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Paper 32

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CURRENT PROBLEMS AND DIRECTIONS IN PLASMA SPRAY PROCESSING

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R.A.Miller, R.Neiser, W.Riggs, S.Sampath, M.Smith and P.Spanne*[1].

ABSTRACT

This detailed report summarizes 8 contributions from a thermal spray conference that was held in late 1991 at Brookhaven National Laboratory (Upton, Long Island, NY, USA). The subject of "Plasma Spray Processing" is presented under subject headings of Plasma-particle interactions, Deposit formation dynamics, Thermal properties of thermal barrier coatings, Mechanical properties of coatings, Feed stock materials, Porosity: An integrated approach, 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, then describe current work that is being performed to investigate this area, and finally to suggest areas of research that may be fertile for future activity.

1. INTRODUCTION*[2]

The roots of plasma technology

Melt-spray processing technology in various forms dates back to the early 1900's 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

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[1] This report is a compilation and editing of individual author submissions. The author(s) of each section will be acknowledged throughout this report with a starred "*" footnote.

[2] Contributed by C.C.Berndt and Herman (SUNY at Stony Brook, The Thermal Spray Laboratory, Stony Brook, NY, 11794-2275), P.Spanne and K.W.Jones (Brookhaven National Laboratory, Dept. of Applied Science, Upton, NY 11973)

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 having mechanical properties approximating wrought materials. In recent years plasma spray processing has become the prime means for the melt-spray 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 hard facing 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 as employed 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 1950's. Small non-transferred 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, 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, not infrequently aware 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.

The Stony Brook / Brookhaven Symposium

A symposium was held at Brookhaven National Laboratory on September 13-15, 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 given 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 Methodologies", "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, NY), Metco Perkin-Elmer (Westbury, NY), and The Thermal Spray Laboratory (Stony Brook, NY) 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 marked with a "*" in Table 1 are included in this report. A detailed paper on the microtomography of plasma sprayed coatings will be presented in a future issue of JTST.

2. PLASMA-PARTICLE INTERACTIONS*[3]

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

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[3] Contributed by M.F.Smith (Sandia National Laboratories, Process Metallurgy, PO Box 5800, Albuquerque, NM 87185)

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 forty 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]

Feed stock entry and air entrainment into plasma plume

Another potential problem with existing commercial torches is that the powder feed stock is normally 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 which follow slightly different trajectories through the jet experience different thermal-kinetic histories prior to their impact upon 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 effects 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 down stream 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.

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 high-value-added production applications. However, such solutions are not cost effective for all commercial applications. In the author's opinion, we should use our improved knowledge of the process to step back and address the root cause of these problems. There is 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 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, yet chambered spray systems are impractical due to cost or work piece size considerations.

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 are currently being developed, tested, and even marketed in various parts of the world including Australia., Canada, Europe, Japan, and the U.S. 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, not all feed materials are available in wire form, so we also need improved plasma torches to spray powder.

As we prepare to enter the 2lst century, the industry is poised for some important refinements in plasma spray torch design. The overall objective is to use our 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*[4]

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 takes 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), determines 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, the 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 were 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.

The dynamics of splat formation

The dynamics of splat formation determine the solidification, microstructure development, and phase formation. Cooling 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}°/sec. Cooling rate determinations for aluminum and nickel through direct and indirect techniques have indicated cooling rates in excess of 10^{7}°/sec. Also the cooling rates are similar in both atmospheric plasma spraying (APS) and vacuum plasma spraying (VPS), even though VPS operates at a much higher deposition temperature; i.e., 900°C in VPS vs 100°C for APS. However, the

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[4] Contributed by S.Sampath (GTE Products Corporation, Towanda, PA 18848)

higher substrate temperatures in VPS influence the deposit through self-annealing and leads 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 towards segregation free splat solidification resulting in solute supersaturation and metastable phase formation.

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 VPS. 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 Ni-splats on copper substrates produced from both APS and VPS processes indicate enhanced flow behavior and spreading of a VPS splat compared to the APS 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 APS and VPS. 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 VPS, instead of the columnar grain structure, a columnar cell structure is observed. This microstructure is produced because of recrystallization occurring during VPS deposition, due to the high substrate temperature during VPS. The formation of a columnar microstructure during plasma spraying is well illustrated, Fig. 4, in the cross-section micrograph of an air plasma sprayed molybdenum.

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 APS and VPS nickel deposits both sprayed onto polished steel substrates, suggest a strong <200> texture in the coating. This is expected since <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.

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-scaled version of splat cooling. The splats undergo ultra-rapid quenching with cooling rates in excess of 10^{6}o/sec. 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. VPS 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*[5]

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 are usually applied by plasma spraying. TBCs have two prime requirements: they must insulate the component from the hot gases in the engine and they must also remain on the part for many thousands of hours. Thus, the most important thermal properties of TBCs are those relating to thermal insulation and those relating to the

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[5] Contributed by R.A.Miller and W.J.Brindley (NASA - Lewis Research Center, MS 24-1, Cleveland, OH 44135-3191)

thermal cycle durability. The thermal insulation of a coating layer is essentially a function of the thermal conductivity, thermal diffusivity, and total emissivity. These are, in turn, related to the coating's composition, thickness, and structure. TBC 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 coating's physical, chemical and mechanical properties, substrate properties and many other factors. Since advances in TBC technology have been paced by durability improvements, materials engineers have tended to focus on maximizing coating durability rather than minimizing conductivity. The following is a brief summary of TBC thermal properties with emphasis on the approaches used to assess and improve the durability of TBCs for gas turbine applications.

Testing of thermal barrier coatings

TBC 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 TBC durability. Added to this are uncertainties associated with our 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 TBC 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 are associated with laboratory testing of TBCs. 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 TBC 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 TBC 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 heated in a open flame, such as in a torch test. Nor is it generally realized that specimens having different emissivities will come to 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 come to 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 TBC evaluation. However, since 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, 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 TBCs tested in furnaces generally tends to match the behavior of TBCs 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.

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 TBC 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 TBCs for specific components and for predicting TBC lives. TBC life prediction was the intent of the NASA-sponsored Hot Section Technology (HOST) TBC programs.[13,14]. The HOST programs yielded models to predict the behavior of bill-of-material TBCs over a wide range of conditions. These models employed 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 we understand it. The models were calibrated against furnace and torch data that was 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 TBC 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 which 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 TBC failure were formulated about a decade ago and, unfortunately, remarkably little detailed knowledge of the failure process has been added since. One field of inquiry that has added to our understanding of the failure mechanism involves the study of non-linear material properties such as bond coat and ceramic stress relaxation.

