Thermal Spraying at the Materials Research Society Fall Meeting

The Fall '97 meeting of the MRS was held in Boston (MA, USA) from 1-5 Dec 1997. A special symposium (BB) was convened on the subject of "The Science and Technology of Thermal Spray Materials Processing." The Chairmen of Symposium BB were Herbert Herman (SUNY at Stony Brook), Emil Pfender (University of Minnesota), Richard Neiser (Sandia National Laboratories), and Richard Teets (General Motors R&D Center). The symposium was supported by Anval, Inc., Applied Materials, Inc., General Motors R&D Center, Praxair Specialty Ceramics, Sandia National Laboratories, Sulzer-Metco Inc., and TAFA.

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Each of the 54 papers presented in this symposium is identified with a unique paper code number and details of the nine sessions are provided in Table 1. An index allows specific authors to be located according to these codes.

1. Advanced Diagnostic Techniques for Thermal Plasmas and Thermal Plasma Spray Processing, by J.R. Fincke, W.D. Swank, D.C. Haggard, and S.C. Snyder, Optical and Plasma Physics, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID. Recent developments in the diagnostics of thermal plasma flow fields and injected particles in the thermal plasma spray process are reviewed. The plasma diagnostic techniques discussed are Rayleigh and coherent Thomson scattering, laser Schlieren, laser-induced fluorescence, coherent antiStokes Raman spectroscopy, and enthalpy probes. The quantities measured are heavy species and electron temperature, ionized fraction, plasma composition, and plasma velocity. Injected particle size, velocity, temperature, and number density are simultaneously measured by phase Doppler laser velocimetry, and high-speed two-color optical pyrometry. Measured particle parameters are contrasted with plasma flow field characteristics and the plasma-particle interactions discussed.

2. Diagnostics of In-Flight Particles under Thermal Spraying Conditions, by P. Gougeon and C. Moreau, Industrial Materials Institute, National Research Council of Canada, Boucherville, Quebec, Canada. The National Research Council of Canada has developed an optical integrated system aiming at improving the control of thermal spray processes. To achieve this goal, this system measures the thermal radiation of the in-flight sprayed particles passing in front of an optical sensor head located near the spray jet. After transmission by optical fibers, the particle thermal radiation collected by the sensor head is measured by near infrared photodetectors. The photodetector output signals are analyzed by PC-based software for particle recognition and measurement of particle parameters. The parameters measurable by using the integrated optical system are the particle velocity, surface temperature, size, and flux. In typical spraying conditions, the particle acquisition rate is higher than 50 particles/s. Depending on the optical system configuration, it is possible to measure particle velocities in the range of 30 to 1000 m/s. In this presentation, some examples will be given on the particle parameters measured during plasma, flame, and HVOF spraying. The range of particle velocities and temperatures reached in these processes are significantly different, which leads to a corresponding adaptation of the diagnostic system. In particular, when achieving particle diagnostics under plasma spraying conditions, it can be necessary to use selective bandpass filters in front of the photodetectors. Using these filters permits limitation of the influence of the intense radiation emit-

Table 1

Session	Title of session	Paper codes	Session Chairs
1	Processing Science A	1-9	H. Herman (SUNY at Stony Brook) C. Moreau (National Research Council Canada)
2	Processing Science B	10-17	R.A. Neiser (Sandia National Laboratories) R.E. Teets (General Motors R&D Center)
3	Processing Science A	18-25	J.R. Fincke (Idaho National Engineering and Environmental Laboratory) K.L. Hollis (Los Alamos National Laboratories)
4	Processing Science B	26-30	J.V.R. Heberlein (U. Minnesota) J. Ilavsky (Institute of Plasma Physics)
5	Science and Technology of Water Stabilized Plasmas	30-35	J.V.R. Heberlein (U. Minnesota) J. Ilavsky (Institute of Plasma Physics)
6	Near-Net Fabrication	36-40	E.J. Lavernia (U. California at Irvine) J.E. Smugeresky (Sandia National Laboratories)
7	Mechanical Properties A	41-43	D. Sordelet (Ames Laboratory) S. Suresh (MIT)
8	Mechanical Properties B	44-48	D. Sordelet (Ames Laboratory) S. Suresh (MIT)
9	Microstructures and Imperfections	49-54	A. Goland (Brookhaven National Laboratory) A.M. Vardelle (U. Limoges)

ted by the plasma gas and the sprayed material vapors on the particle temperature measurement.

