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Ceramic Coatings Metrology Workshop Report

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CERAMIC COATINGS METROLOGY WORKSHOP REPORT

ABSTRACT

The Ceramic Coatings Metrology Workshop was held at NIST to identify the measurement needs of the various industries that manufacture and use ceramic coatings. The industrial perspectives were complemented by reviews of the scientific issues that require understanding to enable the development of valid measurement and characterization methods. The perspectives of the standards community that would implement research results as standard measurement methods were also considered. Properties of importance to specific applications were identified. The importance of the integrity of coating systems, generally described as adhesion, was found to be a common theme. The development of measurement methods for those properties and characteristics that determine system integrity and the ability to predict limits of that integrity by the development of failure mechanism maps based on an understanding of the fundamentals of behavior were recognized as forming a framework for future metrological developments.

INTRODUCTION

A workshop was held at NIST, Gaithersburg, on August 23 and 24, 1999, to identify the metrological issues that are most important to the ceramic coatings industry. The workshop was organized to provide a forum for the views of leading manufacturers and users of ceramic coatings, as well as scientific and standards perspectives.

The varied uses of ceramic coatings and the several methods of application fostered the participation of several scientific and technical societies whose members have an interest in this subject, namely: the Thermal Spray Society of ASM International, the Engineering Ceramics Division of the American Ceramic Society, and the National Institute of Ceramic Engineers.

The goals of the workshop were to identify:

- measurement and characterization methods that would provide the greatest benefit to the coatings community
- the underlying science that must be conducted to develop valid measurements
- cooperative means of resolving both the scientific issues as well as implementation of measurement and characterization methods

About 70 engineers and scientists, the majority from industry and academia, attended the workshop. The first day's format consisted of introductory presentations on materials research in the federal government, the role of ceramic coatings in several markets, and descriptions of the metrological issues associated with ceramic coatings in major industrial applications. The second day was devoted to discussions of the measurement needs of the industries represented.

BACKGROUND

Federal Materials Research

The status of federally supported materials research was described by Leslie Smith, Director, NIST Materials Science and Engineering Laboratory (MSEL), who provided an overview of trends in materials research and development. The information provided was gathered for the 1999 report of the Materials Technology Subcommittee (MatTec) of the Committee on Technology of the National Science and Technology Council.

Several recent studies have recognized the importance of materials as an enabling technology. However, federal support of all forms of R&D, Figure 1, has declined for many years and Federal materials R&D expenditures are now significantly lower than in past years, as shown in Figure 2. Slow growth in Federal academic materials-related funding is reflected in declining numbers of U.S. graduate students in materials related disciplines. The percentage of foreign recipients of PhD's from U.S. institutions who plan to stay in the U.S. has also declined, compounding the problem. These factors have combined to create a situation where U.S. leadership in materials research, development and application is strongly contested.

Shifts in federally funded materials research that impact ceramic coatings include:

- an increased emphasis on biocomplex and "soft" materials,
- increased use of computation and modeling for all aspects of materials research and engineering
- technical advances in nanotechnology, smart materials and electronic materials, and
- an increased demand for sophisticated characterization tools, with life scientists the fastest growing user community at national synchrotron facilities.

Ceramic Coatings

The role of ceramic coatings was highlighted by S. J. Dapkunas, NIST Ceramics Division. Ceramic coatings provide enhanced performance in a broad range of applications from dental restoratives to gas turbines. The markets and 1995 Value of Product Shipments in which ceramic coatings provide significant performance and durability improvements are listed in Table 1. This $70B U.S. market is supported by approximately $0.7B in coating supplies and equipment, as shown in Table 2.

A recent survey of R&D opportunities in the field of surface engineering, conducted by the NIST Advanced Technology Program, found that significant opportunities are present to improve the value and hence competitiveness of products using ceramic coatings if the properties of the coating system could be better controlled and performance better predicted.

Furthermore, it is recognized that improvements in both property control and performance prediction are dependent on better measurement and characterization techniques, which could be implemented as standard methods.

CERAMIC COATING APPLICATIONS

Gas Turbine and Aircraft Engine Applications- Curtis Johnson, General Electric, Corporate Research and Development Laboratory

General Electric's heavy frame gas turbines contain about 3000 parts that receive one or more surface treatments. These treatments include thermal spray coatings, vapor deposited coatings, electroplated coatings and shot peening. Thermal barrier coatings (TBCs), which are generally a stabilized zirconia layer applied by either plasma spray (PS) or electron beam physical vapor deposition (EB-PVD) to a bond coat on a substrate, were the application emphasized. The purpose of a TBC is to allow operation of cooled components in higher temperature combustion gas environments. The benefits of TBC use are higher flame temperatures with attendant efficiency increases, reduced cooling air demands and longer component life. The primary requirements for TBCs are high thermal resistance (insulation) and durability. Measurement issues that bear on these requirements were addressed in terms of (1) physical property measurements, (2) dimensional and state measurements, and (3) durability and performance measurements. These issues are summarized in Table 3, Industrial Views of Ceramic Coating Metrology Needs.

Coating Supplier Perspective- Daryl Crawmer, Praxair Surface Technologies, Inc.

Dr. Crawmer represented the view of a coating vendor and identified historical functions of ceramic coatings as thermal, corrosion and wear related. Future functions are expected to be electronic, bio-compatible, emissive and absorptive related. Coating properties of greatest interest have been, and will continue to be, hardness, porosity and bond strength.

