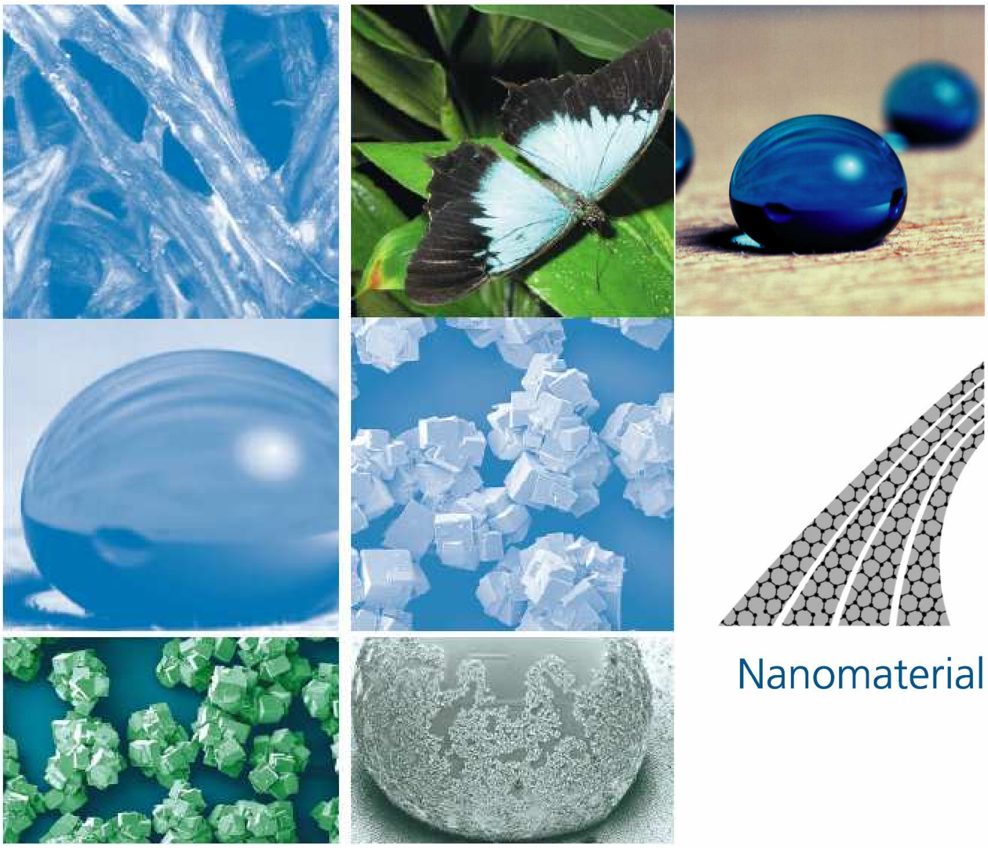

SIXTH FRAMEWORK PROGRAMME

nanoRoad sme

Nanomaterial Roadmap 2015

Overview on Promising Nanomaterials for Industrial Applications

Malsch Techno Valuation

VTT

Fraunhofer Institut Keramische Technologien und Sinterwerkstoffe (IKTS)

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STEINBEIS-EUROPA-ZENTRUM

UPM – Biomaterial laboratory of the Universidad Politecnica de Madrid (Spain)

funded by the European Commission

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Objectives

The objective of the study was to **identify the relevant nano-materials** with high potential for future industrial applications.

Seven main material categories were chosen and for each of them a well-structured report has been prepared which summarizes all the important information on existing studies and national reports, projects, patents and interviews of experts as well as on a literature survey. The R&D studies -divided in seven categories- give an **actual picture** of the nanomaterials domain identifying:

- **trends**
- **properties of the relevant materials**
- **possible applications**

Furthermore, 35 interviews of industrial and research experts of European projects have been carried out. Afterwards, this information have been validated through comparison of the results obtained from the different sources. Finally, the results of the different analysis for each material category were presented in well-structured R&D summary reports[1].

This **brochure** summarizes the relevant results of these seven reports in order to give an short overview of the trends, properties and possible applications in the different material categories.

Classification of nanomaterials

The classification of the nanomaterials should be as simple as possible. For this reason seven main material categories were defined in order to give a good overview of the different nanomaterials in the roadmaps.

The **seven main material categories** are defined as:

1) ***Carbon based nanomaterials***
2) ***Nanocomposites***
3) ***Metals & alloys***
4) ***Biological nanomaterials***
5) ***Nano-polymers***
6) ***Nano-glasses***
7) ***Nano-ceramics***

[1] The R&D summary reports will be available under http://www.nanoroad.net/ at the end of the project.

The R&D studies in the seven nanomaterial categories will give an actual picture (Figure 1) of the domain identifying :

1. Trends,
2. Properties of the relevant materials,
3. Possible applications.

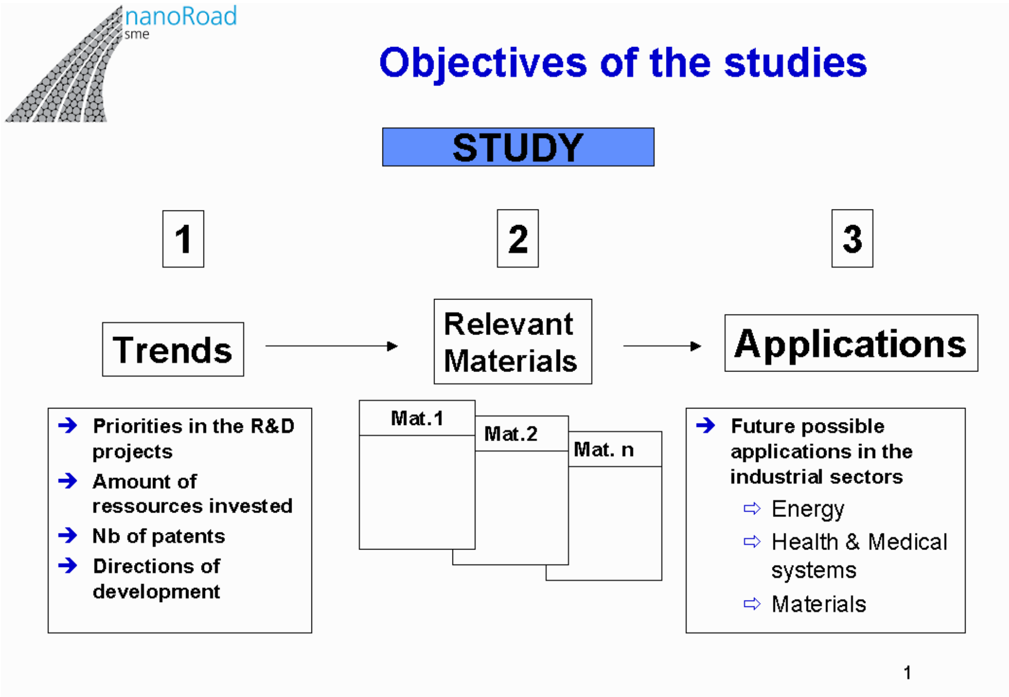


Figure 1: Methodology of the R&D surveys

Trends were defined by answering the questions:

- What are the directions of development?
- What is very actual from a scientific and industrial point of view for this material category?

The answers to these questions are based on reference materials and parameters which validate the choice. The trends have to be identified using the following parameters:

- ✓ Scientific and technical priorities from :
    - the **objectives of R&D projects** identified in Europe
    - **existing studies** and **scientific articles** in the field
- ✓ **Amount of ressources** invested in the R&D projects (number of projects running on these subjects, budget in €, number of organisations involved, manpower...)
- ✓ **Number of patents** in the domain

In the following, a short overview of the R&D summary reports for each of the **seven main material categories** will be presented.

1) Carbon based nanomaterials

1.1 Definition of the material category

This chapter covers **carbon based nanomaterials** and investigates possible avenues of application. Carbon based nanomaterials are defined as materials in which the "nanocomponent" is pure carbon. That means for example that polymers do not count as carbon based nanomaterials. Table 1 lists the carbon based nanomaterials which are under investigation by the scientific community.

Table 1: Most prominently researched carbon based nanomaterials

Single Nanostructures		**Films, Coatings, Nano-Structured surfaces**	**Nanostruc tured bulk material**
Particles	*Nanotubes*		
Carbon Black	SWCNT	Carbon Films	Nano-structured Carbon
Fullerenes	MWCNT	DLC	Nanoporous Carbon
Graphite	Nanohorns	covalent carbides like SiC	Carbon Foams
Nanocluster	Nanowires	metallic carbides like TiC	Carbon Aerogels
	Nanorods	Nano Carbon Nitrides	Carbon Nanocrystals

1.2 References

- 73 relevant national and European **research projects** were analysed.
- The **literature survey** is mainly based on a search in the databases INSPEC and BIOSIS covering 35.559 respectively 3.190 documents on carbon nanomaterials from 1990 to 2003 (see figure 1+2). The patent analysis was made with the WPINDEX database.
- The results of the analysis were validated with published reports e.g of the Royal Society (UK) or TAB and BMBF (Germany) as well as with interviews.

1.3 Summary

Summarizing the results from the searches of national and European funded research projects, the literature and patent searches as well as the interviews with the research experts, the investigated materials have potential for applications in the following areas.

Carbon nanotubes (CNT) are sheets of graphite rolled up to make a tube. The dimensions are variable (down to 0.4 nm in diameter) and it exist also nanotubes within nanotubes, leading to a distinction between multi-walled and single-walled carbon nanotubes (MW- and SWCNT, see figure 1+2). Apart from remarkable tensile strength, nanotubes exhibit varying electrical properties (depending on the way the graphite structure spirals around the tube, and other factors) and so they can be insulating, semiconducting or conducting.
Due to their large surface area CNT are interesting media for **electrical energy storage** and they are still under investigation as a hydrogen storage medium.
CNT show good properties in **electron emission** which could result in large area display applications. Use as sources in electron microscopy, or as tools or tips in scanning probe microscopy are likely and are beginning to come into force.