Thermal properties

Once adequate TBC 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 the properties related to thermal insulation (thermal conductivity, thermal diffusivity, and total emissivity) although seemingly routine are 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.

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 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 of a reliance on engines tests and a stronger attempt to make use of thermal and stress models.

The current interest in using TBCs in a variety of heat engine applications has spurred extensive interest in the TBC 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*[6]

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 since 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

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[6] Contributed by C.C.Berndt (SUNY at Stony Brook, The Thermal Spray Laboratory, Stony Brook, NY, 11794-2275)

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 the 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.

Failure locus determinations

Another aspect of mechanical properties which is not clearly defined concerns the definition of the fracture locus, Fig. 9 There is still some confusion on 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 which 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, since 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 the 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.

Hardness tests

Hardness tests on coatings are also often performed. Caution needs to be exercised in reporting such results; especially if this property is used as a criteria for the acceptance of a particular coatings. 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 for thermally sprayed coatings is susceptible to large errors.

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 that would lead 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. FEED STOCK MATERIALS*[7]

Introduction

The quality of feed stock 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 be used as feed stock. The focus of this report will be on powder feed stock. 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 since complete characterization in terms of particle size, particle distribution, and chemical homogeneity may limit the use of the material.[24]

Production methods and quality assurance

The commonly used methods for producing thermal spray powder[25] are listed in Table 5. All these methods have distinct advantages or disadvantages which 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

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[7] Contributed by D.L.Houck (GTE Products Corporation, Towanda, PA 18848)

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 since 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 the particle size distribution. For example there is often a discrepancy between the particle size distribution of powders which are measured by a light-scattering technique (e.g., "Microtrac" apparatus) compared to that measured by an x-ray cross sectional absorption method (e.g., "Sedigraph" apparatus). It has also been reported that the resin binder of some agglomerated powders may dissolve under severe agitation during the powder size measurement; thus leading to misleading results. It is clear that powder size distributions must be treated with caution.

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 work place 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 where 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*[8]

Introduction

In its recent report on Materials Science and Engineering for the 1990's[27], a National Research Council panel stated as its leading recommendation for strengthening the field that emphasis should be placed on developing the linkage

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[8] Contributed by A.Goland (Brookhaven National Laboratory, Dept. of Applied Science, Upton, NY 11973)

between materials synthesis, processing, and performance. This implies an integrated approach to which plasma spray processing is ideally suited. The purpose of this summary 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.

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 upon concepts in many materials synthesis and processing practices.

Facilities at classify and measure porosity

Special techniques at Brookhaven constituting the core of the program will be 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 (so-named after the authors Brunauer, Deming, Deming, and Teller) adsorption isotherms[28] illustrate the complexity of porous media (Fig. 11; P^o is the condensation pressure), and underscore the importance of utilizing a variety of independent 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.

Fractal concepts of porosity

New ideas utilizing the fractal concept of materials have been applied to small-angle scattering by others[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 $6\text{-}D > 3$. 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}. [$I(q)$ 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*[9]

Introduction

Intermetallic materials are of great interest since, 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 Fe, Ni, and Co, molybdenum di-silicide, and a variety of composites.[34-41] The above materials must be sprayed under VPS 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.

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[9] Contributed by R.Neiser (Sandia National Laboratories, Process Metallurgy, PO Box 5800, Albuquerque, NM 87185)

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 to form macroscopic engineering sections is quite high.

The technology of spray forming is limited at present due to the low through-puts, of the order of kilograms per hour, for the current plasma torches. If higher throughputs can be attained then spray forming of ingots and other raw material stock would become possible. It is necessary to maintain the rapid solidification processing (RSP) character of the deposits since 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 1 atmosphere) 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 where 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 spray forming will be knowledge and control of residual stresses.

The Ni-16Al alloy - an example

The two phase alloy of Ni-16Al is an example of an intermetallic alloy that has been closely examined. 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 gcm^{-3} after 100h 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*[10]

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 non-destructive image of a thermal-spray coating is described here 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 quantities 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 since the pores may not be connected. Synchrotron CMT is an alternative technique which can be used to generate images of the morphology in transverse planes in a sample non-destructively. The limited x-ray brilliance from conventional x-ray tubes, however, generally makes the spatial resolution in CMT much worse than 20 micrometers, which is around the maximum size of pores observed by optical microscopy of thermal sprayed deposits. Synchrotron x-ray sources have orders of magnitude higher brilliance 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

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[10] Contributed by P.Spanne and K.W.Jones (Brookhaven National Laboratory, Dept. of Applied Science, Upton, NY 11973), H.Herman (SUNY at Stony Brook, The Thermal Spray Laboratory, Stony Brook, NY, 11794-2275) and W.L.Riggs (GE Aircraft Engines, Engineering Materials Tech. Lab., 1 Neumann Way, Mail Drop H-85, Cincinnati, OH 45215-6301)

implemented.

Computed microtomography methods

A CMT instrument which can be used for non-destructive microscopy down to a volume resolution of 5 x 5 x 5 micrometers has been developed at the X26 Microscopy Beam Line of the National Synchrotron Light Source.[46]. This instrument is ideally suited to detect voids in small (one mm or less) samples of thermal sprayed coatings. It has been used for a study of voids and material homogeneity in a whole 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 in 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]

An Example of computed microtomography

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 μm × 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 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 Figs. 12 and 13 demonstrate the usefulness of synchrotron CMT for investigation of the 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*[11]

It is difficult to summarize the diverse array of related fields that were addressed in this report. 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 report 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 thermo-fluid 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 <u>manufacturing</u> 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, contribute much to elevate the art of thermal spray to a science.

The report also highlights several areas of research that need attention. Thermal and mechanical property determination are essential for the design and specification of coatings for practical applications. In this fashion it may be possible to gain the full economic potential of thermal spray technology since 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 which 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 while the properties of bulk materials may provide the best guess for the properties of a coating with a similar chemistry; that there is no microstructural justification for such an assumption.

Another major impact of the symposium concerned the strong need for well-

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[11] Contributed by C.C.Berndt (SUNY at Stony Brook, The Thermal Spray Laboratory, Stony Brook, NY, 11794-2275)

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 non-destructive 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 the 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 discussion concerning 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 report, 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 (bar the conference program) were in the capable hands of one person. Thus this conference owes much of it's 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!

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FIGURE CAPTIONS

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 3,500K and nitrogen molecules at about 7,000K rapidly cools the plasma and constricts the isotherm plots for air and nitrogen environments as compared to argon. (from Ref. 2).