He also pointed out that ceramic coatings are unique in that they are generally anisotropic, largely metastable and polyphasic, and prone to be hydroxylic. Measurements of hardness, porosity and bond strength are currently of most interest.

Opportunities to make an impact included the topics cited as well as the ability to measure volume resistivity, dielectric properties, electromagnetic properties, bio-compatibility, residual stress, resistivity, and breakdown voltage. Measurement and characterization methods should ideally be simple, accurate and repeatable tests that are inexpensive. Table 3 includes metrological needs of a coating vendor.

Heavy Equipment Manufacturer- Brad Beardsley, Caterpillar Corporation. Inc.

The advancement to million mile engine warranties, increased availability, and longer service and overhaul intervals for all equipment has necessitated increased attention to the behavior of surfaces and to ceramic coatings in particular. Coating technology to reduce wear and increase thermal efficiency and component durability is a key step in the technical path to meeting future commercial needs such as "Filled for Life" concepts. Coating of large components, particularly for thermally sprayed replacements of chromium plating, presents control and inspection problems. Property measurement methods are critical to implementation of coating technology.

The measurement issues identified for this industry are detailed in Table 3 and are indicative of, primarily, thermal spray deposited coatings.

Adherence was cited as the major issue and the limitations of conventional methods of measurement, such as ASTM 633, were described. These limitations include the inherent strength of the glue (epoxy) used in C 633 and the expense and difficulty of interpretation involved in the plug pull test. The use of data from either of these tests in finite element analysis (FEA) requires the measurement of the elastic modulus and consideration of the anisotropic nature of the coating. Processing factors that affect adherence include surface roughness and surface cleanliness as well as spray/deposition parameters. Beardsley noted that non-destructive inspection (NDI) for adherence during and after coating application would be worthwhile. Thermal property measurement needs included *in situ* measurement of thermal expansion and conductivity, as they influence adherence. The role of surface preparation, particularly grit blasting, in adherence was related to issues of measurement of roughness and extent of blast coverage.

In terms of performance, the difficulty in relating laboratory wear and friction test results to field results was highlighted, as was the poor understanding of microstructure/wear property relationships.

Biomedical applications- David Gaisser, USBiomaterials, Inc,

David Gaisser presented the perspective of the biological applications community, where ceramics are used as implants to minimize rejection by the human body. Bioinert ceramics, generally alumina or partially stabilized zirconia, are better tolerated by the body than metals or polymers, and bioactive ceramics, generally calcium phosphates (alpha or beta tricalcium phosphate, $Ca_3(PO_4)_6$, or calcium hydroxylapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), react with the body to "assist" in the healing process. Ceramic coatings can impart desired surface properties to an implant while maintaining the mechanical characteristics of the substrate, whereas monolithic ceramics are limited in medical applications due to their mechanical properties; e.g., tensile and shear strength. Thin films (1 to µm 10 µm thick) are sputter coated or electro-deposited, whereas "bulk ceramics" (50 µm to 100 µm thick) are flame or plasma sprayed.

Coating properties are specified by ASTM F 1609-95-Standard Specification for Calcium Phosphate Coatings for Implantable Materials. This specification covers chemical purity, phase purity, thickness, porosity and strength. Phase purity is a specific issue since HA content is often reported by manufacturers to describe a coating. However, it is a misleading descriptor since it actually refers to the fraction of crystalline phase that is composed of HA, whereas the actual deposit includes thermal degradation products such as amorphous Ca-P, which may range from 34% to 72 % (by XRD) depending on differences in process equipment and parameters. Coating solubility is obviously important and it varies by crystalline constituent and amorphous content. Reportedly an ASTM Draft Procedure has been developed for solubility measurement. Thickness measurements utilizing ASTM E 376-Practice for Measuring Coating Thickness by Magnetic- Field or Eddy- Current (Electromagnetic) Test Methods are available, as are manufacturer-specific methods such as cross sectioning. Coating porosity is typically analyzed using ASTM C 949- Test Method for Porosity in Vitreous Whitewares by Dye Penetration or cross sectioning and measuring via point counting or digital analysis. Coating strength is measurable by ASTM C 633 or ASTM F 1501-95- Test Method for Tension Testing of Calcium Phosphate Coatings, ASTM F 1658-95- Test Method for Shear Testing of Calcium Phosphate Coatings, ASTM F 1044-95 Test Method for Shear Testing of Porous Metal Coatings, and, ASTM F 1659-95 Test Method for Bending and Shear Fatigue Testing of Calcium Phosphate Coatings on Solid Metal Substrates.

In summary, evaluations are based primarily on ASTM test methods, which are often long in development. Other methods may be too cumbersome for routine use and many manufacturers use proprietary test methods, making comparisons difficult. The perceived measurement needs of the biomedical industry are presented in Table 3.

Cutting Tool Coatings- William Pfouts, Kennametal Corporation, Inc.