3. Using Diagnostic and Modeling Tools to Optimize the HVOF Process, by R.A. Neiser and M.F. Smith, Sandia National Laboratories, Materials and Process Sciences Center, Albuquerque, NM. Noninvasive diagnostic techniques combined with numerical and analytical models greatly enhance our understanding of thermal spray processes. These tools provide an excellent means for improving the robustness of the process and the quality of the sprayed deposits. This paper presents results generated during a cooperative research and development agreement (CRADA) between Sandia National Labs and General Motors that studied a high-velocity oxygen-fuel (HVOF) process for depositing wear-resistant cylinder bore coatings in aluminum automobile engines. The paper discusses how particle diagnostic tools and statistical and analytical models were used to characterize and optimize the process. Wire melting, droplet atomization and acceleration, particle heating in-flight, and the influence of processing parameters on particle size, temperature, and velocity are discussed.

4. Physics of Atomization, Spray Dynamics and Impaction in Spray Processes, by N. Chigier, Spray Systems Technology Center, Carnegie Mellon University, Pittsburgh, PA. Initial spray conditions are characterized by probability density functions of drop size, velocity, number density temperature, and flux intensity gas streams. These point pdfs change as a function of downstream and transverse location in the spray under the influence of atomization, coalescence, vaporization, dispersion, drag, and interaction with high-turbulence intensity gas streams. Differential velocities between drop and gas streams and interdrop interactions result in drop accelerations, decelerations, deflections, and recirculation. A complete control of the impaction process requires control of the spray characteristics during the process of impingement and gas flow deflection. The final deposit is directly dependent on the particle size, velocity, temperature, number density, and flux in the spray immediately prior to impaction. Nonuniform thickness and densities of deposit can be traced to nonuniformities in spray characteristics. The Spray Systems Technology Center at Carnegie Mellon University studies the fundamental physical processes of atomization, spray dynamics, and combustion of sprays with a wide range of industrial applications including combustion in gas turbine, rocket, and automobile engines, spray painting of automobiles, molten metal coatings and spray forming, agricultural spraying, inhalation therapy for respiratory illnesses, pharmaceutical spraying of tablet coatings, etc. Detailed measurements are made in sprays using image analysis, laser diffraction, and phase Doppler interferometry. Measurements are made of single drop size, velocity, and temperature in situ at "points" in the spray. Individual drop measurements are made in 1 μs, yielding very detailed and accurate size, velocity, and temperature distributions and associated number density, flux, and time of arrival measurements. These measurements provide insight to fundamental physical processes and lead to formulation of physical models for highly complex computer codes. The predictions are subsequently validated by the measurements.

5. In-Flight Particle Measurements within a Twin-Wire Electric Arc Spray Plume, by D.L. Hale, D.W. Swank, and D.C. Haggard, Lockheed Martin Idaho Technologies Company, Idaho Falls, ID. A real-time, nonintrusive measurement technique was successfully applied to a TAFA Inc. Model 9000 twin-wire electric arc thermal spray system to simultaneously measure particle size, velocity, and temperature within the spray plume. The purpose of these experiments was to gain an understanding of the physics of the particle-laden spray flow field produced by a twin-wire electric arc spray (TWEA) system. Aluminum wire was sprayed with parametric variations of current from 100 to 300 A and gun pressure (air flow rate) from 40 to 75 psia. For all cases, the average diameter of the molten aluminum particles range from 26 to 52 μm, with the largest particles concentrated at the center of the spray. As the molten metal is stripped from the wires and transported downstream, the droplets initially break up and the smallest particles are flung to the edges of the spray. As expected, the largest velocities and temperatures are found at the spray center due to entrainment from the quiescent, room temperature air. The particles accelerate to peak velocities between 130 and 190 m/s, then decelerate slightly as they travel downstream. The particles exhibit high superheat, with average centerline particle temperatures ranging from 2004 to 2056 °C, and the temperature profile remains fairly flat throughout transport to the substrate. A stagnation pressure probe was used to characterize the gas-flow regime and shock structure in the plume without particles. The wires were found to have a pronounced effect on the flow, resulting in a complex three-dimensional flow field with mixed regions of subsonic and supersonic flow.

