Current Problems in Plasma Spray Processing*

C.C. Berndt, W. Brindley, A.N. Goland, H. Herman, D.L. Houck, K. Jones,
R.A. Miller, R. Neiser, W. Riggs, S. Sampath, M. Smith, and P. Spanne

This article summarizes eight contributions from a thermal spray conference that was held in late 1991 at Brookhaven National Laboratory, Upton, Long Island, New York. Plasma spray processing is discussed in terms of plasma-particle interactions, deposit formation dynamics, thermal properties of thermal barrier coatings, mechanical properties of coatings, feedstock materials, porosity, manufacture of intermetallic coatings, and synchrotron X-ray microtomographic methods for thermal spray materials. Each section is intended to present a concise statement of a specific practical and/or scientific problem. It then describes current work that is being performed to investigate this area, and finally suggests areas of research that may be fertile for future activity.

1. Introduction**

1.1 *The Roots of Plasma Technology*

Melt-spray processing technology in various forms dates back to the early 1900s when melt atomization was introduced for the production of metal powders. The early practitioners used lead and tin and other low-melting-point materials, but the process rapidly gained acceptance when higher melting point metals were introduced. It then occurred to processing engineers that the placement of a substrate in the path of the molten metal flow would permit solidification on the substrate of the still-molten atomized particles. Thus, melt-spray coatings were achieved, and over the next several decades, this evolved into the development of new heat sources, such as arc-plasmas, allowing the melt spraying of refractory materials, including oxide ceramics. It should also be noted that practitioners as early as 1920 actually sprayed enough material to produce thick, free-standing forms with mechanical properties approximating wrought materials. In recent years, plasma spray processing has become the prime means for the melt-spraying of a wide range of high performance materials, including superalloys and refractory intermetallic compounds, and a wide range of ceramics. The primary activity in such work has been the production of protective coatings for diverse industries ranging from hardfacing for the mining industry to corrosion protection in power plants, to various key parts for aircraft gas turbine engineers. More recently, plasma has been used for melt-spray forming of engineered structural materials and will certainly be applied to near-net forming technology.

Plasma technology, although well established and reasonably well understood, remains largely unappreciated by the larger engineering community, especially materials science. We are here speaking of thermal plasmas, comprised of a high density of electrons, ions, and atoms, as opposed to low-pressure plasmas used in plasma-activated processes for chemical vapor deposition, sputtering, etc. The thermal plasma has its roots in electrical engineering and process metallurgy. Arc plasma engineering was used to develop materials extraction and processing systems in the 1950s. Small nontransferred arc DC plasma spray guns were initiated for the production of protective coatings. Somewhat independently, physicists and chemists began to examine thermal plasmas using various spectroscopic techniques to evaluate ionic species and thermal and optical properties, etc.

Plasma processing science and technology has experienced explosive, but unruly, growth. The diversity of disciplines and industry involved with the technology has created both excitement and not a little chaos. There are numerous conferences on special plasma topics attended by focus groups, frequently unaware of other groups with closely related interests. Furthermore, adjacent technologies and sciences have much to offer plasma technology, but too often little cross-fertilization occurs.

1.2 *The Stony Brook / Brookhaven Symposium*

A symposium was held at Brookhaven National Laboratory on 13-15 Sept 1991 to address the situation described above. It was attended by scientists and engineers representing various aspects of the thermal plasma processing science and technology communities. These complex related questions were examined by an interdisciplinary group of 75 from universities, industries, and national laboratories. The program of 13 topics is shown in Table 1 along with the speakers. The speakers were charged with the mission to be controversial and to challenge the audience to question and be critical of all aspects of plasma spray technology.

Several open discussion sessions were convened to address specific deficiencies and needs of selected topics, which included processing science and technology, characterization methods, feedstock materials, adaptive control, porosity: its significance and characterization, and critical views of plasma spraying. Industrial tours of the facilities available at Brookhaven National Laboratory (Upton, New York), Metco Perkin-

Key Words: mechanical and thermal properties, nickel aluminides, plasma processing, porosity and microstructure, powders, review, velocity and temperature diagnostics

---

* This article is a compilation and editing of individual author submissions. The author(s) of each section will be acknowledged by a footnote at the beginning headline of the respective section.

** Contributed by **C.C. Berndt** and **H. Herman,** SUNY at Stony Brook, The Thermal Spray Laboratory, Stony Brook, New York; and **P. Spanne** and **K.W. Jones,** Brookhaven National Laboratory, Dept. of Applied Science, Upton, New York.

Table 1 Speakers and Their Respective Affiliations and Topics

Speaker	Topic
J. Heberlein, University of Minnesota	DC plasma
M. Boulos, Sherbrooke University	RF plasma
M. Smith, Sandia National Laboratory	Particle-plasma interactions*
S. Sampath, GTE Chemical Products	Deposit formation dynamics*
W.L. Riggs, GE Aircraft Engines	Characterization methods
P. Spanne, Brookhaven National Laboratory	Microtomographic methods for microstructure determination*
R. Miller, NASA-Lewis Research Center	Thermal properties*
C.R. Clayton, SUNY at Stony Brook	Chemical properties
C.C. Berndt, SUNY at Stony Brook	Mechanical properties*
D.L. Houck, GTE Chemical Products	Feedstock materials*
R. Smith, Drexel University	Adaptive control
A.N. Goland, Brookhaven National Laboratory	Porosity: an integrated approach*
R. Neiser, Sandia National Laboratory	Intermetallics

* These topics are included in the current article.

Elmer (Westbury, New York), and The Thermal Spray Laboratory (Stony Brook, New York) were held on the third day of the meeting.

The Symposium was divided into three sections: (I) Theoretical and Experimental Studies of the Plasma Flame and Deposit Formation, (II) Deposit Characterization and Properties, and (III) Manufacturing and Process Sciences. This conference report consists of summaries that have been prepared by the authors and reviewed by experts in the subject areas. The presentations in Table 1 marked with an asterisk are included in this report. A detailed article on the microtomography of plasma sprayed coatings will be presented in a future issue of the *Journal of Thermal Spray Technology*.

2. Plasma-Particle Interactions*

2.1 *Introduction*

Plasma spray deposition is a remarkably versatile technology that enjoys a long and successful record as a reliable, cost-effective solution for continuously increasing the range of research and commercial applications. Nevertheless, there is always room for improvement in any technology. In recent years, an improved understanding gained from extensive process diagnostic and modeling research in various laboratories throughout the world is pointing the way to further technological improvements.

Plasma-particle interactions during plasma spray deposition determine the heating and acceleration of individual particles during the deposition process, and these interactions therefore play a crucial role in determining the properties of the spray-deposited material. In an "ideal" plasma spray process (see Table 2), the particles fed into the spray torch would be uniformly heated and accelerated prior to impact on the target surface. Research has shown that the plasma spray torches that are in general commercial use today, although they serve the industry well, may not be optimized for these ideal objectives. The basic design of most "modern" plasma spray torches is very similar to the first commercial plasma spray torches introduced nearly 40 years ago. The typical DC arc spray torch uses a stick cathode (made of thoriated tungsten or a similar refractory metal) surrounded by a hollow, water-cooled copper anode. Such torches produce plasma jets that are characterized by extremely steep radial gradients in properties such as temperature, velocity, viscosity, species distribution, etc.[1,2] As well, the arc attachment point can fluctuate rapidly within the anode bore as the arc repetitively extends and then restrikes through the cold gas sheath adjacent to the nozzle wall. This arc restrike causes temporal variations in the plasma jet in addition to the spatial variations just described.[1,3]

Table 2 Ideal Characteristics of the Plasma Spray Process

Uniform, controllable velocity of particle on impact
Sufficient velocity to produce a high-density deposit without "exploding" the molten or partially molten droplets on impact
Uniform, controllable heating of particles
Attain fully molten or plastic particles without vaporization or undesired reactions
Isolation from or controlled interaction with the ambient environment
Stable process conditions with highly reproducible results

2.2 *Feedstock Entry and Air Entrainment into the Plasma Plume*

Another potential problem with existing commercial torches is that the powder feedstock normally is injected radially at a fairly steep angle relative to the direction of plasma flow, so that small differences in initial particle momentum can cause significant differences in particle trajectory. Powder particles of different size, shape, or density will not follow the same path through the jet, even if injected at the same initial velocity. Due to the steep radial gradients in the properties of the plasma jet, spray particles that follow slightly different trajectories through the jet experience different thermal-kinetic histories prior to their impact on the target surface. This can cause inhomogeneity in the deposited material and reduced deposition efficiency.

Entrainment of air or other cold gases from the ambient environment into the plasma jet also affects the spray deposition process (Fig. 1).[4,5] Entrained air, which accounts for as much as 50% of the spray plume at distances of only a few nozzle diameters downstream from the spray torch, can reduce melting efficiency and promote oxidation of the sprayed material. Although oxidation can be beneficial in some applications, for example by increasing the hardness of the sprayed material, it may be detrimental in other applications.

2.3 *Process Enhancements*

Many of the issues just described have been addressed by process enhancements, such as spraying in controlled-atmosphere chambers and closed-loop process monitor/control systems that have successfully produced very high-quality plasma-sprayed materials for aerospace, medical, and other

---

* Contributed by **M.F. Smith,** Sandia National Laboratories, Process Metallurgy, Albuquerque, New Mexico.