Ceramic coated tungsten carbide cutting tools are an increasingly important application. Coatings in this application are subject to several failure modes, including: mechanical (abrasive) wear, chemical (diffusion) wear, plastic deformation, chipping, built-up edge, thermal cracking and depth-of-cut notching. The composition of the coatings and their microstructure has evolved since they were first used in the 1970's. Early coatings, applied by chemical vapor deposition (CVD) at 850 °C to 1000 °C, included TiN, TiC, TiCN, and Al_2O_3. These coatings are generally multilayer systems of the above compositions with a total thickness of 5 μm to 20 μm and contain tensile residual stresses and cracks due to thermal expansion mismatches with the substrate. Currently, physical vapor deposition (PVD) at 300 °C to 600 °C is used to deposit TiN, TiCN, TiAlN, ZrN, CrN, and TiB_2 monolayer and multilayer coatings of 2 μm to 8 μm thickness. PVD coatings are smoother than CVD and do not contain an eta phase in the interface (as do CVD), are in compressive stress and are crack free. Superhard (e.g., hardness greater than 40 MPa) coatings such as diamond and cubic boron nitride (cBN), as well as nano-layered and nano-composite films are expected to experience wide application in the next decade. Measurement and characterization needs for cutting tools are listed in Table 3.

CVD/PVD Service and Equipment Supplier- Peter Hatto, Multi-Arc (UK)

Multi-Arc/Bernex, is a PVD/CVD service and equipment provider. Multi-Arc provides arc evaporative PVD, magnetron sputtering, thermal CVD and radio frequency plasma assisted CVD (RF PACVD) coatings 2 μm to 10 μm thick but sometimes greater than 50 m thick. PVD monolayer coatings include TiN, CrN, TiCN, TiAlN, AlTiN, MoS_2 and diamond like carbon (DLC). Multilayer PVD coatings of TiCN and zircon are also supplied. Multi-Arc supplies CVD monolayer coatings of TiCN, TiC and Cr_7C_3 as well as multilayer coatings of TiC/TiCN/TiN, MT TiCN+ Al_2O_3, HT TiCN+ Al_2O_3 and TiC/Al_2O_3. These coatings are applied to high speed steel and carbide cutting tools as well as forming tools for stamping, drawing, forging, die-casting and extrusion of metals and plastics. Aerospace and automotive components and biomedical devices, such as bone nails and screws, hip, knee, shoulder and orthodontic implants, are also coated. These applications are typified by complex geometries.

Metrological needs were grouped according to design or certification uses and are so summarized in Table 3.

Peter Hatto also provided a short description of Multi-Arc's Coating Technical Specification (CTS), which ensures the quality of products, and a summary of European Committee for Standardization (CEN) Technical Committee (TC) 184/Working Group (WG)5 activities appropriate to ceramic coating metrology. These activities are summarized in Table 4.

Department of Defense Perspective- Lewis Sloter, Staff Specialist for Materials/Office of the Secretary of Defense

Dr. Sloter provided an overview of the DOD's ceramic coating applications, programs, needs and opportunities. Ceramic coating use and development are driven by the same themes that motivate all materials research in the DOD, namely: lighter weight; faster transition from conception to use, insertion and application; longer life; lower life cycle cost; and lower environmental impact. Table 5 lists the broad categories of applications of interest to DOD. Specific projects described include: water vapor effects on oxidation and hot corrosion of thermal barrier coatings; carbon fiber reinforced iridium oxidation barriers for carbon-carbon composites; development of protective coatings and claddings for IR transparencies; nanostructured coatings for wear resistance in shafts, seals, pumps and hydraulic cylinders; development of wear resistant and thermally insulative materials for diesel engines; low loss hexagonal ferrite films for millimeter wave circulators, and protective films for goggles. Table 6 summarizes the DOD view of ceramic coatings applications, as well as the measurement issues in each of the four broad categories of applications described.

STANDARDS ORGANIZATIONS

ASTM Perspective- Steven Gonczy, Gateway Materials, Inc

Seven Gonczy, representing ASTM Committee C 28-Advanced Ceramics, presented the results of a survey conducted on behalf of C-28 to ascertain the interests of various parties. The survey was sent to 131 individuals. Responses were received from 36 (27%) and were primarily from the gas turbine/aircraft engine community concerned with thermal barrier coatings. The highest priority properties and test methods identified in the survey included: microstructure, thickness, adhesion, conductivity and resistance to thermal cycling. Responses to the survey are provided in Table 7.

Most respondents saw several benefits to the availability of standardized tests. The ability to compare coatings and to improve quality and reproducibility was seen as the most beneficial. The greatest challenge to development of standards lay in the fact that a single standard may not be useful for coatings with different microstructures or mechanisms of failure.

It is significant to note that 15 respondents expressed a willingness to participate in standards development through C-28. The next step in the process will be to present the survey results to

ASTM C-28 in November, 1999. The results of the ASTM survey, in general, were consistent with the views expressed in this workshop by industrial participants.

SCIENTIFIC PERSPECTIVES

Perspectives on the fundamental issues underlying the development of meaningful metrological procedures for ceramic coatings were given by Professor Christopher Berndt of the Thermal Spray Laboratory at the State University of New York (SUNY) at Stony Brook and by Dr. Brian Lawn, NIST Fellow in the NIST Materials Science and Engineering Laboratory.

Brian Lawn addressed the topic in a general sense by discussing the behavior of ceramic coatings on soft substrates, emphasizing dental applications. In particular, he addressed the use of the Hertzian contact technique to investigate mechanisms of failure of these coating systems. In this method, well understood stresses are developed by loading with a spherical indenter. Cracking behavior of the coating can be observed directly when the coating or the substrate is transparent. A significant observation made in this procedure is that separation of the coating from the substrate can result from the formation of cracks in the coating, not only from delamination at the coating-substrate interface.