6. Particle Temperature Measurements in a HVOF Thermal Spray by Two Color Radiant Emission Pyrometry, by W. Yu and B.M. Cetegen, Mechanical Engineering Department, University of Connecticut, Storrs, CT. Thermal spray process diagnostics is vital in facilitating an improved understanding of thermal spray processes and controlling of coating quality deposited by thermal sprays. Key process parameters such as temperature, size, and velocity of thermally sprayed particles have been known to influence coating deposition characteristics and their longevity at their operating environment of high temperature and high mechanical and thermal stresses. Within the work described here, a two-color pyrometer system was first custom-designed utilizing two emission wavelength bands centered around 600 and 700 nm. The pyrometer system was calibrated using a black-body radiation source and a tungsten ribbon lamp before its application to the thermal spray characterization The calibrated pyrometer was used to measure the particle temperatures of various materials sprayed by a commercial HVOF spray system. In these experiments, chromium carbide, stainless steel, ordinary tungsten carbide-cobalt and nano-agglomerated tungsten carbide-cobalt particles were sprayed. Measurements show that the average particle temperature decays with increasing axial distance away from the stoichiometry (or the oxygen-fuel mixture ratio), with highest temperature levels being reached near-stoichiometric conditions. Particle temperatures tend to have a wider range in the early stages of flight towards the substrate, but this range narrows with increasing downstream distance. Nano-agglomerated WC-Co particles show somewhat different temperature behavior from those of ordinary microsized WC-Co particles, which may be attributed to the differences in their microstructure.

7. HVOF Particle Velocity and Temperature and their Relationship to Coating Properties, by S.R. Bekofske and G.S. Settles, The Pennsylvania State University, University Park, PA. Little is currently known of the relationship between HVOF particle temperature and velocity and the properties of the resulting coating. It is useful to have the ability to tailor the kinetic and thermal energy state of sprayed particles to yield certain desired coating properties. Here, particle streak velocimetry and two-color pyrometry are used to measure the particle kinetic and thermal state in flight. Control of these properties over certain ranges has already been demonstrated in our prior work. In the present paper, corrosion-resistant coatings are sprayed and analyzed by metallography and other techniques to determine several pertinent coating parameters. By varying the in-flight particle state, a range of different coating properties is observed. An attempt is then make to define physical relationships among HVOF spray gun parameters, particle thermal and kinetic properties, and the properties of the resulting coatings. This knowledge is expected to contribute both fundamentally and practically to thermal spray technology.

8. Computational Fluid Dynamics Modeling of the High-Velocity Oxygen-Fuel (HVOF) Thermal Spray Process, by B. Hassan, W.L. Oberkampf, and A.R. Lopez, Sandia National Laboratories, Aerosciences and Compressible Fluid Mechanics Department, Albuquerque, NM. An overview of recent computational modeling of the high-velocity oxygen-fuel (HVOF) thermal spray process is presented. The analyses presented are based on the application of computational fluid dynamics (CFD) to solve for the combusting, two-phase, gas and particle flow inside and outside of a HVOF thermal spray torch. Steady-state CFD results are presented and discussed for both axisymmetric and three-dimensional devices used for a variety of coating applications. The gas dynamics of the HVOF process involve the solution of the Navier-Stokes equations for a compressible, reacting, and turbulent gas/particle mixture. The hydrocarbon-air combustion process is modeled using both instantaneous and single-step finite rate chemistry models. A Eulerian-Lagrangian technique is used to couple the fluid dynamics of the combusting gas flow to that of the particles. An implicit, iterative, finite volume numerical technique is used to solve the coupled conservation of mass, momentum, and energy equations for the gas and particulate (solid and liquid) phases in a sequential manner. Details of the reacting gas flow fields and the particle dynamics are presented and discussed for various operating conditions. In addition, the CFD results are compared with experimental measurements of pressure inside the HVOF device and laser velocimetry measurements of the particles in the high-speed jet external to the device.

