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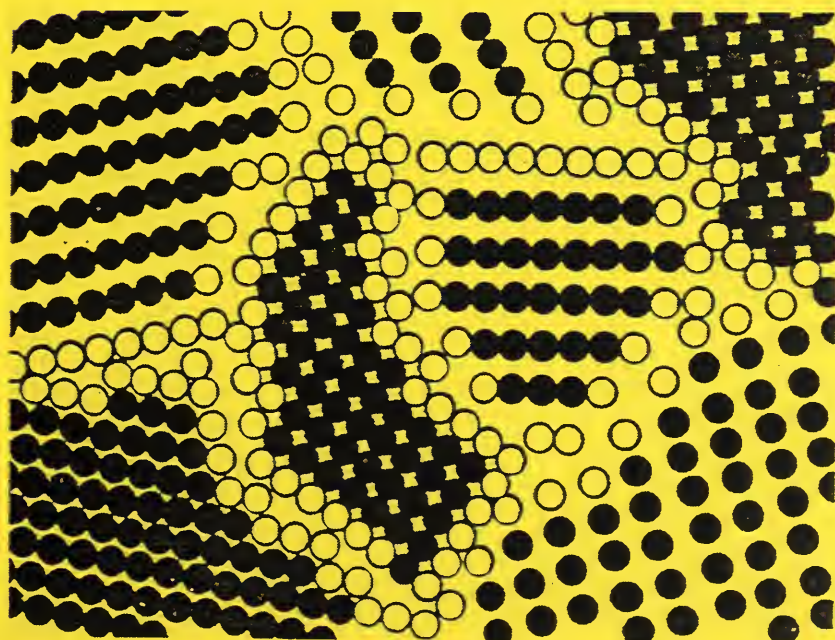
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# **First NIST Workshop on Nanostructured Material**

Report of an Industrial  
Workshop Conducted by the  
National Institute of Standards and Technology

**R. D. Shull**

U.S. DEPARTMENT OF COMMERCE  
Technology Administration  
National Institute of Standards  
and Technology  
Gaithersburg, MD 20899



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**NIST**



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March 1994



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**TECHNOLOGY ADMINISTRATION**  
**Mary L. Good, Under Secretary for Technology**

**NATIONAL INSTITUTE OF STANDARDS  
AND TECHNOLOGY**  
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## WORKSHOP ORGANIZING COMMITTEE:

### Chairman:

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Materials Science and Engineering Laboratory  
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## INTRODUCTION

This workshop, the "First NIST Workshop on Nanostructured Materials," was the first of a series of workshops on the synthesis, characterization, properties, and applications of nanostructured materials to be held every three years at NIST for the first three meetings as developments in the area accelerate, and somewhat less frequently in the following years as the technological area matures.

Nanostructured materials are a class of high technology materials possessing grain sizes, or some other important characteristic dimension, on the order of a few nanometers. Fabrication control of these materials occurs at the nanometer level. Consequently, this class of materials provides one of the better vehicles for the atomic engineering of materials with specific properties and property combinations. For composites, by judiciously controlling the composition at the nanometer scale, the material's properties may be chosen between those of the particular constituents. In recent years it was also found that materials with nanometer dimensions can also possess properties which are uniquely different from that possessed by the same material (or at least by chemically-similar materials) not possessing the characteristic nanometer-scale dimensions. This finding has even prompted some people to refer to this class of materials as a "new state of matter."

The emergence of this field as a major materials science thrust has just begun. At this stage in its development, only glimpses of exciting new properties (e.g., superplasticity, giant magnetocaloric effects, transparency in opaque ceramics, enhanced homogeneity, enhanced wear resistance, unusually soft ferromagnetism, and giant magnetoresistance effects) possessed by materials containing some critical length which has been reduced to nanometer dimensions has been obtained. For many of these cases, it still remains to be determined whether the property changes are due to new physics of the mechanisms at small dimensions or to an extension of larger-scale systematics to small sizes. The available information is still very new and incomplete. Yet, the reported successes have been exciting enough to prompt even industry to begin considering these materials for both new and old applications, despite the great deal of unknown information. Two main pieces of information, however, are required before widespread industrialization is possible: (1) can these materials be prepared in the large enough quantities that will be required for some industrial applications and (2) can these materials be consolidated and fabricated into usable parts and devices without losing their important nanometer-scale dimensions.

This workshop was organized to bring together people from industry, federal agencies, and universities to (1) expedite the flow of information in the field, (2) identify key synthesis and processing methods with scalability potential, (3) acquaint the various communities with the unique properties of nanostructured materials, (4) assist industry in identifying potential application areas, and (5) identify needed areas of study. In addition, it was anticipated that answers to the two industrial application questions posed in the above paragraph would also be forthcoming during the workshop, and that informal contacts at the workshop would result in collaborative research efforts. The workshop also was planned because of our recognition that

in order for the U.S. to take advantage of the promise these materials hold, a concerted effort in this area is needed early. This workshop could highlight this need and provide directions for a concerted effort. Finally, it was felt that this workshop would provide NIST with additional guidance in directing its own programmatic initiative in the area.

The focus of the workshop was on materials whose characteristic dimensions were reduced to the nanometer scale in three directions. Consequently, encompassed in the workshop were powders, thin films, and bulk nanophase materials prepared by physical, chemical, and mechanical processes. Multilayers were not included explicitly in the scope of this workshop since that field is already very mature, and would have detracted from the emerging technology of nanophase materials under consideration here.

In the opening plenary session, Dr. Lyle Schwartz, Director of the Materials Science and Engineering Laboratory (MSEL), welcomed the participants and highlighted the changes that have occurred at NIST in the four years since NBS became NIST. Dr. Robert Shull, Chairman of the Organizing Committee, then set forth the goals of the workshop and two keynote speakers, Dr. Richard Siegel (Argonne National Laboratory) and Dr. Bernard Kear (Chairman of the Department of Materials Science, Rutgers University), surveyed the present status of the field of nanophase and nanostructured materials for materials prepared by vapor condensation and chemical methods respectively. Dr. Shull presented an overview of the present nanophase activities and special facilities at NIST, and Dr. John Gudas, Manager of the NIST Advanced Materials Program, presented an update on the NIST Advanced Technology Program.

In the afternoon three simultaneous working groups were planned in the areas of synthesis and processing, characterization, and properties. However, due to the overwhelming interest of the participants in the first and last of the above areas, it was decided to defer the characterization topic to a later workshop. This disparity in interest is a further indication of how exciting and quickly changing the field of nanostructured materials is. Each group was co-chaired by an expert from NIST and a knowledgeable expert in the area of nanostructured materials from another government agency. Some of the questions which were addressed in these working groups included what research was needed in these areas in both the short term and the long term, where does industry see its role in the development of this class of materials, what are the effective mechanisms for obtaining strong industry, university and federal agency interaction, and what is an appropriate role for NIST in the development of these advanced materials. Each working group also had a recording secretary, a leading scientist from outside the Washington D.C. area, who kept the proceedings of the working group.

The second day of the workshop started with a summary of the previous afternoon's discussions within the working groups, presented by the group rapporteurs. These reports were followed by a discussion on these results and workshop conclusions were formulated. The workshop subsequently ended with a series of conducted tours to various NIST laboratories and facilities actively involved in nanometer-scale materials research. Included in these tours were visits to the Microanalysis, Micrometrology, and Process Measurements Laboratories, the Magnetic Nanocomposites, Interface Characterization, Advanced Ceramic Processing, and Electrodeposited



Compositionally Modulated Alloys Laboratories, the NIST Cold Neutron Research Facility, and the Scanning Electron Microscope with Polarization Analysis Facility.

This report includes summaries of the opening plenary session and of the discussions that occurred in the working groups. Following these reports, are conclusions from the workshop and a list of attendees.



## WORKSHOP CONCLUSIONS

1. Nanostructured Materials, materials possessing nanometer-scale critical dimensions, are a distinct class of materials having unusual properties which potentially represent an important industrial class.
2. Interest in the area of nanostructured materials is increasing at an accelerating rate.
3. A great deal more basic research is necessary in order to fulfill the industrial potential of these materials.
4. There are many methods for preparing nanostructured materials, including several which potentially could provide scalability to large volumes.
5. Methods are available for the fabrication of nanostructured materials into large shapes without excessive grain growth destroying their nanometer dimensions.
6. In addition to properties investigations, a better theoretical understanding is necessary of the materials and of the mechanisms operative at the nanometer scale.
7. Composites represent an important subset of nanostructured materials which can provide unusual property **combinations**, and need increased examination.
8. NIST can provide assistance acting as an interface between industry and basic research, conducting key missing-property-information research and modelling (especially that requiring specialized equipment and expertise), preparing standards, assembling and administering a nanostructured materials information database, making available to outside users expensive national characterization facilities at NIST with their support staff for the synthesis and study of these materials, and supporting key industrial efforts in the area through its Advanced Technology Program.



## WORKSHOP PROGRAM

**MAY 14, 1992**

- 8:00 a.m. Registration
- 8:30 a.m. Welcome  
Dr. Lyle H. Schwartz (Director, Materials Science and Engineering Laboratory, NIST)
- 8:40 a.m. Opening Remarks  
Dr. Robert D. Shull (Metallurgy Division, NIST)
- 8:45 a.m. Overview of Physical Vapor Deposition Processes  
Dr. Richard W. Siegel (Materials Science Division, Argonne National Laboratory)
- 9:45 a.m. Refreshments
- 10:00 a.m. Overview of Chemical Processes  
Dr. Bernard H. Kear (Director, Advanced Technology Center for Surface Engineered Materials, Rutgers University)
- 11:00 a.m. Overview of NIST Nanophase Materials Activities  
Dr. Robert D. Shull (Metallurgy Division, MSEL, NIST)
- 11:45 a.m. Update on the NIST Advanced Technology Program  
Dr. John P. Gudas (Advanced Materials Program Manager)
- 12:15 p.m. LUNCH
- 1:15 p.m. - 2:45 p.m. Break up into Workshop Groups:

A. SYNTHESIS AND PROCESSING

Chairman: Dr. Mike Roco (Program Director, Engineering Directorate, NSF)

Co-Chairman: Dr. Gregory J. Rosasco (Group Leader, Reacting Flows, Process Measurements Division, CSTL, NIST)

Recording Secretary: Dr. Peter Strutt (Director, Nanoprecision Engineering Initiative, University of Connecticut)



**B. PROPERTIES**

Chairman: Dr. Lawrence T. Kabacoff (Scientific Officer, Materials Division, Office of Naval Research)

Co-Chairman: Dr. Neville Pugh (Chief, Metallurgy Division, NIST)

Recording Secretary: Dr. Carl C. Koch (Professor, North Carolina State University)

2:45 p.m. - 3:00 p.m. Refreshments

3:00 p.m. - 4:30 p.m. Return to Working Groups

4:30 p.m. TOURS OF NIST FACILITIES: (1) Microanalysis Laboratory  
(2) Micrometrology Laboratory  
(3) Process Measurements Laboratory (Process Sensing & Reacting Flows)

5:30 p.m. BREAK FOR DINNER

**MAY 15, 1992**

8:30 a.m. Refreshments

9:00 a.m. WORKING GROUP WRAP-UP AND DISCUSSION

Chairman: Dr. Brian Frost [Senior Technical Advisor (formerly Director: Materials Science Division), Argonne National Laboratory]