Chris Berndt, State University of New York (SUNY)/Stony Brook, provided a comprehensive overview of the thermal spray coating industry and identified measurement needs. A key point Berndt recognized is that in the U.S., consensus standards are the appropriate way to implement measurement methods. He also pointed out that the thermal spray industry is not large enough to overcome a "black box" mentality, which limits incentive for consensus development. That is, competition between companies hinders exchange of information on problem resolution, including measurement of properties whose importance is recognized. Specific limitations to growth and barriers to implementation of ceramic coatings, including lack of standards and specifications, were identified and are listed in Table 8.

Berndt provided a classification scheme for thermal spray which described the science, engineering and technology content of the thermal spray process, microstructure, testing and properties, and applications. This classification scheme is shown in Table 9.
He pointed out that it is important to measure (among other attributes) adhesion, roughness, Young's modulus, porosity, residual stress and wear rates or other performance characteristics all based on an understanding of the microstructure as well as the relationships between process conditions, particle parameters and deposit formation.

Berndt noted that the in order to achieve "prime reliant" TBC systems, the following needs must be met: precise knowledge of thermo-mechanical properties (and variation) of TBCs; mechanical and physical models for TBC behavior and performance; mechanical property responses to processing and service environments; and life prediction capability, especially for fatigue.

Process sensors and controls were identified as important measurement capabilities. Berndt provided an analysis, shown in Table 10, that dentifies parameters for which sensing and control are important. These include particle impact properties, residual stress, elastic modulus, real time thickness, surface roughness and direct characterization of microstructure. These needs were further assessed to specify measurement techniques in the research stage or that are commercially available. Practical issues associated with the development and implementation of these methods include: the ability to operate the instrument with minimal operator training or education; instrument affordability; robustness; and, what improvements can accrue through their use.

THE NIST CERAMIC COATINGS PROGRAM

The NIST program was described by NIST staff members who summarized the research and results of the work that has been underway since 1991. The objective of the NIST program is to develop measurement, characterization and modeling methods which support improvement of process control and property/performance prediction. This research is conducted in cooperation with industrial and academic collaborators who provide processing capabilities to complement NIST's analytical skills, and has emphasized thermal spray deposited materials, particularly TBCs. The program was described in terms of microstructure characterization, property measurement, behavior modeling and Standard Reference Materials developed in the program.

Microstructure- Andrew Allen

A.J. Allen of NIST Ceramics Division reviewed the NIST research on the microstructural characterization and phase analysis of ceramic yttria-stabilized zirconia thermal barrier coatings. The use of neutron diffraction to analyze the long-term phase evolution at elevated temperatures was discussed in connection with the need to minimize transformation to the deleterious monoclinic zirconia phase during thermal cycling. Neutron diffraction Rietveld refinement methods, together with the sensitivity to different elements and large instrument range, provide a powerful means of distinguishing between the zirconia phases even when the oxide stoichiometry is not well-known. The results suggest that, at present typical levels of yttria stabilization (7-8%), the deleterious transformation will occur after extended service life at elevated temperatures. The extent to which x-ray diffraction methods can be developed for industrial evaluation of the phase composition is also being explored at NIST.

The application of novel small-angle neutron scattering (SANS) studies, for the void microstructure characterization of plasma-sprayed ceramic deposits has been pioneered at NIST, and was reviewed in some detail. These studies allow the porous part of the microstructure to be described by three major void component systems (cracks, lamellar pores, and globular pores). Each system can then be independently related to the powder morphology, the processing conditions, and the coating properties, to aid in the design of specific coating microstructures for given service environments. Significant changes in coating microstructure were evident during initial exposure to elevated temperatures, in contrast to the long-term effects of the phase transitions, above. The effects of various feedstock and processing variables have been quantified for the annealing of yttria-stabilized zirconia thermal-spray deposits, both ex-situ and in-situ using a purpose-designed SANS furnace. Much of this research to-date has been on thick self-standing deposits. However, near-surface grazing-incidence SANS techniques are also being applied to extend these studies to thinner TBCs on substrates. Possible extension of these methods to near-surface small-angle x-ray scattering may eventually permit a similar characterization of sub-micrometer coatings.

Neutron diffraction measurements of the anisotropic elastic moduli in plasma-spray deposits were also discussed. The high penetrability of neutron beams permits the internal lattice strain to be measured under conditions of known applied load. The relationships among the moduli found by neutron diffraction, those found by indentation, and the microstructural parameters found by SANS, are providing new insights into how the coating properties are governed by microstructure.

Properties- Douglas Smith

Douglas Smith summarized NIST work on the measurement of coating properties. The primary focus was on the measurement of coating hardness and Young's modulus using instrumented indentation, but NIST measurement techniques for residual stress and thermal conductivity were also mentioned. Basic instrumented indentation techniques were described, and results for several coatings systems were presented as examples. These systems included spark plasma sintered functionally graded metal-ceramic coatings, air-plasma-sprayed thermal barrier coatings (APS TBCs), and thin ceramic films being investigated as candidates for standard reference coatings for mechanical testing. The technique was shown to be capable of providing both "average" mechanical property information from coarse or complicated microstructure (such as APS TBC's), through the use of spherical indenters and high indentation loads, and information on individual phases and small volumes of material by using very low loads and sharp diamond indenters (nanoindentation). The effects of annealing time and temperature on the modulus of APS TBC's were shown in some detail. Work on national and international standards for the indentation technique was described. The talk concluded with brief descriptions of NIST work on the measurement of coating residual stress, using microRaman and photoluminescence methods, and on the NIST guarded hot plate facility, which is capable of making direct measurements of coating thermal conductivity.

