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CLUSTER ASSEMBLY OF HIERARCHICAL NANOSTRUCTURES*

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ABSTRACT

In the past few years, atom clusters with diameters in the range of 2-20 nm of a variety of materials, including both metals and ceramics, have been synthesized by evaporation and condensation in high-purity gases and subsequently consolidated in situ under ultrahigh vacuum conditions to create nanophase materials. These new ultrafine-grained materials have properties that are often significantly different and considerably improved relative to those of their coarser-grained counterparts owing to both their small grain-size scale and the large percentage of their atoms in grain boundary environments. Since their properties can be engineered during the synthesis and processing steps, cluster-assembled materials appear to have significant potential for the introduction of a hierarchy of both structure and properties. Some of the recent research on nanophase materials related to properties and scale are reviewed and some of the possibilities for synthesizing hierarchical nanostructures via cluster assembly are considered.

INTRODUCTION

Hierarchical materials are ensembles of structure and function in which scale, interaction, and architecture play a dominant role. Cluster-assembled nanostructures already exhibit simple forms of hierarchy, and more complex hierarchical materials should be possible to synthesize by cluster assembly in the future, but much work remains before this can happen. Nanophase materials appear to have existed since the beginning of time, even before the advent of the beautiful and complex biological hierarchies cited in this Symposium. Evidence from the earliest meteorites suggests that primordial materials with nanometer-scale phase structures condensed from our solar nebula [1-3]. Billions of years later, the man-made synthesis of nanometer size atomic clusters of metals and ceramics by means of the gas-condensation method, followed by their in situ consolidation under high-vacuum conditions, has resulted in a new class of synthetic ultrafine-grained materials where sophisticated control of scale, interaction, and architecture may become possible. For now, such hierarchy is in its infancy.

Increasing interest has focused on a variety of synthetic nanostructured materials, with average grain sizes below 100 nm, during the past several years with the anticipation that their properties will be different from, and often superior to, those of conventional materials that have phase or grain structures on a coarser size scale [4]. This interest has been stimulated not only by the considerable recent effort and success in synthesizing a variety of one-dimensionally modulated, multilayered materials with nanometer scale modulations, but also by the exciting possibility of synthesizing three-dimensionally analogous, bulk nanophase materials via the assembly of clusters of atoms [5].

Atom clusters in the nanometer size regime, containing hundreds to tens of thousands of atoms, can now be produced in sufficient numbers by means of either physical or chemical processes that they can be assembled into materials that can be studied by a variety of conventional experimental methods. These materials have the possibility for taking advantage of and incorporating a number of size-related effects in condensed matter ranging from electronic effects (so-called "quantum size effects") caused by spatial confinement of delocalized valence electrons and altered cooperative ("many body") atom phenomena, such as lattice vibrations or melting, to the suppression of such lattice-defect mechanisms as dislocation generation and migration in confined grain sizes. The possibilities to assemble size-selected atom clusters into new materials with unique or improved properties may thus impact our ability to engineer a wide variety of controlled optical, electronic, mechanical, and chemical properties with attendant useful technological applications.

The present paper focuses on the preparation of atom clusters of metals and ceramics by means of the gas-condensation method and their in situ consolidation under high-vacuum conditions [6-12]. Some aspects of the structure and properties of nanophase metals and ceramics synthesized by this method are considered in relation to hierarchical materials. This appears to be the most generally applicable of the presently available methods for producing size-selected atom clusters in the less-than-100-nm (nanophase) regime, and thus appears to have very broad technological potential.

There are a number of advantages associated with the synthesis of nanophase materials from atom clusters which together offer the potential for the creation of hierarchies of scale, interaction, and architecture. Some of these stem from the nanometer scale of the structures assembled and others arise from the inherent flexibility of dealing with clusters as the building blocks of these materials. Some of these advantages are as follows [12]:

(1) The ultrafine sizes of the atom clusters and their surface cleanliness allow the conventional restrictions of phase equilibria and kinetics to be essentially overcome during material synthesis and processing, by the fortunate combination of short diffusion distances, high driving forces, and uncontaminated surfaces and interfaces.

