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

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Abstract

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

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

1. Introduction

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

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

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

2. Nanostructured metals and alloys

Carbide strengthened steels are widely used for gears, bearings and shafts in gas turbine engines, because of their good resistance to tempering, wear and rolling contact fatigue. In the fully hardened condition, such steels contain a fine dispersion of $M_{23}C_6$, $M_7C_3$ or $MC$ carbide particles in a martensitic matrix. Some of the carbide particles, however, can be as large as several microns in diameter, in which case they can act as favorable sites for crack initiation in fatigue. To circumvent this problem, an attempt is now being made to develop an n-M50 steel, a prototype carbide strengthened steel, in which the dispersed carbide phase is of uniform nanoscale dimensions. The anticipated superior strength, wear resistance and fracture toughness of the n-M50 steel...
An Aqueous Solution Reaction (ASR) method has been developed to synthesize n-M50 steel powder. The synthesis involves three steps: (1) preparation of an aqueous solution of mixed metal (Fe, Cr, Mo and V) chlorides using de-ionized and de-oxygenated water, (2) reductive decomposition of the starting solution with sodium trialkyl-borohydride to obtain a colloidal solution of the metallic constituents, and (3) after filtering, washing and drying, gas phase carburization under controlled carbon and oxygen activity conditions to form the desired nanodispersion of carbide phase in a metallic matrix. A similar procedure has been used to synthesize n-Cr3C2/Ni powders for use in thermal spraying of corrosion resistant hard coatings (3) (see section 6). In both cases, separation of the sodium chloride from the colloidal solution is carried out by repeated washing in a centrifuge. A small amount of an organic passivation agent, such as a solution of paraffin in hexane, which is added to the final wash, provides protection of the high surface area powder against spontaneous combustion when dried and exposed to air.

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

3. Nanostructured ceramics

Silicon-base ceramics, such as SiC and Si3N4, are useful materials for many engineering applications, such as highly stressed components in heat engines, grinding wheels and wear parts, because of their excellent high temperature mechanical strength and good oxidation resistance. Silicon carbide is also useful because of its favorable electrical resistance (heating elements) and thermal conductivity (substrate materials). A limitation of today's processing of these materials is the very high sintering temperature and pressure needed for powder consolidation, which is a consequence of their covalent bonding. Sintering aids can be used, but they frequently degrade properties. An alternative approach is to take advantage of the lower sintering temperatures characteristic of nanostructured powders. This was the approach adopted in our research.

Inert Gas Condensation (IGC) is the most versatile process in use today for synthesizing experimental quantities of nanostructured powders (1). A feature of the process is its ability to generate non-agglomerated n-powders, which are sinterable at relatively low temperatures. In IGC processing, Figure 1(a), an evaporative source is used to generate the powder particles, which are convectively transported to and collected on a cold substrate. The nanoparticles develop in a thermalizing zone just above the evaporative source, due to interactions between the hot vapor species and the much colder inert gas atoms (typically 1-20 mbar pressure) in the chamber. Ceramic powders are usually produced by a two-stage process: evaporation of a metal source, or a metal suboxide of high vapor pressure, followed by slow oxidation to develop the desired n-ceramic powder particles.

Recently, we have modified a conventional IGC processing unit for the purpose of synthesizing...
n-ceramic powders from metalorganic precursors. In this new Chemical Vapor Condensation (CVC) process (4,5), Figure 1(b), the original evaporative heating source is replaced by a hot-wall tubular reactor, which decomposes the precursor/carrier gas to form a continuous stream of clusters or nanoparticles exiting from the reactor tube. Critical to the success of CVC processing are: (1) a low concentration of precursor in the carrier gas, (2) rapid expansion of the gas stream through the uniformly heated tubular reactor, (3) rapid quenching of the gas phase nucleated clusters or nanoparticles as they exit from the reactor tube, and (4) a low pressure in the reaction chamber. The resulting n-ceramic powder particles are non-agglomerated, as in the IGC process, and display low temperature sinterability, as well as other useful characteristics as infiltrants (see section 5.). Non-agglomerated n-TiO$_2$ and n-ZrO$_2$ powders produced by the CVC method can be sintered to theoretical density at temperatures as low as 0.4 Tm. This is in contrast to the ultrafine powders produced by conventional ambient pressure combustion flame and arc-plasma powder processing methods, which yield cemented aggregates that can be consolidated only at much higher sintering temperatures.

