From Safe Nanomanufacturing to Nanosafe-by-Design processes

F Schuster$^1$ and F Lomello$^1$

$^1$CEA Cross-Cutting program on Advanced Materials Saclay, 91191 Gif-sur-Yvette, France

E-mail: frederic.schuster@cea.fr

Abstract. Industrial needs in terms of multifunctional components are increasing. Many sectors are concerned, from the integrated direct nanoparticles production to the emerging combinations which include the metal matrix composites (MMC), ductile ceramics and ceramic matrix composites, polymer matrix composites (PMC) for bulk application and advanced surface coatings in the fields of automotive, aerospace, energy production and building applications. Moreover, domains with a planetary impact such as environmental issues, as well as aspects for instance health (toxicity) and hazard assessment (ignition and explosion severity) were also taken into account. Nanotechnologies play an important role in promoting innovation in design and realization of multifunctional products for the future, either by improving usual products or creating new functions and/or new products. Nevertheless, this huge evolution in terms of materials could only be promoted by increasing the social acceptance and by acting on the different main technological and economic challenges and developing safe oriented processes. Nowadays, a huge number of developments of nanoparticles are potentially industrial up-scalable. However, some doubts exist about the handling’s safety of the current technologies. For these reasons, the main purpose was to develop a self-monitored automation in the production line coupling different techniques in order to simplify processes such as in-situ growth nanoparticles into a nanostructured matrix, over different substrates and/or the nanopowders synthesis, functionalization, dry or wet safe recovery system, granulation, consolidation in single-step, by monitoring at real time the processing parameters such as powder stoichiometry. With the aim of assuring the traceability of the product during the whole life, starting from the conception and including the R&D, the distribution and the use were also considered. The optimization in terms of processing, recovery and conditioning, permits to increase its versatility, thus leading to the increase of the added value to the production. This review put in evidence -by different examples- the progress achieved since the beginning of Nanosafe integrated initiative developed by CEA and its partners as well as promoting, firstly the safety at work place, and then extending to an integrated and controlled in-situ production by of Nanosafe-by-Design controlled processes.

1. Objectives of the R&D

Nowadays, the nanotechnologies applied to the materials science are a strategic issue for almost all the industrial sectors.

CEA took profit on its safety culture knowledge inherited from the nuclear field, in order to carry out multidisciplinary scientific studies regarding the risk assessment related to human health, the environment, final workers and costumers at all stages of the life cycle of nanotechnology. This life cycle involves the starting at the point of conception and including R&D, manufacturing and distribution.

The first step was to verify and quantify the current exposition risks (Nanosafe), followed by reassuring the safe nanomanufacturing (SAPHIR- Safe, Integrated & controlled production of high-tech multifunctional materials and their recycling) and then evolving up to a single step production and in-situ integration of nano-objects without any handling - Nanosafe-by-design processes.
This allowed the development of self-monitorated, integrated and controlled production of high-tech multifunctional nanostructured products. Furthermore, the principal aim is to produce objects at a unit cost equal or slightly lower than those of existing objects especially for mass production. The industrial demonstration platforms enabled to assess both the technical and economic effectiveness of the concept of the factory for nano’s. The combinatorial approach will also be a powerful tool to select the best candidates reducing time-spent on nanostructured products preparation and thus time-to-market. The different developed tools, techniques and technological demonstrators are resumed in the figure below.

In order to achieve the main aim, Safe Nanomanufacturing tools and Nanosafe-by-Design processes were developed. In the following lines, the examples regarding the safe processes are given.

![Figure 1. The Safe Nanomanufacturing and Nanosafe-by-Design processes.](image-url)

### 2. Introduction: some definitions regarding nanopowders

During the 80s, the nanopowders production was initiated on large scale and the attention was focused on nanopowders processing. In the following decade, the effort was emphasized to develop reproducible processing methods for manufacturing nanopowders into useful components taking profit on its new properties. During the second part of the 90s many significant advances in the production of nanometric objects were achieved as they present new interesting properties. However, the handling of nanopowders and the possible industrial production created new challenges. Generally, nanomaterials could be classified into different groups as shown in the figure below.
According to Gleiter [1], nanomaterials are classified into twelve groups depending on their shape (dimensionality) and chemical composition of the structural elements. On one hand, as a function of crystallites shape, three categories of nanocrystalline materials could be distinguished: layer-shaped crystallites, rod-shaped crystallites with layer thickness or rod diameters in the order of a few nanometers and nanocrystalline materials composed of the equiaxed nanometer-sized crystallites.

On the other hand, depending on the chemical composition of the crystallites, the three categories of nanocrystalline materials could be divided into four families.

2.1. Brief description and properties regarding the nanomaterials

Nanomaterials and in particular nanopowders are composed of individual particles having sizes between 1 to 100 nm according to cf. standard ISO/TS 27687. The particles in nanopowders are smaller than the wavelength of the visible light. Nanopowders are characterized of having an extremely high surface area to volume ratio [2]. Specific surface area of the particle is related to the average particle size, based on a geometrical consideration. In case of spherical particles, the formula [3] is given below.

$$SSA_{sphere} = \frac{SA_{sphere}}{m_{sphere}} = \frac{4\pi r^2}{\rho V_{sphere}} = \frac{3}{\rho \cdot r}$$  \hspace{1cm} (1)

where SSA is the specific surface area (generally measured in m$^2$/g), SSA is the surface area, m is the mass and V is the volume. Generally, the rougher the particle surface, the greater surface area regardless of the particle size. The equation underestimates the surface associated with the surface texture.

Regarding the new properties, size effects on nanomaterials, for example in case of Ni$_3$Al crystallites dispersed in a NiAl matrix lead having a different of flow stress as a function of the precipitates size (Fig. 3 a). Similarly, quantum size effects are observed allowing a blue shift in the absorption and luminescence spectra as it is corroborated for instance when CdS nanoparticles when dispersed in an aqueous solution.
When light quantum is absorbed, an electron is transferred from the valence band into the conduction band, leaving behind a positive hole. In small particles, the wave functions of the electron and the hole are confined to the particle volume.

Another characteristic of nanomaterials is their incoherent interfaces which introduce misfit between the crystallites. This is responsible for modifying locally the atomic microstructure by reducing the atomic density and the coordination [1]. The relative coordination number for interatomic spacing is less than one. This fact is thought to be responsible for changing the properties in nanostructured materials (Fig. 4).

The third aspect, which differs the nanosized powders from the classical, micronic ones is the morphological metastability related to fine grain size. This metastability in nanocrystalline materials could be divided into three categories: compositional (extended solution ranges), structural or topological (alternate crystal structure or amorphous phases) and morphological (finely divided structures) [4].

However, the influence in some fields are not clear, for example in the mechanical field it has not been proved yet the benefits in keeping the nanoregime [5].

2.2. Aspects related to nanopowders

The potentialities of nanostructured powders can be affected by some drawbacks, first of all by their inherent agglomeration, due to Van der Waals forces [6]. Therefore, in order to produce dense...
materials, with tailored microstructure, it is important to control all the elaboration steps, beginning with the dispersion.

Most nanocrystalline powders are not composed of single nanometer sized particles. Such particles known as crystallites are bonded together to form agglomerates or aggregates as it is illustrated in Fig. 5. The distinction between the agglomerate and the aggregate is usually based on the degree of bonding.

Soft agglomerates in which the particles are bonded by weak Van der Waals and hard agglomerates or aggregates in which particles show necks between adjacent particles [8].

![Diagram of primary particle, agglomerates, and pores](image)

**Figure 5.** Schematic illustration of nanocrystallites and agglomerates/aggregates [7].

Those agglomerates and/or aggregates, could present two different types of pores: inter-agglomerate pores (micronic) which coexist with smaller inter-crystallite pores (nanometric).

3. **Risk evaluation tools during the entire products’ life-cycle: development of secure industrial systems and workplaces**

3.1. **Quantification of individual protections: efficiency of personal protective equipment**

It is thought that the exposition of workers to nanoparticles will be increased in a near future. Indeed, the National Science Foundation in the USA has estimated an overall market for nanoproducts exceeding 1 trillion of dollars in 2015.

As a consequence, the potential human exposure to nanoparticles can occur by inhalation, dermal contact and ingestion during processing should be considered. Actually, for non developed fibrous media, the maximum penetrating particle size (MPPS) is about 200-300 nm [8].

In many cases, nanoparticles under 200 nm tends to re-agglomerate by the Van der Waals forces. Although, the electrostatic filters allow reducing the MPPS down to 50-60 nm. These filters are fabricated by fibers electrically charged by corona or triboelectric effect.

In addition, Balazy et al. reported a MPPS near 40 nm for N95 electrostatic filters exposed to a NaCl monodispersed aerosol [9].

Golanski et al. tested FPP3 electrostatic filters (according the EN 149) with graphite and TiO$_2$ aerosols [10,11]. The researchers employed a nanoparticle penetration device, as shown in the figure below.

The **through diffusion bench** was designed so as to reproduce the conditions of workers’ clothing. In the upper cell, the concentration of nanoparticles is maintained constant. A differential pressure of few megabars is kept between the two parts. The particle flow was accurately measured in order to estimate the efficiency of the protective clothing. Finally, the $^{85}$Kr was employed with the aim of neutralizing the aerosol into the test filter or the diffusion cell.
On one hand, the graphite particles were generated by spark plasma discharge between two graphite electrodes with an average distribution of around 35 nm. On the other hand, TiO$_2$ and Pt particles are produced by condensation from supersaturated vapour obtained with an average distribution of 40 and 10 nm, respectively.

Firstly, the authors tested the efficiency of the HEPA filters. The results regarding the penetration are presented in Fig. 7. The HEPA filter shows higher efficiency for graphite nanoaerosols, if compared with TiO$_2$ and Pt, for particles ranging from 10 to 20 nm. A difference of one order of magnitude is observed for a given particle diameter. TiO$_2$ nanoaerosols show the highest penetration through the filter: the maximum penetration for 19 nm particles is around 0.2%.

An increase of fibrous filter efficiencies inversely proportional particle size is predicted by the classical filtration model, considering the Brownian diffusion and the Van der Waals forces [12].

Figure 6. Schematic diagram of the nanoparticle penetration device [11].

