

Toward Applications of Ceramic Nanostructures

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Guest Editors

Abstract

This article serves to introduce the January 2004 issue of *MRS Bulletin* on progress toward applications of ceramic nanostructures. Conventional ceramic materials are widely used today in areas ranging from structural to biological applications, and in devices as diverse as lasers, semiconductors, sensors, and piezoelectric components. Such materials include oxides, carbides, nitrides, mixed oxides, and composites. Over the last decade, the use of ceramic nanostructures has already changed the approach to materials design in many of these applications, by seeking structural control at the atomic level and tailoring of the engineering properties. The articles in this issue review the advantages of nanoceramics, their application in various fields, and the challenges involved in their fabrication.

Keywords: bioceramics, consolidation, nanoceramics, nanocomposites, nanostructure, nanotubes, photovoltaics, semiconductors.

Materials scientists today are being challenged to discover, build, control, and test structures whose dimensions range in the nanometer scale and to demonstrate the potential of these nanostructures in scientific, industrial, or medical applications while keeping in mind their potential impact on society. The resulting so-called nanotechnology, which implies the control of matter at the atomic and molecular level, is requiring researchers to work across not only the boundaries of classical scientific disciplines, but also those of other fields, including the social sciences and education.^{1,2} Figure 1 gives a basic scheme of the interdisciplinary character of nanotechnology by showing the overlaps between the science of nanotechnology and various application fields.

As often happens in the early stages of a promising new technology, strong hopes have been placed on nanomaterials to solve all the current problems in many scientific fields, from electronics, optoelectronics, and photonics to energy storage, medicine, and biology. It is indeed true that many nanoscale approaches that have been proposed can in principle provide solutions to difficult scientific problems; successful

demonstrations of this have been made in laboratories throughout the world (see References 3–9 for examples). Some applications that have already benefited from

nanomaterials and nanotechnology are mentioned in Figure 1. However, a delicate point to address is that the integration of nanotechnology in current industrial processes remains a challenge.

Gaining an understanding of and, ultimately, control over the properties and behavior of a wide range of materials at the nanoscale is now a major theme in materials research. The properties of the resulting products and devices ultimately depend on how the atoms are arranged in the material. For example, atoms in coal can be rearranged to make diamond; atoms in sand can be manipulated (with the addition of a few other trace elements) to make computer chips. As researchers' ability to synthesize materials and fabricate structures at the nanoscale improves, effective characterization becomes a stringent requirement. Although new instruments with enhanced sensitivity and resolution may be necessary, innovative approaches are essential for tackling the problems, addressing the difficulties, and finally reaching solutions that will lead to new products and devices fabricated on the nanoscale.

This issue of *MRS Bulletin* specifically deals with ceramic nanostructures. Ceramics have been known since the early days of human civilization. The word "ceramic" comes from the Greek *keras*, meaning horn. In prehistoric times, animal horns were used as containers; later, containers made out of clay were used to store food, water, wine, and oil. *Keramika* describes the working of the clay into pottery. Observing the hardening of the clay under the hot desert sun may have given our ancestors the idea that clay would

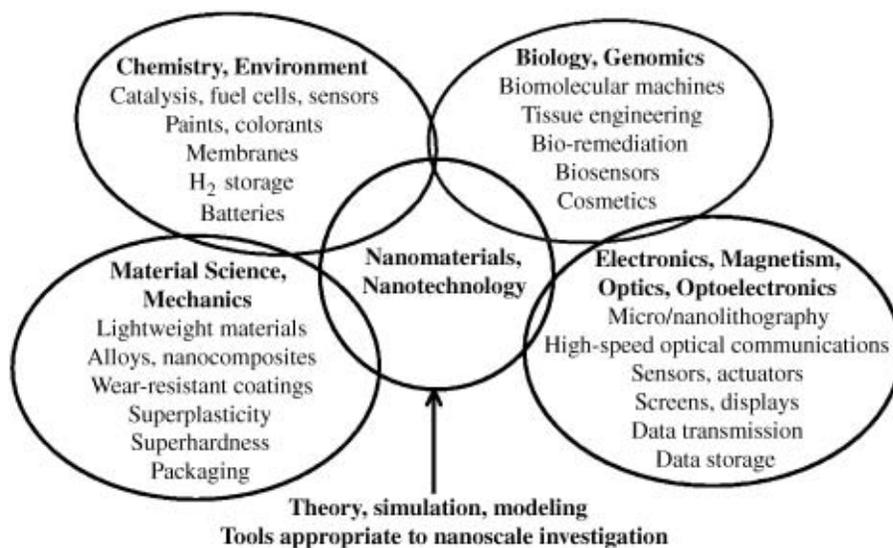


Figure 1. Schematic illustration of the interdisciplinary character of nanotechnology, showing the overlaps between the science of nanomaterials and application fields.

harden even more if subjected to firing. Over the centuries, the technology of ceramic fabrication, at the macroscale at least, evolved to high levels of sophistication and artistry (Figure 2).

