



# ObservatoryNANO report

## WP2 - Science and Technology Assessment Automotive and Aeronautics

Final report  
June 2009

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## Executive Summary

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Both automotive and aeronautics sectors are important industrial sectors in Europe. The European automotive industry produces 17,1 million passenger cars yearly, which is 32% of the worldwide vehicle manufacturing (ACEA, EU-27 data, 2008). The European Aerospace and defence industry had a turnover of € 132.2 billion in 2007, of which around 52% was related to military applications. Excluding defence, the European Aerospace industry had a turnover of around € 90 billion in 2004, of which 91% came from aircraft manufacturing and the remaining turnover from missiles and space. Within aircraft manufacturing, the biggest share came from large civil aircrafts (around 22% of total EU aerospace industry turnover) and military aircrafts (around 17%). Aircraft engines represented 9% whereas aircraft maintenance represented above 19%

Accordingly, there have been significant research and development activities in these sectors. In addition to competition, efficient use of energy resources, reduction in CO<sub>2</sub> emissions, relevant regulations and increased safety and comfort are important drivers for these industries' investment in R&D. To give an example, in Europe automotive industry invests 5% of its annual turnover in R&D while this figure reaches 14.4% in the case of aeronautics sector.

Industry aims to decrease weight while increasing engine efficiency and overall performance of the vehicles to be able to reduce CO<sub>2</sub> footprint and therefore, energy consumption. Consequently, research activities are focused on using lighter materials with improved performance for lighter vehicle components, increasing engine efficiency via reducing energy losses due to friction or via developing more efficient combustion systems, and, increasing the safety via improving the mechanical properties of various parts, etc.

This report provides an overview on processing technologies of nanostructured metals, polymer nanocomposites and tribological coatings for automotive / aeronautics applications.

Bulk forms of nanostructured metals and alloys exhibit extraordinarily high strength and high corrosion resistance as compared to their microstructured counterparts. Besides their exceptional properties, they are preferred for applications in automotive and aeronautics part due to their ease of manufacturing via reduced machining times and forging temperatures. These exceptional properties of nanostructured metals would make replacement of steel with a lighter material e.g. aluminium, magnesium, etc. So far, the most promising technologies to produce nanostructured metals are Severe Plastic Deformation (SPD) and among them Large Strain Extrusion Machining (LSEM). The biggest challenge for these technologies' feasible applications in transport industries is to be able to produce large parts with nanostructured metals at competitive costs.

Polymer nanocomposites, which are nanofillers incorporated polymer composites, can find applications in both structural and non-structural parts of the vehicles and also on parts, like fuselage where electrical discharge is a problem. Most common nanofillers that have been investigated for their applications in PNCs are nanoclays, carbon nanotubes and carbon nanofibers, graphene. Use of small amounts, 5-10%, of these nanofillers instead of their glass counterparts in polymer matrices bring drastic improvements while leading to a considerable weight reduction. Main research challenges for use of nanofillers is the dispersion, compatibility with the polymer matrix and homogeneous alignment in the case of nanotubes and nanofibers. Challenges regarding to their widespread use in vehicle applications are cost, availability of these materials in large amount with good quality.

Tribological coatings of different materials containing carbides, nitrides, metals or ceramics play a key role in the performance of internal mechanical components of a vehicle, such as the engine and power train. By reducing wear and friction tribological coatings increase the lifetime of the working material at the same time that they reduce the dissipation of energy as heat, thus increasing the efficiency of the vehicle. Coatings can increase tool productivity (longer tool life, higher cycle frequencies, less workpiece finishing), reduce manufacturing costs, improve the quality of products (due to smoother surfaces, better dimensional stability, higher degrees of metal deformation and fewer manufacturing steps) and reduce lubricant consumption.

Thermal spraying processes eg. atmospheric plasma spraying and high velocity oxygen fuel, and vapour deposition processes eg. physical vapour deposition (PVD) and chemical vapor deposition (CVD) processes are the common processing technologies for tribological coatings. The most important challenge to overcome in relation to application of tribological coatings on vehicle parts is the chamber sizes for large parts and accordingly long processing times where vacuum is required.

This report does not contain any economic data about the processes (production costs, production rates and investments necessary). This is a field that should be analysed in a separate study, so that the industry could evaluate the cost-benefit balance associated to the processes for bulk nanostructured metals.

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## 1.1 Technologies to produce bulk nanostructured metals

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### 1.1.1 Definition

In this report we provide information on the processing technologies that could potentially be used in the automotive and aeronautics industry to produce nanostructured metals and alloys.

The nanostructured metals and alloys considered are **aluminium, magnesium and titanium**.

The report introduces the following techniques used to produce nanostructure metals: **severe plastic deformation (SPD), nanopowder sintering, melt spinning and electrodeposition**.

Most of the techniques presented in this report are used mainly in **lab-scale** production for now. Very few exceptions where there have been final products are for small parts like bolt or screws used in the automotive or aeronautics industries. For their use in structural applications in the industrial scale, these novel materials have to be obtained in bulk forms with **large dimensions**, often in **large volumes** and always with **competitive costs** compared with the current solutions. Technically it is not possible yet to comply with all the above mentioned constraints at the same time, but the perspectives are optimistic, as the **development of nanostructured materials is a fast-growing** field and the **potential of these materials is very important**, as explained in the report.

This report does not contain any economic information about the processes (production costs, production rates and investments necessary). This is a field that should be analysed in a separate study, so that the industry could evaluate the cost-benefit balance associated to the processes for bulk nanostructured metals.

## 1.1.2 Short description

**Nanostructured metals and alloys** are defined as solids having structural features in the range of 1-100 nm in at least one dimension. In an ordinary metal the grain size is typically in the range of a few to hundreds micrometers.

Bulk forms of nanostructured metals and alloys exhibit improved mechanical properties (e.g. extraordinarily high strength) and have been studied extensively for several decades. According to Lux Research, the total market of nanostructured metals in 2010 will be around 200\$ million (assessed in 2007).

The most relevant nanostructured metals to be applied for transport applications are aluminium, magnesium, steel and titanium.

Due to their structure, bulk nanostructured metals and alloys exhibit different physical properties i.e. higher strength, higher corrosion resistance, and lower ductility than their conventional counterparts. To give an example, nanostructured nickel is 5 times harder than conventional nickel. This is because the properties of metals are governed by **the Hall-Petch relationship** - as grain size decreases, strength increases. Nanocrystalline materials are characterized by significant increases in *yield strength*, ultimate *tensile strength*, and *hardness*. For example, the *fatigue lifetime* can be increased by 200-300 % by using nanomaterials with a significant reduction of grain size in comparison with conventional materials.

Not only high strength but also high *ductility* is essential for the use of metals in automotive and aeronautics sector. Nanostructured metals normally have very limited ductility, but thanks to recent developments in the processing technologies it is possible to reduce ductility losses in nanocrystalline metals.

Besides the superior properties shown by nanostructured metals, their potential in the automotive and aeronautics applications is driven by their superior *manufacturability* properties too, such as in some cases the reduction of machining times and forging temperature, and the improved superplastic forming.

However, the current part sizes and volumes (and cost) that can be achieved are not sufficient to be used in most of the automotive or aeronautics structural parts, that is where nanostructured metal could have the highest impact.

### 1.1.3 State of R&D

A bulk nanostructured metal can be produced by two complementary approaches: The first one is the "Bottom-up" approach, in which bulk nanostructured materials are assembled from individual atoms or from nanoparticles, like **nanopowder sintering** and **electrodeposition** fall in this category. In the opposite direction, nanostructured metals can also be produced with a "Top-down" approach, i.e. the existing coarse-grained materials are processed to produce substantial grain refinement and nanostructures. The most successful of this later category is **Severe Plastic Deformation (SPD)** and **Melt spinning**.

The final characteristics of the material will be different depending on the technique chosen and the parameters adjusted.

#### Severe Plastic Deformation

Processing by Severe Plastic Deformation (SPD) refers to a method of metal forming where very high strains are applied on materials. It leads to exceptional grain refinement in the metal, without any significant change in the overall dimensions of the work piece.

The metallurgic principle for this technique to achieve nanostructured materials has been commonly used in the past: When a high pressure in the order of several GPa is applied on the work piece, the dislocations which evolve into boundaries to form finer grains are generated in the metal. There is a discussion in the scientific community about what is more important in the process, the pressure or the plastic strain. The materials produced by SPD techniques usually have grain sizes in the range of 100-1000 nm. However, they have subgrain structures, such as dislocation cells and X-ray coherent diffraction domains (crystallites), which are often smaller than 100 nm. Therefore, they can be called nanostructured (NS) materials.

Regarding the possible techniques, the strain can be applied in a number of ways, such as extrusion, bending, twisting, or rolling. The most common SPD methods available for automotive and aeronautics applications are equal-channel angular pressing (ECAP), large strain extrusion machining (LSEM), high pressure torsion (HPT), repetitive corrugation and straightening (RCS), friction stir processing (FSP), accumulative roll bonding (ARB), cyclic extrusion and compression (CEC) and asymmetric rolling (ASR).

#### Equal-channel angular pressing (ECAP)

ECAP is one of the most common SPD techniques, mainly based on straining a material by simple shear force. Simple shear deformation is repeatedly imposed in materials without changing the cross-sectorial dimensions of the work piece. Despite being a simple process, microstructure evolution during ECAP is quite complex and depends on the process parameters. Also improper use of ECAP may lead to defect generation.

ECAP is an appropriate technique to produce wires and rods. In a recent study, use of ECAP to produce strengthened Al wires with a micrometer scale grain structure was reported, using a miniaturized ECAP die with a millimetre-scale channel.

The main **limitation** in this process is the length of the billets that can be produced: while it is possible in soft tested materials, like plasticine or modeling clay, when a metal billet is used, due to elastic deformation and the Poisson effect, there is a lateral expansion of the billet in the entrance channel, and very high frictional forces develop between the work-piece and the channel walls. The force required to press a billet through the die increases

very rapidly with the length of the billet. Correspondingly, there is also a large increase in stresses experienced by the die. These two factors limit the length of the billet that can be practically processed by ECAP. In practise, the billets produced do not have more than 20 cm in any dimension.

### **Large strain extrusion machining (LSEM)**

LSEM is a method of SPD. This method combines inherent advantages afforded by large strain deformation in chip formation by machining, with simultaneous dimensional control of extrusion in a single step of deformation.

An important advantage of LSEM is that even high strength, low ductility materials can be subjected to SPD at ambient temperature.

A promising solution for SPD is **Continuous Severe Plastic Deformation (CSPD)**, where several SPD techniques can be combined to be able to overcome part of their limitations. For example to increase the length of the billets produced by ECAP. A usual sequence is the consecutive setting of ECAP and extrusion and drawing operations.

As different materials could be combined in the SPD techniques, "multimaterials" would be possible, like for example sheets with aluminium, titanium and magnesium. These kind of materials could be very suitable for the automotive and aeronautics industry, as different properties like high strain, magnetism, lightweight, etc. could be combined in one single material.

## **Nanopowder sintering**

Nanopowder sintering is the second of a 2-step process, comprised of nanopowder synthesis and then the consolidation process when the nanoscaled particles which are subsequently fused together using combinations of pressure and heat.

Sintering can be defined as the consolidation of a dispersed material under the action of heat, without total melting of the material. If part of the matter reaches its melting point during this densification, we speak of liquid-phase sintering; otherwise, it is called solid-state sintering. Moreover, if the material is chemically synthesised during sintering, this is called reactive sintering; otherwise, it is called non-reactive sintering.

The densification process for conventional powders is well known theoretically and practically. However, the densification of nanopowders poses significant challenges:

- *Chemical contamination* due to high reactivity of metallic nano powders leading to oxidation. Therefore, it has required developing oxygen-free in situ technologies for synthesis of powder and its sintering.
- Another more important aspect in the *sintering* for nanostructured materials is how to achieve full density while simultaneously retaining a nanoscaled microstructure. The relaxation of defective structure and grain growth under mechanical loading is probable, which results in loss of nanostructure. Therefore, the process to compact the nanopowder while conserving the nanostructure is strongly required. Besides, full densities are more difficult to achieve in metals than in ceramics.

**Warm sintering** is the preferred technique of sintering for nanometals, because it can combine high densities and grain sizes less than 100 nm.

Warm sintering temperatures are up to 675 K (402°C), and for most metal nanopowders, these temperatures are still in the cold working regime. Selection of such temperatures below recrystallization temperature is purposely sought to prevent grain growth. Only in low-melting-point materials may sintering at room temperature induce recrystallization and sintering effects.

Experimentally, densities obtained by warm sintering have exceeded 95%.

As well, **hot pressing** can achieve full densities and minimal grain growth in nanograined metals. Remarkable results -consistent theoretical and near theoretical densities and grain sizes less than 100 nm - have been achieved by hot pressing of mechanically alloyed powders (e.g. Fe(2-10%)Al, Al(0-10%)-Ti, etc.)-

Example of process: to make Cu-Fe alloys, mixtures of iron and copper powders having the composition  $\text{Fe}_{85}\text{Cu}_{15}$  are ballmilled for 15 hours at room temperature. The material is then compacted using a tungsten-carbide die at a pressure of 1 GPa for 24 hours. This compact is then subjected to hot compactation for 30 min at temperatures in the vicinity of 400°C and pressure up to 870 MPa. The final density of the compact is 99,2% of the maximum possible density.