Figure 7. Evolution of graphite, TiO$_2$ and Pt nanoparticle penetration for the same HEPA fibrous filter as a function of particle size (nm) for a face velocity of 5.3 cm/s [11].

Figure 8. Penetration as a function of the particle size of FPP3 electrostatic filters [11].
The efficiency of an FPP3 electrostatic filter was investigated for TiO$_2$ and graphite particle diameters ranging between 15 and 75 nm at the flow speed of $v = 5.3$ cm/s. The authors reported MPPS values around 35 nm in case of TiO$_2$, five times higher if compared with graphite as shown in Fig. 8. A shift of the MPPS toward smaller particles is consistent with the theory: the fiber charge has an effect on the particle deposition [8]. A difference in terms of efficiency between different materials was noted. The electrostatic forces in the graphite could enhance the nanoparticles’ capture in comparison with TiO$_2$ nanoparticles. Subsequently, the diffusion through the protective clothing was also measured. The results concerning the efficiencies of cotton, polyester and polyethylene are shown in Fig. 9.

![Figure 9](image_url)

**Figure 9.** Evolution of particle flow for TiO$_2$ and Pt nanoparticles as measured by through diffusion technique [11].

The results indicated that cotton and polyester present almost the same efficiency when tested with TiO$_2$ and Pt particles with mean geometric diameter of around 10 nm. Non-woven fabrics (air-tight materials) present the best efficiency against Pt and TiO$_2$ nanoparticles centered around 10 nm. These results are in good agreement with those published by Golanski et al., who reported similar results for graphite nanoparticles of 40-80 nm [10]. Finally, the authors analyzed three types of gloves i.e. nitrile, latex and neoprene with thicknesses 100, 150 and 700 µm.

![Figure 10](image_url)

**Figure 10.** The number of particles as a function of time for a nitrile exposed to TiO$_2$ [11].

No TiO$_2$ penetration through nitrile glove after exposing for 5 minutes is observed, as shown in Fig. 10. Furthermore, no TiO$_2$ and Pt penetration were found when the gloves are exposed at
10^5-10^6 particles/cm³. As a conclusion, nitrile, latex and neoprene gloves are efficient for TiO₂ and Pt around 10 nm.

3.2. Monitoring by means of the Laser-Induced Breakdown Spectroscopy (LIBS)

Amodeo et al. studied the particle physicochemical characteristics by means of a spectral imaging-aided Laser-Induced Breakdown Spectroscopy (LIBS) coupled with a Scanning Mobility Particle Sizer (SMPS) [13]. They employed the technique for detecting sodium chloride and metallic particles ranging from 40 nm to 1 µm.

![Experimental set-up of the second device](image)

**Figure 11.** Experimental set-up of the second device [13].

As shown in Fig. 11, the general experimental set-up combines the LIBS technique and the SMPS. Two nanoparticle generators were used during our experiments. An atomizer and a spark generator were utilized for particle generation. With both generators, a flow of clean air was obtained connecting the laboratory compressed air line to a filtered air supply unit.

Particle sizes, number and concentration were measured using a Differential Mobility Analyzer (DMA) combined with a particle counter (CPC). On one hand, the DMA connected with a particle counter allowed to measure the granulometry and total mass concentration. On the other hand, the particle number involving polydispersed flows was detected by another particle counter - designed for counting the particles whose sizes were inferior to 10 nm.

Time-resolved plasma imagery on laser-induced sparks, generated in air subsequent to single shots was recorded, in order to determine temporal evolution of plasma characteristics such as size, shape and lifetime. An example is given in the figure below.

Shortly after the end of the laser pulse, the cone-shaped plasma expands rapidly longitudinally in the radial direction between 0 and 20 ns. From 1500 ns to 4500 ns time delay, the plasma expansion slows down, stabilizes in shape and plasma dimensions are approximately 4.5 mm long and 2.5 mm wide. The plasma lifetime value was estimated to be more than 60 µs.

In all cases three regions within the laser induced plasma are distinguished. The size effects do not occur during LIBS measurements on particles with sizes ranging from 60 nm to 500 nm, due to a span incomplete vaporization.
Figure 12. Laser-induced plasma spatio-temporal evolution as a function of time delay using laser shots of 120 mJ – Above the images are indicated the delays, optical densities (OD) and Gate widths. [13].

Carranza and Hahn reported that an incomplete vaporization of micrometric-sized particles even for high laser irradiance. The authors confirmed the existence of an upper particle size of 2.1 µm beyond which, the vaporization was not completed thus leading a LIBS signal saturation for short time delays closer to vaporization times [14,15].

Figure 13. Evolution of LIBS intensity as a function of the mass concentration [13].

The LIBS intensity is linear as a function of the mass concentration as it is reported in Fig. 13. The authors concluded that no particle size effect is observed. As reported in literature, the dependency on LIBS signal and the size effects were detected by employing carbonaceous nanoparticles in the 30-100 nm at early time delays (5-10 µs) closer to vaporization times [15].

With the aim of characterizing the particle size in-situ, the LIBS technique was successfully coupled with the transmission electron microscopy (TEM) in a pilot production of carbon nanotubes (CNT) - by the catalytic chemical vapor deposition technique (CCVD) -, as reported by R’mili et al. – Fig. 14 [16].

Two TEM samplers were connected in order to measure the particle size and the morphology. The two TEM samplers were designed by Technical Research of Finland [17].
The first sampler is based on aspiration through holey TEM grids and collects particles without particle size selection. The second sampler works on diffusion assisted with thermophoretic repulsion as shown in the figure above. In the latter the temperature gradient of few degrees, between the TEM grid and the sampling pipe, helps to repel the micrometric particles. The authors were successfully able to separate by the thermophoretic –by repulsion– the carbon nanotubes as it is compared in Fig. 15. Moreover, LIBS measurements presented detection inconvenience, as in the previous case due to lower-upper particle size limits. In their study, the authors claimed that no efficient results were obtained over the 1-80 µm range, due to an incomplete vaporization.

![Figure 14. Experimental set up of TEM and LIBS systems [16].](image)

**Figure 14.** Experimental set up of TEM and LIBS systems [16].

3.3. **NanoBadge**

The NanoBadge was developed during *Nanosafe project* in order to measure the personal exposure as well as the indoor and outdoor air quality assessment. The two generations are presented in the Fig. 16.

![Figure 15. TEM micrographs by using (A) the aspiration and (B) the diffusion assisted with thermophoretic repulsion sampler [16].](image)

**Figure 15.** TEM micrographs by using (A) the aspiration and (B) the diffusion assisted with thermophoretic repulsion sampler [16].

3.3. **NanoBadge**
It is a compact solution for measuring, the inhalation exposure to engineered nanomaterials in the worker zone, in order to determine the particle mass concentration. The workplace exposure to airborne nanoparticles and their aggregates are quantified by means of elemental quantification and mass concentration in the respiratory fraction (alveolar).

The NanoBadge sampler collects particles with cut-off aerodynamic diameter < 4 µm with 50 % efficiency in order to fit the alveolar fraction (Fig. 17). The inlet size selection stage is a home-made impactor designed specifically for NanoBadge. The nanoparticles are then collected on the filter downstream.

In parallel, additional data such as user identity, timestamp, flow rate, events and errors are also recorded. Subsequently, an *ex-situ* analysis is made extracting the filter from the cassette. All the possible characterization techniques are contained in the figure below.
3.4. Health and hazard assessment: in vitro toxicity tests

During the Nanosafe project, the toxic effect of 24 different nanoparticles with similar equivalent spherical diameter and various elemental compositions were evaluated on 2 human pulmonary cell lines: A549 and THP-1 [18]. A secondary aim was to elaborate a generic experimental set-up that would allow the rapid screening of cytotoxic effect of nanoparticles. By comparing 2 cytotoxicity assays (MTT and Neutral Red) and by analyzing 2 time points (3 and 24 hours) for each cell type and nanoparticle. The data treatment allowed the TC50 (Toxic Concentration 50 i.e. nanoparticle concentration inducing 50% cell mortality) calculation.

The MTT assay on THP-1 cells exposed for 24 hours allowed assessing the cytotoxic effect of one type of nanoparticles. Results revealed that Copper- and Zinc-based nanoparticles were the most toxic. Titania, Alumina, Ceria and Zirconia-based nanoparticles show moderate toxicity, and no toxicity was observed for Tungsten Carbide. No correlation between cytotoxicity and the physico-chemical characteristics such as the equivalent spherical diameter and/or specific surface area was found.

3.4.1. Development of a physiologically based kinetic model for $^{99mTc}$-labelled carbon nanoparticles – In Silico computer model

Particulate air pollution is associated with respiratory and cardiovascular morbidity and mortality as it was reported by Péry et al. [19]. The researchers proposed a model which simulates the translocation of nanopowders into the bloodstream in humans. The authors based the model Technegas® distribution data on 5 healthy male volunteers from 24 to 47 years old reported by Nemmar et al. [20]. The male volunteers were exposed to 100 MBq in 3 to 5 acts of breathing - intake of nanoparticles occurs initially through breathing. Technegas® is an aerosol suspension of $^{99mTc}$-labelled carbon nanoparticles (5 to 10 nm) produced in high purity argon. The blood radioactivity data was measured at 1, 5, 10, 20, 30, 45 and 60 min in order to observe the concentration evolution. A gamma-camera enables to identify the radioactivity distribution at the liver, stomach, urine and blood. Based on these results, Péry et al. [19] developed a parameter estimation in the Bayesian context with the Markov chain Monte Carlo (MCMC) techniques. The authors developed a physiologically based pharmacokinetic (PBPK) model, adapted to imaging data analysis of Nemmar et al. which simplifies the mechanisms of absorption, distribution and elimination of technetium-labelled nanoparticles.

