SAPHIR – EUROPEAN PROJECT
Safe, integrated and controlled production of high-tech multifunctional materials and their recycling

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Industrial needs in terms of multifunctional components are increasing. Several sectors are concerned, ranging from mature high volume markets like automotive applications, high added value parts like space & aeronautic components or even emerging activities like new technologies for energy. Domains with a planetary impact like environment, new products and functions for health and safety of people are also concerned. Nanotechnologies could play a key role in promoting innovation in design and realisation of multifunctional products for the future, either by improving usual products or by creating new functions and new products. Nevertheless, this huge evolution of the industry of materials can only happen if the main technological and economic challenges are solved with reference to the societal acceptance. It concerns the mastering, over the whole life cycle of the products, of the potential risks, by an integration of the elaboration channels, while taking recycling into account.

At the present time, the manufacture of nanostructured products is not integrated so that each step entails a loss of time and money as well as potential release of nanoparticles in the atmosphere. SAPHIR aims at implementing direct production of nanoparticles through the development of a global integrated concept (from the synthesis to the final products) with a responsible approach. Indeed, the main breakthrough is to connect individual processes so that the handling of the produced powders is avoided. By means of safe recovery and conditioning systems, such as suspensions or nanostructured granulates, nanoparticles can be manipulated without risk. The transformation of these suspensions or granulates through conventional and emerging processes needs to be adapted, as far as most of these processes have only been developed for the manufacture of micro-structured components.

Description:

There is a huge number of developments and applications involving nanoparticles. The nanotech industry is moving from research to production with over 500 consumer nano-products which are already available. Nanotechnology is not tomorrow's technology anymore; nanoproducts are focused on today's market opportunities. Some previous limitations have been solved thanks to improvements in particular in the technic of dispersion of nanoparticles and the decrease of the production costs.
Nanoparticles production quantity increases (world wide market: 700-1000 billion Euros) with the consequence that more and more workers are exposed while toxicity aspects are still unknown.
NIOSH (National Institute for Occupational Safety and Health) recommends a prudent approach for manufacturing and using nanoparticles in industry. Employers should take precautions to minimize workers' exposure until more information is available.
At present no regulation exists which refers specifically to the production and the application of nanomaterials or nanoparticles. A lot more knowledge has to be generated on how nanomaterial based processes and products may interfere with human health and the environment, before any regulation in this field can be established.
In the meantime we have to apply the principle of precaution.

The development of nanotechnologies appears to be a real innovative solution in order to improve existing technologies and create new products of the future. However, at the present time, the manufacture of nanostructured products is not integrated so that each step entails a loss of time and money as well as potential release of nanoparticles in the atmosphere. SAPHIR aims at implementing direct production of nanoparticles through the development of a global integrated concept (from the synthesis to the final products) with a responsible approach as shown in fig 1.

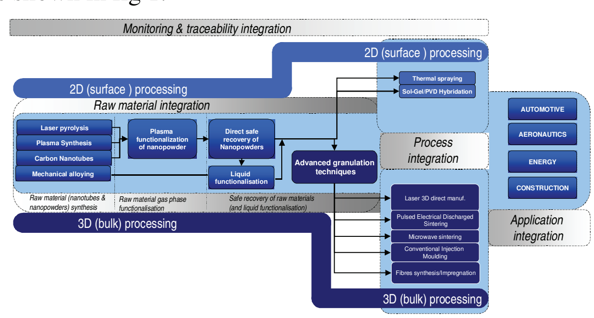

Fig 1: global integrated concept

Indeed, the main breakthrough is to connect individual processes so that the handling of the produced powders is avoided. Thanks to safe recovery and conditioning systems, suspensions or nanostructured granulates processing, nanoparticles can be manipulated without risk. The transformation of these suspensions or granulates through conventional and emerging processes needs to be adapted,

