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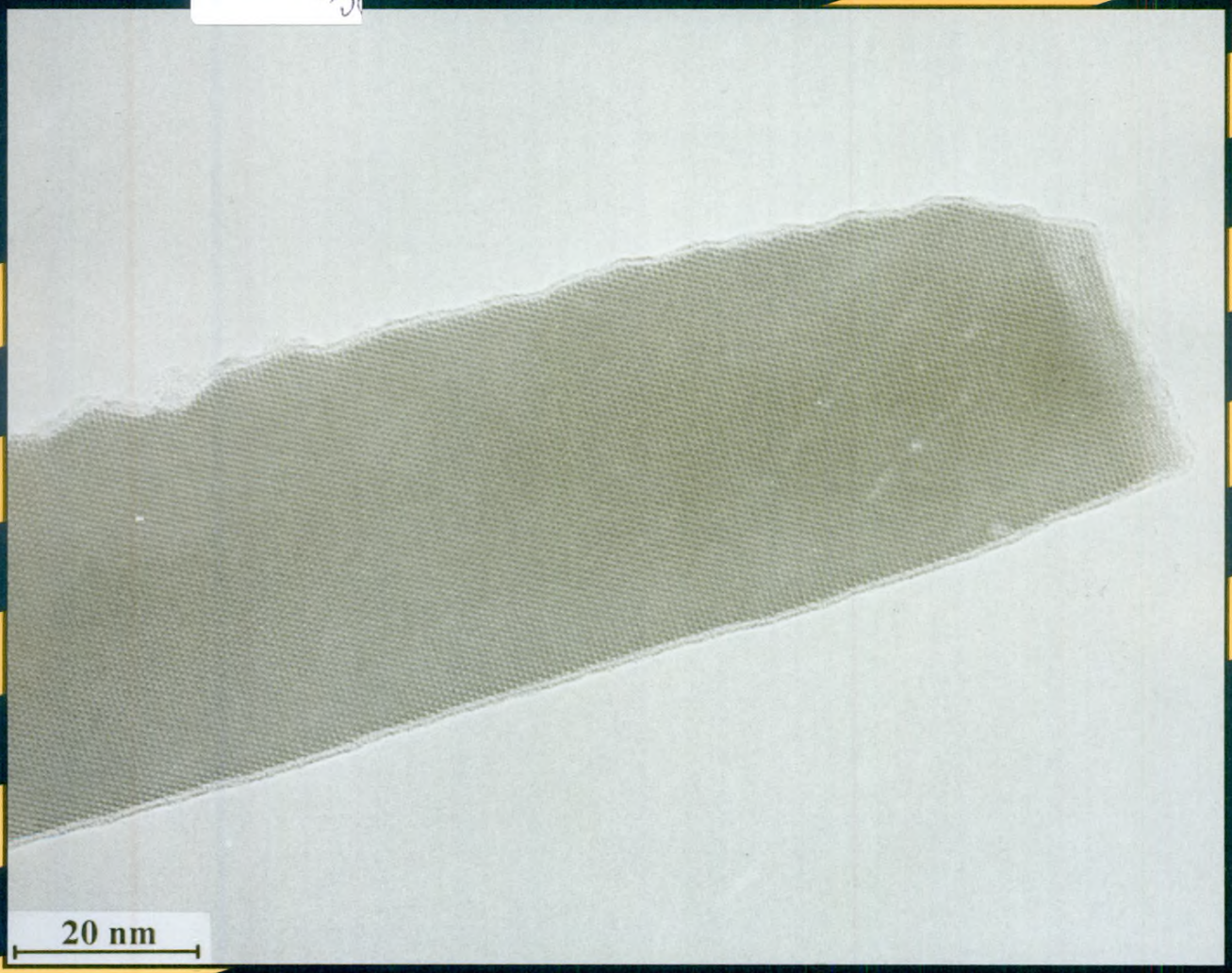

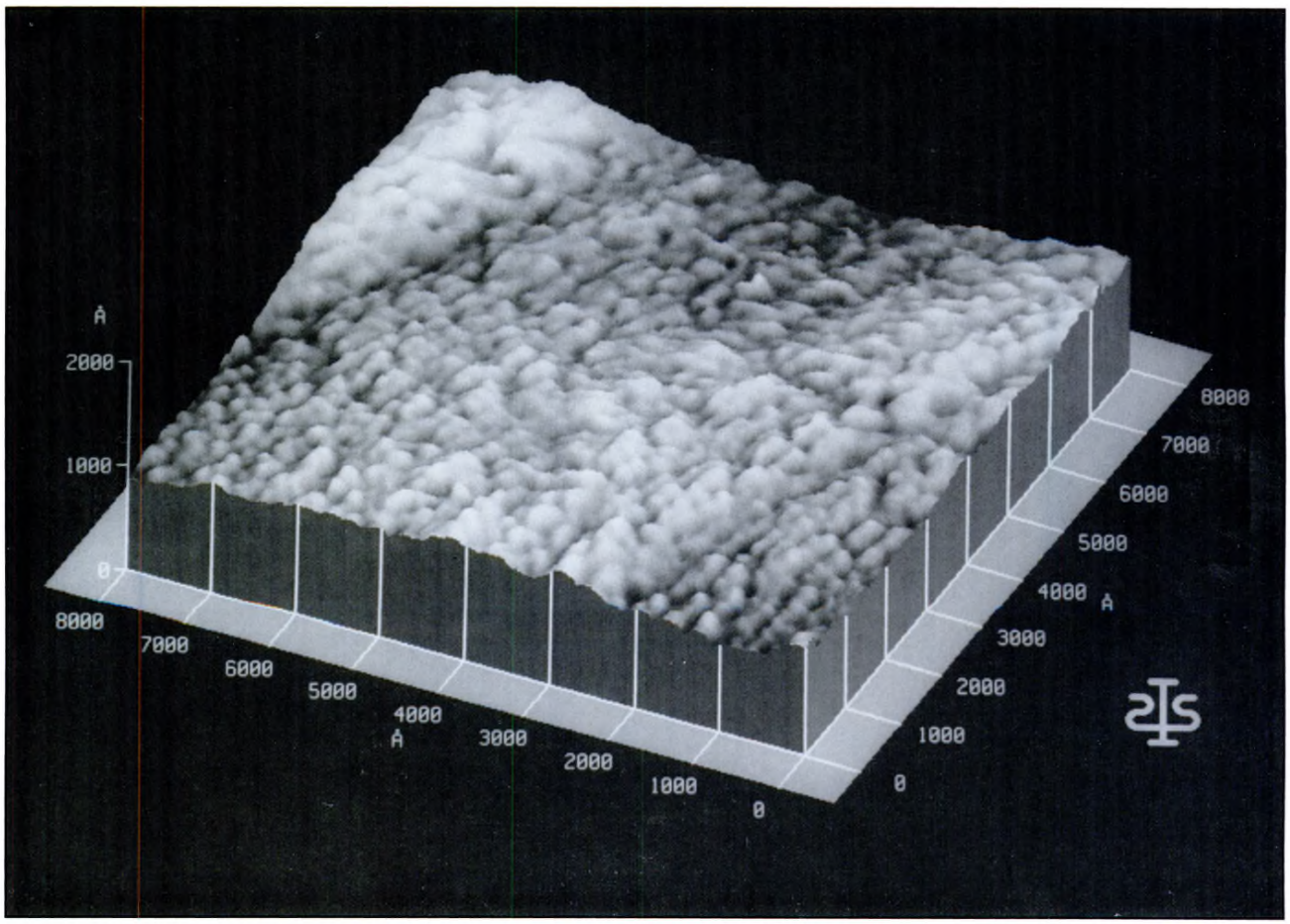

Atomic force microscope image of a green body formed by cold compaction of nanoscale TiO_2 powder. Nanoscale particles exhibit greatly enhanced catalytic properties. See article by Ying.

Articles

Departments

About the Cover

High resolution transmission electron microscope (HRTEM) image of a nanoscale single crystal Si_3N_4 whisker. Whiskers are formed rapidly from nanoscale Si-C-N powder and NH_4 in the presence of small liquid silicon droplets. Such fibers are important in the development of high strength, high toughness ceramic matrix composites. See article by Kear and Strutt.

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Introduction

Lawrance Kabacoff, Guest Editor
Materials S&T Division
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It has been conservatively estimated that the performance of more than half of the systems used by the Navy are materials limited. Development of a new material with properties superior to those already available can significantly enhance the performance of many of these systems and have a major impact on the capabilities of the fleet. Some advances in materials science can be revolutionary (as opposed to evolutionary). Such "breakthroughs" are generally greeted with skepticism both because of negative past experience with revolutionary advances that didn't live up to their advanced billing, and because of an ingrained belief that anything too good to be true probably isn't. Nevertheless, the field of nanoscale materials, which is currently experiencing explosive growth, appears to be living up to its early promise.

Quite simply, nanoscale materials are defined as any material with a physical length scale in at least one dimension less than 100 nm. This dimension can be the diameter of a particle, thickness of a film layer or fiber, or the average grain size in a polycrystalline materials. While the choice of 100 nm is not absolute, it is not as arbitrary as it may seem. There are several reasons why the properties of materials begin to radically change as one goes below this limit. For one thing, physical phenomenon tend to have a characteristic length scale. This length scale might be, for example, the magnetic exchange correlation length, the spatial extent of the quantum mechanical wave function of an electron, or the distance between pinning sites in a Frank-Reade dislocation source. If the physical dimension of the material is smaller than this characteristic length, the mechanical, optical, electronic, and/or magnetic properties of the material are greatly altered. Another important factor is the very high surface area (either free surface or interfacial) in a nanoscale material. In a polycrystalline materials with a 10 nm grain size, for example, nearly half of the atoms are at grain boundaries. This leads to very high diffusion rates coupled with very short diffusion distances, with strong implications for such processes as sintering and superplastic deformation. The effect of the high surface area on catalysis is obvious, as is the effect on gas sensors which require adsorption of a gas onto a surface. The properties of nanoscale materials *really are* significantly different from even those of so-called sub-micron materials.

Actually, nanoscale materials have been in use for decades. The carbon black in automobile tires is a nanoscale powder, as is the titania (TiO_2) in paint. Fumed silica is yet another example. The particles making up these materials are highly agglomerated, i.e. the individual particles are welded together to form long chains and branching networks which are very difficult to process either into coatings or bulk materials. The current interest in nanoscale materials began in the mid 1980's with the synthesis of unagglomerated pure metal and oxide powders by Herb Gleiter at Saarlandes University in Germany. In his process, a metal is evaporated to form a supersaturated vapor. Particle growth and agglomeration are controlled by using convection currents to carry the particles out of the supersaturated region to a cold surface where they are collected. Gleiter was able to consolidate these powders into bulk solids which exhibited some remarkable properties.

The number of techniques for synthesizing nanoscale materials has greatly expanded in recent years to include spray conversion processing, chemical vapor condensation, detonation synthesis, various aerosol based processes, and laser pyrolysis, just to name a few. The Flieter process has been commercialized and kilogram quantities of oxide ceramics and some pure metals are readily available. The spray conversion process has also been commercialized for the production of cermets such as Co/WC, which are available in quantities

approaching tons. Today, more than sixty companies (including over forty small businesses) are actively engaged in research and development on synthesis of nanoscale material.

The list of potential applications of nanoscale materials is much too long to describe in a single issue of this journal. The articles presented here provide a brief summary of some of the work in this field being carried out of ONR sponsored researchers. The first article, by Bernard Kear (Rutgers University) and Peter Strutt (University of Connecticut), presents some of the recent progress in synthesis of nanoscale powders by chemical routes and their processing into coatings and bulk structures. It also discusses some of the applications for these materials currently under development, such as wear resistant and thermal barrier coatings, ceramic matrix composites with no fiber damage ore fiber/matrix reactions, and net shape forming of ceramics and cermets. Professor Kear, in addition to being a major driving force in the development of nanoscale materials technology, has also been an advocate for the establishment of better vehicles for the transfer of university developed technology to industry. Following the first article, a brief biographical sketch of Professor Kear is presented together with a description by him of his activities in establishing such a vehicle. The next article, by Gan-Moog Chow and Alok Singh, described their research at the Naval Research Laboratory on synthesizing nanoscale particles with precisely controlled size using a technique which mimics a biological process, namely, the use of artificial membranes to form reverse micelles within which the particles form. This is followed by a paper by Robert Schwerzel (Georgia Institute of Technology) on "capped" colloidal quantum-dot semiconductor. Finally Jackie Ying (Massachusetts Institute of Technology) describes some of her work on developing an understanding of the surface chemistry of nanoscale catalysts.

Nanostructures: The Next Generation of High Performance Bulk Materials and Coatings

B. H. Kear, Rutgers University
P. R. Strutt, University of Connecticut

Abstract

This paper presents an overview of recent research performed at Rutgers University and the University of Connecticut on the synthesis and processing of nanostructured materials. Highlights of this collaborative research program include: (1) synthesis of carbide strengthened steel and hard cermet powders from aqueous solution precursors, (2) synthesis of ceramic powders and ceramic matrix composites from metalorganic precursors, (3) densification of powder compacts by liquid phase sintering, (4) formation of high quality coatings by thermal spraying, and (5) demonstration of superior hardness and wear resistance in bulk cermet materials and coatings.

Nanostructured bulk materials with designed multifunctional coatings present unprecedented opportunities for advances in materials properties and performance for a broad range of structural applications.

Introduction

For generations, materials with fine-scale microstructures have been recognized to exhibit remarkable and technologically attractive properties. In the past few years, interest has been growing in a new class of materials that are composed of ultrafine grains or particles[1]. A feature of such 'nanostructured' materials is the high fraction of atoms that reside at grain or particle boundaries. Although much of today's research in the nanomaterials field is focussed on the synthesis and processing of bulk materials, there is also growing interest in the preparation of coatings.

Research on nanostructured materials (hereafter n-materials) has been a major activity at Rutgers University and the University of Connecticut since the late 1980's. Progress has been made in the synthesis of (1) n-metal powders by the Aqueous Solution Reaction method, (2) n-cermet powders by the Spray Conversion Processing method, and (3) n-ceramic powders by the Chemical Vapor Condensation method. Advances have also been made in the consolidation of n-powders by solid and liquid phase sintering methods (for bulk materials) and by thermal spraying (for coatings), while preserving the desirable nanostructures.

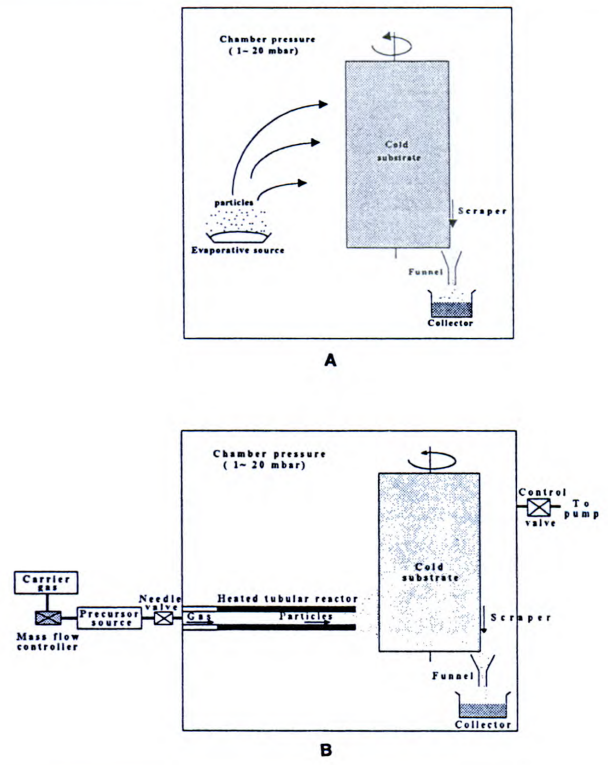
In what follows, we will describe highlights of this research, with the emphasis on synthesis and processing methods and the characteristics of the resulting nanostructured materials. One example will be cited that illustrates the performance advantages to be gained by substituting 'nanograined' material for conventional 'micrograined' material in a cutting tool application.

Nanostructured metals and alloys

Carbide strengthened steels are widely used for gears, bearings and shafts in gas turbine engines, because of their good resistance to tempering, wear and rolling contact fatigue. In the fully hardened condition, such steels contain a fine

Figure 1.

Schematic representation of (a) inert gas condensation (IGC) process, and (b) chemical vapor condensation (CVC) process.



dispersion of $M_{23}C_6$, M_2C, or MC carbide particles in a martensitic matrix. Some of the carbide particles, however, can be as large as several microns in diameter, in which case they can act as favorable sites for crack initiation in fatigue. To circumvent this problem, an attempt is now being made to develop an n-M50 steel, a prototype carbide strengthened steel, in which the dispersed carbide phase is of uniform nanoscale dimensions. The anticipated superior strength, wear resistance and fracture toughness of the n-M50 steel is expected to significantly enhance its properties and performance.