The authors distinguished and modeled three different fractions of nanoparticles according to the particle sizes: small $^{99mTc}$ bonded particles (i.e. able to translocate), large $^{99mTc}$ bonded particles (i.e. unable to translocate) and free $^{99mTc}$. On one hand, large nanoparticles are supposed to remain at constant concentration in the respiratory tract, lungs and the stomach. On the contrary, nanoparticles in the lung are transferred to blood by diffusion. Furthermore, the free $^{99mTc}$ is able to translocate from the lung into the gastrointestinal tract. These phenomena were taken into account in the model. Generally, nanoparticles diffuse into the various organs excepting the brain, since experimental measurements do not confirm the of $^{99mTc}$ presence. The elimination is supposed to occur by means of the renal elimination (urine). Nonetheless, during the time of exposure, the renal elimination of particle bound-$^{99mTc}$ was not observed, since only free $^{99mTc}$ was found in urine.

3.4.2. Rapid screening in vitro tests

The screening of nanoparticles toxic effects in humans was studied and a device was developed that it is able to detect them. These nanoparticles are thought to be able to enter into the human body by the lung-blood barrier. The translocation of nanoparticles by the in vitro model implies increased risks of toxicity, because the internal organs are also exposed to nanomaterials due to the blood stream.
The developed system consists in a microchip containing an internal biological system and a data detector. The nanoparticles screen is based on an in vitro translocation test using a model of pulmonary epithelium, i.e. a watertight layer of epithelial cells.

![Figure 19](image)

**Figure 19.** (a) Photo & (b) schematic view of the chip.

A chip contains an internal gap in which the epithelial cells (CaLu-3 cells) are cultured forming a tight layer that simulates the human lung epithelium. The microfluidic system feeds the cell culture media with the nanoparticles representing the interior of the lung. Nanoparticles cross into the lower compartment allowing the detection by measuring the electrical resistance on the on-chip electrodes (‘TransEpithelial Electrical Resistance’ or ‘TEER’). The silicon chip is fabricated using standard photolithography and silicon microfabrication techniques. The fluidic layers were casted in PDMS using a microfabricated master in silicon and SU8 photoresist.

With the aim of calibrating the device, the researchers employed four elemental standards: Cd, Te, Au, and Ti were used. These elements were chosen because of the possibility of analyzing nanoparticles such as Cd/Te, Au and TiO$_2$. For instance in Fig. 20, a test done with a mixture of TiO$_2$, Au (with sizes of 20nm) and CdTe nanoparticles of 590 nm is presented.

![Figure 20](image)

**Figure 20.** Calibration curves for Cd and Te detection.

As illustrated in Fig. 20, the system allows to quantify the nanoparticles detection in a culture medium. Similar results were obtained employing different powder mixtures.
3.5. Flammability and explosivity risks: nanopowders & multiwall carbon nanotubes

Many powders in suspension in air tend to ignite, burn and propagate as the powder nature influences the explosion propensity [21]. This phenomenon depends on the concentration, the degree of agglomeration and turbulence.

Several studies were devoted to the micro-sized powders [21]. However, the study of flammability hazard was extended to nano-sized powders in the EU Nanosafe 2 project. Bouillard et al. compared and tried to establish some correlation by using carbonaceous nanoparticles, aluminium particles as well as multiwall carbon nanotubes (MWNTs) [22,23].

The authors centred the attention on the dependencies between the particle size, the ignition temperature and minimal explosive concentration (MEC), since nanopowders are thought to present higher potential inflammation and explosion risks.

Generally, nanopowders are heavily agglomerated due to the Van der Waals forces as mentioned in the previous section. The fact of presenting voids in the bulk state increases the required storage volumes. According to the Geldart’s classification, nanopowders belong to the cohesive type since their difference in terms of the particle density $\rho_s$ and the fluid density $\rho_g$ [24]. For the sake of clarity in Fig. 21 the different groups are presented.

![Geldart’s classification](image)

**Figure 21.** Geldart’s classification [24].

As shown in Fig. 21, they present low bulk density that involves a low thermal conductivity which enables a higher self-heating and ignition risks.

Bouillard et al. claimed that nanopowders present two combustion regimes kinetically controlled (chemical) for small sized ones i.e. nanopowders and diffusion controlled for large sized one (micro). Both regimes for carbon (a) and aluminium (b) are presented in Fig. 22.

![Combustion time $\tau_B$ versus particle size](image)

**Figure 22.** Combustion time $\tau_B$ versus particle size: (a) carbon [22] and (b) aluminium [25] particles.
Carbonaceous nanoparticles present well separated the two combustion mechanisms as it is shown in Fig. 22 (a). Indeed, the phenomenon was corroborated in case of the aluminium in Fig. 22 (b), in good agreement with the research of Huang et al. [25].

In addition, Bouillard et al. claimed that aluminium oxidation at low temperatures (1000°C<) is essentially ruled by diffusion mechanisms. Furthermore, their work and the observation of Huang et al. [25] put in evidence how the particle size affects the ignition temperature. As a matter of fact, the decreasing of the particle size is accompanied by a reduction of the ignition temperature as it is shown in Fig. 23.

**Figure 23.** Ignition temperature versus particle diameter for (a) aluminium [25] and (b) carbonaceous particles [26,27].

Nonetheless, by comparing figures 23 (a & b) a minimum ignition temperature is observed in nanosized agglomerated carbonaceous such as black carbon and MWNTs Fig. 23 (b). In fact, the agglomeration and/or aggregration in nanoparticles oblige counting additional energy required to oxidize the powder. This fact explains the higher MIT observed in the nanosized range Fig. 23 (b).

The minimum explosible concentration (MEC) and the minimum ignition energy (MIE) as a function of the particle size are also important factors to be taken into account Fig. 24. On one hand, many studies were devoted to the minimal explosive concentrations. Bouillard et al. found that no significant differences regarding the minimum explosible concentration exists between the nanopowders’ types.

**Figure 24.** Minimal explosible concentration versus the particle size of (A) aluminium and (B) carbonaceous nanoparticles [22].

An almost constant MEC is noted at low particle size range being 30 gm⁻³ in the case of aluminium.
On the other hand, a second factor is the minimum ignition energy (MIE), which is determined by the energy required for a given cloud of particles to sustain ignition and in a medium at an initial temperature $T_u$, while the burning temperature is at the final temperature $T_{ad}$ (the flame adiabatic temperature).

As reviewed by the authors from the information found in literature, the two combustion regimes the kinetically and the diffusion controlled regimes are distinguished in Fig. 25. The former depends on $d_p^3$ and the latter $d_p^{3/2}$, respectively. In aluminium particles, a transition in a range of 400-2000 nm is noted. No experimental data was found by the authors for the carbonaceous nanoparticles. Bouillard et al. have shown that the particle diameter influences the explosion severity in terms of maximum pressure. Indeed, the maximum pressure rise is determined by the particles concentration and the specific surface area (SSA). In Fig. X the explosion pressure is presented as a function of both factors corresponding to different aluminium nanopowders.

As a conclusion, the combination of both parameters defines the maximum explosion pressure. However, the SSA is not the only factor to be considered. The chemical elements of the compound should be pondered. From their study, Bouillard et al. claimed that MWNTs and black carbon have higher SSA. MWNTs are heavily agglomerated if compared with black carbon as it is shown in Fig. 27, thus hindering the risk explosivity. Nevertheless, the contribution of particle size is lower if compared with the parameters as shown before.
The degree of agglomeration is the principal parameter to be controlled in order to increase the safety regarding nanopowders’ handling. As a conclusion, the carbon nanopowders tend to explode while metallic powders have the propensity to ignite in air (self-heating). Vignes et al. focused the attention on the kinetics of combustion of MWCNTs with the purpose of clarifying the global risk assessment regarding the production and storage inside the EU Nanosafe 2 project in reply to the needs of the European directive 1999/92/EC [37,38]. The different parameters were measured by means of thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results indicated that the single step reaction is accompanied by a cylindrical shrinking.

Furthermore, the authors determined the activation energies by the Kissinger method being 150 kJ mol$^{-1}$ [39]. The calculated value was higher if compared with SWCNTs [40]. The authors confirmed that the explosion severity of these materials is limited. In fact, the authors performed the tests as well as adiabatic calculation, as presented in Fig. 28. By comparing the black carbon and the MWCNT behaviour, it is possible to observe a lower maximum explosion pressure in the latter one. Although, good storage facilities should be required in order to avoid self-heating and dust explosions as well as ignition sources such as hot surfaces, electric sparks and smouldering combustion.

![Figure 27. SEM and TEM micrograph of MWCNTs at different magnifications [38].](image-url)

![Figure 28. Maximum explosion and adiabatic calculated pressure as a function of the CNTs concentration [38].](image-url)
3.6. Releaseability of nano fillers from different nanomaterials during the entire products' life-cycle

In the Nanosafe project, CEA developed a specific bench abrasion test using normalized Taber equipment – according the ASTM C1353-07 method- in order to quantify the nanomaterials before their market introduction in terms of their constitutive nanoparticle release-ability.

Firstly, Guiot et al. focused the attention on the calibration and the determination of the nanoparticles release of PET layer coated with a PVC layer and nanoclays as fillers [41]. As shown in the figure below, the scanning mobility particle size (SMPS) is coupled with a condensation particle counter (CPC) so as to permit the particle measurement in a range of 5-1000 nm. These tests revealed a release of 50 nm nanoparticles corresponding to the nanofillers size.

In a second publication, Golanski et al. reported the abrasion results regarding four types of paints containing nano-TiO$_2$, calcium carbonate and a TiO$_2$ pigment [42]. The paints were deposited on PVD substrates.

In this particular research, the abrasion tests were done adding a liquid solution on the coating in order to generate a dynamic friction. The Taber 5131 standard tool was employed. During the tests, the resulting nanoparticles were collected on filters for SEM analysis. At the same time, an Electrical Low Pressure Impactor (ELPI) was coupled with the aim of determining the number size distribution in the range of 7 nm-10 µm.

No nanoparticle release was measured during wet abrasion tests by the ELPI granulometer, only agglomerates in their matrix of around 100-300 nm were detected. This fact was confirmed by SEM observations.

In a third study, the nanoparticles release was measured in polycarbonate (PC), epoxy, and PA11 polymers containing carbon nanotubes (CNT) up to 4 % wt as fillers in polymers, paints, and fabrics are mechanically solicited [43].

Especially in the case of paints, hard abrasion tests were performed in non-optimized paint containing SiO$_2$ (12 nm) nanoparticles up to 35 %wt.