The CVC process has been used to synthesize n-powders of a variety of ceramic materials, which cannot easily be produced by the IGC process, because of their high melting points and/or low vapor pressures. Examples are n-SiCxNy powders, for which there are many suitable organosilicon precursors, such as hexamethyl-disilazane (HMDS). In a particular case, the actual composition of the resulting powder is strongly influenced by the choice of carrier gas. Thus, HMDS/H$_2$O, HMDS/H$_2$ and HMDS/NH$_3$ give n-ceramic powders with compositions close to SiO$_2$, SiC and Si$_3$N$_4$, respectively.

Consider the CVC synthesis of Si-rich powders from HMDS/He, in which the temperature of the tubular reactor is varied over the range 1100-1400 C in 100 C steps. With the flow rate of He fixed at 8.55 x 10$^{-3}$ mole/min, the HMDS concentration in the gas stream is about 16.4 mole % at ambient temperature. Under these conditions, about 2 grams of amorphous n-SiCxNy powder is collected in several minutes. Relevant data on powder characteristics and compositions are presented in Tables 1 and 2. The average particle size from TEM ranges from 6-10 nm, with the smallest particle size corresponding to the highest reaction temperature. The density of the particles increases with decomposition temperature, indicating a higher degree of precursor pyrolysis at the highest temperature. A noteworthy feature is the unexpectedly large amount of oxygen in the powders, which decreases with increasing pyrolysis temperature. In contrast, the concentration of carbon and nitrogen in the powders increases with pyrolysis temperature. The atomic ratios of the constituent elements of the powders are clearly at variance with the atomic ratios in the original HMDS precursor. Furthermore, there is substantially more carbon in the product powders than that of stoichiometric SiC. In all cases, annealing the amorphous powders at 1600 C in flowing high purity argon for 2 hours causes crystallization to

### Table 1 Some Important Characteristics of As-synthesized N-SiCxNy Powders

| Sample name | Reactor Temp. (C) | Powder Density* (g/cm$^3$) | Powder appearance | Surface area** (M$^2$/g) | BET (nm) | TEM (NM) |
|-------------|-------------------|-----------------------------|------------------|-------------------------|----------|----------|
| S-1         | 1100              | 2.64                        | brown            | 568                     | 4        | 10       |
| S-2         | 1200              | 2.737                       | dark-brown       | 555                     | 4        | 30       |
| S-3         | 1300              | 2.781                       | brown-black      | 360                     | 6        | 8        |
| S-4         | 1400              | 2.783                       | jet-black        | 272                     | 8        | 6        |

* measured by pycnometry using He gas  
**measured by single point BET adsorption

### Table 2 Chemical of As-synthesized Amorphous n-SiCxNyO$_2$ Powders, as Determined by Rutherford Backscattering Spectroscopy

| Sample name | Experimental Condition | X  | Y  | Z  |
|-------------|------------------------|----|----|----|
| HMDS        | as-received precursor  | 3.00| 0.50| 0.00|
| S-1         | synthesis at 1100C     | 1.26| 0.35| 0.28|
| S-2         | synthesis at 1200C     | 1.35| 0.40| 0.47|
| S-3         | synthesis at 1300C     | 1.45| 0.48| 0.29|
| S-4         | synthesis at 1400C     | 1.51| 0.49| 0.28|
| A-1         | annealing at 1600C     | 1.60| 0.00| 0.00|
Fig. 2 XRD patterns of as-synthesized amorphous n-SiCxNy powders after annealing in flowing argon. The crystallization process is initiated at about 1100-1200°C and is essentially complete at 1400°C. Figure 2.

