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NEWS METHODS OF SYNTHESIS OF NANOSTRUCTURED MATERIALS

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Abstract: The nanostructured materials, including ceramics can be obtained by different methods: mechanical methods, chemical, physical methods and mixed methods. This procedures are been described evidencing the method's principle, their advantages and disadvantages and also the tips of materials obtained by each method. This present work proposes to review the methods of synthesis of the materials for which a phase at least, determining for certain properties, has dimensions lower than 100 nanometers.

1. Theoretical considerations

Nanostructured materials are materials with a microstructure the characteristic length scale of which is on the order of a few (typically 1-100) nanometers. The microstructure refers to the chemical composition, the arrangement of the atoms (the atomic structure), and the size of a solid in one, two, or three dimensions. A nanomaterial consists of nanoobjects (of which the size is between 1 and 100 nm) - particles, fibers or tubes which present specific properties of the nanometric scale.

The nanometric field is governed by numerous phenomena of surface (photosynthesis, catalyze, precipitation, reactivity, deformation, reflection, luminosity,..). In these news materials the number of atoms which are localized on surface is greater than the number of atoms localized inside the grain. The present and futures applications of these materials are extremely various in all the fields of our life: electronics, aeronautical industry, medicine, foods, and army.

2. Nanomaterials classification

The nanobjects are used like catalyst, to transport drugs, for the polishing of wafers and hard disks in micro-electronics, or in order to work out materials - gathered according to 3 families of products:

- materials nano-charged or nano-reinforced,
- materials nano-structured in surface (couches minces)
- materials nano-structured in volume.

3. Methods to produce nanomaterials

For producing nanomaterials in bulk powders a number of processes are used, coatings, thin films, laminates and composites. The current processes allowing the development of nano-objects are classified in four main categories:

- Synthesis by mechanical method,
- Synthesis using physical methods,
- Synthesis by chemical way,
- Mixed methods.

For one half-century approximately have appeared new techniques of fast cooling, of chemistry known as soft, technical techniques ground-freezing for example, which give access at sizes of grain much lower than the micron, in the field of nanomaterials. The other methods of production under electric arc, laser, plasma or microwaves product materials of very small size. In parallel of this step of miniaturization, known as " signal-down ", develops another step, known as " bottom-up ", which consists in building in a controlled way from atoms and molecules the new buildings and structures. Effects controlling the properties of nanostructured materials include size effects (where critical length scales of physical phenomena become comparable with the characteristic size of the building blocks of the microstructure), changes of the dimensionality of the system, changes of the atomic structure, and alloying of components (e.g., elements) that are not miscible in the solid and/or the molten state.

Mechanical alloying represent a process where high-energy ball milling is used to grin and refine the structure to produce highly mixed, ultra-fines powders. Grain size are partially depend on time, where extended milling times result in more uniform grain size. One of the advantages of the mechanical alloying process is the producing large quantities of nanostructured material. But the contamination from the milling hardware and environment, non-uniform particle size and non-homogeneous chemical composition due to incomplete milling reaction are the main disadvantages of this process. [1,2]

In the physical methods category are included: the solid state reaction, chemical vapor deposition (CVD), physical vapor deposition (PVD), jet vapor deposition, etc.

The solid state process consists in the reaction in solid phase of the components at high temperatures for producing the new phase at a conveyable speed. The advantages are the simple dosage and exact dosage of components involved in reactions that can make possible the obtaining of rigorous composition. The disadvantages consist in the apparition of non-homogeny particles and the using of high temperature reaction. One of the most important processes utilized in fabricated nanostructured film is chemical vapor deposition. This process involves a gas-phase chemical reaction which forms a solid material on a substrate. Nanostructured ceramics and composites are the most nanomaterials produced by CVD. [2-4]

The most used chemical methods for producing the nanomaterials are: the precipitation and coprecipitation (hydrolyze method), sol-gel process, hydrothermal process. These processes consist in reactions in aqueous solutions of electrolytes or organics solution. Depending of parameters process: pH, temperature, concentration can precipitate solid precursors. By calcinations of these precursors can be obtained nanopowders with homogeneous composition, which grain size are depending of the reaction conditions.

The simple oxides are produced by hydrolyze process by adding a mineralizing agent. The coprecipitation process is utilized for synthesis of mixed oxides. The advantages of these processes are: the accessibility of precursors, the producing of nanopowders with homogenous chemical composition. The agglomeration of powders and the simultaneous coprecipitation of all cations from solution are the main disadvantage of hydrolyze method.

The sol-gel process is a solution phase processing technique that is used more often to fabricate nanostructured materials that any other liquid phase process. This is a process capable of producing nanostructured ceramics and composites. A disadvantage to this process is that the starting materials can be expensive. The advantages are: the excellent control it provides over the chemical composition, which leads to a more homogeneous composition, large quantities (to be commercially viable) relatively cheaply, capacity of synthesize almost any material and co-synthesize two or more materials simultaneously, obtaining the coat of one or more materials onto other materials, capacity to produce extremely homogeneous alloys and composites, synthesis ultra-high purity materials and precisely control the microstructure of the final products.