Modeling- Edwin Fuller

Dr. Fuller described the development of an Object Oriented Finite Element program (OOF) intended to compute and investigate macroscopic properties of complex material microstructures. OOF, a tool for materials scientists, is publically available software developed at NIST in collaboration with other government laboratories, universities and industry. OOF has been used to elucidate the effect of pores and microcracks (their spacial and size distribution) on the elastic behavior of plasma sprayed deposits of yttria stabilized zirconia. This tool was further refined to examine the role of interfacial roughness on residual stress distributions in plasma sprayed thermal barrier coatings (TBCs) and to model damage evolution of nano-crystalline coatings with soft grain boundaries. OOF is now being adapted to incorporate thermal behavior of TBCs.

The development of a "Physics-Based TBC Life Prediction Model" by the Optimal Corporation under a Small Business Innovation Research (SBIR) grant from NIST was also described. This model links equations of oxygen diffusion, oxide scale formation, materials creep, crack growth and other micro-material damage to a work potential, through many damage parameters. Phase two of this project is expected to be completed in the next year.

Standard Reference Materials- James Kelly

This presentation outlined the need for NIST certified particle size distribution reference materials for calibrating instruments, quality control in powder manufacturing, and to help industry satisfy ISO 9000 requirements for measurement devices. These SRM's are now available in a wide range of powder sizes and materials. They have been certified using a variety of sizing techniques such as electron and optical microscopy, sieving, laser diffraction, electron sensing and sedimentation. The zirconia powder SRM 1982 was produced in response to an identified need within the thermal spray community. The material was characterized using sieving, scanning microscopy/image analysis, and a nine-laboratory round robin study using several laser diffraction instruments. The results of these size studies were presented, along with data from Sandia National Laboratory on the variation in particle velocity and temperature in spray tests using size splits of SRM 1982 powder. Two new tungsten carbide/cobalt powder SRMs are being developed. SRM 1984 is a sintered and crushed material, and SRM 1985 is a pray dried and sintered powder. Preliminary results of round robin testing by laser diffraction were presented and compared with NIST results using SEM/image analysis.

DISCUSSION

The measurement of many properties of coatings were identified as important in both the formal presentations and in subsequent discussions. Clearly, however, the coating property with greatest interest is "adhesion." "Adhesion," in the most general sense, is the ability of a coating to remain in place and function as planned.

In the broadest sense, measurement of adhesion could require understanding the physical phenomena that affect lifetime. Mechanistic understanding would enable the development of "design diagrams" which allow prediction of lifetime. This diagram requires not only knowledge of mechanisms of delamination but also the properties and conditions which drive or control the mechanism.

It is not clear that the properties or conditions that determine adhesion in one application, say cutting tools, is appropriate or operable in other applications, say TBCs. However, the range of basic properties required includes: interfacial toughness, microstructural effects, residual stress, thermal conductivity, coefficient of thermal expansion, and surface steriology (e.g., roughness, cleanliness, "state of surface").

Adhesion tests suitable for gathering data necessary for design purposes as well as tests suitable for gathering information for controlling product manufacture are required. It was also noted that a single test may not meet both needs. There was also a strongly expressed need for an adhesion test whose results (i.e., property measured) could be related to behavior in an application.

ASTM C633 (or company proprietary tests) may be useful in terms of quality control to highlight changes in processing or materials but it does not provide information of use to designers, e.g. data to be used as input to finite element codes. Specifically, elastic properties are critical to the use of finite element codes but these properties are not generally measured when coatings are evaluated (by C633 for example). The value of a simple, and perhaps non-destructive test of adhesion was noted.

The discussion of adhesion was augmented by a brief presentation by Dr. Wang of Northwestern University on his research on measurement of adhesion. He approaches the issue by separating those parameters which further adhesion and those which reduce adhesion. He described the micromechanics analysis that could serve as the basis of a measurement method.

It was suggested that a summary of properties critical to adhesion measurement be compiled into a table. Test methods to measure these properties will be included in the table. These tests will be further evaluated in terms of those that have been advanced to the point of being a standard, those ready to be standardized, and those not yet ready to be standardized. The list of volunteers who have offered to work on ASTM C28 for development of standardized tests will be given to Johnson by Steven Gonczy. Offers to provide critical comment were received from participants from Sulzer, Kennemetal, Caterpillar, Praxair, Northwestern University and the Army Research Laboratory.

There was limited interest expressed for chemical analysis, phase analysis, or the provision of SRMs.

Several of the participating companies expressed a willingness to collaborate in the development of measurement methods. This participation might consist of providing material specifically for the purpose of making measurements or as partners in a collaborative effort. The Thermal Spray Society of ASM International has a Recommended Practice Committee which would be an appropriate partner as would ASTM C-28. In this latter regard, the survey conducted by C-28 identified 15 individuals who would actively participate in the development of standard test methods for ceramic coatings.

SUMMARY

A workshop was held to identify those aspects of metrology that industry views as most important in improving the reproducibility and predictability of ceramic coatings. Perspectives were gathered from the gas turbine, heavy equipment, biomedical and cutting tool industries as well as the measurement, standards and scientific communities, and the Department of Defense. Key points for each of the above parties were identified. Foremost among these points is that coating systems, not the ceramic overlay, determine usefulness in any application and that characterization and measurement methods should be developed recognizing this fact.

