

Chapter 7

APPLICATIONS: CONSOLIDATED NANOSTRUCTURES

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7.1 VISION

Nanostructure science and technology (nanotechnology) is fundamentally changing the way that materials and the structures made from them will be manufactured in the future. Our increasing ability to synthesize and assemble nanoscale building blocks with precisely controlled sizes and chemistries into consolidated nanostructures and nanocomposites with unique properties and functionalities likely will lead to revolutionary changes in industry.

7.2 CURRENT SCIENTIFIC AND TECHNOLOGICAL ADVANCEMENTS

A number of major scientific and technological advances in the area of consolidated nanostructures have occurred in the past decade, and many more are expected. Such advances, some of which are listed below, have already led to commercial scale-up of some nanostructured materials and also to products incorporating them:

- Production of layered nanostructures with control of thickness at the atomic level and the subsequently developed ability to engineer the resisto-magnetic-field response by varying nanoscale architecture to make useful devices for magnetic recording
- Development of processes to net-shape-form nanophase ceramics and ceramic-based composites into finished parts while maintaining ultrafine grain size and nanoscale properties when desired
- Discovery and development of unique nanostructured hard and soft magnetic materials for a variety of applications, including information technology hardware
- Development of nanoscale cemented-carbide, hard materials for improved cutting-tool performance with superior wear resistance and fracture toughness
- Development of direct methods for fabricating nanostructured coatings yielding exceptional electrical, chemical, thermal, mechanical, and environmental protection of the coated parts
- Creation of a wide range of nanocomposites, such as nanoparticle- or nanotube-filled polymers, with enhanced or fundamentally new and controllable engineering performance, including significantly increased strength and reduced flammability
- Development of biological templating for the directed growth and patterning of nanostructures for biomedical and electronic applications
- Engineering of scaled-up and economical industrial processes for production of nanopowders and nanostructured bulk materials in the multi-tonnage range

7.3 GOALS FOR THE NEXT 5-10 YEARS: BARRIERS AND SOLUTIONS

In order to move nanostructure science and technology forward effectively during the next five to ten years, there are a number of significant issues that must be considered.

Significant Issues

- Nanostructured systems will be manufactured primarily from the bottom up using nanoscale building blocks and not from the top down as in conventional manufacturing methods.
- Up-front costs may be higher, but net commercial savings will result from more efficient design and processing, use of only necessary material, and decreased and less deleterious effluent.
- New scale-up methods will be required, along with novel scenarios for processing and handling of materials and parts.
- Statistically driven process controls with real time diagnostics and precise reliability standards will also be needed.
- Realistic multiscale theoretical modeling of nanostructuring and the properties and functionalities of the resulting nanostructures and systems will be important to their ultimate success.
- Understanding of the structure and properties of surfaces and interfaces and how to control these in a variety of nanostructure assembly strategies will need to be significantly increased.

Many new applications in the area of consolidated nanostructures will become available when these issues are faced and the appropriate barriers surmounted. Some examples follow:

- Ultrahigh-strength, tough structural materials
- Novel soft and hard ferromagnets
- Ductile and strong cements
- High-brightness displays based on nanotubes
- Bio-inspired medical prostheses
- Self-assembled arrays of biomolecular single-electron devices
- Drugs from consolidated nanoparticles

Several additional opportunities can be suggested that will lead to a wide range of useful developments:

- High-pressure sintering of nanophase oxide ceramics should be extended to difficult-to-sinter non-oxide ceramics for a variety of industrial applications, including high-efficiency automotive parts.
- Magnetic nanocomposites with 5-10-fold increases in magnetocaloric effects should be used to develop magnetic refrigerators that operate at room temperature.

- A unique new class of nanostructured permanent magnets with higher saturation magnetization values than are presently available should be developed for many information technology applications.
- Textiles and plastics filled with dispersed nanoparticles should be created that will enhance the materials' mechanical performances while reducing their flammability.
- Lithium-ion batteries composed of nanodispersed ceramics in polymer matrices should be developed for the next generation of lightweight rechargeable batteries for cellular telephones, laptop computers, and transportable CD players and radios.