4. Nanostructured cerments

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

For several years, Rutgers University has been conducting research on the preparation and consolidation of n-WC/Co powders (7). Concurrently, a tribology group at Stevens Institute of Technology has been evaluating their friction and wear properties (8). More recently, the University of Connecticut has established a complementary research activity on thermal spraying of n-WC/Co and other cermet powders (see section 6). Highlights of this tripartite collaborative research program include: (1) synthesis of n-WC/Co powders with WC grain size controllable down to about 50 nm, (2) densification of powder compacts by liquid phase sintering in vacuum or hydrogen, (3) mitigation of WC grain growth during liquid phase sintering by the use of potent grain growth inhibitor carbide phases, such as VC or Cr₃C₂, (4) demonstration of hardness in fully sintered nanograind WC/Co (with inhibitor carbide phase) that is twice that of conventional micrograined material, (5) confirmation of enhanced wear resistance and cutting performance in sintered materials of high hardness, and (6) demonstration of the feasibility of thermal spraying n-WC/Co powders.

Recent research has shown that incipient melting in VC- and Cr₃C₂-doped WC/Co alloys occurs at temperatures about 250°C below the melting point of the undoped alloy (9). Moreover, we have found that these alloys can be deformed in the semi-solid state, provided that the volume fraction of the dispersed carbide phase does not exceed about 75%. Such ‘semi-solid forming’ is not a new concept. Several processes were introduced in the 1970’s, based on pioneering work done at MIT. The desired structure is produced by cooling a molten alloy to form a slurry, which is mechanically stirred to break-up the dendrites. The roughly spherical morphology of the granular structure of the semi-solid alloy leads to a low shear strength, even with a relatively high solid fraction, which permits the semi-solid to be shaped in a die. In Rheocasting, a slurry is produced in a mixer and delivered directly into a die. In Thixocasting, a billet having the required microstructure is first cast and, at a later time, a slug cut from the billet is heated to the semi-solid state and forged in a die. The present semi-solid processing method differs from the MIT method in several respects: (1) a slurry is formed by heating a powder mixture into the semi-solid region of the phase diagram, (2) no mechanical stirring is required to obtain the desired semi-solid state, with a roughly spherical grain or particle morphology, and (3) an ultrafine structure is obtained by utilizing a nanocomposite powder produced from a chemical precursor.
Currently, we are investigating semi-solid forming of Cr3C2-doped n-WC/Co alloys, because of the unusually low melting point of the Co-rich eutectic liquid phase. An interesting aspect is the effect of subsequent directional solidification of the eutectic liquid phase, which is confined to narrow channels between the WC phase in the bicontinuous structure. The possibility exists of being able to generate a single crystal Co-rich matrix that is isotropically reinforced with a rigid network of nanograined WC phase.

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

Another interesting observation has been the striking difference in response of micrograined and nanograined materials to a scratch test (8), Figure 5. The micrograined material shows evidence for combined plastic deformation and fracture of the WC

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**Fig. 4** (a) Hardness vs. wt.% VC (grain growth inhibitor) in WC/7 wt.% Co alloys, (b) hardness vs. wt.% Co binder phase in WC/Co alloys, comparing data for conventional “micrograined” and “nanograined” materials

**Fig. 5** Comparison of response of (a) micrograined, and (b) nanograined WC/Co samples to a scratch test (100 gm load, using a diamond indentor)
grains, whereas the nanograined material yields by pure plastic deformation, despite its high hardness. Evidence for superior abrasive wear resistance of n-WC/Co, as well as for improved cutting performance of n-WC/Co drill bits has been obtained \((10)\).

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

5. Nanostructured composites

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

![Micrograined Zirconia Matrix](1400°C, 15 KSI)

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

![Nanostructured Zirconia Matrix](1040°C, 16 KSI)

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

**Fig. 6** Comparison of sinterability of (a) micrograined, and (b) nanograined \(ZrO_2\) matrix in an \(Al_2O_3\) fiber-reinforced composite

![Ni Particles](CH_2SiCl_2 + H_2 → SiC Nanowhiskers (upward growth) → Infiltrated composite structure (unidirectionally reinforced))

![Graphite substrate](H_2 + NH_3 → SiC Nanowhiskers (upward growth) → Infiltrated composite structure (isotropically reinforced))

**Fig. 7** Schematic diagrams showing two different approaches for synthesizing whisker-reinforced ceramic matrix composites; (a) unidirectionally reinforced, (b) isotropically reinforced
pre-form and its lower sintering temperature.