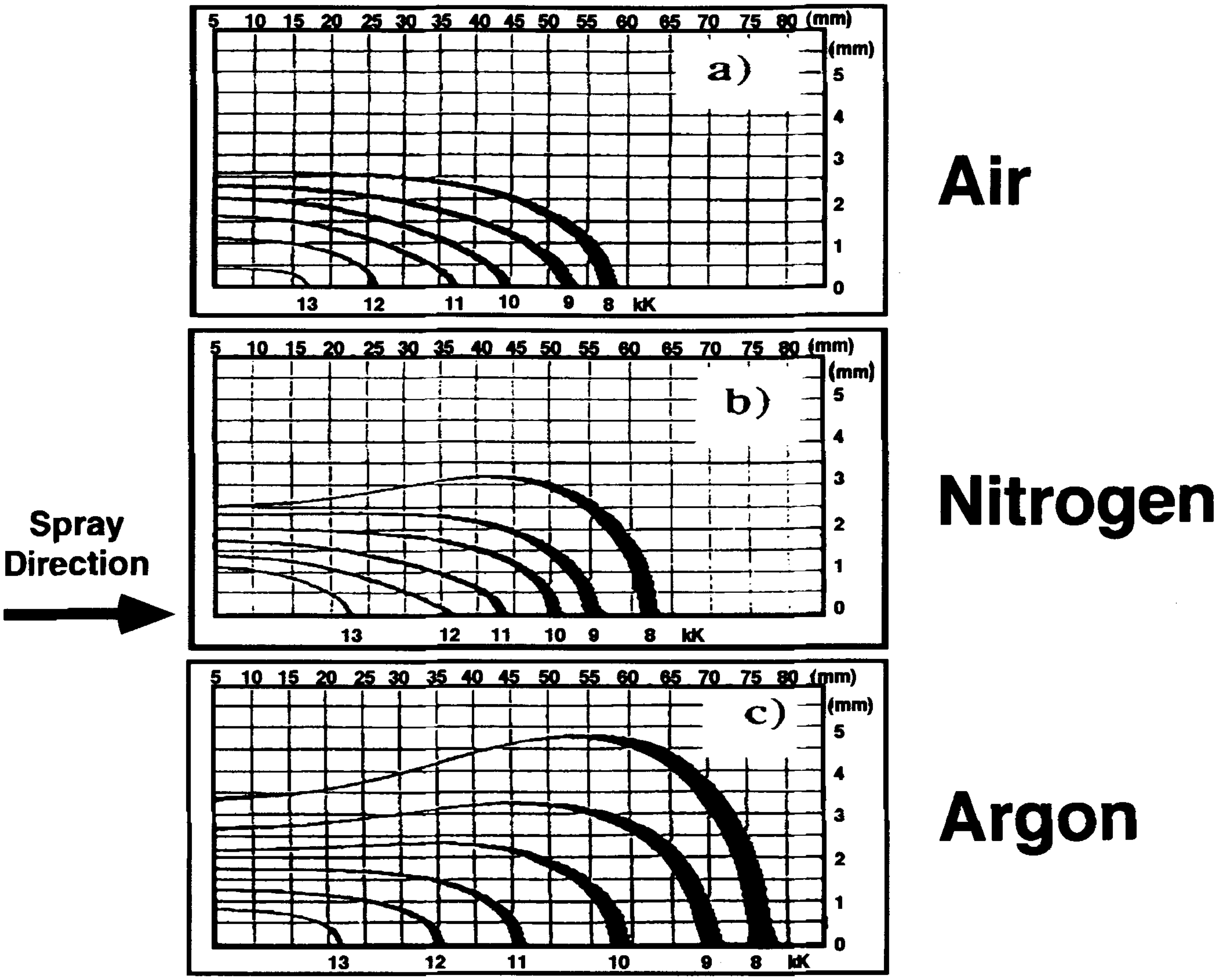

Fig. 1 Temperature distribution for Ar-H_2 plasma jets flowing in ambient air (**a**) or under a controlled atmosphere of nitrogen (**b**) or argon (**c**). The dissociation of oxygen molecules at approximately 3500 K and nitrogen molecules at about 7000 K rapidly cools the plasma and constricts the isotherm plots for air and nitrogen environments as compared to argon. (From Ref 2)

high-value-added production applications. However, such solutions are not cost-effective for all commercial applications. In the author's opinion, current knowledge of the process should be used to address the root cause of these problems. There is a need to develop new spray torch designs that inherently provide more uniform and consistent melting and acceleration of the feed material(s). There is also a need to develop more effective mechanical shrouds, boundary layer gas shrouds, or other cost-effective methods to mitigate the effects of ambient gas entrainment for applications where entrainment control is desirable. However, chambered spray systems are impractical due to cost or workpiece size considerations.

2.4 *Future Development and Understanding*

The good news is that interest and activity in plasma torch design has grown rapidly in recent years. Novel spray torch designs currently are being developed, tested, and even marketed in various parts of the world including Australia, Canada, Europe, Japan, and the United States. These emerging designs feature various methods to improve the uniformity and stability of the plasma jet, and many feature axial injection of powder (or wire) along the center line of the jet. For example, Fig. 2 illustrates a relatively uniform droplet velocity distribution achieved with a new plasma spray torch that uses a secondary, high-velocity gas jet to atomize and accelerate the molten droplets after they are formed by melting from the tip of a consumable wire feedstock.[6] Melting and acceleration of the spray material is inherently more uniform and consistent by virtue of its design. However, because not all feed materials are available in wire form, there is also the need for improved plasma torches to spray powder.

As the 21st century approaches, the industry is poised for some important refinements in plasma spray torch design. The overall objective is to use the improved knowledge about the spray process together with better diagnostic and modeling tools to design truly robust plasma spray torches that are inherently much less sensitive to normal variations in feedstock and other process variables. This is a key to opening new applications and markets by further improving the quality, reliability, and utility of the process, while at the same time further reducing process costs.

3. Deposit Formation Dynamics*

3.1 *Introduction*

The physical properties of plasma-sprayed coatings are directly related to the deposit microstructure. Plasma spraying is a high-velocity impact deposition process in which melting, quenching, and consolidation take place in a single step. A deposit is produced by successive impingement of micrometer-sized drops of material (referred to as "splats") upon a prepared substrate. The dynamics of formation of these splats and the interaction of these splats with the substrate (or previously solidified splats) determine the overall microstructure of the plasma-sprayed coating.

There are essentially two considerations relative to deposit formation dynamics during plasma spraying. The mechanistic or physical aspects of splat formation deals with the spreading of the molten droplet, interaction with the substrate, and heat transfer to the substrate. These characteristics are affected by the temperature of the splat, splat viscosity, surface tension, heat transfer coefficient, and other properties. The metallurgical or material aspects of splat formation deal with the cooling rate of the splat, solidification criteria, nucleation and growth of crystals, and phase formation. Additionally, both of the above aspects are interrelated.

Houben has detailed the mechanistic aspects of splat formation through thermodynamic and mechanical models.[7] The various types of splat morphologies have been described as "pancake type" and "flower type." The splat morphology is dependent on the velocity of the impinging droplet. Thus, increased velocity produced particles with more flattening and spreading of the droplet.

3.2 *Dynamics of Splat Formation*

The dynamics of splat formation determine the solidification, microstructure development, and phase formation. Cool-

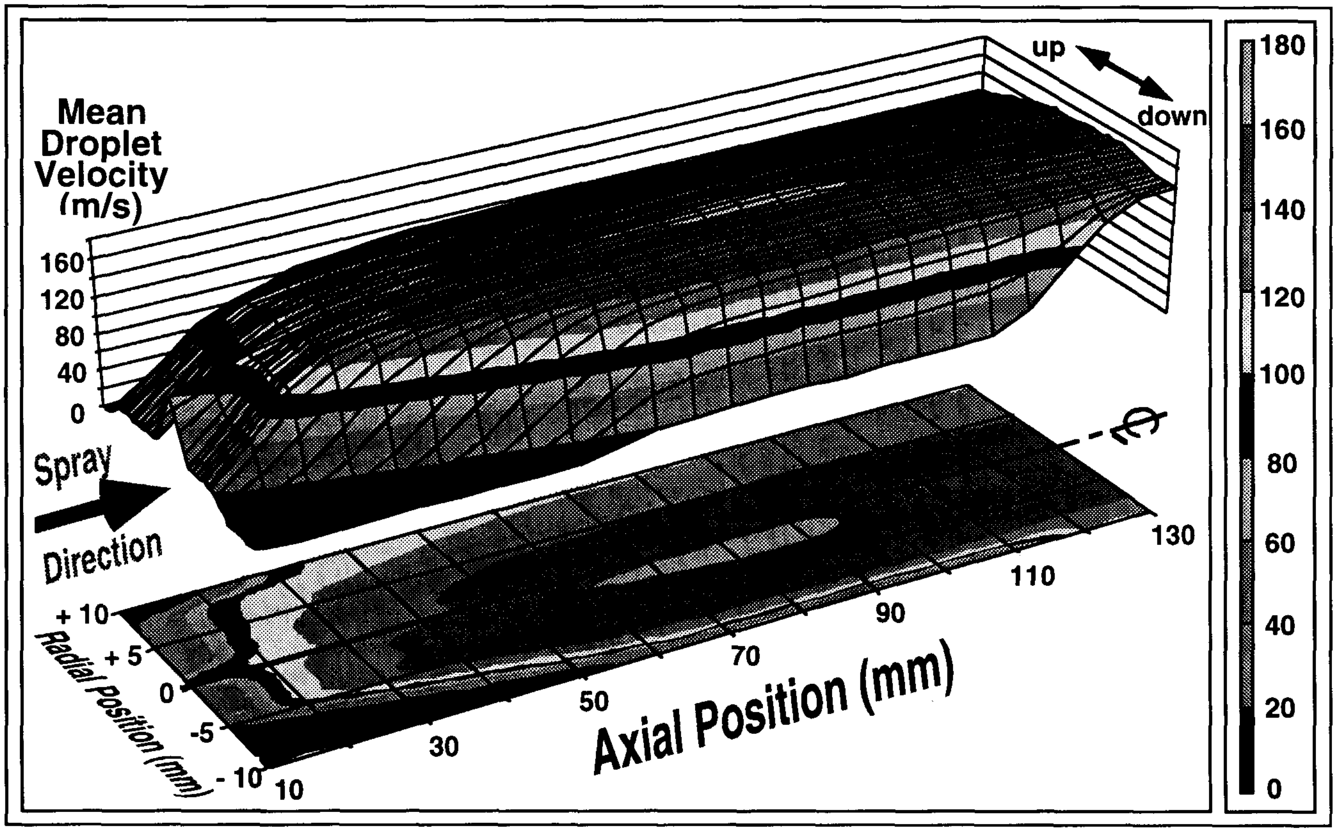

Fig. 2 Two-dimensional droplet velocity plot for aluminum wire sprayed with a wire arc plasma spray device. Because the droplets consistently enter the jet at essentially the same position with little or no initial velocity component, the velocity profile is inherently relatively uniform. (Based on research described in Ref 6)

---

* Contributed by **S. Sampath,** GTE Products Corp., Towanda, Pennsylvania.

ing rate is the most important variable, which determines the solidification parameters. Several studies[8-10] have concluded that plasma spraying yields rapid solidification with cooling rates in excess of 10^6 °C/s. Cooling rate determinations for aluminum and nickel through direct and indirect techniques have indicated cooling rates in excess of 10^7°C/s. Also, the cooling rates are similar in both atmospheric plasma spraying (APS) and vacuum plasma spraying (VPS), even though vacuum plasma spraying operates at a much higher deposition temperature, i.e., 900 °C in vacuum plasma spraying versus 100 °C for atmospheric plasma spraying. However, the higher substrate temperatures in vacuum plasma spraying influence the deposit through self-annealing and lead to phase transformations, thus altering the rapidly solidified structure.

The solidification parameters of direct relevance to the structure, such as solidification rate (interface velocity), undercooling, and interface stability criteria, are derived from cooling rates and are described in Table 3. The characteristic ratio of G_l/R determines whether cellular, dendritic, or plane front solidification would follow. The large values of G_l/R represent a regime close to absolute stability in the solidification front. This suggests plane front growth as the likely mode of solidification of the splat during plasma spray deposition. This solidification mode has implications toward segregation-free splat solidification, resulting in solute supersaturation and metastable phase formation.

