# Introduction and Overview:
# Physical Properties of Nanostructured Materials

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This special issue of Journal of Electroceramics contains a subset of articles from a Research Needs Assessment commissioned by the U.S. Department of Energy, evaluating ''Future Use of Nanostructured Materials in Energy Applications,'' chaired by Y.-M. Chiang and J.Y. Ying. The study was stimulated by the increasing emphasis worldwide on the manipulation of materials structure and properties at the 1–10 nanometer size scale, and the recognition that certain special properties which arise at such length scales could have important impact on energy-related technologies. The written reviews in this study are the culmination of extensive communications by the individual authors with active researchers in the field, initiated at a Workshop held at MIT in December of 1994.

In defining the scope of the study, we took a broad view of ''energy applications,'' seeking to identify research areas in which nanostructured materials could benefit not only the perpetually important areas of energy production, conversion, conservation, and storage, but also energy-intensive processes such as waste remediation, chemicals production, and materials manufacturing. The articles in this issue address topics likely to be of particular interest to the readers of this journal: Nanostructured Catalysts (J.Y. Ying and T. Sun), Photochemistry of Nanostructured Materials (B. Levy), Nanostructured Carbons (M.S. Dresselhaus and G. Dresselhaus), and Solid State Electrochemical Systems (H.L. Tuller). Additional reviews on Physical Properties of Ultrafine Crystals (Y.-M. Chiang), Structural Nanostructured Materials (W.S. Owen), Separations (W.S.W. Ho and J.Y. Ying) and Nanostructured Magnetic Materials (R.S. O'Handley) will appear in the completed report.

Approximately a decade has passed since Gleiter [1] and co-workers suggested that compacts of very small crystallites (<10 nm) might possess unique physical properties which could be exploited in a variety of engineering applications. These predictions applied to properties other than the well-known effect of quantum confinement on electronic structure, which is the exemplar of a size-dependent physical property. At present, many materials can be fabricated as nanometer-size clusters using processes such as vapor-phase condensation, wet-chemical precipitation, high-energy mechanical alloying, and micellar templating. Furthermore, there is a developing ability to organize such crystallites, into non-interacting or interacting arrays, porous aggregates, and densely-consolidated solids. We may ask at this juncture, what are the unique physical properties of ultrafine crystallites? The remainder of this introduction attempts to summarize and classify some of the identifiable phenomena, using examples particularly relevant to inorganic crystals and electroceramics.

## Structure, Thermodynamics, and Defect Properties

When novel processing results in the creation of entirely new structures, it is no surprise that unique properties result. Such is the case with fullerenes, which exhibit unique mechanical, thermal, and electronic properties, as discussed in the article by M.S. Dresselhaus and G. Dresselhaus. For mesoporous oxides prepared by micellar organization [2,3], the pore size control useful for selective filtering, ion-exchange, and catalysis also derives from unique structure, as discussed in the article by J.Y. Ying and T. Sun. In polymorphic systems, surface stresses alter the relative stability of phases at ultrafine crystallite sizes; well-known examples include the stabilization of higher-temperature polymorphs of zirconia [4] and barium titanate [5] upon reduction of particle size into the submicron regime. In nanostructured magnetic composites, it is the single-domain state that is

stabilized at ultrafine size (or film thickness, for a multilayer). By controlling the interactions between nanoparticles, a variety of responses including superparamagnetism can be manipulated, with existing or likely applications in ferrofluids, toners, inks, and magnetic refrigeration [6,7].

However, a significant fraction of the work on nanocrystalline metals and ceramics over the past decade has centered on densified nanocrystalline compacts. Phase stability aside, the precise structural uniqueness of such materials has not been so clear. We now know that the characteristics of such materials depend strongly on the method of preparation and consolidation. In general, materials prepared by the consolidation of ultrafine powders, whether prepared by inert-gas-condensation, mechanical alloying, or wet chemical methods, appear to differ significantly from those produced by atom-by-atom deposition techniques, severe plastic deformation, or higher-temperature consolidation. Lower elastic modulus [8,9], increased coefficient of thermal expansion, and increased heat capacity [10] are amongst the effects observed in compacted nanocrystalline metals which are suggestive of greater disorder, i.e., a higher grain boundary free volume. Positron annhilation experiments on compacted nanocrystalline metals indicate the existence of considerably porosity on the scale of 1–15 atomic volumes [11]. It is notable that in contrast, electrodeposited Ni of ~10 nm grain size exhibits negligible enhancement of thermal expansion coefficient and minimal increase in heat capacity [12]. Annealing of compacted materials without significant grain coarsening appears to relax to some extent, but not entirely remove, these differences. Molecular dynamics simulations [13] of nanocrystalline grains are constrained from rotation and translation during ''crystallization'' from the melt result in disordered grain boundary regions of nearly 1 nm thickness. This simulation may in fact approximate the preparation of nanocrystalline compacts under conditions where the *crystallite* mobility (as opposed to atom mobility) is low. Despite the variability in properties which comes with the strong dependence on processing technique, compacted nanocrystals appear to remain stable for long periods, depending on the specific material and temperature, and may be a potentially useful metastable state.