**Hot Isostatic Pressing (HIP)** is another relevant technique. By design, HIP densification required longer times and therefore grain growth is more likely to occur than in hot pressing. However, a careful control of the parameters, particularly temperature, can result in satisfying grain sizes (e.g. 100-300 nm in ball milled TiAl, Cu, etc.). Although the temperature exposure experienced during hot isostatic pressing is extreme, it has been shown that nanograins can be retained in alloys such as TiAl by low temperature HIP while achieving full density. With nanostructured material, full density can be achieved around 600-800°C compared to around 1000-1200°C for materials with micron-sized grains.

Nanopowder sintering can also be combined with Severe Plastic Deformation techniques to process nanostructured metals.

## Melt-spinning

Melt-spinning process is characterised by pouring a metallic melt on a water-cooled rotating wheel, thus leading to the formation of a metal ribbon film of less than 100 micrometers thickness or flakes of it. The cooling rates vary from  $10^4$  till  $10^7$  Kelvin/s.

Once they have solidified, the flakes need to be compacted and pressed into the desired shape. During this step, their microcrystalline structures must remain intact. The method the researchers use in this case is spark plasma sintering: High-frequency current pulses inside the press compact the material in a very short space of time so that the fine microstructures are preserved. The very fast cooling of the molten metal leads to a nanostructuring of the metal. This results in new material properties of known alloys. The strength increases dramatically without changing the formability. This process gives the freedom of designing complex alloys in a flexible manner.

Another advantage of this process is its controllability. Therefore, the need for advanced modelling technologies is not considered so essential in this case as it was in SPD.

## Electrodeposition

Electrodeposition is a well-known technique and has long been used to produce coatings (electroplating) and to create freestanding entities (electroforming). In addition, it can also be used to form **metal sheets**.

Electrodeposition technologies have been developed for many different applications, including large thick-walled (>1 mm) electroformed products such as moulds for thermoplastic composite component manufacture.

The basic components required to form a cell for electrodeposition are an anode, cathode, electrolyte, and direct-current source.

For example, a sheet of nanostructured Cu can be fabricated by putting two electrodes in an electrolyte of  $\text{CuSO}_4$  and applying a voltage between the two electrodes. A layer of nanostructured Cu will be deposited on the negative titanium electrode. A sheet of 2 mm thick Cu can be produced by this process, having an average grain size of 27 nm, and an enhanced yield strength of 119 MPa.

The main processing parameters for obtaining nanocrystalline materials include the **basic composition of the electrolyte, addition of grain nucleators, stress relievers and grain growth inhibitors, the pH value, the deposition temperature, the current density, and the type of current cycles** such as continuous direct-current plating, pulsed direct-current plating, or periodic current-reversal plating.

The advantage of this technique is that it has been already tested for coatings, and that it can be processed at room temperature. On the other side, the costs and the cycle time are still too high to be scaled up to mass production in the automotive or aeronautics industries.

### 1.1.4 Additional demand for research

**Ductility:** An important point where more research is needed is to keep ductility in nanostructured metals. All of the nanostructured metals have very high strength, much stronger than ordinary metals, but they normally have very limited ductility. To make the nanostructured metals ductile, research suggests how to use deformation instead of annealing. Moderate annealing after SPD processing may improve the ductility without significantly sacrificing the strength, thereby improving the low-cycle fatigue life. Surface hardening techniques such as shot-peening are generally effective in improving the fatigue life of coarse-grained materials but appear to be ineffective in improving the fatigue life of nanostructured metals.

**Characterisation and simulation:** The scientific community is also asking for more developments in process characterisation. The structural characterisation of nanostructured materials has progressed importantly in the previous years. However, investigations are still ongoing to deeper understand the grain refinement mechanisms. A promising field for the development of nanostructured metals is the simulation "*ab initio*", also known as atomistic simulation, as it would reduce the uncertainties of the behaviour of nanostructured metals during the forming processes. It is said that these modelling techniques, when developed, could accelerate the investigations on SPD.

**Application in high-strength metals:** It is easier to process low strength metals like aluminium or copper. However, the automotive and aeronautics industry also demand high strength metals, like steel, and this is a field that still needs further research.

**Scale-up:** Another necessary point for the industrial application is to reduce the cycle times to produce nanostructured metals. For example processing of nanostructures by SPD techniques is a non-trivial problem, it requires special experimental and theoretical investigations of plastic flow mechanics, thorough characterization of the processed nanostructures and establishing the processing guidelines. A winning horse to increase the efficiency of the technologies to produce nanostructured metals would be to achieve continuous processing. To do that, existing technologies to produce nanostructured metals should be adapted to avoid batch production and use continuous production.

**Nanostructure control:** For improving sintering technologies, further research is needed to control the grain size and distribution. While suitable for making powders and small compacted samples with excellent control over particle size, the condensation method is at present not practical for most applications other than experimental. A particularly limiting aspect is the inability to form nanocrystalline materials of alloys because of the difficulty of controlling the composition of the material from the vapour phase. Another important challenge is that high grain densities are much harder to achieve as a result of the nanosized particles produced. Other methods that have been explored to synthesize nanocrystals include aerosol, sol-gel, high-energy ball-milling, and hydrothermal processes. However, these techniques cannot produce nanocrystalline materials at a cost acceptable for practical applications. Vacancies are also produced in large numbers during SPD, but have received much less attention. Using transmission electron microscopy, a high density of unusually large vacancy Frank loops in SPD-processed Al has been demonstrated. They are shown to impede moving dislocations and should be a contributor to strength. Related to this, grain boundary engineering is also an important field of research.

**Cost-benefit analysis to communicate with the industry:** To complement the metallurgic research, economic analyses for these technologies should be performed. Realistic scenarios for scaling up the technologies and data like process cycle time, possible dimensions, necessary investment and final part costs should be described and shared with the industry. This cost-benefit overview would facilitate the adoption of the nanostructured metals in the automotive and aeronautics industry, and would ease the selection of the most appropriate technique for each specific case.

### 1.1.5 Applications and perspectives

The technologies explained in the previous chapters exist basically at the laboratory level and have been used for very few final products in the automotive or aeronautics industry (small parts like bolts or screws). Taking into account the additional demands for research mentioned, there is an important potential for nanostructured metals to be industrially applied. Since the production of bulk nanostructured metals and alloys by SPD require a **modest investment** in capital equipment, compared to other technologies, the most common and suitable technology to produce bulk nanostructured metals and alloys for automotive and aeronautics applications is Severe Plastic Deformation (SPD). This is because nanostructured metals and alloys are produced using equipments that have similarities with the ones used in conventional deformation processes. In fact, machinery producers have incorporated ECAP into conventional rolling mills for continuous processing.

A big limitation for the industrial application is the **size of the parts** that can be produced. All the techniques explained in this report produce lab-size metal ingots. In the literature reviewed, there is only proof of parts of 20 mm in diameter and 100 mm in length that can be currently produced.

For example, in ECAP the length of the billet that can be practically processed is limited. In 2005, the largest billet of nanostructured aluminium that could be processed by ECAP was 5 cm by 10 cm at the U.S Air Force Research Laboratory (AFRL), and most scientific studies had been conducted on samples with 10 mm diameter or smaller. With LSEM, bulk nanostructured materials in the form of foils, plates, and bars of controlled dimensions are shown to result by appropriately controlling the geometric parameters of the deformation in large strain extrusion machining.

Small parts like **bolts, fasteners and screws** can be readily manufactured from the billets made with SPD technology, but the size the technologies can achieve in their nanostructured metals semifinished products has to be increased for large scale applications. Other shapes like **wires and rods** will soon probably be manufacturable using SPD techniques.

SPD has a significant potential for producing nanostructured materials at rates, and therefore at costs, comparable to conventional material production methods. The incorporation of ECAP into continuous production techniques also holds out the promise of producing nanostructured materials with a competitive low **cost**. Current costs to produce 5 to 20 mm diameter round bar of nanostructured titanium and titanium alloys by non-continuous ECAP range between \$50 / kg and \$150 / kg. These costs are comparable to those for intensive thermomechanical size reductions of conventional metals as in, for example, the production of wire. However, they are not competitive for many larger-dimension higher-volume applications.

Another issue is that to be applied in the industry, **safe working conditions** need to be guaranteed. While nanopowder sintering can have the presence of potentially hazardous nanoparticles, SPD techniques could have problems related to the high pressures involved in the process (e.g. potential equipment or piping explosions).

To finish with the **industrial post-processing**, it is important to highlight that nanostructured metals formed by SPD show improved characteristics, i.e. following formability processes:

- **Machining:** For products that are directly machined to shape from SPD-processed mill products, the feed rates and cutting depths can be increased because of the manner in which the deformation occurs under the machining conditions. Processing by SPD lead to a smoother surface finish and a reduction in tool wear. In some cases the superior surface finish from machining of the SPD-processed metals may obviate the need for subsequent surface finishing steps. This will reduce the manufacturing costs by eliminating or simplifying the processing steps.
- **Forging:** It is often used to create product shapes in the aerospace and automotive industry and there is evidence that the forging temperatures can be significantly reduced when forging SPD-processed aluminium alloys for aerospace applications. In addition, the times for subsequent heat treatments may be reduced by as much as 50%, implying time and energy savings.
- **Annealing:** In a report published in the April 14 2006 issue of Science, a team of scientists reported that a nanostructured metal can be hardened by annealing and softened when subsequently deformed, which is in contrast to the typical behaviour of a metal.
- **Superplastic forming:** Nanostructured metals can be processed until 100 times faster than conventional superplastic forming. This is an important feature for the aeronautics industry, because complex parts can be achieved.

### Nanostructured metals in automotive and aircraft industry

The most relevant metals for the automotive and aeronautics industry where nanotechnology can have an impact are the light materials, like aluminium, magnesium, titanium and their alloys.

Nanostructured metals, particularly aluminium and titanium alloys can improve the mechanical properties and enhance corrosion resistance.

Conventional **aluminium alloys** are currently spread in a wide variety of automotive and aeronautical applications. Their current limits are their low tensile properties compared to steel and their low melting temperature (~660°C).

For the SPD processing of Al, special applications requiring limited-production volumes will undoubtedly initiate the first applications of these materials. Later, after the economics of SPD processing are well established, it is reasonable to assume that high volume production will become attractive.

Since in the automotive and the aeronautics sector the weight reduction is a driver, lightweight structures of nano-Al alloys will probably be very important, mainly in structural parts.

Forging is used to create product shapes in the aerospace and automotive industry and there is evidence that in some cases the forging temperatures can be significantly reduced when forging SPD-processed aluminium alloys for aerospace applications.

**Magnesium** is also an attractive material for automotive use, primarily because of its lightweight (36% lighter per unit volume than aluminium and 78% lighter than iron (Fe)). When alloyed, Mg has the highest strength-to-weight ratio of all the structural metals.

Magnesium has a long tradition of use as a lightweight material in the field of commercial and speciality automotive construction. On the other side, it also has some critical drawbacks, like corrosion, reactivity, low melting point, flammability and price instability.

Further growth is forecast over the next 10 years. In Europe, the increase in using magnesium as a structural lightweight material is being led by the Volkswagen Group. However, magnesium is not currently used in civil aircrafts.

Nanostructured magnesium could overcome one of the most important barriers for magnesium nowadays: the corrosion.

Besides its application in other areas like the medical industry, titanium is also used in the aeronautics industry. Conventional **titanium alloys** are strong, stiff, and corrosion resistant and have low density (density of pure Ti is  $4,5 \text{ g/cm}^3$ ). Titanium alloys are stiffer than aluminium alloys and thus titanium components can be smaller in size than a comparable aluminium component. They are used in the aircrafts in applications where the volume is important, such as landing gears and attachment points and where the temperature is too high for aluminium, such as near the engine. In the automotive industry, titanium is not as important as in aeronautics, but still has been used since more than 10 years in springs, valve springs, valves, connecting rods and exhaust systems. On the other hand, the biggest restriction on titanium is its higher density than Al and its high cost (approximately 7 times that of aluminium or steel).

Titanium with nanograins is thermally stable at temperatures up to  $300^\circ\text{C}$  and shows good corrosion resistance properties. It is foreseen that nanograined titanium will be used for strong light weight body parts.

### 1.1.6 Current Situation within the EU

Even though Japan and USA have been leading the investigations about nanostructured metals, there are also a big number of active research groups carrying out promising developments in this area in Europe.

In Europe, the most relevant countries are Russia and Germany, but also Finland, Spain, Italy, Sweden and Norway have important research groups.

### 1.1.7 Key projects

- FP6 CA IPMMAN: Improvement of Industrial Production Integrating Macro-, Micro- and Nanotechnology.
- NAOMITEC: Nano and Micro- technology SMEs in EC projects (dedicated reports to individual sectors: Automotive, Environment, Aerospace, Health and ICT, as well as to individual countries)
- PRONACOM: Nanocomposites can reduce weight, enhance performance and improve production conditions for automotive and other industrial components. PRONACOM is exploring the relationship between processing conditions, structures and properties.
- FP6 BEARINGS: New generation of aeronautical bearings for extreme environmental constraints (2006-2009)
- FP6 NADIA: New automotive components designed for and manufactured by intelligent processing of light alloys. (2006-2010)
- German Funded Project BMBF: Melt spinning technology
- INTAS NANOLIGHT: High performance nano-structured Al alloys (2005-2007)

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## 1.2 Technologies to produce polymer nanocomposites

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### 1.2.1 Definition

In this report brief information on polymer nanocomposites and processing technologies of polymer nanocomposite parts that are used in automotive and aeronautics industry is provided.

