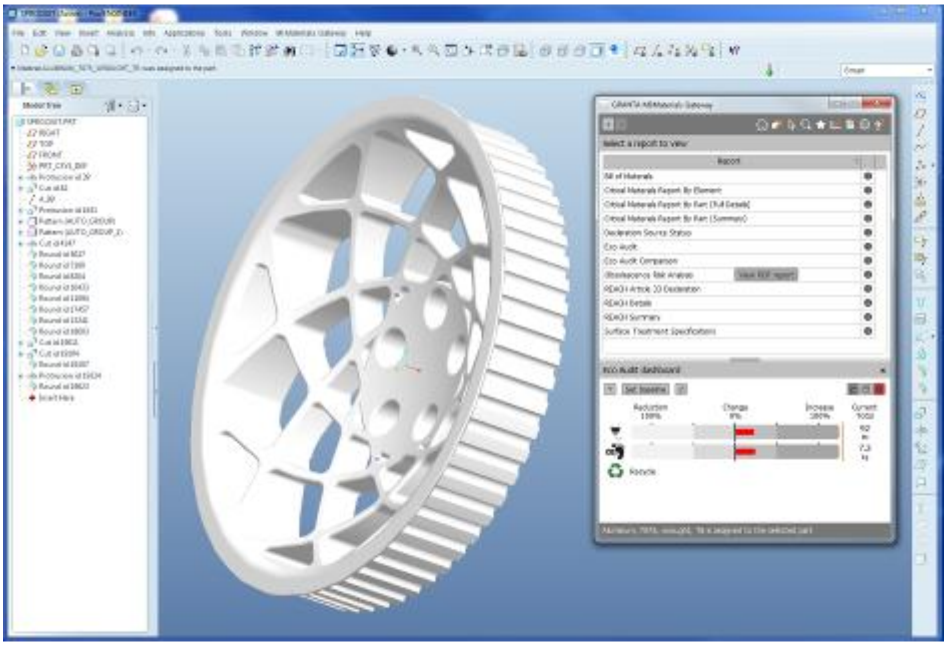


Figure 1: Comparison of two substrate-coating systems in the Eco Audit Dashboard in CAD (ProEngineer)

<u>Life cycle analysis (the contribution will be inserted in the part of aeronautical and biomedical components)</u>

EcoAudit™ was used to perform a streamlined-LCA (energy, CO_2 equivalent) for the material and manufacturing life cycle phases for aeronautical and biomedical applications. Specifically, powder producing process, coating manufacturing and application process has been modelled from primary data (gaps filled by Ecoinvent v.2.2). Use and transport phases were not considered, nor recycling of the coating. Recycling of the substrate was included for the aeronautical application.

Biomedical case study: a comparison of results for the benchmark (TiCN/TiN coating on Co-Cr-Mo substrate) and the Ti-nano-composite coating system developed in Supersonic resulted in a 250% increase in energy use, 270% increase in CO_2 footprint, 63% reduction in water, and 17% reduction in cost. The environmental performance is reduced for the new system, primarily due to the intensive energy and CO_2 cold gas spray process. Gas consumption, particularly the use of Helium, is the major reason for this (168 MJ/kg, 9.5 kg CO_2eq/kg of gas [Ecoinvent v2.2]). Nitrogen as a carrier gas could decrease this impact.

Aeronautical case study: a comparison of results for the benchmark coated bearing (Ag coating on Stainless steel substrate) and the NiSn coating system developed in Supersonic resulted in a 17% reduction in CO_2, 9% reduction in energy use, 97% reduction in water use, and 93% reduction in cost. Nickel (Ni) is listed in Annex XVII of REACH, and should be treated with caution if used in a spraying process for which human contact is possible. Tin (Sn) is a conflict mineral according to the U.S. Dodd Franck Act. The environmental analysis above gained a credit for the ability to recycle the substrate, and hence the manufacturing phase (370% increase in energy) is still a hot spot and the recommendation to exchange Helium for Nitrogen persists.

- The potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and exploitation of results (not exceeding 10 pages).

Potential impact (socio-economic impact)

Cold Spray is a relatively young process but many companies have involved considerable R&D efforts in the last years to understand and control this process due to the promising results that this technology can produce. SUPERSONIC project removes the technical barriers that prevent the opening of the wide-scale introduction of nano-featured coatings and technologies in a wide range of sectors creating the basis of a new European manufacturing platform able to produce high performance products.