9. Controlling the Plasma Spray Process: Practical Issues and Possible Solutions, by D.E. Crawmer, Praxair Surface Technologies, Appleton, WI. This presentation focuses on the level of plasma spray technology as it is generally practiced. Emphasis is placed on what is right and wrong with specifications, materials, and processes. Potential solutions/directions to present and future needs are offered. Today's thermal spray industry, plasma spray specifically, is living with the legacy of thirty years of ill-defined coatings and materials specifications. Coupled with that problem is a user base which, generally speaking, has failed to advance as rapidly as has technology. Apart from an elite group of service shops, job shops, and captive (OEM) shops, the industry has evolved little in three decades. New tools, which are in development, have the potential to revolutionize the thermal spray industry. However, in their present form, these control and measurement devices are intrusive and expensive. Some truly adaptive controls and advanced measurement devices are commercially available, but much work remains to be done. In spite of the above issues and limitations, for the present, thermal spray remains a powerful tool for materials processing and design engineers. To remain competitive, the thermal spray community at large must begin in earnest to address these concerns.

10. Intelligent Control in Thermal Spray Processes, by C. Moreau, P. Gougeon, L. Leblanc, M. Prystay, M. Viens, A. Blouin, D. Drolet, and J.-P. Monchalin, National Research Council Canada, Industrial Materials Institute, Boucherville, QC, Canada. Consistency and reproducibility of the physical properties of coatings are among the most important characteristics of thermally sprayed materials currently being used in some demanding applications. Spraying the same coating, day after day, on the production line becomes a key factor for success in these critical applications. To achieve this goal, not only the sources of variability in the deposition processes must be identified, but also their influence on the coating properties must be understood and eventually minimized on the production line. In this presentation, we review some recent developments on sensors for monitoring the state of key spray parameters such as the temperature and velocity of the sprayed particles and the substrate temperature during spraying. The influence of these parameters on the characteristics of the coatings are emphasized. We discuss also techniques for nondestructive testing of the deposited coatings based on laser-ultrasonics and thermography.

11. Closed-Loop Feedback Control of the Thermal Spray Process, by J.R. Fincke, W.D. Swank, and D.C. Haggard, Optical and Plasma Physics, Idaho National Engineering Laboratory, Idaho Falls, ID. The implementation of closed-loop control requires the direct real-time monitoring of process performance, via real-time sensing of particle temperature and velocity and the taking of corrective actions rather than the traditional approach of setting process variables and post-process examination. A real-time digital controller that is capable of setting and maintaining particle velocity and temperature at designated set points is developed and demonstrated on a plasma spray process. The ability to adjust particle impact velocity over a range of 80 to 120 m/s while maintaining a constant particle temperature and to vary particle temperature by 500 K while maintaining a constant particle velocity are demonstrated.

12. Transport Phenomena and Reaction Rates in the Impact and Solidification Processes of Plasma-Sprayed Droplets, by A. Vardelle, University of Limoges, Laboratoire Materiaux Ceramiques et Traitements de Surface, Limoges, France. In the plasma spray process, when particles impinge on the substrate, they undergo severe deformation and rapid solidification. Particle spreading determines the geometry of the resulting splat and porosity formation while the cooling process controls the cooling rate, selection of crystalline phases, crystal growth, and thus the microstructure. The transient behavior of the molten droplet in the flattening and freezing processes controls the quality of the contact between the splat and the underlying layer, and the properties of the coating. The need for final products with closely controlled and reproducible properties requires that the design and control strategy of thermal spraying methods be based on a broad understanding of the transport and chemical reaction phenomena that occur during the residence of particles in the plasma jet and after impact on the substrate. This paper examines the role of the parameters of both particles at impact and substrate on splat formation and the properties of coating. This is done in light of transport phenomena theory and experimental evidence, by considering the formation of splats and the solidification and overlaying of splats that form the final coating.