Polymer nanocomposites included are nanofiller incorporated polymeric composites. Nanofillers covered in detail are nanoclays, carbon nanotubes, carbon nanofibers and graphene. In-situ polymerization, solution exfoliation and melt intercalation are the main processing methods included in this study.

## 1.2.2 Short description

Automotive and aeronautics industry uses high amounts of advanced plastics. For example an average car has about 160 kilograms of plastic parts. For this reason, any further change in the plastic materials that would result in weight reduction of vehicles' components is very important and accordingly one of the main drives behind the research in polymer nanocomposites. Since PNCs have low amounts of additives which are lighter than traditional additives like glass fibers, they decrease the weight of the vehicles in considerable amounts.

### Composite

Composite materials are a combination of two or more materials with *different properties* in the form of a **matrix** (metal/ceramic/polymer) material and a **reinforcing material** (glass/carbon/etc) or filler materials or additives to core materials. Composite materials exhibit different physical properties than their constituents even if the constituting materials retain their pristine structural properties. Reinforcing materials are surrounded by the matrix materials. The matrix holds the reinforcing material together while protecting it from external damage and stress. Reinforcements carry the load along the length of the fiber or to provide strength and stiffness in one direction.

In composites where the matrix is a polymeric material then matrix is named as resin. Resins are divided into two groups according to their behaviours as thermosets and thermoplastics.

**Thermosets** are usually liquids or low melting point solids in their pristine form. They are cured by the use of a catalyst, heat or a combination of the two when they are used to produce finished goods. Once cured, thermoset resins cannot be converted back to their original form. Accordingly, recyclability of pieces made out of thermosets is not possible. The most common thermosets used in the polymer industry are unsaturated **polyesters** (PE), **epoxies**, **vinyl esters** and **phenolics**. Applications of thermosets are very common due to their ease of processing.

*Epoxies* are usually used for fabricating high performance composites with superior mechanical properties, resistance to corrosive liquids and environments, superior electrical properties, good performance at elevated temperatures, good adhesion to substrate, or a combination of these benefits.

*Vinyl Esters* were developed to combine the advantages of epoxy resins with the better handling / quicker curing, which are typical for unsaturated polyester resins. Vinyl esters offer mechanical toughness and excellent corrosion resistance.

*Phenolics* are a class of resins commonly based on phenol (carbolic acid) and formaldehyde. Phenolic composites have many desirable performance qualities like high temperature resistance, creep resistance, excellent thermal insulation and sound damping properties, corrosion resistance.

A **thermoplastic** is a polymer that melts to a liquid when heated and freezes to a brittle, glassy state when cooled enough. Thermoplastic polymers can be remelted and remoulded; therefore, reshaped on the contrary to thermosets. Therefore, they can be recycled which makes their use more preferable. Among thermoplastics, **polypropylene** is commonly used in both plastic and composite auto parts. High performance engineering thermoplastics, used in more demanding applications include **polyphenylene sulfide (PPS)**, **polyether ketoneketone (PEEK)** and several formulations of polyamide, commonly called **Nylon**.

## Polymer nanocomposite

A 'polymer nanocomposite' (PNC) is a two-phase material where one of the phases has at least one dimension in the nanometre range. PNCs can have enhanced mechanical and electrical properties in terms of their strength, weight, flame retardancy and electrical conductivity due to the very high surface / volume ratio of its reinforcements. The interfacial properties and the interfacial area have a crucial role to obtain good final properties in composites. The interfacial area in PNCs is much higher compared to the traditional composites due to the 'nano'size of the fillers which provide them those abovementioned advanced properties.

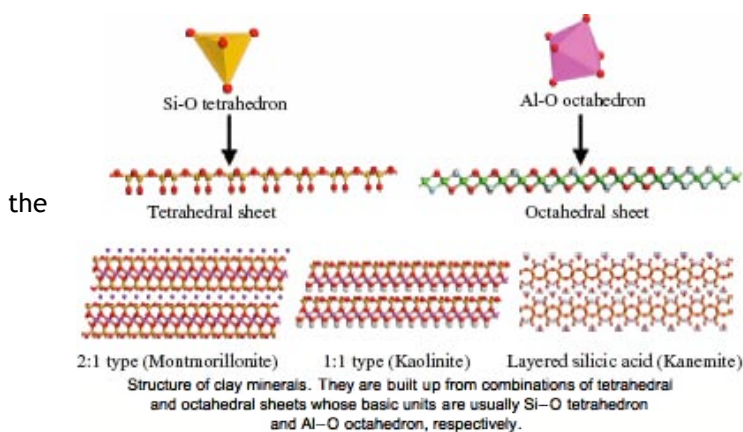
Today in automotive/aeronautics industry most commonly applied polymer nanocomposites are nanoclay incorporated polymers. They are preferred due to their enhanced physical properties eg. *light weight, corrosion resistance, low thermal conductivity, low coefficient of thermal expansion, flame retardancy, noise dampening, high impact strength, high strength to weight ratio, dimensional stability, long term durability, directional strength, and etc.* Another important reason for the interest in nanoclays is their cost and their availability in large scales.

In addition to main constituents of composites, resins and reinforcements, use of additional fillers has become very common both for composites and nanocomposites. Fillers not only improve the mechanical properties of the composite but also reduce the cost of it. Fillers can improve mechanical properties including fire and smoke performance by reducing organic content in composite laminates. Many other properties like water resistance, stiffness, dimensional stability and temperature resistance, etc. can be improved using fillers. One of the most common fillers used in nanocomposites is nanoclay. There have been also huge interest for using carbon nanofibers, carbon nanotubes, graphene and core shell as fillers for PNCs. Accordingly, many research groups from both industry and research institutes have been working on this field. However, so far there has been no industrial scale applications of nanofiller incorporated PNCs.

In addition to these filler materials, POSS (Polyhedral oligomeric silsequioxane) is researched as an alternative nanofiller to be used in polymer nanocomposites after its compatibilization.

Halloysite nanotubes (HNT) are also seen as promising filler materials that can be used in PNCs. HNTs,  $\text{Al}_2\text{O}_3\text{Si}_2\text{O}_4 \cdot 4(\text{H}_2\text{O})$ , are sort of clays which belong to Kaolin Group. They carry all the advantages of nanoclays. Additionally, they are more suitable for industrial processing due to their broad compatibility, low viscosity and better packaging features.

### Nanoclays



Most common clay mineral structures are montmorillonite, kaolinite and kanemite whose structures could be seen on left image.

Montmorillonite is a natural clay which has a crystal structure consisting of nanometer thick layers

(platelets) of aluminium octahedron sheet sandwiched in between two silicon tetrahedron sheets. Its formula is  $M_x(\text{Al}_{2-x}\text{Mg}_x)\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  where M could be metal cations like Na, Ca, Mg, Fe and Li.

Kaolinite  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  is another natural clay structure which consists of one aluminium octahedron sheet and one silicon tetrahedron sheet. Kanemite  $\text{Na}_2\text{Si}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$  is a layered silicic acid which is both naturally and synthetically available. The clays consist mainly of silicon tetrahedron sheets with different layer thickness.

### Carbon nanotubes

*Please check Chemistry-Materials sector for detailed information about carbon nanotubes' processing methods, properties and other application areas.*

Carbon nanotubes are promising materials for use in PNCs due to their enhanced mechanical and physical properties (thermal stability, barrier properties, electrical properties i.e. for the dissipation of electrical charges). Since chemical vapour deposition (CVD) allows higher product output compared to other methods, CVD grown CNTs are preferred for polymer nanocomposite applications. Also CVD produced CNTs can be functionalized which is necessary for their incorporation into resin.

### Carbon nanofibers

Carbon nanofibers are cylindrical nanostructures with graphene layers arranged as stacked cones, cups or plates. *Please see Chemistry-Materials sector draft report for details.*

### Resin transfer moulding (RTM)

This method is also known as liquid moulding. RTM is a simple process which combines compression, moulding and transfer-moulding processes. It is comprised of a pairing, two part closed mould. Usually reinforcements fibers or a preform are placed in the mould in advance. Later on resin is pumped into the mould under low to moderate pressure. Resin should have low viscosity so as not to have problems during its injection into the mould. RTM is a practical method which is suitable for automated, serial manufacturing processes with a high efficiency. ([http://en.wikipedia.org/wiki/Transfer\\_molding](http://en.wikipedia.org/wiki/Transfer_molding))

### Vacuum assisted resin transfer moulding (VARTM)

In VARTM resin is drawn into the mould under pressure through the special inlets designed on the mould. This is a very common method that is used in manufacturing composite automotive parts.

### Prepreg

Prepregs are fibrous reinforcements like sheets, fabrics or mats which are already pre-impregnated with a pre-catalysed resin. Prepregs can be stored in cold places to be used later on. Prepregs are usually activated by heating. Prepregs are used by aeronautics and automotive industry in addition to wind energy, sporting goods and construction industries.

### 1.2.3 State of R&D

Polymer nanocomposites (PNCs) are expected to find applications in automotive and aeronautics industries. Polymer nanocomposites comprise polymer matrixes (resins), mainly thermosets, thermoplastics and elastomers, that are reinforced with nano-sized particles which have high aspect ratios.

Common processing technologies to produce polymer nanocomposites are *incorporating nanoparticles into a polymer matrix* and also through *obtaining nanostructured polymers via modification of the polymer structure during the synthesis by nanopatterning*. Automotive / aeronautics industry mainly use the former technology via dispersing inorganic or organic nanoparticles into either a thermoplastic or thermoset polymer. In this way it is not necessary to develop new resin systems and the main changes on the composite manufacturing processes are related to processing parameters.

Vacuum assisted processing (VAP) technologies are very favourable by the industry due to its cost, processing speed and environmentally friendliness. However, so far this method is not compatible for processing polymer nanocomposites.

For their widespread industrial application, PNCs should be net-shape mouldable and may be extruded, allowing consolidation of parts and reduction in assembly step. For example, nanofillers need to be easily incorporated into resin, which would be followed by forming pellets to be translated into automotive parts. Each step has great challenges to be met to produce competitive parts for specific uses. Each application may require variations in the process to match the part specifications and the processing methods used to make the part.

Hand lay-out and injection moulding methods are very common for the production of composite automotive parts. There are different structural injection moulding methods. Structural reaction injection moulding (SRIM), reinforced reaction injection moulding (RRIM) and sheet moulding compound (SMC) are the most common ones. Resin transfer moulding (RTM) is another common method used to manufacture both internal and external structural parts like floors, doors, side frames and bumpers and also under hood parts.

Nanoparticles used in PNCs can be three-dimensional spherical and polyhedral nanoparticles (e.g. colloidal silica), two-dimensional nanofibers (e.g. nanotube, whisker) or one-dimensional disc-like nanoparticles (e.g. clay platelet).

*Dispersion of the nanofillers* in the polymeric matrix is critical to make most out of their potential. The nanofiller dispersion can be obtained only by a fine optimization the processing. In fact the nanofillers show a tendency to remain agglomerated due to different kinds of physicals-chemicals interaction. The separation of nanofillers is in many cases difficult due to the dimensions of the polymer chains. Apart from dispersion, compatibility with the resin is very critical.

In the rest of this section different nanofillers and relevant processing technologies are explained in detail.

#### Nanoclays:

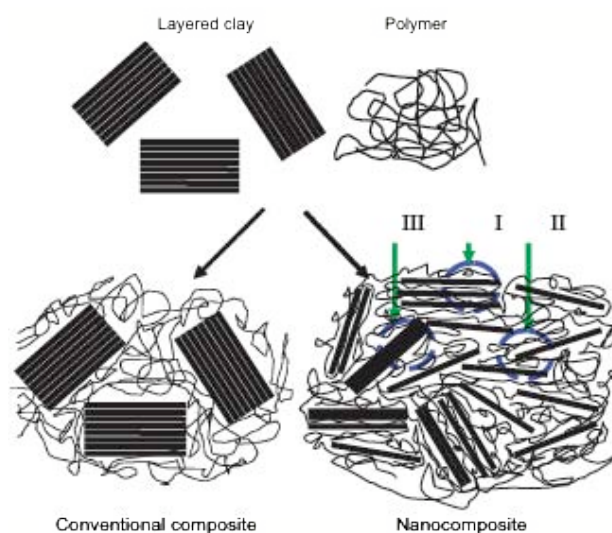
Nanoclays play an important role in composites due to their enhanced flame retardancy, barrier properties and improved balance of stiffness and toughness. Moreover, the fact that nanoclays are cheaper than other nanomaterials is a reason for their extended use in automotive and aeronautics industry. Nanoclays are produced in existing, full-scale production facilities which make them cheaper. Automotive and aeronautics industry uses

nanoclays as fillers in polyolefin nanocomposites, thermoplastic olefin (TPO) clay nanoolefins, etc.