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as far as most of these processes have only been developed for the manufacture of micro-structured components.
The general objective of the SAPHIR project is the safe, integrated and controlled production of high-tech multifunctional nano-structured products including their recycling, and ensuring competitiveness.
It means that:

i) all along the production sequence; no nanoparticle release will be encountered. This includes synthesis, recovery (direct liquid recovery), conditioning (advanced granulation), processing and handling;
ii) ii) the whole production sequence will consist in linking in a safe way existing or emerging elementary processes (direct plasma spraying, laser 3D direct manufacturing, and powder consolidation techniques);
iii) iii) the production sequence will be controlled by innovative systems covering process efficiency, product reliability, global safety production, & traceability; recyclability issues will be addressed by proposing routes for the next future

First, the functionalization of nanoparticles will improve the properties of the final products as well as their "processability" for the next steps by a coating process (plasma treatment or fluidized bed technology are evaluated).
Then, the conditioning in suspension and the granulation will considerably reduce the risk of emission of nanoparticles in the air.
Granulation is performed by:

i) spray drying where the powder is dispersed in a liquid (water or organic solvent) and then sprayed into a chamber with hot air where the drops (granules) are shaped and dried.
ii) freeze granulation, a recently developed technology in which drops are freezed in a vessel containing liquid nitrogen or by
iii) mechanical alloying to combine alloying with CNT or nanopowders produced in a separate way.

These emerging combinations will allow the elaboration of new generation of metallic matrix composites (MMC), ductile ceramics and ceramic matrix composites (CMC), plastic matrix composites (PMC).

In order to guarantee the reliability of the chain, we have to focus on the development of on-line monitoring instrumentation (fig 2). Two parts will be developed in this field: process monitoring and traceability.
This double approach will allow to eliminate corrective actions, to do "the right things the first time" thus insuring a safe and competitive production

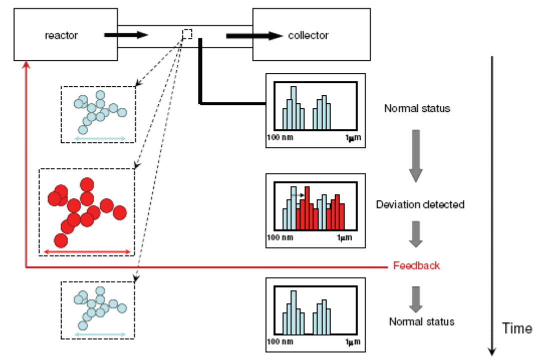

Fig 2: process monitoring

Work is done to address bulk and surface applications:

Bulk materials:
Existing processes as SPS, HIP, microwave, laser 3D processes were analyzed. SPS and HIP were successfully proven to produce nanostructured parts; the structure of these parts was studied and the properties evaluated.
Work was performed successfully towards of application of MWCNT in polymer matrices for automotive field and bipolar plates in fuel cells in the energetic field.
Main processes that are studied and developed during the project are extrusion and injection moulding; fibre synthesis/processing and direct growth of carbon nanotubes on carbon textures.
The aim of this work is to improve, in function of thermal, optical or mechanical properties, the final product.

Surface coating:
Work is performed in the field of surface engineering to improve properties for different applications.
Titanium oxide coatings were prepared by different technologies (sol-gel, thermal spray methods) using suspensions and their photocatalytic activity was studied. Hard metal coatings were prepared by thermal spraying and laser cladding, work focusses here on the in-situ formation of nanoparticles during the coating process. Performed studies contributed significantly to the understanding of the processes. As well titanium oxide coatings were prepared from powders and their photocatalytic behaviour was studied. Thermal spray coating was addressed by plasma spraying TiO_2 P25 as a suspension. Induction plasma technology was used and attention was given to the phases and to the atomisation of the suspension in the plasma torch.

SIGNIFICANT NEW ACCOMPLISHEMENTS

After the third year, the SAPHIR project now shows clearly a large number of very valuable results in 3 main domains which are:

The manufacturing of high performance raw material like ODS nanostructured powders, nanosized ZnO particles (see fig. 3) or Al/nano SiC nanostructured powders.