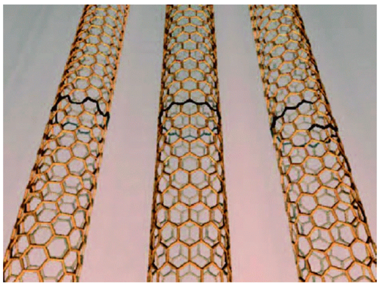


Fig. 1: Single wall carbon nanotubes of different types: armchair- (left), zigzag- (middle) and chiral-type (right) which show different electronic behavior because of their structure.[2]

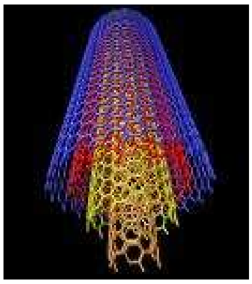


Fig. 2: Multi wall carbon nanotube where the several nanotubes have different diameters.[3]

The infra-red vibration of nanotubes is being investigated for the possibility of using infrared radiation to enable the manipulation of carbon nanotubes. Their use as **molecular pincers** in actuators is under investigation.
Prof. Strunk mentioned the potential of the **optical properties** of carbon nanotubes in his interview.
The excellent electrical and mechanical properties of carbon nanotubes like electrical conductivity, heat transmission capacity, heat stability, high strength or low density makes them candidates for use as fillers and many other applications.
A growing application potential field is the exploitation of these properties in **composite materials**.
Also in the medical&health sector CNT could play an active role. Recently, a CNT were used as needles to bring active agents into living cells. This process could be applied e.g. as a new way to a therapy against cancer.
CNT are the most intensively researched carbon nanomaterial (see fig. 3+4), however applications are expected in the mid-term view.

Carbon nanotubes / polymer composites can be prepared of composites of carbon nanotubes and polymers which have high electrical conductivity, with applications in a conventional cold cathode or a polymer LED. They can also introduce electrical conductivity to materials which additionaly indicate an improved mechanical performance.
Incorporated into a polymer matrix CNT can produce composites with a very high strength and high elastic modulus which may lead to the development of ultra-resistant materials for use as reinforcement fibres.

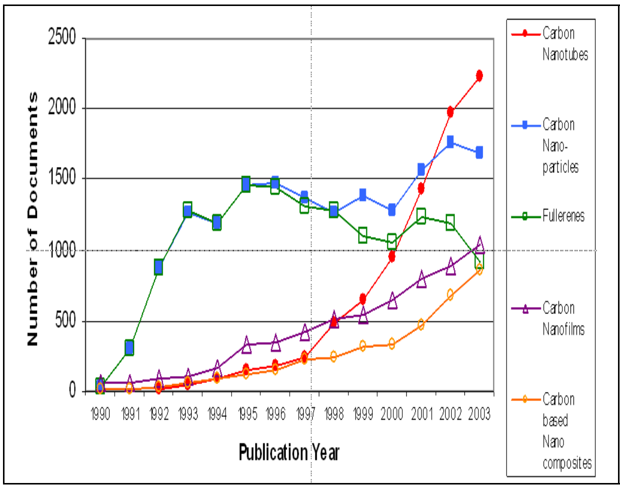


Fig. 3:Publication activity for different carbon based materials

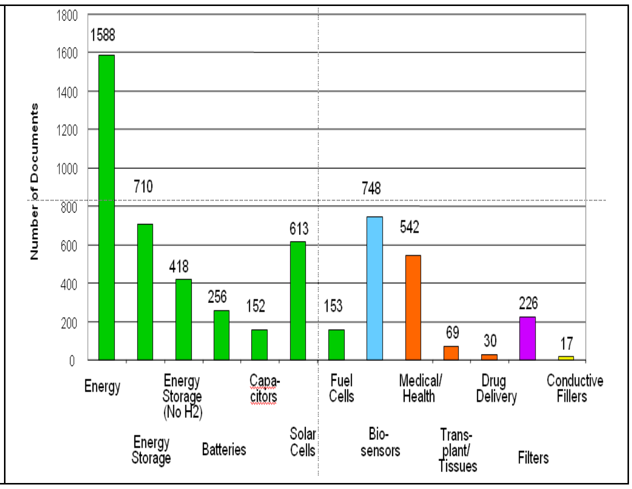


Fig. 4: Number of publications concerned different applications in the field of carbon based materials

[2] Image credit: Physik Journal 3 (2004) Nr. 10, p. 39; Wiley-VCH Verlag GmbH&Co. KgaA, Weinheim
[3] Image credit: www.ee.surrey.ac.uk/Personal/C.Poa/nanotubes.htm

Carbon nanotubes and polymer composites can form foams. These materials are just at an early stage of investigation and lightweight foams will be produced with improved electrical, mechanical, and thermal properties.
Conducting polymers may be able to be optimised for electrical energy storage applications and may have higher electrical capacitance than pure CNT films or pure electrically conducting polymers.

Carbon black is currently the most widely used carbon nanomaterial, it has found **application in car tyres**, **antistatic textiles** and is used for **colour effects**.

Fullerenes are a class of cage-like carbon compounds composed of fused, pentagonal and/or hexagonal sp^2 carbon rings (see fig. 5). Fullerenes are however, like all pure carbon structures insoluble in water. The literature search showed a **decrease in activity** in fullerene research and indeed a low level of interest was reflected in the projects. The interview with Dr. Lebedkin also confirmed this finding. Although there are still some open questions, fullerenes are now well understood systems. The **applications of fullerenes appear limited**. Earlier it was expected that tribological properties of fullerenes would make application as lubricants possible but the fullerene molecules are too small. There is potential that fullerenes can be used as fillers.
In the longer term, applications as drug deliverers either by the attachment of functional ligands to the carbon cage or by trapping molecules inside has been predicted. Research in this field is in the very early stages and applications are not expected in the next ten years. The trapping of metals inside the cage such as Lanthanides could enable the application of fullerenes as **tracer molecules**.

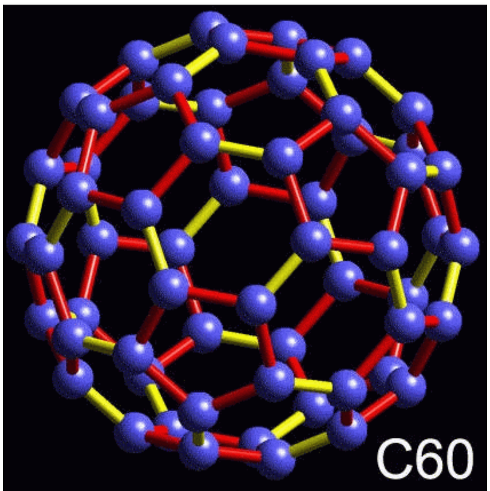


Fig. 5:C_{60} molecule called “buckminsterfullerene”.[4]

Fishbone Carbon Nanofibres can be manufactured in large quantity and at low costs. Their strength and graphite structure makes them suitable for application as **catalysts support materials**. The low costs may make them an attractive alternative to carbon nanofibres from carbon nanotubes.

Nanoporous carbon can be used as **storage media for electrical energy** because of its large surface area. The large surface area also makes it suitable for use as an anode in Lithium ion batteries.

Carbon based nanofilms are very promising materials. Several properties can be adjusted separately so that the coatings can be optimized for specific applications. They can be used

[4] Image credit: http://www.xray.uu.se/cluster/images/c60.gif

for **wear protection** and to **reduce friction**. There are several elements which can be used to build up **Carbid Nanofilms** and **Nanocristalline Carbonfilms** like "**Diamond Like Carbon" (DLC)**, these are: C, Si, N, B, Ti. Combination of these elements like C_3N_4 and Si_3N_4 lead to several materials with different characteristics. Two groups of these binary compound materials are of extra ordinary interest. These are covalent carbides like SiC and B_4C and metallic carbides like TiC or LaC_2.
Nanocrystalline diamond in an amorphous carbon matrix deposited in a nanocomposite film as well as Carbid Nanofilms **combines the properties of diamond with very low friction**, **high toughness and biocompatibility**. Applications in the medical & health area of replacement joints are foreseen. A further advantage of these materials is that the adjustment of the properties of the films can be done without the need to adapt the production process. The preparation process is based on a well established technology (CVD, PECVD, PVD). Therefore there is already considerable expertise at hand for the development of new materials. Most of the techniques are however at the laboratory level. A major break through in the next three to five years is not expected. There is need for the investigation of the composition and structure of the films produced as well as the properties of the film (Interview Prof. Holleck). Applications are also expected in **scratch resistant surfaces** with a low friction coefficient where e.g. the thin layers have a good balance of grip hardness and friction.

1.4 List of nanomaterials with actual industrial applications

Extracted from literature survey and the analysis of recent and current research projects on carbon based nanomaterials, the following list of current and potential applications could be extracted (see Table 2).

It was distinguished between two categories: one very specific category, in which the material is used for a specific purpose and another more general category. The general category for applications is used to link the specific application to the branches energy, medical & health, and material.

Table 2: List of current and potential applications in the field of carbon based nanomaterials.