A recent test performed on an Al2O3-fiber weave infiltrated with ‘nanograin’ ZrO2 powder has demonstrated the feasibility of both low temperature sintering and ideal infiltration of the fibrous structure (11), Figure 6. A fully dense composite was achieved at 1040 C/16 ksi, with no indications of fiber-matrix reaction. In contrast, the fibrous material infiltrated with conventional ‘micrograin’ ZrO2 powder, and sintered at 1400 C/16 ksi, showed high porosity and severe fiber-matrix reaction, as well as gross fiber damage. Another interesting feature displayed by the nanograin matrix composite was that cracks initiated by microhardness indentations tended to follow fiber-matrix interfaces. In other words, the fiber-matrix interfaces appeared to be acting as effective crack blunners. The possibility of enhancing fracture toughness by this mechanism is being explored.

Looking ahead, an interesting extension of this technology would be to fabricate nanostructured whisker-reinforced CMC’s entirely from metalorganic precursors. Two options have recently emerged from our research, Figure 7. Using trichloromethyl-silane as precursor compound and a nanodispersed nickel catalyst on a graphite support, the feasibility of growing SiC nanowhiskers at practical growth rates of several mm/hr at temperatures of 1100-1400 C has been demonstrated. (12) Whisker growth occurs by the so-called vapor-liquid-solid (VLS) mechanism, where the silicon source gas reacts with the Ni nanoparticles to form a liquid Ni/Si eutectic; thereafter, whisker growth occurs by transport of the silicon through the liquid droplet to the growing whisker at its base, Figure 8. Because this is in effect a growth-from-the-melt process, a typical SiC whisker displays a high degree of crystalline perfection and exceptionally high strength. Recently, we have also explored:

Fig. 8 Illustration of three types of whisker growth mechanism

Silicon Nitride Nanowhiskers

a) HREM image of as-synthesized Si3N4 whisker, (b) whiskers after thickening by CVD, (c) evidence for powder liquid-solid whisker growth mechanism, and (d) whisker pre-form
discovered that CVC-synthesized n-SiCxNy powders, prepared by thermal decomposition of hexamethyldisilazane, can also be transformed into nanowhiskers by a simple heat treatment in a reactive gas stream (5). Thus, heating the n-powders in flowing H₂ at 1200°C yields SiC whiskers, whereas heating in flowing NH₃/H₂ gives Si₃N₄ whiskers. Rapid growth of the whiskers occurs by two different mechanisms: by a new powder-liquid-solid (PLS) growth mechanism and by the more familiar VLS growth mechanism. **Figure 8.** An interesting feature of the thermochemical conversion of the n-powders into whiskers is the formation of a three-dimensional random weave, which replicates the shape of the original powder bed from which it is derived. In fact, the whisker pre-form, which is both strong and resilient, can be removed intact from its container, say a ceramic crucible, **Figure 9,** and used for subsequent processing. We are now attempting to infiltrate whisker pre-forms with nanoparticle slurries in order to investigate the possibilities for n-CMC sheet fabrication, **Figure 7.**