An Aqueous Solution Reaction (ASR) method has been developed to synthesize n-M50 steel powder[2]. The synthesis involves three steps: (1) preparation of an aqueous solution of mixed metal (Fe, Cr, Mo and V) chlorides using de-ionized and de-oxygenated water, (2) reductive decomposition of the starting solution with sodium trialkyl-borohydride to obtain a colloidal solution of the metallic constituents, and (3) after filtering, washing and drying, gas phase carburization under controlled carbon and oxygen activity conditions to form the desired nanodispersion of carbide phase in a metallic matrix. A similar procedure has been used to synthesize n-Cr_3C_2/Ni powders for use in thermal spraying of corrosion resistant hard coatings[3]. In both cases, separation of the sodium chloride from the colloidal solution is carried out by repeated washing in a centrifuge. A small amount of an organic passivation agent, such as a solution of paraffin in hexane, which is added to the final wash, provides protection of the high surface area powder against spontaneous combustion when dried and exposed to air.

Procedures for the low temperature consolidation of the as-synthesized n-M50 powders are being investigated.

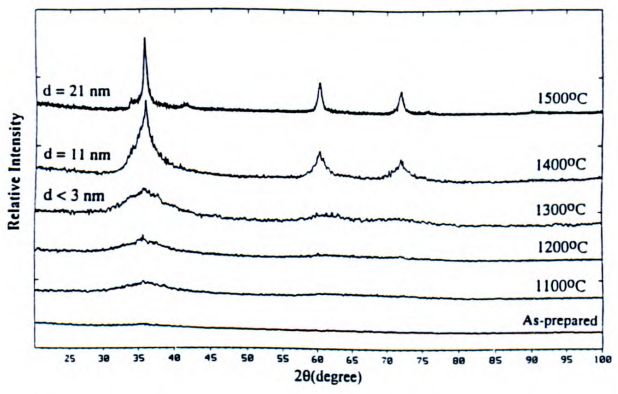
Nanostructured ceramics

Silicon-base ceramics, such as SiC and Si_3N_4, are useful materials for many engineering applications, such as highly stressed components in heat engines, grinding wheels and wear parts, because of their excellent high temperature mechanical strength and good oxidation resistance. Silicon carbide is also useful because of its favorable electrical resistance (heating elements) and thermal conductivity (substrate materials). A limitation of today's processing of these materials is the very high sintering temperature and pressure needed for powder consolidation, which is a consequence of their covalent bonding. Sintering aids can be used, but they frequently degrade properties. An alternative approach is to take advantage of the lower sintering temperatures characteristic of nanostructured powders. This was the approach adopted in our research.

Inert Gas Condensation (IGC) is the most versatile process in use today for synthesizing experimental quantities of nanostructured powders[1]. A feature of the process is its ability to generate non-agglomerated n-powders, which are sinterable at relatively low temperatures. In IGC processing, Figure 1(a), an evaporative source is used to generate the powder particles,

Figure 2.

XRD patterns of as-synthesized amorphous n-SiC_xN_y powders after annealing in flowing argon.



which are convectively transported to and collected on a cold substrate. The nanoparticles develop in a thermalizing zone just above the evaporative source, due to interactions between the hot vapor species and the much colder inert gas atoms (typically 1-20 mbar pressure) in the chamber. Ceramic powders are usually produced by a two-stage process: evaporation of a metal source, or a metal suboxide of high vapor pressure, followed by slow oxidation to develop the desired n-ceramic powder particles.

Recently, we have modified a conventional IGC processing unit for the purpose of synthesizing n-ceramic powders from metalorganic precursors. In this new Chemical Vapor Condensation (CVC) process[4,5], Figure 1(b), the original evaporative heating source is replaced by a hot-wall tubular reactor, which decomposes the precursor/carrier gas to form a continuous stream of clusters or nanoparticles exiting from the reactor tube. Critical to the success of CVC processing are: (1) a low concentration of precursor in the carrier gas, (2) rapid expansion of the gas stream through the uniformly heated tubular reactor, (3) rapid quenching of the gas phase nucleated clusters or nanoparticles as they exit from the reactor tube, and (4) a low pressure in the reaction chamber. The resulting n-ceramic powder particles are non-agglomerated, as in the IGC process, and display low temperature sinterability, as well as other useful characteristics as infiltrants. Non-agglomerated n-TiO_2 and n-ZrO_2 powders produced by the CVC method can be sintered to theoretical density at temperatures as low as 0.4 Tm. This is in contrast to the ultrafine powders produced by conventional ambient pressure combustion flame and arc-plasma powder processing methods, which yield cemented aggregates that can be consolidated only at much higher sintering temperatures.

The CVC process has been used to synthesize n-powders of a variety of ceramic materials, which cannot easily be produced by the IGC process, because of their high melting points and/or low vapor pressures. Examples are n-SiC_xN_y powders, for which there are many suitable organosilicon precursors, such as hexamethyl-disilazane (HMDS). In a particular case, the actual composition of the resulting powder is strongly influenced by the choice of carrier gas. Thus, HMDS/H_2O, HMDS/H_2 and HMDS/NH_3 give n-ceramic powders with compositions close to SiO_2, SiC and Si_3N_4, respectively.

Consider the CVC synthesis of Si-rich powders from HMDS/He, in which the temperature of the tubular reactor is varied over the range 1100-1400C in 100C steps. With the flow

Figure 3.

Schematic diagram of scaleable process for the preparation of nanostructured powders, starting from aqueous solution precursors.

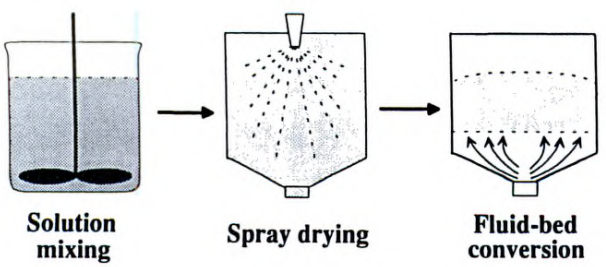
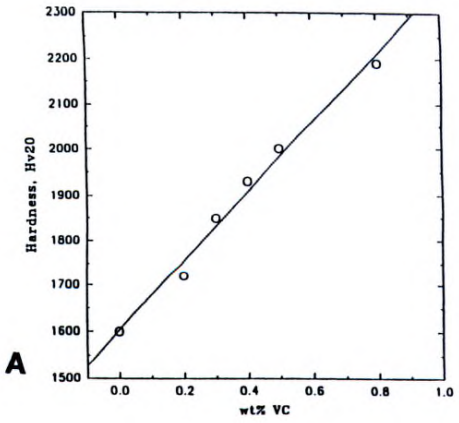


Figure 4.

(a) Hardness vs. wt.% VC (grain growth inhibitor) in WC/7 wt% Co alloys, (b) hardness vs. wt.% Co binder phase in WC/Co alloys, comparing data for conventional 'micrograined' and 'nanograined' materials.



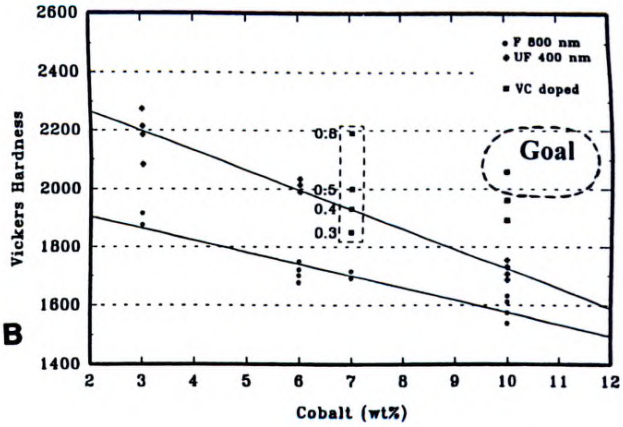
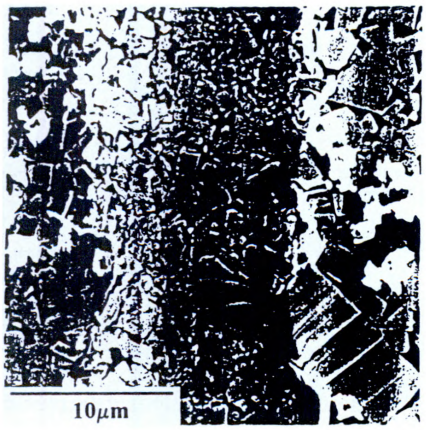


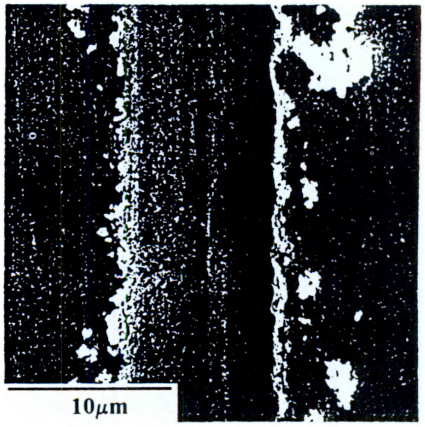
Figure 5.

Comparison of response of (a) micrograined, and (b) nanograined WC/Co samples to a scratch test (100 gm load, using a diamond indentor).



Micrograined

* Hv_2 : 1220 Kg/mm^2
* Fracture of WC particles
* Deformation of WC particles
* Loose WC particles



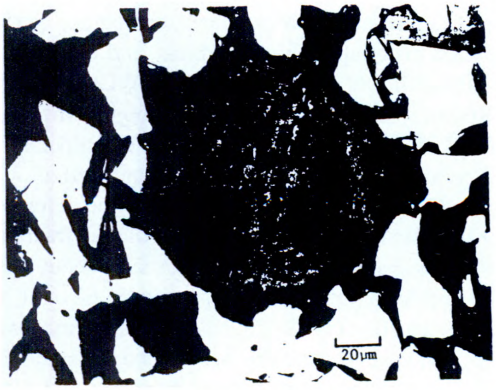
Nanograined

* Hv_2 : 2260 Kg/mm^2
* Purely ductile deformation not seen before at this hardness

Figure 6.

Comparison of sinterability of (a) micrograined, and (b) nanograined ZrO_2 matrix in an Al_2O_3 fiber-reinforced composite.

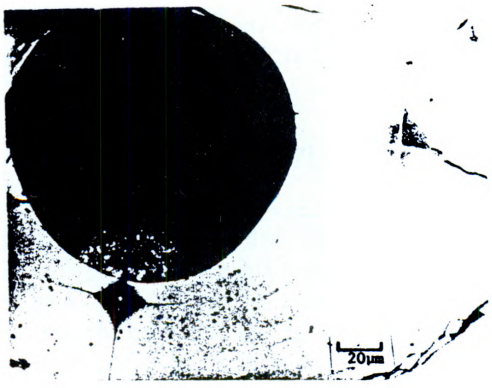
Micrograined Zirconia Matrix (1400°C/16 KSI)



A

- High Porosity
- Severe Fiber-Matrix Reaction
- Fiber Damage

Nanograined Zirconia Matrix (1040°C/16 KSI)



B

- Fully Dense
- No Indications of Fiber-Matrix Reaction
- Indentation Generated Crack follows Interface

Figure 7.

Schematic diagrams showing two different approaches for synthesizing whisker-reinforced ceramic matrix composites; (a) unidirectionally reinforced, (b) isotropically reinforced.

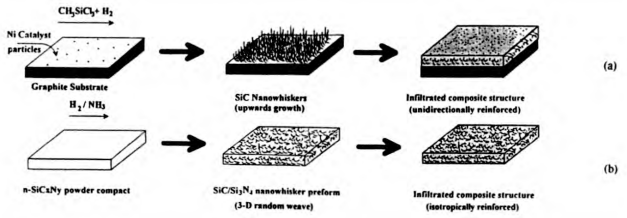
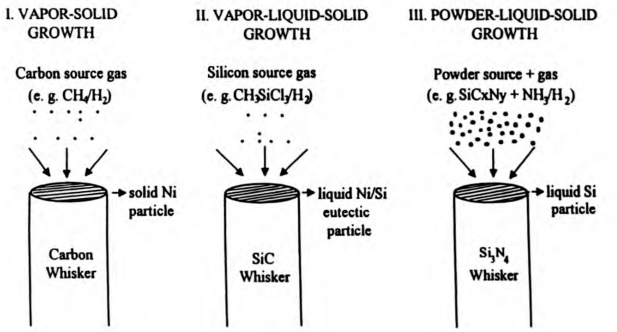


Figure 8.

Illustration of three types of whisker growth mechanism.



rate of He fixed at 8.55x10-3 mole/min, the HMDS concentration in the gas stream is about 16.4 mole % at ambient temperature. Under these conditions, about 2 grams of amorphous n-SiC_xN_y powder is collected in several minutes. Relevant data on powder characteristics and compositions are presented in Tables 1 and 2. The average particle size from TEM ranges from 6-10 nm, with the smallest particle size corresponding to the highest reaction temperature. The density of the particles increases with decomposition temperature, indicating a higher degree of precursor pyrolysis at the highest temperature. A noteworthy feature is the unexpectedly large amount of oxygen in the powders, which decreases with increasing pyrolysis temperature. In contrast, the concentration of carbon and nitrogen in the powders increases with pyrolysis temperature. The atomic ratios of the constituent elements of the powders are clearly at variance with the atomic ratios in the original HMDS precursor. Furthermore, there is substantially more carbon in the product powders than that of stoichiometric SiC. In all cases, annealing the amorphous powders at 1600C in flowing high purity argon for 2 hours causes crystallization to essentially phase pure SiC. The crystallization process is initiated at about 1100-1200 C and is essentially complete at 1400C, Figure 2.

Nanostructured cermets

Ceramic/metal composites (cermets) are the materials of choice for cutting tools, drill bits and wear parts. Typically, such materials are produced by mechanical mixing of powders of the constituent phases, followed by cold compaction and liquid phase sintering. This limits the attainable structural scale of the composite material to about 0.3 microns, so-called 'micrograined' cermets. Recently, a new chemical process, called Spray Conversion Processing (SCP), has been introduced, which is capable of synthesizing 'nanograined' cermets[6], Figure 3. The new process involves three steps: (1) preparation of an aqueous solution mixture of salts of the constituent elements, (2) spray drying of the starting solution to form an homogeneous precursor powder, and (3) fluid bed conversion (reduction and carburization) of the precursor powder to the desired n-cermet powder.

For several years, Rutgers University has been conducting research on the preparation and consolidation of n-WC/Co powders[7]. Concurrently, a tribology group at Stevens Institute of Technology has been evaluating their friction and wear properties[8]. More recently, the University of Connecticut has established a complementary research activity on thermal spraying of n-WC/Co and other cermet powders. Highlights of this tripartite collaborative research program include: (1) synthesis of n-WC/Co powders with WC grain size controllable down to about 50 nm, (2) densification of powder compacts by liquid phase sintering in vacuum or hydrogen, (3) mitigation of WC grain growth during liquid phase sintering by the use of potent grain growth inhibitor carbide phases, such as VC or Cr_3C_2, (4) demonstration of hardness in fully sintered nanograined WC/Co (with inhibitor carbide phase) that is twice that of conventional micrograined material, (5) confirmation of enhanced wear resistance and cutting performance in sintered materials of high hardness, and (6) demonstration of the feasibility of thermal spraying n-WC/Co powders.

Recent research has shown that incipient melting in VC- and Cr_3C_2-doped WC/Co alloys occurs at temperatures about 250C below the melting point of the undoped alloy[9]. Moreover, we have found that these alloys can be deformed in the semi-solid state, provided that the volume fraction of the dispersed carbide phase does not exceed about 75%. Such 'semi-solid forming' is not a new concept. Several processes were introduced in the 1970's, based on pioneering work done at MIT. The desired structure is produced by cooling a molten alloy to form a slurry, which is mechanically stirred to break-up the dendrites. The roughly spherical morphology of the granular structure of the semi-solid alloy leads to a low shear strength, even with a relatively high solid fraction, which permits the semi-solid to be shaped in a die. In Rheocasting, a slurry is produced in a mixer and delivered directly into a die. In Thixocasting, a billet having the required microstructure is

first cast and, at a later time, a slug cut from the billet is heated to the semi-solid state and forged in a die. The present semi-solid processing method differs from the MIT method in several respects: (1) a slurry is formed by heating a powder mixture into the semi-solid region of the phase diagram, (2) no mechanical stirring is required to obtain the desired semi-solid state, with a roughly spherical grain or particle morphology, and (3) an ultrafine structure is obtained by utilizing a nanocomposite powder produced from a chemical precursor. Currently, we are investigating semi-solid forming of Cr_3C_2-doped n-WC/Co alloys, because of the unusually low melting point of the Co-rich eutectic liquid phase. An interesting aspect is the effect of subsequent directional solidification of the eutectic liquid phase, which is confined to narrow channels between the WC phase in the bicontinuous structure. The possibility exists of being able to generate a single crystal Co-rich matrix that is isotropically reinforced with a rigid network of nanograined WC phase.