On one hand, an abrasive paper was rubbed on the sample to generate a dynamic friction on the surface of the sample. On the other hand, the Taber Abrader was employed for the abrasion tests in air. A bench test with several techniques disposed in a clean glove box was designed for these specific experiments – Fig. 29.

![Figure 29. Schematic view of the bench test [43].](image)

As in the previous examples, the debris finished in a sampler- a transmission electron microscopy (TEM) grid.

Firstly, an important release of nanopowders was detected in the nanometric range for polymers PA6, PC containing CNT. The release of CNT from epoxy was only observed when instantaneous shocks induce the CNT separation from the matrix thus overcoming the *Van der Waals* forces. A very low release of CNTs was only detected in samples showing the better dispersion of CNT. The lower CNT agglomerates population in the matrix reduced probability of aerosolizing and releasing.
Secondly, nanoparticles release when induced by scratching of two commercial fabrics made of PVC containing nanoparticles. An important release of nanoparticles was detected in the nanometric range indicating the removal efficiency of the metallic rake. The release of nanoparticles by abrasion in different materials was tested. A very low release of micro- and sub-micronic agglomerates of nano-SiO$_2$ was measured in some products. As a conclusion, the authors agreed that it is still necessary to pursue the studies regarding the nanoparticle release in order to assure nanosafety.

4. Safe Nanomanufacturing 2-D & 3-D processes: Development of Safe Nanomanufacturing generic tools

As it was illustrated in Fig. 1, the different Safe Nanomanufacturing generic tools were integrated into the existing technologies. The second aim was to keep the nanoparticles properties during the new different processes. Finally, after the optimization of the actual processes it is was possible to obtain new advanced multifunctional properties.

4.1. Direct liquid recovery and granulation by CEA

In order to avoid the dissemination of nanoparticles after synthesis, a liquid recovery system was developed. The liquid recovery allows a significant reduction of nanoparticle emissions during powder recovery and bagging operations, thus increasing the safety for the workers. CEA was the responsible for developing the suitable equipment with the aim of collecting the TiO$_2$ nanoparticles in a liquid medium after a laser pyrolysis synthesis [44]. These nanoparticles were produced by decomposing a mixture of titanium isopropoxide (TIP) and Argon. Indeed, it was demonstrated that is possible to recover and collect the nanoparticles in water medium- i.e. one-step process. The Liquid Recovery system is presented in the figure below.

![Liquid Recovery System](image-url)
4.2. *Granulation, liquid phase functionalization & dispersion by GEA Niro/SU*

The *SAPHIR* consortium centered the efforts on the development of versatile nanoparticles production routes allowing the integration into safe modules. The principal aim was to package the nanoparticles in its dry form or *redispersible nanoparticles retaining their properties*. Dispersing the particles as a concentrated suspension reduces the health hazards associated with the respiratory intake [45]. Different approaches were developed in order partially-agglomerate the nanoparticles. New technologies, such as spray drying and freeze granulation, allow to achieve the safe production of free flowing (low dusty granules) from suspensions of nanoparticles.

GEA Niro focused the attention on developing safe processing routes for the production of non-dusty micron-sized granules so as to obtain a safe handling of nanopowders. The GEA Niro Test Centre in Copenhagen has an important experience in producing nanoparticles’ granules employing different materials, i.e. SiC, SiO\(_2\), TiO\(_2\), Hydroxyapatite and carbon nanotubes.

With the aim of characterizing the performance, the Drying Kinetic Analyzer™ was employed, since this apparatus enables to determine drying behaviour. The GEA Niro conducted the investigation using a commercial Degussa Aerioxide TiO\(_2\) P25 which possess a specific surface area of 50 m\(^2\)/g dispersed in an aqueous solution of Dispex N40 and 2-Octananole as foam reducer (37 wt. % of solid content).

The atomization of the slurry was conducted by means of a GEA Niro two fluid nozzle coupled with a Malvern Spraytec (Malvern Instruments) in order to characterize the kinetic measurements and morphology. Both devices are shown in Fig. 31.

![Figure 31. – Schematic illustration of the GEA Niro set-up. [46]](image)

A Mobile Minor™ developed by the GEA Niro was used in four different configurations, as it is reported in the figure below.

![Figure 32. - Different configurations of the Mobile Minor: A: SD-MM configuration with product outlets from cyclone and a bag filter; B: SD-IF-MM configuration with bag filters placed inside the drying chamber and with product outlet under the chamber; C: SD configuration with fine return from the cyclone to the atomization zone and main powder outlet under the chamber & D: IFD-MM](image)
configuration with bag filters placed inside the drying chamber and with powder outlet from the integrated fluid bed [46].

After spray drying, an important volume reduction of $\approx 45\%$ was observed. By analyzing the spraying performance, it was observed that the droplet size is dependent on the liquid/atomization gas flow rate as it is shown in Fig. 33. The ratio between the atomization mass flow rate and the liquid mass flow rate (ALR) is frequently used to quantify the performance of two fluid nozzles.

![Figure 33. Suspension droplet sizes calculated from the measured granule sizes using the volumetric reduction at the A configuration determined by means of Drying Kinetic Analyzer\textsuperscript{TM} [46].](image)

In fact, different configurations allow to vary the granules’ morphology from $D_{50}$ equal 26-43 $\mu$m. From all the tested configurations, the B solution (SD-IF-MM) was the most suitable as it presents the lower shear and less system complexity.

In a second work, the same authors evaluated the effect of the different dispersants employing several techniques such as rheology, particle size and electrokinetic measurements [47]. Different commercial polymeric dispersing agents were tested and one commercial titania the P-25 is produced by hydrolysis of titanium tetrachloride in a $\text{H}_2/\text{O}_2$ flame at 985 $^\circ$C [48,49].

From these dispersing agents, only the Dispex N40 (polycarboxylate) was able to stabilize the primary aggregates of the titania nanoparticles at 2.4 wt. % lower content and over a relatively large pH-range. The carboxylate has a great affinity with the titania surface [50]. These aggregates exhibited lower sizes if compared with the initial powder agglomeration.

It is well known that higher surface charge may present a stronger and longer range electrostatic repulsion which is related to the low viscosity and long-term stability of the TiO$_2$ suspensions at low ionic strength. The Dispex N40 is believed to create steric interactions due to the observed slurry behaviour.

The nanotitania suspension was dispersed by Dispex N40 in an aqueous medium and then spray dried. In order to quantify the influence on granulometry distribution after redispersion, the spray dried was submitted to ultrasonication. Indeed, a similar granulometry (in volume) was measured in the spray dried nanopowder. After redispersion the spray dried powder exhibited an average particle size of 160 nm if compared with the raw powder 180 nm – Fig. 34.
After spray drying, the powder was submitted to FTIR measurements. The FTIR spectra revealed that the powder contained polymeric chains imputed to the dispersing agent. This fact is favorable, since the dispersing agent could act as a binder even at dry state [51,52].

The final granulated powder analyzed by SEM is shown in the figure above (Fig. 35).

4.3. Development of a complete monitoring strategy at workplace

The Safe monitored system was one of the most important objectives of the SAPHIR project. The main target was to control the size and the chemical composition during synthesis. Two different on-line characterization techniques, i.e. scanning mobility particle sizer (SMPS 3936, TSI) and the long path multiwavelength extinction sensor (LPME, Wizard Zahoranski), were proposed as promising Nanosafe safety tools for the existing laser pyrolysis production lines at CEA Saclay [53]. The first solution consisted in an APTL coupled with an aerosol dilution system with the aim of allowing the SMPS measurements. A fixed tunnel Venturi vacuum generator and a customized ejector type diluter were tested. A data acquisition system was especially developed for the LPME technique. The preliminary tests have been performed during the carbon nanoparticles production, in which the particle size distribution was analyzed by means of the LPME and the SMPS. However, these on-line measuring techniques were not tested in the laser pyrolysis production line. Finally, this system was replaced by a nanoparticle impactor, provided by NanoMoudi, MSP. A
A thermophoretic precipitator was installed in order to collect the SiC aggregates/agglomerated particles on TEM grids with the aim of performing the *ex-situ* primary particle size distribution analysis. The analysis of the raw data of SiC nanoparticles produced in CEA laser pyrolysis line has been performed by employing fractal development theory.

In order to achieve this objective, a complete monitoring strategy was built up and tested by the partners on the CEA Pyrolysis platform, as shown in the following Fig. 36.

![Figure 36. Integration of the different Nanosafe safety tools on the CEA Pyrolysis Platform.](image)

As shown in Fig. 36, many techniques such as LIBS, RFPM, Nanomoudi and MALLS were employed. The LIBS permits to monitor different vapour nanopowders synthesis (combustion, laser pyrolysis and plasma) and estimate the chemical composition at the *workplace*. For this purpose, temporarily-resolved emission spectroscopy has been successfully employed for controlling the Si/C\textsubscript{x} stoichiometry as reviewed by Amodeo *et al.* [54].

LIBS method assures the real time stoichiometry control during the production of different materials such as solid, liquid, gas and aerosols [54,55,56,57,58,59,60]. In fact, the method has been already tested in the steel production [61,62]. LIBS has been integrated into the laser pyrolysis existing equipment at the French Atomic Energy Commission. The technique is thought to be a promising candidate for workplace surveillance in industries producing nanosized-based materials.

Laser pyrolysis is known to be an interesting technique for producing various carbide nanopowders [63]. This latter already developed for large production rates (more than 2 kg/hour for SiC) has been extensively studied since its development for the synthesis of SiC [64]. The gaseous process, using the decomposition of silane mixed with a gaseous carbon precursor as acetylene or ethylene, allows to control the final grain size and degree of crystallization [65]. The synthesis was analyzed by the temporarily-resolved emission spectroscopy. In Fig. 37, the experimental set-up is shown.
Figure 37. Schematic illustration of the LIBS unit integrated into the laser pyrolysis reactor [54].

As it is shown, an analysis cell mounted at a by-pass line of the up-stream permits to record the data. A Q-switched Nd-YAG laser at 20 Hz is focused on that cell in which a LIBS signal (originating from the plasma created in the argon-nanoparticles mixture) is collected by an Echelle spectrometer equipped with a fast intensified CCD camera. The elemental composition is then obtained through optical emission spectroscopy analysis. The plasma at a local thermal equilibrium state (LTE) allows to calculate the stoichiometry $S$ from the intensity and the density ratios recorded during the LIBS spectroscopy measurement. Essentially, as claimed by the authors, stoichiometry determination consists of measuring the ratio of the total number of atoms.