13. Modeling of Microstructure Development of a Single Splat in Plasma Thermal Spray Deposition, by G.-X. Wang and V. Prasad, Process Modeling Laboratory; S. Sampath and H. Herman, Center for Thermal Spray Research, State University of New York, Stony Brook, NY. In plasma thermal spray deposition, millions of molten particles impinge on a solid substrate to form a coating or a deposit layer, whose properties are ultimately controlled by the microstructure of individual splats formed and by the bonding and connection between the splats. It is, therefore, essential to understand the microstructure formation mechanism of each individual splat. We have developed an integrated method for modeling the microstructural development of a single splat on a solid substrate or a predeposit layer. This method is based on a one-dimensional heat and mass transfer model, but including the classic nucleation theory, the nonequilibrium crystal growth kinetics, and the linear stability theory of a planar interface. The model calculates the nucleation rate from which one can determine the nucleation temperature, grain density, and size distribution at the end of the nucleation. The kinetic melt undercooling is introduced at the solid/liquid interface based on linear crystal growth kinetics. The solidification morphology, i.e., planar or dendritic, is determined by comparing the model predicted solid/liquid interface velocity with the absolute stability velocity obtained from the stability theory. Once dendritic morphology is selected, the heat transfer model introduces the dendrite tip growth kinetics based on a single dendrite tip growth model available in the literature, which includes the solute diffusion around the tip, capillarity undercooling, and kinetic undercooling. The marginal stability criterion is used to determine the dendrite tip velocity and the tip radius. A supplement microsegregation model with local recalescence and solute trapping is also employed to calculate the solute redistribution and solute segregation. This integrated model has been applied to investigate the microstructure development in thermal sprayed AlCu, molybdenum, and Al_2O_3 splats under varying process conditions. Selected results are presented to explain the controlling mechanisms of structure formation in plasma thermal spray. This work was supported by the MRSEC Program of the National Science Foundation under Award No. DMR-9632570.

14. Experimental Investigation of Droplet Spreading on Substrate During Plasma Thermal Spray, by X.Y. Jiang, S. Sampath, and G.-X. Wang, Center for the Thermal Spray Research, Department of Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, NY. Spreading of molten ceramic or metallic droplets is the first step of coating buildup on the substrate in thermal spray. The comprehensive understanding of the spreading and solidification process is important for controlling coating microstructure and, therefore, the coating properties. In this experimental study, the spreading behavior of molybdenum and PSZ droplets are investigated. The morphologies of the splats, ranging from starlike with severe splashing to regular disklike shape are sensitive to the process conditions such as plasma parameter, distance between the nozzle and the substrate, particle size substrate materials and temperature. The formation mechanism of different splat morphologies and the droplet splashing pattern is suggested in relation to the process parameters. The flattening ratio and the thickness of the disklike splats are measured quantitatively and compared with the values predicted by existing models. The interaction between the splat and the substrate is discussed on the basis of the observed splat morphologies and heat transfer modeling. This work was supported by the MRSEC Program of the National Science Foundation under Award No. DMR-9632570.