Thanks to the achievements of the SUPERSONIC project it is possible now to deliver:

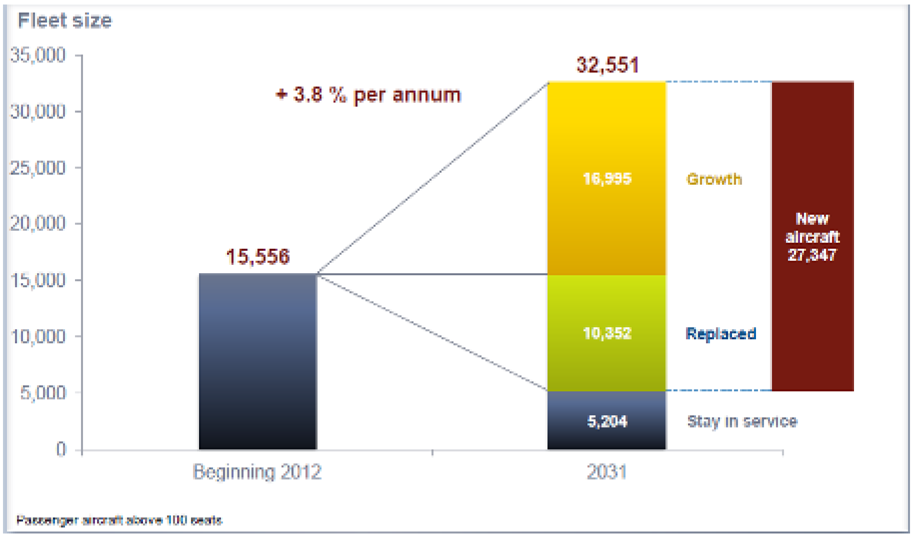
1. Nanostructured coatings and surfaces with outstanding tribological properties in several metallic and composites systems;
2. Deposition of hard and dense CerMet coatings via CGS using the SUPERSONIC innovative concept;
3. Structural integrity of the substrates and coatings thanks to localized reaction with limited thermal effect;

4. Fully industrial powders manufacturing and coating technology with a very high degree of innovation themselves;
5. Reliable equipment developed to produce and deposit reactive powders in totally safe manner;

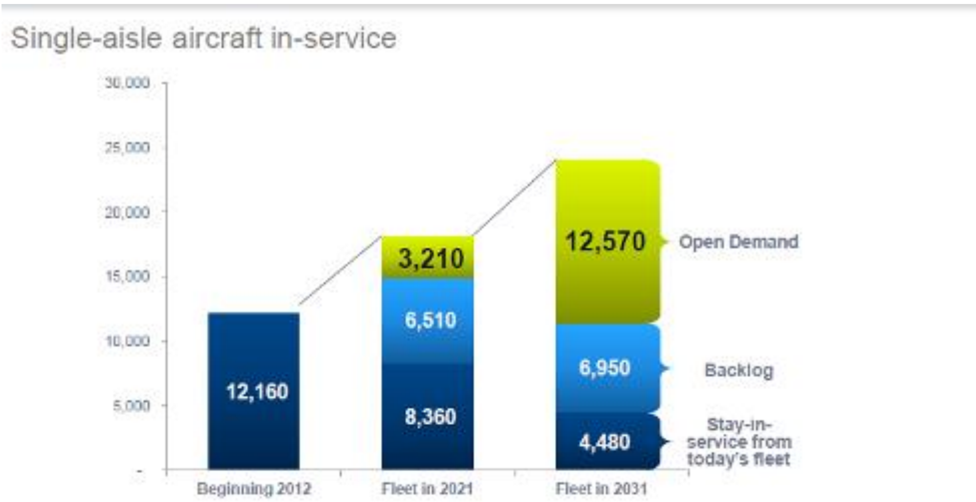
The integration of HEBM and CGS in a reliable manufacturing chain represents the proper way to appeal the interest of the market by increasing the potential impact of the achieved outcomes. Following these considerations, the possibility to produce real pieces with innovative technologies, integrated in a manufacturing chain, has represented a key point of the project development. Aiming this result, the consortium has developed and validated the integration of HEBM and CGS processes thanks to the outcomes described in the S&T results. The achievement of these ambitious targets has been performed by exploiting the cooperative effect of innovation on both the deposition technology and material performances. Three specific industrial areas have been used to demonstrate the possibility to replace conventional products and to introduce new solutions for unsolved problems.

Thanks to the validation activities performed by the industrial partners it been has proved the concreteness of the project results and, moreover, it has been possible to evaluate the potential impact of these outcomes thanks to carried market analysis.

Concerning the aeronautical case study it results that in the next 20 years, aircraft fleet will continue to growth. The market demand has been stimulated by increasing global demography, by emerging market such as Asia-Pacific (more first time flyers, a growing middle class, Liberalisation and Low cost model growth) and by the replacement of the less eco-efficient aircraft (2/3 of existing fleet will be replaced).