**A. SYNTHESIS AND PROCESSING**

Rapporteur: Dr. Peter R. Strutt (Professor, University of Connecticut)

**B. CHARACTERIZATION**

Rapporteur: Dr. Julia Weertman (Professor, Northwestern University)

**C. PROPERTIES**

Rapporteur: Dr. Carl C. Koch (Professor, North Carolina State University)

11:00 a.m.    WORKSHOP CONCLUSIONS AND FUTURE AGENDA  
                  Dr. Robert D. Shull (Metallurgy Division, NIST)

11:30 a.m.    LUNCH

12:30 a.m. - 3:00 p.m.                    TOURS OF NIST FACILITIES

- (1)    NIST Cold Neutron Research Facility
- (2)    Magnetic Nanocomposites Laboratory
- (3)    Advanced Ceramic Processing Laboratory
- (4)    Interface Characterization Laboratories: X-ray Standing Wave &  
          Scanning Scattering Microscope facilities
- (5)    Scanning Electron Microscope with Polarization Analysis Facility
- (6)    NIST Laboratory for Electrodeposited Compositionally Modulated  
          Alloys



## PLENARY SESSION

### I. Introduction by Dr. Lyle H. Schwartz

Director, NIST Materials Science and Engineering Laboratory

After welcoming the participants to NIST, Dr. Schwartz (Chairman of COMAT, the intergovernmental committee on materials science and engineering) stated that in the last four years (since the name change from NBS) there have been many changes at NIST. However, some things have not changed, including its long history of attention to fundamental issues in science. But, he stated that it's equally appropriate that we extend the issues we address at a workshop such as this from basic science and the fascination of understanding what's going on at the nanoscale to the ultimate application of these materials for the benefit of society. He was especially happy that this workshop was addressing not only the understanding of the materials but also ways to make them in ways that makes them commercially viable.

With regard to the things which have changed, Dr. Schwartz indicated that various parts of the US government now recognize NIST's strength is important to maintaining the health of the US industry establishment, and that recognition is resulting in a number of new programs at NIST, one of which is the Advanced Technology Program (ATP). About the ATP program Dr. Schwartz mentioned that it was developing very nicely, and as a result of that development it has created linkages between NIST and a number of the most dynamic companies in the US. In the Congressional authorization of NIST signed by the President last February, the Director of NIST is now allowed to use up to 10% of the ATP budget for activities within the laboratory. As a consequence of that change, NIST is now defining how to use those resources, which, although not enormous, will allow NIST to tune programs to be more responsive to industrial needs. Due to the new recognition of the importance of NIST's activities, the Office of Management and Budget has even stated an interest in doubling the budget for the NIST laboratory, perhaps in the next five years. Dr. Schwartz also mentioned that NIST will soon be given its first ever capitalization fund for refurbishing its 26 year old facilities (40 year old at Boulder). This will result in a major change of the facility in the next 10 years. This means ultimately that the NIST laboratories would match the pretensions of this institution and that would probably be good for the whole nation. With those very positive words, Dr. Schwartz said NIST appears to be doing pretty well, and he was happy to host this workshop since it also helps NIST determine the proper direction for its own programs.

### II. "Overview of Physical Vapor Deposition Processes"

Dr. Richard W. Siegel, Materials Science Division, Argonne National Laboratory

Dr. Richard Siegel, Co-Chairman of the 1988 Blue-Ribbon DOE panel on "Clusters and Cluster-Assembled Materials" and present Chairman of the International Committee on Nanostructured Materials (ICNM), described nanostructured materials as possessing three general characteristics:



(1) they are a synthetic material containing a modulated structure (modulation distance  $\leq 100$  nm); (2) they possess size constraints and confinement effects in three dimensions; and (3) they possess a significant ( $> 1\%$ ) volume fraction of interfaces. These characteristics, which also result when a material is made from cluster building blocks, are responsible for changing the properties of these materials from those they would possess if not nanostructured. Confinement is important both in the quantum mechanical sense, where the size of a system of atoms is shrunk down below the size of an excitonic state, and also in the sense of its value relative to the critical length scale of the mechanism that drives the property of interest. Every property has a critical length associated with it. Mechanisms operative at larger length scales freeze out as the size of the materials is reduced. For example, consider the ductility of a metal. In addition to the non-directional atomic bonding, a metal is ductile because of the easy formation of dislocations and the easy glide of these dislocations through the metal. The critical length scale here is the critical distance between pinning points that activate Frank-Read sources for the easy formation of dislocations. As the size of the system is reduced, the distance between pinning points becomes smaller, causing the stress required to drive the Frank-Read source to increase. For dimensions less than a critical length, the material is no longer able to generate dislocations, thereby drastically affecting the material's ductility. Because in nanostructured materials there is a high volume fraction of interfaces, a large fraction of the atoms in the material will be at "defect" sites (i.e. at interfaces or "not normal" lattice sites). Since these atoms will possess new atomic arrangements over a significant volume of the material, the material's properties will relate to the defect structure, not to the long range bulk structure. Interfaces become important in determining the material's properties when the percentage of atoms residing at interfaces becomes large, as occurs in nanostructured materials. By taking a width of the interface boundary (such as a grain boundary) as 0.5-1 nm (i.e.  $\pm 1-2$  atom planes), the percentage of atoms in the grain boundary ( $N_B$ ) may be calculated as a function of grain diameter ( $d$ ). Such a calculation showed an increase in  $N_B$  as  $d$  decreased. For example, at grain diameters near 100 nm, 10 nm, and 5 nm  $N_B$  had values between 1-3%, 15-30%, and 25-50% respectively. As first suggested by Gleiter in the early 80's, when you make a 3 dimensional array of small clusters to make a monolithic material, the clusters form small grains having very small radii of curvature. Consequently, there are very high chemical forces between the clusters, as well as very short diffusion distances; therefore, the kinetics for interactions between clusters is rapid. Because of this combination of high driving forces you have the ability to overcome normal synthesis conditions in making materials.

One way to make a nanostructured material is to consolidate small atomic clusters as in the assembly of CdS and ZnS clusters contained inside zeolite cages. As one changes the concentration (via precipitation or ion exchange), one increases the cluster loading to the point where the clusters begin to interact (even though they never actually physically touch). At high enough loading an ordered array of the CdS or ZnS clusters forms inside the zeolite cages. Simultaneously, the optical absorption of the material changes from that of the individual clusters (at very low loading) to that due to cluster-cluster interactions, resulting in a shift of the optical absorption edge to higher wavelengths. At the highest loading, the optical absorption edge is that of the bulk CdS. Other methods for making nanostructured materials include mechanical attrition, spark erosion, plasma synthesis, sol-gel, flame and aerosol methods, and micelles routes.

One of the simplest methods for making clusters (which can be assembled into a bulk material) under controlled conditions is via gas condensation. In this process, a precursor material (either a liquid metal or a solid with a high vapor pressure) is vaporized into a system containing cold gas atoms. Upon collision with the cold gas atoms, the vapor atoms lose energy sufficient to allow them to condense into small solid clusters. This process generally occurs within a millimeter or two of the evaporation source where there is high supersaturation of the vaporizing species. In order to keep these atom clusters small, one needs to move them out of the supersaturated region after condensation. There are only three rates involved in this process: (1) the feed rate of atoms (i.e., the evaporation rate), (2) the energy removal rate by collision resulting in condensation, and (3) the removal rate of the clusters from the condensation region. These rates may be easily controlled. Experimentally, you can create the vapor by joule heating, laser ablation, and electron beam heating. In the original Argonne National Laboratory system built six years ago, a cold finger is used to cool the gas and to collect the clusters. In this apparatus, a toroidal flow of the gas due to gravity and convection occurs, and near the cold finger there is a huge temperature gradient. (Natural convection is too slow for industrial processes, so in scale-up operations forced flow methods would be used.) The clusters fall down this temperature gradient by the process of thermophoresis and stick near the cold finger by weak Van der Waal forces. These clusters may then be scraped off the cold finger and compacted. Small atomic clusters are obtained when the feed rate of vapor into the supersaturated region is low and also when the atomic weight of the cold inert gas is low (e.g., He rather than Ar or Xe). This latter condition is advantageous because of the small energy loss per collision. Low inert gas pressure also increases the rate of natural convection and reduces the probability of precursor-gas interactions. Using this process, one obtains a narrow log-normal size distribution ( $\pm 25\%$  FWHM) which scales with the size. Room temperature consolidation results in metals and ceramics having 97% and 75-85% theoretical densities respectively. In these compacts, the pore size distribution scales with the grain size distribution. Full densities can be obtained with increased consolidation temperature.

For nanometer-sized ( $d=10$  nm)  $\text{TiO}_2$  particles, high resolution TEM does not indicate any dislocations in the material, presumably because individual glissile dislocations would be pulled out of a particle so small by image forces. Electron microscopy on these particles also showed they were equiaxed and stay that way as they are consolidated. Similar observations have been made in nanometer-sized metals (e.g., 6-7 nm sized Pd). High resolution TEM on compacted nanophase Pd showed lattice fringes which were both straight and flat upon entering the grain boundaries. Consequently, any distortions occur either in the boundary plane or within 1 atomic plane of the boundary plane. This is similar to high angle grain boundaries in conventional materials; not so surprising since these types of boundaries are the low energy configurations. However, elimination of local strains at the boundaries requires atomic motion. Due to the small size of the clusters only a small amount of atomic motion is necessary, and apparently this motion is possible in the consolidation process. This situation should be true for metals, ceramics or composites.

Dr. Siegel concluded by reiterating the exciting potential provided by cluster-assembled materials. In addition, the ability to make individual clusters of different types also allows one



great flexibility to make very interesting composites with unique properties. Large opportunities also exist using these processes for making multifunctional materials.

### III. "Overview of Chemical Processes"

Dr. Bernard H. Kear, Director, Advanced Technology Center for Surface Engineered Materials, Rutgers University

Dr. Kear, past Chairman of the National Materials Advisory Board and also Chairman of the 1989 NRC Panel on "Research Opportunities for Materials with Ultrafine Microstructures," described chemical methods broken into two categories: (1) those using gaseous precursors [including laser pyrolysis (powders), chemical vapor synthesis (powders and films), and catalytic decomposition (filaments)] and (2) those requiring liquid precursors [including gel synthesis (porous media), electrodeposition (films), and reductive pyrolysis (powders)]. Emphasis devoted to reductive pyrolysis is well on the way toward full scale commercialization.

The idea behind laser pyrolysis is to use the focused energy of the laser (usually a continuous CO<sub>2</sub> gas laser) as the energy source to drive a specific reaction from the gas phase. One of the most common arrangements is the "cross-flow" type: the laser beam enters from the left to a "partial focus" in the reaction zone (where the reacting gas with an inert carrier gas like Ar enters). At Rutgers, nanoparticles of Si<sub>3</sub>N<sub>4</sub> are being made this way using silane and ammonia precursor gases. The laser beam generates effectively a controlled sustainable plasma flame (or plume) in the reaction region and the product species are rapidly quenched out long before they can aggregate into large clusters. The residence time in the reaction region is the key to the control of the particle size. Typically, d=17 nm or smaller. Because these are SiN, invariably the particles are amorphous and spherical. Powder handling is performed external to the system; this could be either good or bad. One also obtains a very narrow pore size distribution in these materials, as determined by porosimetry or nitrogen gas desorption. Due to the small particle size, one can densify the material to fairly high densities. This can be performed at relatively low temperatures, including in liquid N<sub>2</sub> (the liquid acts as a lubricant). This process could also conceivably be used to prepare nanodiamonds!