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

6. Nanostructured coatings

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

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

Recent research at the University of Connecticut has demonstrated the feasibility of thermal spraying of n-WC/Co powders, prepared by SCP technology (see section 4). A procedure has also been devised to reprocess as-synthesized powders into sprayable powder agglomerates, suitable for use in standard powder feed systems, irrespective of whether they have been prepared by chemical or physical methods. Important differences in the thermal spraying of ‘micrograined’ and ‘nanograined’ WC/Co powders can be appreciated from **Figure 11.** Micrograined particles experience surface melting only, which contrasts with homogeneous or bulk melting of nanograined particles. Thus, when the particles impinge on the substrate, the semi-solid nanograined particles flow more freely, thereby forming a much denser coating, which has a completely uniform nanocomposite structure. Because of the rapid kinetics of WC nanograin dissolution in the liquid Co, the relative amounts of these two phases can be predicted using the equilibrium phase diagram. Thus, a controlling factor is the degree of superheat above the pseudo-binary eutectic in the WC-Co system. The higher the particle superheat the lower its viscosity, and hence the higher the deformation rate when it collides with the substrate. Under appropriate conditions, the semi-solid particles should display thixotropic behavior, i.e. the dynamic viscosity should decrease with increasing shear rate. The turbulent flow created in the impacting particles should be
useful in disintegrating particle agglomerates and thus promoting structural homogeneity in the deposited coating.

Tests have shown a much higher hardness in the nanograined composite coating, provided that precautions are taken to avoid decarburization in the flame or plasma. One method of accomplishing this is to use low pressure plasma spraying, where the powder particles are naturally protected from oxidation in the plasma flame. High density coatings, with reproducible high hardness values, can be achieved by this means.

In high cobalt alloys, the resulting 'splat-quenched' coating consists of nanodispersed WC grains in an amorphous Co-rich matrix phase(15). The problem of decarburization in thermal spraying of WC/Co powders is less acute in high velocity oxy-fuel (HVOF) spraying, because of the lower particle temperatures and shorter particle residence times, compared with plasma spraying.

Important recent innovations in HVOF and plasma spraying have been the introduction of (1) yttria stabilized zirconia (YSZ) thermal barrier coatings,
either as an overlay coating on an MCrAlY bond coat or as a continuously graded composite coating, and (2) Cr$_3$C$_2$/Ni hard coatings that display hot corrosion resistance superior to that of conventional WC/Co. We have been investigating the use of nanostructured powders of these materials, prepared by ASR and CVC methods (see sections 2 and 3), as feedstocks in thermal spraying. Preliminary work has underscored the need to develop improved means of delivering the ceramic powders to the combustion flame or plasma. Our research is leading us towards the use of nanoparticle slurry feeds, formed by ultrasonic dispersal of the as-synthesized powders, and delivered directly to the spray guns. A multiple source nanoparticle delivery system is now being developed in order to generate multilayer or continuously graded coating structures. The coatings will be designed to minimize thermal expansion mismatch stresses between the different layers, which is a prerequisite to enhance resistance to coating spallation under thermal cycling conditions.

7. Future perspective

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

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

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

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

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Author’s short biography

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Bernard H. Kear received his B.Sc., Ph.D. and D.Sc. degrees in Materials Science and Engineering from the University of Birmingham, England. From 1958-63 he was with the Franklin Institute in Philadelphia where he studied the effects of long-range ordering on the plastic properties of crystals. From 1963-81 he was with the Pratt & Whitney Division of United Technologies Corporation where he investigated the interrelationships between structure/properties/processing in superalloys, participated in the development of single crystal turbine blade technology, and spearheaded the development of laser surface modification treatments. From 1981-86 was Scientific Advisor at Exxon’s Corporate Research Center, where he conducted research in chemical vapor deposition and its applicability to large scale in-situ surface modification of reactor vessels and the up-grading of the surface properties of steel structures. In 1986 he assumed his present position as State of New Jersey Professor of Materials Science and Technology. Presently, he is Chairman of the Department of Mechanics and Materials Science. His current research activities are focused on chemical vapor deposition of ceramics, chemical synthesis of nanostructured composite materials, and MOCVD synthesis of high Tc superconductors. Kear has published .90 technical papers, has edited 9 books in the field of materials, and has been granted 30 patents. He was awarded the Mathewson Gold Medal of TMS-AIME in 1971, and the Howe Medal of ASM in 1970. He was elected to the National Academy of Engineering in 1979. From 1983, he served as a member of the National Materials Advisory Board and was chairman from 1986-1989. Currently, he is co-editor of the journal Nanostructured Materials.