In tests performed on VC-doped n-WC/Co materials, the measured hardness increases with VC concentration up to a maximum of 2190 VHN at 0.8 wt.% VC[7], Figure 4. These data correlate with a reduced mean free path for the cobalt binder phase (i.e.reduced WC grain size), as determined by magnetic coercivity measurements (also confirmed by TEM). This is striking evidence for the potency of VC as a WC grain growth inhibitor in liquid phase sintering of n-WC/Co alloys. Recent measurements show that nanograined materials possess superior hardness at all compositions. The relatively high hardness (1850 VHN) at high Co content (10 wt% Co) raises interesting questions about the prospects of being able to achieve improved hardness in n-WC/Co without sacrificing fracture resistance. We are investigating the relationship between hardness and fracture resistance, including both transverse rupture strength and fracture toughness, in fully sintered n-WC/Co, with varying amounts (3-30 wt%) of the ductilizing Co phase.

Table 1.

Some important Characteristics of As-Synthesized N-SiCxNy Powders.

Sample name	Reactor Temperature (C)	Powder density* (g/cm^3)	Powder appearance	Surface area** (M^2/g)	Particle size from BET (nm)	Particle size from TEM (NM)
S-1	1100	2,614	brown	568	4	10
S-2	1200	2,737	dark-brown	555	4	10
S-3	1300	2,781	brown-black	360	6	8
S-4	1400	2,783	jet-black	272	8	6

*measured by pycnometry musing He gas

**measured by single point BET adsorption

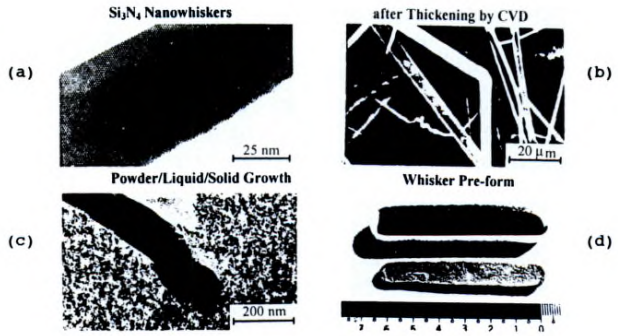
Table 2.

Chemical Compositions of As-synthesized Amorphous n-SiCxNyO$_2$ Powders, as Determined by Rutherford Backscattering Spectroscopy.

Sample name	Experimental Condition	SiCxNyOz X	Y	Z
HMDS	as-received precursor	3.00	0.50	0.00
S-1	synthesis at 1100C	1.26	0.35	0.61
S-2	synthesis at 1200C	1.35	0.40	0.47
S-3	synthesis at 1300C	1.45	0.48	0.29
S-4	synthesis at 1400C	1.51	0.49	0.28
A-1	annealing at 1600C	1.00	0.00	0.00

Figure 9.

(a) HREM image of as-synthesized Si_3N_4 whisker, (b) whiskers after thickening by CVD, (c) evidence for powder liquid-solid whisker growth mechanism, and (d) whisker pre-form.



Another interesting observation has been the striking difference in response of micrograined and nanograined materials to a scratch test[8], Figure 5. The micrograined material shows evidence for combined plastic deformation and fracture of the WC grains, whereas the nanograined material yields by pure plastic deformation, despite its high hardness. Evidence for superior abrasive wear resistance of n-WC/Co, as well as for improved cutting performance of n-WC/Co drill bits has been obtained[10].

Using SCP technology, Nanodyne Inc. is producing industrial-scale quantities of n-WC/Co powders, with compositions extending over the range of commercial interest (3-25 wt% Co). Advances are also being made by several companies in the fabrication of cutting tools, drill bits and wear parts.

Nanostructured composites

Ceramic matrix composites (CMC's) are the materials of choice for high temperature structural applications in the next generation of high performance gas turbine and internal combustion engines. Typically, CMC's are fabricated in three steps: (1) the fibers are woven into the desired 2-D or 3-D structures, (2) the woven structures are infiltrated with ceramic matrix powders, and (3) the composite preforms are consolidated by high temperature sintering. Because of the relatively large particle size and the extent of particle agglomeration in commercially available ceramic powders, it is difficult to completely infiltrate the interconnected pores in the woven structures. Thus, the resulting sintered composites can contain many flaws. In addition, because of the high temperature required for sintering, severe fiber-matrix reaction and even fiber damage often occurs. Recent research has shown that these problems can be overcome by utilizing IGC- or CVC-synthesized n-ceramic powders as matrix infiltrants, because of the ease with which a nanoparticle slurry can be infiltrated into a woven pre-form and its lower sintering temperature.

A recent test performed on an Al_2O_3-fiber weave infiltrated with 'nanograined' ZrO_2 powder has demonstrated the feasibility of both low temperature sintering and ideal infiltration of the fibrous structure[11], Figure 6. A fully dense composite was achieved at 1040C/16 ksi, with no indications of fiber-matrix reaction. In contrast, the fibrous material infiltrated with conventional 'micrograined' ZrO_2 powder, and sintered at 1400C/16 ksi, showed high porosity and severe fiber-matrix reaction, as well as gross fiber damage. Another interesting feature displayed by the nanograined-matrix composite was that cracks initiated by microhardness indentations tended to follow fiber-matrix interfaces. In other words, the fiber-matrix interfaces appeared to be acting as effective crack blunters. The possibility of enhancing fracture toughness by this mechanism is being explored.

Looking ahead, an interesting extension of this technology would be to fabricate nanostructured whisker-reinforced CMC's entirely from metalorganic precursors. Two options have recently emerged from our research, Figure 7. Using trichloromethyl-silane as precursor compound and a nanodispersed nickel catalyst on a graphite support, the feasibility of growing SiC nanowhiskers at practical growth rates of several mm/hr at temperatures of 1100-1400C has been demonstrated.[12] Whisker growth occurs by the so-called vapor-liquid-solid (VLS) mechanism, where the silicon source gas reacts with the Ni nanoparticles to form a liquid Ni/Si eutectic; thereafter, whisker growth occurs by transport of the silicon through the liquid droplet to the growing whisker at its base, Figure 8. Because this is in effect a growth-from-the-melt process, a typical SiC whisker displays a high degree of crystalline perfection and exceptionally high strength. Recently, we have also discovered that CVC-synthesized n-SiC_xN_y powders, prepared by thermal decomposition of hexamethyl-disilazane, can also be transformed into nanowhiskers by a simple heat treatment in a reactive gas stream[5]. Thus, heating the n-powders in flowing H_2 at 1200 C

yields SiC whiskers, whereas heating in flowing NH_3/H_2 gives virtually perfect single crystal Si_3N_4 whiskers. Rapid growth of the whiskers occurs by two different mechanisms: by a new powder-liquid-solid (PLS) growth mechanism and by the more familiar VLS growth mechanism, Figure 8. An interesting feature of the thermochemical conversion of the n-powders into whiskers is the formation of a three-dimensional random weave, which replicates the shape of the original powder bed from which it is derived. In fact, the whisker pre-form, which is both strong and resilient, can be removed intact from its container, say a ceramic crucible, Figure 9, and used for subsequent processing. We are now attempting to infiltrate whisker pre-forms with nanoparticle slurries in order to investigate the possibilities for n-CMC sheet fabrication, Figure 7.

As an extension of this work, we have also initiated research on n-MMC's and n-PMC's. The feasibility of processing n-MMCs by electro-chemical infiltration of whisker pre-forms has been demonstrated, using electroless nickel plating as the means to infiltrate the woven structures[13]. The hardness and wear behavior of the electrochemically infiltrated material has shown a several fold increase over the value of the bulk matrix. Research in n-PMC's is still in its infancy, but a novel approach to composite fabrication has been successfully tested.

Nanostructured coatings

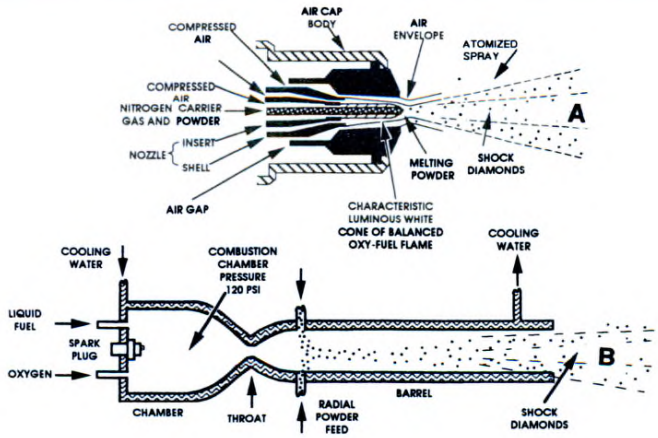
Thermal spraying is a widely used industrial process for applying protective coatings to materials surfaces. An attractive feature of the process is its ability to produce coatings, ranging in thickness from 25 microns to several millimeters, of almost any desired material. Historically, thermal spray deposition of metal, ceramic and composite coatings was developed for applications in aircraft gas turbine engines. During the past ten years, the range of applications has rapidly expanded into other areas, including land-based gas turbines, diesel engines, automobiles, surgical implants and wear parts.

In thermal spraying, powders are fed into a combustion flame or plasma arc spray gun, where they are rapidly accelerated by the high velocity gas stream exiting from the gun nozzle, Figure 10. During the short residence time in the flame or plasma, the particles are rapidly heated to form a spray of partially or completely melted droplets. The large impact forces created as these particles arrive at the substrate surface promotes strong particle-substrate adhesion and the formation of a dense coating. Even so, problems arise from the inability to reproducibly control coating composition, structure and grain morphology, presence of residual porosity, and technical difficulties associated with delivering powder at a uniform rate to the thermal spray gun. Furthermore, it appears that there is no possibility using existing technology to further refine the coating structure, which is the most direct route to enhance properties and performance, nor for that matter can the powder delivery problem be easily resolved. To overcome these limitations, we have been investigating the use of nanostructured powder feed, delivered to the gun in the form of a slurry or generated in-situ from a metalorganic precursor[14]. Some progress has already been made, but more work is needed to realize the full potential of uniform and continuous delivery of nanoparticle powders to the thermal spray gun.

Recent research at the University of Connecticut has demonstrated the feasibility of thermal spraying of n-WC/Co powders, prepared by SCP technology. A procedure has also been devised to reprocess as-synthesized powders into sprayable powder agglomerates, suitable for use in standard powder feed systems, irrespective of whether they have been prepared

Figure 10.

Schematic diagram of two types of HVOF gun, (a) low pressure throat type (Metco Diamond Jet) and (b) high pressure chamber type (Hobart Tafa JP-5000).



by chemical or physical methods. Important differences in the thermal spraying of 'micrograined' and 'nanograined' WC/Co powders can be appreciated from Figure 11. Micrograined particles experience surface melting only, which contrasts with homogeneous or bulk melting of nanograined particles. Thus, when the particles impinge on the substrate, the semi-solid nanograined particles flow more freely, thereby forming a much denser coating, which has a completely uniform nanocomposite structure. Because of the rapid kinetics of WC nanograin dissolution in the liquid Co, the relative amounts of these two phases can be predicted using the equilibrium phase diagram. Thus, a controlling factor is the degree of superheat above the pseudo-binary eutectic in the WC-Co system. The higher the particle superheat the lower its viscosity, and hence the higher the deformation rate when it collides with the substrate. Under appropriate conditions, the semi-solid particles should display thixotropic behavior, i.e. the dynamic viscosity should decrease with increasing shear rate. The turbulent flow created in the impacting particles should be useful in disintegrating particle agglomerates and thus promoting structural homogeneity in the deposited coating.

Tests have shown a much higher hardness in the nanograined composite coating, provided that precautions are taken to avoid decarburization in the flame or plasma. One method of accomplishing this is to use low pressure plasma spraying, where the powder particles are naturally protected from oxidation in the plasma flame. High density coatings, with reproducible high hardness values, can be achieved by this means. In high cobalt alloys, the resulting 'splat-quenched' coating consists of nanodispersed WC grains in an amorphous Co-rich matrix phase[15]. The problem of decarburization in thermal spraying of WC/Co powders is less acute in high velocity oxy-fuel (HVOF) spraying, because of the lower particle temperatures and shorter particle residence times, compared with plasma spraying.

Important recent innovations in HVOF and plasma spraying have been the introduction of (1) yttria stabilized zirconia (YSZ) thermal barrier coatings, either as an overlay coating on an MCrAlY bond coat or as a continuously graded composite coating, and (2) Cr_3C_2/Ni hard coatings that display hot corrosion resistance superior to that of conventional WC/Co. We have been investigating the use of nanostructured powders of these materials, prepared by ASR and CVC methods, as feedstocks in thermal spraying. Preliminary work has underscored the need to develop improved means of delivering the n-ceramic powders to the combustion flame or plasma. Our research is leading us towards the use of nanoparticle slurry feeds, formed by ultrasonic dispersal of the as-synthesized powders, and delivered directly to the spray guns. A multiple source nanoparticle delivery system is now being developed in order to generate multilayer or continuously graded coating structures. The coatings will be designed to minimize thermal expansion mismatch stresses between the different layers, which is a prerequisite to enhance resistance to coating spallation under thermal cycling conditions.

Future perspective

Looking ahead, it is clear that whatever the processing route selected to produce a specific nanostructured bulk material or coating, property optimization will require in-situ monitoring and feed-back control. Anticipating this need, an effort has been initiated to probe the environment in which the materials processing occurs.

Currently, attention is focussed on the mechanisms involved in thermal spray deposition of nanostructured coatings,

Figure 11.

Comparison of thermal spray deposition of conventional and nanostructured WC/Co powders.

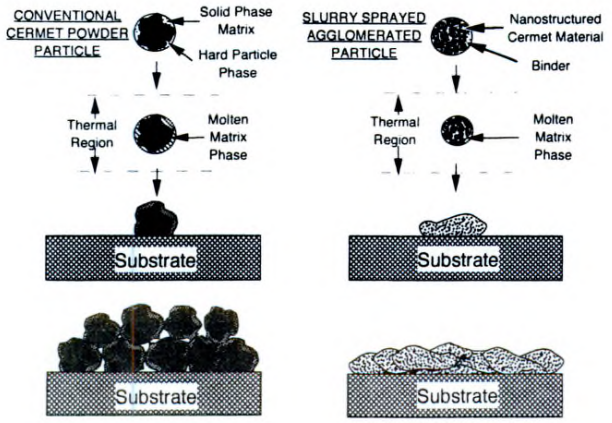
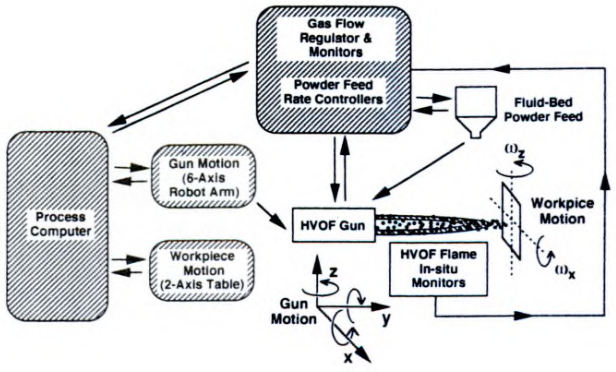


Figure12.

Intelligent processing of nanostructured coatings using an HVOF thermal spray system.



using the high velocity oxy-fuel (HVOF) method. The overall sensing and control system envisioned for an HVOF system is shown schematically in Figure 12. The use of diagnostic techniques is required to establish (1) the spatial and velocity distributions of the particles in the combustion flame, (2) the temperature profile and nature of the chemical reactions occurring in the flame, and (3) the characteristics of the splat quenching phenomena as the particles impinge on the substrate. A convenient method for determining spatial and velocity distributions of in-flight particles is by thermal imaging or laser strobe illumination, whereas spectral sensors may be used to establish the nature of the chemical reactions occurring in the flame, which is a critical factor in spray deposition of coatings of n-WC/Co and other materials. A powerful technique for detailed investigation of combustion phenomena is laser-induced fluorescence, which may be used to determine the nature of chemical species in the high velocity gas stream, and to provide data on the shock front associated with the gas stream. As can readily be appreciated, the entire thermal history of the nanoparticles while in transit in the HVOF flame largely determines the structure of the resulting deposited coating.