Application I (specific)	**Application II** (general)
on large scale for composite material	
	Composites
	Polymers
conductive fillers	conducting polymers
	strong lightweight material
large area displays	electronic device
	FED
anode material in Li ionic batteries	energy storage/supply
electro-mechanical transducers	electronic device
cathodes	electronic device
cathode for HF-microwave generator	electronic device
SET	electronic device
single electron memory	electronic device
logic gate	electronic device

quantum computer	electronic device
spin polarized electronics	electronic device
photonic crystals/device	optoelectronical devices
sensors	electronic device
actuators	electronic device
magnetical and electrical application	electronic device
high capacity capacitor	energy storage/supply
fuel cells	energy storage/supply
solar cells	energy storage/supply
hydrogen storage	energy storage/supply
coatings for prothesis	coatings
coatings for surgical tools	coatings
coatings for fixed orthopedic devices	coatings
antiscratching coatings	coatings
sorting of NP/NT	
positioning of NP/NT	nanostructuring
templates	nanostructuring
AFM-Tips	SPM
molecular tweezers	
	electrochemistry
gas adsorbents	
catalysts	
nanoreactors	
	low cost production route
investigation/characterization of the properties	fundamental research
tuning the properties (of e.g. CNT)	

Carbon based nanomaterials most widely mentioned in the field of **energy applications** and have predicted applications in the fields of hydrogen storage and electrical energy storage. **Batteries** and **capacitors** are the most prominent applications in the field of energy storage. **Solar cells** and **fuel cells** are further potential areas of application of carbon based nanomaterial in the field of energy related applications.

Biosensors are the next most common application mentioned having more publications than the wider topic of medical & health. In the category **medical & health** two applications are specified. It was also recognized that for carbon based nanomaterials the investigation of **transplants** and **tissue engineering** is of more interest than drug delivery systems. A further interesting application is its use for **filters**. Of relatively low interest is the use of carbon based nanomaterials for conductive fillers for compound materials.

1.5 Trends and relevant nanomaterials for future industrial applications

The major emphasis in research activity of carbon based nanomaterials in recent years has been in their **production and characterisation** which is observed in national and EU funded projects collected in this survey and in scientific review articles. In the editorial of a special edition of MRS Bulletin Prof. M.S. Dresselhaus observed that main emphasis in **carbon nanotube research** has been in the **synthesis towards the well defined production of nanotubes of a precisely determinable structure** and hence precisely determinable properties. She comments that research has now achieved a good understanding of the structure and many basic properties of Single Wall Nanotubes (SWNT), and their interrelation. Many of the properties of SWNT are not observed in graphite.
Basic understanding of nanotube growth mechanism is still lacking however. This information is important because of the close dependence of nanotube properties and their geometric structure. This approach was confirmed in an interview with Prof. Strunk of the University Regensburg (Germany) as a particular prerequisite for the application of nanotubes in electronic devices.
Major breakthroughs in the production of nanotubes are emerging. For example Thomas Swann & Co Ltd have recently begun commercial production of high purity single and multi-walled nanotubes. The breakthrough was achieved as a result of ongoing collaboration with Cambridge University (UK) which resolved technical issues in scaling up laboratory procedures for the production of nanotubes. The produced nanotubes have an average diameter of 2 nm and a length of several microns, a purity of 70-90% and cost 200 UK Pounds/g.
Field emission is seen as one of the **most promising applications for carbon based films**. The most attractive forms of carbon for this application are **carbon nanotubes** which are capable of emitting high currents (see fig. 6). Controlled deposition of nanotubes on a substrate has recently become possible. There is concern however for the **long term stability** of the films. Investigations have shown that the film can degrade due to resistive heating, bombardment from gas molecules by the emitted electrons, or arcing. Electrostatic deflection or mechanical stress can cause a change in the local shape of the emitter and a decrease in its effective-ness.
Applications in nanotube **flat panel displays** have been anticipated and a demonstration model has been produced by Samsung. **Field emitting diode (FED) displays** will counter the draw backs of liquid crystal flat screens, such as low image quality and a restricted field of view. The viability of nanotubes for such applications are in question, problems in the correct deposition of the tubes, phosphor lifetime and charging of the spacers need to be overcome.
There are also **applications in lighting elements** as well as in **microwave amplification** and early examples are commercially available. Materials for energy storage is a major area of research for carbon nano-materials. Nanoporous carbon and carbon nanotubes are the important materials in this field.

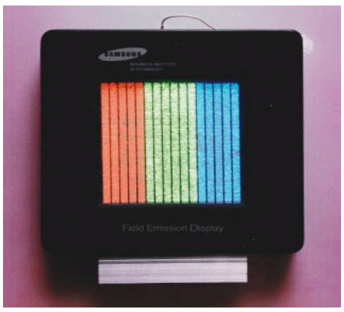


Fig. 6: The Samsung 4.5” full-color nanotube display. Emitting image of fully sealed SWNT-FED at color mode with red, green, and blue phosphor columns.[5]

[5] Source: From W.B. Choi et al., Appl. Phys. Lett. (1999).

The literature search showed most activity for **carbon nanotubes** concerning the last three years, while interest in **nanoparticles** and **fullerenes** decreasing. **The model category for application of carbon nanomaterials in the literature is energy storage.**

The low level of activity in fullerene research is reflected in the list of current and recent research projects, where they are not a major subject of investigation.

Other important materials with respect to publications are **carbon nanofilms** and **carbon based nanocomposites**, with **diamond like carbon layers** being an important material.

Nanocomposites and nanofilms are very important areas in research and the impression is that there is currently growing interest in developing new materials in this category.

The patent activity shows the most success in research for carbon nanofilms. The ability to produce pure carbon nanomaterials and a growing understanding of the growth processes is leading in an upsurge in the investigation of composite materials and an investigation of the effects of incorporating carbon nanomaterials in other materials.

2) Nanocomposites

2.1 Definition of the material category

Nanocomposite materials can be subdivided in different ways. Some nanocomposite materials consist of a non-nanocrystalline matrix of one material filled with either nanoparticles or nanofibers of another material. Nano-nanocomposites also exist: in this type of composite material, the size of all constituent materials grains is in the nanometer range. In this study we only include composite materials including at least two different materials. We consider metal oxides as part of the metals category.
Finally, we make a distinction between nanoparticles, coatings, and bulk materials. In the category nanoparticles, we include nanowires, nanowhiskers, etc. Surface nanostructures are included in the coatings and in the category bulk materials 3D nanostructures are outlined.

2.2 References

The conclusions in this study with respect to relevant nanomaterials are mainly based on literature researches, projects, patents and interviews. In this context, 71 projects from 10 different countries were taken into account all funded by the EU or the corresponding national funding bodies. Regarding the 71 projects surveyed, nine of them involve nanoparticles, twenty coatings and 42 bulk materials. The number of patents in this study, which were considered, are 71. The patent queries are mainly based on the EPO databases accessed through espacenet. For the validation of this study 11 interviews were carried out.

2.3 Trends and future applications

In the following, an overview about the topics of the trends and future applications in this category is given, which were considered in this study:

- General trends influencing the uptake of nanomaterials in products:
  - Risks of nanoparticles and materials for health and environment and new or adapted norms and regulations
  - Need for surveillance of environmental and security risks
  - Ambient intelligence
  - Ethics of science and technology
  - Investment in technology development
- Trends in **energy applications:**
  - Need for sustainable energy production and consumption
  - Need for energy security
  - Energy production / transformation
  - Energy storage: Polymer matrix composites may be applied in energy storage for mobile as well as electrical transport technologies. Bottlenecks (in 2000) were durability, reliability, the absence of recycling facilities.
  - Energy saving: For the energy sector nanocomposites can be used to improve the features of electrical cables.
  - In energy applications including electrically conducting composites; fuel cells / batteries; hybrid systems, conducting polymers can be applied. For these two types are being investigated. The polymer itself can be made electrically conducting, or conducting ions can be added to the polymer. This is an emerging area.
- Trends in **medical & healthcare applications:**
  - Ageing
  - Need for better and cost effective healthcare

  - Legislation
  - Investment
  - General materials for healthcare
  - Drug delivery: Nanoclay-based composites may be applied in medical applications such as protein delivery, but other materials may also be useful, such as core-shell materials.
  - Imaging
  - Tissue engineering, active and passive implants: hydroxyapatite, calcium carbonate, ceramics most likely.
  - Diagnostics
  - Biomimetic and biological materials
  - Dental materials
  - Nanosensors under skin (>2010)
- Trends in materials for **automotive and aerospace applications:**
  - Light and strong materials
  - Transparency windshield
  - Lacquers
  - Safety
  - Polymer matrix composites
- General trends in materials
  - Processing technology
  - New materials
  - Costs of production

2.4 *List of relevant nanomaterials for future industrial applications*

The materials which are to our best knowledge most promising for the relevant applications are:

Matrix materials filled with nanoparticles or fibres:

1) **Polymer matrix nanocomposites**
   - Polymer matrix filled with nanoclays:
     - POSS in polymers
     - Rubber with clay
     - Polyolefin with layered clays
     - Hydrophobic fumed silica
   - Polymer nanocomposite matrix filled with normal fibres
   - Polymer / resin / textile matrix filled with carbon nanotubes (coating and bulk, see fig. 7)
   - Polymer matrix filled with metal and ceramic nanoparticles
     - Hydrated Alumina in Polymer

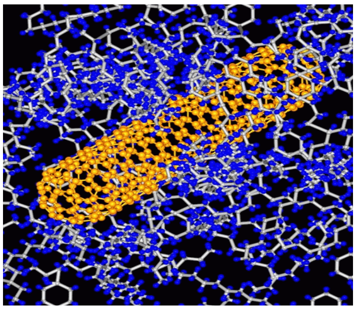


Fig. 7: Carbon nanotube / polymer matrix nanocomposite.[6]