7.4 SCIENTIFIC AND TECHNOLOGICAL INFRASTRUCTURE

In order for nanostructure science and technology, including the area of consolidated nanostructures, to reach fruition in the coming years, a number of infrastructure issues need to be addressed:

- Research funding in nanotechnology should focus on individuals or groups of researchers in universities with interdisciplinary interests, alone or coupled with industry in research/training partnerships, with the national laboratories providing support through unique major facilities and capabilities.
- The research funding process needs to be streamlined by reducing agency timelines, minimizing the proposal writing and reviewing logjam, and increasing significant inter- and intra-agency funding efforts, for example with shorter proposals and greater use of panel reviews.
- It is imperative to create a new breed of researchers who can think "outside the box" of traditional disciplines.
- Educating this new breed of researchers, who will either work across disciplines or know how to work with others across disciplinary lines in the interfaces between disciplines, is vital to the future of nanotechnology.
- Significant opportunities need to be created for academic training, to include industrial internships.

7.5 R&D INVESTMENT AND IMPLEMENTATION STRATEGIES

Besides the single investigator and group research programs, a national nanotechnology network should be established between existing and new nodal points at university centers, while at the same time extending the links to industry and the national laboratories. Research and training in nanostructure science and technology should be given high priority.

University nanostructure science and technology centers should be funded at a level in the range of \$1-5 million per year, with opportunities for renewal after 5 years. Matching funds from industrial partners must be a strong consideration. Additional funds should be earmarked annually in the Federal budget for these nanotechnology centers, without decreasing the normal program funding in this area.

The National Science Foundation's Grant Opportunities for Academic Liaison with Industry (GOALI) program provides an excellent model for university-industry collaborations in fundamental research. The Small Business Innovative Research (SBIR) and Small Technology Transfer Research (STTR) programs supported by Federal agencies remain attractive means for promoting technology transfer and implementation to put university research into industrial practice. The Department of Commerce's Advanced Technology Program (ATP) is another example of targeting research on industrial needs.

7.6 PRIORITIES AND CONCLUSIONS

The area of consolidated nanostructures has seen a great deal of progress in the past decade, with several commercially scaled-up processes now a reality, new jobs created, and new applications already in the marketplace. These successes have been based on the scientific and technological advances that have resulted largely from fundamental research, which then moved toward directed research and development, and from there to manufacturing. The benefits to be gained in the future are enormous compared to those that have been reaped to date. We must focus significant new resources to nurture the fundamental research that will provide the seedbed for future new ideas in consolidated nanostructures; at the same time we must develop new opportunities for training the scientists and engineers needed in this vibrant new field and providing a well lubricated path for technology transfer to industry and the marketplace.

7.7 EXAMPLES OF CURRENT ACHIEVEMENTS AND PARADIGM SHIFTS

Five detailed examples are presented here to elucidate some of the successes and considerable opportunities in the area of consolidated nanostructures. These include various nanostructured layers used in the creation of novel giant magnetoresistance devices for information technology hardware; nanoscale composites of ceramics and metals (cermets) used for hard coatings or wear parts in drilling operations; a novel nanoscale processing route for making a wide variety of ceramic parts; and well-dispersed nanoparticles used for flame retardation in plastics for transportation systems. Some of the examples are already commercial, while others are moving rapidly in that direction.

7.7.1 Nanostructures Used for Giant Magnetoresistance (GMR) Devices

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Giant magnetoresistance (GMR) is a nanoscale phenomenon first discovered in 1988 by A. Fert and coworkers in alternating nanoscale multilayers of Fe and Cr (Baibich et al. 1988). A number of material pairs consisting of a strong ferromagnet (e.g., Fe, Co, NiFe) and a weaker magnetic or nonmagnetic buffer (e.g., Cr, Cu, Ag) have been found to exhibit a similar response magnetoresistance effect in multilayers. The effect results from variations in electron scattering from the interlayer interfaces as an external magnetic field is applied parallel to the multilayers. The spins in alternate magnetic layers in the absence of an external magnetic field are oppositely aligned through anti-ferromagnetic coupling and yield maximum scattering, while in a sufficiently strong positively or negatively oriented external magnetic field, these spins align with the field, and hence, with one another, decreasing the scattering at the interfaces. However, it has

been subsequently observed that such sets of alternating, or one-dimensionally modulated, nanolayers are not the only architecture that exhibits GMR. Random distributions of spherical magnetic nanoparticles in a nonmagnetic matrix give similar results, although the rather large magnetic fields necessary to obtain a minimum resistance in all of these consolidated nanostructures are too large for most practical applications. The discovery that changing the modulation dimensionality of the GMR nanoarchitecture to three dimensions could lead to great reductions in the required magnetic fields has opened the way to the creation of a wide variety of useful GMR devices, some of which are shown schematically below (Barthélémy et al. 1994). Several such devices are now used in commercial information technology hardware, especially in magnetic reading devices.