(2) The large fraction of atoms residing in the grain boundaries and interfaces of these materials allow for interface atomic arrangements to constitute significant volume fractions of material, and thus novel materials properties may result.

(3) The reduced size scale and large surface-to-volume ratios of the individual nanophase grains can be predetermined and can alter and enhance a variety of physical and chemical properties.

(4) A wide range of materials can be produced in this manner including metals and alloys, intermetallic compounds, ceramics, and semiconductors. It is also apparent that they can be formed to contain crystalline, quasicrystalline, or amorphous structures.

(5) The possibilities for reacting, coating, and mixing in situ various types, sizes, and morphologies of clusters create a significant potential for the synthesis of a variety of new multicomponent composites with nanometer-sized microstructures and engineered properties. Most of the research carried out to date, nevertheless, has concentrated on single-phase metals and ceramics.

SYNTHESIS AND STRUCTURE

Certainly, the predominant feature of nanophase materials, shown in the electron micrograph of nanophase Pd in Fig. 1, is their ultrafine grain size and, hence, the large fraction of their atoms that reside in grain boundaries or interfaces and the interactions between the grains. In this regard they can be thought of as the three-dimensional analogues of one-dimensionally modulated multilayered materials. For example, as indicated in Fig. 2, a nanophase material with a 5 nm average grain size will have from about 27 to 49% of its atoms associated with grain boundaries, assuming a simple grain boundary picture and an average grain boundary thickness of about 0.5 to 1.0 nm (ca. 2-4 nearest-neighbor distances). This percentage falls to about 14-27% for a 10 nm grain size, but is as low as 1-3% for a 100 nm grain size. The interface volume fraction is, of course, essentially negligible for conventional grain sizes of 1 μm and above. Therefore, the properties of nanophase materials are expected to be strongly influenced by their grain sizes and the nature (atomic and electronic structure) of their internal boundaries, simply because of the very large number density of these boundaries.

Investigations of nanophase TiO_2 by Raman spectroscopy [15-17] and of nanophase Pd by atomic resolution, transmission electron microscopy [13, 18] indicate that the grain boundary structures in these materials are essentially low energy configurations that are rather similar to those in coarser grained, conventional materials [19]. The nanophase grain boundaries contain short-range ordered structural units representative of the bulk material and distortions that are localized to about ± 0.2 nm on either side of the grain boundary plane. These conclusions are also consistent with the results from complementary small-angle neutron scattering measurements [20-22], and with the expectations for conventional high angle grain boundaries from condensed matter theory [23, 24].

The synthesis of nanophase materials via the in situ consolidation of gas-condensed clusters has been described in detail elsewhere [12]. For the purposes of this paper it is sufficient to give only a brief outline of the process. A precursor material, either metal or compound, is evaporated in a gaseous atmosphere maintained at a few hundred Pa in a back-filled ultrahigh-vacuum chamber. The evaporated atoms or molecules lose energy via collisions with the gas atoms or molecules and

Figure 1. High resolution transmission electron micrograph of a typical area in nanophase Pd [13].

Figure 2. Percentage of atoms in grain boundaries of a nanophase material as a function of grain diameter, assuming that the average grain boundary thickness ranges from 0.5 to 1.0 nm (ca. 2 to 4 atomic planes wide) [14].

undergo a homogeneous condensation to form atom clusters in the highly supersaturated vicinity of the precursor source. In order to maintain small cluster sizes, by preventing further atom or molecule accretion, the clusters once nucleated must be removed rapidly from the region of high supersaturation. Since the clusters are already gas entrained, this is easily accomplished by moving the condensing gas. Such gas motion has generally resulted from natural convection under the action of gravity and the temperature difference between the precursor source and a thermophoretic cluster collector cooled by liquid nitrogen. However, a forced gas flow can also be used, and with significant advantage in terms of cluster size control and process efficiency. The clusters are then removed from the collector under vacuum and consolidated at room temperature at pressures up to about 1-2 GPa by means of a piston-and-anvil device. The resulting samples are usually about 1 cm in diameter and about 0.1-0.5 mm thick, depending upon the amount of precursor material evaporated and the experiment planned.