One general approach to prepare polymer nanocomposites is to employ intercalation chemistry of layered inorganic solids in which polymer is inserted into the interlayer space. Clay minerals are ones that are preferred as fillers for polymer nanocomposites due to their rich intercalation chemistry, high strength and stiffness, high aspect ratio of individual platelets, abundance in nature and low cost. One of the challenges for their use is the incompatibility between hydrophilic clay and hydrophobic polymer which causes agglomeration of clay particles in the polymer matrix. However, this could be overcome either with surface modification of clay through organic treatment or via other mechanical solutions as explained below.

Common methods for processing clay based polymer nanocomposites are in-situ polymerization, solution exfoliation and melt intercalation.

When layered clays are filled into a polymer matrix, either conventional composite or nanocomposite can be formed depending on the nature of the components and processing conditions. Schemes of conventional composite and nanocomposite are shown in Figure 1. Conventional composite is obtained if the polymer cannot intercalate into the galleries of clay minerals. The properties of such composite are similar to that of polymer composites reinforced by microparticles. There are two extreme nanostructures resulting from the mixing of clay minerals and a polymer providing a favourable conditions. One is intercalated nanocomposite (I), in which monolayer of extended polymer chains is inserted into the gallery of clay minerals resulting in a well ordered multilayer morphology stacking alternately polymer layers and clay platelets and a repeating distance of a few nanometers. The other is exfoliated or delaminated nanocomposite (II), in which the clay platelets are completely and uniformly dispersed in a continuous polymer matrix. However, it should be noted that in most cases the cluster (so-called partially exfoliated) nanocomposite (III) is common in polymer nanocomposites.



**Figure 1:** Schemes of clay based polymer composites, including conventional composite and nanocomposite with (I) intercalated, (II) exfoliated and cluster (III) structure.

In **in-situ polymerization**, monomers are intercalated into layered clays and polymerized (cured) via heat, radiation, pre-intercalated initiators or catalysts.

In-situ polymerization is a conventional method for thermoset composites being suitable for low or non-soluble polymers e.g. nylon 6, epoxy, polyurethane, polystyrene, polyethylene oxide, unsaturated polyesters, polyethylene terephthalate. In this method, clay exfoliation depends on the extent of clay swelling and diffusion rate of monomers in the gallery. Oligomer may be formed upon incompletely polymerization which leads to lack of quality.

In the **solution exfoliation** (also known as solution dispersion), layered clays are exfoliated into single platelets using a solvent in which the polymer is soluble. The polymer is then mixed with the clay suspension and adsorbed onto the platelets. Later on, the solvent evaporates leaving the clay-polymer complex. This method is preferable for water-soluble polymers as such epoxy, polyimide, PE, PMMA. However, this method has its disadvantages like (i) use of large quantities of solvent, (ii) unavailability of compatible polymer-clay solvent system and (iii) possibility of solvent and polymer co-intercalation.

In the case of **melt processing** (also known as melt compounding, melt intercalation, melt moulding), layered clays are mixed with the polymer matrix in the molten state. It is a preferred method applicable for thermoplastics due to the fact that no solvent is required and it allows processing of PNCs with conventional plastic extrusion and moulding technology. Nylon 6, PS and PET are some of the polymers that could be processed with this method. Melt intercalation is a convenient method for processing PNCs in industrial applications due to its speed.

All the previously mentioned methods allow use of very low amounts of nanoclay loading for polymer nanocomposites making the overall density similar to pure polymer, therefore does not increase the weight of the part. Also addition of nanoclays improve the processing capability for film or fibers, which is unlikely in conventional polymer composites.

The cost of nanoclay is reasonable for its use in automotive applications, 5 - 7 €/kg and considerably less amounts of nanoclay could replace for example glass fibres in a composite part. In a composite part which is comprised of 35% of glass fibre only a replacement of 7% nanoclay can be used if in-situ polymerization is preferred. In the case of melt processing incorporation of 5% nanoclay would be sufficient. In Europe aluminium trihydroxides (ATH) is usually used to improve flame retardance of composite parts in vehicles. They require loadings of 60 to 65% in composite parts. This loading ratio can be reduced to 15-20% just by adding 3 to 5 percent of the nanoclay.

Apart from decreasing the overall weight of the part, addition of nanoclays has a considerable impact on the processing conditions of the PNCs. For example, introduction of nanoclay, Cloisite 93A into nylon6 caused the melting temperature of the Nylon composite to drop about 3°C. The melting temperature of a polymer is dependent on the size of its crystal lamellae or region. After organoclay nano-sized platelets were introduced into the polymer melt, the platelets were dispersed between the free polymer chains through intercalation and exfoliation effects. As the polymer cools, the platelets may form obstacles restricting the formation of crystalline blocks, forming amorphous regions, and thus reducing the crystal size of the nylon6 in the PNC. As the size of the crystal lamellae decreases, the melting temperature of the polymer decreases.

The most suitable method for industrial applications of polymer nanocomposites is the melt-processing method. The main problem encountered in melt-intercalation is the thorough and uniform dispersion of fillers in the resin matrix to which different solutions have been developed.

In both melt processing and in-situ polymerization there is transition from liquid like behaviour to solid-like behaviour. For this reason, it is crucial to understand this behaviour to be able to better control the process.

#### Industrial case study for use of nanoclays in PNCs:

As mentioned before polypropylene is one of the most widely used thermoplastics in automotive parts. Accordingly, the polypropylene-clay nanocomposite (PPCN) is an attractive material due to its potential effect in weight reduction. Synthesis of PPCN via an *in-situ polymerization* process was reported. However, this method was not found to be fast enough for industrial production. Researchers from Toyota reported the industrial compatibility of the *melt-compounding* process for preparing PPCN. The drawback of this process in its existing form is that pre-treatment of the clay mineral is necessary to achieve a nanometer-scale dispersion of the silicate layers. This pre-treatment process is known as organo-modification and it has to be carried out separately from the melt compounding in an extruder. For organo-modification first, a granular clay mineral is dispersed in water. The organic cation is then added to the dispersion, followed by filtration, drying and milling. This makes the process tedious and costly.

A new production method for PPCN using non-pretreated clay was developed at Toyota. In this method, the nature of the clay material when it was exfoliated in the water was taken into consideration. The basic concept of this method was that clay slurry was achieved in the twin-extruder by adding the clay mineral and the water separately. For this purpose, a new twin-screw extruder was designed (for details of the design please see Kato et al, polymer Eng. and Science). This method facilitated the dispersion of the clay particles even for more than 5wt% clay.

## Carbon nanotubes

As it is the case for nanoclays, also for CNTs, filler dispersion as well as interfacial interactions have been shown to be crucial for both incorporating CNTs into the resin and reaching enhanced mechanical properties in PNCs. One of the biggest challenges is to obtain a homogeneous dispersion of CNTs in a polymer matrix because van der Waals interactions between individual tubes often lead to significant aggregation or agglomeration, thus reducing the expected property improvements of the composite.

Different methods are used to optimize the CNT dispersion within the resin. Some of them are solution mixing, ultrasonification, coagulation, melt compounding, in-situ polymerization and chemical functionalization of the tube surface. The purpose of all of these methods are to separate the individual nanotubes so as to get a homogeneous dispersion throughout the matrix while chemical functionalization intends to bring some adhesion between the nanotubes and the polymer thus enabling effective stress transfer at the polymer interface. It needs to be taken into account that carbon nanotubes have to be functionalized for their incorporation into the resin independent of the method used for dispersion. All of these methods provide dispersion of CNTs within the resin. However, all of them lead to degradation of mechanical properties of CNTs which also effect the final properties and performance of the composite part.

CNT enhanced PNC parts can be manufactured via injection moulding, extrusion, melt compounding, resin transfer moulding, sheet moulding compound, etc. Processing of PNC parts using CNT enhanced preregs is promising.

In the injection moulding process the polymer melt is forced to flow through the gate, runner and mould cavity system. The geometry of the flow channel can significantly affect the end property of the injection moulded products, especially when the materials being processed show anisotropic properties when oriented differently. For example, polymer nanocomposites reinforced with CNTs may show different properties at different directions as the CNTs with high aspect ratios may orient differently at different direction which also effect the final electrical properties of CNT enhanced PNC. In the flow orientation direction, drastic improvement in conductivity can be achieved, while in the transverse directions, no obvious improvement is observed. **For this reason, controlled alignment of CNTs is important to get most out of PNCs when CNTs are used as fillers.**

PNC processing methods that are used for nanoclays can also be used for composites where CNTs are used as fillers. The most common problems encountered are entangling and uncontrolled alignment of CNTs in the resin. And also increased viscosity which decreases the processing speed in all melt processing methods RTM, RIM, Vacuum assisted methods.

Another way to process CNT incorporated polymer composites parts is to prepare prepregs with carbon nanotubes. Vehicle parts can be processed using CNT enhanced prepreg. CNT enhanced prepregs are handled like traditional prepregs. Therefore, use of CNT does not lead to a change in the processing method of parts. Zyvex Performance Materials is the pioneer in use of CNT enhanced prepregs. [Retrieved on 14<sup>th</sup> of May 2009 from <http://www.azonano.com/news.asp?newsID=11449>]

Cost and production of large amounts of good quality CNTs is an important problem for their widespread use in polymer nanocomposites. Besides, there are problems related to their dispersion and also handling and manipulation of them for their incorporation into resins.

One method, which has been heavily investigated to overcome the problems related to integration of CNTs into resins is to grow them directly on carbon fibres. Some experts believe that this would be the real breakthrough. While others point out to the problems occur as a result of this alternative method: The adherence of grown carbon nanotubes onto the substrate, in this case it is carbon fibre, is not really under control. Consequently, it cannot be assured that whole structure is firm. Moreover, after the growth of carbon nanotubes, carbon fibres are partially destroyed which lead to degradation of the mechanical properties.

It is important to overcome the challenges related to processing of CNT incorporated PNCs because of the advances CNTs bring to composites. A recent discovery by Prof. Catalin Picu at Rensselaer Polytechnic Institute shows that addition of CNTs into epoxies lead to tougher, stiffer, harder and more durable composites. Epoxy composites are preferred due to their lightweight. However, their low toughness and fatigue resistance has been a disadvantage until now. Incorporation of treated CNTs in epoxies lead to a 20 fold reduction in the crack growth rate under repetitive stress as compared to an epoxy composite frame made without nanotubes. [Rensselaer Polytechnic Institute (2009, April 3). Fitter Frames: Nanotubes Boost Structural Integrity Of Composites. ScienceDaily]

## Carbon nanofiber:

Vapour grown carbon nanofibers (CNFs), due to their high tensile strength, modulus, and relatively low cost, are drawing significant attention for their potential applications in nano-scale polymer reinforcement. They are synthesized from pyrolysis of hydrocarbons or carbon monoxide in the gaseous state, in the presence of a catalyst. Vapour grown CNFs distinguish themselves from other types of nanofibers, such as polyacrylonitrile or mesophase pitch-

based carbonfiber, in their method of production, physical properties, and structure. Thermoplastics such as polypropylene, polycarbonate, nylon, and thermosets such as epoxy, as well as thermoplastic elastomers such as butadiene-styrene diblock copolymer, have been reinforced with CNFs.

Carbon nanofibres contribute to improve the materials used in automotive industrial applications with the mechanical, electrostatical and tribological properties.

## Graphene:

Graphene is a two-dimensional form of carbon which has attracted huge interest since its entrance into the game since 2006 due to its extraordinary mechanical and electronic properties. Graphene has been researched primarily for its potential applications in electronics. But its foreseen applications in composites especially for automotive and aeronautics industry are also promising. It is the toughest material ever known for now. Since they are two dimensional and have very low aspect ratio (height to length ratio) entanglement problems faced with its other counterparts, CNTs, CNFs and nanoclays do not arise in their use in PNCs. Besides, since two dimensional platelets of graphene can slide over each other, it does not increase the viscosity of the resin in the molten state. Apart from their easier incorporation and processing advantages, graphene is much cheaper than CNTs which makes its industrial uptake / application more realistic. According to a US company XG Sciences which provides graphene it costs 10\$ / lb while SWNT costs 500\$/lb. Graphene is stated to provide more or less the same thermal and barrier properties to a PNC while bringing drastic improvements in electrical and mechanical properties compared to nanoclays. [xgsciences.com/applications] The challenge for use of graphene in PNCs was to be able to have right kind of graphene sheets which was realized by Dr. Brenson et al. at Northwestern University. XG Sciences a spin-off company from Michigan State University, established a pilot plant to produce already graphene incorporated polymers. In this method, instead of individual platelets stacks of platelets are used which is claimed to be stiffer than its individual counterparts. [http://www.technologyreview.com/computing/20821/page2/]

When added into resin, graphene changes the glass transition temperature of the resin and makes lower temperature processing possible. Graphene could be added to thermosets, thermoplastics and elastomers. Melt processing methods, RTM, injection moulding and extrusion can be used for processing graphene platelets incorporated PNCs. [http://www.mfrtech.com/articles/1948.html]

Although graphene is cheap and its incorporation into polymer resin seems to be easier in its lab-scale applications, the research in this field has not been mature enough to state that graphene based polymer nanocomposites would be the most promising ones for automotive and aeronautics industry. Since it is possible to use graphene as a thin coating on different surfaces it would find diverse applications at parts where electromagnetic interference shielding is critical.