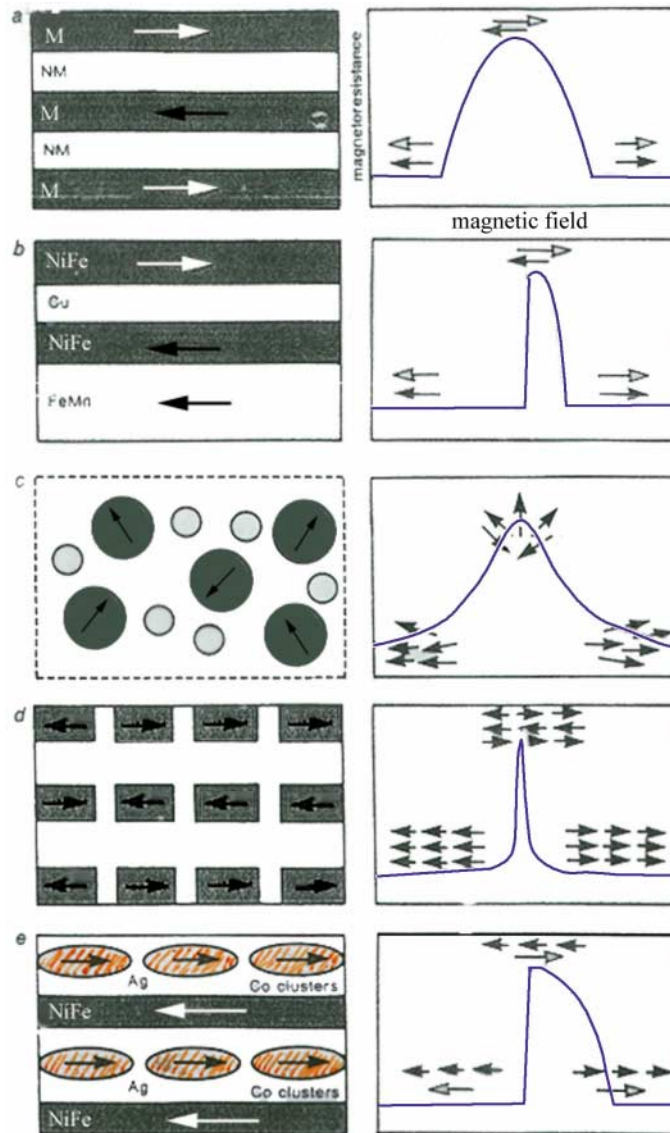


Figure 7.1. Various GMR nanostructures (left) and their magnetoresistance behavior (right—note that all the horizontal scales are different): (a) anti-ferromagnetically coupled multilayer; (b) spin-valve structure; (c) granular alloy; (d) multilayer with discontinuous magnetic layers; and (e) hybrid nanostructure including clusters and layers (reprinted by permission from *Physics World*, Barthélémy et al. 1994).

7.7.2 Nanostructured Hard Materials

Contact person: B.H. Kear, Rutgers University

Nanostructured hard materials are beginning to have commercial impact. It has become possible during the past decade to create cemented carbide nanocomposites, such as WC/Co and TiC/Fe, that have considerably enhanced hardness, fracture toughness, and wear resistance compared to their conventional grain size counterparts that are widely used in the manufacture of machine tools, drill bits, and wear parts. The exceptional properties of nanostructured materials are realized when the constituent WC and Co phases, for example, are interconnected in three dimensions, forming a so-called bicontinuous nanostructure. Typically, WC/Co products are produced by mechanically mixing powders of the constituent phases, followed by cold pressing and sintering. The difficulty of uniformly mixing ultrafine WC and Co powders by mechanical means has heretofore limited the scale of the WC grain size attainable in the final sintered product to about 300 nm. Over the past several years, new chemical methods have been developed for producing pre-mixed powders at the nanoscale level.