3.3 *Splat Formation*

A model for the formation and solidification of a single splat is shown in Fig. 3[9] and this may be extended to vacuum plasma spraying. However, the melt-flow characteristic of the splat can vary from one material to another, depending on the melting point, degree of superheat, viscosity, and interactions with the substrate. Scanning and transmission electron micrographs (SEM, TEM) of nickel splats on copper substrates produced from both atmospheric and vacuum plasma spraying processes indicate enhanced flow behavior and spreading of a vacuum plasma sprayed splat compared to the atmospheric plasma sprayed splat. This is attributed to higher particle velocity, temperature, and absence of surface oxidation. Cross section TEM observations of the central region of splats indicate a columnar mode of solidification in both forms of plasma spraying. This is consistent with the solidification conditions, wherein nucleation occurs on the substrate, with a planar growth of the solid in a direction perpendicular to the substrate. In vacuum plasma spraying, instead of the columnar grain structure, a columnar cell structure is observed. This microstructure is produced because of recrystallization occurring during vacuum plasma spraying deposition, due to the high substrate temperature used during this process. The formation of a columnar microstructure during plasma spraying is well illustrated in Fig. 4, which shows the cross section micrograph of air plasma-sprayed molybdenum.

Table 3 Solidification Parameters Derived from Cooling Rates

Material	Average cooling rate, K/s	Heat transfer, W/m^2	Nusselt's No. ($d = 5\,\mu m$)	Solidification, rate (a), cm/s	G_l/R(b), K/s/cm^2
Nickel	7×10^7	1.4×10^6	0.069	46	2.2×10^4
Aluminum	1.5×10^8	3.5×10^6	0.005	15	3.7×10^4

(a) Assuming no isothermal delay. (b) G_l is the thermal gradient in the liquid; R is the solidification rate of the plane front. The ratio of G_l/R is the degree of constitutional supercooling during solidification.

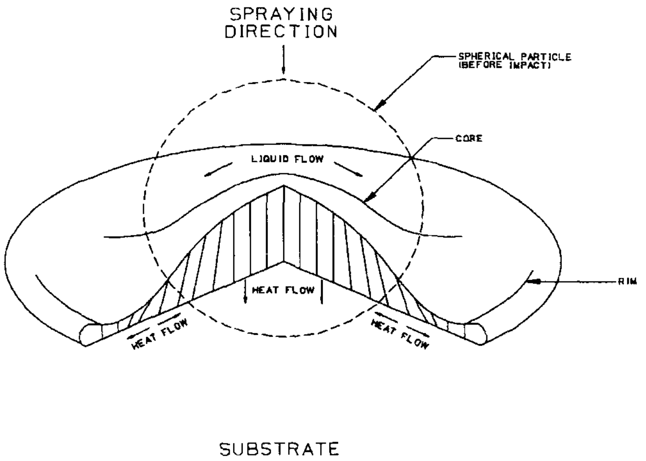

Fig. 3 Schematic showing the relationship between heat flow and microstructure for a molten particle as it rapidly cools on impact against a substrate. (Adapted from Ref 9)

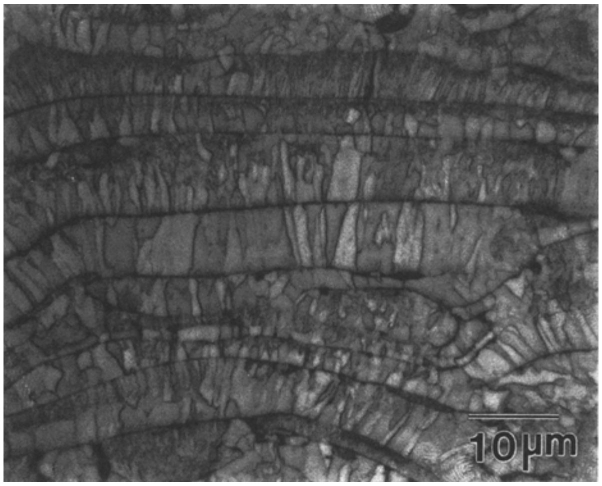

Fig. 4 Plasma-sprayed molybdenum coating exhibiting columnar grain structure over the entire coating cross section.

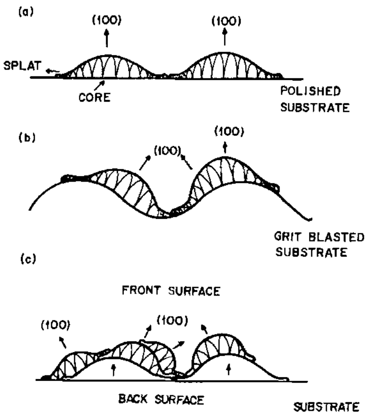

Fig. 5 Morphology and texture development in plasma-sprayed coatings. See text for further details.

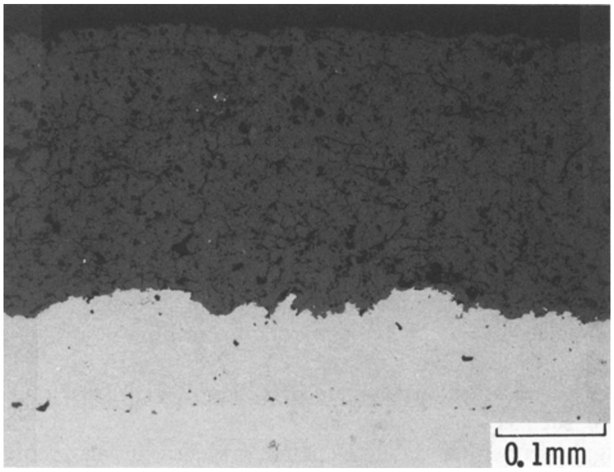

Fig. 6 Cross-sectional photomicrograph of a two-layer thermal barrier coating typically used in gas turbine engines.

Under high solidification rates, it is expected that the fastest crystal growth direction will prevail. X-ray diffraction results from the back side of the atmospheric and vacuum plasma-sprayed nickel deposits, both sprayed onto polished steel substrates, suggest a strong <200> texture in the coating. This is expected, because <100> is the fastest growth direction in cubic materials. Such texture has also been observed for Ni-5wt%Al material, although it is diminished in extent. More recently, <100> texture has also been reported in air plasma-sprayed molybdenum coatings.[11] Although each individual splat may have a texture associated with it, the accumulation of many of these <200> oriented splats develop randomly as a deposit, resulting in the annihilation of most of the preferred orientation. In addition, the substrate interface morphology can also influence the measurement of the preferred orientation (Fig. 5).

3.4 *Summary and Future Research*

A plasma-sprayed coating is a consolidation of many individually solidified splats. The dynamics of splat formation and the interaction between the splats determine the overall microstructure of the sprayed deposit. The solidification of each splat can be treated as an independent event and the plasma spray process can be looked upon as an up-scale version of splat cooling. The splats undergo ultra-rapid quenching with cooling rates in excess of 10^6 °C/s. Morphological stability of the plane front is anticipated, starting with nucleation on the substrate followed by columnar solidification. The columns show preferred orientation; however, accumulation of several splats results in the annihilation of most of the preferred orientation in the overall deposit. Vacuum plasma-sprayed deposits undergo self-annealing, which leads to stress-relief and recrystallization, causing fine, stress-free, and equiaxed microstructures.

Future research in the area of deposit formation needs to be more intimately coupled with plasma and particle parameters such as velocity and temperature. It is envisioned that this will lead to predictive relationships between process and microstructure, microstructure and properties, and property and performance.

4. Thermal Properties of Thermal Barrier Coatings*

4.1 *Introduction*

Thermal barrier coatings (TBCs) are thermally insulating coatings that protect internally cooled components in a heat engine.[12] They generally consist of a layer of ceramic over a layer of a metallic bond coat (see Fig. 6) with intermediate layers of mixed ceramic and metal for some applications. Both layers usually are applied by plasma spraying. Thermal barrier coatings have two prime requirements: they must insulate the component from the hot gases in the engine, and they also must remain on the part for many thousands of hours. Thus, the most important thermal properties of thermal barrier coatings are those relating to thermal insulation and those relating to the thermal cycle durability. The thermal insulation of a coating layer is essentially a function of thermal conductivity, thermal diffusivity, and total emissivity. These are, in turn, related to the composition, thickness, and structure of the coating. Thermal barrier coating durability, on the other hand, is a very complicated function of numerous factors including coating thickness, processing, structure, composition, coating temperature (especially the temperature of the bond coat or other metal-containing layers), environmental effects such as cleanliness of the fuels and air, the physical, chemical, and mechanical properties of the coating, substrate properties, and many other factors. Because advances in thermal barrier coating technology have been paced by dura-

---

* Contributed by **R.A. Miller** and **W.J. Brindley,** NASA-Lewis Research Center, Cleveland, Ohio.