In Fig. 38, a typical recorded spectrum during the vaporization of SiC nanoparticles is presented (time delay 4.2 µs, ICCD gate width 2 µs). It is composed of a carbon line at 247.85 nm and six Si lines.

Figure 38. A typical recorded spectrum during SiC synthesis [54].

In their study, the authors focused the attention on the 247 nm neutral carbon line and the Si 288.157 nm, as they have a better signal to the background ratio if compared with the other detected transitions. The typical spectroscopic characteristics are presented in the following Table I.
The electronic temperature was calculated by using Boltzmann plot method. It is built by using the following formula.

\[
\ln \left( \frac{I_{nm}}{g_n \lambda_{nm}} \right) = -\frac{E_n}{kT} + C
\]  

(2)

\( n \) and \( m \) being the upper and lower levels of the selected transition respectively, \( I_{nm} \) the integrated intensity of the transition, \( \lambda_{nm} \) its wavelength, \( g_n \) statistical weight of the upper state level, \( A_{nm} \) transition probability, \( E_n \) energy of the upper state level, \( T_e \) the electronic temperature, \( k \) Boltzmann constant, and \( C \) a constant. For this experience, it is assumed that the laser-induced plasmas are closer to the LTE condition [66]. Despite the good results, the technique presents some inconveniences related to the limitation for determining the electronic temperature.

Secondly, RFPM employs the low pressure and power plasma RF levitating the particles in plasma by the electrostatic force which counteracts the gravitational one, thus enabling the trapping of particles. The presence of nanoparticles within the plasma modifies the plasma properties allowing the size determination. The nanoparticles arranged in layers of around 10 µm depending on their density.

Thirdly, such as multi-angle laser light scattering (MALLS) was coupled to the laser pyrolysis. It allows to determine the size distribution by means of optical sensors that record the scattered light (in the range of 20-405 nm). A mathematical model determines the final particle size distribution.

Furthermore, a differential mobility spectrometer (DMS) and a mass aerodynamic diameter with a rotating micro-orifice impactor NanoMoudi (MSP) were also tested. On one hand, the DMS measures the particle size by quantifying the electrical mobility of the charge on the particle and its aerodynamic drag. On the other hand, the nano-range cascade impactor NanoMoudi (MSP) collects mass-based size fractioned particles due to their aerodynamic diameter-in a range equal to 10 µm down to 10 nm-.

Finally, the FT-IR in transmission and emission allowed the in-situ monitoring. A laser diode spectroscopy (LDS) was mounted in order to detect the critical impurities such as oxygen. The most promising results are summarized in the following lines:

- Chemical composition & stoichiometric in-situ monitoring by Laser Induced Breakdown Spectroscopy (LIBS) technology.
- Particle size on-line real time monitoring by means of various techniques for gas and liquid. The Radio Frequency Plasma Monitoring (RFPM) technology exhibited the best results if compared with the multi-angle sampling of the scattered intensity (MALLS).
- Real-time Workplace monitoring was also investigated by using the LIBS technology. This technique allows to analyze the nanoparticles - in an air medium - in order to quantify the risk assessment of particles inhalation.

These Nanosafe-by-Design in-situ safety tools allow to evaluate the inherent risks of nanopowders production.
4.4. Safe Nanomanufacturing processes

Safe processing techniques were integrated into the existing processes. As a result, the safe processed nanopowders presented in the section before were employed with the aim of producing new nanocomposites. The principal goal was to demonstrate the production feasibility and the improved properties of the nanostructured materials if compared with conventional materials. These Safe Nanomanufacturing processes were divided into the 3-D (bulk) high temperature and 2-D (surface) processes according their architectures.

4.4.1. 3-D (Bulk) Processes

4.4.1.1. Monolithic ceramic-based matrix nanocomposites

SiC nanopowders synthesized by laser pyrolysis were consolidated by Spark Plasma Sintering. Grain sliding is proposed to be responsible for the fast densification due to the strain rate of around $10^{-3}$ s$^{-1}$. Rapid grain growth is observed in a narrow temperature range, which can occur even in a porous body with a relative density below 80%. The early grain growth inhibits grain sliding which allows the creation of large intergranular pores, thus impeding further densification.

![Figure 39. SiC pellet produced by Spark Plasma Sintering.](image)

A large nano-SiC pellet of 100 mm. was produced keeping a nanometric and homogeneous microstructure, as shown in the SEM micrographs (Fig. 40). Scanning Electron Microscopy (SEM) revealed that the microstructure is mainly composed of grains of around 200-400 nm whereas a second fraction of grains lower than 50 nm is present. The porosity seems to be limited and their size is < 100 nm (closed porosity). However, X-Ray Diffraction confirmed the presence only of the $\beta$-SiC phase in good agreement with the absence of lengthened grains.

![Figure 40. SEM micrographs of the final pellet.](image)
Pure SiC nanoparticles produced by laser pyrolysis at pilot scale were employed. Prior sintering, the pellets were compacted by Cold Isostatic Pressing (CIP) in order to increase the green density up to 45% of theoretical density (TD).

The optimized conditions for the sintering were at temperature of 1890°C, an applied force of 100 MPa using a dwell time of 5 minutes. The final density reached was 98% of T.D. [67].

The same SiC nanopowders were employed in order to produce SiC nanocomposites reinforced with Cfs (carbon fibers). Electrophoretic infiltration (EPI) coupled with Spark Plasma Sintering were employed in order to evaluate an alternative processing route. This technology allows to produce C/SiC nanocomposites with lower associated costs if compared with other techniques such as the Chemical Vapour Infiltration (CVI).

The EPI parameters were evaluated with nanopowders in the system SiCB. The excellent SiCB nanopowders’ suspensions let an acceptable infiltration in the green state. Finally, SPS parameters were determined for each nature of the tested fibres. An example of the final microstructure is presented in Fig. 41.

![SEM micrograph of the Cf embedded in a nano-SiC matrix.](image)

**Figure 41.** SEM micrograph of the Cf embedded in a nano-SiC matrix.

The dynamic grain sliding was studied in this project by Herrmann et al. [68]. Two nitride nanopowders α- and β-Si₃N₄ nanopowders’ mixtures were prepared by mechanical alloying and by radio frequency inductively coupled nitrogen plasma. The nanopowders were subsequently sintered by Spark Plasma Sintering. The consolidation parameters were established in order to avoid the reprecipitation which induces the grain coarsening. The aim of the study was to achieve the dynamic grain sliding by a liquid forming additive (the β-Si₃N₄ nanoparticles are coated by a glassy phase) under mechanical pressure. The authors claimed that is possible to sinter at relatively low temperature of 1400°C for 5 min with an applied force of 75 MPa.

The final average grain size was around 52 ± 10 nm which lead to obtain interesting hardness Hv₁₀ values of around 18.7 GPa.

A third study developed during the project, concerned the processing of Ca-α-SiAlON ceramics prepared by mechanical alloying from Si₃N₄, AlN and CaH₂ precursors [69]. Samples were consolidated by hot pressing in a N₂ atmosphere. In their work, the researchers varied the CaH₂ content in order to obtain different microstructures and Ca-α- and Ca-β-SiAlON contents. By increasing the CaH₂ it is possible to obtain more quantity of elongated Ca-α-SiAlION grains.
Figure 42. A schematic illustration of the forced torsion pendulum [69].

For the mechanical characterization, mechanical spectroscopy measurements were carried out in an inverted forced torsion pendulum working in subresonant mode. In Fig. 42, the schematic illustration of the device is shown.

In this study, by applying an oscillation of 8 MPa at 1 Hz, the sample deformation (torsion angle) by a displacement of a laser beam spot on an optical photocell was measured. The excitation signal is measured by means of a frequency response analyzer. The response parameters phase lag (\(\tan(\phi)\) or mechanical loss) and the ratio between the excitation signal and the strain signal (proportional to the shear modulus \(G\)) is recorded.

As a result, the authors demonstrated the importance of having an equiaxed microstructure since it increases the internal friction thus impeding the displacement.

In contrast, at high temperatures (>1400 K) an \(\alpha\)-relaxation due to the formation of a glassy phase, usually found at grain boundaries in SiAlON. The maximum restoring force intensity (that counteracts the applied load) depends on the glassy phase as well as on the grain elasticity.

In this context, the specimen consisting of equiaxed elongated grains exhibited the lower peak height in comparison with a sample of lower glassy phase content.

4.4.1.2. MWCNTs reinforced polymeric, metal and ceramic nanocomposites

CNTs mechanical and electrical properties are remarkable in comparison with other known materials. These materials are envisaged to reinforce polymers with the aim of increasing their strength as reported by several authors [70]. Composite samples containing acrylonitrile-butadiene-styrene ABS matrix reinforced by Arkema MWCNTs were produced by blending and injection molding at the Centro Ricerche Plast-Optica. Three carbon contents i.e. 3, 7 and 15 wt. % were employed [71,72]. A micrograph corresponding to the ABS 15 wt. % MWCNTs is presented in Fig. 43.

In their study, mechanical spectroscopy was performed by means of the device presented in section monolithic ceramic-based matrix nanocomposites at temperatures varying from 100 to 430 K. Mari et al. identified two relaxations at 189 and 381 K (1 Hz) ascribed to the glass transition of the polybutadiene and the styrene–acrylonitrile (SAN) phases, which are believed to provoke a first \(\beta\)-transition involving the movement of side groups and a second \(\alpha\)-transition related to the chain sliding. The interaction of the MWCNTs with the SAN phase enables the softening of the polymer at higher temperatures. Furthermore, no elastic modulus reinforcing effect was measured - probably due to the method. Indeed, during the tests only shear modulus is measured. A processing inconvenience regarding the reduction of the adhesion between the two constituents could explain this phenomenon.
MWCNTs reinforced magnesium and magnesium-23.5 wt.% nickel nanocomposites were processed by mechanical alloying [73]. The consolidation was achieved by means of hot pressing at 600°C for the magnesium and 430°C under a pressure 50 MPa for 30 min. Prior to mechanical spectroscopy, samples were annealed in a 0.4 MPa hydrogen atmosphere at 620 K thinking about the final application of the hydrogen storage capability. These samples were compared with the pure magnesium.