Chemical Vapor Synthesis (CVS) is useful also for the preparation of fine particles (it already is a well known process for making thin and thick films). There are two alternative approaches: (1) Combustion Flame Reactor (an economical high production rate process) and (2) Plasma Torch Reactor (controlled environment in a high temperature). The later is an extremely mature technology worldwide. Presently, hundreds of thousands of tons (perhaps millions of tons) of carbon-black nanoparticles are produced commercially. Cabosil silica particles as supports for catalysts in the electrochemical business and TiO<sub>2</sub> particles as a pigment for paints are two other commercial examples of materials made by the CVS process. The key to making the nanometer sizes in this process lies in the gas flow through a hot zone from which rapid condensation occurs. The process is also fast and cheap. For example, Cabot corporation makes a months worth of carbon-black in a "ram jet" in a few hours. The simplicity of these processes certainly



compensates for admittedly the moderately expensive precursors (e.g., volatile metal chlorides and fluorides) required. During thin film synthesis, there are hot wall and cold wall processes. The semiconductor device technology invariably uses the cold wall process because of the two competing processes in a CVD reactor: (1) homogeneous nucleation of particles in the gas phase which forms powder and (2) heterogeneous nucleation of particles on cold surfaces which collect and aggregate to form a thin film. Dr. Kear finds there is a "master curve" relating the thin film deposition rate (or powder production rate) to the residence time for each precursor at each concentration and temperature. Film growth is favored at short times while powder formation is favored by longer residence times. If one can live with the low production rates, a low concentration of precursor will give one "powder-free" thin films. When the precursor concentration is high, one always obtains powders because the collision frequency between the reaction intermediates is high. Once decomposition kinetics are established, continuous powder production for any precursor is possible. Therefore, the process can be reactor-length independent, even though it is very temperature dependent. Consequently, the important job is to establish the decomposition kinetics. For the CVD gun process, one just adjusts the temperature of the process so as to increase the residence time to the point where one obtains powders. The advantage of the liquid-feed delivery system in the aerosol method over the gas-feed system in the plasma gun process is that one can introduce much more precursor per unit time in the liquid-feed technique.

For making fine filaments, catalytic decomposition is a good method. In fact in a steam cracker (where ethane is converted to ethylene), the filamentary growth of carbon on the walls of the reactor vessel "chokes" up the reactor. It is a catalytically grown carbon as a result of reaction of the hydrocarbons in the stream with the transition metals in the walls of the reactor, a kind of "arteriosclerosis" of the petrochemical industry! The lower the temperature (which favors double- or triply-bonded hydrocarbons which decompose at the lowest possible temperatures) the finer the structure (or fibers) created. If one uses an alloy catalyst, it is a non-poisoning process. These fibers can fill space, and by this process one can obtain high strength by graphitization at very high temperature. The high strength, high stiffness by graphitization process is presently being used in Japan. General Motors Corporation is also an advocate of this material for future use in making car bodies. Plastic reinforced composites are made with the carbon filaments synthesized by this technique. The trick is to grow the fibers as fine as possible by low temperature growth, followed by a higher temperature stage wherein the fibers are thickened with a graphitic skin. In this process, a hydrocarbon decomposes on contact with the transition metal releasing heat; this exothermic reaction drives the solid state diffusion of the carbon to the base of the metal protrusion leaving the metal top free to repeat the decomposition of the hydrocarbon. The process stops when the carbon so formed soon overgrows and chokes off the catalyst metal tip. To circumvent this latter problem, hydrogen is added to the gas so that it vaporizes the carbon as fast as it forms. If one begins the process with a high surface area material, like fine catalyst particles, in the reactor one can make a lot of interesting structures like a random weave. After the CVD growth of silica with carbon inside, one can oxidize away the interior carbon by changing the gas environment, leaving the silica tubes. Random weaves of such materials with fibers having 2-3 nm diameters fill space and have very low thermal conductivity. Therefore, they possess a potential as thermal barrier coatings (e.g.

for turbine blades).

Reductive pyrolysis is also a viable technique for preparing nanophase materials, and it is just as scalable as the processes described above for making carbon-black. This process is particularly attractive for making nanostructured composites of Co/WC. Such a Co/WC composite combines the high hardness of the WC with the toughness of the Co binder. For this nanocomposite, one may select the desired combination of fracture toughness, hardness, stiffness, and strength by selecting the relative volume fraction of the two phases. It has been known for decades that the properties at a given volume fraction systematically improve as the scale of the microstructure diminishes. But with classic powder metallurgical processing (crushing, grinding, blending, mixing of the powders, and consolidation) one cannot reduce the powder sizes to much below 1  $\mu\text{m}$ . There was, therefore, a window of opportunity here if one could make materials with the small sizes. Chemical methods are a good way if a suitable precursor is found. For synthesis of a Co/WC precursor, a solution was prepared containing two different liquid compounds, each being a source of one of the two species desired in the resultant material (e.g., ammonium metatungstate and cobalt nitrate). To prevent the mixture from phase separating, the solution is sprayed as an aerosol. The process is analogous to rapid solidification preventing the phase separation during solidification of a metal. Each aerosol droplet has the same composition as the original liquid mixture, and therefore results as an amorphous homogeneously mixed precursor powder. The nanometer-sized precursor powder is subsequently thermochemically converted to a composite of the desired structures (e.g., WC/Co). In the case of the WC/Co nanocomposites, improved crack resistance and higher hardness values than the conventional material counterparts were obtained. Liquid phase sintering with VC doping was found to be the key to mitigating WC grain coarsening during sintering of the powders. In these materials, elongation to fracture was also improved by 25% over conventional WC/Co composites.

Gel synthesis is another method which provides a network of material with interconnected porosity which is controllable down to nanoscale dimensions. So one has an opportunity to generate nanophase composites by liquid or gas infiltration of the controlled porosity, or by electrochemical infiltration. By this process, one can make a net shape object or thin films. At NIST it has been found that electrodeposition is also a good way to prepare some materials as multilayers with nanometer size thicknesses having good layer sharpness. By the former technique interesting magnetic nanocomposites have been prepared and by the latter technique improved wear-resistant materials have been made. In summary, (1) there is a wide variety of chemical processes for making nanostructured materials being developed, starting from both gaseous and liquid precursors; (2) a few processes have matured to the point that full-scale commercialization is in sight; and (3) new frontiers for basic research are being uncovered continuously, which bodes well for the future of the field.



#### IV. "Overview of NIST Nanophase Materials Activities"

Dr. Robert D. Shull, Metallurgy Division, Materials Science and Engineering Laboratory, NIST

Dr. Shull, Secretary/Treasurer of the International Committee on Nanostructured Materials, described the preponderance of work on nanophase materials already in progress at NIST. Included in this work was an active effort toward the preparation and characterization of sensors in the Process Measurement Division. Arrays of nanometer-sized metallic islands are deposited onto a semiconducting oxide are being evaluated as catalytic "actuators" for sensing concentration of gaseous species. A scanning tunnelling microscope is presently being installed for the in-situ measurement of both the morphology and electrical characteristics of the nanometer-sized island sensors. In the same division, the flame-combustion process is being used to understand the formation and growth of clusters from the vapor. Dr. Shull showed several laser-induced fluorescence and light scattering measurement results for the formation of nanometer-sized particles of the high temperature superconductor,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , and also for  $\text{SiO}_x$  as a function of time in such a process. Fits of these data to various nucleation and growth models provided a means for determining the formation mechanisms of these materials from the vapor. The Ceramics Division has been developing methods for low temperature sintering. As part of this effort they have been successful at preparing an optically transparent  $\text{Si}_3\text{N}_4$  disc by use of nanophase powders of the material. This material was sintered at only  $1400^\circ\text{C}$  (normally  $2000^\circ\text{C}$  is required) and without sintering aids. This result was possible only because of a liquid nitrogen compaction process developed at NIST. In the Electron and Optical Physics Division a technique for imaging magnetic domains down to the submicron level called scanning electron microscopy with polarization analysis (SEMPA) has been developed. This tool, which provides both magnetic polarization and morphological information on the same area, has attracted a great deal of industrial interest and is presently being extended for nanometer-scale observation. The Metallurgy Division is presently leading the world in both electrodeposited multilayer materials with nanometer layer thicknesses and in magnetic nanocomposite refrigerants, with several patents pending in both areas. Electrodeposited Cu/Ni multilayers with a 4 nm wavelength were even shown to possess a wear resistance comparable to hard chromium! Magnetic refrigerators, long restricted to low temperature and high magnetic field use, may become useful at higher temperatures and lower fields due to the predictions and preliminary data on the enhanced magnetocaloric effects in nanocomposite materials.

Dr. Shull also described several unique facilities located at NIST which are potentially useful for probing materials with nanometer-scale dimensions. In the Precision Engineering Division a device called the "Molecular Measuring Machine" is under construction for mapping areas as large as 5 cm x 5 cm with 0.1 nm resolution. This scanning tunneling/atomic force microscope is operated inside both active and passive vibration isolation stages, with acoustic isolation and 0.1 mK temperature control. Consequently, an absolute precision in location of the probe on the 5 cm x 5 cm area will be better than 1 nm. Microanalysis tools are being used in the Surface and Microanalysis Science Division for obtaining composition analyses of species varying in size down to the nanometer-scale. Techniques such as parallel electron energy loss spectroscopy (PEELS), secondary ion mass spectrometry (SIMS), laser microprobe mass

spectrometry (LAMMS), and laser Raman microprobe (LRM) analysis are used on a regular basis to perform these analyses on nanostructured and other materials. Since these analyses are computerized, compositional maps of surfaces, even at the nanometer scale, are possible using these facilities. In addition, this division has developed an x-ray standing wave technique for measuring the bond distances and angles for atoms of chemisorbed species at surfaces. This is particularly useful for observing reconstructions and defect formation and their role in reducing surface free energy during interface formation. Surface topography with nanometer resolution is also possible through use of the scanning scattering microscope (an IR100 Award Winner) developed in the same division. The cold neutron research facility (CNRF), a national user facility, possesses several capabilities of particular value to nanometer-scale materials research. This facility has just been expanded by 100% with the addition of a guide hall wherein several guide tubes bring in the neutrons from the reactor core. Presently, there is an 8 meter small angle scattering (SANS) facility with two additional 30 meter machines under construction for use at probing density fluctuations at the nanometer-scale. This measurement capability is particularly unique in the US due to the high flux of slow neutrons available because of the cold source installed in the reactor core. Interface structure may be probed using the neutron reflectometer, trace composition levels are possible through prompt gamma activation analysis, and materials dynamics can be probed with the time-of-flight and triple-axis spectrometers under construction. In addition, magnetic spin orientations may be probed using the spin-polarized diffractometer at the reactor. A diagram of the new guide hall with the instruments indicated is shown in figure 1.