Fig. 2: Two-dimensional droplet velocity plot for aluminum wire sprayed with a wire arc plasma spray device. Since 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. (this figure is based on research described in Ref. 6).

Fig. 3. A schematic diagram to indicate the relationship between heat flow and microstructure for a molton particle as it rapidly cools down on impact against a substrate. (Adapted from Ref. 9.)

Fig. 4. Plasma sprayed molybdenum coating showing columar grain structure over the entire coating cross-section.

Fig. 5. An illustration showing morphology and texture development in plasma sprayed coatings. Refer to the text for further detail.

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

Fig. 7. Photograph of a Mach 0.3 burner rig being used to evaluate a carousel of four spinning cyclindrical TBC coated specimens.

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

Fig. 9. Schematic diagram which indicates the various failure loci of a tensile adhesion test specimen.

Fig. 10. A schematic figure to indicate the distinction between random and systematic cracking processes that are revealed by acoustic emission methods.

Fig. 11. Schematic representation of pressure vs volume adsorbed to indicate 5 classifications of porosity distributions. Each type of porosity distribution would be indicative of a different pore microstructure. The curves include adsorption mechanisms based on capilary condensation and interaction between the gas molecules and substrate.

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

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

TABLE 1. LIST OF SPEAKERS, AFFILIATIONS, AND TOPICS

1.	J.Heberlein (University of Minnesota)	The DC Plasma
2.	M.Boulos (Sherbrooke University)	The RF Plasma
3.*	M.Smith (Sandia National Laboratory)	Particle-Plasma Interactions
4.*	S.Sampath (GTE Chemical Products)	Deposit Formation Dynamics
5.	W.L.Riggs (GE Aircraft Engines)	Characterization Methods
6.*	P.Spanne (Brookhaven National Laboratory)	Microtomographic Methods for Microstructure Determination
7.*	R.Miller (NASA-Lewis Research Center	Thermal Properties
8.	C.R.Clayton (SUNY at Stony Brook)	Chemical Properties
9.*	C.C.Berndt (SUNY at Stony Brook)	Mechanical Properties
10.*	D.L.Houck (GTE Chemical Products)	Feedstock Materials
11.	R.Smith (Drexel University)	Adaptive Control
12.*	A.N.Goland (Brookhaven National Laboratory)	Porosity: An Integrated Approach
13.*	R.Neiser (Sandia National Laboratory)	Intermetallics

TABLE 2. SOME IDEAL CHARACTERISTICS OF THE PLASMA SPRAY PROCESS

A uniform, controllable velocity of particle upon impact.
A sufficient velocity to produce a high density deposit without "exploding" the molten or partially molten droplets upon impact.
A 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.

TABLE 3. SOLIDIFICATION PARAMETERS DERIVED FROM COOLING RATES

Material	Average Cooling Rate ^{o}K/sec	Heat Transfer Watts/m^2	Nusselt's Number (d=5 um)	Solidification Rate* cm/sec	G_l/R ^{o}Ksec/cm^2 (see note below)
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

* assuming no isothermal delay.

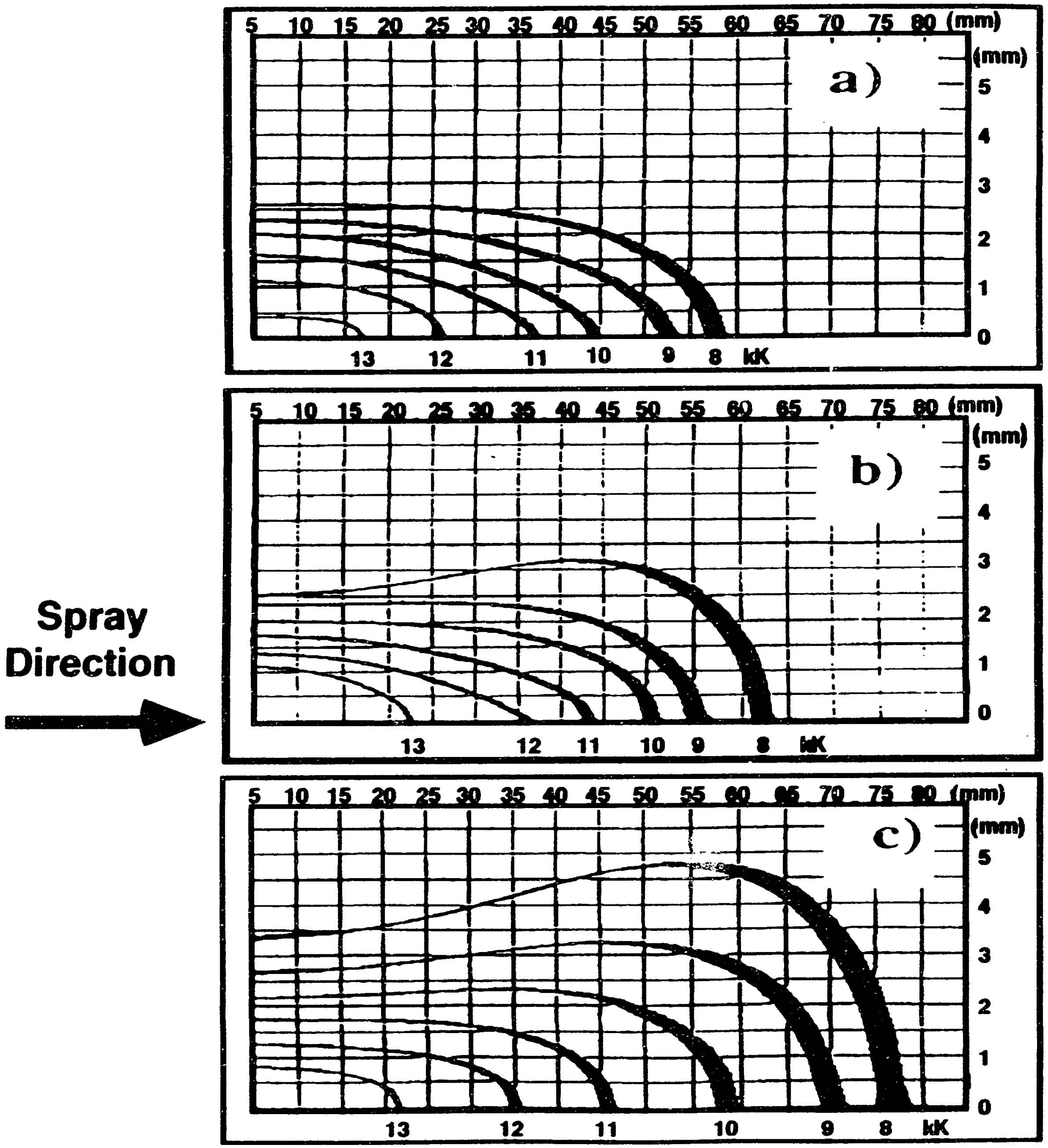
Note: G_l is the thermal gradient in the liquid, R is the solidification rate of the plane front. The ratio of G_l/R is the degree of constitutional supercooling during solidification.