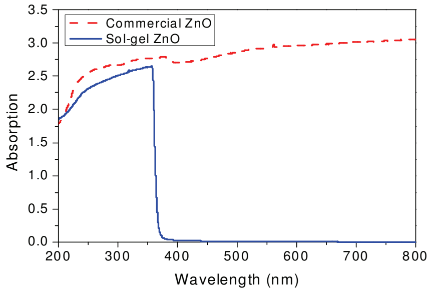

Fig 3: UV blocking capacity

The safe oriented processes which avoid any contacts with workers. Indeed, some developments have been achieved in the manufacturing process itself which is the granulation of the nanopowders (see fig. 4) in order to guarantee no release of nanoparticles at all in the air.

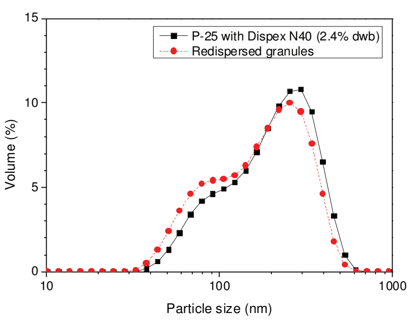

Fig 4: properties of re dispersed granules

The safe recovery system (see fig. 5) has been successfully tested in the phase vapour synthesis application and different forms of paste have been tested for the collection of particles.

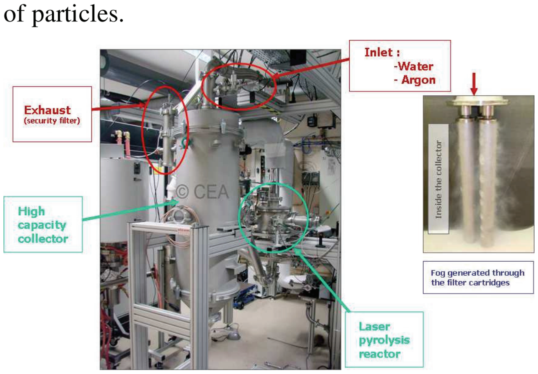

Fig 5: Recovery system

Significant progress has been also made in the field of the monitoring of processes with, in particular, windows monitoring (see fig. 6) coupling LIBS (Laser Induced Breakdown Spectroscopy) technology to the unit of nanopowder synthesis at CEA Saclay.

Fig 6: windows monitoring

Some very encouraging first results were also obtained on RFPM (Radio Frequency Plasma Monitoring) technology.
Applications in surface engineering for example in the nanostructured coatings field for building applications, promising results of photocatalysis were confirmed both by the sol-gel technology and the technology of suspension plasma spraying. Bulk applications were also tested and gave good results as on bipolar plates for PEMFC using carbon nanotubes (see fig. 7).

Fig 7: CNT-containing bipolar plates

Conclusion:

The final goal is to avoid any contact between operators and material.
With regard to potential health and environmental risks dry powders of nanoparticulate materials are to be assessed as most critical, because they can easily form aerosols during production and handling processes, which might lead to human exposure or environmental contamination.
Considering these issues the solution would consist in developing fully automated tools which allow confining the production line in each of it's steps: Raw material

synthesis, functionalisation, dry or wet recovery, granulation, consolidation and finally the processing in surface or bulk applications (fig 8).

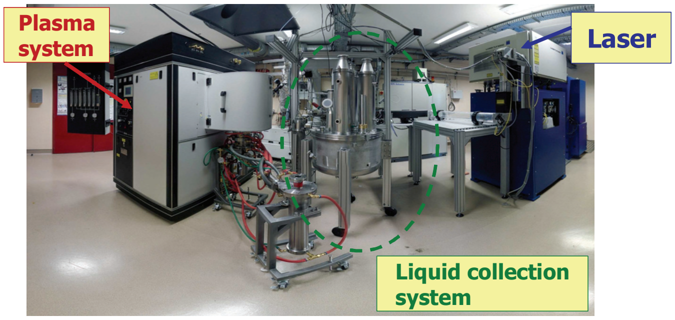

Fig 8: synthesis and recovery of nanoparticles in a safe way

These elements are the foundations of the factory of the future enabling the production of new nanomaterials in conditions of maximum security.