#### V. "Update on the NIST Advanced Technology Program"

Dr. John Gudas, Program Manager for Advanced Materials, Advanced Technology Program Office, NIST

Dr. Gudas described that as a result of the Omnibus Trade and Competitiveness Act of 1988, NIST was given the role to help enhance industrial competitiveness and to promote US economic growth. Part of this augmented NIST activity is represented by the Advanced Technology Program (ATP) wherein monetary awards are provided to industry to support research on precompetitive and generic technology. Generic technology was defined as a concept or process or phenomena which has the potential to be applied to a broad range of products or processes; and precompetitive refers to technological areas where the technical uncertainties are sufficiently large to prevent assessment of commercial potential prior to development. Consequently, projects supported by the ATP involve research and development at a stage between basic research and specific commercial product development. Either single applicants, with possible awards up to \$2x10<sup>6</sup> for 3 years, or joint ventures, with 5 year awards limited by the total funding available, are eligible. Joint ventures, however, must provide at least 50% of the total cost in matching funds. ATP proposals are judged on five criteria: scientific and technical merit (20%), broad based commercial benefits (20%), technology transfer benefits (20%), experience and qualifications of the proposing organization (20%), and the proposer's level of commitment and organizational structure (20%). Proposals initially receive a technical review of the content



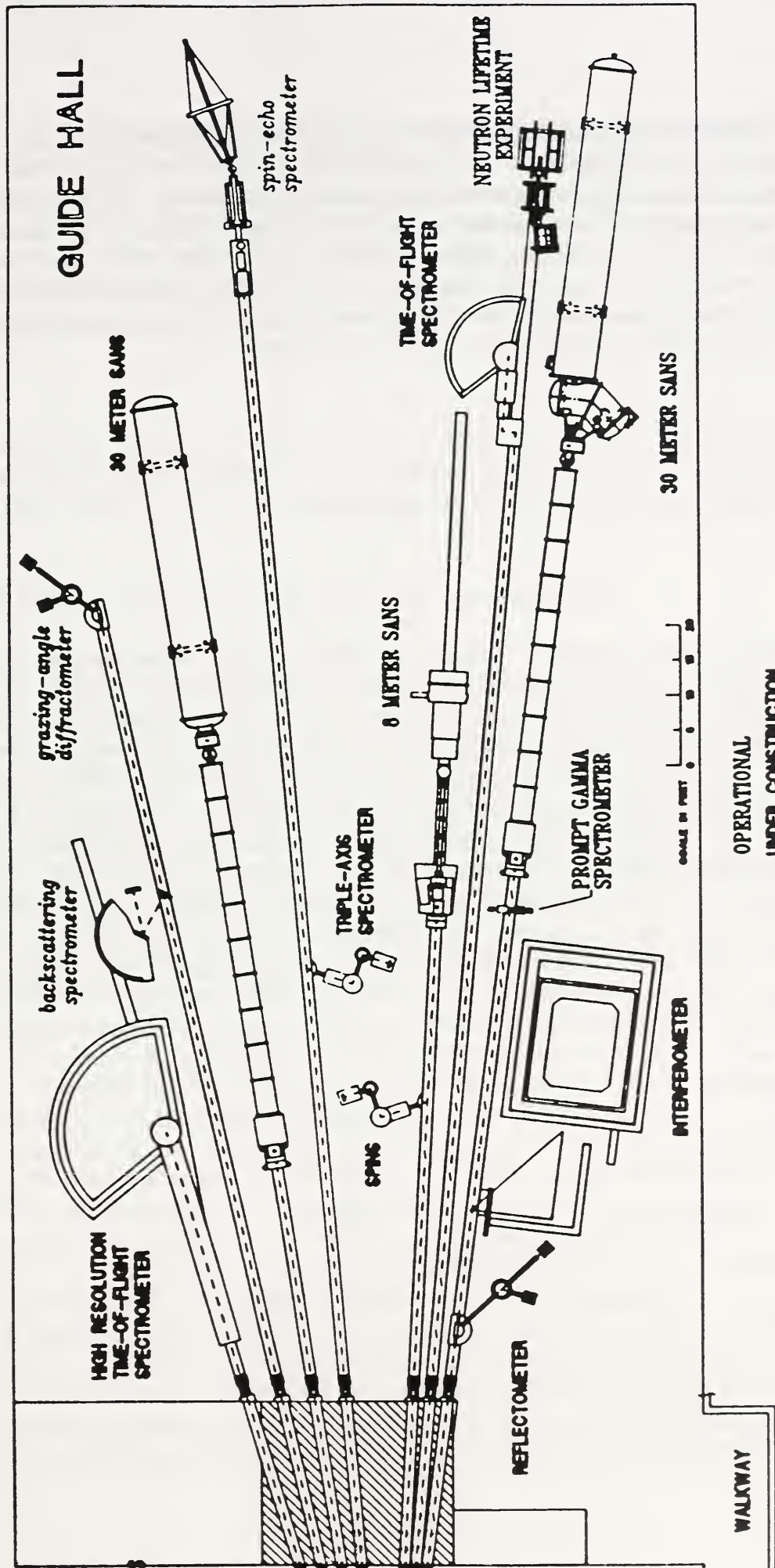


Figure 1. Schematic of the Cold Neutron Research Facility Guide Hall

by up to three reviewers. The top third of these receive a business review, and the top 30 of these are designated as semifinalists. The semifinalists are then invited to make an oral presentation and defense at NIST prior to the final selection of awards. In Fiscal Year 1991, \$35.9 million was appropriated by Congress for the ATP, and in FY92 and FY93 \$47.4 million and \$67.4 million respectively are requested. It is anticipated that further increases in the amount of funds available will occur. Dr. Gudas answered several questions on the application procedure and review process, and encouraged the workshop participants to contact the ATP office to obtain application materials.

## WORKING GROUP A: SYNTHESIS AND PROCESSING

Chairman: Dr. Mike Roco (Program Director, Engineering Directorate, NSF)

Co-Chairman: Dr. Gregory J. Rosasco (Group Leader, Reacting Flows, Process Measurements Division, CSTL, NIST)

Recording Secretary: Dr. Peter Strutt (Director, Nanoprecision Engineering Initiative, University of Connecticut)

This session started with a series of talks on various production methods of nanostructured materials followed by a discussion of key processing problems and of what an appropriate role would be for NIST to play in the development of this field of advanced materials.

### I. Brett Halpern, Jet Process Corp., CT: Jet Vapor Deposition.

Dr. Halpern described a technique which his company is using for the deposition of thin films. They can deposit nanostructured thin films, multilayered structures, and also deposit fine particles. The basic idea they use is to position a vapor source (e.g., via thermal evaporation, microwave discharges, glow discharges, laser vaporization) upstream of a nozzle and to create a pressure difference through the nozzle so that a supersonic jet of the vapor is created. Typically, they have several Torr upstream of the nozzle and inside the nozzle, and a fraction of a Torr downstream of the nozzle. The jet is highly collimated, and the deposits are extremely localized. By varying the pressure drop, the characteristics of the deposit may be controlled. Since the nozzle is typically several centimeters in diameter, when one imposes a pressure difference of at least a factor of 2, a supersonic jet is formed. If one supplies this with a carrier gas, like helium or hydrogen, then the speed of the jet is close to  $10^5$  centimeters per second and the transit time from vapor source to substrate is extremely small. In order to spread the deposit over a larger area, one can either move the substrate in two directions or scan the nozzle, or one can literally move the gas jet itself. A very effective way to uniformly coat a substrate is to mount it on a drum and spin the drum while oscillating the jet. The composition is also uniform since the vapor has no time to diffuse to the walls of the nozzle and also very little time to diffuse out from the jet. In fact, the form of the jet is guaranteed by the slow diffusion relative to the fast axial transport in this regime. A wire feed mechanism has even been found convenient for the deposition of metals such as copper, gold, and aluminum. In these cases, with a source which dissipates 60 watts, a high deposition rate of  $0.1 \text{ cm}^3$  of metal per minute is typical. This means one can coat the thousand square centimeters of a drum 60" in diameter and 3" high to a depth of a micron in about a minute. By coupling one or more jets with these moving substrates, they could generate a number of interesting films, including multilayered films (or microlaminates). For example, using a jet of copper and a jet of gold, the Jet Process Corporation (JPC) was able to build up a repetitive sequence of copper and gold layers (5 nm thick Cu and 5 nm thick Au to a total thickness of 500 nm) by alternating the jets. Improved tensile strength 100  $\mu\text{m}$  thick microlaminates of interleaved Al (50 nm thick) and  $\text{Al}_2\text{O}_3$  (5 nm



thick) have also been prepared. More complex thin films can be obtained by operating the jets simultaneously. For example, JPC has just been awarded a phase 2 contract from DARPA to continue their phase 1 demonstration of making very high quality ferroelectric lead-zirconate-titanate (PZT) by this process. One reason they are successful at making films of such a complex multicomponent system by this process is that despite the fact that there is a high flux from any individual jet, the rotation of the drum guarantees that there will be no more than a sub-monolayer deposited per pass of any jet. There are also no solid state diffusion limitations due to the fine microstructure provided by this process. Silicon nitride films were prepared by using a jet of silane decomposed by a microwave discharge inside the nozzle and a jet of nitrogen. By coupling a similar process with a jet that evaporates organic molecules they were also successful at embedding individual molecules of methyl-red in a 1  $\mu\text{m}$  thick silicon dioxide film. In this film very high concentrations (between  $10^{20}$  -  $10^{21}$  molecules per cubic centimeter) of the organic molecules were embedded, as deduced from its red color. This is equivalent to a one molar solution of methyl-red. Since this film did fluoresce when exposed to ultraviolet light, one concludes the structure of the methyl-red molecule was not been degraded by the trapping in the  $\text{SiO}_2$ . This composite is attractive as a passive wave guide (supported by an NSF/SBIR award). As the masked film is exposed to ultraviolet light, the unprotected methyl-red is destroyed, thereby patterning the waveguide. This JPC method for making a hard film that is comprised of a host that is compatible with semi-conductor technology can be applied to many other combinations. In addition to entrapping molecules, clusters can also be nucleated at the surface by this process. By adjusting the deposition rate of the jets, surface clusters can be made which are then buried in the next layer of the host. One can also make very fine powders by using a liquid target like water, glycerol, or epoxy. Very fine Au, Ag, Cu, and Pt particles have been prepared this way, and they can be kept separated by use of an ionic salt or a surfactant in the solution. By this process, one can make  $100 \text{ cm}^3$  of powders in about 10 minutes. Compare this to the many hours required by chemical reaction techniques, which also commonly leave a residue. JPC does not believe the particles are formed in the gas phase. In order to make clusters one needs three-body collisions. The transit time from the source to the target is about  $10^{-8}$  seconds; while the time it takes to have a 3-body collision between a helium carrier gas and two gold atoms, for example, at the prevailing pressures is something in the order of 0.1 second. Consequently, the probability of 3-body collisions is very low during this fast transit time. Even if one were to form a nucleus that way and by subsequent molecular collisions make it grow, there would still not be enough time to grow a cluster of three nanometer size in the available transit time. By raising the vaporization rate, one can actually grow metal films on the liquid, implying that each individual metal atom has a surface lifetime. They form clusters or rafts, and at some critical size they are pulled under the liquid. In terms of scale up, the size of the nozzles can be scaled-up by a rather large factor, and that the through-puts for this process can be quite large.