Experimental data obtained from the various imaging and flame analysis methods will be used to validate computer simulations of the HVOF process. Global diagnostics of such variables as gas and particle flow rates, gas pressure, stand-off distance (gun to substrate), and substrate temperature will be correlated with coating structure and morphology. This information will be benchmarked with the simulations, leading to reduced or derived process simulators required for intelligent control algorithms and system development. It is anticipated that these studies will provide the basis for the design and construction of a production thermal spray unit, with real-time process control. A feature of this unit will be multi-axis robotic control of the thermal spray gun, which will permit uniform deposition of shape conformal coatings on complex parts in a highly reproducible manner. This is critically important in high volume production of coatings, where detailed inspection of individual components is not possible.

A successful initiative in thermal spraying will lead quite naturally to a consideration of other opportunities for modeling, numerical simulation and diagnostics, particularly in the area of vapor phase synthesis of nanostructured powders from metalorganic precursors.

Biography

B. H. Kear – See Profiles in Science page 14.

P. R. Strutt of the University of Connecticut, is the Director of Nanoprecision Manufacturing in the Precision Manufacturing Center, and Emeritus Professor of Metallurgy. He has 100 scientific publications, of which 28 involve the synthesis of nanostructured materials, using chemical processing and laser processing. His work on laser processing of materials was supported by ONR (1978-1988), continuation of this work has resulted in a patent for making nanofibers. At the Precision Manufacturing Center state funded facility, he has established an industrial-scale facility for synthesizing of nanostructured powders, and depositing nanostructured coatings by thermal spray deposition.

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Profiles in Science

Bernard H. Kear

Bernard H. Kear, who is a principal investigator of the Office of Naval Research, received his B.S. and Ph.D. degrees in Materials Science and Engineering from the University of Birmingham, England. From 1958-63, he was with the Franklin Institute in Philadelphia where he studied the effects of long-range ordering on the plastic properties of crystals. From 1963-81, he was with the Pratt & Whitney Division of United Technologies Corporation where he investigated the interrelationships between structure/properties/processing in superalloys, participated in the development of single crystal turbine blade technology, and spearheaded the development of laser surface modification treatments.

From 1981-86, he was Scientific Advisor at Exxon's Corporate Research Center, where he conducted research in chemical vapor deposition and its applicability to large scale *in-situ* surface modification of reactor vessels and the upgrading of the surface properties of steel structures. In 1986, he assumed his present position as State of New Jersey Professor of Materials Science and Technology. Presently, he is Chairman of the Department of Mechanics and Materials Science. His current research activities are focused on chemical vapor deposition of ceramics, chemical synthesis of nanostructured composite materials, and metal-oxide chemical vapor deposition (MOCVD) synthesis of high Tc superconductors.

Kear has published 200 technical papers, has edited 9 books in the field of materials, and has been granted 30 patents. He was awarded the Mathewson Gold Medal of TMS-AIME in 1971, and the Hower Medal of ASM in 1970. He was elected to the National Academy of Engineering in 1979. From 1983, he served as a member of the National Materials Advisory Board and was Chairman from 1986-1989. Currently, he is co-editor of the journal Nanostructured Materials.

For the last several years, Professor Kear has been engaged in efforts to facilitate the transfer of technology developed by universities to industry without disturbing the independence of individual faculty. In the following brief article, he describes the results of these efforts at Rutgers University.

Methodology for Technology Transfer at Rutgers University

Bernard H. Kear

A major concern in today's increasingly competitive industrial environment is the typically long time from discovery to commercialization. In order to accelerate the innovation process. Rutgers University has been evaluating the effectiveness of a concurrent R&D strategy, where university research is linked to industrial development from the outset of an applications-driven program. This strategy has already been successful in at least one test case. Currently, Rutgers is evaluating a number of options for promoting the rapid advancement, transfer and implementation of new technologies, as they emerge from the various research laboratories and advanced technology centers.

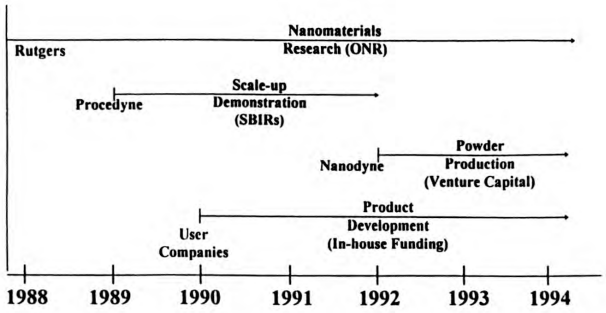
As an illustration of the effectiveness of such a concurrent R&D strategy, we will examine Rutgers' experience with the commercialization of nonostructured WC/Co hard materials, Figure 1. In 1988, pioneering research at Exxon/Rutgers led to the discovery of a new chemical synthesis method for preparing nanostructured WC/Co powders. Next, consultation with chemical engineers at Procedyne Corp. led to a conceptual engineering approach for the commercial scale production of such powders. in 1990-2, this became a reality under an Small Business Innovation Research (SBIR) technology demonstration program, sponsored by ONR. During this period, end-user companies received test quantities of nanostructured WC/Co powders from Procedyne. Thus, two years after the discovery of the basic process, all three necessary components for the rapid development of the technology were in place. It was this early linkage of the on-going university research with process and product development that was the key to the rapid implementation of the new technology.

Today, Nanodyne Inc, established in 1992 as a joint venture of Rutgers University and Procedyne, is producing high quality nanostructured WC/Co powders from aqueous solution precursors. Nanodyne's production process, Figure 2, involves essentially three sequential steps: (1) solution mixing of water soluble tungsten and cobalt salts to fix the composition of a starting solution, (2) spray drying of the starting solution to form an homogeneous precursor powder, and (3) fluid bed thermochemical conversion (reduction and carburization) of the precursor powder to the desired end-product WC/Co powder. Using this technology, Nanodyne has gained considerable experience in producing nanostructured WC/Co powders, extending over the compositional range of commercial interest from 3-20 wt% Co. Among the many end-user companies (over 20 at last count) participating in the development of applications for these powders are Kennametal (sintered parts) and Engelhard Surface Technologies (thermal sprayed coatings).

Building on this experience, a technology transfer organization, dedicated to the commercialization of new nanomaterials technologies, has been established. This new organization, called the Nanomaterials Technology Transfer Center (NTTC), Figure 3, is a subsidiary business unit of Sci-Tech Applications (STA) Inc. The latter is the New Jersey

Figure 1.

Timeline showing concurrent R&D strategy used to rapidly commercialize nanostructured WC/Co powder processing technology.



satellite office of NASA's Northeast Regional Technology Transfer Center. The office provides assistance in the transfer of technology to commercial markets by developing alliances and partnerships between industry and research institutions. A new and major program under an ARPA Technology Reinvestment Program Grant began in February 1994. This program is directed at assisting defense contractors with their defense conversion efforts and the development of dual-use technologies. Through these programs, STA has access to technology transfer networks in industry, federal laboratories and research universities.

The establishment of the NTTC gives researchers at Rutgers University more latitude to advance their research missions without getting embroiled in market decisions, which are best left to industry. In effect, NTTC serves as a 'halfway house' between the technology creators (the university) and the technology users (industry), assuring an efficient and market-driven technology development and commercialization process. The business strategy of the NTTC is:

(1) to establish a flexible and responsive environment to facilitate the development and commercialization of nanomaterials technologies;

(2) to create an environment where market-driven technology can flourish and attract industrial alliances and investments;

(3) to commercialize technologies through collaborative agreements, licensing, joint ventures and spin-off companies.

It is envisioned that federal and state government grants, industrial investments and venture capital will be the principal sources of future funds to operate the NTTC. In the meantime, the Associated Institutions for Materials Sciences (a New Jersey research consortium), and the Northeast Regional Technology Transfer Center are providing resources to operate the center.

Figure 2.

Schematic diagram of Nanodyne's Spray Conversion Processing technology for the production of nanostructured WC/Co powders.

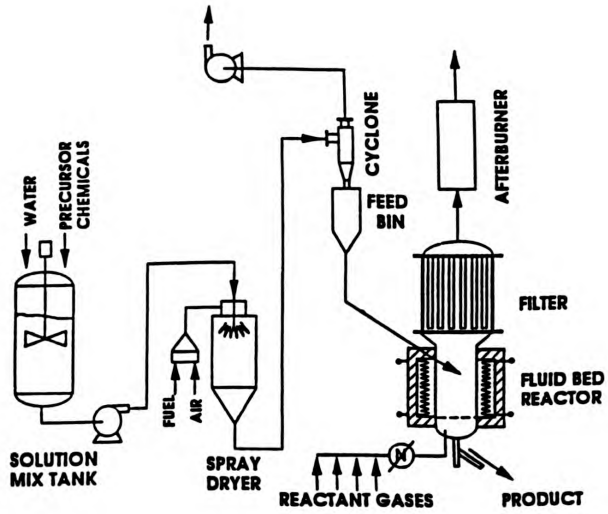
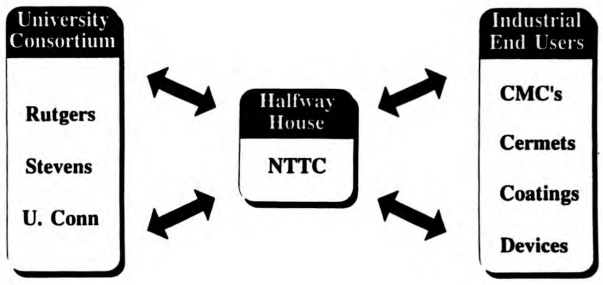


Figure 3.

Concept of 'halfway house' for technology transfer, wherein university research is linked to process and product development from the outset of the innovation process.



Polymerizable Phospholipid Membranes in the Synthesis of Submicrometer and Nanometer Particles

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Center for Bio/molecular Science and Engineering
Naval Research Laboratory

Introduction

This article focusses on recent efforts connecting two emerging technologies: self-organized lipid assemblies and the unagglomerated nanoparticle synthesis. Phospholipids are biologically ubiquitous, chemically-simple molecules that self-organize into molecular assemblies when dispersed in water. These amphipathic molecules (having a polar headgroup and a nonpolar hydrocarbon tail) orient to minimize contact of their nonpolar tails with water leading to self-assemblies of membranes, the minimum energy structures. The phospholipids in membranes are held together by van der Waals forces and hydrophobic interactions. Phospholipids can make membranes with different morphologies and be stabilized by cross-linking the lipid monomers. Figure 1 illustrates various morphologies attained by self-organization of phospholipids. The size, shape, and properties of the organized assemblies are dependent on the lipid structure and the nature of the dispersion medium.[1,2] Closed bilayer assemblies also provide a secluded environment, similar to that of reaction vials, in which different types of reaction chemistry can be accomplished either at the membrane surface or in the free volume of the internal compartment of the microstructures. By designing a phospholipid or an amphipathic molecule and choosing an appropriate mixture of amphiphiles, one should be able to fabricate membranes that are equipped with reactive sites and have predictable properties.

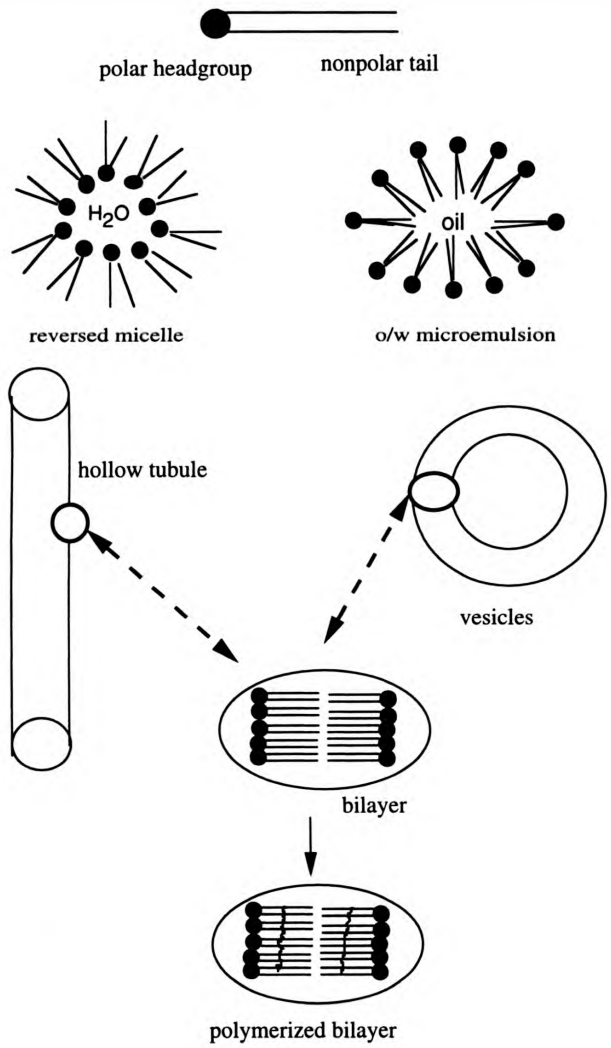
Synthesis of submicron (100 nm < diameter 1 μm) and nanoscale (1 nm ≤ diameter ≤ 100 nm) particles is an important area of research pursued at the basic science as well as on technological levels. Nanoscale particles - also referred to as ultrafine particles, nanostructured or nanophase powders - exhibit volume effects and surface effects which are absent in the same material with dimensions in the micron range.[3-7] Nanoscale particles have potentially unique physical properties (e.g. optical, dielectric, magnetic, mechanical), transport properties (e.g. thermal, atomic diffusion) and improved processing characteristics (e.g. faster sintering kinetics, superplastic forming).[3-7] Conventional methods for making submicron and nanoscale particles include vapor phase synthesis, mechanical milling of solid phases, and solution chemistry. Solution chemistry is more versatile than other two approaches since it allows manipulation of matter at a molecular level and provides better chemical homogeneity of materials, and is cost effective.

Limits of Solution Chemistry

Although solution chemistry can be a practical route to synthesis of both submicron and nanoscale particles of many materials, issues such as the control of particle size distribution, morphology and crystallinity, particle agglomeration during and after synthesis and processing of these particles need further investigation. Materials such as paints, pigments and electronic inks, and ferrofluids, and the processing of advanced functional and structural ceramics require that the particles be uniform in size, and stable against agglomeration. Fine particles, particularly nanoscale particles with significant surface area, often agglomerate to minimize the total surface or interfacial energy of the system. The agglomeration of nanoscale particles defeats the advantages of using ultrafine particles. For example, the agglomeration of nanoscale ceramic particles may lead to differential density after they are compacted; and for magnetic materials, the magnetic properties arising from single domains are diminished if the ferromagnetic nanoscale particles are not isolated from each other. Non-uniform particle size presents a problem of non-uniform material response if particles are used as-synthesized without additional work-up. If they are used as a consolidated part, the green compact often requires sintering at high temperature in order to obtain full density. The particles with a mixed size distribution will undergo abnormal grain growth which adversely affects the densification and properties of the materials.

Figure 1.

A schematic of the hierarchy of lipid microstructures



Surfactant Approach

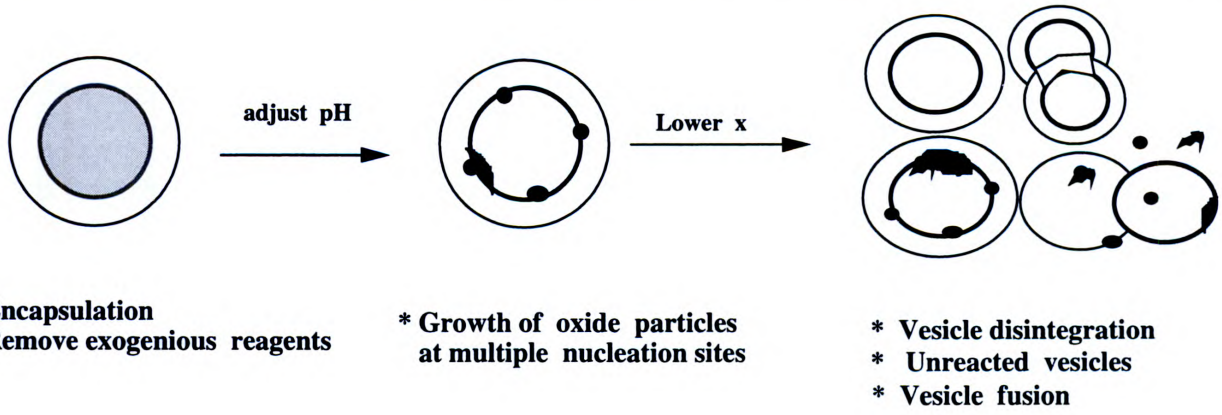
To synthesize stabilized, uniform fine particles, colloidal chemistry offers a possible route. For instance, ferrofluids of amorphous iron nanoscale particles[8] and ceramic hydroxides[9] have been prepared by this route. Colloidal stability can be achieved by either synthesizing the particles in the presence of surfactants or by dispersing as-synthesized particles in surfactants. Many emerging technologies, in particular the stabilization (the prevention of agglomeration) of fine particles in liquid media, involve the use of surfactants.[10,11] The choice of surfactant always depends on the type of materials to be synthesized or dispersed.