## Core shell rubber:

Core shell structure is produced with a tangle of polymerized polyolefin rubber forming a ball with functionalized groups hanging out like bristles. When they are embedded in polymers like polypropylene, nylon, polycarbonate, epoxy resins, etc. these functional groups can combine with the polymer and improve the adhesion of the rubber with the plastic. As a result core shell rubber improved plastics become less brittle.

The researchers manufacture these tiny rubber balls in a one-pot procedure that causes the rubber components to cross-link into the shape of a tiny rubber ball with their functional groups intact. Addition of a surfactant causes the polymers to entangle into a ball with some of the functional groups sticking out from the surface. This way the process can be controlled better and the size of the particles from micron-sized to nanoparticles can be produced in a controlled manner.

## 1.2.4 Additional demand for research

Additional demand for R&D remains with respect to resistance properties and robustness of new composite materials as well as in their automated and large-scale production.

**Dispersion of nanoclays:** Polymer based clay nanocomposites are essential for automotive and aeronautics industry. Dispersion of clays is a standing challenge for making most profit out of them. Further commercial development of clay-based polymer nanocomposites require (i) extended research for the selection of surfactants and the modification of clays for the purposes of targeted polymer matrix, (ii) effective experimental techniques to quantitatively characterize and analyze the microstructure, mechanical, thermodynamic and rheological properties and finally (iii) the understanding of a simple processing-structure-property relationship to facilitate the design, manufacturing and applications of nanocomposites.

**Dispersion and manipulation of CNTs:** There are various techniques applied to further facilitate the dispersion of CNTs in the resin as explained before in **State of R&D** chapter of this report. However, all of them lead to degradation of mechanical properties of CNTs which also effect the final functionality of composite.

For CNTs' use for effective reinforcement of composite materials a large aspect ratio, transfer of interfacial stress, a good dispersion, and alignment is essential. While carbon nanotubes typically have very high aspect ratios, their absolute lengths are still low, which makes them difficult to manipulate and process. Moreover, the high cost and relatively short lengths of CNTs combined with an inability to effectively disperse and align them within a host matrix, currently preclude the development of composite structures that could supplement or replace conventional aerospace components.

Traditionally, blend or composite attempts at multifunctional materials require a trade-off between desired performance, mechanical properties, cost, and processability.

Even if a lot of research activity is going on for the use of carbon nanotubes as fillers in polymer nanocomposites so far there are no applications in the automotive and aeronautics industry due to high price of CNTs and the challenges need to be overcome for processing CNT enhanced composites.

**Self-sensing and self-healing mechanisms:** There is no need to express the importance of safety and therefore maintenance of parts for automotive and aeronautics industry. Hence reliability of parts, pre-detection of any failure / defect and quick repair of these has utmost importance for composite parts. Accordingly, presence of self-sensing and self-healing mechanisms in new developed PNCs is essential. Experts working in this field expressed that the need for extensive research in this field.

**Requirements for uptake of PNCs by the industry:** In addition to the science and technology related demands, common development needs, therefore the drawbacks are related to automation, or large-scale production and economical aspects. Easy and safe handling of materials is also important for the environmental aspects. In terms of economical aspects process yields, low cost materials, ease of implementation and market opportunities are important points to be considered. Also recycling of materials used is an issue to consider both for environmental and economical aspects. Modelling prior to the manufacturing at the design stage is critical in the automotive industry. So far there are no modelling tools which are compatible with nanomaterials. Therefore, new tools need to be

designed for the further integration of nanocomposites into automotive manufacturing right at the design phase.

Most of the companies from where experts were interviewed claimed that they were not keen on investing further in nanomaterials use, etc due to lack of information regarding the safety of nanomaterials and their handling.

## 1.2.5 Applications and perspectives

Automotive / aeronautics industry accounts for nearly 80% of polymer nanocomposite consumption together with packaging industry. Annual growth rate of global composite market is 5% from 2000 to 2005.

Main driver behind use of PNCs in the automotive / aeronautics industry is to decrease energy consumption via reducing the weight of the structural parts. In addition to the energy savings, automotive parts made out of nanocomposites provide stiffness, strength and reliability that could be more advanced than their metal counterparts. Additionally, the use of nanocomposites in vehicle parts and systems is expected to improve manufacturing speed, enhance environmental and thermal stability, and promote recycling.

Polymer nanocomposites are expected to penetrate a number of applications, driven by their improved barrier, strength and conductive properties, as well as reduced weight, possibility to increase production speed of parts and to replace higher-priced materials.

In the automotive industry **Toyota** is the pioneer for both research and use of nanocomposites for automotive applications. In 1990, researchers from Toyota reported that the incorporation of as little as four percent by weight of a layered and nanostructured silicate clay into a polyamide 6 polymer matrix produced a composite material with improved mechanical and barrier properties as well as improved thermal resistance. The first commercial product of polymer nanocomposites is the timing belt cover which exhibited good rigidity, excellent thermal stability and no wrap. Already back in early 90's Toyota Motor and Ube industries developed a polymeric nanocomposite containing only 1.6 vol% nanoclay as an advanced alternative to Nylon with its higher tensile strength (2.1 vs 1.1 GPa) and 50% reduced coefficient of linear thermal expansion ( $6.3 \times 10^{-5}$  to  $13 \times 10^{-5}$ ). Flexural Young modulus of epoxy increased from 45 GPa to 48 GPa when it is filled with nanofiller.

More detailed applications of polymer nanocomposites for automotive applications and the producer companies can be seen in Table 1.

Table 1 Commercial polymer nanocomposites for automotive parts

Product	Characteristics	Applications	Producer
Nylon nanocomposites	Improved modulus, strength, heat distort temperature, barrier properties	Timing-belt cover, engine cover, barrier fuel line	Bayer, Honeywell Polymer, RTP Company, Toyota Motors, Ube, Unitika
Polyolefin nanocomposites	Stiffer, stronger, less brittle, lighter, more easily recycled, improved flame retardancy	Step assist for GMC Safari and Chevrolet Astro vans, heavy-duty electrical enclosure	Basell, Blackhawk Automotive Plastics, General Motors, Gitto Global Corporation, Southern Clay Corporation
Forte™ nanocomposite	Improved temperature resistance and stiffness, very good impact properties	Automotive	Noble polymer

Since the first nanocomposite belt covers, new applications using nanocomposites have been developed - especially for thermoplastic-based nanocomposites - including automotive body panels, interior and under-bonnet parts, electrical parts and appliances, power tool housings, packaging and building components.

Back in 2002 General Motors successfully the first commercial auto exterior application of nanoclay and nanotalc composites on its Safari and Astro Van running boards and now using 300000 kg of nanocomposites annually for various automotive exterior part/panel applications. In addition to thermoplastic olefin/nanoclay composites, GM is exploring the use of CNTs to replace current thermoset structural composites.

**General Motors** and **Montell** have successfully produced thermoplastic olefin (TPO) 'nanocomposites' that promise a number of benefits for interior and exterior automotive applications, including reduced weight, improved dimensional stability, high stiffness and good low temperature impact performance.

**Dow Automotive** (NY, US) has developed a reactive extrusion process to produce nanocomposites based on nanoclay and cyclic buthylene terephthalate (CBT) supplied by Cyclics Corporation.

**Süd ChemieAG** and **Putsch Kunststoffe GmbH** have developed ELAN XP nanocomposite grades based on polypropylene/polystyrene blends for automotive interiors. PP and PS are not normally compatible, but Süd Chemie's Nanofil mineral filler produces compounds with high scratch resistance, a uniformly matt surface, and pleasant tactile properties.

Toughness of resin is really important for Sheet Molding Compound (SMC) in the automotive industry. Common method to increase toughness is incorporating additives into the resin which decrease physical properties. To overcome this problem while toughening its AROTRAN SMC resins **Ashland Specialty Chemical - Composite Polymers** took an unconventional route. Ashland used nanoclays instead of traditional additives to increase the toughness while maintaining all physical properties in Class A toughened resin system.

Recently a new polyketone based nanocomposite has been developed by **OPM** and **NaturalNano** especially to be used on the Boeing 787 aircraft. This new composite, OXPEKK-DRT can be either injection molded or extruded, enabling a broad range of applications. The pleximer additive of NaturalNano consists of halloysite clay nanotubes.

Automotive fuel systems also have started to benefit from nanocomposites. BASF (Germany) has commercialized a conductive polyoxymethylene (POM) with Hyperion nanotubes, specifically for automotive fuel systems.

Apart from CNTs compatible with POM, **Hyperion Catalysis International** has added five resin families of commercial quantity thermoplastic masterbatches containing fibril MWCNTs. The new masterbatches are; Polyetheretherketone (PEEK), Polyetherimide (PEI), Polyphenylene sulphide (PPS), Polystyrene (PS) and Nylon. These thermoplastic compounds containing Fibril CNTs are used for producing Class A body panel and trim parts in automotive industry. Since these CNT incorporating parts would have conductive properties, they would be electrostatically painted. Thus primer steps would be eliminated and it would be easier to paint parts with complex shapes. These nanotubes can be loaded at low rates which allow their use in large exterior panels.

In another application, **Degussa** manufactured CNT-reinforced nylon 6 is used for the tubing in the flexible portion of the fuel line in 70 percent of cars made in North America.

Hyperion also supplies various conductive thermoplastics to manufacturers such as **GE Plastics** for use as injection molding material for electrostatically painted automotive body parts, like mirror housings, door handles and fenders. **Renault Clio** and **Megane** are also using a nanotube filled polyamide/ polyphenylene ether (PA/PPE) blend for their sport fenders.

Nycoa is another company from the US which enhances its nylon-6 based composites with nanoclays. In-situ polymerization is used to make a single layer blow moulded fuel tank. Nanoclays dispersed in the nylon structure increase the toughness and improve the barrier properties making the structure up to 98% less permeable to vapors.

"Industry is becoming more efficient at creating nanoparticles," said Matthew Zaluzec, manager of the Materials Science & Nanotechnology Department for **Ford Research and Advanced Engineering**. He adds: "Our challenge is to take those nanoparticles, separate them and disperse them into existing materials in a way that makes our vehicles lighter, more durable, and more fuel efficient."

With a potential high strength-to-weight ratio and multifunctionality, carbon nanotube reinforced polymer composites may provide a unique option for the aviation industry. Their use can enhance a material's ability to resist vibration and fire. The reinforcement of polymers (thermoplastics, thermosets, elastomers) using fillers, whether inorganic or organic, is common in the production of modern plastics. Carbon nanofiber enhanced PEEK composite are used for underhood automotive and aerospace applications.

Ford Taurus is one of the pioneers incorporating CNFs filled polymer nanocomposites in its mirror housing.

Applied in the automotive industry, the polymer composite makes possible that the composite parts can be painted together with the rest of the auto body and treated in the same process that the metallic materials.

Unidym, Inc and Batelle have collaborated for multifunctional CNT reinforced nanocomposites development for aerospace and automotive applications. They have high performance CNT enhanced carbon fiber composites, CNT based thermoplastics that can be injection molded, and thermoset nanocomposites that can be fabricated with various RTM processes through the compression molding of nanostructured sheet molding compound formulations.

According to experts, for PNCs' industrial application the most convenient way would be to use resin-impregnated fiber (filler) forms which are called prepregs. Using prepregs would be convenient for all kinds of fillers used for PNCs.

## 1.2.6 Current situation within the EU

The US is leading in the fundamental research of polymer nanocomposites. In EU there have been many research groups who have been active in PNC research as well. Also Airbus and EADS have been carrying out many R&D projects in the field.

At the Fraunhofer ICT (Institute for Chemical Technology) there have been polymer composites related research activities focused at the automobile industry for over 20 years, providing research and development services and testing of materials. One the important core topics is lightweight automobile construction. New materials, such as fibre-reinforced thermoplastic-compound materials are achieving increasing market shares in the field of structural and semi-structural components. They are characterised by a high performance potential and are also suitable for recycling. A continual optimisation of plastic components means that optimised materials and innovative material systems are in continual demand. The Fraunhofer ICT carries out intensive research into fibre composite materials and polymer foam technology within the product division Polymer Engineering.

The Polymer and Composites Engineering (PaCE) Group at Imperial College London has focused their research efforts on growth of CNTs on carbon fibers.

European Center for Nanostructured Polymers and Nanocomposites is generated by a EU 6<sup>th</sup> Framework Programme Network of Excellence (NANOFUN-POLY) to be a European Centre to offer the association of various functions required by polymeric materials used in advance applications.

Saab AB (Sweden) has been carrying out close collaboration with MIT under a consortium called 'Nano-Engineered Composite Aerospace Structures Consortium' (NECST). This consortium has been carrying out research activities focused on using carbon nanotubes in composite materials for improving the performance of advanced aerospace materials and structures.

In Germany within Innovationsallianz Carbon Nanotubes (Inno.CNT) there have been collaborative research projects where carbon nanotubes are used in polymeric composites. This initiative brings together important partners both from industry and research institutes in Germany.

CarboCar aims to improve thermoplastic automotive parts using carbon nanotubes via bringing different functionalities. CarboSpace is another project running in this cluster where new carbon nanotube modified materials are developed for aerospace applications.