Since the beginning of the industrial era in the 19th century, ceramics have been steadily integrated in the fabrication processes for technological applications. Conventional ceramic materials are widely used today in areas ranging from structural to biological applications and in devices as diverse as lasers, semiconductors,

sensors, and piezoelectric components. Such materials include oxides, carbides, nitrides, mixed oxides, and metal/oxide composites. Over the last decade, with the successful upscaling of their production, nanoceramics have been revolutionizing traditional materials design in many applications, by the tailoring of their properties via structural control at the atomic level. Some of the advantages of nanoceramics in various fields of application can be highlighted:

- Manufacturing defect-free powder products in all classes of complexity with uniform density;
- Improving the quality and performance characteristics (hardness, plasticity, wear resistance, uniform density, etc.) of sintered ceramic products as a result of their nanostructured formation;
- Reducing the size of electronic devices (transistors), thanks to nanocrystalline gate insulators with higher dielectric capabilities;
- Developing ceramic coatings for greater biocompatibility in medical implants; and
- Using ceramic nanoparticles as drug carriers for site-specific drug delivery.

This issue of *MRS Bulletin* is aimed at addressing the needs in the field of ceramic nanostructures for industrial applications, as illustrated by several articles contributed by researchers from around the world (United States, Europe, Japan, and Australia). Our intent is to provide examples of the development of nanoceramics and their wide range of applications rather than to give a comprehensive treatment of only one aspect of this extremely active and rapidly growing field of research. Several generations of nanotechnology products are expected to evolve from relatively simple nanostructures for products such as ceramic coatings and hard metals, to active components such as nanoscale transistors, and then to nanosystems with new architectures.

The first article, by Seal et al., illustrates the promises and pitfalls of nanotechnology, which are mostly based upon the ability to produce bulk nanostructured parts exhibiting novel properties at the macroscale.¹⁰ The authors describe the present state of knowledge of the fabrication and consolidation of so-called nanocomposites, defined here as a class of materials in which at least one of the constituents is in the nanometer domain. Special emphasis is placed on some encouraging results in the plasma-forming of bulk parts. Future challenges for developing methods for consolidating large nanocomposites while retaining their nanostructure are also highlighted.

The second article, by Kuntz et al., is a complement to the first and focuses on nanocrystalline ceramic composites (defined here as having both phases in the nanometer domain) specifically designed for applications requiring improved fracture toughness. While the models and theory of toughening mechanisms in microcrystalline composites are well developed, the same cannot be said for their nanocrystalline counterparts. The difficulty in producing fully consolidated ceramic composites that retain a nanocrystalline structure is the main hurdle to thorough investigations in this area. Thus, much of the research on “nanocomposites” has actually been on materials with microcrystalline matrices and nanometric secondary phases. This article focuses on the production and testing of composites that have nanocrystalline structures for both the matrices and the secondary phases. The microcrystalline mechanisms and current results are reviewed.

Nanoceramics in biomedical applications constitute the subject of the third article, by Ben-Nissan. An improved understanding of the interactions at the nanoscale between the bioceramics in human implants and the hard or soft tissues in the body could contribute significantly to the design of new-generation prostheses and post-operative patient management strategies. Overall, the benefits of advanced ceramic materials in biomedical applications have been universally accepted, specifically in terms of their strength, biocompatibility, hydrophilicity, and wear resistance in articulating joints. The continuous development of new-generation implants utilizing nanocoatings with novel nanosensors and devices is pertinent for better biocompatibility and improved well-being and longevity for the patients. This article gives a short overview of bioceramics and reexamines key issues of concern for the processing and application of nanoceramics as biomaterials.

Further application of nanoceramics in the biomedical arena is dealt with in the article by Kriven et al. The authors present results showing that bioresorbable nanoceramics can be used for drug delivery. For example, biofunctional molecules can be incorporated between hydroxide layers of clay nanoparticles to form bio-layered double hydroxide (LDH) nanohybrids. Once introduced into the cell, the LDH is purposely removed slowly by dissolving it in a pH-controlled environment, and the encapsulated biomolecules are thus released inside the cell. Preliminary safety studies with rats showed that there were no systemic effects as demonstrated by clinical chemistry and histopathology.