The smallest cluster sizes for a given metal, for example, are obtained for a low precursor evaporation rate and condensation in a low pressure of a light inert gas, such as He [25]. These conditions lead to a lower supersaturation of precursor atoms in the gas, slower removal of energy from the evaporated atoms, via the lighter gas atoms at lower pressure, and more rapid convective gas flow owing also to the lower gas pressure. There are just three fundamental rates which essentially control the formation of the atom clusters in the gas-condensation process [12]. They are (1) the rate of supply of atoms to the region of supersaturation where condensation occurs, (2) the rate of energy removal from the hot atoms via the condensing gas, and (3) the rate of removal of the clusters once nucleated from the supersaturation region. There are other factors that can also affect the clusters finally collected, particularly those that result in significant cluster-cluster coalescence, but these three rates represent the core of the process.

The clusters that are collected on the surface of the collector, and which subsequently become the grains of the consolidated polycrystalline aggregate, have a rather narrow size distribution. A typical grain size distribution, in this case for as-consolidated TiO_2 , is shown in Fig. 3. In order to produce the nanophase TiO_2 with rutile structure, Ti metal clusters condensed in He were first collected on a cold finger and subsequently oxidized by the introduction of oxygen into the chamber [26]. The distribution is quite narrow and has the log-normal shape typical of clusters formed via gas-condensation [25]. This shape is rather typical for the grain size distribution in any of the nanophase materials thus far produced by this method. Oxygen stoichiometry can also be controlled in such material. Raman spectroscopy has been used [16, 17] to calibrate the deviation from stoichiometry in as-produced nanophase titanium dioxide, which could then be easily oxidized to fully stoichiometric TiO_2 , if desired, without sacrificing its small grain size (12 nm). Also, if intermediate deviations from stoichiometry were sought, in order to select particular properties of this material, they could be readily accessed as well.

An important aspect of nanophase materials assembled from atom clusters is their apparently inherent stability against grain growth [27, 28]. Their grain sizes remain rather deeply metastable to elevated temperatures. For example, as also shown in Fig. 3, the 12 nm initial average grain diameter changes little with annealing to elevated temperatures until about 40-50% of the absolute melting temperature (T_m) of TiO_2 is reached. This behavior appears to be rather typical for the nanophase oxides investigated [27] and for nanophase metals [29] also. In the case of the TiO_2 , rapid grain growth only develops above the temperature at which the mean bulk diffusion distance $(D_{\text{Ti}})^{1/2}$ of Ti becomes comparable to the mean grain size, at which temperature any local barriers to grain growth would cease to be significant.

Given the above referenced observations of grain size distributions and grain boundary structures in nanophase materials, it appears that the narrow grain size distributions normally observed in these cluster-assembled materials coupled with their relatively flat and faceted grain boundaries (and also enhanced by their multiplicity of grain boundary junctions) place these nanophase structures in a local minimum in energy (a quasi-frustration) from which they are not easily extricated. They are thus analogous to a variety of closed-cell foam structures, which are stable (really, deeply metastable) despite their large stored surface energy. Under such conditions, only at temperatures above which bulk diffusion distances are comparable to or greater than the grain size, as in the case of nanophase TiO_2 cited above, will this metastability give way to global energy minimization via rapid grain growth. One could, of course, intentionally stabilize against grain growth by appropriate doping or composite formation in the grain boundaries.