TABLE 4. FEEDSTOCK CLASSIFICATION ACCORDING TO CHEMISTRY

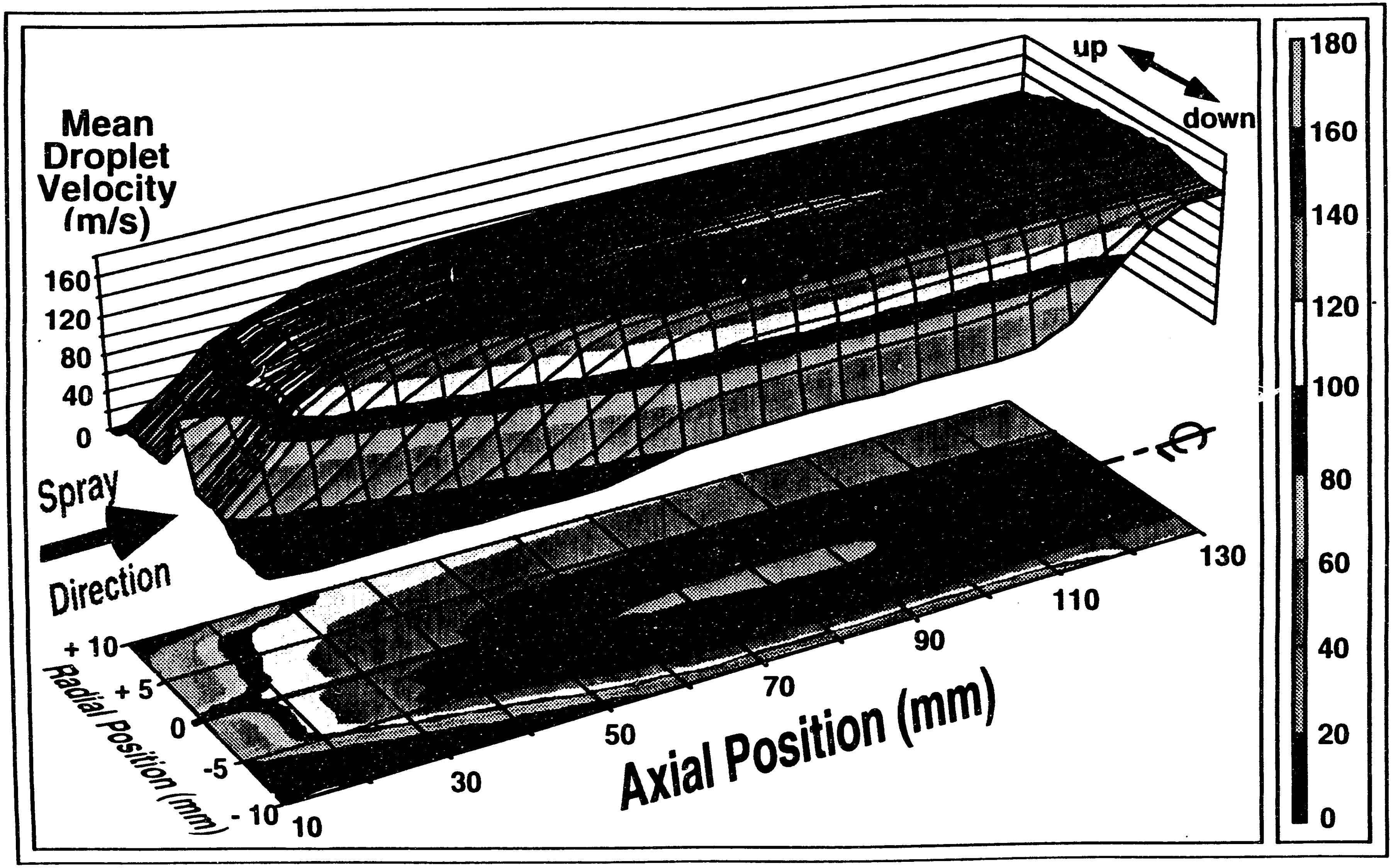
CLASSIFICATION	EXAMPLE OF MATERIAL CONSTITUENTS	
metallic alloys	MCrAlY's (M=Ni, Co, Fe)	
	Co-Cr-W-Co based stellites	
	Ni / Co based self fluxing alloys	
	Ni/Co-Cr-Mo-Si based Laves phase alloys	
	Ni Cr Fe based Inconels	
	Ni Cr Mo based Hastelloys	
	Cu based alloys (Cu-Zn, Cu-Al, Cu-Ni)	
metallic composites	**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 (where M is 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)	
non-metallic hard materials	oxides of Al_2O_3, Cr_2O_3, TiO_2, and ZrO_2	
	non-oxides of B_4C, SiC, and Si_3N_4	

TABLE 5. METHODS FOR 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 - classificaton
sizing - elutriation
sizing - screening
sol gel


Spray
Direction
a)
b)
c)
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 (mm)
(mm)
5 4 3 2 1 0
13 12 11 10 9 8 kK
Air
Nitrogen
Argon