In ceramics, the potential for variations in defect chemistry and nonstoichiometry with size introduces additional complications that are not present in metals. Nonetheless, limited results suggest a similar retention of a non-relaxed structure for long times at moderately high temperature. For example, the electronic conductivity of undoped $CeO_2$, which is a direct measure of the concentration of electrically-active point defects, is several orders of magnitude greater in a fully-compacted 10 nm grain size sample than for conventional materials [14,15]. This excess conductivity is stable for many days at 500°C. However, the excess conductivity relaxes by over $10^2$ upon firing briefly to 700°C, despite insignificant change in grain size, suggesting a relaxation of the grain boundary structure [16]. The excess enthalpy of ultrafine $TiO_2$ polycrystals, measured calorimetrically, increases with grain size and firing temperature in a manner also suggesting size-dependent defect chemistry [17].

**Deviations from Expected Size-Scaling**

For many nanocrystalline metals and ceramics, the phenomena which have aroused interest are *deviations* from known size-scaling laws. Two widely studied examples are the $d^{-1/2}$ grain size dependence of the Hall–Petch yield stress relationship and the $d^{-3}$ dependence of the Coble diffusional creep rate. Accordingly, it was expected that nanocrystalline compacts might be stronger and harder at low temperature where diffusion is quenched, but would creep much faster at elevated temperature than normal polycrystals. The latter attribute, if realized, suggests applications in superplastic forming.

For nanocrystalline metals, both hardening and softening have been observed with decreasing grain size [18–20]. When increases in yield strength have been observed, the increase is less than that expected from Hall–Petch grain size scaling. Results are highly sensitive to annealing, and by inference, the details of processing, and the mechanisms have not been clearly resolved. Observations of shear bands extending over many grains [8] furthermore suggest a similarity with the deformation mechanisms of metallic glasses.

Creep in both nanocrystalline metals and ceramics is expected to occur by diffusional mechanisms since dislocations are neither expected nor observed (by TEM) at grain sizes of a few nanometers. The respective grain size dependences of the Nabarro–Herring (lattice diffusion limited) and Coble (grain boundary diffusion limited) creep rates indicate that

the latter should be preferred at small grain size. However, if diffusional creep becomes limited by the emission/absorption of defects at grain boundaries (i.e., interface-limited creep), as is expected at the finest grain sizes, the creep rate should more weakly size-dependent ($d^{-1}$). Clean experiments have been difficult given the propensity of ultrafine grain structures to coarsen at temperatures where creep measurements are done. In rutile $TiO_2$, dense 40 nm grain sized samples deformed in compression at temperatures where modest grain coarsening occurs exhibit higher stress exponents and weaker grain size dependences suggesting interface-limited creep [21]. Thus, in at least one system, the nanocrystalline behavior seems to approach the limiting mechanism expected at the finest grain sizes, based on previous experience with oxides such as alumina [22]. The absolute creep rates measured for ceramics remain quite low, ~$10^{-3}$ $s^{-1}$ at most, and increases in temperature that might increase creep rate also cause grain coarsening [23]. As a result, superplastic forming seems impractical without development of grain size control measures. In Cu and Pd, two well-studied nanocrystalline metals, creep rates at low temperatures where grain growth is inhibited are two to four orders of magnitude lower than predicted from the Coble mechanism [24]. At higher temperatures where some coarsening occurs, surprisingly, the creep rates are equivalent to or lower than that in coarse-grained samples. TEM observation shows extensive twinning and suggest that some fraction of grain boundaries may be low angle boundaries with low atom diffusivity or interface kinetics. These examples illustrate the complexity of experimental results and the difficulty of mechanistic interpretation encountered in many studies to date.

## Exploiting the Specific Properties of Surfaces

In nanocrystalline powders or compacts, a significant fraction of the total number of atoms resides at the surface or grain boundary. It is reasonable to expect that the surface properties gain greater significance. For instance, the activity of an oxide particulate heterogeneous catalyst may be found to increase in proportion to its surface area. The simplicity of the explanation in no way detracts from its utility; reduction of the particle size to the nanometer regime could be highly useful.

More interesting behavior arises when properties do not scale in direct proportion with surface area, indicating that the *specific* surface properties are varying with size. Several effects can be anticipated and modeled, although experimental confirmation is still sparse.