[6] [6] Image credit: www.ipt.arc.nasa.gov/cntpolymer.html

2) **Ceramic matrix nanocomposites**
   - Ceramic matrix filled with nanocarbon / aquasomes
   - Ceramic matrix nanocomposites for bone
   - Zr or Al based ceramic nanocomposites
   - Ceramic matrix filled with nanopolymer
3) **Metal matrix filled with nanopolymer composites**

Nano-nanocomposites:
1) Quantum dots
2) Core shell nanoparticles (including gold shell nanoparticles)
3) Carbon - nanoceramic coating
4) Carbon nanotube – polymer nano-nanocomposites
5) Textile – nanoceramic or ceramic – polymer nano-nanocomposites
6) Metal – ceramic nano-nanocomposites
7) DNA-linked nanoparticles / polymer-DNA complexes
8) Dendrimer nanocomposites
9) Cerium-oxide nanocomposites
10) Polymer-carbon nanotubes-nanoclay particles nano-nanocomposites

To fabricate the nanocomposites the following **production processes** are established:
1) Standard polymer production processes
2) Sol-gel
3) Coating techniques (e.g. CVD)
4) Printing / imaging

3) Metals & Alloys

3.1 Definition of the material category

The metals were divided into categories according to standard text books on metallurgy:

- Ferrous and
- non-ferrous metals

whereas non-ferrous metals were subdivided as follows (see table 3):

Non-ferrous metals & alloys
Cu and Cu alloys
Ni and Ni alloys
Zn and Zn alloys
Co and Co alloys
Zr and Zr alloys
Noble metals
Light metals
Other

Table 3: Most prominently researched non-ferrous metals

3.2 References

The conclusions in this study with respect to relevant nanomaterials and future trends are mainly based on literature researches, projects, patents and expert interviews. In this study, 302 projects were screened but only 39 were relevant to nanometals and nanocomposites with metal component (247 European FP6 projects, 37 UK, 7 Dutch and Flemish and 11 Polish projects). With respect to the 300 screened publications only 131 were relevant for this study. The patent search was done via the EPO database and approximately 200 patents were found but only 89 were relevant for this study. In addition, for the validation of this study 5 expert interviews were carried out.

3.3 Summary and trends

Statistical analysis of collected data indicate the following main trends in research and for future applications:

- Application of metal nanoparticles, in particular silver (antibacterial) and other noble metals especially in the health protection, but also some special applications (for instance Aluminium).
- Magnetic iron based alloys - reduced loses in energy transmission due to small size of the grains compared to the magnetic domain size and also by interface effects on magnetic properties.
- Structural applications: light metals with superior mechanical properties: Al and Mg alloys, Ti and Ti alloys – radical improvement of various kinds of mechanical properties caused be a change of deformation mechanism comparing to conventional materials
- Coatings - radically improved tribological properties; higher wear resistance, less friction, better corrosion resistance, sustainable production process, etc. The improved properties are connected with uniformity of the structure when it is regarded in the micro-scale.

- Mg and its alloys as a material for hydrogen storage. The promising properties are connected with high diffusion rates for hydrogen and increased solubility limits in the nanoscale material.

The nanostructured and nanocrystalline metal materials offer radical improvements of properties or new functions, that can play a crucial role for SMEs searching for innovative solutions and high competitiveness of the products they offer. This is in some respect reflected by the increasing number of patents in the recent years. The most rapid increase of patents concerns nano-powders, mainly of noble metals as well as aluminium. The powders are suspended in a fluid or another material. In this case the most important property is the high contribution of surfaces of the particle to the properties or function of the material they are embedded in. This results in a high material activity which could be used as catalyst or as source of ions for antibacterial properties, etc.
The second rapidly developing field concerns light metals with improved mechanical properties. Here the specific mechanical properties of nanostructured materials are concerned: high strength, that for some special methods of production can be combined with ductility, high fatigue limits, elevated temperature strength, corrosion or wear resistance, etc. Interestingly however, the number of patents in that field is not as high as it would result from the number of papers.
Much research is focused on magnetic materials. For very fine grain size, the material may become magnetically soft, thus a decrease of energy loses when it is applied as a transformer core or in other applications with oscillating magnetic fields are considered. This leads to energy saving during energy transmission.
The number of patent and papers concerning bulk metals and nanopowders is approximately identical but bulk metals are divided into magnetic materials and structural materials whereas the application of nanopowders is more strongly focused on the antibacterial and catalytic activity. Also the review of industrial applications shows some stronger accents on the application of nanopowders.
On the other hand, it seems that few research projects in the searched data bases concerned metallic nanoparticles with applications in medicine contrary to the number of patents.
The presently **most exploited properties of nanopowders** are based on three phenomena:

- high specific surface area
- soft magnetic properties
- new deformation mechanisms

Experts quoted in this report show a number of other specific phenomena of nanomaterials, that are not yet exploited but may become increasingly important. Here we mention just two:

- Surface treatment of metals: to produce a nanostructure on their surface, increase terminological properties, chemical properties, reduce friction, increase biocompatibility etc.
- Mechanical and multifunctional properties to be exploited in high value in MEMS: structures of the size of some microns, metals in the form of single crystals, amorphous materials or nanomaterials should be used. In the case of conventional polycrystals single grain boundaries would cross the structure element and impair its reliability.
- Wide application of nanoparticles: hydrogen storage, catalysis, production of carbon nanotubes, sensors, getters, optical and electronic devices, biological imaging, besides the already implemented in by industry antibacterial applications.

The trends indicated below are not yet reflected by the patent and papers analysis, but follow from analysis of the basic properties of nano-metals and alloys, that open doors for new applications. The full analysis of such trends is given in the section concerned with **experts reports**.

The forecasts see wide application of nanometals in microsystems, including microelectro-mechanical systems (MEMS), bioMEMS, nanoelectromechanical systems (NEMS), optical, electronic, electrochemical microsystems, for multifunctional devices and systems for chemical and biological analysis/detection, drug delivery/discovery, tissue engineering, chemical and materials synthesis, energy conversion and storage. Here production of micro-parts (microgear, microsprings, complex shapes ...) from nano-metals will be a critical success factor.

As far as surface treatment, wear and corrosion resistant coatings applied by electro-deposition for instance for repair of heat-exchangers, decreased wear and friction. Besides coating, the surface treatment of metal parts to produce a nanostructured layer on their surface will play an important role. Various methods of surface treatment which can be also implemented by SMEs can be envisaged here.

In summary, according to the contribution of experts and our own opinion, nano-metals have an enormous potential for applications in electronics, construction, power transformation, energy storage, telecommunications, information technology, medicine, catalysis and environment protection, with high possible impact in the areas of technology related to energy, health and materials.

3.4 List of relevant nanomaterials for future industrial applications

In the category metals the following nanomaterials are most promising for future applications in which two subcategories are defined:

- Bulk nanostructured metals and powders:
    - Ti
    - Ti-Al
    - Ti-transition metals alloy (Fe or Ni or Cu)
    - Mg-Ni
    - Fe-Cu-Nb-Si-B alloy
    - Fe-transition metal alloy (Co, Ni, Cr, Cu, Zr)
    - Al-transition metal alloy (Fe, Ni, Ti, Zr)
    - Al, Mg, Al-Mg alloy

- Nanopowders of noble metals:
    - Ag
    - Au
    - Pt
    - Pd

4) Biological nanomaterials

4.1 Definition of the material category

The category of **biological nanomaterials** is defined in this study as materials of biological origin that are used for nanotechnological applications. Since the term biomaterials has been used widely, often used also to describe materials of non-biological origin that are used in typically medical applications as bio-compatible materials, the terms need to be defined carefully. In biology, practically all materials can be considered as nano-materials in one way or another. For example enzymes have well defined structures at the nanometer-level and work as nano-machines. However, for the purpose of this study, we have only included materials that have an element of design. That is: materials that mainly comprise biological molecules and that have been chosen or designed for a certain technology (application) that relies on a nanoscale feature. Inorganic nanomaterials, for example alumina, can be used for biological applications, for example as implants. These may be called biomaterials, but are not included here as a biological nanomaterials. They are rather seen as inorganic or ceramic nanomaterials with applications in biosciences.
In molecular biology one can group compounds in roughly four groups:

- Proteins
- nucleic acids
- carbohydrates and
- “small molecules”

While the two first groups are fairly well defined for nanotechnology, the definition of the third group is not very well defined and has only few examples. Into the fourth group we could include lipids, hormones, vitamins, etc. Several examples of biological nanomaterials exist in the groups of proteins and nucleic acids but also for example lipids do constitute parts of nanomaterials. In some cases it may be convenient to add categories such as “viruses” that can contain components of all three previously mentioned groups. Bacterial or animal cells are typically in the micrometer range but they are not included in this study as nanomaterials.
In bio nanomaterials there are two features that are exploited above all:

1) self-assembling properties and
2) specific molecular recognition

The very defined structure of macromolecules are often used i.e. proteins or viruses are large molecules or molecular assemblies but contrary to synthetic polymers they have no (of very little) size distribution. Thus very precise assemblies can be constructed as the building blocks are clearly defined.

4.2 References

The study is mainly based on searches of literature, patents, projects and interviews. In this context, one interview was done. Also, a patent search including 56 abstracts from 11 different countries were taken into account and a listing of 10 projects is included (7 EU and 3 national projects). With respect to literature 13 references are included.

4.3 Actual applications

Applications of biological nanomaterials were searched for by making a patent search on biological nanomaterials.