Currently, components which are coated (particularly TBCs) are not used in temperature, corrosive or stress environments where loss of the coating would cause failure. However, because most of a coating does remain intact, incremental increases in time between inspection or maintenance have been realized. Improved durability in terms of adhesion could enable application to more demanding operating conditions.

The attendees were also clear in pointing out that the types of measurement and characterization that are appropriate for obtaining design data are often quite different from those necessary for quality control or for determining fitness for purposes.

Similarly, the issues of primary interest for biological and cutting tool applications were presented in a defined manner and offer an opportunity to organize cooperative focused metrology projects in these areas.

Within the context of coating system integrity, the attendees identified properties where measurement would most impact product value. System integrity includes not only the maintenance of desired property levels such as thermal conductivity or wear resistance but also, and much more generally, the continued presence of the coating on the substrate. This maintenance of a coating system is generally termed "adhesion."

It was recognized that the specific properties that have bearing on adhesion (or system integrity) vary with coating system, microstructure and use conditions. A longer-range view, which broadly encompasses the development of measurements to quantify those properties inherent in the mechanisms that determine failure as a function of operating conditions, was also suggested. The development of these "design diagrams" that relate material properties to system integrity, particularly adhesion as a function of operating parameter, could enable lifetime prediction.

The principal properties identified that are important for assurance of quality or fitness for purpose include:

Thermal conductivity and diffusivity
Microstructure including porosity and constituent phases
Hardness
Electrical Resistivity
Dielectric properties and breakdown voltage
Stoichiometry
Coefficient of thermal expansion
Thickness

Those properties thought to be related to mechanisms that determine adhesion are:

Elastic modulus
Microstructure
Interfacial strength and toughness
Poisson's ratio
Residual stress
Coefficient of thermal expansion

It is clear that an understanding of the mechanisms of failure is required to guide measurement development. These mechanisms must be understood at the simplest levels where model systems (with controlled but perhaps unrealistic properties) are examined, as well as at the more complex, application-specific level, where realistic materials are examined under operating conditions.

These responses indicate recognition that basic understanding, such as the nature of cracks and sintering behavior, are implicit in characterizing microstructure and microstructural changes of ceramic coatings, as well as the importance of the relation of microstructure to properties such as elastic modulus and performance measures such as thermal cycling resistance.

The importance of high quality metrology to the industrial attendees was verified by their response to the ASTM C-28 questionnaire on ceramic coatings standards. Responses were summarized in the workshop and are reflected in the property measurements itemized above.

That is, without a basic understanding of the fundamental behavior which determines a property such as adhesion, it is unlikely that a metrology standard can be developed that is applicable to more than a singular material-process-service condition.

More importantly, respondees agreed to participate in the development of standards through cooperative prestandards research. As a first action, one attendee agreed to prepare an inventory of available standards, available industrial test methods that can be elevated to standards, and required developments for one application, thermal barrier coatings. Other attendees agreed to review the inventory and cooperate in development of standards.

ACKNOWLEDGEMENTS

The Ceramic Coatings Metrology Workshop was organized and conducted primarily through the efforts of Dr. Gary Fischman, then at the U.S. Food and Drug Administration and currently at the University of Illinois, who brought forth the participation of the biomedical community, the American Ceramic Society, and the National Institute of Ceramic Engineers; and, Drs. Douglas Smith, Andrew Allen, Edwin Fuller, and James Kelly of the NIST Ceramics Division. The participation of the individuals whose presentations provided a broad range of perspectives and the basis for substantial discussion was critical to the success of the workshop. The participation and publicity provided by the Thermal Spray Society of ASM International is appreciated. Contributions to preparation of this report by Douglas Smith and Andrew Allen are recognized; and, the substantial efforts of Mrs. Carolyn Sladic in coordinating the many details attendant in hosting the workshop are greatly appreciated.

Table 1. Market Applications of Ceramic Coatings

PRODUCT	1995 Value of Shipments, $B*
Turbines, Turbine Generators, Turbine Generator Sets	6.1
Machinery and Equipment Farm Construction Mining Oil and Gas Field	35.7
Small Cutting Tools for Machine Tools and Metalworking Machinery	2.7
Aircraft Engines and Engine Parts	15.7
Surgical, Orthopedic, Prosthetic and Therapeutic Appliances and Supplies	10.7

* *1995 Annual Survey of Manufacturers, Value of Product Shipments,* U. S. Department of Commerce, Economics and Statistics Administration, Bureau of the Census, M95(AS)-2, January, 1997

Table 2. North American Market, High Performance Ceramic Coatings

Type	1997 $ M	1997 %	2002 $M	2002 %	AAGR* %
Thermal Spray	380	53.5	510	51.7	6.1
PVD	141	19.8	186	18.8	5.7
CVD	151	21.3	218	22.1	7.6
Other	38	5.4	73	7.4	14.0
Total	710	100.0	987	100.0	6.8

* AAGR= Average annual growth rate; includes dipping, spraying, sol-gel and laser assisted techniques.