## II. Allen Edelstein, Naval Research Laboratory, Wash. D.C.: High Pressure Sputtering.

Dr. Edelstein described the process of making particles in a vapor by sputtering at high pressures. There is a threshold pressure for making the particles, and knowing this threshold

can allow one to control what is made. He showed several transmission electron micrographs of Mo particles formed as a function of sputtering pressure. At low pressures there were no particles in the film; at high pressures one makes cubes of two different sizes. At high pressures the particles are small and the size distribution is broad. The sputtering rate goes down as one increases the pressure, so there are competing effects. As the sputtering rate decreases, the mean-free path also decreases. If one reduces the sputtering pressure, the particle-size distribution narrows, and at the threshold pressure one obtains the bimodal distribution. The big cubes appear to be a 3 x 3 self arrangement of the little cubes. Sometimes one obtains 2 x 2 arrangements. Dr. Edelstein believes that the smaller cubes are made first, and in the vapor they collide with one another making the bigger cubes. In order to understand how that happens, he arranged a series of TEM grids to collect material at various positions in his apparatus. He found that near the target, only films were collected. Only near the cold finger, further away from the target, did he observe the cubes or self organization. In general, Dr. Edelstein concluded that during sputtering there are two regions of concern: a supersaturated region where one gets particle formation, and an unsaturated region. One can move into the supersaturated region by increasing the rate by which particles are added to the vapor, or by keeping the vaporized atoms in the vapor longer by decreasing their mean-free path. Consequently, there is a boundary for forming particles. When sputtering at high rates and with a relatively long mean-free path, particles aren't formed except near the cold finger where it is cold enough to condense. Because the sputtering rate decreases with increasing pressure, one also approaches the boundary at high pressures. The significance of this finding is that the particles are being formed close to where they are collected (i.e., at the cold finger) and therefore don't have much time for growth. In fact, processing anywhere along this critical boundary will probably result in small particles. Secondly, a narrower size distribution will also be obtained via this process since collection will be from a narrow region at low temperatures. Unfortunately, the trade-off is that it is not going to be so obvious how one will make a lot of material by this process.

### III. Laszlo Takacs, Univ. of Maryland, Baltimore County: Mechanical Alloying.

If one puts a couple steel balls into a small vial with powders to be mixed and shakes it very heavily, the metal or non-metal powder particles crack and cold weld together. If repeated many times, the cracks and cold welds occur at random orientations and the two components become mixed together to form a new alloy or compound. Dr. Takacs has been using this process (using a Spex 8000 mill with a ball:powder ratio of 1:10) to make composites of a metal and an oxide (e.g., Fe in  $\text{Al}_2\text{O}_3$ ). However, he uses the process to initiate chemical reactions while mixing the constituents. For example, by starting with  $\text{Fe}_3\text{O}_4$  and aluminum, during the milling process one can initiate the aluminum reduction reaction of the iron oxide, forming aluminum oxide containing Fe particles. He has also performed the opposite reaction: starting with the oxide matrix (e.g.,  $\text{CuO}$ ) and reducing it with Fe to form magnetite in Cu. Understanding the process is very important. Unfortunately, many of the important parameters are not understood, including the thermodynamics of the lattice defects created by mechanical milling and how they affect the chemical activities, the effects of thermal conduction and the heat released during exothermic reactions, and the effects of free surfaces on the thermodynamics of the system. He



showed several x-ray diffraction patterns for the aluminum and iron oxide milled powders, from which the progression of the reduction reaction could be followed. During the ten hours of milling, the magnetite peaks decreased in intensity while pure iron peaks appeared and grew larger with milling time. Dr. Takacs also showed Mössbauer data to indicate that metastable intermediate phases were formed at some intermediate (~20%) milling time. In the Mössbauer spectra one observes after an hour and a half milling additional absorption lines (from some intermediate phase) not observed either at the beginning of the process or at the end of milling. He showed that the magnetic coercivity of the milled material was also very different, depending upon whether one started with a mixture of iron and alumina or with a mixture of magnetite and aluminum. One important parameter which must be considered when using this process is contamination from the balls and vial. For the Fe and Al<sub>2</sub>O<sub>3</sub> system, this was not a problem since Fe was one of the initial constituents. One very attractive aspect of this process is that it is capable of producing large quantities of material if needed.

#### IV. Anthony Pirri, PSI Technology Company, Andover, MA: Aerosol Spray Techniques

A description of the method PSI Technology uses to produce nanophase ceramic powder was presented. Essentially, the process consists of oxidizing at high temperatures an organic carrier material mixed with the ceramic precursor. A common organic carrier is water with dissolved sugar. The solution is passed through an atomization process where it is turned into a spray which when dried creates a carbonaceous particle. This particle is then oxidized at a very high temperature. During oxidation, the ceramic precursor vaporizes and nucleation of the ceramic occurs quickly due to the large temperature gradient between the particle and the outside gas zone. This high temperature process provides for fast reactions while the rapid quenching gives short residence times. By controlling the oxygen flow rate, the concentration of oxygen, and the temperature of the oxygen stream, one can control the residence time and, thereby, control the degree of agglomeration that occurs during the process. So far, PSI has prepared nanophase zirconium oxide, and magnesium oxide by this method. They can obtain a very narrow distribution of particle sizes, with the average diameter on the order of nanometers. This size and distribution is controllable through the processing conditions. Micrographs were shown for cold pressed compacts of this powder and of a commercial powder. The porosity of the nanophase powdered compact was lower. Also the nanophase Zr<sub>2</sub>O<sub>3</sub> powders could be sintered at temperatures below 1500°C (the normal sintering temperature of commercial Zr<sub>2</sub>O<sub>3</sub>). So far PSI has only made a couple grams of material, so scale-up needs to be addressed in the future. It was also stated that even though this process has only been used for making oxide particles so far, it could also be extended to make carbide particles, and possibly nitrides.

#### Ted Morse, Brown University, Providence, RI: Aerosol Spray of Unagglomerated Nanoscale Oxide Particles

In a similar process, Professor Morse described a process whereby an alkoxide/organometallic solution is made into an aerosol via a sonic nozzle, transported into a high temperature reactor with oxygen and propane, and burned. Since the organometallics don't exist above 300-400 K, when the liquid droplets in the aerosol are quickly heated to the 2500-3000 K in the burning

flame, they basically explode. A gas phase reaction subsequently occurs in the turbulent flame which creates fine oxide particles that quickly quench. These particles are spherical and unagglomerated, having no necks, and are tangential to one another. Dr. Morse reports having prepared the oxides of Zr, Ta, Nb, and Si by this process. He showed a particle size distribution for alumina (mean diameter of 40 nm) with the sizes ranging from 5-60 nm. For zirconia particles the room temperature x-ray diffraction data indicated the tetragonal phase. Apparently, it's small size has allowed it to be stabilized in the high temperature tetragonal structure at low temperature. There is also no chlorine in these materials. The production rates are typically 5 g/minute, but Dr. Morse indicated kilogram/minute quantities are possible.

#### VI. Horst Hahn, Rutgers University, Piscataway, NJ: Gas-Condensation of Nanophase Materials

Professor Hahn discussed that for normal gas-condensed powders nitrogen adsorption measurements (BET) indicate the pore size distribution is fairly wide. From those data and the specific surface area, it was also concluded that the particles were 50-70 nm in size, but consisted of 10 nm grains. Consolidation of these materials, however, was more difficult than that for small unagglomerated particles. Dr. Hahn was successful at making this comparison because he had developed a way to prepare unagglomerated gas-condensed yttria powders. The critical step was to control the post-oxidation. He mentioned that even though this is shown here for yttria, one can use the same process to control the post-oxidation of titanium and other materials to the same extent. Dr. Hahn showed a sample of the compacted (at 300 K) unagglomerated yttria powder (300-400  $\mu\text{m}$  thick) which one could see through. Consequently, the pores were smaller than the wavelength of light. A pore size distribution graph for yttria and titania showed that any agglomeration in these materials was also very small. Sintering of those materials was much better than their previous work on titania (even though that was also very good). Dr. Hahn then discussed the creep properties of the compacted powders. The advantage of nanograin materials is thought to derive from the very strong grain size dependence on the creep rate of the material, which leads to high strain rates and high deformation rates at fairly low temperatures (i.e., superplasticity). It is well known that there is a strong creep relationship with volume. Therefore, if one wants to understand the creep behavior of nanostructured ceramics one had better not have any pores. Otherwise that might dominate the whole story. Consequently, in order to study the effect of nanostructure on the creep rate, high density ceramics are needed. For pure titania, it is not possible since one always has grain growth as 100% density is approached. There are, however, two ways to circumvent this problem: dope the material or assist the sintering with pressure. Dr. Hahn prepared 99% dense nanograined (40 nm diameter) titania by pressure assisted sintering. Upon deformation at 800°C, the titania showed no cracking and no opening of pores, thereby showing superplasticity of this ceramic. During deformation there was no density change, but there was grain growth. In order to test the tensile properties, Dr. Hahn prepared a disk sample, put it in between steel blocks, and applied a 4 atm. gas pressure on the opposite side. After heating the sample (15 mm diameter) to 800°C, a ring depression indicating creep deformation under tension was observed on the sample. However, a similar experiment on a sample prepared by a chemical process (reduction of an alkoxide) having the same grain size as the above gas-condensed sample



resulted in no plastic deformation, only rupture. In one of these samples, obviously, something in addition to the grain size effect was being tested.

#### VII. Joanna Groza, Univ. of California, Davis, CA: Plasma Activated Sintering

Professor Groza described a new method called plasma activated sintering (sometimes called gas assisted sintering) for consolidating the nanophase powders prepared by the various techniques. In this process, the loose powder is loaded into a graphite mold and a high temperature plasma is created by applying a large current through the sample (2-25 volts, 750-2000 amps) with the simultaneous application of a 100 GPa uniaxial pressure. For the consolidation of aluminum nitride using this process, Dr. Groza reported achieving densities near 99.2%. These densities were achieved at  $\sim 1730^\circ\text{C}$  without the use of any sintering aides. Normally such aides are required. Also, the particle size (assessed by transmission electron microscopy observation) was not increased during the sintering. Dr. Groza feels the plasma in this process activates the particles making them more susceptible to welding. Compared to microwave-induced plasma sintering, the low uniaxial pressure applied in the present technique is thought to assist particle movement and pore closure. Resistance heating also contributes by liquefying the boundaries between particles, although Dr. Groza did not report observing any interface melting. The plasma activation can also clean off the particle surfaces in situ, thereby assisting the densification process. Simple resistance heating relies upon the high resistance of the oxide surfaces to heat the material to sintering temperatures and therefore provides a different type of consolidated material. Dr. Groza also indicated success at consolidating commercially important  $\text{Nb}_3\text{Al}$  powders to full density using this process.