As an example, in one process that has been scaled up to produce tonnage quantities, spray drying is used to produce a homogeneous precursor powder of mixed tungsten and cobalt salts, followed by fluid-bed thermochemical conversion (pyrolysis, reduction, and carburization) to transform the precursor powder into the desired nanophase WC/Co product powder. Typically, the WC particle size in the agglomerated powder product is about 30 to 40 nm. Using liquid phase sintering and the addition of small amounts of a grain growth inhibitor such as VC, fully sintered nanocomposite products can be produced without inducing significant coarsening of the WC grains. Several hard metal companies are now using these powders in the manufacture of high performance parts, such as microtwist drills used for drilling holes in printed circuit boards (shown below in Figure 7.2); this is an industrial process in which drill tip wear has been a major problem.

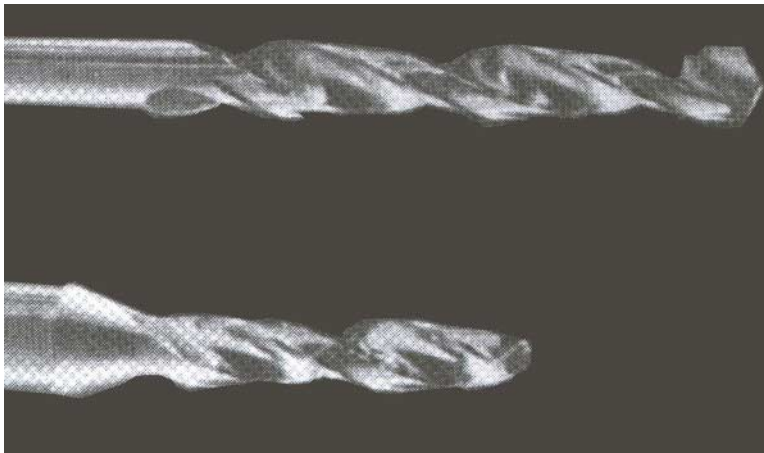


Figure 7.2. Uses for consolidated nanostructured hard materials: nanocomposite microtwist drill bit (top) compared to conventional product after wear for the same use time (courtesy Nanodyne Inc.).

In addition, with the recent availability of industrial-scale quantities of nanopowders of cermets and also ceramics, the use of nanostructured materials as feedstocks for thermal spraying of nanostructured coatings onto conventional parts is being explored through an

initiative of the Office of Naval Research (ONR) to implement the new technology into shipboard systems. Preliminary work has demonstrated that these coatings exhibit superior abrasion and corrosion wear resistance in diverse applications, which could lead to early introduction of such coatings into naval construction.

7.7.3 Ceramic Nanoparticles

Contact person: R.W. Siegel, Rensselaer Polytechnic Institute

A new processing route toward the economic manufacture of ceramic parts has been enabled by ceramic nanoparticles in the past few years. The ability to net shape form ceramics into final parts (as shown below in Figure 7.3) has become a reality in recent years, owing to advancements made in the scaled-up production and processing of ceramic nanoparticles. With the availability now of tonnage quantities of nanophase ceramic powders with their unique rheological and mechanical properties, it is possible to directly form ceramic parts in a sinter-forging mold under sufficient pressure and temperature to yield final parts with all of the definition and precision of the original mold. Nanophase ceramics such as titania and alumina, made from the consolidation of ceramic nanoparticles, have been shown in the laboratory to be readily formable into small samples, and studies of their mechanical behavior indicate that a significant degree of ductile behavior in compression is exhibited in these ultrafine grain size materials.

An understanding of this behavior has been developed in terms of earlier models of grain boundary sliding, in which grains (formerly nanoparticles before consolidation) can slide over one another under the influence of an applied forming stress without breaking the bonds across the boundaries between grains as a result of diffusional (atom transport) healing events taking place at any incipient cracks. This diffusional accommodation in the grain boundary regions over the very short distances involved in nanoscale materials is the key to enabling the net shape forming of nanophase ceramics and nanocomposites based on them. While still in the early stages of commercial activity, such net shape forming technology should have significant future impact.