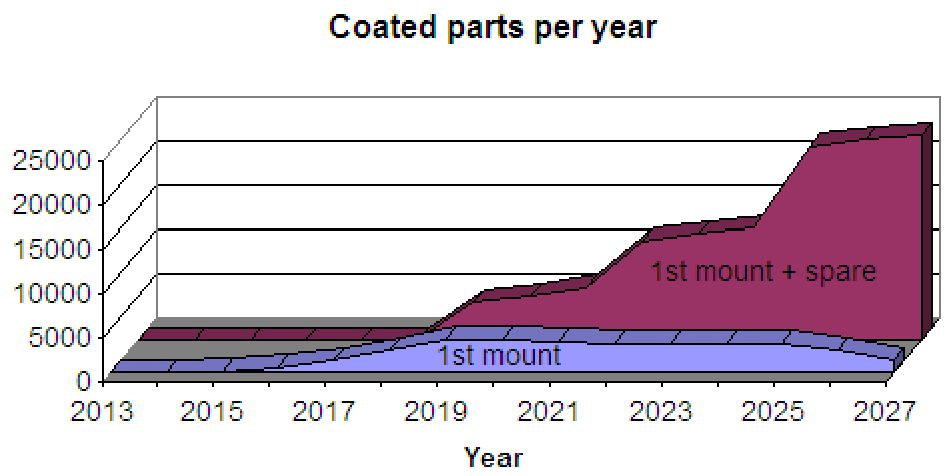


In this global aviation growth trend, the single-aisle aircrafts, as the A320's Aircraft family, represent from the 60 to the 70% of the market. The strongly requested A320 Family is composed of the A318, A319, A320 and A321 and cover the 100-220 seats market and flying up to 4,200nm/7,750km. This bestselling aircraft family has been further enhanced with the offer of new fuel saving engine options, with target enter service end 2015.
The A320 New Engine Option (NEO) will deliver fuel savings of 15%, which represents 3600 tonnes of CO2 savings annually and a double-digit reduction in NOx emissions. A320 NEO customers will benefit from reduced engine noise, lower operating costs and a 500nm increase in range.
In March 2013, already 2052 firm orders for A320 NEO have been confirmed.



A320neo will continue to build on success of the A320 Family

Taking into account that the A320 family has 2 engines per aircraft, that each engine mounts 5 bearings potentially produced exploiting the project results and that the needed of spare parts is commonly predicted after the first mount; the potential market size for the Supersonic bearings can be estimated in about 40.000 parts within the next 20 years.



The biomedical application has been headed by Alhenia: an international leading provider of medical implants and instruments to orthopaedic device manufacturers. The success of Alhenia is based on the focus on medical components, extensive know-how and a OEM driven value proposition. Usual customers are the major orthopaedics / trauma OEM´s and prime distributors in the medical market. The marketability of the Supersonic material for biomedical application can varies in function of the different exploitations of the results available with the Alhenia's markets.

The market size has been calculated with the following assumptions:

- Need to separate captive (OEM internally done) and not captive (externally coating services);
- Captive covers the 59% of Alhenia's market while the not captive is the 41%;
- This diversification includes materials and coating services (Plasma Spray, PVD and EBM);

These assumptions have been made basing on accurate numbers from 2010. In this simulation it has to consider the 10% CAGR for 2011/2012/2013.

Biomedical market represents a niche market thus has particular statements and conditions that have to be considered to execute a correct evaluation. The principal market conditions for the biomedical applications are:

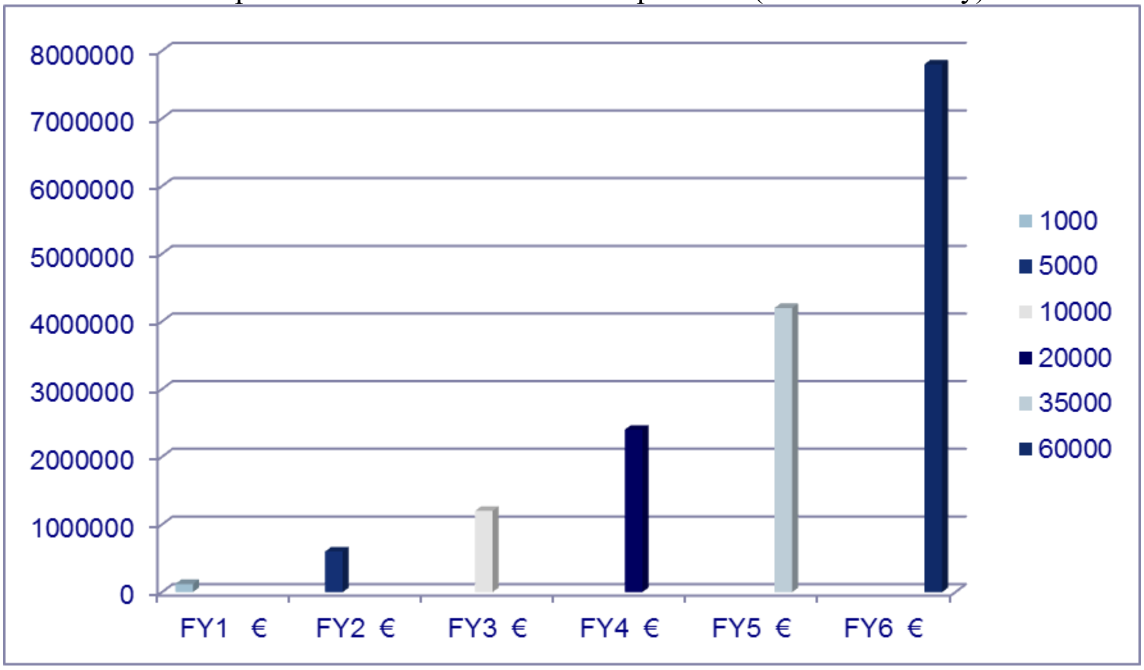
- Coating market is growing extremely fast for the biomedical as well as for other sectors;
- New coating processes will offer product differentiation and additional functionality;
- Coating processes like Plasma, PVD, Sintering, Anodizing etc are recognized and are considered as industry standards;
- Dedicated materials and product solutions for niche applications can be well paid in the biomedical sector;
- Medical industry moves very slowly due to regulatory issues. Time to market is 5 to 7 years in average for new products;

In this scenario Supersonic project helps to bring additional innovation to the existing solutions. The market potential of Supersonic material is influenced by the final target application, in the specific case it is considered the market of the components with wear problems: knee components, shoulder componets, extremities.

Three scenarios have been envisioned by imposing the following boundary conditions:

- If the product is accepted by the market the application will be applied for a Premium Market;
- Market introduction depending of clinical results;
- If regulatory and clinical aspects are successful product introduction will happen in 2016/2017;

Scenario 1: one of the top 5 OEM’s coat their knee components. (With exclusivity)

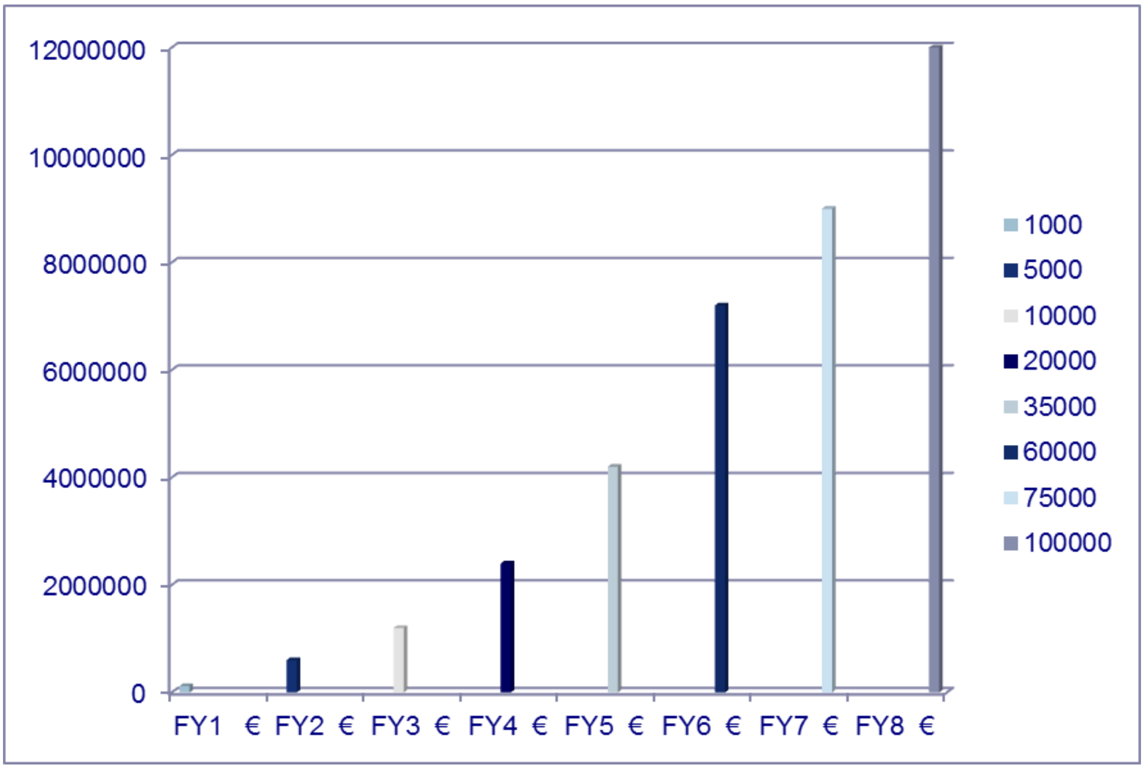


Evidences from the first scenario:

- Potential of around 8 Mio € Sales. Only coating services; coating price 120€/piece
- Quick introduction but stagnation after 5 years
- Lowest Marketing cost

- Minimum return of investment for Supersonic

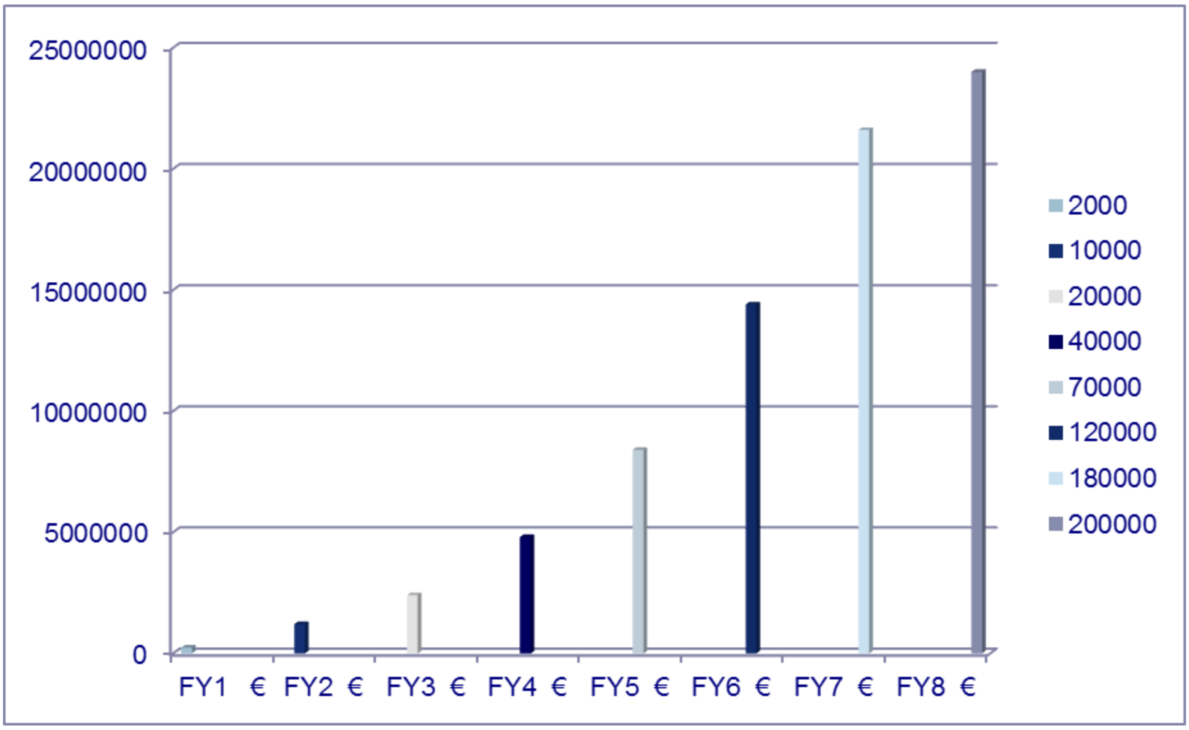
Scenario 2: offer coating services to the orthopedics market with no exclusivity



Main considerations on this scenario:

- Market potential 12 Mio € in coating services;
- Slower market penetration time but steadily growing. High marketing cost;
- Same patern as thermal sprayed coatings. Other applications can be also included in the model;
- Better ROI (return of Investments) for Supersonic consortium;

Scenario 3: offer coating services to the orthopaedics market with no exclusivity. Transfer equipment and technology to major OEM's. (Captive market)



Main considerations on this scenario:

- Market potential of around 25 Mio € on coatings;
- Good compromise with speed and growth;
- Same patern as thermal sprayed coatings. Other applications can be also included in the model;
- Best ROI for Supersonic consortium;

The potential market for these materials has been estimated for three different scenario, starting from the maximum profit for Alhenia and arriving to the maximization of the engages for the Supersonic project. In conclusion we can affirm that there isn't a choice better than another for the exploitation because the analysis has shown that the potential market for the reinforced Titanium materials is very promising independently from the followed scenario.