15. Systematic Studies of Splat-Substrate Interactions by Scanning Electron Microscopy, by T. Chraska, J. Birs, and A.H. King, Department of Materials Science & Engineering, State University of New York, Stony Brook, NY. The adhesion of thermal sprayed coatings to their substrates is determined by the properties and morphology of the splats that compose the first layer of the coating. Therefore, a detailed study of single splats has been conducted. Molybdenum was sprayed on four different polished substrates (steel, copper, aluminum, and glass) preheated to three different temperatures (room temperature, 200 °C, and 400 °C). Specimens were examined in plan view and cross section using SEM and the specimen chemistry was determined by EDS. A number of very different morphologies (e.g., pancake-, flower-, craterlike) has been observed depending on the material and temperature of the substrate. Generally, more splats remained on substrates preheated to the highest temperature. Cracks extending from the splat to the glass substrate or deformation of metallic substrates in the direction of impact were observed, but no signs of alloying were detected. Yttria-stabilized zirconia was sprayed on steel with and without single splats of bond coat (NiCrAl), at room temperature. Powders with four different particle sizes were used. Preliminary results indicate that adhesion of YSZ splats to steel without the bond coat is negligible, and the nature of the bond coat effect is demonstrated in our micrographs. This work is supported by the National Science Foundation MRSEC grant No. DMR 9632570.

16. Transport Phenomena in Droplet-Based Manufacturing Processes, by E.J. Lavernia, Department of Chemical Engineering and Materials Science, Department of Mechanical and Aerospace Engineering, University of California, Irvine, CA. In an effort to optimize the microstructure and physical properties of advanced structural materials, such as composites, a variety of novel manufacturing techniques have evolved over the past few decades. Among these, thermal spray processes offer the opportunity to combine the benefits associated with fine particulate technology (e.g., microstructural refinement, alloy modifications, etc.,) with in situ processing, and in some cases, near-net-shape manufacturing. The manufacture of composite coatings using droplet processes, for example, typically involves the mixing of reinforcements and matrix under highly nonequilibrium conditions, and as a result, these processes offer the opportunity to modify the properties of existing alloy systems and to develop novel alloy compositions. In principle, such an approach will inherently avoid the extreme thermal excursions, with concomitant macrosegregation, normally associated with more classical casting processes. Furthermore, droplet-based processes also eliminate the need to handle fine reactive particulates, normally associated with powder metallurgical processes. In this study, the interrelationship among transport phenomena and the resulting microstructure and mechanical behavior of various thermal sprayed materials are highlighted and discussed. The nucleation phenomena that are associated with the coinjection of ceramic particulates into atomized metal droplets are studied using finite difference analysis. Classical nucleation theory, together with thermal interactions between particulates and droplet, are then used to predict the onset temperature for nucleation. In addition, recent results pertaining to droplet deformation are discussed and compared to those anticipated from currently available theoretical models, paying particular attention to the synergism between transport phenomena and microstructure.

17. Modeling of Spreading and Solidification of Molten Droplets on a Cold Substrate, by H. Zhang, V. Prasad, and S. Sampath, State University of New York, Center for Thermal Spray Research and Process Modeling Laboratory, Stony Brook, NY. Several models have been developed based on the deforming finite-element method with adaptive grid generation and finite difference based volume of fluid (VOF) technique to study the spreading and solidification of splat(s). Both schemes have their own advantages in modeling the spray coating processes. The deforming finite element scheme is more accurate in the tracking of the free surface and solidification interface. However, it is very difficult to handle free surface merger and separation. The phenomena of splashing can be better studied using the VOF or other capturing scheme. To alleviate these problems and build a numerical model capable of handling all aspects of the spray coating process, we have developed a high-resolution numerical scheme based on the finite volume front tracking method and level set formulation (LSF). This model can predict more accurately the melt/solid interface shape and its dynamics due to the use of the front tracking scheme. The contact resistance and kinetics of solidification can also be taken into account by using this scheme. The deforming shape of the splat's free surface is captured by the curvilinear level set function, which is able to simulate the free surface oscillations, merger, and separation. Spreading and solidification of one and two nickel droplets on a cold nickel substrate are modeled, and the effect of the splat temperature, velocity, surface tension, and rate of substrate cooling have been investigated. The simulation begins at the time when the molten droplet comes in contact with the substrate until the entire droplet(s) has been solidified or the deposit layer has been formed. The results have been compared with the analytical solutions of Madejski as well as with experimental data.