## 1.2.7 Key projects

### POCO (FP7; 2008-2012)

POCO is the acronym of the project called 'Carbon nanotube confinement strategies to develop polymer matrix composites'. For detailed information on project please visit <http://www.poco-project.org/home.asp>

### HARCANA (FP7; 2008-2012)

Please visit [www.harcana.eu](http://www.harcana.eu) to learn more about this project on high aspect ratio carbon based nanocomposites.

### NANOTOUGH (FP7; 2008 - 2011)

Nanostructured toughened hybrid nanocomposites for high performance applications (NANOTOUGH) is project which aims to remove technical barriers to producing high performance polymer nanocomposites on the industrial scale, fundamental insight into the dispersion of particles within the matrix is needed. The goal of this project is to gain this insight through a series of carefully designed studies, using the most advanced experimental techniques, theoretical modeling, carried out by very experienced and skilled partners working together in a targeted and interdisciplinary fashion. The basic objective is to obtain a deeper understanding of the interfacial structure of nanocomposites within a polyolefin matrix. This knowledge will enable realization of the great performance potential of these materials through development of novel multiphase and hybrid nanocomposites.

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## 1.3 Technologies to produce tribological nano-coatings

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### 1.3.1 Definition

In this sub-sector of the transport report tribological coatings and relevant processing technologies that are suitable for applying tribological coatings on parts which are used in automotive and aeronautics industry are assessed.

Tribological coatings are coatings that are applied to the surface of a component in order to control its friction and wear. They can be single phase, multi-phase or composite coatings consisting of materials such as carbides (e.g. WC, TiC, SiC), nitrides (e.g. TiN, CrN), metals (e.g. W, Ti, Mo) or ceramics (e.g. Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>). These coatings can be applied to all kinds of substrates (though most of the substrates to be protected are usually metallic and/or ceramic). These coatings can be processed mainly by two different methods, thermal spraying and vapour deposition processes.

Details of these tribological coatings and their processing methods especially for automotive and aeronautics industries can be found in the following chapters.

### 1.3.2 Short description

Tribology is the science and technology of interacting surfaces in relative motion. Tribological properties include friction, lubrication and wear. A tribological system is usually described by the external parameters such as contact load, apparent macroscopic contact area, friction partners, surface textures, lubricant used and the environmental parameters.

Tribological coatings are those coatings that are applied to the surface of a component in order to control its friction and wear. They can be single phase, multi-phase or composite coatings consisting of materials such as carbides, nitrides, metals or ceramics and are applied to all kinds of substrates (although most of the substrates to be protected are usually metallic and /or ceramic).

The final properties of the coating depend on the combination of the coating materials, the substrate they are applied to and the technology and processing parameters. Usual key properties (depending on the application) include good adhesion to substrate, density of the coating (non or low porosity), compressive residual stress, crack-free and smooth surface morphology, optimized heat transfer coefficient, chemical inertness (relative to the workpiece) or crystalline microstructure.

#### **Tribological coatings for automotive and aeronautics**

Tribological coatings play a key role in the performance of internal mechanical components of a vehicle, such as the engine and power train. Besides, they are also key elements of cutting tools, moulds and dies and machinery in general. By reducing wear and friction tribological coatings increase the lifetime of the working material at the same time that they reduce the dissipation of energy as heat, thus increasing the efficiency of the vehicle. When applied to machinery and tools, tribological coatings can reduce (or eliminate) the need for lubricants (dry machining), enable higher material removal rates, increase cutting speeds, reduce maintenance cost or reduce processing cycle times (e.g moulds).

### Materials for tribological coatings

There are a wide variety of materials that can be used in tribological coatings including transition metal carbides (e.g. WC or TiC), other carbides (e.g. SiC), cermets (cemented carbides), metal ceramic oxides (e.g.  $Al_2O_3$  or  $Cr_2O_3$ ), metals (e.g. W, Ti or Mo), nitrides (e.g. TiN or CrN) and diamond and Diamond Like Coatings (usually doped with metals and leading to Me-DLC). While many of the above materials can be processed using thermal spraying techniques, diamond requires more subtle techniques such as CVD or PVD. These material groups, their characteristics and applications are described next. Please notice that not all materials and/or applications described hereinafter are necessarily nano-enabled.

**Carbides** have high hardness and better adhesion than nitrides when deposited via thermal spraying, but lower thermal stability and a higher interaction tendency with other materials compared with Nitrides. Since melting temperature is high, pure carbide powders cannot be properly melted and deposited. Cemented carbides (cermets) are used instead.

**Cermets** are cemented carbides. Cermets' coating consists of an alloy plus the oxides formed during the deposition and usually have thicknesses in the range of 50 microns to 25 mm. Cermets can be processed using a large variety of processes such as flame spraying, atmospheric plasma spraying and high velocity oxygen fuel. To be processed using thermal spraying techniques, carbide particles are embedded into easily melted binder metals with high ductility (e.g. Ni, Co, Cr and mixtures & alloys).

**Metal ceramic oxides** are thermally sprayed ceramic coatings like  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{TiO}_2$ . They exhibit less mechanical strength and fracture toughness (as compared to cermets) and have the disadvantage of low values of the coefficients of thermal expansions and thermal conductivity. However, they exhibit an increase in chemical and thermal resistance as compared to cermets, making them more suitable for applications operating at high temperatures.

**Nitrides** are usually processed by physical vapour deposition. The most common ones are nitrides of Ti and Cr. They exhibit high hardness, good wear resistance, good thermal stability and good chemical inertness which is an essential requirement for cutting tools.

**Carbon based coatings** can be distinguished based on the bonds between carbon atoms ( $\text{sp}^3$ ,  $\text{sp}^2$  or a mix) and the presence of hydrogen, which together with the deposition process and its parameters strongly influence coatings' properties. In the case of diamond,  $\text{sp}^3$  bonds lead to a tetrahedral arrangement with a three dimensional linking whereas in the case of graphite  $\text{sp}^2$  bonds lead to trigonal arrangement and the formation of sheets. Carbon based coatings are referred as **Diamond-like carbon (DLC)**.

The most important classes of Diamond-like coatings (DLC) are hydrogenated amorphous carbon (a-C:H) and tetrahedral amorphous carbon films (ta-C). In general, DLC coatings possess many of the extreme properties of diamond but do not have long-range crystal structure and are typically used for applications where other materials do not provide the required performance.

Tough metal containing, diamond-like carbon coatings (Me-DLC) belong to the same group of coatings as the DLC coatings, there are some important differences between Me-DLC and DLC coatings. Me-DLC coatings have markedly lower compressive stress and can be deposited thicker than DLC coatings without adhesion problems.

Detailed information on hydrogenated amorphous carbon coatings, tetrahedral amorphous carbon films and metal containing diamond-like carbon coatings can be found in the state of R&D of this report in the following pages.

## Processing methods

There are two basic technological approaches for producing tribological coatings, thermal spraying and (vacuum) vapour deposition processes. Both approaches have found their applications in the transport market.

### Thermal Spraying Processes

The principle behind thermal spraying is to give the coating precursor enough thermal and kinetic energy to ensure that, when in contact with the substrate, the material can form a compact coating by particles agglomeration. All thermal spray technologies consist of projecting a stream of molten material (usually supplied to the torch in the form of powder feedstock) towards a substrate, but they differ significantly according to the various heating sources employed for material melting and acceleration the most common being hot plasmas or combustion flames.

The uniqueness of thermal spraying is the ability to deposit thick coatings on an extremely wide range of substrate materials. The density of the coating is dependent on the material, the state of the particle (solid/liquid ratio) on impact and the particle velocity.

In thermal spraying processes when the resulting coating has nanocrystalline structure then we can talk about nanotechnology. In most of the cases the coating thickness is usually between 50 to 300 microns. However, if the powder used in the precursor material is a nanopowder then this could also be regarded as nanotechnology.

Atmospheric Plasma Spraying (APS) and the High Velocity Oxygen fuel (HVOF) are the most common techniques for thermal spraying processes mainly due to the fact that they are non-vacuum processes and they are the simplest to use in different geometries (the equipment is automatically controlled). Other technologies include High Velocity Suspension Flame Spraying (HVSFS), Electric arc spraying or cold spraying. All these technologies are suitable for protection against wear (and also corrosion) but differences exist regarding the processability of material classes, the suitability for coating complex geometries and the possibility of coating internal parts. In general, HVOF tend to produce harder coatings that are applied where mechanical friction is the main concern.

### Atmospheric Plasma Spraying (APS)

APS can be used to coat various substrates with nanopowders. Due to its high temperatures, APS is suitable for ceramics and carbides without metallic components, though thermal degradation is more severe than with HVOF. Due to its lower speed, this process leads to more pores in the coating (as compared to the HVOF).

In APS the material to be deposited (feedstock) – typically as a powder, sometimes as a liquid, suspension or wire – is introduced into the plasma jet, emanating from a plasma torch. In the jet, where the temperature is on the order of 10.000K and up to 15.000K, the material is melted and propelled towards a substrate. There, the molten droplets flatten, rapidly solidify and form a deposit. Speed may reach between 200 and 500 m/s. It is a non-vacuum process (though there are vacuum variants such as the Vacuum/Low Pressure Plasma Spraying (VPS/LPPS)).

### High Velocity Oxygen Fuel (HVOF)

The high velocity oxygen fuel powder spray process uses a combination of a fuel-like kerosene, which burns with large quantities of oxygen to produce a flame which combines a relatively low melting temperature of about 3000°C with an extremely high speed. This speed may reach values of 2000 m/s as opposed to about 100 m/s (flame spraying) to 1000 m/s (plasma spraying) and leads to coating compaction. This can result in very dense, tightly adherent coatings with little or no oxidation during the application and low residual stresses, allowing significantly greater thicknesses to be applied compared to the plasma method, while providing lower porosity, lower oxide content, and higher coating adhesion.

### High Velocity Suspension Flame Spraying (HVSFS)

HVSFS is a new process that omits the granulation step and performs direct spraying of liquid nanoparticle dispersions in a high velocity oxygen fuel-spraying torch with robot-controlled kinematics. Avoiding the granulation step represents a cleaner and cheaper way of producing nanocoatings. Moreover direct spraying of suspensions shows much higher flexibility in combining and processing different materials.

## Vapour deposition process

Chemical vapour deposition (CVD) and physical vapour deposition (PVD) processes are the main methods. Most common CVD processes for tribological coatings are atmospheric plasma

CVD (APCVD) and plasma enhanced / assisted CVD (PECVD / PACVD). PVD processes include thermal evaporation, cathodic arc evaporation (CAE), large area filtered arc deposition (LAFAD), ion implantation, pulsed laser deposition (PLD) and magnetron sputtering.

### Chemical Vapour Deposition (CVD)

A typical CVD system consists of three components, a gas handling system where suitable precursors are vaporized and dosed, a reactor vessel where precursors react and an exhaust system where harmful reaction waste products are scrubbed and the harmless gases are vented. The choice of the process activation method depends on the substrate material used. For thermally stable substrates, thermal activation is preferred as it usually produces superior coating properties for all but polymer-type films.

One advantage of the CVD process is that it is not a line-of-sight process and therefore is capable of coating complex-shaped substrates. Besides, it can uniformly coat large area surfaces and have usually high deposition rates. In general, the deposition rate of atmospheric pressure CVD (APCVD) is faster than for PECVD (which is also faster than PVD processes). In principle, the CVD process can process any coating types (including DLC coatings). The main limitation of CVD processes is the need for a high processing temperature (normally between 800 to 1200°C) that hinders its application on many substrates. For instance, the steel used in cutting tools usually have a melting point around 500°C. Another disadvantage is the use of flammable and/or toxic precursors and the fact that it can generate tensile residual stresses (which limit the thickness of the coating).

However, Plasma Enhanced CVD can drop down the required process temperature for hard coatings to 450 to 550°C by using the energy of the charged particles in the plasma which is basically used to overcome the reaction activation energy barrier. Thus widening the range of substrate materials than can be coated. The drawback is that the adhesion to the substrate is low as compared to the traditional CVD.

### Physical Vapour Deposition (PVD)

A PVD coating is a hard, thin layer of metal or ceramic which is applied under vacuum on metal or plastic substrates. The coating material is vaporized or sputtered in a chamber to produce a flux of atoms or molecules that condenses on the substrate to be coated. PVD processes variants include evaporation, cathodic arc evaporation (CAE), large area filtered arc deposition (LAFAD), ion implantation, magnetron sputtering, etc. Many of these processes were already used in industrial environments, though new processes' set-ups required for benefiting from nanotechnology are usually not widely deployed.

Besides, ion implantation of the substrate surface (by bombarding it with ions) modifies the substrate and the coating protection against wear and corrosion can be improved dramatically.

Because evaporation processes lead to inferior adhesion and chemical purity of the coatings, CAE and magnetron sputtering are the methods usually used to produce nano-enabled tribological coatings. In the case of magnetron sputterings, magnetic fields are used to steer the plasma and resulting on higher deposition rates and good reproducibility.

The main advantages of the PVD process are the possibility to produce hard, wear resistant, and low friction coatings can be produced at relatively low temperatures (200 to 500°C) which enables its use over wide range of substrate selection. Moreover, it can produce coatings with compressive residual stress (which can inhibit crack propagation) and is capable of producing desired compositional coatings and with finer grains (smoother).