Mechanical

The market analysis of the Supersonic coatings tuned for the mechanical applications is made on existing industrial tribological problems based on the feedback provided by the end-user and the know-how of Falex.

Sliding conditions: Piston rings – internal combustion engines

Annually more than 20 billion $ are spent on resources wasted and for repairing of piston rings due to synergetic effect of mechanical loadings and/or oxidation phenomena. Therefore, the automotive industry possess as a major market for applying these sprayed nanostructured coatings. In particular, in this project, FAC-Al CerMet coatings were deposited onto industrial steel alloys in order to improve the scaling and wear resistance of automotive pistons.

The bare and FAC-Al coated pistons were submitted to scaling tests.

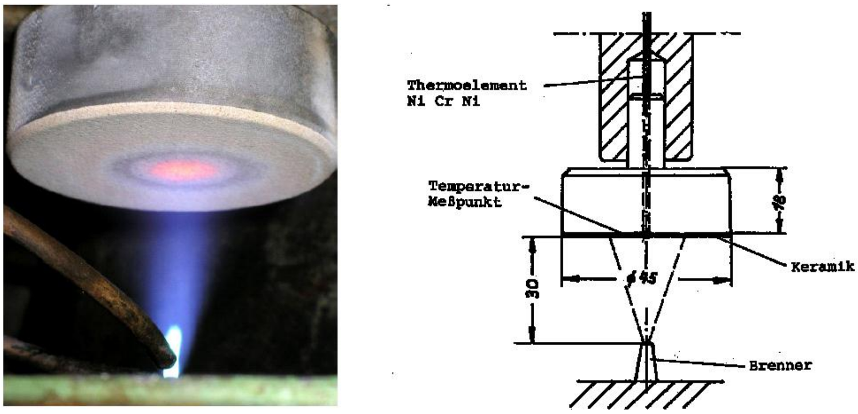


Figure 1: scaling testing of automotive pistons

From the experimental results obtained it is evident that the FAC-Al coated pistons exhibit superior scaling resistance in comparison to the bare pistons.

FAC-Al CerMet are extremely attractive materials for coating pistons. In a market that billions of euro are spend on an annual basis, such supersonic coatings can potentially replace existing steel based alloys in the automotive industry, as they possess improved tribological and scaling characteristics. In addition, they appear to have similar wear characteristics and a much lower cost than some of the most advanced tribo-alloys in the market.

Abrasive conditions - Cylinder bores

One of the main failure of the cylinder bores is due to the abrasive wear. FAC-Al and WC-Co supersonic coatings have been tested and compared to industrial AISI 52100 steel and advanced Plasma transferred wire arc (PTWA) benchmark. While FAC-Al shows a similar behavior, WC-Co-Al CerMet equals the properties of benchmark materials without showing any sticking phenomena during the fretting loops. WC-Co-Al CerMet coatings can be a potential candidate material to replace advanced and expensive PTWA coatings in the automotive industry.

In addition, for other mechanical cases studied, WC-Co-Al and Fe-Al-Cu+Al2O3 CerMet can potentially replace DLC coatings for abrasive applications. The main advantage of these sprayed coatings is their lower cost, complexity of deposition process, deposition on any substrate, and geometry of substrate.

Market prospective

Supersonic sprayed coatings are found to exhibit good tribological characteristics under dry and lubrication conditions. The flexibility of spraying technique, along with the very interesting characteristics of these coatings, is believed to attract significant technological and industrial interest within the following years. Up to now, the use of such coatings in industrial scale was still in its infancy, however, the results obtained present a clear evidence that these materials can be a feasible and economical solution to existing industrial problems and demands. In addition, the established know-how of the consortium can be the starting point of introducing and applying advanced techniques and novel materials to industrial customers.

<u>Dissemination activities</u>

The dissemination of the achievements is performed in order to create awareness about the project concreteness and the technological breakthroughs obtained. The dissemination of the principal outcomes outside the Consortium is one of the primary interests of the involved partners and it can be carried out by information mediums.

One of the easiest way to disseminate data and to publish the reached results is represented by a website properly structured. It allows to disseminate results and, moreover, it represents an excellent way to exchange information among the consortium. The work done for the website can be considered a success inasmuch more than 15.000 visits have been counted up to now. The continuous visit by guest users assures to the achieved results the desired visibility. The website is continuously updated and resumes also the conferences, the exhibitions, the publications, etc. made by the involved partners.

Another important way used to disseminate the obtained results is represented by the publication of scientific papers. The RTD partners has published during the project period almost 20 scientific papers and other are in working.