Vesicles for making Nanoparticles

Increasingly, the trend in the field of nanoparticle synthesis is to use multidisciplinary approaches that involve material synthesis and processing, integrating solution chemistry and bio/molecular science to develop routes for nanoparticle synthesis within "reaction vials" formed from surfactants.[12,13] For example, several groups have used membrane strategy to precipitate particles within vesicles or creating vesicle-sized particles by metallizing the vesicles.[14-22] Vesicles are closed bilayer structures formed from phospholipids and surfactants. There are many types of lipids available for constructing vesicles including some with charged headgroups or headgroups derivatized with other functional groups. The multilamellar vesicles are usually 100 - 800 nm in diameter whereas the single bilayer vesicles are 30 - 60 nm in diameter. Vesicles have a number of useful features including a large number of solubilization sites, a hydrocarbon region able to incorporate hydrophobic molecules, free movement of polar molecules entrapped inside the water pool, and binding of small charged ions to the surfaces of vesicles when charged lipids are present. In addition, the stability of the vesicles can be enhanced by polymerization. This is achieved by cross-link-

Figure 2.

A schematic of intra-vesicular synthesis of nanoscale oxide particles

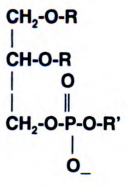


ing the hydrocarbon tails or the head groups which are functionalized by vinyl, methacrylate, diacetylene, isocyano or styrene groups.[23]

Phospholipid vesicles can be used as reaction cages and templates for intra-vesicular precipitation of nanoparticles. This synthetic route is unique in that: (i) intra-vesicular chemical reactions are different from the free solution reaction, thus it is possible to produce new phases, (ii) membrane structures as reaction cages provide a means to vary intra-vesicular supersaturation and nucleation rate, and thus particle size and distribution; (iii) nucleation at the membrane interface can be controlled by the density of functional groups; and (iv) chemical homogeneity of composite materials can be controlled at the level of vesicular dimensions. The membrane also may act as an agglomeration barrier and a lubricant for subsequent consolidation. Desirable membranes have the following features: cost effective, large yield, interfacial chemistry to control nucleation of inorganic phases and diameter less than 100 nm with controllable size distribution. In addition, the permeability of the lipid vesicle membrane is highly selective, i.e. anions can readily cross the membrane. Precipitation of inorganic particles occurs inside the vesicular compartment when the diffusion of appropriate anions occurs. Figure 2 is a schematic of intra-vesicular synthesis of nanoscale oxide particles. If the vesicles are not stable under reaction conditions, they show disintegration, fusion, and no reaction. Nanoparticles such as silver oxide,[17] iron oxides,[18] aluminum oxide,[19] cobalt ferrite[20] and multicomponent mixtures of Y, Ba, Cu and Ag[21] have been synthesized by intra-vesicular precipitation. Much work still needs to be done on characterization, properties, yield and purity of the synthesized particles.

Figure 3.

Chemical structures of diacetylenic phospholipids



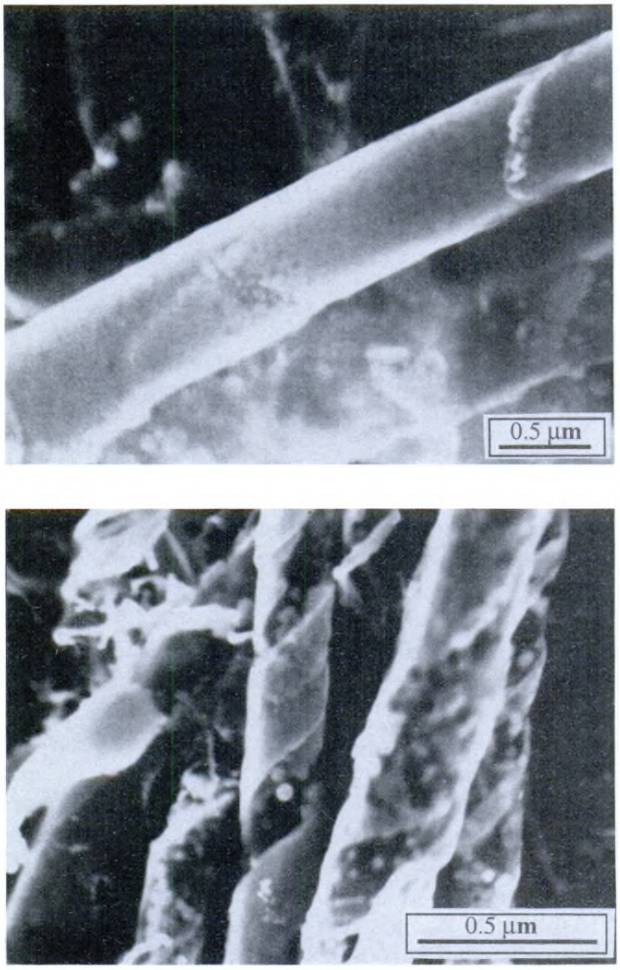
1. R= $OC(CH_2)_8-C\equiv C-C\equiv C-(CH_2)_9-CH_3$; R'= $CH_2-CH_2-NMe_3$ (Charge neutral)
2. R= $OC(CH_2)_8-C\equiv C-C\equiv C-(CH_2)_9-CH_3$; R'= CH_2-CH_2-OH
3. R= $OC(CH_2)_8-C\equiv C-C\equiv C-(CH_2)_9-CH_3$; R'= $CH_2-CH_2-CH_2-OH$
4. R= $OC(CH_2)_8-C\equiv C-C\equiv C-(CH_2)_9-CH_3$; R'= H (dibasic acid)
5. R= $OC(CH_2)_{14}-CH_3$; R'= CH_2-CH_2-OH (saturated analogue)
6. R= $OC(CH_2)_{16-18}-CH_3$; R'= CH_2-CH_2-OH (unsaturated, inexpensive analogue)

Mixed Phospholipid Membranes Mediated Nanoscale Particle Synthesis

Although the efforts described in preceding paragraph provided only low yields of nanoparticles of uncertain purity, they did provide the proof of principle that this approach was feasible. A probable cause of the unacceptable performance is the stability of the lipids and lipid membranes under experimental conditions. Small changes in phospholipid structure or dispersion medium have been demonstrated to produce large changes in membrane morphology and stability.[24-27] Molecularly engineered phospholipid assemblies have been used as models to design and prepare template structures for controlled formation of higher ordered materials.[28,29] The headgroup geometry, surface charge density, and spatial arrangement of

Figure 4.

TEM micrograph of Ni plated tubules



the phospholipids define the interaction of the membrane surface with other molecules such as ions or biomolecules. Synthetic chemistry can be effectively used, once the relationship between the molecular level of assembly of matter and its macroscopic properties is understood, to prepare membranes which have the desired morphological and functional properties.

In our laboratory, phospholipids with modified headgroup structure and charges are used to prepare reactive membrane surface which are suitable for molecular interactions advantageous for nanoparticle synthesis. Membranes used in this approach consist of two morphologies, vesicles and tubules. Vesicles are bilayer membranes in spherical morphology. The tubules are bilayers membranes in open ended, hollow, cylindrical morphology with a diameter of ~0.5 m and variable length that gives an average aspect ratio of 200. Figure 3 illustrates the structures of charged and uncharged phospholipids that have been used in the formation of microstructures with reactive interfaces.

The selective metallization of vesicles formed from mixtures of 1,2-bis(tricosa-10,12-diynoyl)-*sn*-glycero-3-phosphocholine and negatively charged diacetylenic and non-diacetylenic phospholipids (**1** and **2**) helped us to develop a model of how complexes of negatively charged phospholipid surfaces and metal ions in a variety of microstructures can be utilized as catalysts for the selective nucleation and growth of inorganic particles. Such a process could be used not only to define the spatial arrangement of the deposited materials but also to provide a framework for fabricating composite materials. Phospholipids, with different headgroup geometry and charges, used in the formation of membranes containing reactive sites essential for initiating metallization process were

synthesized by following well worked out procedures.[30-32] A similar protocol was used for metallization of both tubules and vesicles.[33] The particle characterization was carried out by using transmission electron microscopy (Zeiss EM-10 and JEOL JEM200CX microscope), electron diffraction, and X-ray diffraction (Rigaku DMAXB X-ray diffractometer).

Our approach for the reactive templates encompasses the use of synthetic vesicle membranes made from polymerizable diacetylenic phosphocholine and phospholipid with modified polar headgroups.[34,35] Previously, we had observed that a bivalent palladium ion can catalyze both formation and metallization of tubules from negatively charged diacetylenic phospholipids.[36,37] In that work, tubules were formed from a negatively charged diacetylenic phospholipid (**2**) in the presence of tetraamine palladium (II) chloride ($Pd(NH_3)_4Cl_2$) and then dialyzed against water to remove excess palladium ions. Upon addition of a metallization bath containing $NiCl_2$ or $CoCl_2$ and the reducing agent dimethylamine borane complex ($((CH_3)_2NH.BH_3)$), palladium ions were first reduced to Pd^o, which then initiated the autocatalytic electroless deposition of the metal (Figure 4). Palladium complexes have also been used as molecular catalysts for the electroless metallization of nanoscale rhapidosome cylinders.[38] In the case of microstructures formed from mixtures of neutral and negatively charged lipids, palladium ions bound to the negatively charged lipids would act as the catalyst to metallize selective areas of bilayer surfaces. Selective metallization of anisotropic microstructures such as tubules or a vesicle surface could produce materials with interesting electrical or magnetic properties.[39-42]

Recently, the external membrane surface of polymerized vesicles formed from mixtures of negatively charged and zwitterionic diacetylenic phospholipids have been selectively plated with gold nanocrystals.[43] Both headgroup shape and degree of vesicle polymerization had a significant effect on the stability of the vesicles to the metallization process. Vesicles containing polymerizable phospholipids with phosphohydroxyethanol (**2**) or phosphohydroxypropanol (**3**) headgroups were stable to electroless metallization and yielded partially plated vesicles. Since the vesicles were formed from a miscible mixture of phospholipids comprised of 75 % **1** and 25% **2**, the negatively charged phospholipids were well separated on the vesicle surface. This is in contrast to the surface of the tubule which is completely covered with negatively charged headgroups and was completely metallized by this procedure. However, the initial coverage of electroless deposits is determined by the number and spatial arrangement of the catalytic sites (palladium ions bound to the negatively charged headgroups) as clearly shown by contrasting the vesicle and tubule cases. It was also observed that gold metal clusters formed on the vesicle surface. This cluster formation may be due to the growth of the metal particles over time. Each nucleation site gave rise to a growing metallic particle which initially was like an isolated island. The particles grow not only in thickness but in width. Coalescence of the islands may lead to the appearance of clusters. In addition, the observation that the metal covers more area of the vesicle surface than can be accounted for by the number of nucleation sites indicates that once nucleation has taken place on the negatively charged phosphate-$Pd(NH_3)_4$2+ complex, the plated metal will grow over the zwitterionic phosphocholine headgroup which does not contain bound palladium ion.

On the other hand, vesicles containing polymerizable phospholipids with the less sterically hindered phosphatidic acid headgroup (**4**) yielded fully plated, agglomerated metal vesicles (Figure 5). The palladium ion may be more accessible for further reaction when bound to the phosphatidic acid headgroup than to the more sterically hindered **2** or **3** headgroups. Therefore, metallization could occur at a much faster rate leading to rapid metal deposition over the vesicle surface and rapid agglomeration of the metallized vesicles. Electroless metallization of vesicles containing polymerizable zwitterionic phosphocholine and negatively charged non-polymerizable phospholipids (**5** and **6**) also resulted in the formation of agglomerated metallized particles. In this case, the unpolymerized phospholipid molecules may be pulled out from the vesicles due to membrane disruptions resulting from the evolution of H_2 that occurs during the reduction of the metal ions. Also, metallization may produce localized heating which may result in disruption of the vesicles by causing the acyl chains of the non-polymerizable lipids to become more fluid.

The inner as well as the outer surfaces of vesicles can be selectively metallized. Figure 6 is a TEM micrograph showing nanoscale crystalline gold particles synthesized within polymerized vesicles formed from a mixture of negatively charged phospholipid and **1**. The particles ranged in size from 4 nm to 10 nm. (Reference 44)

Figure 5.

Metallized vesicles

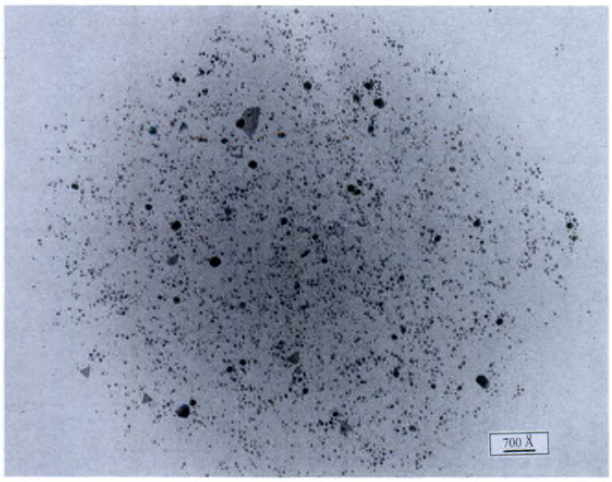
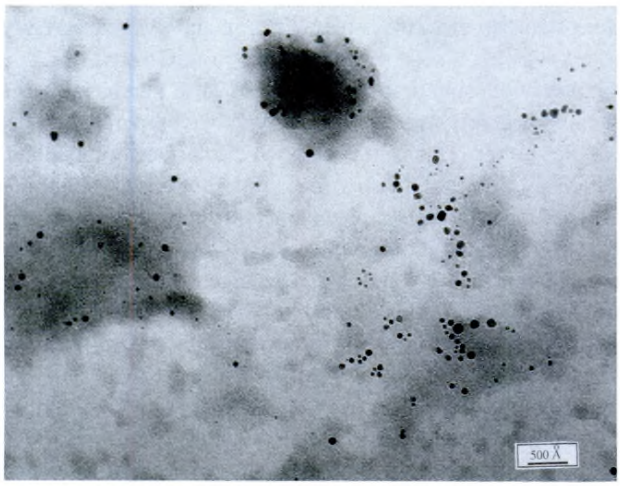


Figure 6.

TEM micrograph of nanoscale gold particles synthesized



Future Trend

It has been demonstrated that self-assembled membrane structures can be used as templates and reactors to fabricate submicron and nanoscale particles. This synthetic and processing approach is multidisciplinary, and though at its infancy, is receiving growing interest. Questions such as cost effectiveness and connection to practical processing technology remain to be addressed. Our current efforts in nanoscale particle synthesis and processing using polymerized lipid and other surfactant membranes are focusing on these critical issues.

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Biographies

Dr. Alok Singh is a Research Chemist at the Center for Bio/Molecular Science and Engineering. He is currently leading an NRL program on *Membrane Structure and Functions*. This research is focussed on the study of lipid self-assembly and the development of stabilized membranes for technological applications. His research interests include – membrane morphology control through molecular architecture, development of stimuli responsive membranes for controlled release applications, nano-particle synthesis, molecular recognition, and method development for making new materials.

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"Capped" Colloidal Quantum-Dot Semiconductors: New Opportunities for the Design of Materials with Tailored Optical and Electronic Properties

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Introduction

In recent years, much progress has been made in the development of new techniques for the synthesis and stabilization of colloidal "quantum-dot" semiconductor nanocrystallites. These are tiny, crystalline clusters of compound semiconductors that occupy the size regime between molecular monomers and bulk semiconductors. The term "quantum dot" is used to convey the fact that the physical size of the crystallites – typically 20 to 100 in diameter – is smaller than the wavefunction of the electron orbitals in the crystallite, with the result that the electrons are confined within the particle to a degree that depends on the size of the crystalllite. This quantum confinement causes the crystallites to exhibit the size-dependent optical and electronic properties that are responsible for the current surge of interest in these materials.