Figure 3. Grain size distribution for an as-consolidated nanophase TiO₂ (rutile) sample compacted to 1.4 GPa at room temperature, as determined by dark-field transmission electron microscopy (inset) and the variation of this average grain size with sintering temperature (0.5 h at each) [26].

Figure 4. The ac conductivity of Pt-doped nanophase TiO₂ as a function of temperature. The sample was pre-annealed in air at about 500°C for 4 h prior to the conductivity measurements; the electrical response is reversible with temperature [30].

PROPERTIES

Nanophase materials have a variety of properties that are different and often considerably improved in comparison with those of conventional coarse-grained structures. For example, nanophase TiO_2 (rutile) exhibits significant improvements in both sinterability and resulting mechanical properties relative to conventionally synthesized coarser-grained rutile [26, 31-33]. Nanophase TiO_2 with a 12 nm initial mean grain diameter has been shown [26] to sinter under ambient pressures at 400 to 600°C lower temperatures than conventional coarser-grained rutile, and without the need for any compacting or sintering aid, such as polyvinyl alcohol, which is usually required.

Atomic diffusion in nanophase materials, which can have a significant bearing on their mechanical properties, such as creep and superplasticity, and electrical properties as well, has been found to be very rapid. Measurements of self-diffusion and impurity-diffusion [31, 34-37] in as-consolidated nanophase metals and ceramics indicate that atomic transport is orders of magnitude faster in these materials than in coarser-grained polycrystalline samples. However, the very rapid diffusion in as-consolidated nanophase materials appears to be intrinsically coupled with the porous nature of the interfaces in these materials, since the diffusion can be suppressed back to conventional values by sintering samples to full density [31]. Nonetheless, there exist considerable possibilities for efficiently doping nanophase materials at relatively low temperatures via the rapid diffusion available along their ubiquitous grain-boundary networks, with only short diffusion paths remaining into their grain interiors, to synthesize materials with tailored optical, electrical, or mechanical properties.

Little work has been carried out so far on the electrical properties of nanophase materials. However, there appear to be interesting prospects, if the results shown in Fig. 4 are any indication [30]. Nanophase TiO_2 was doped at about the 1% level with Pt diffused in from the surface. After annealing in air for 4 h at about 500°C, the ac conductivity of the sample was measured as a function of temperature. The strongly nonlinear, and reversible, electrical response shown, caused presumably by the Pt doping into the band gap of this wide band gap (3.2 eV) semiconductor, suggests that the rather easy doping of nanophase electroceramics may lead to a wide range of interesting device applications in the future. However, much work remains to be done in this area.

In the area of mechanical behavior, it has been observed that nanophase ceramics are easily formed [26, 38-40]. However, the degree to which nanophase ceramics are truly ductile is only beginning to be understood. Nanoindenter measurements on nanophase TiO_2 [33] and ZnO [41] have recently demonstrated that a dramatic increase of strain rate sensitivity occurs with decreasing grain size, as shown in Fig. 5. Since this strong grain-size dependence is found for sets of samples in which the porosity is changing very little, it appears to be an intrinsic property of these ultrafine-grained ceramics. The strain rate sensitivity values at the smallest grain sizes yet investigated (12 nm in nanophase TiO_2 and 7 nm in ZnO) thus indicate ductile behavior of these nanophase ceramics, as well as a significant potential for increased ductility at even smaller grain sizes and elevated temperatures. The maximum strain rate sensitivities measured in these studies, about 0.04, are already approximately one-quarter that for lead at room temperature, for example. However, no superplasticity has yet been observed in nanophase materials at room temperature, which would yield m values about an order of magnitude higher than the maximum observed. Nevertheless, it already seems clear that in the future, at smaller grain sizes and/or at elevated temperatures, superplasticity of these materials will indeed be observed.