Source: Business Communications Co., Inc, Norwalk, CN

Table 3. Industrial Views of Ceramic Coating Metrology Needs [#]

Aircraft Engines/Gas Turbines	General	Heavy Equipment	Biomedical	PVD Service Vendor	Cutting Tools
Physical Property				*Design*	*Adhesion*
Thermal conductivity/diffusivity	Hardness	Adherence	Chemical purity	Adhesion-Interfacial Shear Str.	Interfacial adhesion
Adsorptivity/emissivity (vs wavelength)	Porosity	Strength	Phase purity	Modulus-x,y,z directions	Residual stress
Elastic Modulus	Bond strength	Modulus	Thickness	Poisson's ratio	Substrate surface topo.
Adhesion strength	Residual stress	Wear and friction	Porosity	Intrinsic stress w/thickness	Substrate surface stress
Shear strength	Resistivity	Thermal properties	Strength	Preferred orientation	Substrate cleanliness, Porosity
Interfacial toughness	Dielectric properties		- Tensile	Fatigue behavior	Elastic properties
	Breakdown voltage		- Shear	CTE	CTE
			- Fatigue	Yield stress,intra- and inter- granular	
Dimensional/State Measurement				Wear rate	*Wear resistance*
Topcoat thickness				Coefficient of friction	Room to Hi Temp Hardness
Temperature				Oxidation and corrosion behavior	Coating Grain size
					Coating Shear strength
Durability/Performance Measurement				*Certification*	Reactivity with workpiece
Durability testing in high thermal gradient				Assurance of minimum adhesive strength*	Surface Energy
Thermo-mechanical fatigue				Thickness*	Coating microcracks
				Surface roughness	
NDT				Composition	*Resistance to microchipping*
Determination of mechanical "integrity"				Hardness/modulus	Thermal conduct.
				Film defect density	Microtoughness of coating/substrate composite
				(*Critical Properties)	

[#] Groupings of needs for some applications, as provided by participant, are italicized.

Table 4. European Committee for Standardization (CEN)
Technical Committee (TC) 184/Working Group (WG) 5 Coating Activities

European Pre-Standard (ENV)

- ENV 1071-1 (1993): Film Thickness by Step Height-Under Review
- ENV 1071-2(1993): Film Thickness by Crater Grinding- Under Review
- ENV 1071-3(1994): Film Adhesion by Scratch Test- under Review
- ENV 1071-4(1995): Determination of Chemical Composition(by EPMA)-Under Review
- ENV 1071-5(1995): Determination of Porosity-Under Review

Current Work Items (W/I)

- 117: Internal Stress by Stoney Formula
- 118: Composition by X-Ray Spectrometry
- 119: Fracture Strain by 4 Point Bending
- 120: Coating Thickness by X-Section
- 121/132: Coating Hardness and Modulus by Depth Sensing Indentation
- 131: Coating Adhesion by Rockwell Indentation

Table 5. DOD Ceramic Coating Applications

- Passive Protection from the Environment
  - Paint-like coatings
  - Oxidation resistant high temperature coatings
  - Diamond erosion coatings

- Active Protection from the Environment
  - Tribological coatings
  - Ablative coatings

- Functional Interfaces
  - Thermal barrier coatings
  - Tunnel junctions
  - Diamond thermal panes
  - Electrical insulation

- Functional Layers
  - Silicon on sapphire
  - Ferrites on silicon
  - Dielectric stacks

Table 6. Summary of DOD View of Ceramic Coatings

- Passive Protection from the Environment
  - Ceramics will play an increasing role
  - Measurement of geometric and chemical properties on application and in service is important to successful application

- Active Protection from the Environment
  - Ceramics are a key element for long life and affordability
  - Measurement of geometric, chemical, physical, and mechanical properties is critical for successful application

- Functional Interfaces
  - Ceramics are among the means to affordable performance
  - Measurement requirements will be focused on all the above plus specific functional requirements

- Functional Layers
  - Ceramics are a great enabler for nanotechnology, afforable tailored functionality, and novel performance
  - In addition to the above, measurement capabilities will need to be integrated into manufacture and service

Table 7. Results of the ASTM Survey, Property Measurement Desired/Number of Votes

Physical Characteristic	Mechanical Property	Durability Tests	Thermal
Microstructure /21	Adhesion/20	Thermal Cycle/18	Conductivity/21
Thickness/19	Elastic modulus/15	Spallation/17	Expansion/12
Porosity/15	Hardness/11	Oxidation/11	Emission/1
Composition/13	Fracture/Toughness/11	Wear/abrasion/10	
Phase/9	Tensile strength/6	Corrosion/10	
Density/8	Residual stress/1	Thermal shock/9	
Roughness/6	Compressive strength/1	Impact/erosion/7	
Permeability/3		Sintering/2	
Cracks/1		Water/steam/1	
		Creep/1	

Table 8. Limitations to Growth and Barriers to Implementation of Thermal Spray Ceramic Coatings