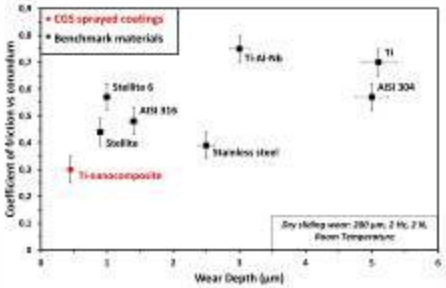
The whole consortium has focused his efforts for the dissemination also by participating to inherent conventions, exhibitions, conferences and workshops. Up to now partners have attended to almost 30 public events and additional participations are already planned for further exhibitions.

Supersonic Project has, moreover, a flyer resuming the most important achievements reached.

Results

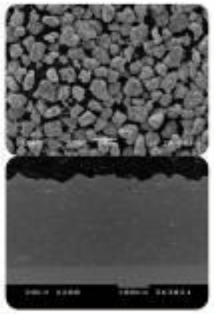
Titanium nanocomposite

The Ti nanocomposite coatings when applied to Ti substrates meets the requirements set by mechanical and biocompatibility ISO specifications.



Coating performances

	Unit	Value
Hardness	HV	640
Adhension F-1147	Mpa	>30
Thickness	μm	350
Porosity	%	<2.0
Taber ASTM F1978	Within standard	



Are you interested?

Join us at the planned exhibition:

ITSC 2014 — International Thermal Spray Conference & Exhibition

May 21-23, 2014| Barcelona, Spain

EURO PM2014 congress & exhibition — Euro PM2014 Congress & Exhibition
The Messezentrum Salzburg, Austria
21 - 24 September 2014
www.epma.com/pm2014

Visit our website to find all the information you may need:

www.supersonic-project.eu

Consortium

CPT · MBN · GRANTA · FALEX TRIBOLOGY · MATRES · IMNR · Alhenia · SKF · impact · KU LEUVEN · AGH

Contact

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Technical Coordinator:
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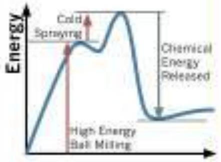
FP7-NMP-2008-LARGE-2
CP-IP 228814-2 SUPERSONIC

SUPERSONIC DEPOSITION OF NANO-STRUCTURED SURFACES

Innovative material and deposition concepts obtained by Mechanical Alloying and Cold Gas Spraying for advanced coatings in aeronautical, biomedical and mechanical applications.

Innovative material concept

Materials can exploit the kinetic energy of the CGS deposition to trigger the formation of ceramic phases and reinforce the metal matrix.



Principle outcomes

Supersonic project ensures:

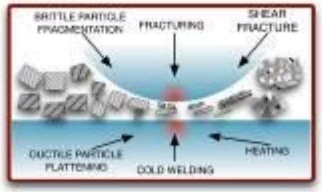
- **Nanostructured coatings** with outstanding tribological properties
- **CerMet via CGS:** Dense metal coatings reinforced with nano-ceramics using the SUPERSONIC concept
- **Structural integrity** of substrate and coating thanks to localized reaction with limited thermal effect
- **Reliable equipment:** developed to produce and deposit reactive powders in totally safe manner

Adopted Technologies

High Energy Ball Milling (HEBM)

The proprietary technology of **MBN** has the following advantages:

- Industrial scale productivity (100 tons/year) for nanostructured powder materials
- Possibility to adjust composition on customer's demand
- Allows the formation of ceramic nano-reinforcements by in situ reaction



Cold Gas Spray (CGS)

The technology developed by **IMPACT** innovation, ensures:

- The maintaining of the nanostructuring achieved thanks to his nature of solid state process
- The deposition of temperature sensitive materials
- The possibility to achieve thick coatings with reduced thermal stresses

Developments - Achievements

Selection of coating constituents, based on eco-design and restricted substances evaluations, has been performed thanks to the modeling software of **GRANTA**.

Development work of IMPACT in the Supersonic Project

IMPACT is partner in the project and focused on engineering and manufactoring components for the Cold Spray process.

Especially equipment for processing reactive powders was developed, tested and supplied to the partners.

- Turbulence Feeder
- Adjustable funnels
- Powder injection 90°
- Central feeding unit
- Air / Water / Liquid cooling device
- Variety of nozzles

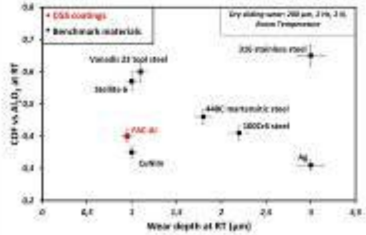
A new software was developed to work off the CG-process easy and comfortable.