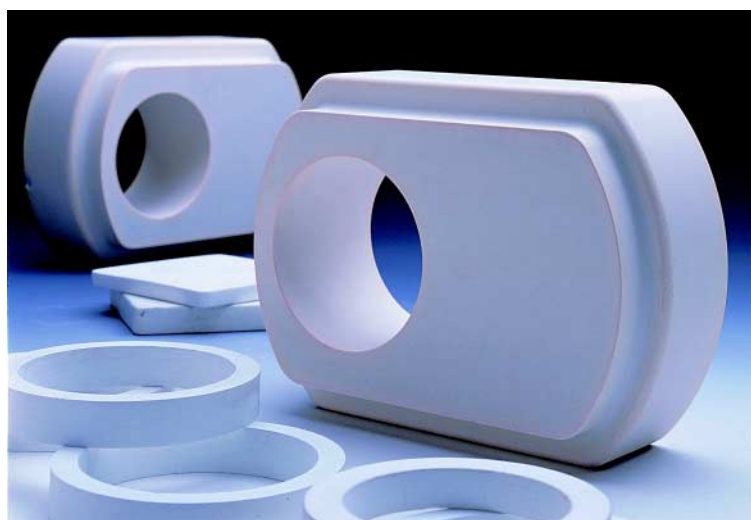


Figure 7.3. Net shape forming via consolidated nanoparticles (courtesy of Nanophase Technologies Corporation).

7.7.4 Fire Retardation in Plastics

Contact person: J.W. Gilman, National Institute of Standards and Technology

Plastics have rapidly infiltrated all aspects of society and have enabled many technologies that are commonplace today, such as aircraft, automobiles, and many consumer goods. However, beyond the many benefits of plastics, their inherent flammability is a continual concern in many applications. In addition to the hazard from fire, the concomitant smoke and toxic combustion products are a serious problem. The flammability of plastics can be considerably reduced by the addition of well-dispersed inorganic nanoparticles to form consolidated nanocomposites. For example, the heat release rates of thermoplastic and thermoset polymer-based materials are reduced by 40-60% in delaminated or intercalated nanocomposites that contain only 2-6 wt% silicate clays.

An example is shown in Figure 7.4. The nanocomposite structure of the char appears to enhance the performance of the char layer, which apparently acts as an insulator and a mass transport barrier, slowing the escape of the volatile products generated as the polymer decomposes. This marked reduction in flammability results in self-extinguishing characteristics and is achieved without the commonly observed decrease in mechanical properties and increase in evolution of carbon monoxide, soot, and toxic compounds associated with conventional flame-retardant additives: physical properties are not degraded, and processability is maintained. Beyond their flammability resistance, such nanocomposites have also demonstrated ablation resistance comparable to current state-of-the-art solid rocket motor ablatives. Ablative materials are critical for insulation applications in space and launch systems in order to protect aerodynamic surfaces, propulsion structures, payloads, and ground equipment from the severe effects of very high temperatures ($>2000^{\circ}\text{C}$), incident heating rates, and chemically oxidizing atmospheres with gas and particulate velocities that may range from Mach 0.01 to 10+. As little as 1.6 vol% of well-dispersed nanoscale layered silicate in nylon 6 is needed to form a relatively tough, inorganic char during ablation. This protective char results in at least an order-of-magnitude decrease in the mass loss (erosion) rate relative to neat nylon 6.

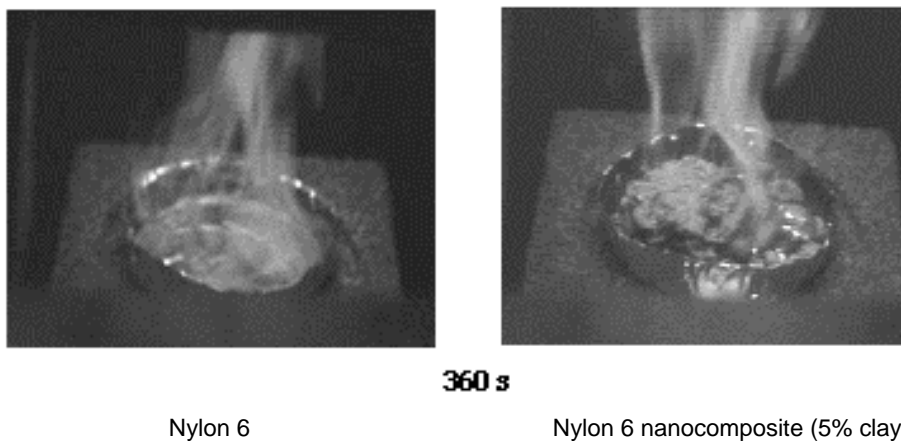


Figure 7.4. Flammability and thermal stability studies of polymer layered silicate (clay) nanocomposites (Gilman 1999; reproduced by permission).