As in the previous case, Schaller et al. indexed two relaxation peaks at ≈190 and ≈330 K (≈6 kHz) in the magnesium-23.5 wt.% nickel. The authors reported that H atoms destroy the crystalline order in the Mg₂Ni phase of the hexagonal structures, precipitating as Mg₂NiH₄ hydrides. Hydrogen occupies the tetrahedral interstitial sites within the hexagonal structure. This fact is increased in 25 orders in magnesium-23.5 wt.% sample containing magnesium 23.5 wt.%. Nevertheless, no hydrogenation was detected in a sample which contained pure magnesium.

Finally, the study was extended to production of MWCNTs reinforced nanoceramics. For this purpose, nanosized ZrO₂ (Y-stabilized) with 0, 0.5, 1.5, 3 and 5 wt% CNT contents were consolidated by SPS. The characterization was conducted by means of the mechanical spectroscopy.

The measurements were performed at 10⁻³ Pa either as a function of temperature up to 1600 K at a fixed frequency or as a function of frequency (10⁻⁴ to 10 Hz) at a fixed temperature. Schaller et al. processed polycrystalline 3Y-TZP mixed either with CNTs or SiCₖ via attrition milling with the aim of producing ceramic nanocomposites [74]. Samples compacted by cold uniaxial pressing at 100 MPa were naturally sintered in argon atmosphere.

Figure 43. SEM micrograph of the ABS 15 wt.% MWCNTs microstructure [71].

Figure 44. Mechanical-loss (tan φ) spectra for two zirconia samples: pure (curve 1) and reinforced with carbon nanotubes (curve 2) [74].
In Fig. 44, shows the theoretical mechanical-loss spectra of the pure zirconia and the composite. Indeed, an exponential increase of the mechanical loss (tan $\phi$) is observed when the temperature increases in both samples. It was corroborated that the MWCNTs improve the restoring forces, since the pinning effect on the GB sliding was measured. This allows to obtain a better final creep resistance (in factor 2) in the sample containing 1.5 wt. % MWCNTs, as less angular displacements were measured.

The higher creep resistance was attributed to the presence of MWCNTs pinning grain boundaries at high temperatures.

Moreover, Schaller et al. produced 3Y-TZP/MWCNTs composites varying as in the previous case the MWCNTs content [75]. In contrast, in the second study, samples were consolidated by Spark Plasma Sintering. The different microstructures of the 3Y-TZP/MWCNTs composites are shown in Fig. 45.

![Figure 45. SEM micrographs of the 3Y-TZP/MWCNTs composites: (a) 0.5, (b) 1.5, (c) 3 and 5 wt. % (the arrows indicated the MWCNTs position) [74].](image)

The authors measured an important increase of toughness $K_{IC}$ by means of single edge V-notch bean (SEVNB), being $6.1 \pm 0.15$ for monolithic zirconia and $11 \text{ MPa.m}^{1/2}$ for 5 wt. % CNT reinforced zirconia composite. Furthermore, a significant enhancement of electrical conductivity (14 order of magnitude) is observed with 5 wt.% MWCNT addition due to the percolation network through the insulating zirconia matrix [76].

As reported in the previous study, the increasing of MWCNTs content allows to enhance the mechanical resistance at high temperatures as presented in Fig. 46.

![Figure 46. Mechanical-loss (tan $\phi$) spectra and the dynamic shear modulus $G/G_{ref}$ as a function of the MWCNTs content [76].](image)
4.4.1.3. Aluminium-based matrix composites

The principal aim was to develop nanoparticle reinforced Al-based Metal Matrix Composite. In this context, Al2009-15%SiC (nano) powders have been milled and consolidated by SPS, HIP and extrusion. The latter was selected as the forming preindustrial demonstrators. The final bars exhibited a dimension of about 13 mm (diameter) and 1500 mm (length) – Fig. 47. The bars were consolidated at CEA and Mecachrome.

![Figure 47. Al2009-15%SiC preindustrial extruded bar.](image)

The mechanical properties of the bars were measured by the final user (EADS). The results were compared with the commercially available Al + 15% micro-SiC (SiC mean size 6 µm). A strong improvement of the yield and tensile strength were measured. Indeed, the yield strength (R 0.2) was increased in >2 order of magnitude from 350 to 747 MPa. Nevertheless, the strain to failure was reduced taking into account the final applications’ tolerances. On the contrary, the fatigue behavior was improved by employing the nano-SiC dispersion in the Al matrix. As shown in Fig. 48, the Al nano-SiC sample exhibited higher fatigue strength if compared to a commercial micro-MMC (in a factor 1.6).

![Figure 48. Comparison of the S-N curves between the Al micro/nano SiC samples.](image)

4.4.1.4. Direct growth of aligned MWCNTs on substrates without manipulation

Aligned multi-walled carbon nanotubes (MWCNT) carpets can be successfully synthesized on both carbon fibres and any metal substrates compatible with the injection-CVD process. This injection-CVD process involves two stages, including fibre pretreatment by depositing a SiO₂-based sub-layer
from an organometallic precursor followed by CNT growth from toluene/ferrocene precursor mixture as illustrated in Fig. 49 (b).

![Figure 49](image)

**Figure 49.** (a) FEG-SEM micrograph of CNTs grown on SiO\textsubscript{2}-based coated stainless steel substrate & (b) injection-CVD experimental set-up [77].

Nowadays, this technique was up-scaled into an injection-CVD demonstration for the safe production of aligned carbon nanotubes in an A4 format Carbon Fiber Fabric.

4.4.1.5. **Complete integrated PEM fuel cell bipolar plate**

ZBT developed an industrial scale-up production of highly filled carbon compounds for bipolar plate materials at high temperatures (up to 200°C) PEM Fuel Cells – Fig. 50 (a) [78]. The bipolar plate production is achieved by compression and injection moulding lead to achieve a substantially increase of the performances in terms of electrical conductivity. The process of compression moulding enables a higher filling load due to the perfect alignment of graphite and spherical flakes or the carbon nanotubes within an injection moulded plate - Kraus Maffei KM500-.

A handling of the carbon based compounds was assured by feeding the fillers in an enclosed environment via bag-dumpers. The same quality of compound material could be achieved on a twin screw extruder. A fully robotized plate removal from injection moulding was developed in order to prevent the operator exposition to CNTs.

![Figure 50](image)

**Figure 50.** (a) Injection molded CNT-based bipolar plates & (b) Polarization curve of the 5-cell PEM stack at 70°C under a cathodic/anodic pressure of 1.2/1.04 bars.

A 5-cells stack PEM cell containing CNTs was assembled. After testing in humidified hydrogen and air, an interesting behaviour was observed. The polarization curves at 70 °C are presented in Fig. 50 (b). The power output was about 125 W at 0.5 V single cell voltage and a current of 50 A.
As a conclusion, among all the carbon based nanoparticles, the CNTs exhibited the best operational performances and a better rheological behaviour. The latter leads to facilitate the fabrication.

4.4.2. 2-D (Surface) Processes

4.4.2.1. Photocatalytic activity of the spray dried nanopowders

Initially, the main purpose was to develop technical solutions for the industrial demonstration of functionalized flat products, like antibacterial or self cleaning panels and/or anti-corrosion panels. The different coatings were evaluated by the industrial partner Arcelor.

On one hand, the first aim was to integrate the spray dried nanoparticles into the existing solution as they allow the fabrication of transparent coatings. On the other hand, they also permit to employ crystalline phases such as TiO$_2$ anatase which possesses interesting photocatalytic activity. The latter is difficult to obtain at low temperatures.

Moreover, the nanoparticles should have a direct contact with the air molecules as well as to be cohesive, adherent, flexible and reliable. In addition, the coatings require a second phase in order to serve as a matrix, without avoiding the contact between TiO$_2$ and atmosphere.

The application of the photocatalytic coatings was for indoor air purification devices as illustrated in Fig. 51.

![Figure 51. Air purification wall.](image)

The Fraunhofer IWS tested different thermal spray technologies which showed interesting photocatalytic characteristics. In fact, the suspension deposited by HVOF kept the active TiO$_2$ anatase phase despite the high temperatures involved [79,80]. The researchers from Fraunhofer IWS employed a TiO$_2$ Degussa P25 composed of mainly anatase (80 vol. %, 25 nm) and rutile. The powder was spray dried by using the IFD Minor Plant (Niro A/S, Denmark) in an Ar–H$_2$ and Ar–H$_2$–He plasma.

Suspensions were injected into the Atmospheric Plasma-Sprayed (APS) and High Velocity Oxy-fuel (HVOF) flame. In fact, it was demonstrated that it is possible to limit the surface overheating at 150°C on substrates such as hot dip galvanized steel.

Moreover, the HVOF technology was adapted for the desired applications with a robotized arm. It is well known, that this technique exhibits better results in 3-D pieces.

IWS employed different substrates such as stainless steel and hot dip galvanized steel in which it was subsequently measured a high/constant photo catalytic activity. In their study, the photocatalytic efficiency was evaluated by means of decolouration of the pink dye Rhodamine B (performed at LABEIN Tecnalia) and degradation of gaseous acetaldehyde (Arcelor Mittal Liège R&D).
As shown in Fig. 52, during UV irradiation the pink colour continuously decreases in intensity. After 120 min, the UV light leads to fully deteriorate the Rhodamine B in coating deposited by APS. In contrast, uncoated steel completed the degradation without UV irradiation after 96 hours. For the sake of clarity, the comparison between the different titanium oxide sprayed coatings regarding the photocatalytic decolouration of the pink dye Rhodamine B is presented in Fig. 54.

![Figure 52. Photocatalytic decolouration of pink dye Rhodamine B on TiO₂ coating deposited by APS as a function of the irradiation time [79].](image)

A second photocatalytic test revealed new encouraging results – Fig. 54. Indeed, the samples processed by HVOF using non spray dried powder showed a very low degradation (10%) of the pollutant. In contrast, spray dried samples exhibited a final degradation of 140 min and 80 min in the case of HVOF and APS samples, respectively.