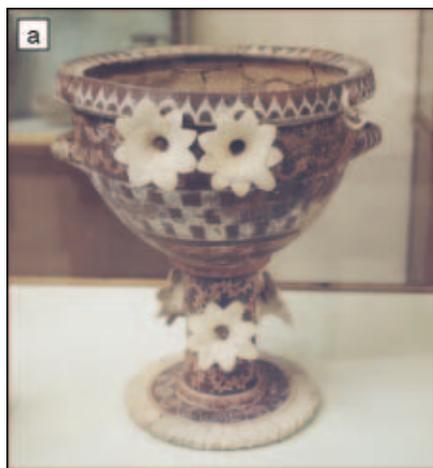


Figure 2. Examples of the high level of sophistication and artistry achieved in ceramic technology on the macroscale over the centuries. (a) Ceramic vase in the Kamares style from Phaestos, Greece, 1900–1700 BC (Archaeological Museum, Heraklion, Greece). Height, approximately 70 cm. (b) Limoges porcelain dish, France, 1834 AD (Adrien Dubouche Museum, Limoges, France.) Height, approximately 30 cm. Note that these two works are separated by an interval of almost 40 centuries. Photographs courtesy of M.-J. Baraton.

In vitro studies indicated that pristine LDH nanohybrid material had no cytotoxic or growth-inhibitory effects. From the pharmacokinetic *in vivo* studies, the possibility of using the bio-LDH nanohybrids as a device for slow-release intravenous drug administration can be suggested.

The fifth article, by Golberg et al., presents nanotubular structures in the B-C-N ceramic system that represent an intriguing alternative to conventional carbon nanotubes (CNTs). Because of the ability to widely vary nanotube chemical composition within the B-C-N ternary phase diagram and to change the stacking of C-rich or BN-rich tubular shells in multiwalled structures, a wide horizon opens up for tuning nanostructure electrical properties. Pure CNTs are metals or narrow-bandgap semiconductors, depending on the helicity and diameter of the nanotubes, whereas BN nanotubes are insulators with a ~5.0 eV gap independent of these parameters. Thus, the relative B/C/N ratios and/or BN-rich and C-rich domain spatial arrangements, rather than tube helicity and diameter, are assumed to primarily determine the B-C-N nanotube electrical response. This characteristic is highly valuable for nanotechnology because while tube diameter and helicity are currently difficult to control, continuous doping of C with BN,

or vice versa, proceeds relatively easily due to the isostructural nature of layered C and BN materials. In this article, recent progress in synthesis, microscopic analysis, and electrical property measurements of a variety of compound nanotubes in the ceramic B-C-N system is documented and discussed.

Besides structural materials, nanoceramics are intended to play a major role in photovoltaic devices, representing a potentially huge market. In the last article, Brabec et al. consider nanostructures, nanoparticles, and nanoceramics for novel photovoltaic devices and show that by controlling the morphology of organic and inorganic semiconductors on a molecular scale, nanoscaled *p-n* junctions can be generated in a bulk composite. Such a composite is typically called a "bulk heterojunction composite" and can be considered as one virtual semiconductor combining the electrical and optical properties of the single components. Solar cells constitute one attractive application for bulk heterojunction composites. The *p*-type semiconducting class encompasses conjugated polymers or oligomers, while for *n*-type semiconductors, inorganic nanoparticles as well as organic molecules are investigated. Due to the solubility of the single components, production relies on printing techniques.

The nonexhaustive examples of ceramic nanostructures presented in this issue demonstrate that multidisciplinary research in nanotechnology is not an option, but rather a necessity. It becomes therefore critical and urgent that researchers from various areas share their expertise and develop a common language. This will ensure faster integration of nanotechnology in industry, in the best interests of society.

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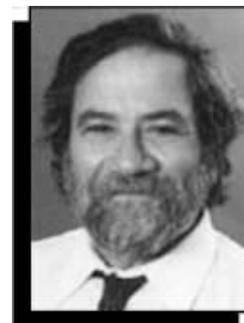
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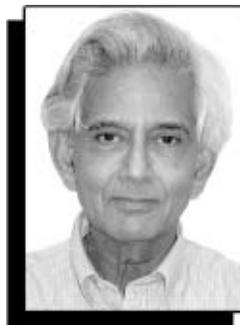


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