Because there is a strong tendency for clusters in this size range to aggregate together to form larger particles, it is important that the surface of the crystallites be treated in such a way as to prevent agglomeration. While lipid vesicles[1,2] and bilayers[3] have been used to isolate and stabilize the nanocrystallites, as have Langmuir-Blodgett films[4], a particularly useful medium for the synthesis and stabilization of these particles has proven to be reverse micelles[5-10], in which aqueous solutions of the inorganic ions needed to form the particles are dispersed in non-aqueous solutions of surfactant. The advantage of this technique is that the surface of the crystallite is acessible during the synthetic procedure, so that one can easily make modifications to the structure and composition of the particle as it grows. In particular, one can arrest the growth of the particle and stabilize it against agglomeration by "capping" the particle with a monolayer (or partial monolayer) of organic reagents (typically thiols)[9] that bind tightly to the particle surface. One can also use the technique to prepare layered particles, in which one or more shells of semiconductor are added to the original core particle prior to capping[11]. The reverse-micelle approach thus provides a tool for manipulating both portions of capped colloidal semiconductor particles – the

core semiconductor crystallite and the organic (or organometallic) capping reagent.

In recent years, a promising alternative method of preparing capped semiconductor crystallites has been developed[12-14], in which the metal ions (such as cadmium) compete for sulfide ions and for thiol anions, both of which are present simultaneously in homogeneous, non-micellar solution. Quite good size control can be achieved by controlling the ratio of sulfide to thiol ions, although the preparation of layered particles does not appear possible with this technique because capping occurs in parallel with crystallite growth.

The possibilities for tailoring the optical, electronic, and mechanical properties of materials containing capped quantum-dot semiconductor particles are only now beginning to be explored. It is the purpose of this article to review the recent progress that has been made in the synthesis and characterization of these particles, with emphasis on the preparation and properties of capped particles that can be isolated from their growth medium, and to describe some of the potential applications that lie in wait for future generations of these novel materials.

The Reverse-Micelle Synthetic Technique

In the reverse-micelle procedure developed by Steigerwald and Brus[9], an aqueous solution of the surfactant dioctyl sulfosuccinate ("Aerosol OT", or "AOT") is dispersed in heptane, typically at a concentration of around 0.5 M. This results in the formation of inverted, "reverse" micelles, with the fatty hydrocarbon "tails" of the surfactant extending into the heptane solvent and the polar "head" groups clustered around localized microdroplets of water. When the concentration ratio is chosen properly, completely homogenous, transparent solutions of reverse micelles can be prepared in this way.

In practice, two such solutions are prepared, one containing (for example) cadmium ions, typically as $CdCl_2$, and the other containing (for example) sulfide ion, typically as Na_2S. Stirring these two solutions together in heptane leads to ion exchange as the micelles collide with one another, and results in the formation of small crystallites of cadmium sulfide within the micelles. The micelles serve to provide a controlled environment for the crystallite When the crystallites have grown to the desired size, which can be controlled to some extent by varying the ionic concentrations and/or the stirring time, as well as by controlling the molar ratio of water to surfactant, they can be "capped" by the addition of an organic reagent, such as thiophenol[5-9], that binds strongly to the cadmium ions on the surface of the crystallites. The "capped" particles precipitate from solution, and can be collected by centrifugation or filtration. After purification by repeated washings with heptane, they are obtained as a dry, free-flowing powder. With proper experimental procedure, the size distribution of the particles can be quite narrow[9], although not truly monodisperse.

The reverse-micelle process is illustrated in cartoon fashion in Figure 1. Other types of particles, such as CdSe, CdTe, or ZnS, can be made in the same way, as can silver halide (AgX), with some modifications to the procedure[15]. As noted before, the primary benefit of the reverse-micelle technique is its flexibility in tailoring the structure and composition of the resulting particles. Examples of this flexibility will be provided below.

The Competitive-Reaction Synthetic Technique

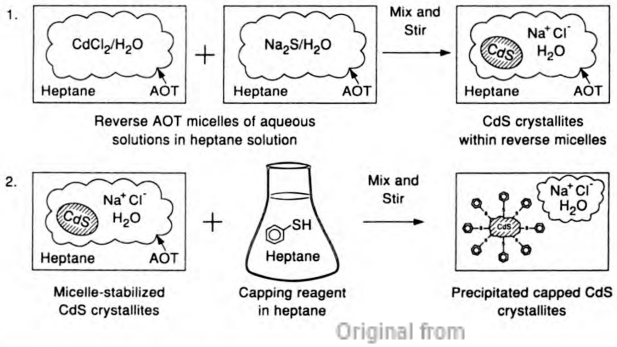
In contrast to the reverse-micelle technique, the competitive-reaction technique developed by Herron, Wang, and Eckert[12,13] relies on the kinetic competition between the reactions of (for example) cadmium ions with sulfide ions and cadmium ions with thiophenolate (or other thiolate) ions. This process is quite similar to that proposed by Meisel[14] for controlling the size of CdS clusters grown by pulse radiolysis of thiol solutions in the presence of cadmium ions.

In the Herron-Wang-Eckert procedure, the cadmium, sulfide, and thiolate ions are mixed simultaneously in a non-micellar fluid solution (typically methanol-water or methanol-water-acetonitrile) with continuous stirring. The capped particles precipitate quickly, and are isolated either by direct filtration (for methanol-water solutions, where the molar ratio of sulfide to thiolate is greater than 1.0) or by extraction into actonitrile followed by filtration to remove insoluble by-products and vacuum evaporation of the resulting clear filtrate (for methanol-water-acetonitrile solutions, where the molar ratio of sulfide to thiolate is less than 1.0).

This technique offers the advantage that the size of the capped particles can be controlled reasonably well by varying the sulfide/thiolate ratio[12,13]. As might be expected, low ratios

Figure 1.

Reverse-Micelle Synthesis of Capped Colloidal CdS Particles



of sulfide to thiolate (less than 1.0) yield small particles, with diameters in the 15-20 Å range, since the relatively high concentration of thiolate serves to cap the particle at an early stage of growth. High rations of sulfide to thiolate (from 1.0 to nearly 4.0) yield larger particles, with diameters up to around 35 Å; evidently, at these higher concentrations of sulfide, crystallite growth is able to compete more effectively with capping, so larger particles are formed before the surface becomes blocked with bound thiolate.

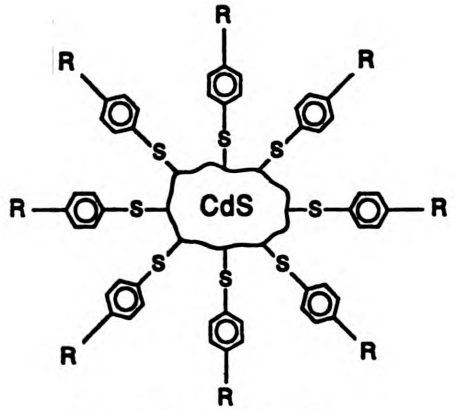
The competitive-reaction technique is considerably less flexible than the reverse-micelle method, though, in that by its very nature it is unsuited to the fabrication of multi-layer quantum-dot quantum-well particles consisting of concentric shells of different semiconductors[11,16]. Since it appears that much control over the optical properties of the particles may be gained by having the ability to design and fabricate such structures[11,16], it seems likely that the competitive-reaction technique will be used primarily for the study of monolithic semiconductor particles when the control of particle size is of paramount importance.

Variations on Particle Composition and Structure

The majority of studies on capped semiconductor crystallites have concentrated on thiophenol-capped chalcogenides, such as ZnS, CdS, or CdSe, both because these materials are interesting in their own right and because the experimental procedures for their synthesis have become well established in recent years, as noted above. More interesting possibilities have begun to appear in recent years, however, as the synthetic procedures and theoretical understanding of the particles have evolved.

Figure 2.

Functionalized Thiophenol-Capped Cadmium Sulfide Crystallite



One type of variation on the theme is represented schematically by Figure 2, which shows a CdS crystallite capped with derivatized thiophenol molecules. This is intended to symbolize the fact that one is by no means restricted to "plain-vanilla" thiophenol groups as capping reagents, and the ability to functionalize the capping reagent allows one to tailor the organic component of the particle in a wide variety of ways, to alter the solubility, reactivity, or other properties. We have found, for example, that thiols bind far more strongly than aromatic amines to the surface of growing cadmium sulfide srystallites, and that the resulting differences in surface coverage translate directly into significant differences in the solubility of the particles in organic solvents[17].

Other workers have found that simple aliphatic amines, such as triethylamine, can greatly enhance the luminescence of cadmium sulfide or cadmium arsenide crystallites, presumably through modification of midband gap states[7]. It has also been reported that colloidal cadmium sulfide particles can complex with diethyldithiocarbamate, with the result that a new, broad absorption band is formed at around 600 nm wavelength and a decrease in the emission quantum yield for the particles[18]. This is perhaps not true "capping" in the sense that the particle is stabilized through the surface interaction, since it was suggested that the crystallites are partially decomposed in the course of complexing with the thiocarbamate[18]. Nonetheless, these extreme examples serve to illustrate the diversity of effects that can be obtained through appropriate modification of the capping reagent.

An alternate approach, which we have taken recently in our development of composite "nonlinear-nonlinear" optical materials[19], is to incorporate capped crystallites of cadmium sulfide in a Langmuir-Blodgett multilayer structure of polydiacetylenes. A proposed structure for the resulting composite materials is shown schematically in Figure 3[19]. This combination of materials was chosen as the first example of this new class of nonlinear optical materials because the absorption spectra of the capped CdS and of the polydiacetylene form a natural transmission window between the band edge of the CdS, at around 510 nm, and the absorption peak of the polydiacetylene, at around 628 nm. The nonlinear refractive index of both components is negative within this wavelength regime, and since the nonlinear refractive index changes more slowly with wavelength than does the absorbance, the two reinforce to give a relatively large value of n_2 (on the order of 11 x 10^{-8} cm^2/MW) over a wavelength range where the absorption of the composite system is at a minimum. It is anticipated that with further development, materials of this type may have significant applications in all-optical device applications; this is because the semiconductor component and the nonlinear organic component can be chosen, at least in principle, to give

a transmission window at a wavelength optimized for specific device requirements.

Other interesting modifications in the structure and properties of capped colloidal particles can be obtained by altering the core semiconductor portion of the particle, rather than the capping reagent. A classic example, which also illustrates the synthetic flexibility of the reverse-micelle technique, is the recent work by Brus and co-workers on the growth of thiophenol-capped two-layer particles, with CdSe on a ZnS quantum-dot core, and vice versa[11]. In this work, core particles of ZnS were grown by standard reverse-micelle procedures, and were then treated with sufficient amounts of cadmium and selenide ions to (ideally) form a complete shell around the ZnS cores. The resulting particles were then capped with thiophenol and isolated by filtration. The same procedure was used to grow capped CdSe core particles with a shell of ZnS. X-ray analysis indicated that the particles of $(CdSe)_1(ZnS)_4Ph$ had a CdSe core diameter of around 35 Å, with a ZnS outer layer only around 4 Å or so thick, while the particles of $(ZnS)_1(CdSe)_4Ph$ had a ZnS core diameter of approximately 15-18 Å and a CdSe outer layer of approximately 12-14 Å thickness. In both cases, the overall semiconductor particle diameters were around 40-45 Å, not counting the contribution of the capping groups.

The striking effects of these compositional changes on the optical properties of the particles are illustrated by Figures 4 and 5, both of which are adapted from Reference 11. Figure 4 shows the absorption spectra of "seed" particles of (a) CdSe, (b) ZnS, and (c) CdS in micellar solution, along with the spectrum that results (d) when cadmium ion is added to the ZnS seed, still in the micellar solution.

Figure 5 shows the effect of adding the ZnS shell on the room-temperature luminescence spectrum of a core particle of CdSe, in both cases after the particles had been annealed by refluxing at 169 C in 4-ethylpyridine[11]. It can be seen that the luminescence shifts strongly to the blue upon growing the layer of ZnS, and the quantum yield of luminescence increases by more than an order of magnitude. This is attributed to the recombination of carriers in deep surface traps[20]. Effects of this type may have obvious applications to the development of improved polymer-compatible phosphors, with potential applications in a wide variety of displays.

New Directions

It is clear from the work described here that the surface has only just been scratched in learning what effects can be obtained from the controlled manipulation of the core particle and the capping groups in capped quantum-dot structures. However, some trends in future research appear evident. First of all, there is a clear incentive to explore the behavior of layered particles, with the objective of developing a family of quantum-dot quantum-well ("QDQW") materials along the lines recently pioneered by Weller's group in Germany[16]. While their particles were not capped, and so far have only been studied in micellar solution, they have nonetheless reported the synthesis of the first true three-layer QDQW structure: CdS/HgS/CdS[16]. They find that the addition of Hg^+ ions to a micellar solution of CdS particles results in a significant red shift of the absorption spectrum, which is extended still further (out to 700 nm) by the subsequent addition of H_2S and additional Cd^{2+}. The spectra observed correspond to increases in overall particle size from around 52 Å to around 80Å during this process.

More recently, Nozik and co-workers have reported the formation of colloidal dispersions of indium phosphide capped with trioctylphosphine oxide[21]. This is a significant development, because it ushers in the synthesis of quantum-dot particles of semiconductors other than the II-VI family. These particles were prepared by the reaction of indium chlo-

Figure 3.

Schematic Representation of Composite CdS/PDA Multilayer Film

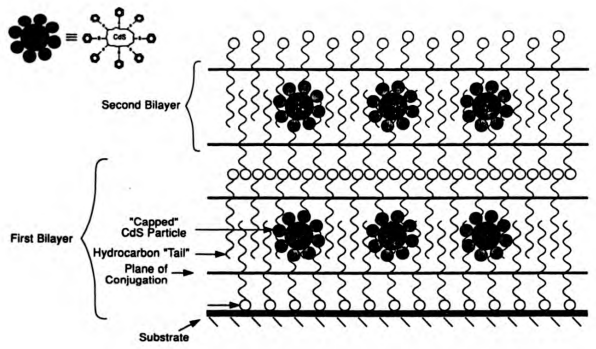


Figure 4.

Absorption Spectra in Micellar Solution of: (A) Bare CdSe Seed Particles; (B) Bare ZnS Seed Particles; (C) Bare CdS Seed Particles; and (D) ZnS Seed Particles with Added Cd Ions (Adapted from Reference 11)

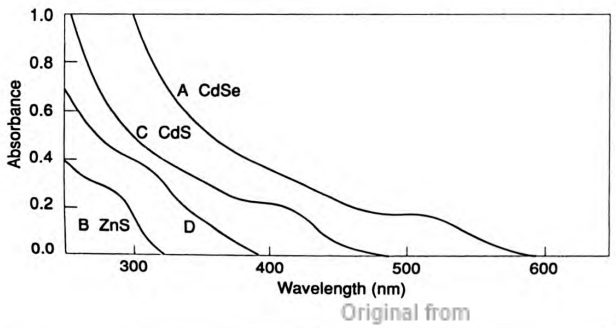
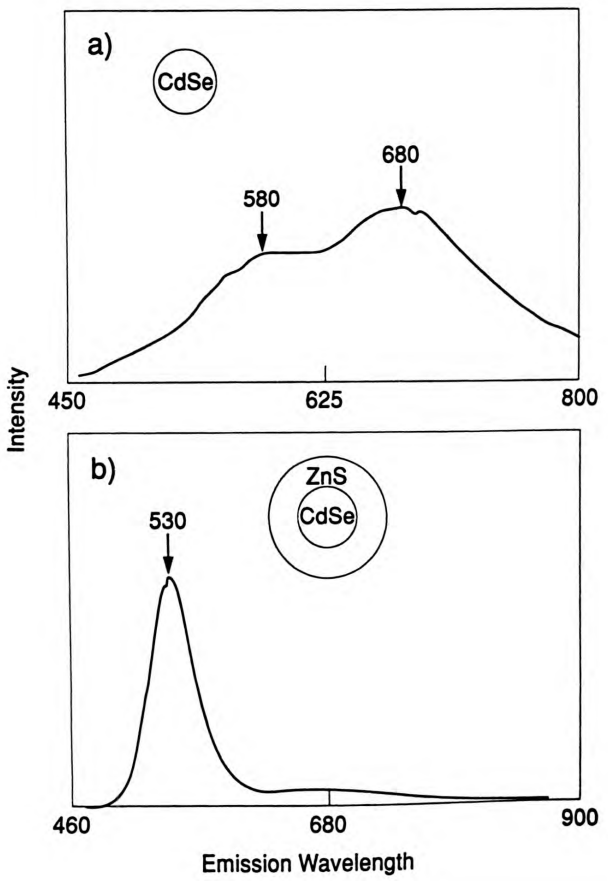


Figure 5.

Room-Temperature Luminescence Spectra of (a) Thiophenol-Capped CdSe and (b) Thiophenol-Capped $(CdSe)_1(ZnS)_4$ (Adapted from Reference 11)



ride with sodium oxalate in acetonitrile to form a chloroindium oxalate complex, which was then mixed with $P(SiMe_3)_3$ in acetonitrile and heated with a mixture of trioctylphosphine and trioctylphosphine oxide for several days. The resulting particles had a mean diameter of around 25 Å, with a very narrow size distribution (1.9 Å).