7.7.5 Manufacturing of Nanostructured Coatings

Contact person: E. Lavernia, University of California, Irvine (UCI)

Thermal spraying of nanostructured coatings represents a potentially revolutionary approach to capitalizing on the unusual mechanical and physical attributes of nanostructured materials (e.g., hardness, toughness, and resistance to corrosion). When grain size is in the nanoscale range, the number of atoms at the grain boundaries becomes comparable to the number of atoms inside the grains. Because specific grain boundary area increases, the amount of impurities per unit grain boundary is lower than for larger-grained materials with the same bulk impurity concentration. This purification of the grain boundaries has been associated with more uniform corrosion morphology and higher intergranular corrosion resistance than larger-grained materials.

Recent work (Lau, Jiang, et al. 1998; Lau, Strock, et al. 1998) has demonstrated that it is possible to achieve dramatic enhancement in the physical behavior of nanostructured coatings, that is, coatings having grain sizes smaller than 100 nanometers (e.g., see Figure 7.5). Available results suggest that the nanometric grains are not only inherently thermally stable (Huang et al. 1996), but they also effectively block dislocation movement, giving rise to ultrahigh hardness, and in some cases, ultrahigh toughness values. Additional benefits of the nanometric grain sizes of the coatings include a reduction in the residual stress state of the coatings, which effectively allows, for the first time, the generation of thicknesses heretofore unobtainable—in some cases, four times thicker than those achievable with conventional materials. For example, various nanostructured coatings (Ni, Ni-based superalloy and stainless steel; $\text{Cr}_3\text{C}_2/\text{NiCr}$; and WC/Co) have been successfully thermal sprayed in UCI laboratories using high velocity oxygen fuel (HVOF) spraying. Comparison of the nanocrystalline coating characteristics to those of conventional coatings showed larger micro-hardness values for the as-sprayed nanocrystalline coatings than for the conventional coatings, an increase of 16 to 63%, depending on the gas composition and the milling method.

Potential applications span the entire spectrum of technology, from thermal barrier coatings for turbine blades to wear-resistant rotating parts. The potential economic impact is several billion dollars per year, and development of this technology will likely involve the aerospace industry (e.g., Boeing Corporation), the jet engine industry (e.g., General Electric), and the automotive industry (e.g., Ford) (Cheung et al. 1996, 479).

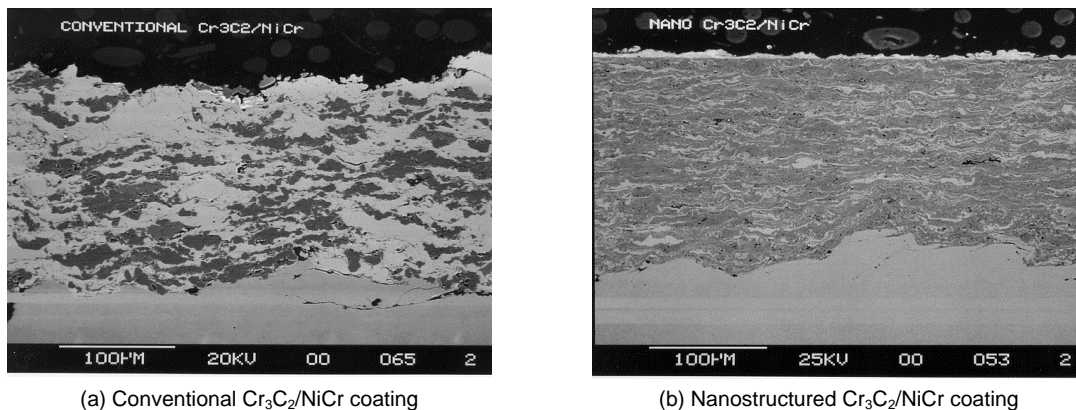


Figure 7.5. SEM morphology of conventional and nanostructured coatings.

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