#### VIII. Ronald Ziolo, Xerox Corporation, Webster, NY: Polymeric Nanocomposites

Dr. Ziolo described his activities in the nanophase field since 1975 in order to make see-through magnets. Conventional magnets are opaque for the same reason they are magnetic. It turned out that the secret to getting around that problem was through nanophase materials. Two processes were discovered at that time. One involved a porous  $\text{SiO}_2$  matrix and the other which he described here involved the polymer-matrix-mediated synthesis of these nanocomposites. This material is comprised of nanometer-sized  $\gamma\text{-Fe}_2\text{O}_3$  particles in an ion exchange resin which is commercially available in the form of 140-160  $\mu\text{m}$  diameter beads. To prepare these materials, one starts out with a cross-linked sulfonated polystyrene which has either protons ( $\text{H}^+$ ) or Na ions that are exchangeable with  $\text{Fe}^{2+}$  ions. Upon wet chemical treatment with sodium hydroxide (taking the ph to about 11), one basically goes through an intermediate state where one sees the emerald green formation of Fe hydroxide in the matrix. If hydrogen peroxide is added at about 60 C,  $\text{Fe}_2\text{O}_3$  particles are precipitated (1-10 nm). Their growth can also be controlled up to 25-30 nm and larger. These particles are equiaxed and in the unusual gamma form of  $\text{Fe}_2\text{O}_3$ . The polymer offers a medium for controlling the particle size. This material turns out to be relatively transparent compared to bulk  $\gamma\text{-Fe}_2\text{O}_3$ , and because the magnetic particles are so small in size, the material superparamagnetic. One, therefore, has the unusual combination of magnetism and optical transparency. It is thought that there are sites in the polymer matrix that provide cluster nucleation sites, inhibit particle aggregation, and set an

upper limit to the particle size. An interesting aspect of the material is that when the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> loaded material is subjected to the same process over again, the particles do not grow in size, but instead increase in number! Therefore, one can easily increase the number density of particles in this material. Xerox has so far been successful at cycling the material 10 times. The 10-cycle material has a magnetic strength equal to about 1/4 of that of elemental Fe. Dr. Ziolo also mentioned he has been able to scale up the process to provide kilogram quantities. This material also enables one to color magnetic image light. One can mix colors (reds, blues, and greens) with it and come up with a powder that is colored and at the same time is magnetic. Therefore, it can be magnetically pushed around in the machine, and is very attractive for use as advanced toner materials.

#### IX. Mike Roco, NSF, Washington D.C.: NSF Programs on Processing

This area is supported by two NSF divisions: the Division of Material Research and the Division of Chemical and Thermal Systems. The Chemical and Thermal Systems Division has an initiative on ultra-fine particle engineering. Supported under this initiative are several interdisciplinary groups. These groups are typically formed by a "critical mass" of three professors from different departments to develop a basic understanding of various fine particle processes. It is envisioned that after five years, sufficient understanding of the processes would have been achieved that industry could immediately begin applying the processes. Their intention is to support basic research but in processes which are suitable for large scale industrial use. Presently, they have made six awards: (1) a high production plasma process (control of the residence time in the nozzle to thereby control the particle size), (2) spark erosion, (3) a colloid and microemulsion method, (4) a combined combustion and colloid method, (5) laser ablation, and (6) a study of clusters and cluster interactions. The money available at NSF for these types of programs are taken from a special "fix-it" initiative which is called this year "Materials Synthesis and Processing" and next year it will be called the "Advanced Materials and Processing Program". The basic award given was about \$200K per year for three years.

#### X. Discussion on Processing Problems

There was much discussion about agglomeration of the powders prepared by the various techniques, especially via vapor phase processes. Agglomeration of particles is undesirable primarily because it retards subsequent sintering due to the difference in annihilation rates of small and large pores. It was pointed out that low residence times of the particles in the vapor favor less agglomeration. Similarly, lower particulate densities favor less agglomeration. Aggregation is thought to occur by coagulation processes, so if the probability of collisions between particles decreases, the probability of agglomeration also decreases. Fast quenching processes are desirable since they reduce the time available for aggregation, and once the temperature of the particles is reduced their reactivity is also reduced.

Dr. Gregory Rosasco (NIST) started a discussion on diagnostics by describing the NIST interest in both measuring and understanding what goes on during the processing (e.g., the gas phase reactions and particle formation). One role NIST could provide to this area is the development



of in-situ monitoring techniques for understanding the mechanistic of the process or for use as feed back mechanisms to control the process. For example, one of his present programs is directed toward the development of sensors that in real-time provide oxygen and carbon activities in a gas stream or for monitoring the ph of a solution. The possibilities for on-line measurement of the particle size distribution would be particularly valuable since this job is normally very labor intensive. It was also mentioned that the use of non-intrusive laser diagnostics in powder atomization or aerosol processing to obtain this information would be invaluable. However, it was brought up that since the nanometer regime is smaller than the wavelength of light, the development of very short wavelength "lasers" would be required! Present lasers can allow particle sizing down to 40 nm. However, one can use the present laser technology to give valuable information on **where** the particles are being formed. It is not always necessary that one uses a diagnostic tool to provide a hard number; a range of values or limits to the value may be sufficient. In general, however, there is unfortunately a problem with characterization techniques not being useful at the nanometer scale. When people go to apply the traditional tools to the nanometer regime (whether it is to diagnose the process or for analyzing the materials themselves), they are very frequently at the limit of applicability of the techniques. For example, one would like to be able to make a chemical analysis of the nanophase samples but on a scale which is small compared to the grain size. However, the conventional equipment for performing chemical analyses do not have that sort of lateral resolution. In microscopic techniques there is a similar need for development of techniques with nanometer resolution if one is really going to understand these materials. The detection of flaws and voids in these nanometer-sized materials presents even further problems. It was mentioned that one needs to "pull out all the stops" to probe these materials. Clean room facilities (e.g., class 10 type or better) for examining and consolidating nanometer-scale materials are also needed due to the high surface area of these materials. One suggestion was that due to the large expense of such facilities, perhaps it would be useful for NIST to develop a resource space of this type which outside users could access to explore ultra-clean materials.

A common theme at the workshop was that with regard to technology transfer, it was felt to be particularly important for a university/industry/NIST joint effort to be started and pursued. Otherwise it was felt that technology transfer would not happen very quickly. There was also interest in having NIST utilize its extraordinary resources in modelling to study this area. However, it was cautioned that innovative modelling routes will need to be pursued since the cost of modelling on the micro-scale in a straight forward fashion will be exorbitant. Even twenty-atom cluster modelling can be prohibitive, let alone hundred-atom clusters. Not only direct theoretical simulations are needed, but also improvements in the theoretical understanding at the microscopic level is needed. It was felt in general that the theory of modelling was very important to the progress of development of this field. Otherwise one must wait a very long time for all the experimental data to be measured to fill in the knowledge gaps. In the final analysis what one is interested in is the bulk property of the material. That property is going to be made up of the properties of the smaller building blocks and by their interactions, and one would like to be able to model this. However, once one starts talking about large scale modeling one is already assuming there is a large body of available data. Unfortunately, that is not yet the case in this field. All the information presently available is very small compared



to the number of materials being considered. There will be a need to collect the reliable data and to make it available to the scientific community. It was suggested that perhaps NIST could also provide this role.

It was also suggested that NIST make contributions to this field in the area of standard reference materials and standard reference data? It was felt that "we are at the tip of a very exciting iceberg." Consequently, since the field is just emerging, there is also very little data assembled so far. Caution was stressed about extrapolating into that "iceberg" from what is available now which may be unreliable since it has been unchecked. NIST could help the reliability question through the preparation of standard reference materials and collection of reference data.

The committee also addressed the question of what the most important development will be in the next five years. The consensus was that it would be very important to the field to get something rapidly commercialized. Just one thing; it doesn't matter what it is. Successfully commercialize it and that will bring industry into the field in a big way. Such a demonstration would make the field much more believable and show that scale-up can be accomplished. In order to accomplish this goal, it was felt that the money being invested by the government is tremendously important, but should be accelerated. The SBIR programs of many agencies is a particularly good vehicle through which to accomplish this goal. It was also suggested that perhaps NIST could also play a catalytic role in the implementation and integration of technology through its ATP program.



## WORKING GROUP B: PROPERTIES

Chairman: Dr. Lawrence T. Kabacoff (Scientific Officer, Materials Division, Office of Naval Research)  
Co-Chairman: Dr. Neville Pugh (Chief, Metallurgy Division, NIST)  
Recording Secretary: Dr. Carl C. Koch (Professor, North Carolina State University)

This working group was conducted slightly differently from that addressing the processing of nanostructured materials. Here, a particular application (the jet engine) is initially described as a laboratory for use in finding an important niche for nanometer-scale materials, and as a mechanism for initiating the subsequent discussion of the important properties of these materials. Following this introduction each of the property areas are addressed separately, and an assessment in each area was made as to what is known and what are some of the key unanswered questions.

### I. JET ENGINE APPLICATION:

Dr. Maurice Gell (Pratt & Whitney Company) mentioned that an equivalent (but opposite) approach to researching the application of nanostructured materials might be to look at the requirements for a given application and decide where these materials can demonstrate those properties. He suggested using the modern jet engine as a representative application with a sufficiently wide range for potential application of nanostructured materials. Starting at the front of the engine, one finds polymeric materials working at ambient temperature (e.g., graphite fibers in an epoxy), followed by titanium alloys in the compressor section. In the combustor section a little further back, one finds high temperature ferrous materials and in the high turbine section at the back of the engine are found nickel and cobalt superalloys. For certain non-structural applications, ceramics are used either as thin or thick coatings. In this industry, there is a large driving force to continually develop future generation materials. Examples systems are the titanium aluminides, high temperature intermetallics, ceramics, and composites. One way to look at this area of nanostructured materials is that it provides an alternate path for materials development to the traditional ones that have been pursued for the past 10-20 years.

What counts in this industry is performance and energy efficiency. If the turbine can spin faster, it can do more work. So one needs higher strength materials. However, at the front end of the engine one doesn't need high temperature properties. That is why the jet engine provides such a nice vehicle for exploring this new area of advanced materials: because the temperature applications vary from ambient all the way to beyond 1200°C. One may ask why the previous systems, like the titanium aluminides, ceramics, and composites for providing a low density structure with higher temperature capability, not worked? Those materials are brittle, have little fracture toughness, and little crack resistance. Of course, nobody wants to fly in an airplane powered with engines having low or limited ductility. One of the features pointed out in the plenary session was that nanostructured materials have the possibility of providing ductility in the materials that traditionally have not been useful because of their brittleness. This is what



makes the area of nanostructured materials exciting. As one begins to look at the higher temperature applications, then the thermal stability and retention of properties at elevated temperatures is clearly one of the major barriers associated with these materials. One is continually obtaining evidence for properties in these materials that have surprised us; there is better thermal stability than one initially thought. For example, as Bernie Kear described this morning relative to the tungsten-carbide reinforced cobalt hard facings (which are used in jet engine applications), the addition of vanadium carbide to prevent coarsening of the fine structure on heating was successful. If one wants to define the barriers to the success of this area, then long time thermal stability would clearly be one.

One of the characteristics of nanoscale materials is the reduction of defect sizes to very small values. With ceramic materials, these small defects would be expected to enhance the fracture strength, but not necessarily the ductility. When questioned about this paradox (since enhanced ductilities are being obtained in the nanoscale ceramics), Dr. Gell replied by paraphrasing Dick Siegel's suggestion in his morning talk: there is likely an entirely new method of deformation in nanograin materials, which instead of occurring in the bulk grain and having to be accommodated at the grain boundaries is occurring directly at the grain boundaries (which are present in very large numbers in nanophase materials) and being accommodated by the grains. The resulting enhanced ductility in nanophase materials has been observed over a temperature range from room temperature up to the point where the grains start growing. This is a very wide range for enhanced ductility. Dr. Gell felt it was clear that in practice one will need to balance the ductility with the toughness and all the other properties possessed by these materials. There will certainly be some trade-offs.