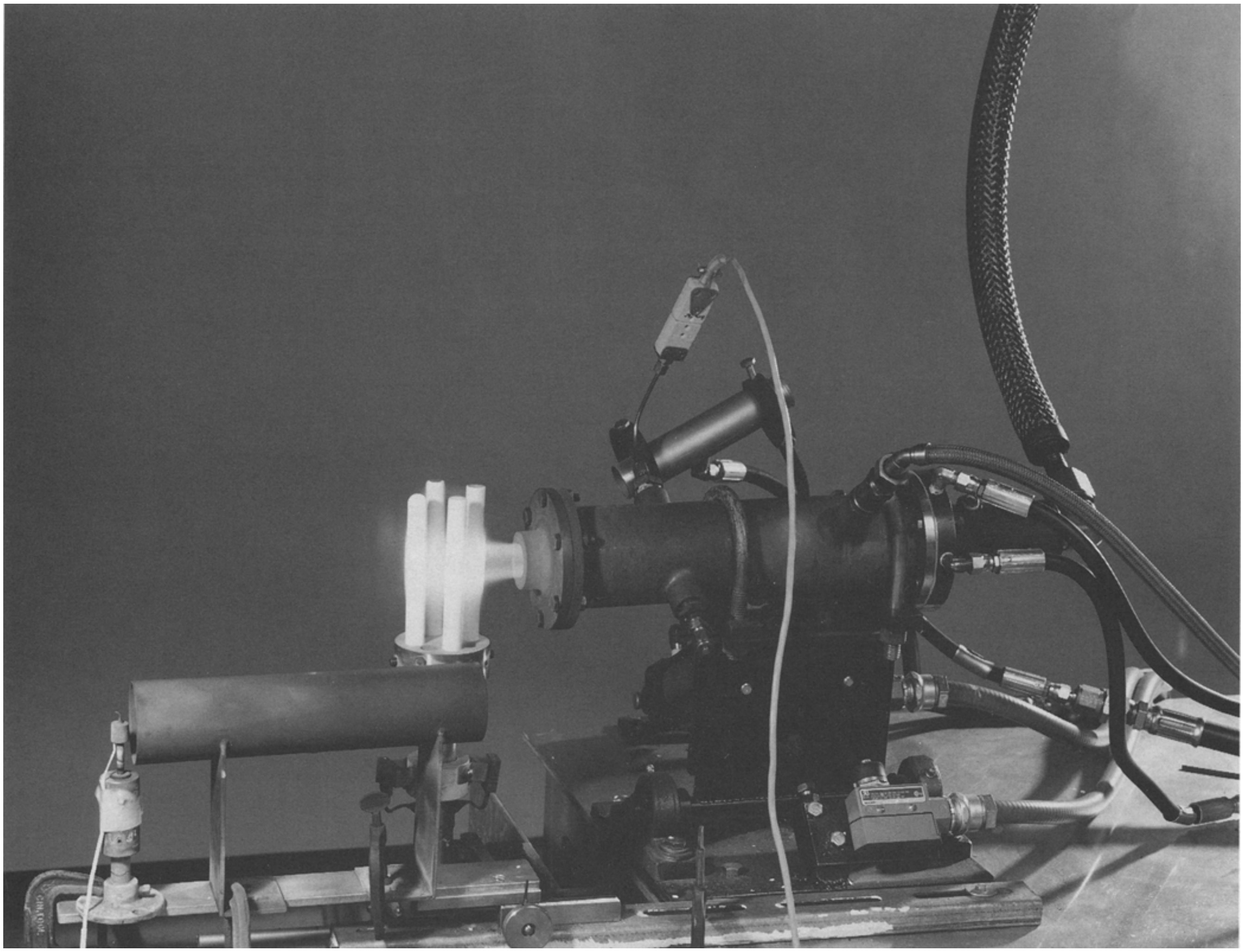

Fig. 7 Mach 0.3 burner rig used to evaluate a carousel of four spinning cylindrical thermal barrier-coated specimens.

bility improvements, materials engineers have tended to focus on maximizing coating durability rather than minimizing conductivity. The following is a brief summary of thermal barrier coating thermal properties, with emphasis on the approaches used to assess and improve the durability of thermal barrier coatings for gas turbine applications.

4.2. *Testing of Thermal Barrier Coatings*

Thermal barrier coating durability basically refers to thermal cycle life under engine operating conditions. Thermal cycle life can be further divided into thermal fatigue (due to thermal expansion mismatch and any transient effects) and time-at-temperature degradation (oxidation, creep, etc.). The thermal fatigue and the time-at-temperature aspects of durability are known to interact synergistically, which further complicates the subject of durability. Added to this are uncertainties associated with the current understanding of engine operating conditions. Thus, it is clear that durability cannot be assessed from simple tests or modeling. In fact, the only fully creditable approach for assessing durability is an engine test. However, the expense of engine tests generally makes them unsuitable for routine screening or for assessing the fundamentals of thermal barrier coating behavior. Furnace tests and torch tests (such as a Mach 0.3 burner rig test, shown in Fig. 7) are the most common laboratory-scale approaches for durability assessment.

An entirely new set of complications is associated with laboratory testing of thermal barrier coatings. Most of these complications relate to the test method being used to assess durability and not directly to durability itself. The most important factor is temperature measurement, because specimen temperature (especially bond coat temperature) has been found to be the most important factor controlling durability. For example, the measured durability of a thermal barrier coating system decreases by a factor of about two for a 25 °C increase in bond coat temperature.[13] To put this another way, a 2% error in the measurement of temperature (relative to room temperature) can yield a 100% decrease in thermal barrier coating life, as illustrated in Fig. 8.

It is much more difficult than generally realized to measure the temperature of a low-emissivity specimen that is being

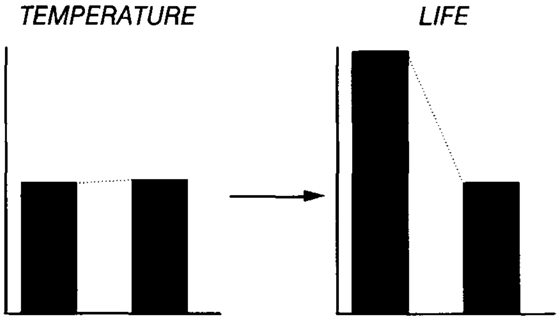

Fig. 8 Schematic of the strong effect that a relatively small error in temperature measurement (about 2%) can have on the life of thermal barrier-coated specimens (about 100%).

heated in a open flame, such as in a torch test. Nor is it generally realized that specimens having different emissivities will reach different temperatures when tested in the same flame. In an open flame (cool-wall) environment, specimens with higher total emissivities attain lower temperatures (because of greater radiative cooling) than specimens with a lower emissivity. The opposite effect can occur if at least a portion of the surroundings are at a higher temperature than the coated specimens (hot-wall environment). If, on the other hand, uncooled specimens and their surroundings are at the same temperature, then all specimens will reach the same temperature regardless of their emissivity. A furnace is approximately an isothermal environment. Thus, emissivity differences should not be a factor, and temperature is more easily measured in a furnace. Therefore, from a temperature control viewpoint, a furnace test is often the best choice for thermal barrier coating evaluation. However, because a specimen tested in the low heat flux environment of a furnace is generally isothermal, it is hard to design a furnace specimen that is not subject to edge-effect failures. Also, the furnace is less amenable to hot-salt corrosion testing, short time-at-temperature cycling, and internal cooling of the specimen. Furthermore, the higher velocity and higher heat flux associated with a torch test gives it a certain credibility over furnaces, even though velocity and heat flux are believed to be far less important to durability than bond coat temperature.

Fortunately, even with all of the above difficulties, the behavior of thermal barrier coatings tested in furnaces generally tends to match the behavior of those tested in torches, which in turn match the behavior of coatings tested in engines. The actual testing approach used is best decided on a case-by-case basis. Regardless of which approach is used to collect data, there will be variability associated with that test and with the coating. Therefore, it is necessary to use statistical methods so that the variability associated with the durability of the coating can be assessed.

4.3 *Stress Modeling and Failure*

Simple tests or stress modeling are generally inadequate for assessing durability due to the complexity of the failure mechanism(s) and the lack of a single, independent critical component of the failure mechanism around which one could build a simple test or model. Stress modeling and simple mechanical tests do, however, play two important roles in thermal barrier coating research. The first important role is the use of modeling and simple tests as an aid for understanding failure mechanisms. The second role is the use of models for designing thermal barrier coatings for specific components and for predicting thermal barrier coating lives. Thermal barrier coating life prediction was the intent of the NASA-sponsored Hot Section Technology (HOST) thermal barrier coating programs.[13,14] The HOST programs yielded models to predict the behavior of bill-of-material thermal barrier coatings over a wide range of conditions. These models used finite- element stress models (which were driven by measured thermophysical and thermomechanical properties) and semi-empirical life models that were based on the failure mechanism as it is currently understood. The models were calibrated against furnace and torch data that were collected over a wide range of conditions for a specific coating system. These models were developed so that engine designers could predict the response of specific coating systems in an engine environment. They were never intended to be used by materials engineers for coating development.

Much more work is needed to help isolate the individual components of thermal barrier coating failure, and many of these efforts may be based on simple tests. Testing conducted in areas that appear most relevant (i.e., fracture toughness, crack propagation, microstructural characterization, oxidation, thermal expansion measurement, etc.) is expected to be the most fruitful. In fact, simple experiments have shown that failure is most strongly associated with thermal expansion mismatch stresses that arise in the ceramic upon cooling after exposure to high temperatures. Processes such as bond coat oxidation contribute to degradation at high temperatures, and heating stresses are not the prime drivers of failure unless rocket conditions are considered. These basic concepts of thermal barrier coating failure were formulated about a decade ago, and, unfortunately, remarkably little detailed knowledge of the failure process has been obtained since that time. One field of inquiry that has added to the understanding of the failure mechanism involves the study of nonlinear material properties such as bond coat and ceramic stress relaxation.

4.4 *Thermal Properties*

Once adequate thermal barrier coating durability has been demonstrated for a gas turbine or diesel application, the thermal properties related to thermal insulation become important to the engine designer. The measurement of properties related to thermal insulation (thermal conductivity, thermal diffusivity, and total emissivity), although seemingly routine, is very difficult to perform on a reliable basis from laboratory to laboratory. For instance, the approach of measuring thermal diffusivity by the flash method[15,16] is attractive because, when done correctly, it is fast, accurate, and suitable for small specimens. However, the practitioner quickly learns that the operational and data analysis techniques for this method are not trivial and can lead to significant errors. Thus, the designer using these properties must understand the uncertainty that may be associated with a given property. These types of problems must be addressed if these properties are to be used with confidence in engine designs.

4.5 *Heat Engine Applications*

The above comments pertain primarily to gas turbine applications. For the case of thick thermal barrier coatings for diesel engine components, there is even less agreement on the details of coating failure, and no general agreement has been reached on an appropriate laboratory-scale test.[15] However, the cost of diesel engine tests are relatively low compared with gas turbine tests. As a result, there has been more reliance on engine tests and a stronger attempt to make use of thermal and stress models.

The current interest in using thermal barrier coatings in a variety of heat engine applications has spurred extensive interest in the thermal barrier coating properties of thermal insulation and thermal cyclic durability. The brief summary presented here points out some of the difficulties associated with assessing these properties, particularly thermal cycle durability. It is clear that durability testing will continue to be the prime concern for engine manufacturers. It is also clear that the most intelligent and economical use of these coatings dictates that more attention be paid to thermal insulation properties, stress and life modeling, and to understanding of the failure mechanism.

5. Mechanical Properties of Coatings*

5.1 *Why Perform Mechanical Property Tests?*

The relevance of performing mechanical property tests on coatings must be correlated to the anticipated information that is gained. Thus, the determined properties of bond strength and elastic modulus are often required by design engineers so that modeling studies, life prediction, and component (i.e., coating/substrate) design can be performed. The definition of "modulus" for a thermally sprayed coating may also be somewhat misleading, because the tile-like structure of coatings allows these coatings to deform in a pseudo-elastic fashion.[17] Thus, the coatings may appear to have a linear stress-strain response; however, on unloading, it is observed that there is a residual extension indicative of permanent set deformation.

There are limitations to the present testing methods. It is generally accepted that the present tensile adhesion test (TAT) methodology, as required by AFNOR NF A91-202-79, ASTM C633-69, DIN 50 160-A, and JIS H8666-80 (among other standards and specifications), is not a good indicator of true coating adhesion.[18] These usual methods of testing are limited by the strength of the epoxy and are not adequate for the *higher strength* coatings that are now being produced. Other methods such as fracture toughness testing[19] are more suited to research applications for studying fundamental structure/property relationships of materials.