The main disadvantage of PVD is that it is a line of sight process, 2D or 3D rotation deposition is necessary for coating complex shape components. Besides, vacuum chambers can be as large as one to two meters and the larger they are the more expensive they get. This may limit the size of the parts to be coated.

### 1.3.3 State of R&D

In this section information on state of R&D of the tribological coatings and their processing methods will be provided.

#### Carbon based coatings

Hydrogenated amorphous carbon (a-C:H) coatings are deposited by plasma enhanced CVD and physical vapour deposition. Regarding a-C:H coatings, the amorphous network composed of carbon and hydrogen consists of strongly cross-linked carbon atoms with mainly sp<sup>2</sup> (graphitic-like) and sp<sup>3</sup> (diamond-like) bonds. For a-C:H coatings, under tribological conditions and due to its graphitic nature, wear products are transferred to the counter-face forming the so-called transfer layer that protects the softer material from wear.

Ta-C coatings (>80% carbon sp<sup>3</sup> hybridized) are mainly produced from pure carbon targets by filtered vacuum arc. Ta-C coatings are mainly used for systems where the two moving parts do not continuously slide within a restricted area. In such a system the formation of a transfer layer would not occur.

However, there are also some drawbacks: DLC suffers from brittleness, high stress, poor adhesion, and poor resistance to fatigue (due to high stresses or poor adhesion), and is often limited in its thickness due to stress build-up in thicker layers. Moreover, amorphous carbon-based coatings often possess poor thermo-mechanical stability, as the coatings are susceptible to hydrogen loss and rapid wear and graphitization at elevated temperatures limiting the maximum service temperature of DLC to 250-350°C.

#### Atmospheric Plasma Spraying (APS)

APS can be used to coat various substrates with nanopowders. Due to its high temperatures, APS is suitable for ceramics and carbides without metallic components, though thermal degradation is more severe than with HVOF. Due to its lower speed, this process leads to more pores in the coating (as compared to the HVOF).

The intensive heat and mass transfer during thermokinetic deposition of nanopowders contains the risk of grain coarsening as a consequence of droplet formation in liquid state. This is most evident in single-phase powders under the extreme thermal conditions of plasma spraying. For HVOF flame spraying there is a much higher potential to trigger the heat transfer and dwell time to obtain, at least partially, the nanostructure of the original nanopowder source.

For Zirconia, during the coating process the nanostructure can be preserved at elevated temperature, if the heating rate is high enough. However there is always some degree of grain growth during the plasma spray as a consequence of droplet formation in liquid state. In terms of mechanical properties, the resulting nanocoating exhibits higher hardness and toughness compared to traditional microcoatings.

#### High Velocity Oxygen Fuel (HVOF)

The nanopowders used in advanced surface technologies, such as APS and HVOF, must have been previously produced by spray drying in order to form spray nanoparticles with appropriate grain size that are suitable for standard powder feeding technology.

Tough nanopowders agglomerate and may have several microns, the coating ends up having nanocrystallites. A general problem is that during the melting process in the flame the

agglomerated particles lose their nanostructure (in case of a single phase agglomerate) so it is not yet clear if there is any benefit as compared to using standard powders.

HVOF coatings produced from powder or nanopowder cermet can be used to replace hard chromium coatings (e.g. used on steel cylinders). Nanopowders (e.g. 75Cr3-25NiCr) display a smaller weight loss value with respect to hard chromium and conventional HVOF coatings. This is due to the lower surface roughness and to the better distribution of carbides in the metal matrix and also to the lower porosity of the coating. CrC-NiCr and WC-CoCr coatings deposited over steel, aluminium and reinforced aluminium substrates are dense and homogeneous and seem to exhibit a good adherence and continuity on the different substrate.

The higher velocities and lower temperatures experienced by the nanopowders when using in HVOF (as compared to the APS) makes this process more suitable for depositing feedstock powders such as WC-CoCr and CrC-NiCr because it results in less decomposition of the carbides during spraying. Consequently, this results in higher quality, more wear-resistant coatings (with higher levels of reinforced material and less porosity).

HVOF-sprayed nanostructured  $\text{Al}_2\text{O}_3$  powders provide moderate improvement compared to HVOF-sprayed conventional  $\text{Al}_2\text{O}_3$ , since porosity is somewhat lower and toughness is slightly higher. However, the improvements are not particularly significant, since HVOF-sprayed conventional  $\text{Al}_2\text{O}_3$  already displays excellent micromechanical properties and interlamellar cohesion. Oxide based nanopowders are supplied by several companies, whereas cermet based powder materials containing hard phase particles like carbides or borides are relatively rare and expensive.

### **High Velocity Suspension Flame Spraying (HVSFS)**

The coatings obtained from HVSFS are dense and if desired very thin coatings of various oxide-based nanocomposites and cermets for tribological applications in automotive engineering can be produced.

When suspensions are used in thermal spraying, the liquid is atomised into small droplets not necessarily having the size of the primary nanoparticles. The goal is to optimise the atomisation in the combustion chamber to achieve as small as possible suspension droplets. This leads to finer splats in the coating, to a better interlamellar adhesion and, thus, to better mechanical properties of the coating (e.g. Young's modulus, hardness).

Experimental tests have been reported on HVSFS application onto steel, aluminium and titanium by spraying  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , YSZ and  $\text{TiO}_2$  that have nanoscale grain sizes.  $\text{Cr}_2\text{O}_3$  was coated onto a steel substrate with no significant changes in the crystallographic structure as compared to the initial powder material though the crystal size had increased. However, researchers reported significantly lower hardness as compared to coatings obtained through APS and HVOF. For YSZ the coating appeared totally dense and homogeneous. In all cases, coatings exhibit lower surface roughness value as compared to APS and HVOF.

### **Chemical Vapour Deposition**

Hard coatings, such as TiN, TiC, TiCN,  $\text{Al}_2\text{O}_3$  deposited by thermal chemical vapour deposition (CVD) on machining tools have been used since 1960 in order to increase their life time. However, due to the required process temperature, this technique was mainly limited to cemented carbides coated tools. Only through dense plasma the temperature could be

reduced but was difficult to scale-up with dense plasma. Around 1980 it was already reported the use of PACVD for producing a self-lubricating low friction coating such a-C:H.

In the mid 90s, it was reported that the columnar morphology of refractory, hard coatings deposited at a relatively low homologous temperature disappears upon the addition of silicon to the TiN and W<sub>2</sub>N coatings, when the nc-MenN/a-Si<sub>3</sub>N<sub>4</sub> nanocomposites with the maximum hardness are formed by plasma enhanced CVD. With the effect of the plasma nanocrystals become randomly oriented which further increases their hardness. More recently, the same researchers confirmed it also for nc-TiN/a-Si<sub>3</sub>N<sub>4</sub> nanocomposites deposited by PECVD (and also by reactive sputtering).

Despite the fact that carbon layers can be produced by several PVD approaches, hard carbon layers of TiC/a-C have been recently obtained by combining closed field unbalanced magnetron sputtering and PACVD. The carbon presence in the deposition process forms a matrix in which nanocrystalline TiC particles are embedded. The TiC/a-C layers are characterized by a high hardness, a low friction coefficient and a low abrasive wear.

According to the literature, several tribological studies have revealed a close correlation between the friction and wear coefficients of DLC films and the chemical composition of the source gases used in the CVD. Films grown in source gases with very high hydrogen led to superlow friction and wear coefficients, whereas those grown in hydrogen-poor plasmas exhibited relatively high friction and wear. These DLC films have been deposited on steel by using PECVD process at room temperature, though there are no references to them being nanostructured.

Already in the 90s, researchers reported on the detrimental role of impurities which, when incorporated into the coatings during the growth, make it impossible to achieve superhardness or even any hardness enhancement at all. According to available data from three different PECVD deposition units (but also for different sputtering units), the detrimental role of oxygen is almost independent of the deposition technique used. For PECVD, hardness of 50-60 GPa is achieved in the binary systems (e.g. nanocrystalline-TiN/a-Si<sub>3</sub>N<sub>4</sub>) only when the impurity content is less than about 0.1 at %.

## Physical Vapour Deposition

PVD tribological coatings are engineered for a specific set of properties including high wear resistance, high hardness (normally at high operating temperatures), high oxidation resistance, low friction, anti-sticking and high scratch resistance. Since the mid 80s the development of the PVD processes has enabled its use in a wide range of coating materials such as TiN, TiCN, TiAlN, MoS<sub>2</sub>, TiB<sub>2</sub>, WC-C, Al<sub>2</sub>O<sub>3</sub> and many others. These (without being nano) already provided coated surfaces with drastically enhanced performance. Actually, it has been reported that the market for PVD processes (including equipment, materials and services) was worth \$ 9 billion in 2007 and is expected to grow to \$ 16.7 billion in 2013 (with equipment being the largest market and semiconductors the largest end-user market). In the field of hard coatings (e.g. used in cutting tools) great progress has been achieved in the previous years. Single-layer coatings of transition metal nitrides and carbides (e.g. TiN) and multicomponent hard coatings (e.g. TiAlN) have been replaced in some cases with nanostructured (superlattice, nanocomposite, nanogradient) and other superhard coatings (e.g. diamond, c-BN, CN<sub>x</sub>). Various multilayer coatings have been also introduced in industrial production. They consist of a periodic structure of two different materials. The thicknesses of individual layers are in the range of a few nanometers up to few hundred nanometers.

Recently, the NCPVD Centre has developed a new variant of the PVD called HIPIMS (High Power Impulse Magnetron Sputtering (HIPIMS) for adhesion-enhancing substrate pre-treatment by improving the corrosion resistance due to a defect-free interface between CrN/NbN nanoscale multi-layers. This process has already been implemented on an industrial scale (Cathode area > 1.200 cm<sup>2</sup>) with the help of an industrial size power supply. The Centre claims it is the main breakthrough in PVD technologies for the last thirty years.

According to the literature, sputtering enables the ionisation of the sputtered material and these ions can be used to improve the quality of the films. If combined with low ion energies at the substrate it should allow the deposition of films with low stresses. Thus, it would be possible to produce coatings up to 20 to 30 microns and expand the range of potential applications of PVD films.

The up-to-date research activities on diamond-like carbon (DLC) films have been devoted to investigate various functional properties of DLC doped or alloyed by elements such as Si, N, F or metals (films labelled "a-C:X"). The challenge is to extend the properties of conventional DLC (a-C and a-C:H) through an accurate control of the film composition and nanostructure, to achieve design reproducible properties. Pulsed laser deposition (PLD) has proved to be an effective technique for low temperature deposition of a wide variety of thin film materials, including DLC, oxides and various nanostructured materials. These investigations show that the incorporation of a few atomic percent of doping elements strongly modifies the electrical, optical, mechanical and tribological properties, in comparison to pure a-C films. However, several laser systems need to be applied simultaneously to get high deposition rates and thickness uniformity over the substrate requires special equipment for target or substrate movement so hybrid approaches have been also reported.

Recently, several attempts have been made to improve the properties of DLC films. Nanocomposite DLC coatings based on crystalline TiC and amorphous carbon phases show potentials as high-strength material due to the grain boundary effect, which is dependent on the average grain size. Their mechanical properties depend on the ratio of TiC<sub>x</sub>/a-C:H. Nanocomposite coatings of TiC<sub>x</sub>/a-C:H have been deposited by different combined plasma assisted PVD/CVD techniques and sputtering systems showing that the phase composition of the coatings, as well as their surface quality, is sensitive to the deposition conditions and methods.

### 1.3.4 Additional Demand for Research

Though it is complicated because of the presence of too many variables, there is need for modelling tools for all processing methods to produce tribological coatings. Good modelling tools exist for micrometer range. These need to be refined and adapted for use in nanometer scale.

Automated processing technologies are missing in some applications especially where big pieces need to be coated or in place surface treatment is required.

#### **Atmospheric plasma spraying:**

In general, in the APS process there are several factors limiting the quality of the coatings (e.g. density, adhesion to the substrate) that have been widely reported. Because it is a non-vacuum process, turbulent mixing with external air soon reduces gas jet velocity and temperature leading to defective coatings. Moreover, the limited velocity of the sprayed particles has also a negative effect on coatings density. The Low Pressure Plasma Spraying (vacuum process) enhances coating cohesion, because plasma jet speed increases but disadvantages are higher production costs, higher substrate temperatures (up to  $\geq 500^{\circ}\text{C}$ ) and possible oxygen loss from oxide ceramics.

When looking at nano-specific issues, a reduction of particle size below 5 microns requires an extraordinary effort in powder feeding machines because fluidisation of the spray powder gets more and more challenging when particle size decreases.

It has also been reported that conventional powder feeder technologies are not suitable. Furthermore refilling or cleaning would be associated with a potential health hazard. There are now three approaches to solve this problem: **(1)** spraying of granulated powders, **(2)** spraying of molecular chemical precursors and **(3)** direct injection spraying of suspensions.

#### **High velocity oxygen fuel (HVOF):**

Developing high throughput processes for pure nanopowders is a difficult and expensive task especially if safe protection measures have to be applied. Powders of this kind have recently become available but at extremely high prices. Today it is assumed that at least most oxide nanoparticles (e.g. zirconia, alumina, titania, etc.) are available in sufficient amounts and at reasonable costs. In case of non-oxides this is still problematic as neither the quality nor the price and availability of the powders is enough to cover the demand from the ceramics industry. If milling or grinding of ultra-hard or abrasion-resistant materials is required, then processes become absolutely uneconomical.