Size-dependent segregation of solutes to interfaces is expected to occur as the impurity content of a material decreases, and/or its specific surface area increases. This occurs simply because the amount of solute competing for energetically favorable interfacial sites becomes limited; there is not enough segregant to go around. The size-dependence of surface concentration can be predicted using a statistical thermodynamic model based on Langmuir adsorption, in which the number of surface and bulk sites is taken into account [25,26]. The essential parameters of such a model are the numbers of the respective sites, the free energy for segregation to the interfacial sites, and temperature. It is found that with decreasing crystal size, a sharp transition to a size-dependent segregation regime occurs, below which the surface coverage varies linearly with size. This behavior has been experimentally confirmed for Ca segregation in ultrafine $TiO_2$ [26] and Si segregation in Ca-$ZrO_2$ [27]. Furthermore, within the size-dependent regime, the fraction of the available solute atoms which reside at surface sites increases rapidly to unity. An interesting implication of this result is that the crystal interior can be ''undoped'' simply by decreasing the crystal size. This effect may explain the observation that $CeO_2$ containing sufficient $Gd_2O_3$ to yield extrinsic ionic conduction in a conventional polycrystal instead exhibits, at 10 nm grain size, electronic conductivity characteristic of much lower doping levels [28].

A related property is the increased solid solubility of nanocrystalline compacts. The equilibration of a material containing interface sites of lower chemical potential with a solute source of a given activity results in increased solubility, without requiring any change in the bulk solubility. It is therefore expected that any solute which has a propensity to segregate will also have increased solid solubility in a nanocrystalline host. Increased solubility of hydrogen in various metals has been reported [1] and is a potential mechanism of hydrogen storage; other systems in which the effect has been characterized include Bi in Cu [1] and Ca in $TiO_2$ [26].

A second size-dependent interfacial phenomenon

occurs when internal space-charge fields impinge. Assuming no other changes in the system, the volume-averaged defect concentration, and associated transport properties, increase when the grain size (or film thickness, for a thin film) approach the scale of the Debye length [29–31]. The implications for space-charge conduction parallel to the interfaces have been extensively modeled by Maier [31–33]. In the case of $CaF_2$, increased ionic conductivity at nanocrystalline grain sizes has been attributed to this effect [33]. Additional discussion appears in the article by Tuller.

Space-charge models treats the spatial distribution of internal defects and solutes for given boundary conditions defined by the surface defect formation energies and site densities. It is important to recognize that the existence of space-charge phenomena is a consequence of the fact that the defect thermodynamics of surfaces and interfaces differ from those of the bulk crystal. Consequently, at sufficiently fine crystallite size, nanocrystalline solids can be dominated by the defect properties of their interfaces. $CeO_2$ has been a particularly useful model for exploring these effects through the use of transport measurements, as it is a small-polaron conductor in which the mobility of electrons is less impacted by the presence of interfaces and defects than in high carrier mobility solids. (For instance, in ultrafine metals the electrical resistivity always increases with decreasing grain size due to increased scattering, whereas in oxides, size reduction can increase conductivity.) By analyzing the transport properties of fully-dense nanocrystalline $CeO_2$ compacts [14–16], it was concluded that the mechanism of reduction remained the same as for bulk single crystals and polycrystals (i.e., oxygen vacancy compensation), but that the volume-averaged heat of reduction was less than one-half the bulk value. It is natural to attribute the sites of reduced defect formation enthalpy to the grain boundaries. The existence of surface sites of low reduction enthalpy explains qualitatively the catalytic activity of $CeO_2$ for heterogeneous reactions involving extraction of surface oxygen (e.g., oxidation of CO). However, there remain many unexplored effects, particularly involving the behavior of specific free surfaces, which computations for $CeO_2$ [34] indicate will have great anisotropy in the heat of reduction, and the role of heterojunctions in the behavior of multiphase catalysts, as discussed further in the article by Ying and Sun.

We can also speculate on an additional type of surface defect which may become important at small crystallite size. It is widely recognized that the anisotropy of crystal surfaces results in faceting. The shorter diffusion lengths for small crystallites suggest that they are likely to reach the equilibrium or Wulff shape rather easily. Under-coordinated edge and corner sites must then result where atomically flat facets meet, and for a small crystallite, the fraction of such sites is increased relative to the number of bulk and surface sites. For processes involving site-specific surface reactions, these sites may be energetically favored, and nanocrystalline particles may represent a route for their utilization. It also seems possible, although we know of no clear data to support the contention, that the Wulff shape may change at very small crystallite size due to the increasing relative contributions of edge energies.

These brief examples illustrate the complex and varied behavior found in nanometer-scale microstructures, and also the close relationship between processing and measured physical properties in studies to date. It is clear that a variety of size-dependent effects arise that are often not clearly understood, are sometimes hard to precisely control, but which offer additional variables by which properties can be manipulated. The following reviews discuss many additional examples in greater detail, and their technological relevance for specific applications.

## Acknowledgments

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