Droplet Velocity Distribution
for Aluminum Wire Arc Plasma Spray



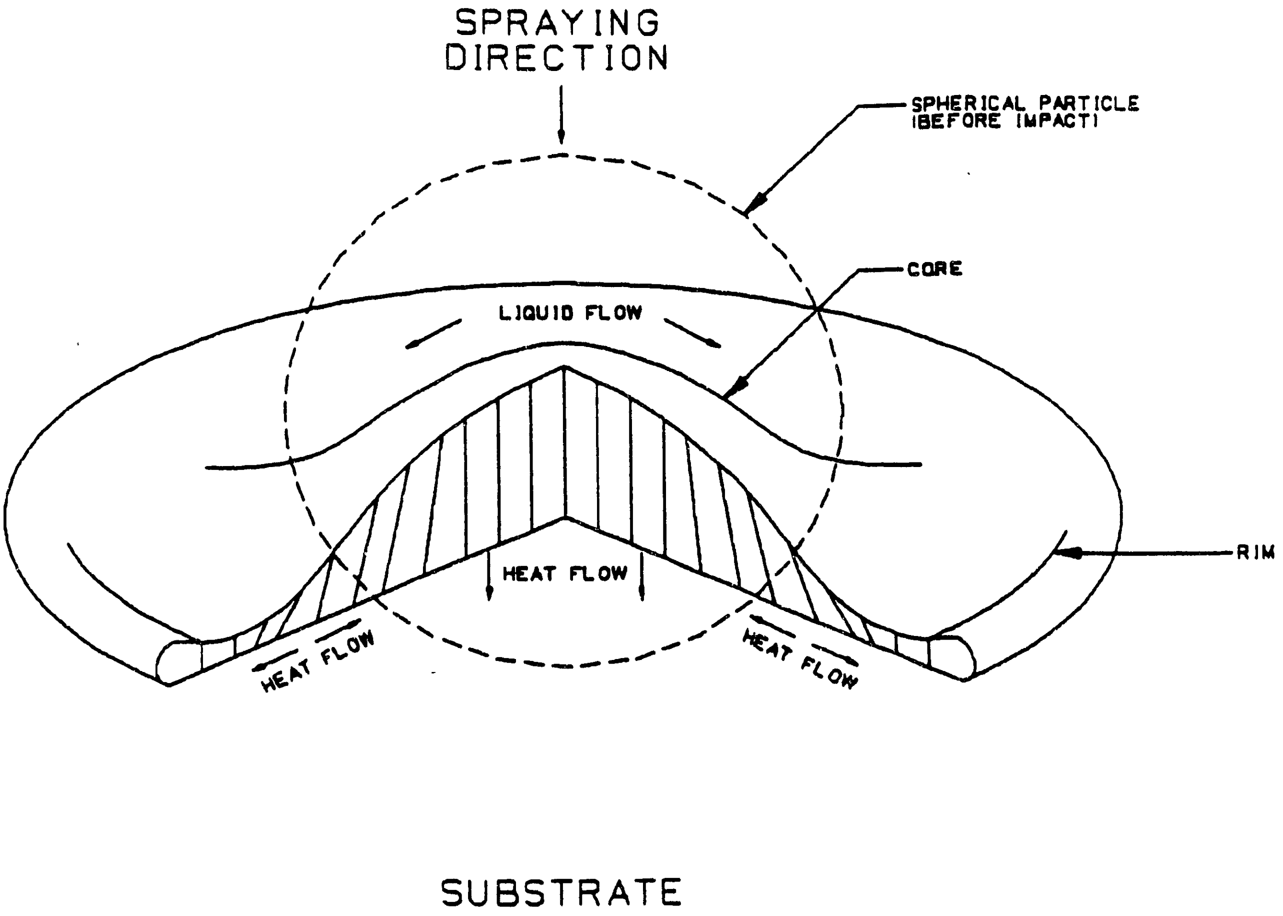

SPRAYING DIRECTION
SPHERICAL PARTICLE (BEFORE IMPACT)
CORE
LIQUID FLOW
HEAT FLOW
HEAT FLOW
HEAT FLOW
RIM
SUBSTRATE

Fig 3


10 µm

[illegible]