Nanostructures have grown up out of the thin film area and the current jet engine uses coatings extensively. Consequently, Dr. Gell felt that was likely to be the first application for nanostructured materials. Hot corrosion resistance (especially oxidation) is one potential area for application, and another is as thermal barrier coatings (e.g., in the combustor to coat the turbine air foils). Advanced thermal barrier coatings would allow the use of higher gas temperatures for increased engine efficiency. The jet engine is also a pretty hostile environment in terms of erosion since there are many rotating and rubbing metal parts. In order to have low thermal fatigue, high strength coatings are required so that thermal deformation is elastic rather than plastic. If one is successful in the use of nanostructured materials as coatings, then the effort can be directed toward building nanophase materials into thicker parts and using them as structural materials. In addition, nanophase materials can be built as fine sensors into the engine components and used to provide real-time monitoring of operating conditions like temperature, pressure, and environment. Optimally, such sensors would also allow one to determine the residual life remaining in a component without disassembly.

## II. PHASE EQUILIBRIA: THEORY AND MODELLING

In the area of phase equilibria there is a dearth of information. One needs to calculate metastable phase diagrams for nanostructures with an emphasis on the melting, crystallization,

and critical temperatures of stability. The nucleation and growth of ceramic nanocomposites and metals prepared by gas condensation or other methods also need to be analyzed. What is the structural stability of nanoparticles with respect to temperature, composition, and gas interactions? This would probably entail use of existing thermodynamics with the addition of large surface terms. Such thermodynamics would be useful in providing phase diagrams for fine particles. However, special problems would be confronted when describing mixtures, as in nanocomposites. Separate thermodynamics need to be developed for these materials. For example, look at a magnetic material like nickel and make it into a nanocomposite over a range of composition with silica (i.e., the classical granular metal). As one adds silica all that happens is the addition of small particles of silica into the nickel since these are immiscible materials. Consequently, one might think that the magnetic changes would be easy to understand: (1) one would have less magnetism per unit volume because of the addition of the non-magnetic material and (2) the Curie temperature would be unchanged since that is a function of the internal structure of the nickel. However, the Curie temperature ( $T_C$ ) actually decreases linearly with the addition of the silica. There is no theory that explains that effect. It has been suggested that maybe there was some pressure effect which caused a change in lattice constant and thereby  $T_C$ . However, the data on this system does not support this theory. If one continues, of course, adding silica to the system, one gets in a range where nickel is in small particles in the silica and the material possesses superparamagnetism. For this system, one can plot something that looks like a phase diagram, but it's more analogous to the oil and water phase diagram. There are no models whatsoever for explaining how one can change the Curie temperature of a material by putting holes in it! Most of the material is not even near the holes. This is an example for magnetism, but it is suspected that for any property similar unusual systematics will be measured. In addition, with respect to immiscible systems, there is a lot of evidence both in gas condensed materials and in those prepared by mechanical attrition, that one may obtain extremely large metastable solubilities in systems that are normally immiscible. These enhanced solubilities can be enormous. For example, one can have systems that have less than 0.1-1% mutually solubility and get tens of per cent solubility when nanoscale mixtures are prepared. What is the thermodynamics of this? Presumably this material is metastable, but how can this be explained by existing thermodynamic models?.

### III. MAGNETISM

In terms of the magnetic properties, there are two phenomena which need to be addressed. The small size of grains and the large volume of grain boundaries. The latter effect is thought to be reflected by the very high coercivities (tens of  $\text{Wb/m}^2$ ) which have been seen in some nanograined materials. Even though the feeling is that this effect is related to domain pinning of the grain boundaries, no models exist for it. In particular it would be important to know whether there is an optimum grain size for coercive force compared to the domain wall thickness. The Nd-Fe-B magnets, which are made by two different processes, are a good example material. Here the coercive forces are similar even though microstructurally the materials made by the two processes are different. The General Motors Corporation material (crystallized metallic glass) consists of very small particles which are interacting through grain



boundaries. The Sumitomo Corporation material is a very fine powder. Both companies have learned to optimize the coercive force for each process by the trial and error method, adding impurities to grain boundaries and changing the sizes of the particles. However, there is no fundamental understanding of the coercive force in these materials, and certainly no model for it. Magnetic domains in these materials are felt to be probably much larger than the particle size. To confuse the coercivity issue even further, there are also the surprising results recently measured on a rapidly solidified Fe-Cu-Nb-Si-B alloy. This material is initially a metallic glass as solidified. As it is crystallized into a nanocomposite the coercivity decreases, and also becomes extraordinarily low. Why the presence of grain boundaries in this material does not impede domain wall motion is not understood. However, these results indicate a potential future application for magnetic nanocomposites as very soft ferromagnets, an area now dominated by Fe-Si alloys and metallic glasses.

In terms of the effect of the smallness of the particles on magnetism, two effects were noted. One was the effect noted above on the Curie temperature variation of Ni when in small particles mixed with silica (there have also recently been unchecked reports of a similar phenomena in single phase materials as their grain size was reduced) and the other was the magnetocaloric effect described by Bob Shull earlier in the day in superparamagnetic nanocomposites. Dr. Shull showed that composites containing nanometer-sized magnetic species can possess much enhanced magnetocaloric effects over conventional refrigerants. These enhancements are largest at both higher temperatures and lower magnetic fields, and are due to it being easier for a magnetic field to align a group of magnetic spins than to align single spins as in conventional paramagnetic refrigerants. These enhancements derive directly from the size of the particles and not the boundaries between them. These small particle magnetocaloric effects have important ramifications for magnetic refrigerators. Magnetic refrigeration is a highly efficient cooling technology that until recently only works at temperatures below 15K because the magnetocaloric effects upon which the technique is based are not large enough in conventional refrigerants at the higher temperatures. Consequently, these new advanced materials are opening up a whole new field of materials research on magnetic refrigerants. One of the major costs in this technology is the requirement for high magnetic fields, which means a big superconducting magnet needs to be attached to the refrigerator and needs to be kept cool. One of the exciting possibilities of the magnetic nanocomposite refrigerants is that of reducing the size of the magnetic field required, thereby providing huge savings in energy. Consequently, there is expectation that through the use of magnetic nanocomposite refrigerants, the historical limitations of low temperature and high magnetic field on the use of this technology will be overcome.

Another poorly understood area is that of recent reports in some layered magnetic materials of interactions across layers which are a factor of 10 or greater than in normal materials. These "superexchange" effects can give rise to materials with very high magnetization, very high magnetostrictive effects and very large magnetoresistance effects. Industrially, these enhancements are potentially important. There are also some layered magnetic materials which have effective "g" values (gyromagnetic splitting ratios) of 200. A value of 2 is normally found for the normal free-electron materials. The origin of these anomalously large values still remains to be explored. In the multilayered materials another activity is directed toward



changing the crystal symmetry restrictions of conventional magnetic materials by making very thin atomic layers. For example, to reduce the cubic symmetry normally obtained in the equilibrium Laves phase,  $\text{TbFe}_2$ , Tb-Fe multilayers with each layer only 1-3 monolayers thick are being prepared. This is being prepared in order to reduce the large, normally 2500 ppm, magnetostriction of the cubic  $\text{TbFe}_2$ .

The potential application of nanograined materials, especially nanocomposites, in the magnetic recording area was also discussed. Finer crystal sizes of magnetic materials can provide higher storage density on things like magnetic disks. However, the major problem with application of this technology then becomes a reading and writing problem as the existing technology doesn't possess the nanometer-scale resolution. Also, one will have a stray field problem (i.e., preventing the magnetization of one particle from affecting the other particles). By using nanometer-sized magnetic particles, one has solved the storage material problem, but has created an instrument problem which still remains to be solved.

#### IV. TRANSPORT PROPERTIES

The question was raised about how the thermal conductivity of materials varies as the grain size is reduced to finer and finer sizes. Because of the increased grain boundary scattering with smaller grains, one might expect the thermal conductivity (and electrical conductivity) to decrease with the decreasing grain size. However, when the grain size becomes small compared to the appropriate wavelengths, the phonons may not "see" the nanoscale at all and then just propagate through the structure without scattering. At this point, the thermal conductivity might be expected to increase. In addition, some old work on aluminum superconductors indicates that the phonon spectrum is actually changed by the nanoscale. Bulk aluminum, which has a superconducting transition temperature of about 1 K, possesses a transition temperature of about 3 K when in the form of a nanocomposite, thereby indicating the excitation of higher and higher energy phonons. Perturbations to the phonon spectrum are also easy to accomplish. For example, diamonds in their natural state have a very high thermal conductivity relative to copper. However, if one purifies the diamond by removing the  $^{13}\text{C}$  isotope (which represents only 1% of the carbon atoms), the thermal conductivity is increased by a factor of three. Consequently, it doesn't take much of a change to disrupt the phonons. No one has yet properly explained the effect, as attempts to calculate the magnitude have been off by an order of magnitude. Accordingly, it would not be unexpected to find unusual effects in the transport properties of materials with nanometer scale grains. However, there is not much information yet available on this property.

The phonon spectrum also affects the heat capacity of the material. One might expect that as the grains of a material are reduced to nanometer-sized dimensions, then the "boxes" inside which the electrons are contained would also become smaller. This occurrence would have important ramifications on both the atomic energy levels and the phonon spectrum. Consistent with this consequence, it was mentioned that there was some preliminary data available on nanometer scale particles which showed evidence for an enhanced heat capacity at low

temperatures. As enhanced heat capacities were also observed in amorphous materials (perhaps the limiting case of size reduction), it was also suggested there may be some connection between that class of materials and nanocrystalline materials. In the amorphous materials there was an extra linear term in the heat capacity at low temperatures, implying additional electronic contributions due to changes in the density of states. It was suggested that the preliminary data available on the nanocrystalline material be viewed closely for the presence of such an additional linear term, and also for an increased Debye temperature. Further measurements on other systems was also encouraged.

The electrical resistivity, which is easy to measure but difficult to predict, was also discussed. In some nanocrystalline materials the residual resistance has been found to increase like expected from the increased grain boundary scattering, but that the thermal coefficient of resistivity (TCR) decreased. In some cases the TCR became negative or flat, similar to that found in many amorphous materials. With composite materials, one can mix materials of different types (e.g., a metal with a non-metal) and upon reducing the size of the species, end up with a nanocomposite which possesses a resistivity that can be tailored by varying the mixing ratio. For instance, one can prepare a metallic nanocomposite (with a positive TCR) at high metal concentrations, an insulating material (with a negative TCR) at large non-metallic concentrations, or a zero TCR material at some intermediate composition ratios. Other properties can be similarly changed with composition, an easy variable to control, in nanocomposites. In amorphous materials one obtains a negative TCR when the electron mean-free-path becomes comparable to the interatomic distance. At that point, the electrons will scatter off every atom they see regardless of whether it is vibrating or not. Consequently, as the temperature goes up and the atom vibrates more, the resistivity would be unaffected. Other effects on the resistivity then become more important. In a nanocrystalline material, the mean-free-path is also comparable to atomic distances. However, it was expressed that the mechanism for the negative temperature coefficient of resistance in amorphous materials is not necessarily the same as that for the same effect observed in nanocrystalline materials, since factors other than the mean-free-path appear to be more important in determining this phenomenon.