Most of the patents can be grouped into

- Self-assembling systems
  - Peptides
  - DNA
  - proteins

- Actuators
- Motors
- Sensors
- Drug delivery
- Specific filtration
- Memory devices

Almost half of the patents concerned different immobilisation strategies rather than actual self-assembling based on the properties of the biomolecule. Three different strategies can be categorised as follows:

1. Non-organised surface + self-assembling biomolecule
2. Organised surface + biomoleclule
3. Self-assembling biomolecule + inorganic material

Biomoleclules can be peptides, proteins, DNA, lipids or combinations of them. E.g. single-stranded DNA can be used as a tag to immobilise peptides and proteins in an ordered array format to a oligonucleotide coated immobilisation surfaces. These surfaces can be 2D surfaces or 3D particles or beads made of various materials e.g. glass, silica, polymers and metals. Site-directed, ordered immobilisation is advantageous in biosensors, micro/nanoarrays, biochips and nano-composite materials which can be used in applications such as detection and quantification of genes, diagnostics of various compounds, assaying protein target interactions, proteomics, drug development and screening or using of catalytic enzymes. Immobilised biomolecules can be used to modify the properties of the surface or to introduce an functionality e.g. binding activity.

Most of the examples are dealing with 2D crystallisation and 3D self-assembly of proteins and peptides making lattices. Such 3D constructions can be used as structural or functional elements such as molecular sieves or to be used for drug delivery. Peptides can form different types of nanostructures such as nanopillars, -crystals, -rods, -wires, -tubes, -filaments, -fibres and -shells. The self-assembling protein or peptide can be inserted by a functionality e.g. binding activity for a semi-conducting material or an antigenic determinant for immunisation purposes. Possible applications for semi-conducting materials might be optical detectors, biological sensors, well-ordered liquid crystal displays, light-emitting displays and nanometre scale computer components. Nucleic acid molecules can be used to form nanoscale devices e.g. resistors, capacitors, inducers, transistors, wires, switches, memory devices and nanoscale containers for drug or other materials. Also nanoscale filters and molecular sieves can be constructed. In addition 3D assemblies of surfactants or lipids can be used to deliver biomolecules across cell membranes.

Advantages of protein and peptide based nanomaterials is their homogeneity over organic and inorganic materials producing structures with predictable geometry and stochiometry.

Examples:

- Producing a self-assembled protein microarray useful in rapid diagnostic applications comprises localizing oligonucleotide-addressed synthetic proteins onto an oligonucleotide tag microarray device
- Manufacture of film or controlling cholesteric pitch of nanoparticle, by using self-assembling biological molecule that has been modified to possess amino acid oligomer capable of specific binding to semiconductor material.
- Forming spatially organized nanostructures by applying an external perturbation with preset magnitude on localized regions of smooth thin film of bistable or multistable molecules and forming nanostructure by self-organization of molecules.
- Screening peptides that bind to nanographite structures like carbon nanohorns for producing various functional materials applicable in e.g. nanobiotechnology,

comprises oxidation, biotinylation and immobilization.
- Detecting a conformational change or binding event in a targeted molecule by combining a magnetically active nucleus sensor with a targeted molecule and recording the detectable signal upon the conformational change or binding event.
- Staged assembly of nanostructures, useful e.g. in biosensors or as catalyst supports, using assembly units derived from pilin proteins, also new hybrid pilin proteins**.**

From the patent search most applications seem to be in an early phase and the patents are more at a proof of principle level.

4.4 Trends and future applications

One of the main trends for biological molecules is the use of molecular self as a means to manufacture nanostructures for various nanodevices. There are a magnitude of different materials and approaches that are being investigated. However, altogether it seems that bio-analytical applications are most developed. This is perhaps due to the large effort on biosensors that has been going on for already a few decades, and that is now getting a new boost from nanotechnology.

The use of biomolecules in the **energy sector** has so far been rather limited. Although there are in principle possibilities for applications such as using biological light-harvesting complexes for solar energy capture, the formats are so far not very compatible. If such applications were to be realized it is very likely that they would rely heavily on biological nanomaterials. Lately there has been focus on fuel cells for using chemical redox reactions for production of electricity. Some success has been reported for such devices that include biomolecules. It this case it can be seen that performance of such devices might be boosted by nanostructured biomaterials.

Most of the applications are related to **health & medical areas**. Typical examples include arrays (chips) for large scale DNA or protein screening. Drug delivery is another much studied example. Various self assembled peptide structures can be designed to release compounds under specific conditions.

In the sector **materials** mainly the self assembling properties of the biomolecules are utilized. Examples include biological arrays for formation of 2D organization of semiconductor nanoparticles. Self-assembly is seen as a route to designing materials with tailored properties, such as responsive materials. The biological recognition of various molecules (such as the antibody antigen interaction) can be used to build nanomaterials with specific permeation selectivity. Several of the biological materials that have interesting properties are nanostructured composite materials that involve biomineralization. Examples of materials that scientists are trying to mimic include bone, tooth or mollusc shells.
For materials where mechanical action is desired, many groups have been studying biological molecular machines. Biomolecular motors are envisioned to be able to be part of materials in such roles as: molecular assembly lines, construction of nano-networks, or part of adaptive materials. Some of the possibilities that are being pointed out are based on proteins such as:
- actin networks
- kinesin motors
- myosin motors
- ATP synthease motors

4.5 List of relevant nanomaterials for future industrial applications

Based on the above mentioned results some categories of biomaterials have been grouped which are the following:

- **PROTEINS-based materials**
  - self-assembling materials:
    - Proteins that form 2D structures:
      - S-layer protein
      - Hydrophobins
      - Chaperones
    - Self assembly based on avidin-biotin interactions, barnase-barstar interaction etc..
    - Nanocontainers
  - functional protein units:
    - Bacteriorhodopsin
    - Nanopores
    - Proteins for molecular recognition
      - antibodies, single chain antibodies
      - Specific molecular recognition
      - antifreeze protein
    - Conformation switching proteins
      - periplasmic carbohydrate binding protein, calmodulin
    - Biological nano-motors (see fig. 8+9)
      - Kinesin
      - Actin-myosin
      - DNA interacting enzymes
      - ATP synthase (see fig. 8)

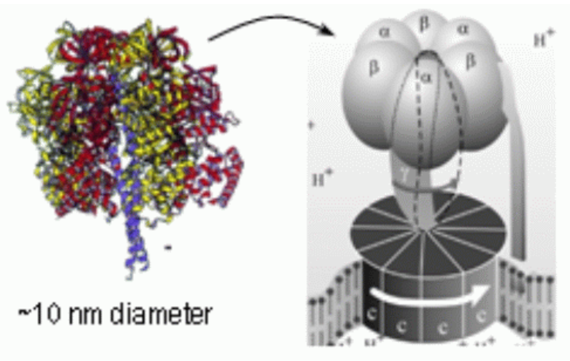


Fig. 8: Structure (left) and functionality (right) of ATP synthase.[7]

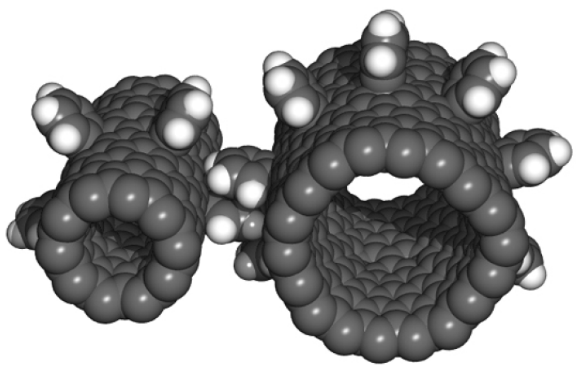


Fig. 9: A nanogear with benzyne molecules bonded as teeth.[8]

- **PEPTIDES**
  - Peptide-based self-assembling materials
    - Nanostructured peptides (nanopillars, -crystals, -rods, -wires, -tubes, -filaments, -fibres and -shells)
    - nanocontainers
    - metallic nanowire
    - peptides templates for silicon particle formation
  - Peptides for molecular recognition
    - peptides recognizing metal surfaces, carbon nanotubes
  - Template forming peptides

[7] Image credit: www.science.doe.gov/bes/scale_of_things.html
[8] Image credit: NASA: http://www.ipt.arc.nasa.gov/carbonnano.html

- Metal nanowires, silicon particles

➢ **CARBOHYDRATES**
  - crystalline cellulose
  - lectins for molecular recognition

➢ **VIRUS PARTICLES**
  - structured materials using virus as structural components

➢ **LIPIDS**
  - nanocontainers and Liposomes
  - lipid bilayers as support or template for self assembly

➢ **DNA**
  - 2D DNA lattices
  - 3D cages and networks
  - Hybrid structures of DNA and protein
  - DNA templates (see fig. 10+11):
    - Nanowires
    - Nanomechanical DNA device

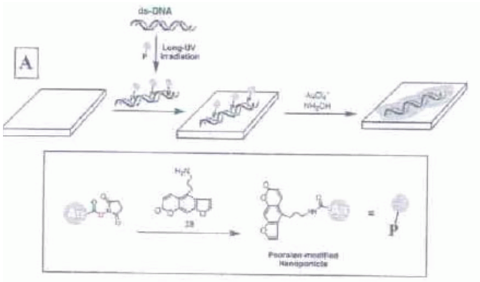


Fig. 10: DNA templated nanocircuitry: DNA can function as a template for a variety of structures.