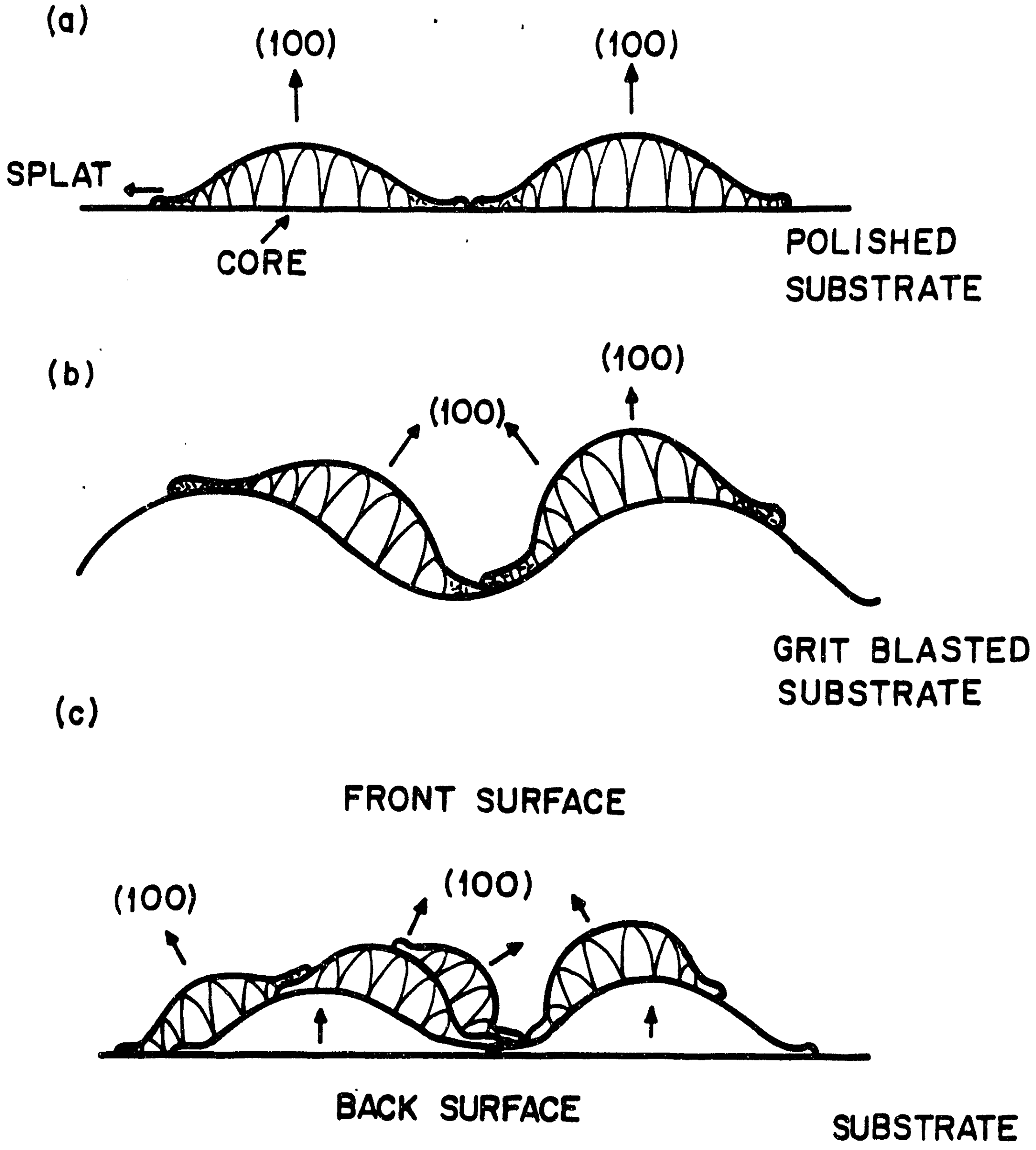
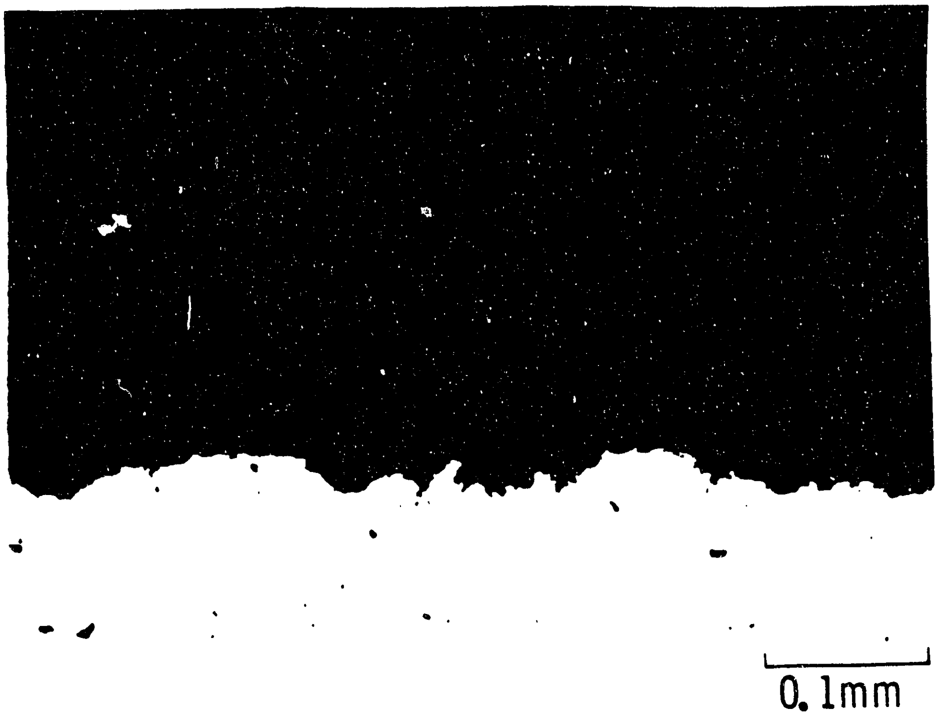
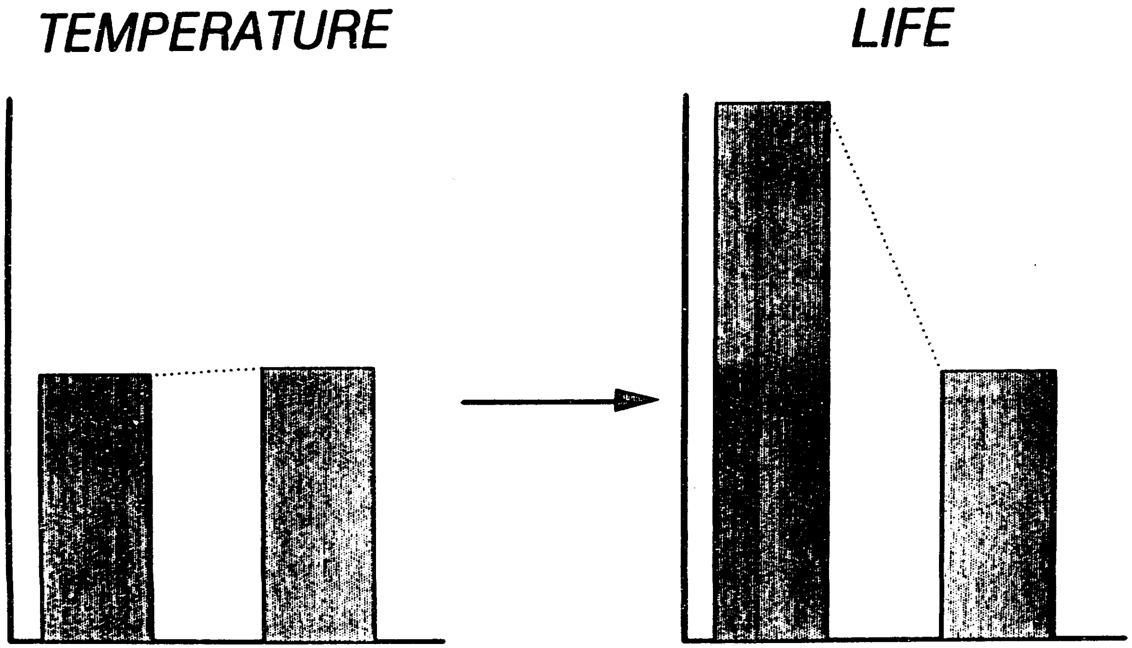
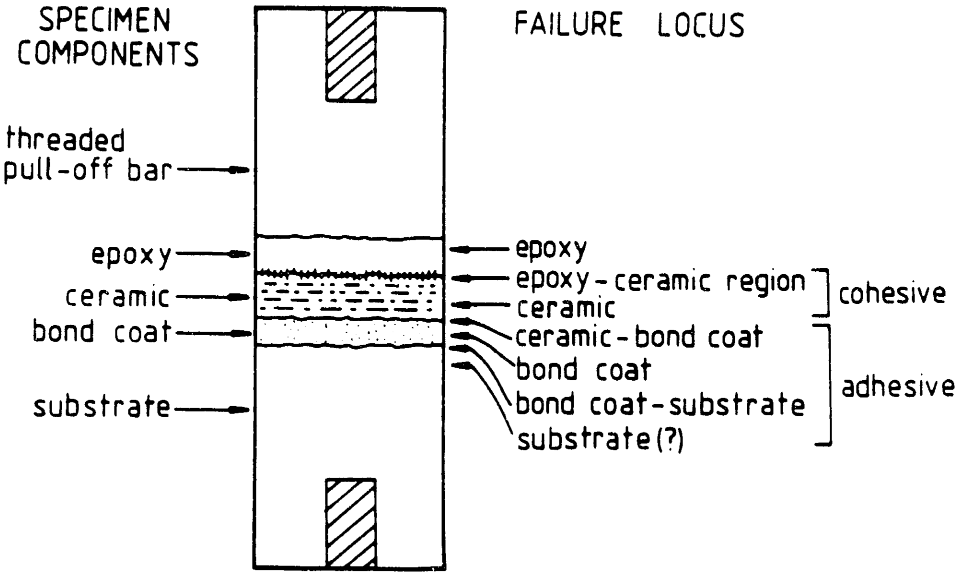