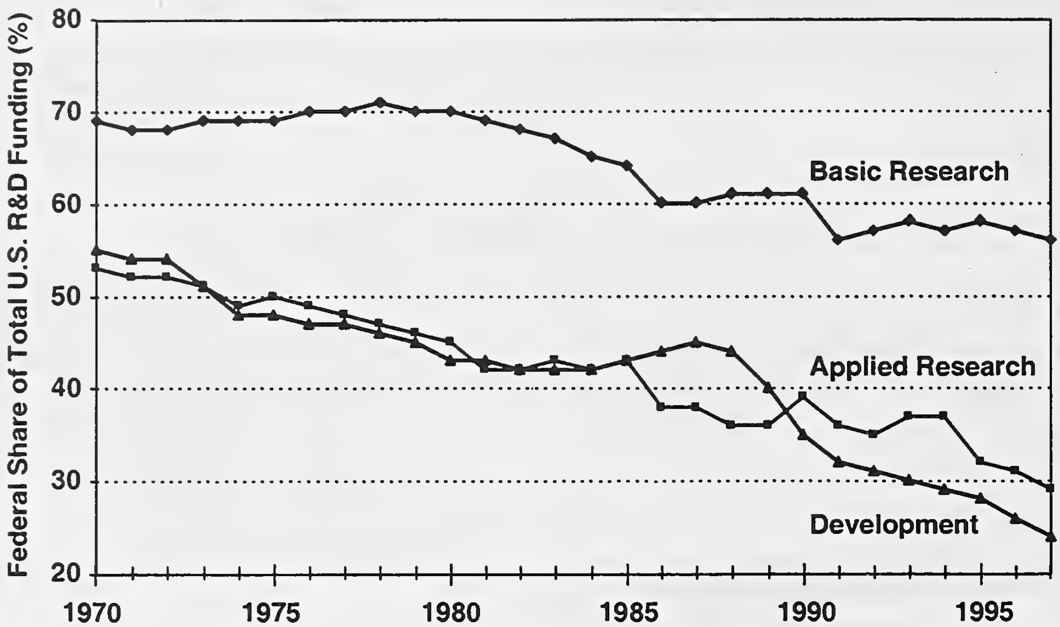
- Lack of hard unbiased data for life cycle costs
- Non-cognizant engineers and managers
- Lack of standards and specifications for materials, processes and applications
- Lack of inspection methods
- The field has developed emperically on an application-by-application basis
- The field is characterized by a band-aid philosophy, not a prime reliant view
- There is inadequate process control
- Understanding of process-microstructure property relationship is limited

Table 9. A Classification Scheme for Thermal Spray Disciplines

<table>
<tr><th></th><th>Science</th><th>Engineering</th><th>Technology</th></tr>
<tr><td>Process</td><td>Plasma arc physics
Combustion
Diagnostics</td><td>Design & manufacture of:
Torches
Equipment</td><td rowspan="2">Process control
thermal spray
tables</td></tr>
<tr><td>Microstructure</td><td>Characterization of
chemistry, porosity, phases, etc.
Modeling of process</td><td>Quality control
Residual stresses
Powder production</td></tr>
<tr><td>Testing and Properties of Coatings</td><td rowspan="2">Mechanical properties
Thermal properties
Corrosion behavior
Electrical properties
Interface with constituency
Emerging applications</td><td>Mechanisms
Modeling
Prediction</td><td>Suitability of coating
Interface with
consumers</td></tr>
<tr><td>Applications</td><td colspan="2">Solve and advise on specific problems/
Applications
Design coating</td></tr>
</table>

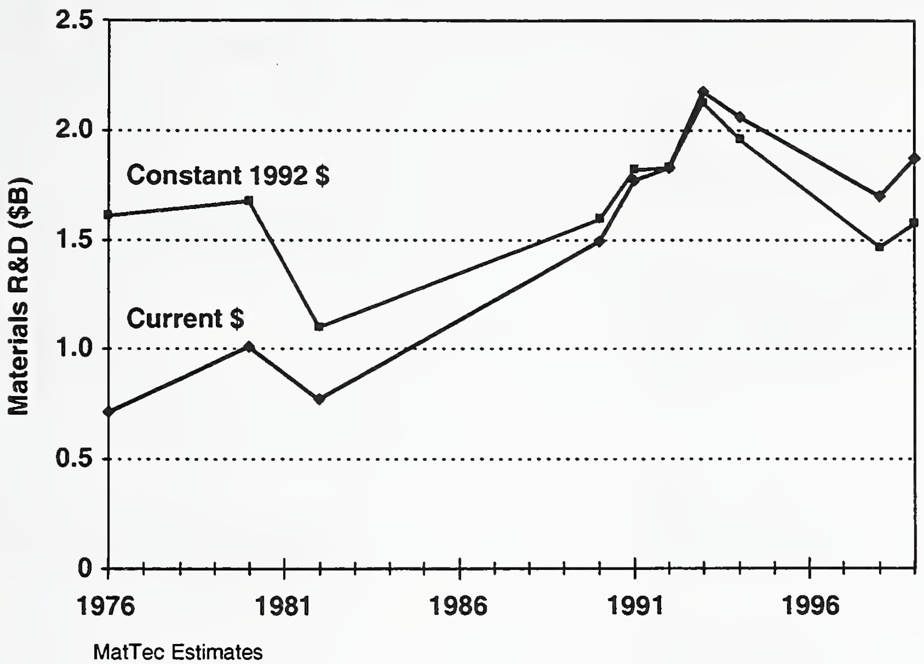
Table 10. Summary of Sensors/Controls

Parameters or Properties Important to Sense or Control	Sensors or Controls in the Research Stage	Sensors or Controls Currently Available	
Impact properties (temp, vel, size)		In-flight particle Pyrometer Tecnar DP2000 for measuring temperature	Who is using these tools besides research institutions?
Residual stress/strain, Elastic modulus			Who will pay for control/tools sensors?
Real time thickness	Laser thickness gages		Are tools robust?
A "direct microstructure" sensor, e.g. porosity	Acoustic emission to measure torch performance and erosion, implying microstructure Laser nondestructive methods		Does the work-force need an advanced degree to use?



Science and Engineering Indicators – 1998

Figure 1 The Federal Government Has Smaller Share of All Forms of R&D



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