5.2 *Failure Locus Determinations*

Another aspect of mechanical properties that is not clearly defined concerns the definition of the fracture locus (Fig. 9). There is still some confusion over the nomenclature of "adhesive" and "cohesive" failure. Most investigators agree that adhesive failure can be defined as occurring between the coating and substrate, whereas cohesive failure occurs within the thermally sprayed deposit. However, these definitions are confusing when used to describe failure of mixed component systems that use a bond coat and ceramic overlay, or systems that consist of a cermet-type of structure. Thus, failure between the bond coat and ceramic overlay can be considered as either adhesive, because it occurs between two different materials; or as cohesive, since failure lies completely within the coating system. Such confusion can be reduced by clearly defining the failure mode in each report. An alternative remedy is for workers in this area to agree on a standard set of definitions for every morphology of failure. It is generally perceived that such a "standard" will be essential, because there is a strong need to succinctly describe coating failures. Service failures of coatings are also described as "delamination" or "segmentation" cracking. These modes of failure can be directly related to the probable causes of failure and are thus invaluable in assisting a physical description of failure processes.

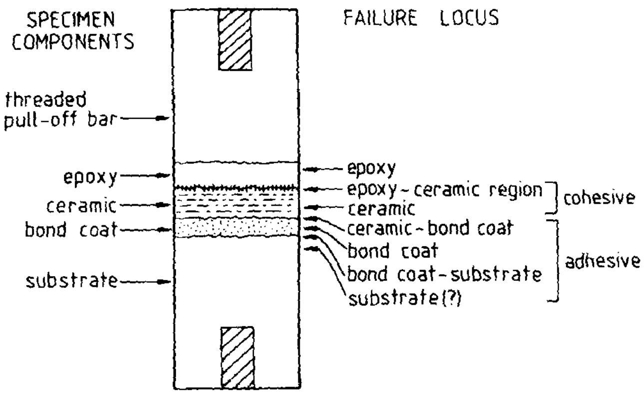

Fig. 9 Schematic showing the various failure loci of a tensile adhesion test specimen.

5.3 *Hardness Tests*

Hardness tests on coatings also are often performed. Caution needs to be exercised in reporting such results, particularly if this property is used as a criteria for the acceptance of a particular coating. Recent work[20] has shown that the variability of hardness tests is quite high and often extends to variances of 35%. This result can be compared to a typical variance of, at most, 25% for equivalent mechanical properties on bulk materials. There is also strong evidence that the use of indentation fracture mechanics for determining a fracture toughness value for thermally sprayed coatings is susceptible to large errors.

5.4 *Future Research*

The future of mechanical property measurements lies in performing fundamental studies that can be used for design and development purposes. Thus, acoustic emission studies[21] have a strong potential of enabling correlations to fracture mechanism measurements. For example, Fig. 10 indicates that it may be possible to distinguish microcracking, which may be tolerated in a certain application, from macrocracking, which could lead

---

* Contributed by **C.C. Berndt**, SUNY at Stony Brook, The Thermal Spray Laboratory, Stony Brook, New York.

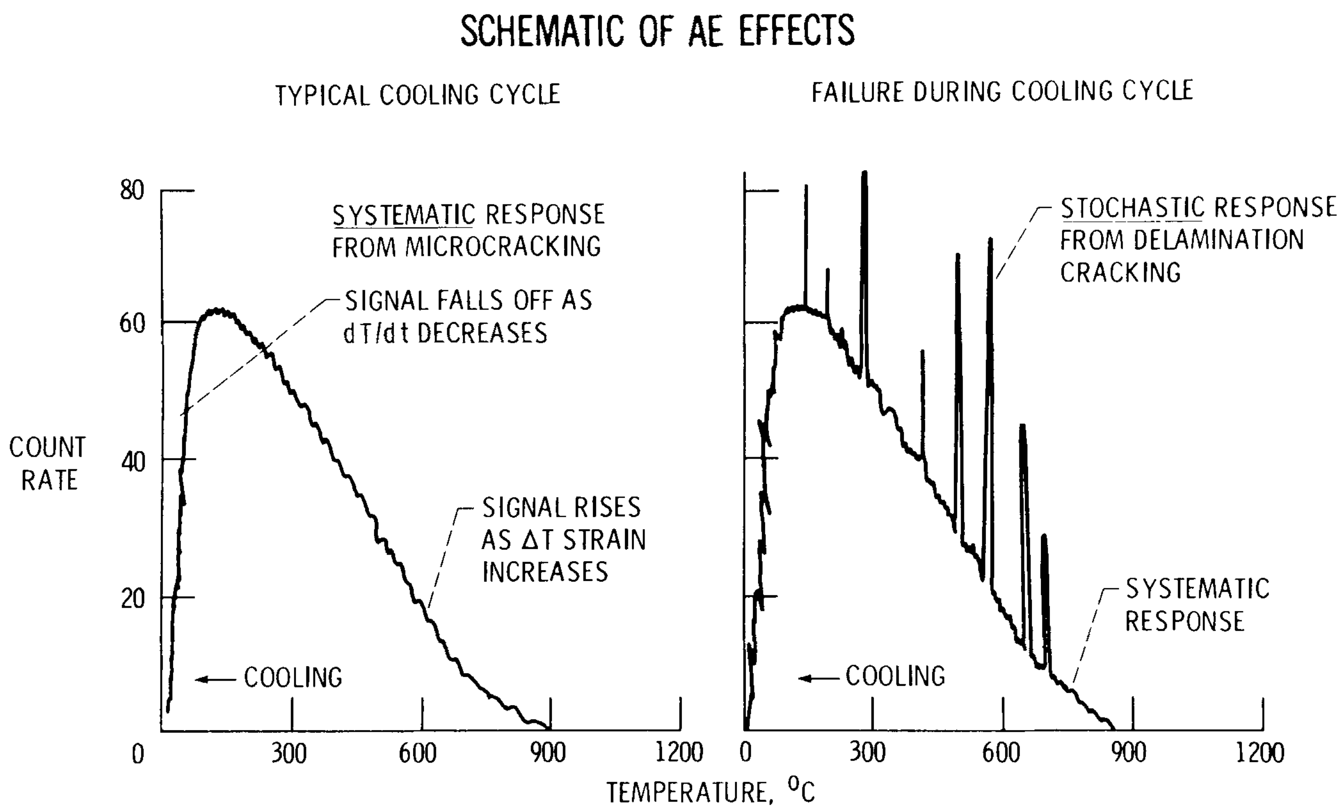

Fig. 10 Schematic illustrating the distinction between random and systematic cracking processes that are revealed by acoustic emission methods.

to catastrophic failure of the coating system. The quantitative analysis of the fracture behavior of plasma-sprayed coatings will ultimately lead to significant improvements in their design and therefore broaden the scope of their application.

6. Feedstock Materials*

6.1 *Introduction*

The quality of feedstock materials is an integral part of the plasma spray process. These materials can be classified according to their general chemical compositions, as indicated in Table 4. Of course, one of the major advantages of thermal spray coating methods is that almost any material can be produced in wire or powder form and thus may be used as feedstock. The focus of this section will be on powder feedstock. The chemical classifications are only a guide to potential applications of the so-formed coatings, i.e., WC for wear resistance,[22] zirconia-based ceramic alloys for thermal barrier applications,[23] etc. Two powders of identical composition may still be of variable quality because complete characterization in terms of particle size, particle distribution, and chemical homogeneity may limit the use of the material.[24]

6.2 *Production Methods and Quality Assurance*

The commonly used methods for producing thermal spray powder[25] are listed in Table 5. All of these methods have distinct advantages or disadvantages that may bring about certain attributes or deficiencies in the powder product. For example, the fusing and crushing method of powder production is quite economical; however, it produces particles of angular characteristics that may be unreliable in terms of powder sizing and powder feeding characteristics. Future powder applications will require narrow particle size distributions, and the production of such powders is a prime research area for technology.

The quality assurance of powders is one area of powder technology[26] that still requires attention because these specifications are poorly defined. Thus, the acceptable range of particle sizes and the distribution within this range is a critical vendor specification for the optimum plasma spray processing of the material. It can be noted that there is no universally accepted control technique for the analysis of powder chemistry and for measuring particle size distribution. For example, there is often a discrepancy between the particle size distribution of powders that are measured by a light-scattering technique (e.g., "Microtrac" apparatus) compared to those measured by an x-ray cross-sectional absorption method (e.g., "Sedigraph" apparatus). It also has been reported that the resin binder of some agglomerated powders may dissolve under severe agitation during powder size measurement, thus causing misleading results. It is clear that powder size distributions must be treated with caution.

---

*Contributed by **D.L. Houck**, GTE Products Corp., Towanda, Pennsylvania.

Table 4 Feedstock Classification According to Chemistry

Classification	Material constituents	
Metallic alloys	MCrAlY (M = Ni, Co, Fe)	
	Co-Cr-W-Co-based stellites	
	Ni/Co-based self-fluxing alloys	
	Ni/Co-Cr-Mo-Si-based Laves phase alloys	
	Ni-Cr-Fe-based Inconels	
	Ni-Cr-Mo-based Hastelloys	
	Cu-based alloys (Cu-Zn, Cu-Al, Cu-Ni)	
Metallic composites	**Cladding material**	**Core material**
	Al	Ni
	Al-Mo	NiCr
	Co-Al	NiCrFe
	Ni-Al	FeCr
	Ni	Al
	Co-Al-Y_2O_3	Fe-Ni
Intermetallics	Ni-Al	
	Ni-Ti	
	M-Cr-Al-Y types (M = Ni, Co, etc.)	
	Triballoys	
	Superalloys	
Cermets	Ni/Co/Fe-based alloys + Al_2O_3, ZrO_2, etc.	
	Ni/Co/Fe-based materials + WC-Co, TiC, Cr_3C_2, etc.	
	Al/Ni based-materials + graphite (abradables)	
Refractory metals	Carbides of Ti, Zr, and Hf (group IVa elements)	
	Nitrides of V, Nb, and Ta (group Va elements)	
	Borides of Cr, Mo, and W (group VIa elements)	
Nonmetallic hard materials	Oxides of Al_2O_3, Cr_2O_3, TiO_2, and ZrO_2	
	Nonoxides of B_4C, SiC, and Si_3N_4	

6.3 *Environmental Issues and Future Activities*

Another aspect of powder technology that is most important concerns the environmental issues. It is necessary to have effective dust collection to ensure healthy practices in the workplace, and any hazardous materials must be segregated, either during the powder manufacture stage or during plasma spraying. The collection of spray residue (i.e., the spray material that is not deposited and collected in the wet collector or cyclone) can be considered a fertile area in which increased efficiency can be gained by recycling of these materials.