Taken together, these results suggest that research in this field will progress rapidly in several closely related directions in the next few years. Independent studies on the effects of modifying the core composition, the core structure, and the capping groups are likely to merge as clearer structure-activity relationships become apparent. The great advantage of capped particles is that they can not only be isolated from their growth medium, but they can be redispersed in a variety of solvents or polymer hosts. Future research may therefore lead to new generations of novel semiconductor-polymer nanocomposite materials, having optical, electronic, and mechanical properties tailored to specific device applications. Regardless of whether or not commercial aspirations are borne out, however, it is clear that there is much fundamental new knowledge to be gained from the manipulation of materials in this tiny, quantum-confinement size regime.

Biography

Robert E. Schwerzel received his B.S. degree in chemistry from Virginia Polytechnic Institute and State University, and his Ph.D. in physical organic chemistry from Florida State University. He then conducted postdoctoral research programs in photochemistry at Cornell University and in chemically induced dynamic nuclear polarization at Brown University. He then conducted research on stable free radicals for immunoassay applications at Syva Research Institute in Palo Alto, California (1972-1973). Dr. Schwerzel directed the research programs in photochemistry and nonlinear optical materials at Battelle's Columbus Operations, in Columbus, Ohio for nearly 20 years, from 1973 to 1993. He then moved to Georgia Tech Research Institute, where he is responsible for the development and guidance of the research efforts in advanced photonic materials. His research interests range from photochemistry and spectroscopy to nonlinear optics and photonic materials for integrated optics applications. He is currently serving as the U. S. Treasurer for the European Photochemistry Association, and is actively engaged in the study of quantum-dot-quantum-well materials under contract to ONR.

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Nanocrystalline Processing of Surface Reactive Materials: Effects of Non-Stoichiometry and Dispersion

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Abstract

Nanocrystalline materials are associated with remarkably high surface reactivity. Unique processing routes have been developed to provide such systems with an unusual control of stoichiometry and dispersion. The high concentration of oxygen vacancies in nanocrystalline CeO_{2-x} is illustrated to give rise to greatly enhanced catalytic activity in SO_2 reduction. By having Cu_2O highly dispersed on CeO_{2-x} nanocrystals, one can further create semiconductor Schottky junctions between the two oxides to lower the enthalpy of oxygen vacancy formation. The resulting material achieved successful catalytic SO_2 reduction and CO oxidation at significantly lower temperatures. The non-stoichiometry and dispersion effects in nanocrystalline materials may be very useful in improving a variety of structural and functional characteristics in ceramic systems.

Non-Stoichiometric Oxides

In a variety of applications, oxide stoichiometry directly affects the properties of materials. The defect concentration in oxides may be varied by dopant concentration and oxygen partial pressure. Typically, high non-stoichiometry cannot be easily achieved or stabilized without going to high temperatures and reducing atmospheres. The ability to tailor oxygen vacancy concentration will present a number of possibilities for novel or improved material characteristics. For example, defect concentration in ceramics directly affects ionic and/or electronic conductivity. Non-stoichiometric oxides can provide unique enhancement in oxygen-conducting applications, such as sensors, fuel cells, and ceramic membrane reactors.

Oxide non-stoichiometry is also important in catalytic applications. We have found that in a number of redox catalytic reactions, the catalytically active sites are associated with oxygen vacancies[1,2]. The availability of a high concentration of oxygen vacancies in a catalytic material will provide excellent activity at lower reaction temperatures. One such example is selective SO_2 reduction by CO[1,2],

$$SO_2 + 2\,CO \Rightarrow S + 2\,CO_2.$$

In this redox reaction, one needs to first reduce the catalyst surface through the oxidation of adsorbed CO species. Having two oxygen vacancies in the vicinity will then enable an adsorbed SO_2 to be fully reduced. This important reaction can convert the major cause of acid rain to valuable elemental

sulfur. However, the conventional perovskite catalysts would require at least 650 °C for high conversion of SO_2.

The reaction mechanism suggests that availability of oxygen vacancies and high oxygen mobility are critical to the surface reaction[1]. We have chosen CeO_2 as the catalytic material[1,2] since it (i) has high oxygen vacancy mobility associated with the fluorite-type crystal structure, and (ii) can undergo large deviation from stoichiometry upon reduction at high temperatures in low oxygen partial pressure[3,4]. If one can synthesize a highly non-stoichiometric high surface area CeO_{2-x} catalyst, there would be a great deal of surface reactivity without the need for high-temperature reduction which could cause sintering. This concept was realized through nanocrystalline processing[5].

Nanocrystalline Processing of CeO_{2-x}

Nanocrystalline processing was first developed by Gleiter and co-workers who utilized Joule-heating[6-9] to vaporize a metallic precursor in a resistively heated crucible (Figure 1(a)). Collision of the supersaturated metallic vapor and the molecules of a cool inert gas in the reaction chamber leads to nucleation, followed by cluster growth through coalescence[10]. The aerosol of ultrafine particles may be collected via natural gas convection and thermophoresis on a liquid-nitrogen cooled rotating cold-finger.

Joule-heating can be used to synthesize nanoclusters of materials with intermediate melting point and relatively high vapor pressures. A greater variety of materials may be obtained with inert gas condensation using dc- or rf-magnetron sputtering, a technique conventionally utilized in thin film deposition[11,12]. During sputtering, ions of a suitable substance (such as Ar or Kr) accelerated to high energies are directed toward a surface, from which atoms and clusters, both neutral and ionic, are ejected. By controlling the synthesis parameters, such as the type of gas, gas pressure and sputtering condition, we can obtain the desirable nanoclusters of the same composition as the sputter target. For particle formation[9,13-17], a relatively high gas pressure of 1 Pa is needed compared to the 10^{-1}-10^{-2} Pa pressure range typically employed in thin film deposition processes. At such pressure, deposition in the line-of-sight of sputtering was rather low, whereas that in the plane of the sputter gun was significant. We have therefore modified the ground shield of the sputter gun for use as an effective collection substrate[5] (Figure 1(b)). For synthesizing non-stoichiometric CeO_{2-x} nanocrystals, we first sputtered Ce nanoclusters from a metallic target in argon atmosphere. The pyrophoric metallic nanoclusters collected on the liquid-nitrogen cooled modified substrate were then carefully oxidized to a controlled degree. The resulting nanocrystalline CeO_{2-x} powders were scraped off the rotating substrate under vacuum. They have an olive color, and their oxygen deficiency remained remarkably stable under room conditions.

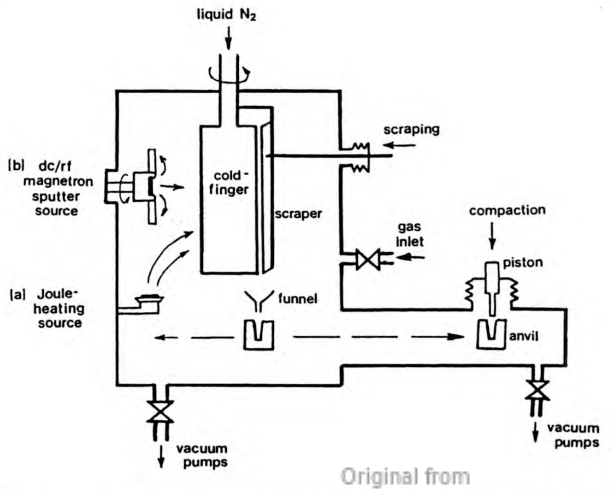
The nanocrystalline CeO_{2-x} was characterized by X-ray diffraction (XRD) to have an average grain size of 7 nm. B.E.T. nitrogen adsorption indicated that the sample has a high surface area of 70 m^2/g, which is very attractive since catalytic reactions occur predominantly on the surface of a catalytic material. The presence of oxygen vacancies was characterized by X-ray photoelectron spectroscopy (XPS) and photoacoustic Fourier-transform infrared spectroscopy (PA-FTIR). Nanocrystalline cerium oxide, oxidized at 475 °C in 1 kPa CO_2/He for 12 hours exhibited the typical 6-line XPS spectrum of CeO_2 (Figure 2(b))[5]. The as-prepared nanocrystalline cerium oxide materials showed two strong peaks, u' and v' (Figure 2(a)), which corresponded to the $4f^1$ initial state of Ce^{3+}[18,19]. From the relative integrated intensity of the deconvoluted u' and v' peaks, a Ce^{3+} component of about 22% was calculated for the as-prepared CeO_{2-x}[20]. After oxidation at 475 °C, the Ce^{3+} component was reduced to less than 5%.

The molecular structure of nanocrystalline CeO_{2-x} was analyzed by PA-FTIR[21]. This specially developed technique is particularly suitable for studying both the surface and bulk phonon structure of solid samples[22,23]. The as-prepared CeO_{2-x} nanocluster (Figure 3(a)) has a great deal of adsorbed species associated with its large surface area, including hydrogen-bonded water and hydroxyl groups, adsorbed hydrocarbon and water from atmosphere, and carbonate species. These surface adsorbates were gradually removed with heat treatment due to reduction of surface area. They were completely eliminated when the sample was sintered at 1400 °C in O_2.

The sample heated to 950 °C and 1400 °C consisted of CeO_2 phonon vibrations and superoxide (O^-_2) species. The superoxides were adsorbed species that formed on the surface

Figure 1.

Schematic drawing of a gas-condensation chamber for the synthesis of nanometer-sized clusters by: (a) Joule-heating and/or (b) modified dc-/rf-magnetron sputtering[25].

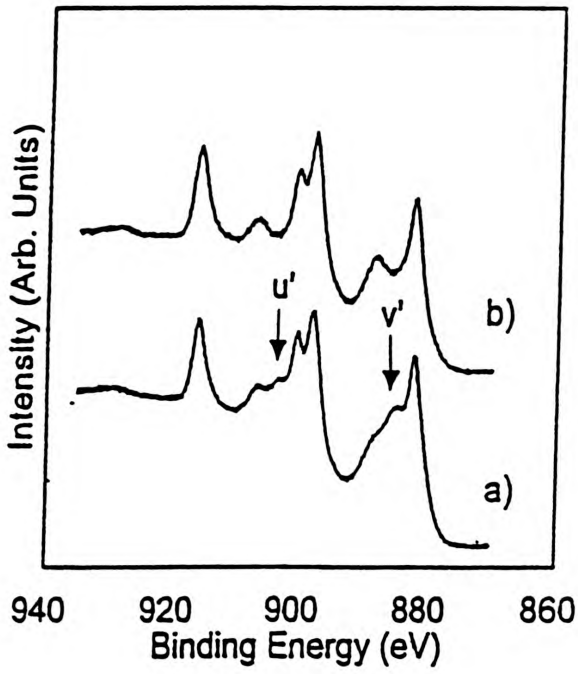


defects of cerium oxides. Electrons were supplied to these adsorbates by the coordinately unsaturated Ce^{4+} ions, which would then stabilize the formed species[24]. The as-prepared sample possessed additional phonon and adsorbate vibrations uniquely associated with its non-stoichiometry. It has phonon bands identified with sub-stoichiometric CeO_{2-x}, and peaks of adsorbed peroxides (O_2^{2-}). The peroxide species were only formed on Ce^{3+} ions or on Ce^{3+} and Ce^{4+} with oxygen nests[24]. They might be generated via O_2^- formation on a surface defect site and subsequent interaction with a Ce^{3+} site in the vicinity to gain the second electron. The presence of O_2^{2-} adsorbed species and CeO_{2-x} vibrations in the as-prepared nanoclusters confirmed the high concentration of surface defects and oxygen vacancies in this sample.

Indeed, the O_2^{2-} adsorbates were linked to the desirable catalytic sites that would allow SO_2 to be fully reduced to elemental sulfur. The nanocrystalline CeO_{2-x} catalyst we designed achieved excellent catalytic activity in selective SO_2 reduction by CO. 100% conversion to S was attained at 500 °C, compared to 600 °C required by ultrafine stoichiometric CeO_2 powder[2]. The availability of oxygen vacancies in close vicinity and the high vacancy mobility in this novel catalyst enabled the bottleneck in the redox mechanism to be overcome. This study demonstrates the surface reactivity associated with the non-stoichiometry which can be tailored by nanocrystalline processing of materials.

Figure 2.

Ce-3d XPS spectrum of nanocrystalline CeO_{2-x} (a) before and (b) after annealing at 475°C for 10 hours in 1% CO_2/He at a total pressure of 50 Pa. The peaks u' and v' in (a) which are absent in (b) indicate the reduced Ce^{3+} component[5].



Dispersion in Multicomponent Oxides

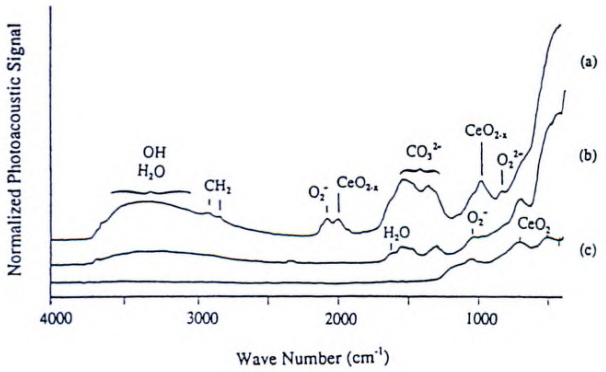
Multicomponent oxide systems may exist as a solid solution or as a mixture of different components. In a number of materials applications, it is desirable to have an intimate mixture of different components or phases to engineer the surface interaction and interfacial chemistry in the multicomponent systems. Conventionally, a mixed component system is obtained through physical mixing of different constituents, or through chemical co-precipitation of the corresponding metallic salt precursors. As expected, homogeneous mixtures of multicomponent systems are not easily achieved through these conventional routes, and undesirable bulk phase separation may occur upon heat treatment.

The objective of this study is to explore novel means of processing materials to achieve ultrahigh dispersion in tailoring the interfacial characteristics of materials. In heterogeneous catalysis, reacting species would typically adsorb on the surface sites of an active component such that surface reaction could proceed. The active component may be a metal or a metal oxide, which is usually present in a small quantity. It relies on a relatively inert support component to disperse it over the large support area, and to stabilize it as a reactive phase. The interaction between the active component and the oxide support component directly influences the catalytic activity, and the long-term resistance of the supported catalyst against sintering and poisoning effects. In ceramic applications, a second component is commonly added to the major ceramic component for several functions: (i) as a sintering aid to promote low-temperature sintering; (ii) as a 'pinning' secondary phase that suppresses grain growth during heat treatment to facilitate the final stage of densification; and (iii) as a reinforcing agent that interacts synergistically with the matrix component for greater structural strength and toughness. The dispersion of the secondary component in the matrix component is extremely important since the interfacial chemistry governs the structure of the grain boundaries, and impacts on the overall mechanical, thermal, electrical, and optical behavior of the ceramic materials.

In both catalytic and ceramic applications, achieving an ultrahigh dispersion of the different components would ensure that the resulting multicomponent material has a uniform property, with maximum surface contact between the different phases such that the desirable interfacial characteristics can be attained with minimal use of the secondary component. Nanocrystalline processing offers the possibility to design model multicomponent systems with an ultrahigh level of mixing that provides nanometer-scaled uniformity. Figure 4

Figure 3.

PA-FTIR spectra of CeO_{2-x} nanoclusters: as-prepared (a); and after annealing in O_2 at 950°C(b), and 1400°C(c)[21].

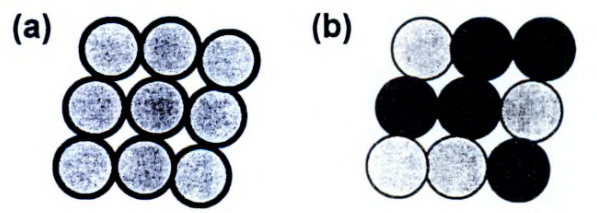


depicts two types of mixing that would give rise to unique surface interaction between different components[25]. In Figure 4(a), each grain has a surface coating which consists of a different component from that of the core crystallite. The amount of interaction between the surface component and the core component is maximized when the crystallite size is minimized. The complexity involved in direct deposition of a coating layer on fine crystallites is rather formidable, so unique means of materials engineering has to be developed to generate such surface dispersion features.

Figure 4(b) illustrates a uniform random mixing of grains of different composition, which is difficult to achieve mechanically without alloying effects, or chemically without being compromised by agglomeration. It can however, be attained by vapor synthesis routes through simultaneous or sequential materials generation from different sources[9,25]. Ideally, the level of mixing would be highest if the grain sizes are of an ultrafine nature. In Figs. 4(a) and (b), the grains may be

Figure 4.