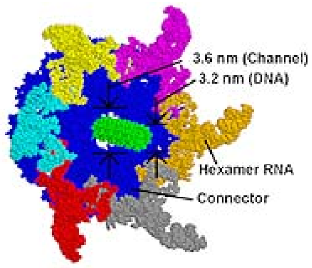


Fig. 11: A prototype of the "Viral Protein Nano Motor" based on DNA which is expected in 2007.[9]

➢ **COMPOSITES**
  - Magnetsomes
  - ferritin
  - Ca-biomolecule composites

[9] Image credit: http://www.spacedaily.com/news/nanotech-03zw.html

5) Nano-polymers

5.1 Definition of the material category

The study focuses on nanopolymers and polymer nanocomposites.
Nanopolymers are nanostructured polymers. The nanostructure determines important modifications in the intrinsecals properties. Multiscale nanostructuring and the resulting materials properties across the hierarchy of length scales from atomic, to mesoscopic, to macroscopic is an absolute necessity as we go down the road in the next decades to realizing the tremendous potential of nanostructure science and technology. We need to learn the control of nanostructure size and size distribution, composition, and assembly.

The term polymer covers a large, diverse group of molecules, including substances from proteins to high-strength kevlar fibres. A key feature that distinguishes polymers from other large molecules is the repetition of units of atoms (monomers) in their chains. This occurs during polymerization, in which many monomer molecules link to each other.

Because polymers are distinguished by their constituent monomers, polymer chains within a substance are often not of equal length. This is unlike other molecules in which every atom is accounted for, each molecule having a set molecular mass. Differing chain lengths occur because polymer chains terminate during polymerization after random intervals of chain lengthening (propagation).

The attractive forces between polymer chains play a large part in determining a polymer's properties. Because polymer chains are so long, these interchain forces are amplified far beyond the attractions between conventional molecules. Also, longer chains are more *amorphous* (randomly oriented). Polymers can be visualised as tangled spaghetti chains - pulling any one spaghetti strand out is a lot harder the more tangled the chains are. These stronger forces typically result in high tensile strength and melting points.

Polymer nanocomposite (PNC) is a polymer or copolymer having dispersed in its nanoparticles. These may be of different shape (e.g., platelets, fibers, spheroids), but at least one dimension must be ca. 1 to 50 nm (diameter of pencil lead is about 1 mm, or 1,000,000 nm). PNC with all three types of nanoparticles have been prepared (e.g., polycarbonate with carbon nanotubes, polyamide with iron oxide spheres), but only PNC with clay platelets are on the market for the structural (high volume) applications. These PNC's belong to the category of multi-phase systems (MPS, viz. blends, composites, and foams) that consume ca. 95% of plastics production. The key to industrial success of MPS is the desired and stable morphology. Thus, these systems require controlled mixing/compounding, stabilization of the achieved dispersion, orientation of the dispersed phase, and optimization of interactions in the finished product. In spite of differences in the nature of the dispersed phase, the compounding strategies for all MPS, including PNC, are similar.

Today, we must be able to manipulate matter at ever finer size scales, and we must eventually use computational approaches in directing this, if we are really going to take full advantage of the available opportunities. Theory and modelling are essential. Fortunately, this is an area in which the sizes of the building blocks and their assemblies are small enough that one can, with the ever increasing capabilities in computational sciences.

Multiscale nanostructuring and the resulting materials properties across the hierarchy of length scales from atomic, to mesoscopic, to macroscopic is an absolute necessity as we go down the road in the next decades to realizing the tremendous potential of nanostructure science and technology.

Furthermore, we need to understand the critical roles that surfaces and interfaces play in nanostructured materials. We need to know in detail not only the structure of these interfaces, but also their local chemistries and the effects of segregation and interaction between the nanoscale building blocks and their surroundings. We need to learn the control of nanostructure size and size distribution, composition, and assembly.

5.2 References

The trends in this report are mainly based – as in the other reports – on patents, projects, literature search. In this context, around 44 patents were found for this topic via the EPO database acceded through espacenet. Furthermore, 41 references mentioned in a literature survey as books and 42 European and national R&D funded projects are listed in this report. Also, 73 references are listed in the part for the classification of the nanopolymers. In addition, for the validation of this study 5 expert interviews were carried out.

5.3 Trends and future applications

When nanoparticle becomes a great topic in enhancing polymer's mechanical property, it is a natural combination into microcellular foam. Nanoparticles could be an ideal nucleating agent and even dispersion can generate interfacial volume as nucleus for microcellular morphology. This nano-microcellular polymer could be a great product with an impressive performance/weight ratio; excellent physical, mechanical and thermal properties.

The nanopolymers are one of the most important nanomaterial for the future. Nanopolymers has applications in medicine, energy and materials science.

5.4 Market analysis

The other challenge is to explore the finest cell size, highest cell density, and MCF density. Is nano-cellular possible? It will then be a pure material development. The main advantages of CPNC (clay-containing polymeric nanocomposites) stem from the improved stiffness (by a factor of 2 at 5 wt% loading), reduction of gas and vapour permeability (by a factor of 100 at 10 wt% loading), and reduced flammability. Since these enhancements are achieved with only a slight increase of density, the transport, and packaging industries are expect to be the first to profit from this new technology.
Up to now two principal obstacles hindered progress of CPNC into the market: the cost and reproducibility of performance. The demonstrated by Kato et al. suitability of Na-MMT reduces the cost of the nano-filler from ca. $7 to $2 per kilogram, and at the same time reduces the probability of thermo-mechanical degradation during processing and forming. Many questions remain the foremost being whether the achieved improvement of technology is sufficient to lower the cost and improve stability to satisfy the industry standards. Evidently, the future of CPNC technology hinges on the intelligent application of the available compounding and processing technologies, adopted for the specific needs of the nano-scale mixing.

5.5 List of relevant nanomaterials for future industrial applications

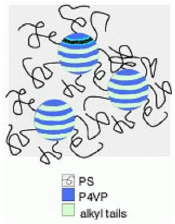
Nanopolymers are a new area in the materials science, in which it is difficult to realize a material classification, the next list is a primary approximation.

CLASSIFICATION:

- SELF-ASSEMBLED STRUCTURES:
  - Lamellar
  - Lamellar-within-spherical (1)
  - Lamellar-within-cylinder (2)
  - Cylinder-within-lamellar (3)

- o Spherical-within-lamellar (4)
- o Construction units types for self-assembly structures

(1)



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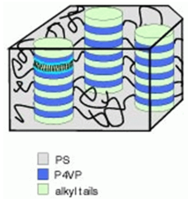

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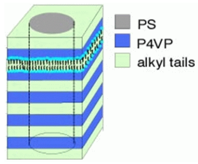

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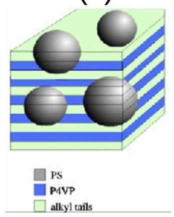
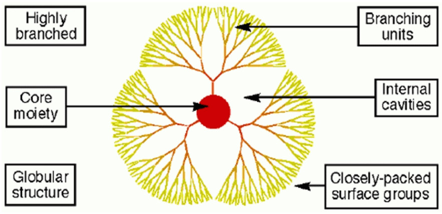
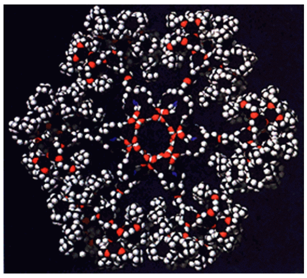


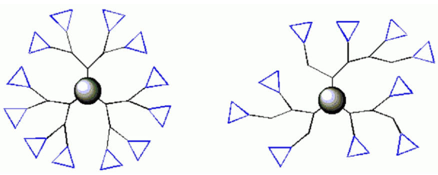
- ➢ NON SELF-ASSEMBLED STRUCTURES:
  - o Dendrimers (5)
  - o Hyperbranched polymers (6)
  - o Polymer brushes (7)
  - o Nanofibers (8)
  - o Polyphosphazene
  - o Polymeric nanotubes (9)
  - o Nanocapsules (10)
    - ▪ Eudragit: poly (methylacrylic acid-co-methylmethacrylate)
    - ▪ P(MAA-g-EG): poly (methacrylic-g-ethylene glycol)
    - ▪ HPMC-AS: hydroxypropylmethylcellulose acetate succinate



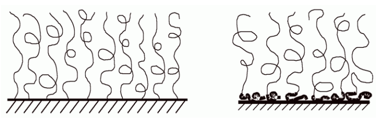
(5) Dentritic structure



e.g. Poly(amidoamine) (PAMAM)



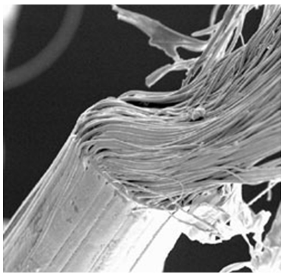
(6) Schematic comparison between a perfect dendrimer and a hyperbranched polymer with a central core and multiple functional endgroups in the periphery e.g. amphiphilic hyper-branched polyblycerols.



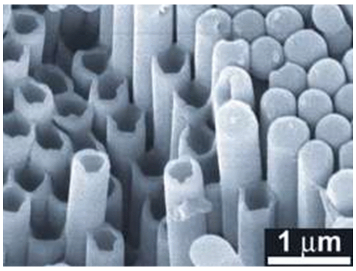
(7) Polymer brush systems: (left) end-grafted polymers and (right) adsorbed diblock copolymers e.g. Polystyrene/ Poly methyl methacrylate (PMM).