Future activities in the area of powders will include the development of unique materials combinations that are designed specifically to capitalize on the versatility of thermal spray processing. There are also expected gains in improved methods of production. These advances will be engendered by a more complete understanding of the relationship between the feedstock and coating properties.

7. Porosity: An Integrated Approach*

7.1 *Introduction*

In its recent report[27] on Materials Science and Engineering for the 1990s, a National Research Council panel stated as its leading recommendation for strengthening the field that emphasis should be placed on developing the linkage between materials synthesis, processing, and performance. This implies an integrated approach to which plasma spray processing is ideally suited. The purpose of this section is to describe a plan developed jointly by Brookhaven and Stony Brook to pursue such an integrated program focused on one key parameter in plasma spray coating: porosity.

Table 5 Methods of Producing Thermal Spray Powders

Agglomeration, sintering
Agglomeration, spray drying
Atomization
Crushing
Densification/spheroidization, e.g., "GTE" method
Densification/spheroidization, e.g., Metco's HOSP process
Fusing, three-phase arc
Fusing, three-phase resistance
Fusing, vacuum arc skull
Particle coating, e.g., "Metco" method
Particle coating, e.g., "Sherritt-Gordan" method
Reduction/co-reduction of oxides
Sizing, classification
Sizing, elutriation
Sizing, screening
Sol gel

Porosity is a unifying theme for materials scientists at Brookhaven, because they are currently engaged in other programs on carbon-based gas storage systems and on cementitious materials in addition to plasma spray coatings. Porosity is an important attribute of all these materials, and an understanding of how to characterize it in one material will benefit all of them. It is also easy to identify other energy-related fields in which porosity plays a key role, e.g., the coal industry, the oil and gas industry, and the ceramics industry, and all of these are of major importance to the U.S. Department of Energy. Thus, a program that concentrates on characterizing porous media can be global in its influence on concepts in many materials synthesis and processing practices.

7.2 *Facilities to Classify and Measure Porosity*

Special techniques at Brookhaven, constituting the core of the program, are X-ray and neutron scattering at the National Synchrotron Light Source (NSLS) and the high flux beam reactor (HFBR), respectively. The x-ray work will include small-angle scattering and computed X-ray tomography. Supplementary experiments appropriate to a specific material will be performed with experimental apparatus available for electrical resistivity, infrared absorption, SEM, electron energy loss spectroscopy (EELS), TEM, and gas porosimetry measurements. A fully automated gas adsorption apparatus is also available for determination of adsorption isotherms, from which surface areas and other relevant properties can be deduced.

The diverse forms of the classic BDDT adsorption isotherms [28] (so-named after the authors Brunauer, Deming, Deming, and Teller) illustrate the complexity of porous media (Fig. 11) and underscore the importance of using a variety of independent

---

* Contributed by **A. Goland,** Brookhaven National laboratory, Department of Applied Science, Upton, New York.

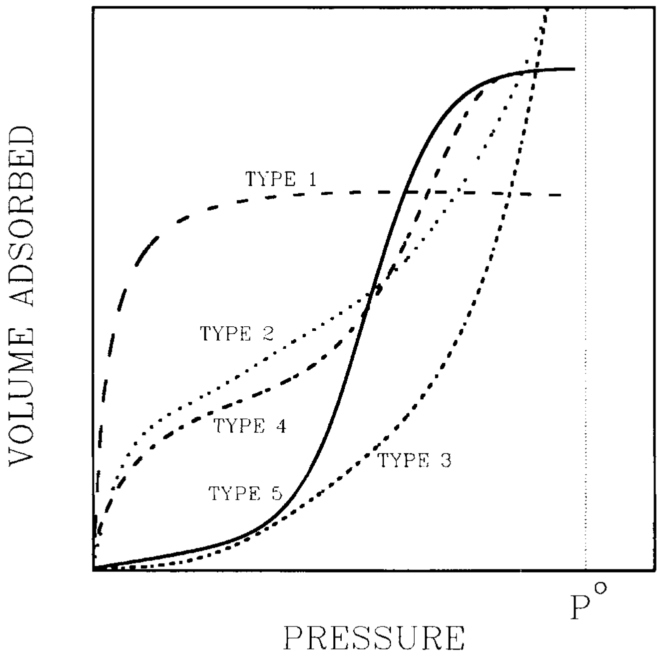

Fig. 11 Schematic representation of pressure versus volume adsorbed to indicate five classifications of porosity distribution. Each type of porosity distribution is indicative of a different pore microstructure. The curves include adsorption mechanisms based on capillary condensation and interaction between the gas molecules and substrate. P^o is the condensation pressure.

methods to characterize these materials definitively. It is also well known that porosimetry alone is not the answer, because different kinds of porosimetry can yield different answers. A complete picture will only emerge from a combination of experimental techniques, and it appears that small-angle scattering of X-rays or neutrons can be a powerful analytical tool. Because of the existence of major user facilities at Brookhaven, small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) will be emphasized in the plasma spray program.

7.3 *Fractal Concepts of Porosity*

New ideas using the fractal concept of materials have been applied to small-angle scattering,[29-33] offering some promise of an eventual scientific basis for a comprehensive description of porous media. The application of a fractal description of porous media to analysis of small-angle scattering permits a distinction to be made in some cases between surface and volume (mass) fractal materials. For volume fractals $I(q) \sim 1/q^D$, where $D < 3$, and for surface fractals: $I(q) \sim 1/q^{6-D}$, where $6-D > 3$. It can be noted that when $D \sim 2$, then $I(q) \sim q^{-4}$ and the Debye-Porod rule implies a smooth surface on the length scale of q^{-1}. Note that $I(q)$ is the intensity of the length scale used in determining the fractal dimension and D is a constant.

This kind of systematic classification, as well as understanding why some porous media apparently cannot be described by fractal concepts, will lead ultimately to a sound scientific basis for a comprehensive model of porous media that can guide plasma spray technology.

8. Manufacture of Intermetallics*

8.1 *Introduction*

Intermetallic materials are of great interest, because in their bulk form they exhibit high elastic moduli, high strength, low creep rates, and high recrystallization temperatures. These high-performance characteristics are somewhat moderated by their low ductility and low toughness. It is generally assumed that some of these properties will be carried over into a thermally sprayed deposit.

The systems that have been studied include the nickel aluminides, superalloys based on iron, nickel, and cobalt, molybdenum disilicide, and a variety of composites.[34-41] The above materials must be sprayed under vacuum plasma spraying conditions to reduce the formation of oxides and improve interparticle bonding. Fine grain sizes (which improve deposit ductility), the elimination of chemical segregation , and the reduced fabrication costs associated with near-net shape forming are some of the significant advantages accrued when intermetallics are spray formed.

8.2 *Spray Forming Advantages and Limitations*

The disadvantages of the plasma-deposited structures are that the fine-grained microstructures have low creep resistance and that the bonding between particles is poor, and thus, strength may be limited. The plasma spray process also gives rise to metastable structures, such as martensites, that may cause unwanted aging effects at high operational temperatures. Full densification is difficult to achieve by thermal spraying, and the process time required to form macroscopic engineering sections is quite high.

The technology of spray forming is limited at present due to the low through puts (on the order of kilograms per hour) of the current plasma torches. If higher throughputs can be attained, then spray forming of ingots and other raw material stock would be possible. It is necessary to maintain the rapid solidification processing (RSP) character of the deposits, because these microstructures are believed to confer optimal properties to the coating.[38,41]Research in the area of using liquid feedstock material or alternative torch designs may lift the barrier of high deposition rates, while at the same time maintaining the rapid solidification processed nature of the deposit. Another technological barrier is the need to process intermetallics under inert atmosphere conditions. Hyperbaric spraying (i.e., greater than one atm.) may be beneficial for spray processing high melting point materials.[42] Other process methods to enhance interparticle cohesion include using transferred arcs to surface clean the substrate as well as to elevate the substrate temperature. The technological limit of near-net-shape forming of deposits will be the creation of complex geometries in which new masking methods will be required, and the tolerances for maintaining or achieving a certain edge profile and the dimensional stability of the form will need to be ascertained.[43] One of the prime material variables that is the root cause for these engineering limits of

---

* Contributed by **R. Neiser,** Sandia National Laboratories, Process Metallurgy, Albuquerque, New Mexico.

spray forming will be knowledge and control of residual stresses.

8.3 *The Ni-16Al Alloy*

The two-phase alloy of Ni-16Al is an example of an intermetallic alloy that has been examined closely. The NiAl phase is distributed uniformly, with an equiaxed grain structure among the Ni_3Al after a homogenizing anneal at 1100 °C. This anneal also has the benefit of increasing density from 6.70 to 7.06 g/cm^3 after 100 h at temperature. This spray-formed alloy exhibited no ductility up to 600 °C, but exhibited an elongation to failure in excess of 75% at 800 °C. The microstructures of spray-formed intermetallics will, in general terms, exhibit metastability, porosity, be fine grained, exhibit minimum segregation effects, and have residual stresses. The upshot of such structures of intermetallics are good mechanical properties and good ductility; however, there is the potential for dimensional instability and poor creep resistance.

9. Synchrotron X-Ray Microtomography of Thermal Spray Materials*

9.1 *Difficulties with Conventional Microscopy Methods*

The structure of materials prepared using thermal spray methods is difficult to determine using conventional microscopy or porosimetry methods. The difficulties inherent in these approaches can be circumvented using synchrotron computed microtomography (CMT). An example of the use of CMT to produce a high-resolution nondestructive image of a thermal spray coating is described in this section to illustrate the power of this technique.

Thermal spray technology is used to fabricate coatings of different types of materials that will improve the thermal properties or wear resistance of the substrate material. The quality of the coating is affected by its homogeneity, porosity, adhesion to the substrate, etc. The determination of these properties is often attempted using conventional optical microscopy methods. This necessitates sectioning and polishing the coating, which can produce artifacts that obscure the true nature of the section. Use of conventional porosimetry methods is also hazardous, because the pores may not be connected. Synchrotron CMT is an alternative technique that can be used to generate images of the morphology in transverse planes in a sample nondestructively. The limited X-ray brilliance from conventional X-ray tubes, however, generally makes the spatial resolution in CMT much worse than 20 μm, which is around the maximum size of pores observed by optical microscopy of thermal sprayed deposits. Synchrotron X-ray sources have brilliance that is orders of magnitude higher than x-ray tubes and have made possible CMT with much higher spatial resolution.[44,45] The construction of third-generation synchrotron X-ray sources now taking place makes CMT with sub-micrometer spatial resolution conceivable, although it still has yet to be implemented.