(a)
(100)
(100)
SPLAT
CORE
POLISHED SUBSTRATE
(b)
(100)
(100)
(100)
GRIT BLASTED SUBSTRATE
(c)
FRONT SURFACE
(100)
(100)
BACK SURFACE
SUBSTRATE

Fig 5

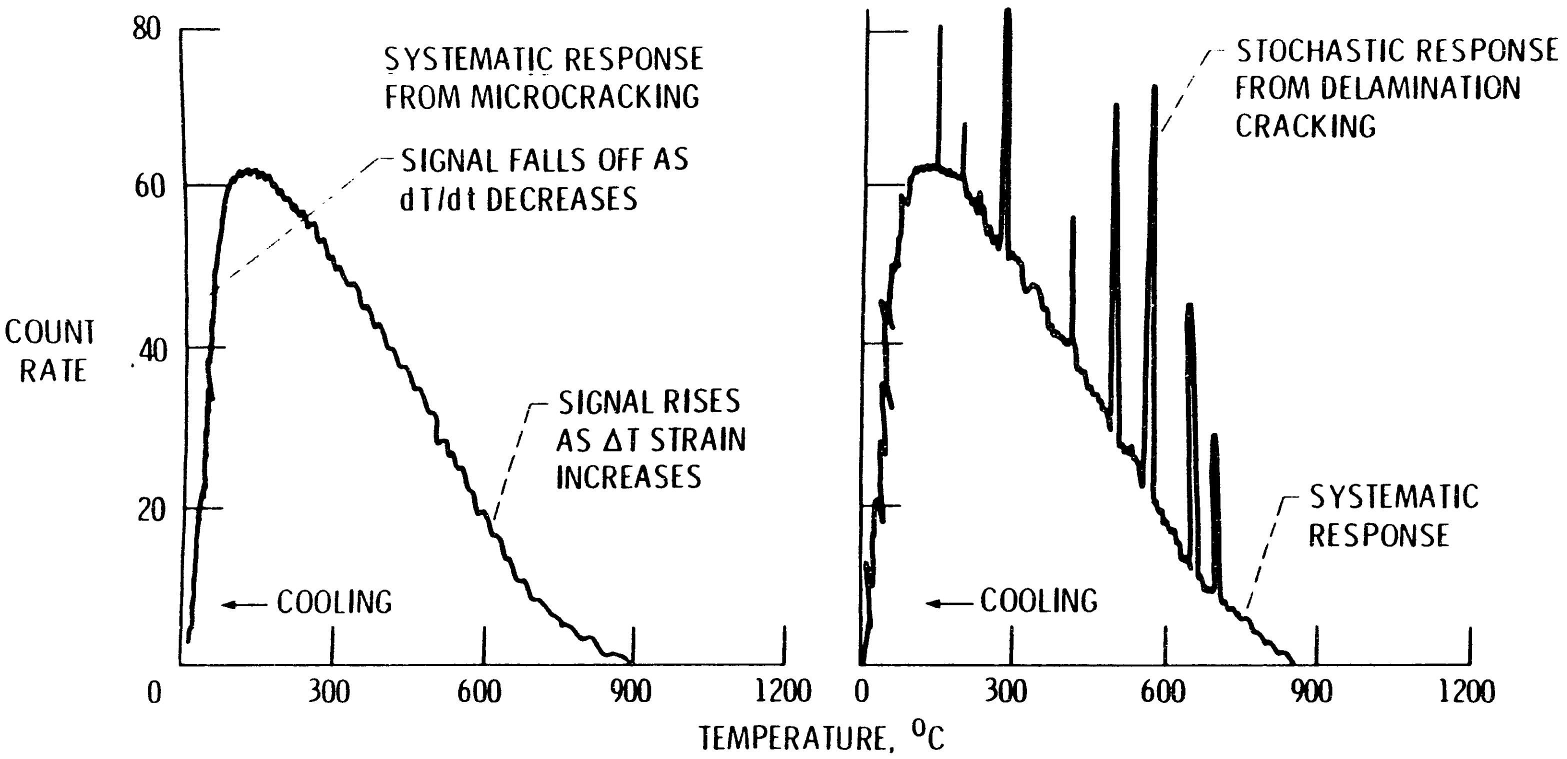

0.1mm

2% TEMPERATURE CHANGE ≈ 100% LIFE CHANGE




SPECIMEN COMPONENTS
FAILURE LOCUS
threaded pull-off bar
epoxy
ceramic
bond coat
substrate
epoxy
epoxy-ceramic region
ceramic
cohesive
ceramic-bond coat
bond coat
bond coat-substrate
substrate (?)
adhesive