The hydrothermal synthesis became in the last decade a very interesting route for the synthesis of different nanostructured materials as powders and thin films controlled composition, grain size, texture. The principal advantages of hydrothermal process concerning the mechanism and the homogenous kinetic of reactions consist in: versatility, reduction of technological operations number, the energy cost and chemicals agents, elimination or reduction of effluents, fabrication of nanocristallins powders, monodisperses whit high reactivity, low cost and energy.

The mixed process to produce nanostructured materials are: electrodeposition, hydrotremal-electrochemical process, hydrothermal-mecanochemical process. These involved the combination or two or three process. The more used technique for producing the nanostructured materials is electrodeposition process. This process is capable of producing a nanocrystalline material with grain size down to 5 nm. The factors affecting the resulting grain size include pH, temperature and current density. Moreover, electrodeposition is a less expensive process that can be used for large-scale production.

The properties of nanostructured materials deviate from those of single crystals (or coarse grained polycrystals) and glasses with the same average chemical composition. This deviation results from the reduced size and dimensionality of the nanometer-sized crystallites as well as from the numerous interfaces between adjacent crystallites.[1,2] Consequently, it was possible to reduce the sizes of grain at dimensions characteristic of the defects which control some properties like dislocations (mechanical properties) or the walls of Bloch (ferromagnetic properties), or the phenomena which do not interfere only on the scale of the nanometer or below (tunnel effect, effects of "restraint" when the size of the particles is lower than the length of wave of the particles — electrons, photons... — which intervene in the phenomenon studied). These dimensions, according to cases vary between some nanometers and 100 nanometers.[3-5]

An attempt is made to summarize the basic physical concepts and the microstructural features of equilibrium and non-equilibrium nanostructured materials. When the size of crystallites is of the order of the nanometer, the fraction of atoms located at the surface of the grains becomes significant. Grain boundaries make up a major portion of the material at nanoscales, and strongly affect properties and processing. The structure of the grain boundaries of nanomaterials is very different of that of materials of current size of grains. The development of applications in correlation with their unique properties in a very large industry scale made possible the development of the synthesis techniques.

2. Structure of the joints

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grain, there exist many phenomena which are controlled by the properties of the grain boundaries:
— those which result from the diffusion to the grain boundaries, mainly growth of the grains and mechanical properties.
— certain changes of crystallographic structure which interfere on a nanometric scale.

Nanocrystallites of bulk inorganic solids have been shown to exhibit size dependent properties, such as lower melting points, higher energy gaps, and nonthermodynamic structures. In comparison to macro-scale powders, increased ductility has been observed in nanopowders of metal alloys. In addition, quantum effects from boundary values become significant leading to such phenomena as quantum dots lasers.

Also thermodynamic and kinetic properties of materials, in this case, are primarily controlled by the joints of grains. They may be in or far away from thermodynamic equilibrium. For example, nanostructured materials consisting of nanometer-sized crystallites of Au or NaCl with different crystallographic orientations and/or chemical compositions vary greatly from their thermodynamic equilibrium. Nanostructured materials synthesized by supramolecular chemistry yielding nanoassemblies are examples of those in thermodynamic equilibrium. [1]

3. Conclusions

Nanomaterials possess many unique chemical, physical, and mechanical properties. Due to these beneficial properties, nanomaterials are being favorably considered for a wide variety of structural, non-structural, biomedical, and microelectronic applications. However, widespread application of nanomaterials is severely hampered by the lack of suitable commercial-scale production techniques and high manufacturing costs. Furthermore, the applications are limited by the lack of suitable processing techniques to consolidate these nanocrystalline powders into shapes without any significant grain growth. New applications for nanomaterials in all the sectors of industry are also being discovered almost daily.

REFERENCES

[1]. Kerber Michael B., Shafler Erhard, Zehetbauer Michael J., Processing and evaluation of X-ray line profiles measured from nanostructured materials produced by sever plastic deformation, Rev. Adv. Mater. Sci. 10, 2005, pag. 427-433;
[2]. Matijevic E., Ultrastructure Processing of Advanced Ceramics, Ed. J.O. McKenzie, 1988, pag. 429-431.
[3]. H.ZhaQ.X. , Klason P., Solid and soft nanostructured materials: Fundamentals and applications, Microelectronics Journal, No. 36, 2005, pag. 940–949.
[4]. Wang Z. L., Kang Z. C., Functional and Smart Materials, Structural Evolution and Structure Analysis, Plenum Press, New York, 1998.
[5]. Byrappa K., Yoshimura M., Handbook of Hydrothermal Technology, A technology for Crystal Growth and Materials Processing,William Andrew Publishing, LLC Norwich, New York, 2001.