![Figure 53. Normalised data for photocatalytic degradation of Rhodamine B as a function of UV irradiation time [79].](image)

![Figure 54. Photocatalytic removal of acetaldehyde (C/C₀) during the UV irradiation [79].](image)
This phenomenon is attributed to the higher anatase content in the spray dried samples (>65 vol.%) if compared with the non-spray dried HVOF samples (15.9 vol.%). But if the deformability is promising, the adhesion of the coatings is still low, even if it can be improved by an optimization of the surface temperature or by pretreatment of the substrate.

5. **Nanosafe-by-design processes**

The Nanosafe-by-Design processes concern the development of new 2-D and 3-D nanostructured materials. The main purpose is to generate and integrate *in-situ one-step* nano-functional objects, avoiding any risk of dispersal into the environment. In addition, it leads to redesign the current industrial value chains since some processing steps could be removed and/or skipped. In the following lines, the Nanosafe-by design processes developed by CEA and other examples found in literature are presented.

5.1. **2-D Surface Processes**

5.1.1. **Nanostructured thin films processed by physical vapour deposition**

The production of nanostructured superlattice hard coatings with different periods could be easily upscaled into industrial cathodic arc reactors only by varying the substrate rotation as shown by Ducros *et al.* [81,82]. In the following Fig. 55, the TEM cross section of these coatings is shown.

![Figure 55. TEM images of the cross-section of TiN/AlTiN [81].](image)

The authors measured important hardness values ≈ 55 GPa and good elastic properties. Furthermore, authors demonstrated that the nanocoatings on cutting tools were the optimal solution for reducing the forces during machining.

Nanolayered superlattice coatings are well known due to their enhanced mechanical properties if compared with single-phase coatings. These are often called the fourth generation of hard coatings when hardness is >40 GPa [83,84]. Many authors concentrated the studies around the superlattice coatings after the publication of Koehler [85]. The author suggested that by creating an alternated architecture, it would be possible to create an efficient dislocation barrier. The second condition is to decrease layer thicknesses with the aim of avoiding the dislocation generation (≈ 100 atomic layers or less) and the dislocation pile-up.
The strength improvement is explained by applying the formula $Q = \frac{(G_A - G_B)}{(G_A + G_B)}$ where $G_A$ and $G_B$ are the shear moduli of the superlattice single constituents [86]. The second explanation of the inhibition of dislocation is attributed to the layer coherency strains due to the increase of interface area which allows to glide throughout the layers [87].

Another interesting example of multilayered nanocomposites was given by Kamath et al. [88]. TiAlCN/VCN multilayered coatings were prepared combining the one operating in high-power impulse magnetron sputtering (HIPIMS) with the other in unbalance magnetron sputtering (UBMS) mode. These coatings possess low friction ($\mu = 0.42$) and high hardness ($N_{K0.25} = 2800$), which enables an increase of the tool life 4 times more, when aerospace grade Al 7010-T7651 alloy is dry machined. The XTEM microstructural observation (Fig. 56) revealed that the period was 2.2 nm.

![Figure 56. XTEM cross section of TiAlCN/VCN [88].](image)

5.1.2. Antibacterial titania-based nanostructured thin films processed by DLI-MOCVD

TiO$_2$–Cu and TiO$_2$-Ag nanocomposite films were grown by pulsed direct liquid injection-metalorganic chemical vapor deposition (DLI-MOCVD) on different substrates at 683 K [89,90]. The aim of the study was to develop new antibacterial surfaces. As a matter of fact, it is well known that the addition of metals (Cu, Ag, Au, Co, Fe, etc.) to anatase TiO$_2$ improve the photocatalytic activity [91,92,93]. The two metalorganic precursors as Cu/Ag and Ti sources were employed in a conventional MOCVD reactor: copper bis (2,2,6,6-tetramethyl-3,5-heptadionate) (Cu(TMHD)$_2$) or (silver pivalate (CH$_3$)$_3$CC(O)OAg (namely AgPiv) and titanium tetra-iso-propoxide (TTIP). The precursors were introduced through injectors to a flash vaporization chamber and then the reactive vapors followed the deposition zone under low pressure using N$_2$. A schematic view of the reactor is shown in Fig. 57.

![Figure 57. DLI-MOCVD reactor [90].](image)
After deposition, the TEM microstructural observation revealed that the microstructure is composed of a TiO$_2$ matrix with crystallites of about 50-150 nm embedding Ag or Cu dispersoids (indicated with an arrow in the image), as is illustrated in Fig. 58.

![Figure 58](image)

**Figure 58.** Bright field TEM cross-section image of (a) TiO$_2$–Ag & (b) TiO$_2$–Cu [89,90].

In their work, the authors were capable to alter the metal content inside the TiO$_2$ matrix as a function of the precursor content. This fact indicated that is possible to control the anti-bacterial activity without UV irradiation only varying the metal content determined by secondary ion mass spectroscopy (SIMS) as shown in the following Fig. 59.

![Figure 59](image)

**Figure 59.** Anti-bacterial activities against Gram-positive *Staphylococcus aureus* as a function of the metal content: (a) TiO$_2$–Cu & (b) TiO$_2$–Ag [89,90].

In the case of TiO$_2$–Cu, the authors reported a slight decrease from 100% to 70% of the bactericidal property which only changes after 5 months of storage.

A second advantage of TiO$_2$–Ag is the photo-induced self-cleaning behaviour. With the aim of evaluating the photocatalytic behaviour, the degradation of Orange G in aqueous solution ($10^{-3}$ mol L$^{-1}$) under UV irradiation (365 nm) was studied. In Fig. 60, the photocatalytic behaviour is reported. As a conclusion, in this particular case the silver content above >0.1 substantially affected the photocatalytic activation of the films.

![Figure 60](image)

**Figure 60.** Photocatalytic decomposition kinetics of Orange G under UV light [90].
5.2. Hybridization of different the physical - and chemical- deposition methods

5.2.1. Cathodic arc coupled with plasma enhanced chemical vapour deposition

The hybridization of the physical (PVD) and a plasma assisted chemical vapour processes (PECVD) lead to produce in one step TiN-α-Si₃N₄ nanocomposites, as reported by Bendavid et al. [94]. The experimental set up is shown in the following Fig. 61.

![Experimental set-up of the PVD and CVD hybridation technologies](image)

**Figure 61.** Experimental set-up of the PVD and CVD hybridation technologies [94].

The nanocomposite TiN-Si₃N₄ thin films are formed by the reactive deposition of Ti produced from a classical cathodic arc and the Si from a liquid precursor, the tetramethylsilane (TMS). This technique consists of combining both the cathodic arc and chemical vapour deposition technologies employing a nitrogen atmosphere.

In their study, the researchers varied the TMS flow rate on the structure which lead to obtain different mechanical properties. The film was composed of TiN crystallites surrounded by amorphous α-Si₃N₄.

By increasing TMS flow, a decrease in the TiN crystalline size was measured passing from 33 nm to 4 nm - Fig. 62 (a). Indeed, the Si content enables to obtain different hardness values, being 41 GPa when the Si content was 5%, corresponding to a pressure of TMS of 0.8 Pa.

Hardness enhancement was ascribed to the crystallite size evolution when the presence of the amorphous α-Si₃N₄ phase is increased Fig. 62 (b). This increase is the result of the creation of additional interfaces between both phases which hinders dislocation movement allowing the energy dissipation and crack deflection.

![Graphs](image)

**Figure 62.** (a) Hardness and (b) Grain size evolution as a function of the Si content in TiN-Si₃N₄ films [94].
The decreasing from the maximum value - when the Si content evolves - is ascribed by the authors to some stress relaxation. The microstructural morphology was analyzed by high resolution transmission electron microscopy (HRTEM) analysis – Fig. 63, which confirmed the existence of well orientated nc-TiN/α-Si₃N₄ (~10 nm grains) microstructure in the case of the sample containing 5 at. % Si.

![Image of HRTEM micrograph](image)

**Figure 63.** HRTEM micrograph of nc-TiN/α-Si₃N₄ (the orientation is indicated with an arrow [94]).

An interesting phenomenon reported by the authors, is that in samples containing more than 4 at. % of silicon, their hardness is retained after annealing at 500°C in vacuum. This fact is ascribed to the percolative nature of the Si₃N₄ phase segregation, which creates one monolayer protection around TiN crystal allowing no changes in terms of grain sizes [95].

### 5.2.2. Laser Pyrolysis coupled with magnetron sputtering

*Leconte at al.* at CEA developed a system that combines two nanoparticles processes for producing Si Q-Dots embedded in a SiO₂ matrix [96]. The purpose was to create a one *single-step process* for applications related to photovoltaic solar cells. The technique has an interesting versatility regarding the large size range (2-100 nm) and different possible chemical compositions. It is a safe process, since it presents no worker exposure to nanoparticles.

As a matter of fact, similar films were processed by sol-gel and spin coating. However, they present limitations in terms of chemical composition, film thickness and a process step complexity. The single step process consists in forming Si quantum dots by laser pyrolysis in the expansion chamber. Subsequently, a supersonic expansion in the intermediate chamber enables to increase the particles’ energy.

Finally, these particles arrive to the deposition chamber in which the supersonic jet is destroyed but keeping their energy (2 keV). The quantum dots are deposited on a substrate. Simultaneously, the magnetron sputtering leads to create the SiO₂ matrix. The following schematic illustration resumes the process - Fig. 64.
5.2.3. Hybridization of supersonic cluster beam combined with cathodic arc deposition

Piazzoni et al. produced nanocomposite thin films consisting of a titanium nitride matrix with embedded molybdenum disulphide fullerene-like (IFLN) nanoparticles [97]. The nanocomposite layer was deposited by combining an industrial cathodic arc evaporator (for TiN) with a pulsed microplasma cluster source (PMCS) for the production of supersonic MoS$_2$ cluster beams.

In Fig. 65, TEM images of multilayer MoS$_2$-TiN sample deposited on Si substrates are presented. Two phases of IFLN-MoS$_2$ nanoparticles of 10–50 nm and TiN matrix were observed.