The dominant mechanical property change resulting from reducing the grain sizes of nanophase metals is the significant increase in their strength [42-44]. While the microhardness of as-consolidated nanophase oxides is reduced relative to their fully-dense counterparts, owing to their significant porosity in addition to their ultrafine grain sizes, the case for nanophase metals is quite different. Figure 6, for example, shows recent microhardness results for several samples of nanophase Cu and a coarser-grained counterpart [44]. The smallest grain size (6 nm) sample is seen to exhibit about a 500% increase in hardness over the coarser-grained (ca. 50 μm) sample. Similar results have been observed in nanophase Pd as well [42, 43].

The increased strength in ultrafine-grained nanophase metals, although superficially analogous to conventional Hall-Petch strengthening observed with decreasing grain size in coarser-grained metals, must result from fundamentally different mechanisms. The grain sizes here, after all, are

Figure 5. Strain rate sensitivity of nanophase TiO₂ [33] and ZnO [41] as a function of grain size. The strain rate sensitivity was measured by a nanoindentation method and the grain size was determined by dark-field transmission electron microscopy.

Figure 6. Vickers microhardness measurements at a number of positions across several nanophase Cu samples ranging in grain size from 6 to 50 nm, compared with similar measurements from an annealed conventional 50 μm grain size Cu sample [44].

smaller than the necessary critical bowing lengths for Frank-Read dislocation sources to operate and smaller than the normal spacings between dislocations in a pile-up, as well. It appears that as the grain-size scale is reduced into the nanoscale regime, the energetic hierarchy of microscopic deformation mechanisms or paths is successively accessed, with easier paths (such as dislocation generation from Frank-Read sources) becoming frozen out at sufficiently small grain sizes and more costly paths becoming necessary to effect deformation.

The enhanced strain rate sensitivity at room temperature found in nanophase oxides [33, 41] appears to result from increased grain boundary sliding in this material, aided by the presence of porosity, ultrafine grain size, and probably rapid diffusion as well. The increased strength of nanophase metals [41-43], on the other hand, indicates that dislocation generation, as well as dislocation mobility, may become significantly difficult in ultrafine-grained metals. It may thus be that the increased strength of nanophase metals and the increased ductility of nanophase ceramics indicate a convergence of the mechanical response of these two classes of materials as grain sizes enter the nanometer size range. In such a case, grain boundary sliding mechanisms, accompanied by short-range diffusion assisted healing events, would be expected to increasingly dominate the deformation of nanophase materials, and superplasticity in a wide range of nanophase materials including metals and alloys, intermetallic compounds, ceramics, and even semiconductors could result. Accordingly, increased opportunities for high-deformation or superplastic near-net-shape forming of a very wide range of materials could result.

CONCLUSIONS

We are just now beginning to take advantage of the opportunities for synthesizing nanophase materials with new architectures at the nanometer scale via the assembly of atom clusters. The future appears to hold great promise for these materials, based upon the limited knowledge that has already been accumulated, but much work remains to be done. The cluster sizes accessed to date indicate that the high reactivities and short diffusion distances available in cluster-assembled materials can have profound effects upon their processing characteristics and the interactions that take place across their many interfaces. The ability to gain greater control over these characteristics in developing the wherewithall to create more sophisticated hierarchical materials should be further enhanced as even smaller and more uniformly sized clusters become available in sufficiently large numbers to effect their assembly into usable materials.

Combining the various aspects of scale and properties of cluster-assembled nanophase materials to make a variety of multifunctional and functionally-gradient hierarchical materials will be a great challenge for the future. For example, the enhanced atomic diffusivities available along the grain boundary networks of nanophase materials, with only few atomic jumps separating grain interiors from grain boundaries, should enable efficient impurity doping of these materials. Nanophase insulators and semiconductors could be easily doped with impurities at relatively low temperatures, thus allowing efficient introduction of impurity levels into their band gaps and control over their electrical, chemical, and optical properties. These materials could be assembled with controlled porosity and high surface areas or made into fully dense parts that are readily formable and exhibit ductility, all of which could have significant technological impacts in a wide variety of applications. It is a challenge well worth the effort.

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