SIXTH FRAMEWORK PROGRAMME

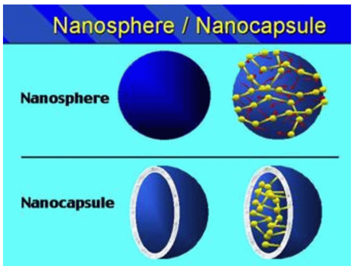
nanoRoad sme



(8) Nanofibers: e.g. Polyethylene nanofiber



(9) Polymeric nanotubes: e.g. Polystyrene nanotubes



(10) Nanocapsules

- Porous materials
  - Polystyrene-block-poly (4-vinylpyridine) (PS-block-P4VP)
  - Poly(α-methylstyrene)-block-poly(2-vinylpyridine) (PMS-b-P2VP)
  - Poly (2-vinylpyridine) (PVP)
  - PS-PVP hybrid nanolayers
- Nano-objects

➢ OBTAINING NANOSTRUCTURES ON POLYMERIC SURFACES: NANOLITHOGRAPHY
- Nanoimprint
- Soft lithography
- Electron-beam lithography
- Dip-pen lithography

6) Nano-glasses

6.1 Definition of the material category

In this study a series of amorphous nanomaterials has been considered. Amongst them SiO_2 is the most relevant for optical applications as opaque pigment, for the manufacture of light diffusers in LEDs, band gap photonic materials, paintings, etc. Also, other non-amorphous materials are of great importance in optical applications, such as ITO and nanostructured materials, such as nanofibers and nanotubes.

In addition to nanomaterials also the processes and applications in a nanometric scale, such as nanolithography, design of optical nanodevices (lenses, diffraction gratings, etc.) are of a crucial relevance in nanooptics and they will also be considered in this work.

6.2 References

The conclusions in this report are mainly based on the search of EU and national projects, patents and literature survey. In this report, 58 EU, 23 national projects and 54 references in the literature survey are included. The patent search was done via the INSPEC database (EPO), they found approximately 57 patents, which were relevant for this study. Further, for the validation of this study 5 expert interviews were carried out.

6.3 Trends and future applications

Nano- and photonics technologies hold the potential for highly efficient communication and information systems of the future, both for defense and commercial applications. Nanooptics, a newly emerged combination of these technologies, opens new horizons in photonics, with a plethora of new phenomena, new materials, new designs and new attractive applications. Many materials- and performance-related problems in photonics engineering that cannot be solved today, because of the limitations due to the properties of the natural materials employed, have a potential to be successfully solved tomorrow, owing to the emergence of, and recent progress in, nano-science, nano-materials and nano-technologies.

Optical technology is Olympus's core technology that has been successfully incorporated in our digital cameras, binoculars, endoscopes, optical disks, and a number of other products. Concurrently, Olympus has built up enormous knowledge and experience in nanoprecision processing and measuring technology for the processing of high-performance lenses. Other innovations based on MEMS (micro-electrical-mechanical systems) include devices for measuring at the molecular level and scanning mirrors with nanopositioning capability. This technology has proven successful in the use of tissue samples, DNA, and genetic material in nanobiology. Bringing together leading-edge research in Japan and abroad, fusing nanooptics, nanomaterials, and nanodevices to create nanostructures with new functions and then researching how they can be applied in biosensing devices.

Current devices are the initial applications of SOEs, but the possibilities are expanding in several directions. SOE-based building-block functionality will be introduced both as chips and as packaged devices. Demonstrated SOE functionality spans polarizers, polarization beam splitters/combiners, filters, photodetectors and photonic bandgap devices. Dynamic control for switching, attenuation and tuning is also possible.

Monolithic integration of SOEs can be achieved by stacking SOE layers to create aggregated optical effects. Nano-imprint lithography permits direct layering on of SOEs without resorting to lamination techniques. Combining SOEs with optically active layers allows optical control circuits to be built, resulting in complex optical components "on-a-chip." Multilayer SOE integration has already been demonstrated by combining filters with photodetector arrays to create dynamic optical feedback loops.

Because SOEs are self-compatible and fabricated via wafer-scale manufacturing with relatively minor differences from device to device, the means exist to implement them.

Near-field optical microscopy shows great promise for achieving subwavelength optical resolution. Theoretical models of NSOM images are essential to utilize NSOM for nanoscale metrology. Our computational tools to model and interpret NSOM images, including finite difference and element approaches, mode expansion techniques, and scattering techniques, will be integrated into a general computational package to best exploit each technique. Specific applications will include tip design and optimization, scanning of evanescent fields by small metal tips, diagnostic imaging for optical waveguides, and local nanoscale engineering of optical waveguides. Nanooptics modelling of optical nanostructures will continue to identify and engineer structures optimal for use in quantum computing and local, intradevice optical communication.

6.4 Conclusions

Nanotechonology materials, like could be glasses, crystals, and amorphous have a direct application in optics. The optical response of these materials in nanostructure format has contributed to constitute the nano-optics.

Nano-optics is a branch of optics that describes the phenomena that occur when light interacts with nanostructures. That is, nanostructures are pieces of matter that are either very small in themselves or exhibit features of sub-wavelength dimensions down to a few nanometres. Small particles, sharp tips, single molecules or atoms, and semiconductor quantum dots are just a few examples that fall into this category. A major finding of nano-optics is that strongly enhanced and spatially confined optical fields can exist under certain conditions in the vicinity of nano-matter. The understanding and exploitation of such effects will have a major impact on future optical technology because it will strongly influence such important fields as high-resolution optical microscopy, optical data storage, nonlinear optics and optical communication. The recent progress in nano-optics and nano-photonics is based strongly on the ever-improving understanding of how to tune the properties of nano-matter, i.e. its geometrical shape and material composition, and how to manipulate the incident light in the right way to achieve desired effects, such as extreme local-field enhancement or control of the flux of light at sub-wavelength dimensions. Concomitantly, modern techniques for material processing on the nanometre scale, such as high-resolution focused-ion-beam milling, become more widely available, and novel, more complex (prototype) material structures can be created. A number of papers in this subjet issue deal with this task of getting better control over nano-optical fields.

The current trend towards nanoscience and nanotechnology makes it necessary to address the key issues of optics on the nanometer scale. The interaction of light with matter renders unique information about the structural and dynamical properties of matter and is of great importance for the study of biological and solid-state nanostructures. Near-feld optics and nano-optics in general address the key issues of optics on the nanometer scale covering technology and basic sciences. The technological side is represented by topics such as nanolithography and high-density optical data storage, whereas topics like atom-photon interactions in the optical near-field are representative for the basic sciences side. Of great importance are optical microscopy and spectroscopy which aim at selectively interacting with nanostructures and probing their physical properties on a nanometer scale.

Three branches can be considerated:
a) **Characterization** of optical devices to study the optical properties of new materials (near-field microscopes: AFM, confocal, optical near-field microscopy, tunnel microscopy).
b) **Production** of nanostructures by optical methods (nanolithography).
c) **Traitment** of materials by laser tools (ablation process).
Characterization of optical devices could be tunneling-electron luminescence microscopy for multifuncional and real-space characterization of semiconductor nanostructures. Time - resolved luminescence microscopy offers many advantages over conventional transmission and fluorescence microscopy. As well as the improved sensitivity inherent in luminescence microscopy, time-resolution offers the possibility of gating out short-lived fluorescence emanating from biological chromophores.
Nanolithography for production methods is the most extended technology to make nanostructured materials. Today, there is two main technologies: ion etching and electron beam, but others, like could be EUVL lithography and evanescence field based methods, are now being considerate as very good alternatives in the lithography area. EUVL uses extrem ultraviolet (EUV) radiation with a wavelength in the range of 10 – 14 nm. to carry out proyecting imaging. Currently, and for the last several decades, optical proyection lithographic techniques used in the high-volume manufacture of integrated circuits. Evanescence waves are used in lithography to make relief in many materials, it use the total reflexion situation to write at nanometer scale.
In the material treatment we find a extremal importance in the surface technology with coatings configurations. New materials are developed to ensure the aspect-ratio configuration at the nanometer scale when we would like to write on it by lithographic techniques. Laser ablation is a promising tool to create micro and nano-structures in polymers. Due to several drawbacks (i.e. high ablation thresholds, low ablation rates) it is only used in a limited number of industrial applications (i.e. drilling of nozzles for ink-jet printers and drilling of holes for multi-chip modules).
Other emergent technologies that we have found are Dip-Pen Lithography (using a Tip to write nanostructured motives) and hidrofobic materials, both can be used in microfluidic and interface surfaces for masive optical devices (mirrors, architecture, lighting,...)

6.5 List of relevant nanomaterials for future industrial applications

In the project the following nano-optical materials are taken into consideration:

- Metallic glasses (fig. 12)
- Electrochromics (fig. 13)
- Nano-Resist for lithographyc technologies (fig. 14)
- Nanoporous glasses
    - o Micropores of less than 2 nm in diameter
    - o Mesopores between 2 and 50 nm
    - o Macropores of greater than 50 nm
- Nanochannel glass materials
- Photonic glasses

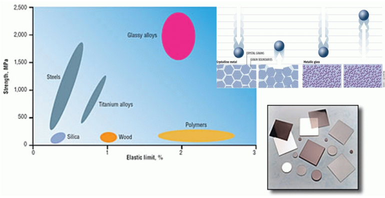


Fig. 12: Metallic glasses[10]

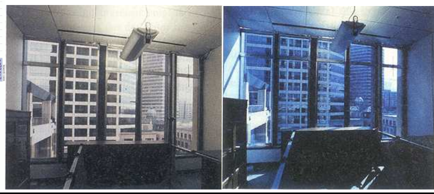


Fig. 13: Electrochromic glasses.[11]

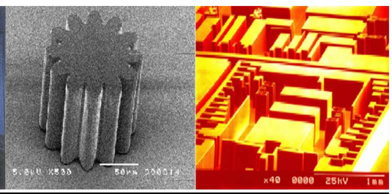


Fig. 14: Nano-Resist: Nano SU-8.[12]

[10] Image credit: http://www.er.doe.gov/Sub/Accomplishments/Decades_Discovery/images/26b.jpg
[11] Image credit: http://windows.lbl.gov/comm_perf/electroSys.htm
[12] Image credit: www.micro.me.gunma-u.ac.jp/www2000/micro-nano/

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7) Nano-ceramics

7.1 Definition of the material category

Materials which have been considered in the study are oxide and non-oxide ceramic materials, silicates and hard metals such as composites of these material groups.