5.3. 3-D Processes

5.3.1. Oxide dispersed strengthened steels four fuel cladding pins (ODS)

The objective was to produce a demonstrator of a fuel cladding pin made of ODS steel by mechanical alloying for the RNR nuclear reactor (Gen IV) [98]. Two different consolidation routes were proposed with the aim of producing steel-based matrix composites with dispersed nanometric Y$_2$O$_3$ reinforcements; i.e. hot extrusion and Spark Plasma Sintering [99]. The optimization of consolidation route was successfully achieved by means of Spark Plasma Sintering. Different samples diameters 60 & 100 mm. were sintered. An optimal reproducibility in terms of final density was obtained.
Interesting results regarding the microstructure were obtained. Indeed, in sample processed by extrusion, the microstructure was mainly composed of fine grain elongated along the extrusion direction.

After extrusion, the tube was machined up to the right dimensions. Subsequently, an annealing step (1050°C for 1 hour) was employed in order to reduce the strain to the desired hardness (380 HV). A further cold rolling step allows to increase the hardness up to 400HV.

However, intermediate heat treatments on the tube at 1200°C during 1 hour are required to reach the recrystallization state. The dimensions of the finished tube are 1500mm in length, 10.7mm in diameter and 0.5mm of internal thickness as shown in the figure below.

![Figure 66. (A) First prototype of ODS steel and (B) the evolution of the oxides’ distribution after irradiation tests [99].](image)

From the impact tests, an important decrease in terms of the ductile-brittle transition temperature (-150°C) was measured – if compared with a PM 2000 industrial ODS steel (+100°C). The encouraging tensile tests revealed that the 18Cr ODS steel behaviour is quite similar between in the 20-750°C range if compared with the industrial ODS steels.

### 5.3.2. Oxide dispersed strengthened alloys by EBPVD

Srinivasan et al. processed NiCr alloys reinforced with nanoscale yttria and alumina dispersoids by electron beam physical vapor deposition (EBPVD) [100].

For this purpose, targets containing master alloys of Ni-20 wt% Cr (NiCr) and Y₂O₃/Al₂O₃ were evaporated in order to produce the nanocomposite-ODS sheets. These sheets were processed at the International Center for Electron Beam Technology (ICEBT), Ukraine.

With this technique it is possible to fabricate ODS alloys in a *one-step process*. In their work, the produced samples NiCr-4% Y₂O₃ and NiCr-4% Al₂O₃ alloys were submitted to a TEM microstructural observation, as presented in Fig. 67.

As shown in the figure above, it is possible to process ODS alloys containing 50–200 nm grains of the NiCr matrix with well dispersed of Y₂O₃ and Al₂O₃ nanoparticles of 5–20 nm.

A second study employing the NiCr-Y₂O₃ nanocomposites revealed that it is possible to tailor the mechanical properties [101]. The ultimate tensile strength and elongation percentage measured in the as-processed ODS nanocomposite are 1060 MPa and 0.07.

By aging the sample at 800°C for 3 h, it is possible to increase the ultimate tensile strength up to 1220 MPa due to the formation of Cr₂₃C₆. Whereas samples heat treated at 1100°C for 0.5 h or at 800°C for 16 h exhibited an ultimate tensile strength reduction down to 960 MPa. The same phenomenon was corroborated in the sample treated at 1100°C for 3 h in which a diminution down to 930 MPa was measured.
On the contrary, the latter treatment allows the formation $Y_3Al_5O_{12}$ (YAG) precipitates which are believed to enhance the final ductility.

Another interesting study regarding the mechanical properties was reported by He et al. [102]. Indeed, the researchers submitted a similar ODS thin film of 0.1 mm by hot isostatic pressing (HIP). The treatment was performed at 1100°C, with an applied pressure of 1100°C for 1 h. After the treatment, no significant differences regarding the microstructure were found. Only dislocations located at the grains and along the grain boundaries were observed. As a result, the treatment provokes an increasing of tensile strength and elongation evolving from 725 MPa and 0.49 to 1230 MPa and 0.92, respectively.

5.3.3. Thermal plasma in-situ synthesis of TiC-Al(Ti) nanocomposite

Another example of single-step process is the TiC-Al (Ti) nanopowders’ production by thermal plasma technology. As reported by Tong et al., the process consists in vaporizing Al (sizes ranging 45 to 375 µm), Ti (45 µm) and CH$_4$ in a thermal plasma plume followed by a supersaturated product gases quenching [103]. The thermal plasma unit is composed of a power source and plasma torch, powder processing system (including reactor, condenser and filter), starting material feeder and data acquisition system – Fig. 68.

First, the reinforcement particles with a high melting point are nucleated from the supersaturated gas phase during shock quenching (Fig. 69). Along the nanopowders production, a particle size was
measured. In fact, the nanoparticles collected in the coil I/II and the filter zone confirmed this phenomenon. For the sake of clarity the SEM observations performed with powders collected in the filter zone are presented in Fig. 69.

Figure 69. SEM micrographs of particles collected at the: (a) filter zone, (b) quenching zone 2 and (c) quenching zone 1 (A-B-C: indicates typical particles) [103].

The condensed ceramic particles act as heterogeneous nucleation seeds for the condensation of the metallic phase. The condensed metallic phase grows and encapsulates ceramic reinforcement particles in order to form composite powders with grain sizes >100 nm. Subsequently, nanopowders are collected, pressed and sintered with the aim of producing the Al (Ti) alloy matrix composites with a uniform distribution of TiC reinforcements.

5.3.4. Reactive mechanical milling of TiC/Ti-Al nanocomposites

TiC/Ti-Al nanocomposite powders were synthesized in one step by mechanical alloying from a mixture consisting of elemental Ti (30 µm), Al (16 µm), and graphite powder (30 µm) - Ti$_{50}$Al$_{25}$C$_{25}$ - as reported by Gu et al. [104]. During the mechanical alloying in an argon atmosphere, Ti and Al form a primary hcp solid-solution, whereas the TiC is formed by a rapid interdiffusion and an abrupt reaction between the Ti and C elements (Ti + C = TiC).

The authors found that by varying the milling time, it is possible to observe a refinement of the crystallite size accompanied with an increase of lattice strain as shown in Fig. 70 (a). The lattice strain directly influences the hardness of powder particles – Fig. 70 (b).

Figure 70. Average crystallite size and lattice strain and microhardness as a function of milling time [104].
In order to explain the mechanism for the formation of *in-situ* TiC/Ti-Al nanocomposites, the authors proposed the following a→d steps as presented in Fig. 71.

![Mechanism for the formation of *in-situ* TiC/Ti-Al nanocomposites](image)

**Figure 71.** Mechanism for the formation of *in-situ* TiC/Ti-Al nanocomposites [104].

TEM and EDX-spectroscopy allowed identifying the TiC nanoparticles within the Ti-Al matrix. Indeed, in the MET micrograph - Fig. 72 (a)- two zones A and B were analyzed. By observing the matrix (zone A), on Al-Ti with an equal atomic proportion is measured by EDX - Fig. 72. On the contrary, the zone B with ≈8 nm revealed the formation of the stoichiometric TiC reinforcements, since the atomic ratio of the C element and the residual Ti element is near 1:1.

![TEM micrograph on the 32 hours milled nanopowders](image)

**Figure 72.** TEM micrograph on the 32 hours milled nanopowders (Cu is due to the copper-mesh grid) [104].

5.3.5. Nanocomposites processed *in-situ* by solid state reaction

Surface doping of two commercial alpha alumina powders was performed in order to prepare an Al₂O₃-5 vol.% YAG (Y₃Al₅O₁₂) composites. These materials were composed of micronic or highly
sub-micronic alumina particles and very fine YAG grains, yielded by \textit{in-situ} reaction as reported by several researchers \cite{105,106,107}.

Two different $\alpha$-alumina powders were dispersed in aqueous suspensions by ball-milling and then doped with an yttrium chloride solution. A spray drying step was carried out by atomization in order to avoid the dopant segregation. Fast heat treatments were carried out in order to partially induce the crystallization of yttrium-aluminates on the alumina particles surface, minimizing the crystallites growth and the aggregates formation during heating. Subsequently, the powders were re-dispersed by ball milling and slip casted in porous moulds.

Samples were uniaxially pressed with the aim of increasing the green density and then consolidated by three sintering routes: Pressure-less Sintering, Hot-Pressing (HP) and \textit{Spark Plasma Sintering} (SPS).

The complete formation of the YAG phase was only yield after sintering. The final microstructures were analyzed by field emission scanning electron microscopy (FESEM) are shown below– Fig. 73. They correspond to the commercial alumina powder characterized by the finer crystallite size (150 nm).

![Figure 73. ESEM micrographs of polished surfaces: (a) Pressure-less Sintered, (b) Hot Pressed and (c) Spark Plasma Sintered [107].](image)

As shown in Fig. 74, the microstructures are composed of equiaxed alumina grains with submicronic YAG grains (brighter in the micrographs) located at inter- and intra-granular positions (along/inside grain boundaries).

As reported by the authors, the YAG formation allowed the enhancing of the creep behaviour in these composites, since it is believed that $\text{Y}^{3+}$ reduces the grain boundary diffusivity \cite{108}.

6. Conclusion

In this review, many examples regarding the \textit{Safe-Nanomanufacturing} and \textit{Nanosafe-by-Design} are given. As a matter of fact, ten years ago the CEA and its partners began the development of an integrated multidisciplinary \textit{nanosafety} approach.

As a consequence, different generic tools were set-up in the frame of three European projects: \textit{Nanosafe}, \textit{Nanosafe 2} and \textit{SAPHIR}. In these projects, the risks associated with the \textit{nanomanufacturing} were not considered as drawbacks.

On the contrary, they were the \textit{driving force} for developing new advanced measurement, monitoring and \textit{Safe-Nanomanufacturing} tools. These tools were designed taking into consideration the entire products’ life cycle: nanostructured materials or nano-objects.

The latter are believed to be the reaction intermediaries, which allow the microstructure and final properties tailoring. Finally, as reviewed in the last section, the \textit{Nanosafe-by-Design} processes are thought to overcome the associated risks of dispersal into the environment. Furthermore, by implementing these processes, the \textit{nanoproducts’ manufacturers} will be able to skip some processes in their value chains.
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