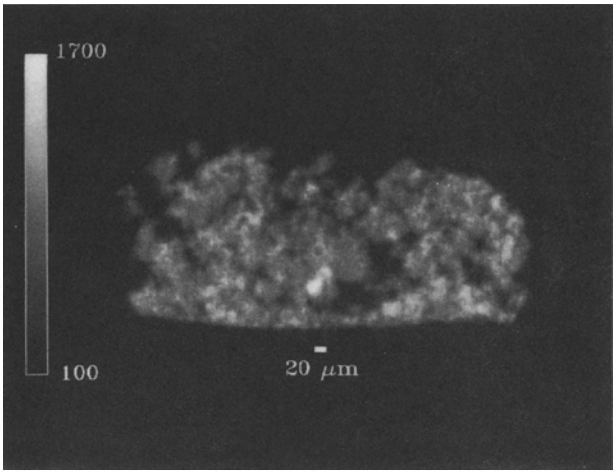

Fig. 12 Tomographic section through a specimen of Cr_3C_2/NiCr produced using thermal spray technology under nonoptimal conditions. The different gray levels indicate that voids are present within the material.

9.2 *Computed Microtomography Methods*

A CMT instrument that can be used for nondestructive microscopy down to a volume resolution of 5 × 5 × 5 μm has been developed at the ×26 Microscopy Beam Line of the National Synchrotron Light Source.[46] This instrument is ideally suited to detect voids in small (1 mm or less) samples of thermal sprayed coatings. It has been used for a study of voids and material homogeneity in a series of thermal sprayed deposits, produced at different temperatures and using different feedstock materials. The imaged quantity was the linear attenuation coefficient averaged over the energy spectrum of the synchrotron X-rays. The linear attenuation coefficient depends on both the material composition as well as the density of the samples. For elements having a photoelectric absorption edge at an appropriate energy in relation to the sample size, it is possible to map the two-dimensional distribution for a selected element by making a subtraction image from images generated using two different X-ray energies straddling the edge energy.[47]

9.3 *An Example*

To illustrate the application of CMT, a thermal spray coating of Cr_3C_2/NiCr was prepared. The conditions were chosen to produce a coating with high porosity so that the ability of the CMT method to differentiate between the material and voids would be most evident. The tomographic section that was produced is shown in Fig. 12. The pixel size for this image is about 5 × 5 μm, with a slice thickness also of 5 μm. The gray scale used to produce the image shows regions of high linear attenuation coefficients as lighter gray than regions of low attenuation coefficients (voids).

The relative quality of the specimen can be shown by constructing a histogram giving the frequency of occurrence of the

---

* Contributed by **P. Spanne** and **K.W. Jones,** Brookhaven National Laboratory, Department of Applied Science, Upton, New York; **H. Herman,** SUNY at Stony Brook, The Thermal Spray Laboratory, Stony Brook, New York; and **W.L. Riggs,** GE Aircraft Engines, Engineering Materials Tech. Lab., Cincinnati, Ohio.

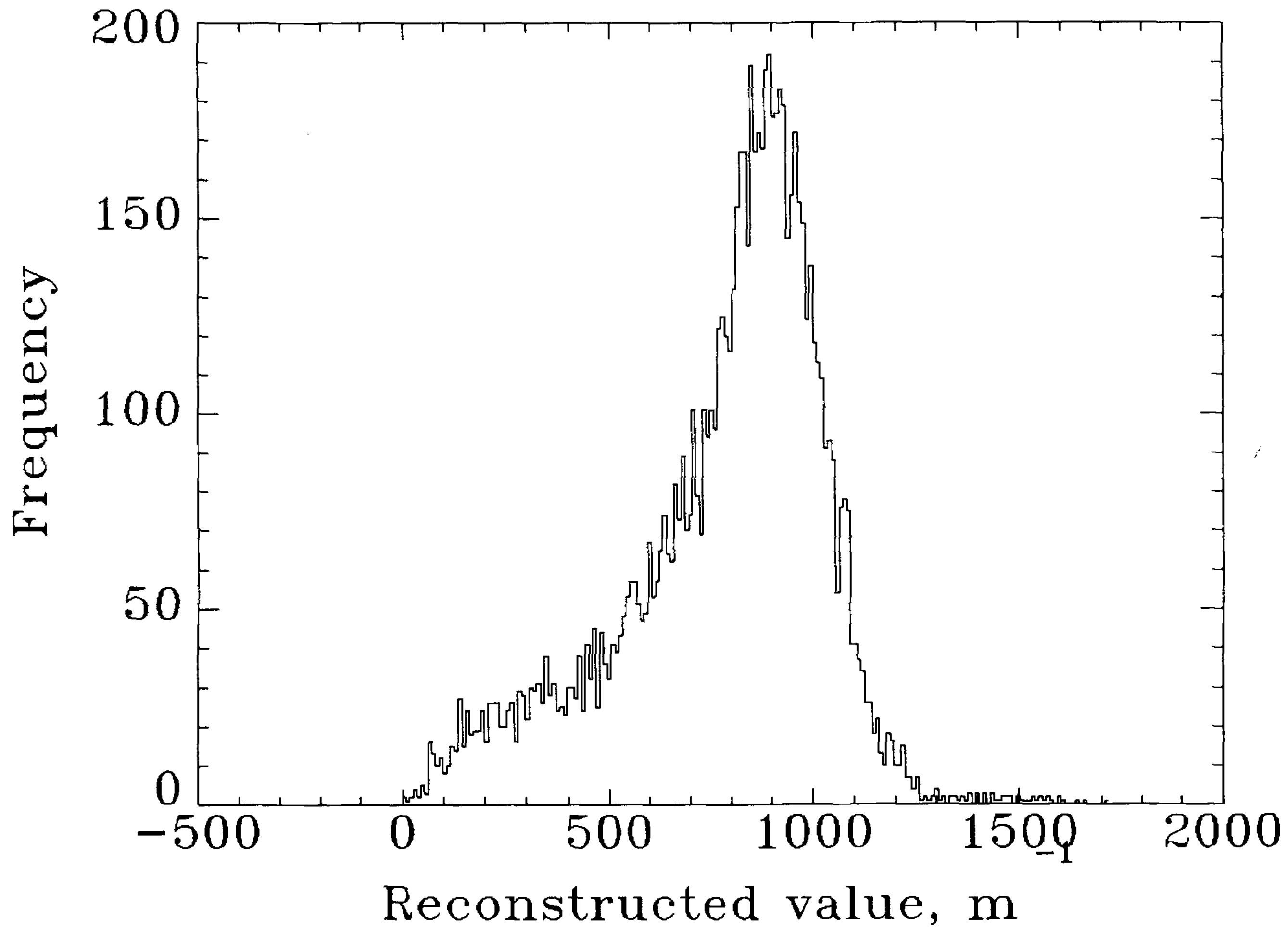

Fig. 13 Histogram showing relative distribution of linear attenuation coefficients in the specimen. The coefficient for air is centered around zero attenuation coefficient.

linear attenuation coefficients within the specimen. The results obtained for the section shown in Fig. 12 are shown in Fig. 13. The area under the two peaks, the one for void space not being very distinct, can be used to estimate the porosity of the sample. The results shown in Fig. 12 and 13 demonstrate the usefulness of synchrotron CMT for investigation of thermal spray coatings. A systematic application of the method to investigate thermal spray materials should give new insights into the quality of coatings produced under different conditions. This will make possible a correlation between quality and preparation conditions, which has not been previously possible and should thus lead to improved coating methods.

10. Concluding Remarks*

It is difficult to summarize the diverse array of related fields that were addressed in this article. The full range of topics— from plasma diagnostics to thermal and mechanical testing— as well as microstructural determinations is covered and would, if complete, present a true "unified approach" to thermal spray science and technology. The purpose of each contribution has been to present a short status report and a few key comments about future directions of research.

Thus, the present article is best used to focus on several issues of thermal spray that are complementary and/or related. For example, plasma diagnostics have been used by scientists for decades to ascertain particle thermofluid characteristics within the plasma effluent. However, only recently, has there been the potential to create control algorithms, in real-time, so that the process control of plasma spray manufacturing may become a production reality rather than a sophisticated laboratory experiment. In an alike fashion, the potential of real-time CMT (or a similar diagnostic tool) to analyze for microstructure defects will be a boost to instituting quality control, assessing metallographic standards and generally, will contribute much to elevate the art of thermal spray to a science.

The article also highlights several areas of research that need attention. Thermal and mechanical property determination are essential for the design and specification of coatings for practi-

---

* Contributed by C.C. Berndt, SUNY at Stony Brook, The Thermal Spray Laboratory, Stony Brook, New York.

cal applications. In this fashion, it may be possible to gain the full economic potential of thermal spray technology, because coatings will be designed as an integral part of an engineering component rather than as a coating that is just added to an existing part. There are many pitfalls in performing material property measurements on coatings. For example, a common mistake is to assign bulk material properties to coatings that have the same chemistry (e.g., PSZ, alumina, NiCrAlY, etc.). Another is to assume that the properties so-determined are isotropic. All scientists and engineers should recognize that, although the properties of bulk materials may provide the best guess for the properties of a coating with a similar chemistry, there is no microstructural justification for such an assumption.

Another major impact of the symposium concerned the strong need for well-established and routine methods for the microstructural characterization of coatings. Aspects of measurement such as quantitative phase determination, the measurement of porosity, and protocols for the nondestructive determination of microstructural integrity within the bulk of the coating are essential if coatings are to be accepted into critical applications where reliability, reproducibility, and standardization may be a question for concern. The methods that were addressed, including the definition and determination of porosity and understanding the evolution of the thermal spray microstructure as a rapidly solidified material, will enable the universal application of coatings. For instance, the aspect of forming net shapes by thermal spray deposition methods represents one application that will benefit from an increased understanding of the coating structure and its relationship to processing parameters.

This workshop was able to bring together some 75 participants who strived to shed light on fundamental and practical issues of plasma spray. This meeting was very successful in that basic questions of plasma spray technology were asked, and in some cases, answers were provided. The meeting also provided a framework for the rational development and interaction between many diverse disciplines, for example, by establishing strong links and defining interaction between the scientific theory and engineering applications of plasma spray technology.

Acknowledgments

The work on the porosity (Section 7) and microtomography studies (Section 9) mentioned in this article, as well as the conference itself, was supported in part or whole by the US Department of Energy, Division of Materials Sciences, Office of Basic Energy Services, under Contract No. DE-AC02-76CH00016.

All of the organizational and logistical tasks of this conference (except the conference program) were in the capable hands of one person. Thus, this conference owes much of its success to Lore Barbier for her "beyond the call of duty" help in all professional matters. All the conference attendees, especially the conference program organizers, thank her!