Schematic of two types of mixing for ultrahigh dispersion of different components[25].



consolidated to form a bulk solid compact. If the grains are synthesized as non-agglomerated nanocrystals, we acquire not only an ultrahigh level of mixing between different components, but also a nanostructured compact with a high volume fraction of grain boundaries and a microporous network. The significant grain boundary component provides a further opportunity to tailor the interfacial chemistry of the multicomponent system. The pores give rise to high surface area for enhanced catalytic activity, and their small diameter may offer catalytic selectivity like the zeolitic structures. A ceramic green body with such fine porosity has greater mechanical reliability associated with small flaw sizes, and may be sintered at much lower temperatures due to the shorter diffusion distances involved in the nanostructure.

Ultrahigh Dispersion of Cu_2O on Nanocrystalline CeO_{2-x}

The application of nanocrystalline processing to attain an optimized dispersion in a multicomponent system is illustrated in our attempt to further improve the catalytic properties of CeO_{2-x} in SO_2 reduction. The concept is to create a supported oxide catalyst whereby semiconductor Schottky junctions are formed between two different oxides to lower the formation enthalpy of oxygen vacancies. We chose Cu_2O to be the secondary oxide - it is an inexpensive base metal oxide (compared to oxides of noble metals such as Pd and Pt), has a suitable electronic structure, and is immiscible with CeO_2. The interaction between Cu_2O and CeO_{2-x} may also enhance the adsorptivity of reacting species on the catalyst through spillover effects from Cu_2O to CeO_{2-x}. We set out to create the optimum dispersion of Cu_2O on CeO_{2-x} through deriving a mixed multicomponent system depicted in Figure 4(a). A coating of Cu_2O on CeO_{2-x} nanocluster cannot be easily achieved in a direct vapor synthesis process in the reactor shown in Figure 1. Our idea is to make use of surface segregation effects to achieve the Cu_2O coating on CeO_{2-x}[5]. By starting with a mixed 15 at% Cu/85 at% Ce target, Cu-Ce nanocrystals with a uniform alloy composition were generated by dc-magnetron sputtering at a power of 160 W in an argon pressure of 20-30 Pa. The alloy nanoclusters were then carefully post-oxidized by slowly back-filling the ultrahigh vacuum chamber with 500 Pa of oxygen. As Cu and Ce were gradually oxidized, they lost their miscibility in their respective oxide forms, and we anticipated that the minor component, copper oxide, would be segregated to the surface of the CeO_{2-x} crystallites.

Characterization by XRD and XPS confirmed the structure of model Cu_2O/CeO_{2-x}[5]. Figure 5(a) illustrates the XRD pattern of nanocrystalline Cu-Ce sample after annealing in an oxidizing atmosphere at 500 °C. The pattern only displays the diffraction peaks associated with the face-centered cubic structure of the cerium sublattice for the fluorite-structured cerium oxide. Cu peaks were not obtained presumably because: (i) Cu

was in solid solution with Ce, and/or (ii) Cu was highly dispersed in the grain boundaries or on the surfaces of the nanocrystallites. Separate copper phase in the form of CuO was found only after heating at 550 °C. This phase became more distinct upon further heat treatments to 600 °C and 650 °C. The mean crystal size of the cerium oxide phase was determined from the (111) and (222) reflection peak broadening by Kochendorfer analysis. The as-prepared sample has a grain size of 7 nm. Annealing at 600 °C led to a minor grain growth to ~10 nm. Significant grain coarsening did not initiate till the sample was heat treated at 700 °C.

XPS illustrated the surface stoichiometry and chemical composition of the samples (see Figure 6). Both Ce-3d lines (870-920 eV) and Cu-2p lines (920-960 eV) were found in the XPS spectrum. The as-prepared sample has the special peaks u' and v' which corresponded to Ce^{3+}[18,19] (Figure 6(a)). These peaks became less distinct for samples oxidized at increasing temperatures. The position of the Cu-2p line and LMM Auger line, after correcting for peak position using C-1s, shows that Cu was in +1 oxidation state[26]. There was a distinct increase in the Cu peaks in the XPS spectrum when the sample was heated to 450 °C. Since XRD did not reflect separate copper phase formation until treatment 500 °C, the large increase in Cu-2p line in XPS at 450 °C was interpreted to be associated with surface segregation of Cu_2O in the CeO_{2-x} crystallites.

The different analytical sensitivity to crystalline and surface structure of XRD and XPS could be complemented to demonstrate the following structural evolution in nanocrystalline Cu/CeO_{2-x}: (i) copper-doped CeO_{2-x} existed as a solid solution up to at least 300 °C (Figure 7(a)); (ii) copper was segregated to the surface of the CeO_{2-x} nanocrystals when heated between 300 °C and 450 °C, producing a surface copper enrichment as illustrated in Figure 7(b); (iii) copper existed as Cu^{+1} to at least 450 °C, and Ce^{3+} was still detected in the sample at this temperature; (iv) copper was finely dispersed below 550 °C, so that only cerium oxide crystalline phase but no bulk copper oxide phase was detected by XRD; (v) distinct copper oxide phase (CuO) was developed when the sample was treated between 500 °C and 550 °C (Figure 7(c))[5,25]. The change in copper oxidation states and Ce^{3+} peak intensities could be attributed to the extent of oxidation.

Figure 5.

X-ray diffraction pattern for Cu-doped CeO_{2-x} after annealing at (a) 550°C, (b) 55 C, (c) 600°C, and (d) 650°C. The main peaks are due to the cerium fee sublattice whereas the smaller peaks at 35.5° and 39° correspond to CuO. Notice that the Ce peak after annealing at 500°C is still broadened as compared to higher temperatures[5].

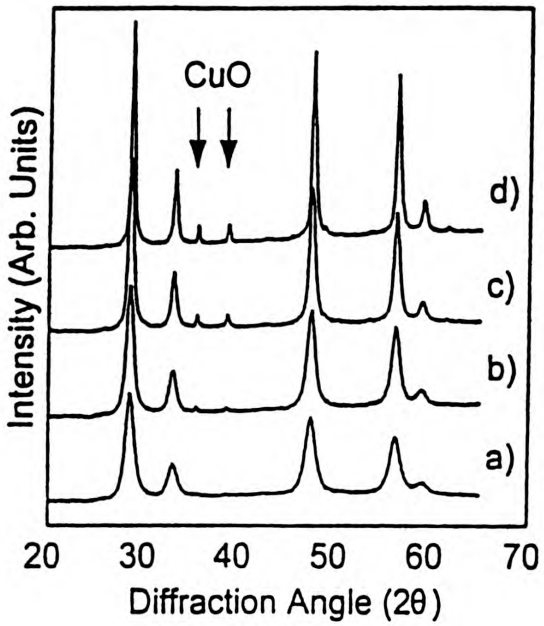


Figure 6.

XPS spectrum of Cu-doped CeO_{2-x}: as prepared (a), and after annealing at (b) 150°C, (c) 300 °C, and (d) 450°C. The two distinct lines in curve (d) are Cu-2p and their increase in relative intensity with respect to Ce-3d indicates Cu segregation[5].

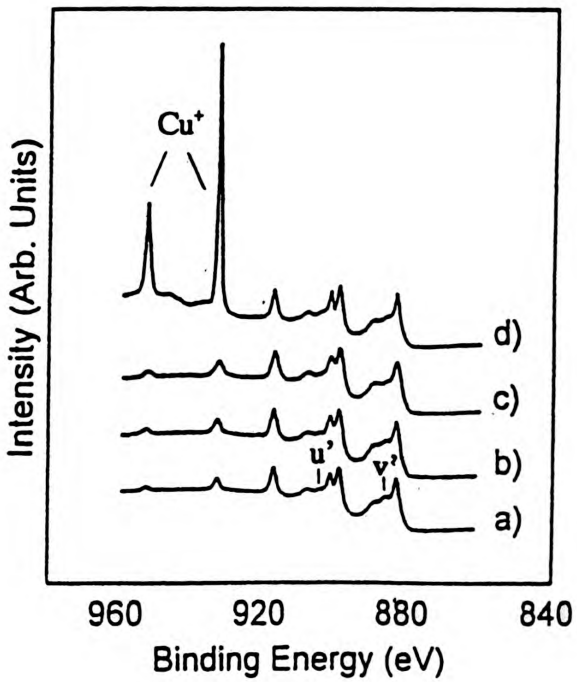
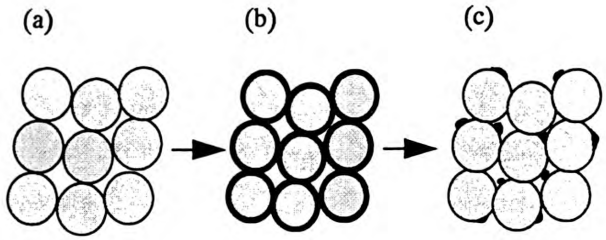


Figure 7.

Synthesis of Cu_2O/CeO_{2-x} nanocrystalline supported catalyst: (a) nanocrystals of a Cu-CeO_{2-x} solid solution, (b) surface segregated Cu_2O in CeO_{2-x} nanocrystals, and (c) phase separated CuO in CeO_{2-x} nanocrysals matrix.[25]



This experiment illustrates that through a controlled post-oxidation process, one may tailor different level of dispersion of one component in another for model supported oxide catalyst. The Cu_2O/CeO_{2-x} nanocrystals derived by surface segregation of Cu between 300 °C and 450 °C in O_2 enabled unusually high catalytic activity for SO_2 reduction and CO oxidation. The novel catalyst achieved full conversion of SO_2 to S and of CO to CO_2 at a remarkably low temperature of 420 °C and 80 °C, respectively[2].

Non-Stoichiometry and Dispersion in Nitride Ceramics

The nitride family of ceramics demonstrates great promise in a number of engineering applications. Si_3N_4 for example, is one of the most potentially useful ceramic materials of the future because of its hardness and high temperature properties. Its high fracture toughness provides for superior fatigue life in high speed, high stress ball bearing applications. Its high strength and resistance to oxidation and thermal shock enable reliable structural performance in advanced heat engine and ballistic applications. Si_3N_4 allows operating temperatures to be extended beyond the limits of metallic systems, creating light-weight components while reducing our dependence on strategic materials used in superalloys.

AlN on the other hand, is particularly attractive as a high thermal conductivity material for electronic packaging. It has excellent electrical resistivity, high dielectric strength, and low dielectric loss. It is expected to demonstrate the performance and dependability needed to accommodate the packaging of large Si-based, high density, multichip interconnects.

The common problem in processing nitride ceramics lies in the high temperature and/or pressure needed in the sintering process of these covalent materials. To successfully densify these ceramics to reliable components, oxide sintering aids such as Y_2O_3 and Al_2O_3 are typically added to promote liquid phase sintering. However, these additives often left behind glassy intergranular phases in the densified ceramics, greatly deteriorating the high-temperature strength and thermal conductivity of the nitride materials. We are currently examining the potential of improving the nitride ceramic properties through nanocrystalline processing.

Nanocrystalline Processing of Advanced Ceramics

There are two ways that one can minimize the detrimental effects of oxide additives in nitride ceramics. First of all, one can achieve maximum dispersion of oxide additives for effective wetting of nitride grains if non-agglomerated nanocrystalline sintering aids are employed. This would minimize the quantity of oxide additives needed, and subsequently limit the formation of oxide glassy phases. Secondly, one can tailor non-stoichiometry in oxide additives to control the surface tension of the sintering aids. This may allow us to vary the wetting behavior of intergranular oxide films in nitride ceramics, such that the oxide films can be removed after sintering. The ability to derive non-stoichiometric oxide sintering aids, and make use of such interfacial reactivity in the wetting and de-wetting phenomena in multicomponent ceramics will offer tremendous potential in the processing of superior nitride ceramics. This study was recently initiated in my laboratory.

The more complex processing and high demand of nanocrystalline materials call for the design of an advanced materials synthesis reactor. Our objective is to develop flexibility in making highly dispersed multicomponent ceramics in large quantities while achieving a narrower particle size distribution. We have constructed a novel continuous forced flux reactor, which has Joule-heating crucible at one end of the reactor (Figure 8)[27]. A forced flow of inert gas is established at the other end of the reactor by a booster pump to carry a large population of ultrafine particles quickly out of the hot evaporation zone without significant particle coalescence and sintering. This gas flow deposits nanocrystals on a liquid-nitrogen cooled plate by thermophoresis. The microstructure of the nanocrystalline particles can be controlled by the type of gas, gas pressure, evaporation rate, as well as gas flow rate and reactor length. The rotating substrate allows nanocrystalline powders to be scraped off *in situ* during synthesis.

The flexibility of this reactor design is associated with its tubular nature. Crucibles could be positioned and reactive gases could be introduced at different points along the reactor length. One can create a sequence of reactions that would achieve an optimum dispersion of oxide sintering aids on nitride grains. For example, Si can be evaporated from one end of the reactor, be nitrided shortly after the evaporation zone; be coated with Y, which is oxidized to a controlled degree shortly after; and finally the Y_2O_{3-x}-coated Si_3N_4 particles are

collected on the cooled substrate. The evaporation rates, different temperature zones and manner of introducing reactive gases will determine the grain size, stoichiometry, and nature of dispersion (as described in Figure 4(a) or (b)) for silicon nitride and its oxide additive. Such processing flexibility would allow us to achieve novel systems that would elucidate the importance of non-stoichiometric and ultrahigh dispersion effects in nitride ceramic sintering, and the potential to derive superior strength and thermal conductivity in the final Si_3N_4 and AlN components.

Summary

Nanocrystalline processing was employed in the derivation of novel non-stoichiometric oxides, and ultrahigh mixing in multicomponent systems. These effects were shown to be extremely important in the catalytic reduction of SO_2, and may have significant impact in improving processing of advanced nitride ceramics. The surface reactivity offered by nanocrystalline processing may be flexibly applied to a wide variety of systems, provided that fruitful reactor design is incorporated as part of the processing scheme. The potential of nanocrystalline processing in creating useful novel structures needs to be realized through an interdisciplinary approach that draws upon materials science and reaction engineering for conception of new ideas and successful scale-up in materials generation.

Acknowledgment

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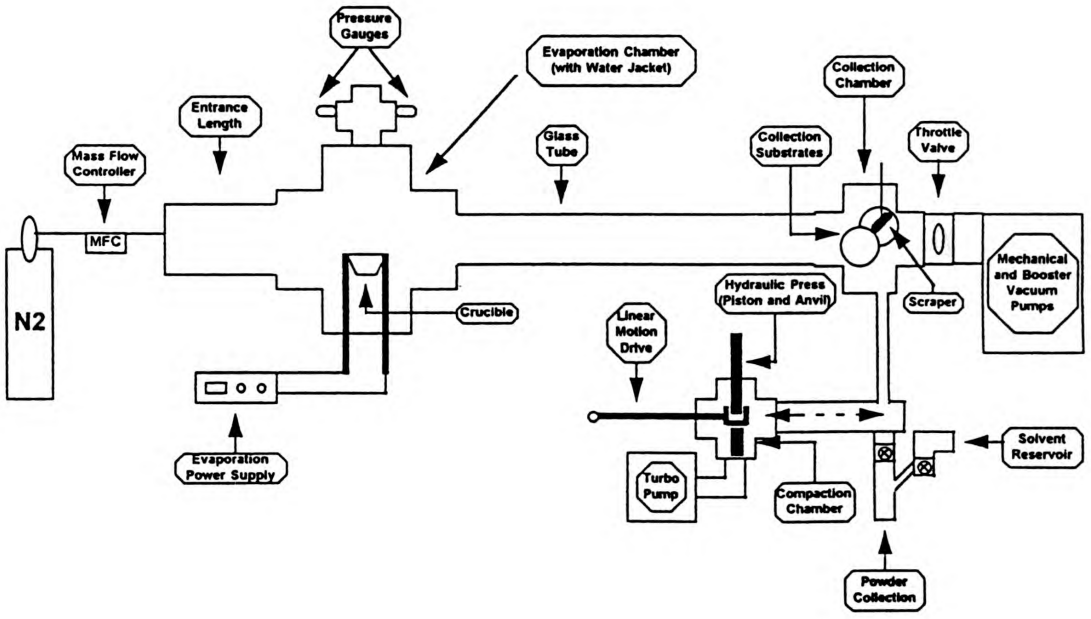
Biography

Jacke Y. Ying is a Cabot Assistant Professor of Chemical Engineering at M.I.T. Her research interest lies in ultrafine materials processing for ceramic, catalytic, and inorganic membrane applications. She is the principal investigator for an ONR grant on nanocrystalline processing and interface engineering of SI_3N_4-based ceramic. Through nanostructurtal tailoring and surface chemistry control, her group is developing new methods to achieve low-temperature sinterable and high ductility covalent composites for advanced structural ceramic

Figure 8.

Schematic of the tubular forced flow reactor for nanocrystalline synthesis[27].



applications. She is a 1995 recipiant of an ONR Young Investigator Aware.

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