SCHEMATIC OF AE EFFECTS

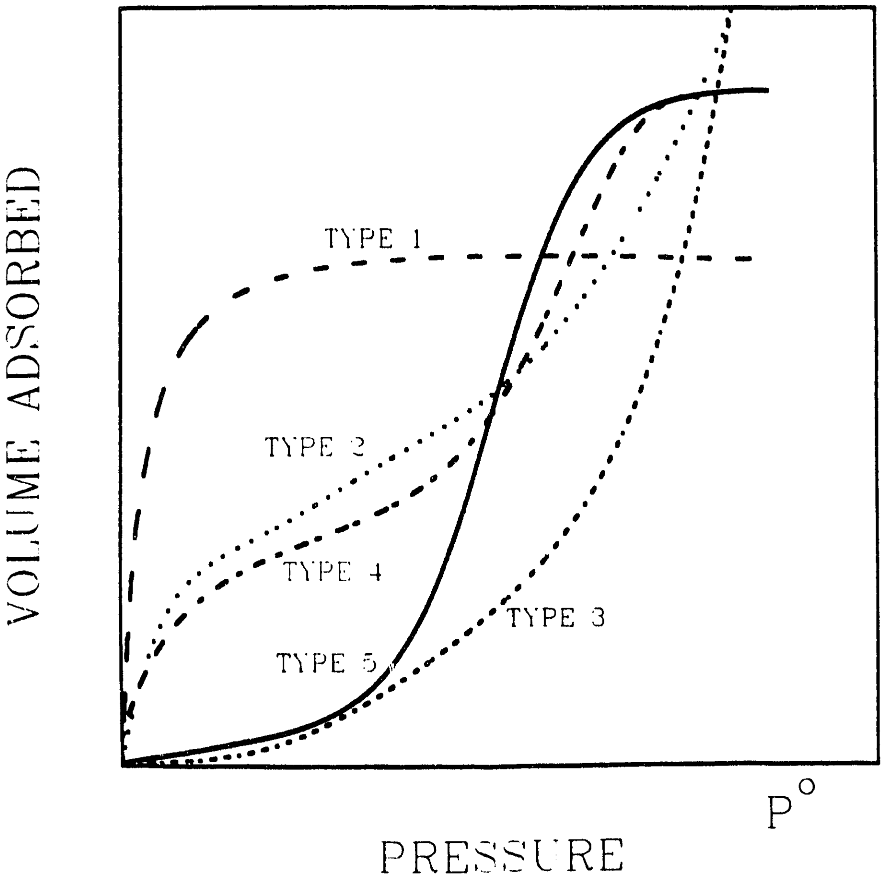


TYPICAL COOLING CYCLE

FAILURE DURING COOLING CYCLE

V-1979

CS-84-4291


VOLUME ADSORBED
TYPE 1
TYPE 2
TYPE 4
TYPE 3
TYPE 5
P°
PRESSURE

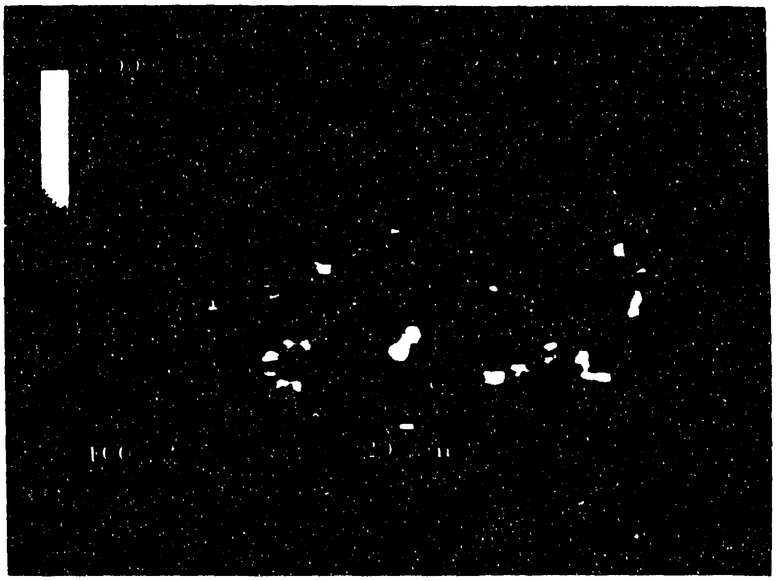


Figure 1

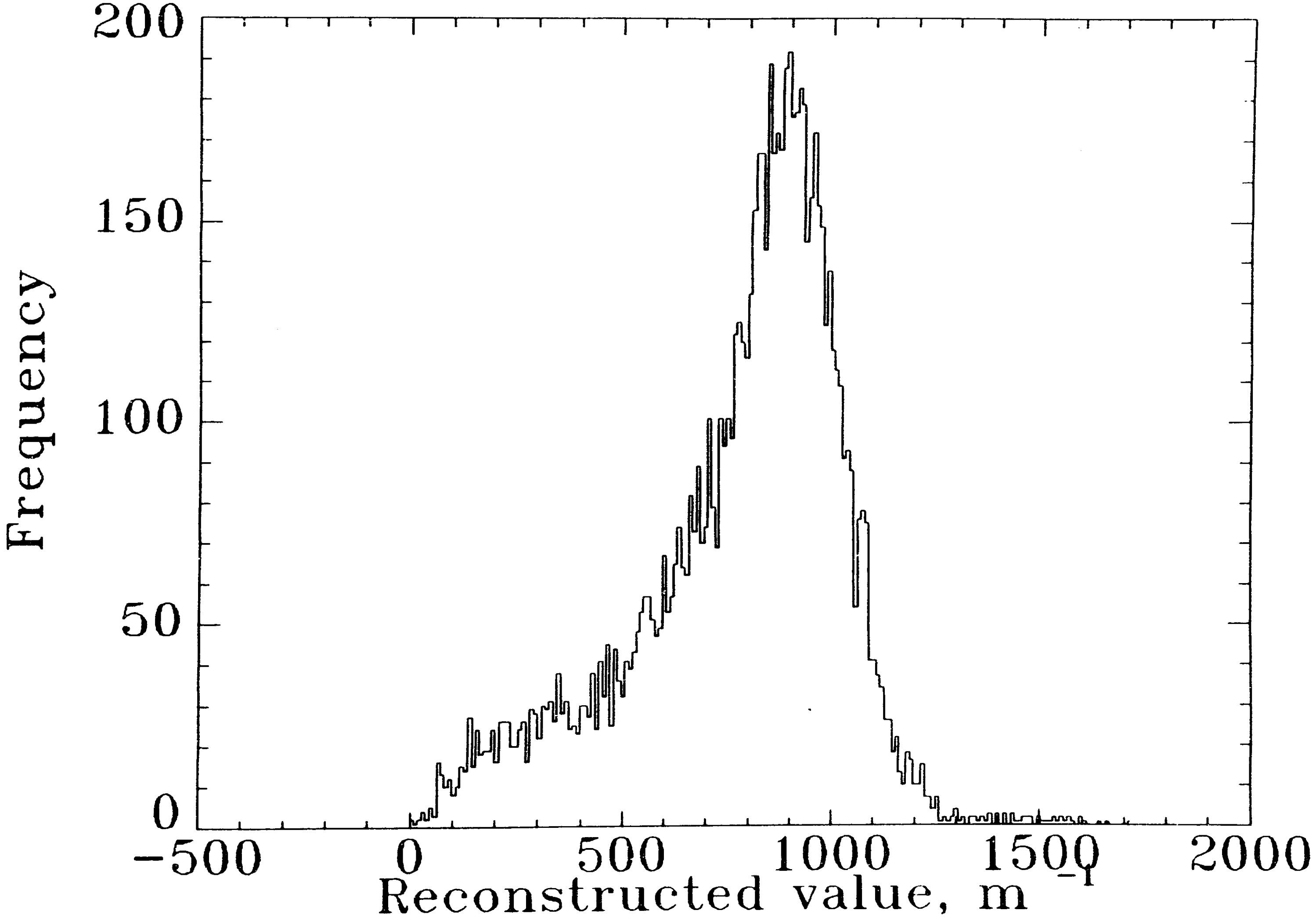

200
150
100
50
0
Frequency
−500
0
500
1000
1500
2000
Reconstructed value, m^{-1}

Figure 2

END

DATE FILMED

3/23/93