Results

FAC-Al

Nanostructured cermet coating consisting of alumina dispersed in a Fe-Cu-Al matrix exhibits a superior wear behaviour thanks to the lubricating effect of soft areas (Cu) while harder areas (Al2O3) contributes to the good resistance to abrasion.

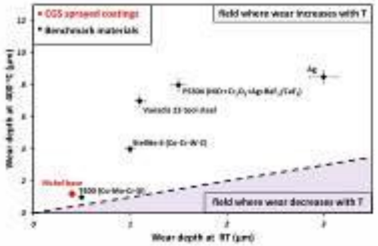
Coating performances	Unit	CGS
Hardness	HV	650
Adhension	Mpa	>60
Thickness	µm	<300



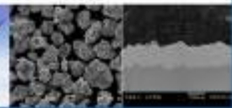
Nickel base

Nickel reinforced with intermetallic phases forms a dense coating to be used in the aeronautical applications providing:

- Self-lubricant behaviour at high temperature
- Enhanced mechanical properties at high temperature
- Enhanced tribological properties both at RT and HT



Coating performances	Unit	Value
Adhension	Mpa	>60
Thickness	µm	>500
Coefficient of friction		<0.3



Exploitation

Thanks to the outcomes achieved during the Supersonic project and to the collaboration among the involved partners, the foundations for the creation of solid assets, able to continue and improve the work started, have been laid.

The optimization of the used technologies for the biomedical devices opens, for the asset MBN-UB-IMPACT-ALHENIA, several opportunities of exploitation for the orthopaedics market.

MBN has optimized the Ti-system material by producing powder able to follow the biocompatibility requirements and it will exploit this result by proposing to the biomedical market its high technological content materials.

UB can support the interested companies by consultancy activities on the coating processes and the materials behaviour while IMPACT will be able provide the same consultancy offers as well as the devices and the apparatus for the spraying.

ALHENIA can exploit the obtained results by the three different ways explained above.

The work done for the aeronautical application has brought to SKF the possibility to introduce in its facilities a manufacturing chain that exploits non-conventional technologies. Supersonic project has inserted the deposition via CGS of Nickel materials but the validation of the so obtained components involves several and severe tests. In case of positive results SKF can think to start the utilization of the HEBM-CGS manufacturing chain by opening new a new market scenario for MBN and IMPACT.

In the mechanical application FALEX will act as intermediary between the consortium partners and those companies that are interested in these technologies or that require particular solutions resolvable by the HEBM-CGS approach.

Outside of these application fields MBN and IMPACT can exploit the achieved outcomes by, respectively, selling powder and equipment to CGS utilizers.

From the point of view of the software adaptations performed during the project, GRANTA has and will continue to exploit the obtained results in order to improve his software programs.

- The address of the project public website, if applicable as well as relevant contact details.

Ref. website: www.supersonic-project.eu

Powder production and technical project management:
MBN Nanomaterialia S.p.A. (Italy)
+39 0422 447311
Website: www.mbn.it
Mail to: research@mbn.it

CGS equipment:
IMPACT Innovations (Germany)
Website: www.impact-innovations.com

Coating optimization:
CPT Barcelona (Spain)
Website: www.cptub.com

Software development:
Granta Ltd. (United Kingdom)
Website: www.grantadesign.com/contact/

Microstructural evaluation:
AGH - University of Science and Technology (Poland)
Website: www.agh.edu.pl

Thermal evaluation:
IMNR – National institute (Romania)
Website: www.imnr.ro

Tribological evaluation:
KU-Leuven University (Belgium)
Website: www.kuleuven.be

Wear test analysis:
Falex Tribology (Belgium)
Website: www.falexint.com

Furthermore, project logo, diagrams or photographs illustrating and promoting the work of the project (including videos, etc…), as well as the list of all beneficiaries with the corresponding contact names can be submitted without any restriction.

FINAL REPORT ON THE DISTRIBUTION OF THE EUROPEAN UNION FINANCIAL CONTRIBUTION

This report will be submitted to the Commission within 30 days after receipt of the final payment of the European Union financial contribution.

Report on the distribution of the European Union financial contribution between beneficiaries

Name of beneficiary	Final amount of EU contribution per beneficiary in Euros
AGH	*477 859,69*
MBN	*750 675,37*
KUL	*461 293,68*
CGT	*114 618,60*
UB	*550 593,82*
MATRES	*451 321,95*
SKF	*160 675,37*
ALHENIA	*363 033,70*
IMNR	*273 847,84*
GRANTA	*374 145,03*
FALEX	*294 397,38*
IMPACT	*330 074,99*
TOTAL	***4 602 537,42***