References

1. E. Pfender, W.L.T. Chen, and R. Spores; A New Look at Thermal and Dynamic Characteristics of a Plasma Jet, in *Thermal Spray Research and Applications*, T.F. Bernecki, Ed., ASM International, 1991, p 1-10.
2. Ph. Roumilhac, J.F. Coudert, and P. Fauchais, Designing Parameters of Spraying Plasma Torches, *Thermal Spray Research and Applications*, T.F. Bernecki, Ed., ASM International, 1991, p 11-18.
3. J.R. Fincke and W.D. Swank, The Effect of Plasma Jet Fluctuations on Particle Time-Temperature Histories, *Thermal Spray Coatings: Properties, Processes and Applications*, T.F. Bernecki, Ed., ASM International, 1991, p 193-198.
4. M. Vardelle, A. Vardelle, Ph. Roumhilac, and P. Fauchais, Influence of the Surrounding Atmosphere under Plasma Spraying Conditions, *Thermal Spray Technology New Ideas and Processes*, D.L.Houck, Ed., ASM International, 1989, p 117.
5. J.R. Fincke, R. Rodriguez, and C.G. Pentecost, Measurement of Air Entrainment in Plasma Jets, *Thermal Spray Research and Applications*, T.F. Bernecki, Ed., ASM International, 1991, p 45-48.
6. K.A. Kowalski, D.R. Marantz, R. Neiser, and M.F. Smith, Diagnostic Behavior of the Wire-Arc-Plasma Spray Process, *Thermal Spray: International Advances in Coatings Technology*, C.C.Berndt, Ed., ASM International, 1992, p 337-342.
7. J.M. Houben, Ph.D. thesis, Eindhoven University of Technology, Eindhoven, Holland.
8. M. Moss, Dispersion Hardening in Al-V by Plasma-Jet Spray Quenching, *Acta Metall.*, Vol 16, 1968, p 321-332.
9. S. Safai and H. Herman, Microstructural Investigation of Plasma-Sprayed Aluminum Coatings, *Thin Solid Films*, Vol 45, 1977, p 295-307.
10. S. Sampath and H. Herman, Microstructural Development of Plasma Sprayed Coatings, Paper 53, *Proc. 12th Int. Thermal Spraying Conference*, Vol 1, Welding Institute, London, 1989.
11. S. Sampath, Ph.D. thesis, "Rapid Solidification during Plasma Spraying," SUNY at Stony Brook, Aug 1989.
12. W.J. Brindley and R.A. Miller, Thermal Barrier Coatings for Better Engine Efficiency, *Adv. Mater. Proc.*, Vol 136 (No. 2) Aug 1989, p 29-33.
13. J.T. DiMasi, K.D. Sheffler, and M. Ortiz, "Thermal Barrier Coating Life Prediction Model Development, Phase I—Final Report," NASA Contractor Report CR 182230, Pratt & Whitney, Dec 1989.
14. R.A. Miller, Life Modeling of Thermal Barrier Coatings for Aircraft Gas Turbine Engines, *Trans. ASME J. Eng. Gas Turbines Power*, Vol 111, 1989, p 301-305.
15. R.A. Miller, Assessment of Fundamental Materials Needs for Thick Thermal Barrier Coatings (TTBC's) for Truck Diesel Engines, *Proc. 1990 Coatings for Advanced Heat Engine Workshop*, Aug 6-9, 1990, Castine, ME, also NASA Technical Memoranda TM-103130, May 1990.
16. R.E. Taylor, Things Mother Never Taught Me (about Thermophysical Properties of Solids), in *Thermal Conductivity 21*, C.J. Cremers and H.A. Fine, Ed., Plenum Press, 1990, p 41-49.
17. C.C. Berndt, Tensile Adhesion Testing Methodology for Thermally Sprayed Coatings, *J. Mater. Eng.*, Vol 12, 1990, p 151-158.
18. S. Amada, H. Yamada, S. Yematsu, and T. Saotome, Modelling and Measurements of Adhesive Strength of Thermally Sprayed Coatings, *Thermal Spray: International Advances in Coatings Technology*, C.C. Berndt, Ed., ASM International, 1992, p 915-920.
19. C.C. Berndt and R. McPherson, Assessment of the Adhesion of Plasma Sprayed Coatings, *Surf. J. Int.*, Vol 1(No. 2), 1986, p 49-52.
20. C.C. Berndt, J. Ilavsky, and J. Karthikeyan, Microhardness—Lifetime Correlations for Plasma Sprayed Thermal Barrier Coatings, in *Thermal Spray: International Advances in Coatings Technology*, C.C. Berndt, Ed., ASM International, 1992, p 941-946.
21. C.C. Berndt and R.A. Miller, Failure Analysis of Plasma-Sprayed Thermal Barrier Coatings, *Thin Solid Films*, Vol 119, 1984, p 173-184, also NASA TM 83777.
22. E. Lugscheider, Plasma Spraying for Wear Applications, in *Thermal Spray: Advances in Coatings Technology*, D.L.Houck, Ed., ASM International, 1988, p 173-184.

23. G. Schwier, Plasma Spray Powders for Thermal Barrier Coatings, *Advances in Thermal Spray*, The Welding Institute of Canada, Montreal, Canada, 1986, p 277-286.
24. D. Chauxian, R.A. Zatorski, H. Herman, and D. Ott, Oxide Powders for Plasma Spraying—The Relationship Between Powder Characteristics and Coating Properties, *Thin Solid Films*, Vol 118, 1984, p 467-475.
25. D.L. Houck, Techniques for the Production of Flame and Plasma Spray Powders, *Modern Developments in Powder Metallurgy*, Vol 12, 13, and 14, 1980, p 485-504.
26. A.R. Nicoll and H. Eschnauer, Retesting Thermal-Spray Powders, *Surf. Coat. Technol.*, Vol 30(No.1), 1987, p 95-106.
27. *Materials Science and Engineering for the 1990s*, National Academy Press, 1989.
28. S. Brunauer, L.S. Deming, W.E. Deming, and E. Teller, On A Theory of the Van der Waal's Adsorption of Gases, *J.Am. Chem. Soc.*, Vol 62, 1940, p 1723-1732.
29. S. Brunauer, *The Adsorption of Gases and Vapors*, Princeton University Press, 1945.
30. P.W. Schmidt, in *The Fractal Approach to Heterogeneous Chemistry*, D. Avnir, Ed., John Wiley & Sons, 1989.
31. Po-zen Wong and A.J. Bray, Small Angle Scattering of Rough and Fractal Surfaces, *J. Appl. Crystallogr.*, Vol 21, 1988, p 786-794.
32. J.K. Kjems, T. Freltoft, D. Richter, and S.K. Sinha, Neutron Scattering from Fractals, *Physica*, Vol 136B, 1986, p 285-290.
33. A.J. Hurd, D.W. Schaefer, and J.E. Martin, Surface and Mass Fractals in Vapor-Phase Aggregates, *Phys. Rev. A*, Vol 35, 1987, p 2361-2364.
34. R.H. Ericksen, J.C. Swearengen, and R.E. Allred, Mechanical Properties of Plasma Sprayed 1100 Aluminum as a Composite Matrix, *Sampe Quart.*, Vol 7(No. 1), 1975, p 1-8.
35. M.R. Jackson, J.R. Rairden, J.S. Smith, and R.W. Smith, Production of Metallurgical Structures by Rapid Solidification Plasma Deposition, *J. Met.*, Vol 33(No. 11), 1981, p 23-27.
36. M. Scholl, P. Clayton, E. Elmore, and J. Wooten, Sprayforming by High-Power High-Velocity Plasma Spraying, *Thermal Spray Coatings: Properties, Processes and Applications*, T.F. Bernecki, Ed., ASM International, 1992, p 281-288.
37. D. Stover, D. Moulatsiotis, W. Diehl, E. El-Magd, and R. Hecker, Low Pressure Plasma Sprayed Bulk Superalloy UDIMET 700: Mechanical Properties and Microstructure, *Thermal Spray Research and Applications*, T.F. Bernecki, Ed., ASM International, 1991, p 375-381.
38. R. Tiwari, H. Herman, S. Sampath, and B. Gudmundsson, Plasma Spray Consolidation of High Temperature Composites, *Mater. Sci. Eng.*, Vol A144, 1991, p 127-131.
39. T.N. McKechnie, Y.K. Liaw, F.R. Zimmerman, and R.M. Poorman, Metallurgy and Properties of Plasma Spray Formed Materials, *Thermal Spray: International Advances in Coatings Technology*, C.C.Berndt, Ed., ASM International, 1992, p 839-846.
40. R. Tiwari, H. Herman, and S. Sampath, Vacuum Plasma Spraying of $MoSi_2$ and Its Composites, *Mater. Sci. Eng.*, Vol A155, 1992, p 95-100.
41. S. Sampath, R. Tiwari, and H. Herman, Rapid Solidification Processing of Intermetallic Composites Through Plasma Spray, *Proc. TMS Fall Meeting Symp. on Microstructural Design by Solidification Processing*, Nov 1992, to be published.
42. D.A. Jager, D. Stover, and W. Chlump, High Pressure Plasma Spraying in Controlled Atmosphere up to Two Bar, *Thermal Spray: International Advances in Coatings Technology*, C.C. Berndt, Ed., ASM International, 1992, p 69-74.
43. L.E. Weiss, F. Prinz, and D. Adams, Solid Freeform Fabrication by Thermal Spray Shape Deposition, *Thermal Spray: International Advances in Coatings Technology*, C.C. Berndt, Ed., ASM International, 1992, p 847-852.
44. P. Spanne and M.L. Rivers, Computerized Microtomography Using Synchrotron Radiation from the NSLS, *Nucl. Instrum. Methods Phys. Res.*, Vol B24/25, 1987, p 1063-1067.
45. K.W. Jones, P. Spanne, W.B. Lindquist, W.C. Conner, and M. Ferrero, Determination of Polymerization Particle Morphology Using Synchrotron Computed Microtomography, *Nucl. Instrum. Methods Phys. Res.*, Vol B68, 1992, p 105-110.
46. K.W. Jones, R.S. Bockman, B.M. Gordon, M.L. Rivers, A.J. Saubermann, G. Schidlovsky, and P. Spanne, Biomedical Applications of Synchrotron X-Ray Microscopy, *Proc. 2nd Int. Workshop—XRF and PIXE Applications in Life Science*, R. Moro and R. Cesareo, Ed., World Scientific Publishing Co., Singapore, 1990, p 163-174.
47. K.W. Jones, P. Spanne, S.W. Webb, W.C. Conner, R.A. Beyerlein, W.J. Reagan, and F.M. Dautzenberg, Catalyst Analysis Using Synchrotron X-Ray Microscopy, *Nucl. Instrum. Methods Phys. Res.*, Vol B56/57, 1991, p 427-432.