Due to the nature of the process, to ensure proper coatings it is usually required to have moving supports for pieces. This leads to higher equipment costs. Process can be automated using spraying torches with robot-controlled kinetics (also for APS and other thermal spray processes). However, the process is very noisy (around 120 dB) and needs noise insulated facilities to fulfil EU regulations (max noise level 80 dB).

#### **Physical vapour deposition**

For applications in automotive and aeronautics parts multifunctional coatings that could detect defects and wear problems (as known as self-sensing) and then accordingly heals (self-healing) these defects and problems is more and more looked for.

Testing and characterization of tribological coatings is an important area where more research and development is needed. In most of the cases advanced and industrially applicable analysis / characterization methods are missing. For example, techniques to measure hardness at high temperatures, analysis methods to help better understanding of the wear behaviour of coatings during use in industrial applications. In the case of very thin, nanosized coatings measuring tools where very small loads can be applied for nanoindentation testing is required. There are commercially available tools for nanoindentation testing. However, due to their cost and long testing time, they are not sufficient for use in industrial applications.

Existing nanoindentation test tools are satisfying for measuring hardness in perpendicular direction. However, on cutting tools shear forces also play an important role on hardness which can not be tackled just using perpendicular forces.

For multifunctional coatings it is common to have multilayer coatings. Then these coatings exhibit very complicated behaviours. These coatings can only be tested and characterized via trial / error methods with existing technologies. Therefore, much iteration is needed before these coatings can be applied industrially.

It is very important to produce / synthesize new materials with new functionalities for different applications. However, it is not enough just to synthesize these materials. One should be able to test them under different applications.

### 1.3.5 Applications and Perspectives

Tribological coatings find diverse applications both for automotive / aeronautics parts and also for the tools that are used for forming these parts. Tribological coatings not only increase the lifetime of the parts but also have a drastic impact in energy efficiency. Nanotechnology and use of new materials for tribological coatings would bring further improvement in lifetime, reliability, damage tolerance and safety via self-sensing and self-healing.

Below more information is provided for applications of specific coatings and also their processing technologies.

#### Carbides

Existing tribological applications of transition metal carbides in the aircraft industry include, but may not be limited to, propulsion systems, hydraulic components or wing parts (e.g. WC or CrC) and provide enhanced wear and abrasion reduction or anti-fretting while can also contribute to corrosion protection.

#### Cermets

(Potential) applications of cermets include valves, pistons and piston rings but also cutting tools (their original use) and other processing machinery. For instance, it has been reported that thermally sprayed (by HVOF) CrC-NiCr and WC-CoCr can be coated over steel, aluminium alloys and aluminium matrix composites moulds used in plastic parts production thus contributing to reduce the cycle time. In general, cermet coatings are good candidates to substitute hard chroming galvanised processes, which are toxic.

If the coating needs to operate at high temperatures (and especially in humid environments), cermet coatings do not stand up well to chemical degradation and metal ceramic oxides should be used instead.

#### Metal ceramic oxides

Ceramic coatings  $Al_2O_3$ ,  $Cr_2O_3$  and  $TiO_2$  can be coated onto metallic substrates such as steel (HVOF, APS) or aluminium and titanium alloys (by using HVOF, APS or HVSFS). However, the adhesion to metallic substrate is compromised by the non-metallic bonding character of the oxides.

#### Nitrides

Hard coatings of TiN are applied in various powertrain components such as tappets, cams, and gears and also to several components of aircrafts' turbo-reactors (e.g. compressor). CrN coatings can be applied in engine's piston rings.

#### Carbon based coatings

DLC applications in the automotive industry include wrist pins, spur gears, plungers (of injector pumps), pistons, valve train, beamshafts, injector needles and more. Typical industrial applications where Me-DLC coatings are used today include diesel fuel injection systems, gearboxes and such as plunger, roller pin in fuel injection pump, gear and valve train, which serve at high-applied loads and high speeds.

## BALINIT®

Oerlikon Balzers has a series of coatings known with the trade name of BALINIT®. These series of coatings include nitrides, carbides and carbon based coatings which are processed via physical vapour deposition (arc-cathodic evaporation and sputtering) and plasma assisted chemical vapour deposition methods. For a detailed list where all varieties of BALINIT® coatings can be found please visit [http://www.oerlikon.com/ecomaXL/index.php?site=BALZERS\\_EN\\_balinit\\_coatings](http://www.oerlikon.com/ecomaXL/index.php?site=BALZERS_EN_balinit_coatings) . BALINIT coatings are applied on automotive and aerospace parts; also they find applications on the tools that are used for machining different parts.

In general, for ease of application and widespread use of advanced coatings on automotive and aerospace parts, there needs to be a reasonable market demand for building chambers that could allocate big parts. Oerlikon has machines which can coat very big parts i.e. 5-meters by 10-meters. In some cases geometry of the parts could create problems to have homogeneous coatings on parts.

## Thermal Spraying Processes

For all thermal spraying processes the bond between a sprayed coating and the substrate is primarily mechanical (not metallurgical or fused). Good adhesion between the substrate and the coating is essential for thermal shock resistance and in APS and HVOF the bond strength is a strong function of residual stress (a strong function of the coating thickness) and surface roughness prior to coating. Thus, substrate surface must be roughened and this is normally done by grit blasting and cleaned thoroughly prior to spraying. A novel approach consists of using simple cutting or grinding tools to produce an average surface roughness of 2-10 microns.

### Atmospheric Plasma Spraying

For  $Al_2O_3$  and  $Cr_2O_3$  produced using APS (but also HVOF), the tribological behaviour is dominated by tribofilm formation mechanisms, leading to smooth and compact surface films that protect underlying materials. These mechanisms mainly depend on the chemical composition. At high temperatures, stresses are increased and brittle fracture may occur, mainly by interlamellar cracking. HVOF are tougher and resist cracking better than APS.

Estimated global sales of thermally sprayed coatings (not necessarily nano) are in the US\$5 billion range per year, 50% of which are achieved by APS.

For instance, APS is in use at several carmakers for cylinder bores coating. It has been reported that in 2006 more than 60 % of the engines for passenger cars are produced in cast aluminium alloys; however, there is the need to improve Aluminium poor tribological coatings in order to avoid the need of having cast iron sleeves in the cylinder bores. An example is Ford's European Research Lab. in Aachen (Germany) that is developing a thermally sprayed nanocoating that could replace the heavier cast iron liners that provide the necessary wear resistance of cylinder bores in aluminium block engines. Already in 2000, production machines using rotating plasma spray guns which are capable of coating 800 engine blocks per day had been built.

APS is also used for Thermal Barrier Coatings (TBC) of nickel based super alloy components in aero and gas turbine engine components. However, material issues such as adherence to substrate, porosity or residual stress for thick coatings still offer a lot of room for improvement.

## High Velocity Oxygen Fuel

The HVOF technique is most used for hard, abrasion resistant coatings where adhesion is the main concern, but it can be used for any material available in powder form. The characteristics of the process enable processing almost all kinds of metals and alloys with melting temperatures below 2000°C and even permit the use of polymeric materials of low melting temperature (e.g. polyester). HVOF-spraying is recognised to be superior to plasma spraying for manufacturing metallic and cermet coatings.

For cermets, only the metallic phase is melted. The high velocity of the process means less time under high temperatures, which enables processing materials suffering from thermal degradation (e.g. WC). It is known that some HVOF torches are able to spray ceramics as well; the torch must provide a sufficiently hot flame and adequately long particle residence time in the jet in order to achieve full -or near-full melting of particles.

To continue using Aluminium alloys in engine blocks (due to its lightweight) and improving wear resistance in the engine bores (without using cast iron liners/sleeves), several techniques have been explored. These techniques are dedicated to form new composite and / or monolithic coatings on the bore substrate and include HVOF and APS. By obviating the need for cast iron liners, the engine dimension can be significantly reduced by reducing its weight around 1 kg.

Replacing steel moulds and tools (used in the production of plastic parts) by aluminium alloys coated with wear resistance coatings. This should enable a reduction in the injection time and increase the mould lifetime (as a result of the improvement in thermal conductivity - Aluminium has 4 times better conductivity than steel) and wear resistance of cermet coatings. In general, lightweight metals exhibit very poor tribological properties resulting in a severe surface wear. Other potential applications (may) include piston liners.

Another example is that of the steel body of aircraft wheels, that can also be protected from corrosion by applying HVOF technique a wear and corrosion resistant cemented WC-Co coating to the side portion of the wheels and a metallic-ceramic coating to the body portion of the wheel.

## Chemical vapour deposition process

The global market for chemical vapour deposition (CVD) is expected to increase from \$7.0 billion in 2007 to an estimated \$7.3 billion by the end of 2008 and reach \$11.8 billion by 2013. However, semiconductors are the largest market for CVD processes due to the high quality epitaxial growth of the films.

According to the literature, tribological nanocomposite films made of PECVD are already into the market and have had a very fast transition from the laboratory to the commercial markets. However, specific applications have not yet been found on the literature.

Besides tribological coatings, laser CVD processes can be applied to produce thermal barrier coatings (e.g. YSZ over Ni-base superalloys) used in gas turbines' blades or, out of the transport sector, on Titanium medical implants.

## Physical vapour deposition process

The best-known applications of PVD technology are decorative coatings and tribological (coatings on cutting and forming tools. With PVD coatings, one can increase tool productivity (longer tool life, higher cycle frequencies, less workpiece finishing), reduce manufacturing costs, improve the quality of products (due to smoother surfaces, better dimensional

stability, higher degrees of metal deformation and fewer manufacturing steps) and reduce lubricant consumption. All these advantages can be reached in metal cutting, sheet metal work, cold forming, pressure die-casting and plastic processing. For instance, nanoscale (superlattice) coatings of TiAlN/VN onto steel used in aluminium cutting tools have shown reduced adhesion to the aluminium to the tool substrate due to reduction (or non-existence) of built-on edge in the tool.

The NCPVD Centre claims to have developed coating families such as TiAlYCrN, CrAlYN/CrN, CrN/NbN, TiAlN/VN, TiAlCN/VCN and Me/C and that most of these have been successfully transferred to industrial coating companies.

Regarding the application of materials (not necessarily nano) in the automotive sector, Me-DLC (e.g. used to have low friction coating for Diesel injectors) counts for more than 40% of the PVD coatings while CrN (e.g. used for hard coatings for piston rings) counts for more than 20%. TiN coatings are used for hard coating of various components (tappets, cams, gears) and AlSnSi as a self-lubricating coating for journal bearings. Other parts routinely being coated are used in fuel pumps, valves and power train, needles, piston pins, connecting rods or journal bearings. Though it is not clear which of these applications is already benefiting from nanotechnology, superlattice coatings for injector components in diesel engines are being developed to address the challenges posed by higher operating pressures.

### 1.3.6 Current Situation within the EU

Many research groups and companies have been working in the area of tribological coatings for automotive and aerospace industries in the EU. Relevant projects could be found in the next section of this report.

### 1.3.7 Key projects

#### CORRAL (FP7 2008-2011)

Corrosion protection with perfect atomic layers (CORRAL) aims to develop high density defect-free ultra-thin sealing coatings with excellent barrier properties and improved corrosion resistance. The application areas include high precision mechanical parts, aerospace components and gas handling components.

#### MUST (FP7 2008 - 2012)

Multi-level protection of materials for vehicles by smart nanocontainers (MUST) is a project which aims to provide new technologies based on active-multilevel protective systems for future vehicle materials. A multi-level self-healing approach will combine - in a same system - several damage prevention and reparation mechanisms, which will be activated in response to environmental conditions. For details please visit <http://www.sintef.no/Projectweb/MUST/>

#### APPLICMA (FP7 2008-2011)

APPLICMA is the acronym for the FP7 project called Development of wear resistant coatings based on complex alloys for multifunctional applications. Please visit <http://www.applicma.eu/applicma/> to get detailed information about this project.

#### MATECO (FP6 2004-2007)

Within the scope of this project (New Coatings Based by PACVD for Corrosion protection) smart multifunctional coatings based on [Is-O-N] materials have been developed.

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## Annex: Expert Engagement

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This report has been partially based on interviews done with the following experts:

Dr. Gotzon AZKARATE, INASMET Spain

Prof. Dr. Thilo BEIN, EARPA European Automotive Research Partners Association

Dr. Matthias GEISTBECK, EADS Innovation Works Germany

Prof. Dr. Hakan GÜR, METU Turkey

Dr. Jürgen HIRSCH, Hydro Aluminium Germany

Dr. Gordon KELLY, GE Dowty Propellers UK

Prof. Dr. Jose KENNY, University of Perugia Italy

Dr. Hans LUINGE, EADS Innovation Works Germany

Dr. Meinherd MEYER, EADS Innovation Works Germany

Prof. Dr. J. J. MOORE, University of Colorado Mines US

Dr. Jürgen RAMM, Oerlikon Balzers Liechtenstein

Dr. Yoram RAMI, ALUBIN Israel

Prof. Dr. Hans ROVEN, SINTEF Norway

Mr. Alex SANCHEZ, GESTAMP Spain

Dr. Jan SCHULTE zur HEIDE, Alcan Composite Structures Switzerland

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