7.2 References

In this report, the results are mainly based on the research of project, literature and patents. In the part of the project research, 41 R&D projects funded by the EU and 18 national R&D projects are considered. The literature research is mainly based on 39 publications of 7 different countries by a search in the FZK Technik since 1986. In the part of the patent research two different patent researches were carried, where one table is shown, in which the patents in this field are assigned to which application. In the first patent research in the field of “nano and ceramic”, 381 patents were found by using Delphion data base, where only 8 % belongs to EU. In the second patent research in the field of “nano and particles” 1482 patents were found. The patents belong to the following countries and parts of the world: WO, US,CN, JP, EU and DE. For the validation of this study 6 expert interviews in 6 different countries were carried out.

7.3 Summary

Nanocrystalline materials exhibit increased strength/hardness, enhanced diffusivity, improved ductility/toughness, reduced density, reduced elastic modulus, higher electrical resistance, increased specific heat, higher thermal expansion coefficient, lower thermal conductivity, and superior soft magnetic properties in comparison to conventional coarse-grained materials.
Since nanocrystalline materials contain a very large fraction of atoms at the grain boundaries, the numerous interfaces provide a high density of short-circuit diffusion paths. The enhanced diffusivity can have a significant effect on mechanical properties such as creep and superplasticity, and ability to efficiently dope nanocrystalline materials with impurities at relatively low temperatures. The increased diffusivity leads to increased solid solubility limits and increased sinterability of nanocrystalline powders.
The methods which have been commonly employed to synthesize these materials include both the top-down approach (breaking up larger microparticles by external forces) and the bottom-up approach. The latter is more effective since it provides a substantially wider spectrum of possibilities. Furthermore, chemical bottom-up methods allow to achieve high purity products, impurities introduced by comminution steps are prevented. The chemical synthesis routes can be further divided into liquid-solid transformations (e. g. sol-gel processing, co-precipitation, micro emulsion routes, electrochemical deposition or decomposition of liquid precursors) and gas-solid transformations (e. g. inert gas condensation, plasma processing, laser ablation or flame pyrolysis). Generally, the latter yield less agglomerated nanoparticles.
According to the experts from science and industry the German ministry of education and research (BMBF) defined five main lines of development, which are presented in the following: 1) production and application of ultra thin layers, 2) manufacturing and usage of lateral nanostructures, 3) fabrication and application of nanomaterials and molecular architecture, 4) ultra precise machining of surfaces and 5) measurement and analysis of nanostructures.

The main present task which has to be solved is an up-scaling of the most successful synthesis methods from lab scale to standard production processes able to provide monodisperse morphologies of powders in reliable quality in production scale. Today the question is, whether sales increase in the field of nanomaterials can be achieved by forward integration or by extension and improvement of production processes of the nanomaterials. Widespread application of nanocrystalline materials requires production of the powder in tonnage quantities and also efficient methods of consolitating the powders into bulk shapes. After solving this task, the whole potential of these powders must be used by coating techniques and functionalization. A remaining step which has to be gone in future will be to address and to align single particles. This would be necessary for manufacturing of nano capacitors or nano transistors.

7.4 Trends and future applications

Although products related to NT are already on the market (ceramics made of oxide nanomaterials, light filter substances, effect pigments, coatings, data storage layers, etc.), most areas of NT are still in the basic research stage. Still the market qualification carried out by analysts and experts has been vague and full of discrepancies; however, market-relevant applications in the fields of optics, precision engineering, analytics, chemistry, automotive and mechanical engineering, materials management and medical engineering, pharmaceutics and biology are anticipated.

Analysis of the state of the art of ceramics, identification of advantages and comparison of the various production methods for nanopowders allow the conclusion to be made that for nanopowders, realistic market opportunities exist primarily in those areas where materials with novel property combinations or at least with remarkably improved tribological, mechanical or corrosion properties can be produced. Realization of the market potential will only be possible if the following basic prerequisites are met:

- Reproducible powders having constant properties and acceptable prices must be able to be produced on both small and commercial scales.
- Powder processing, structural formation and materials production must be controllable.

The analysis of worldwide research activities has shown that both public funding of basic research and specific application-related research and development for the manufacture of marketable products and venture capital funds for the establishment of startups and spinoffs are needed. It is also recognized that targeted public funding and raising of the budget for Ceramic NT - especially in USA, Europe and Japan - allow a solid foundation for future competitiveness to be laid, since competitiveness and the technological basis required for it hinge upon the availability of capital and human resources. There is relatively good agreement among experts that the year 2005/2006 should see first market breakthroughs in Ceramic NT.

Significant advances in almost every area of technology can only be made if ever-smaller structures and increasingly complex systems composed of the widest possible range of materials are available. Experts and analysts see particularly great potential in high-performance and functional ceramics, due in part to the high annual growth rates of these materials. For expansion and opening up of new application fields in the future, these ceramics will have to exhibit novel property profiles. Through the use of nanopowders, the current disadvantages of ceramics - especially the high brittleness (low fracture toughness) - that are generally persistent at high temperatures and which result in low defect tolerance of ceramic materials and parts can be minimized. Emphasis was placed on nanoscale nonoxide ceramics and nonoxide nanopowders, which, contrary to oxide nanopowders, are not currently available on a commercial scale. The reasons lie especially in the necessity of:

- a low-cost production method for preparing deagglomerated powder of constant quality and particle size distribution (a significant barrier to further development in many areas);
- adaptation, redesign and development of innovative production technologies; and
- continuous cooperation between all links in the value-added chain, i.e., from raw material suppliers through powder, ceramic and parts manufacturers to the user, as well as the technology providers and research institutes.

Future samples key parts for the work with nonoxides are a ball bearing for silicon nitride and a drawing die for titanium carbonitride. The market analyses, research and expert interviews revealed the following trends, especially for ceramics and hard materials:

1. Due to relatively high powder prices and processing difficulties, applications for nanopowders are focused primarily on films or components of composite materials, in which the nanopowders produce specific effects. Nevertheless, apart from being used in powder form as fillers, thickening agents, insulation materials and support materials in pharmaceutics and medicine, for example, ultrafine particles are increasingly being used in the form of compact ceramic materials. Applications are not oriented solely towards thin and ultrathin films - they are also aimed at sensor materials, membranes and catalysts, transparent Al_2O_3 ceramics and superplastic ceramics, to name a few. Nanopowders can furthermore play a role in transparent polymers as UV absorbers or diffusion barriers, or they can be used to attain specific magnetic or dielectric properties in polymers.

2. Increasingly prominent is the use of nanopowders to reduce sintering temperatures and produce materials possessing submicrometer-sized structures. Use of these structures allows properties such as hardness and wear behavior to be improved, the sintering process and the resultant structure to be decoupled from one another and non equilibrium composite materials to be synthesized.

3. The market whose potential lies in the most distant future (and which currently has the smallest market size) is represented by the actual nanomaterials, that is, materials that possess nanoscale structures after being sintered. Such materials place extremely high demands on powder, processing and sintering technology. In the short term, considerable growth is expected to occur, especially in the area of composite materials in which one component is nanocrystalline.

4. The markets mentioned here can only be developed if a reproducible method for producing deagglomerated nanopowders possessing narrow grain size distributions exists. Such a method has been partially realized on a commercial scale for certain oxide powders (e.g., SiO_2, TiO_2); nonoxide nanopowders have yet to be produced on an adequate scale.

5. In order for nanoceramics to be successfully produced from powders, the powder processing step (deagglomeration, low-defect forming) must be controllable. Over the last few years basic knowledge has been acquired and the foundations for new technologies (e.g., the so-called colloidal methods of producing ceramics) have been laid.

6. A prerequisite for reduction of grain growth is an extremely narrow grain size distribution - which is currently far from being realized. The extent to which improvements in sintering technology (microwave sintering, SPS, etc.) can effect a reduction in grain growth and allow these processes to be implemented commercially is presently indeterminable.

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The individual trends listed here depict the increasing importance of nanotechnology and, especially, the reproducible production of nanopowders of sufficient quality as the key to further and broader application of such technologies. Oxide nanopowders are already being produced on a commercial scale for various applications (pigments, insulation materials, etc.), and the demand for nonoxide nanopowder products that realize the improvements in properties shown to be possible here is increasing.

7.5 List of relevant nanomaterials

- Tungsten cabide

Products already in use

- Alumina
- Zirconia
- Titania
- Silica
- Zinc oxide

already mass production of powders

- Silicon nitride
- Magnesia
- Ferric oxide
- Ceria
- Hydroxyapatite (HAP)
- Yttria
- Silicon carbide
- Boron nitride

Powders are developed, basic research and early applications

- TiC
- Amorphous silicon nitride
- AlN, TiN, ZrN, TiC_XN_{1-x}, ZrC_xN_{1-x}, $MgAl_2O_4$
- Si_3N_4-TiN, Si_3N_4-AlN, Si_3N_4-ZrN, AlN-TiN, AlN-ZrN
- Si_3N_4-Y_2O_3, Si_3N_4-MgO, AlN-Y_2O_3
- ZrO_2-Y_2O_3, ZrO_2-MgO, ZrO_2-Al_2O_3, $YBa_2Cu_3O_{7-x}$
- TiC_XN_{1-x}-Fe, Ni

Powders are commercially available in kilogramme scale

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