The effect of grain size on chemical diffusion was also addressed. In particular, it was wondered whether the effect was scalable with the grain size and whether the increases in diffusivity that have been quoted in these materials are due to increased grain boundary area or increased diffusivity. The general feeling was that since nanostructured materials are essentially all boundary, one is most likely measuring the grain boundary diffusion value on such materials. It is, however, a very tricky thing to determine the diffusion coefficient in a grain boundary because what is measured is the width times the diffusivity. In larger grain materials, it is also somewhat arbitrary what thickness is assigned to the grain boundaries. This arbitrariness also comes from the fact that there is a continuous change in diffusivity as a function of position as one crosses the grain boundary. Consequently, there is no discontinuous change in the diffusivity which would allow an easier definition of grain boundary diffusivity. It is also possible, however, that the mechanism of diffusion along the grain boundaries may change as one reduces the size of the grains since the grain boundary structure would be expected to similarly vary. If the grain boundaries stay the same for nanograin materials, as possibly



indicated by the few available high resolution transmission electron micrographs (HRTEM), then it was felt the diffusivity mechanism should also be unchanged. A consensus opinion was that more HRTEM observations are needed along with high resolution composition analyses in order to answer this latter question.

## V. MECHANICAL PROPERTIES

### A. CREEP

For high temperature stability, creep is a phenomena which will need to be controlled. Since grain boundary sliding is a major creep mechanism, with many grain boundaries present in nanograin material, creep may be a potential problem in these advanced materials. Virgil Provenzano (Naval Research Laboratory) indicated one solution to avoiding creep while still possessing ductility is to move away from single phase materials toward composites. The loss of ductility in composites is not a law of nature. It depends upon what sort of composite one has. It was a consensus opinion that in nanophase materials, creep was a largely unexplored and poorly understood area. For nanocomposites, the understanding was much worse than for single phase materials, although there was a guess that the composite nature of the material would provide some additional creep resistance. The workshop attendees mentioned some creep experiments on single phase nanometer-scale metals and on single phase ceramics, but the attendees were unaware of experiments on nanophase composite materials. At low temperatures, the single phase materials do not creep.

For conventional materials, the combination of high strength and high temperature stability have been provided by single crystal superalloys (which are also composites, containing a gamma prime phase in solution). However, in that case the strengthening comes from the fact that dislocations go through a splitting mode once they go into the gamma prime, not because of the composite nature of the materials. Continuing the analogy between composites and superalloys, Bernie Kear (Rutgers University) reminded the attendees that during creep of a solution-treated quenched alloy, the morphology of the gamma prime precipitation which occurred could be drastically altered. By this mechanism, the gamma prime crystals could be coarsened into plates rather than cuboids when under tension, but became rods under compression. It is an intriguing possibility that in a nanophase superalloy, the coarsening which would occur under stress (as in a creep experiment) would form unusual morphologies like plates and rods. The properties of such morphologies, especially at the nanometer scale are unknown. Unfortunately, there is also no theoretical model to guide such work. In the case of large scale materials, there are good theoretical explanations for stress-induced morphological changes in specific orientations when there is coherency, but not for incoherent systems.



## B. SUPERPLASTICITY

The mechanism of superplasticity in the materials being discussed in this workshop is still wide open. In conventional materials, the morphological changes which occur during superplastic forming involves dislocation motion and dislocation accommodation. However, in nanograin material, dislocations are not observed after superplastic deformation. Also, it was pointed out that even though in ceramic materials (even coarse-grained ceramics) dislocation generation and motion is difficult to start with, these same ceramics show superplasticity when fine grained. Consequently, it was thought that even if dislocations are present during the deformation, other deformation mechanisms would be more important. In ceramic materials the fact that one doesn't see any dislocations is not new even though some ductility is observed before fracture. One explanation is that some grain boundary diffusion during deformation provides some accommodation of phases, especially since one certainly doesn't find too many voids forming. It was suggested that in future work, one should become very careful about this question of whether or not dislocations are present during the deformation. These are very small systems where the image forces on the dislocations after one relieves the stress are very large. It may well be that dislocations either inside the grains or at the grain boundaries are operating under stress, but when the stress is removed, they quickly move out of the material and one doesn't see them. Consequently, it was cautioned that one needs to be very cautious in post-mortem analyses, and particularly so in these fine systems. For deformation at elevated temperature, another problem with post-mortem observation is the effects which occur during the cool-down period from the high temperature. In simple work on aluminum, if one takes more than 2 minutes to cool the sample down, one will measure an entirely different effect. The dislocation density in a slowly cooled sample, even under load, is vastly different from the dislocation arrangement and density in a sample cooled rapidly. Similar effects have been seen in copper, even if they only experienced 4 seconds at one half the melting temperature during cool down. In the case of a ceramic matrix, rapid cooling may thermally shock the material. One must even be cautious of in situ observation of deformation in a microscope because one must use a thin film in such a study. In thin films, there are surface effects which are not present in the bulk. Another suggested method for studying the presence of dislocations was to use radiation damage to pin dislocations while the sample was under stress. Upon removal of the stress, the dislocations cannot move since they are no longer glissile. Consequently, it was decided that the deformation mechanism in nanoscale materials needs to be examined much more closely in the future. In particular, one needs to determine if new physics is involved, or is the deformation behavior just a natural extension to small sizes of the phenomenology of coarser-grained materials?

## C. ELASTIC MODULUS

In the literature are conflicting reports on the presence or absence of an enhanced ( $\sim 200\%$ ) modulus of elasticity (i.e., the "supermodulus" effect) in nanograined materials. Unfortunately at the present time, the samples have been too small to be useful in sorting out this question. There was also a lot of attention a few years ago on an enhanced modulus observed in

multilayers. John Cahn (NIST) mentioned that such an effect is not totally unlikely. For example, look at beer foam. This material is a composite of two fluids (gas and liquid) which have no sheer rigidity. However, when put together in a broth as in beer foam, one obtains something that has structural rigidity to it. In the foam, the many surfaces present impart a rigidity to the system. Such may also be the case in nanograined materials.

#### D. HARDNESS

Some people have seen an inverse Hall-Petch relationship (i.e., where the hardness increased with increasing grain size) in some nanograined materials. Since the sample sizes of nanophase materials most investigators possess are in general very small, hardness has been used as an indicator of material strength. Consequently, a degradation in hardness with decreasing grain size is not a desirable finding. Julia Weertman (Northwestern University) described that it appeared from the literature on the inverse Hall-Petch effect that whenever other people saw the inverse Hall-Petch relationship, they performed the experiments in a particular fashion. Specifically, those studies involved the measurement of the microhardness on a very fine grain material which was sequentially heat treated to coarsen the grains. Somehow in the heating process, those materials became stronger. Investigators who measured the normal Hall-Petch relationship, however, generally measured the microhardness on a series of as-prepared specimens containing different grain sizes (i.e., on companion samples). In order to test this idea, Dr. Weertman took one of her fine grain samples, which was one of her original series of samples that had given the normal Hall-Petch equation relationship, and conducted a series of heat treatments (at not too high a temperature:  $\sim 100^{\circ}\text{C}$  for Cu and  $\sim 250^{\circ}\text{C}$  for Pd) on it to coarsen the grains similar to the methodology followed by some of the previous studies. For both pure nanograin Cu and Pd, once one started to change the grain size by heating the sample, it became stronger (by both microhardness tests and tensile tests) while the grains grew in size. The reason for the strengthening was not known. Creep measurements were also performed to determine whether this strengthening was a result of the Coble creep mechanism, but found the samples did not creep. Density measurements were also performed to see if porosity was decreased. Unfortunately, even though no densification was measured, the samples were so small that only 2% precision was obtained in the data. It may be that during the heat treatment necks are forming between the grains which contribute to the strengthening, and so small angle neutron scattering (SANS) studies are planned. By comparison, however, microhardness measurements on a series of electrodeposited materials prepared with different grain sizes have also shown the inverse Hall-Petch effect. Since, these are samples which have not been heat treated, other explanations for this unusual behavior are needed. There was also mention of some work on nanophase materials prepared by mechanical attrition and compacted by an electrodischarge technique. Depending on the compaction parameters, different grain sizes were obtained, and microhardness analysis of these samples gave the inverse Hall-Petch phenomenon. This might not be too surprising since the compaction scheme obviously employs a heating of the sample.



## VI. CORROSION

It wasn't obvious to the workshop participants what the effect of the nanostructure would be on the corrosion resistance of these materials. For amorphous materials, there was great excitement initially for their supposed oxidation and corrosion resistance. However, that attraction turned out to be only if the materials had the right chemistry; only if they made passive films. For the materials under consideration here, many of them contain ceramics that are oxidation resistant. For conventional coarse-grained materials, oxidation and hot corrosion resistance is composition dependent. The question of what happens to these properties when the structure is reduced to the nanometer scale while keeping the same chemistry is unknown. It was mentioned that increases in diffusivity at the nanometer scale might deleteriously effect the corrosion behavior since there are more grain boundaries in such materials and, therefore, more paths for penetrating species to follow. On the other hand, for hot corrosion by  $\text{SO}_2$  (which is a localized phenomena), for example, enhanced diffusivity might be expected to make it more uniform and less damaging. It was a consensus opinion that this was another area that needed exploration, as corrosion behavior would be an industrially important consideration, especially if high temperature application is envisioned.



## WORKING GROUP WRAP-UP AND DISCUSSION

Chairman: Dr. Brian Frost [Senior Technical Advisor (formerly Director: Materials Science Division), Argonne National Laboratory]

The workshop was concluded with reports to the whole group of attendees from the recording secretaries of the previous day's two working groups (described above) and a discussion of the workshop conclusions (presented at the beginning of the report). There was a general feeling that materials with nanometer-scale dimensions were an important new class of materials which need to be quickly assessed. Most of the properties of these materials are not known at present, but there are a few exciting findings including superplasticity, enhanced magnetocaloric effects, superparamagnetism, unusually soft ferromagnetic characteristics, enhanced wear resistance, transparency in opaque materials, and enhanced diffusivity. Unfortunately, there are more questions than answers, and virtually no theoretical basis for much of the phenomena observed. There are many methods for the production of nanometer-scale materials, and some of them are capable of providing large industrial quantities, including chemical methods, mechanical attrition, electrodeposition, and aerosol methods. Key barriers would include retention of nanostructure during consolidation and elevated temperature use, failure analysis of nanosystems, better understanding of mechanisms, development of diagnostic capabilities at the nanometer scale, and a better understanding of the thermodynamics of small systems. It was also felt that if the end user was linked to the materials producer and developer from the beginning, progress in the field would be much faster. Consequently, there is a need to form partnerships between industry and both governmental and university laboratories. Concurrent engineering of all the participants from the manufacturer to the designers to the fabricators and to the end user must be involved from the very beginning. Success in any area could then be the driving force for further development of the field. One vehicle for forming these partnerships is through Cooperative Research and Development Agreements (CRADA's) with government agencies. Another mechanism is through joint proposals to the Department of Commerce's Advanced Technology Program (ATP). This latter program provides funds for supporting research in industry in precompetitive generic technologies. It was also suggested that NIST could provide a needed service by helping bring these different groups together through organization of further workshops in the area.

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**FIRST NIST WORKSHOP ON NANOSTRUCTURED MATERIALS**

National Institute of Standards and Technology

May 14-15, 1992

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