18. Extending the Range of Plasma Spraying: Low-Pressure Fine Particle Spraying, by J.V.R. Heberlein, H.C. Chen, N. Rao, S. Girshick, and P. McMurry, University of Minnesota, Dept. of Mechanical Engineering, Minneapolis, MN. In the adaptation of the thermal spray process to the generation of coatings with specific materials properties, two new approaches are being investigated that extend the parameter range that is conventionally being used in plasma spraying. In the low-pressure central-injection spray process, fine powders (10 to 30 μm diameter) are injected into the plasma formed by three plasma jets from three independently operated torches in an environment of 50 torr. This process has been demonstrated to yield yttria-stabilized zirconia films with a porosity less than 0.5%, which are impermeable at a thickness of 30 μm. The films have been evaluated as dielectric layers in a solid oxide fuel cell. The second process, hypersonic plasma particle deposition, involves the synthesis of nanosize particles in a plasma jet that is subsequently quenched through acceleration in a supersonic nozzle, acceleration of these particles to hypersonic speeds and deposition on a substrate in front of the nozzle. On-line measurement of the particle size distributions show that the distributions peak around 10 nm. Deposition of these particles using this process has shown to yield films with nanosize structures of silicon and silicon carbide. These new processes are compared with conventional plasma spraying and with other emerging plasma coating processes.

19. Kinetic Spray Coatings, by J.R. Smith, T.H. Vansteenkiste, R.E. Teets, and J.J. Moleski, General Motors R&D Center, Warren, MI. Coatings can now be made from powders via a high-velocity spray technique without the requirement of melting or thermally softening the powders prior to impingement onto the substrate. Not only is the process simplified by not requiring arcs, flames, or plasmas, but also desirable coating properties such as low oxide content and low thermal stress can be obtained. In this process the powders are entrained in a gas, which is usually air, and accelerated through a nozzle. Mechanisms by which this kinetic energy source can yield good coatings are discussed. The optimization of coating properties by variation of process parameters are also described for coatings including elements such as copper, aluminum, and iron.

20. Microstructural and Physical Characteristics of Copper Deposited by Cold Gas-Dynamic Spraying, by R.C. McCune, O.O. Popoola, E.L. Cartwright, and W.T. Donlon, Ford Motor Company—Ford Research Laboratory, Dearborn, MI. A technique for developing thick metallic layers using relatively low-temperature, high-velocity spray nozzles has been reported by Alkbimov, et al. (1990). An exploratory study of this process was subsequently undertaken by a consortium of companies organized under the National Center for Manufacturing Sciences (NCMS). This paper reports on outcomes of that program as related to the development of high-purity copper deposits produced by cold gas-dynamic spraying. The utility of thermally sprayed copper metallizations for electrical applications is often limited by the purity of the deposit, which may be degraded by formation of oxides, voids, or other inhomogeneities that are a consequence of the high temperatures used in arc, flame, or plasma processes. This work reports on coatings produced from two different starting copper powders: one manufactured by direct reduction, having a large fraction of surface oxide coverage, the other produced by gas atomization, being more regular and limited in the extent of surface oxidation. The microstructural aspects of the two resulting coatings are compared at the level of optical, scanning, and transmission electron microscopy. Mechanical and physical properties were obtained through use of microhardness, electrical conductivity, Young's modulus, and residual stress measurements. Results of studies on the microstructural evolution and damage reduction during annealing are presented.

21. Plasma Spraying Using the Supersonic Induction Plasma Torch, by K. Mailhot, F. Gitzhofer, and M. Boulos, Plasma Technology Research Centre, Department of Chemical Engineering, Universite de Sherbrooke, Sherbrooke, Quebec, Canada. Induction plasma technology has long been known for its potential use in materials processing whether for powder densification and spheroidization, reactive in-flight processing of materials, or the plasma deposition of protective coatings and near-net-shape parts. Its principal features are the absence of electrodes, which results in the great flexibility that it offers for the control of the chemical composition of the atmosphere under which the treatment takes place. Reactive plasma deposition is a typical example where the chemical nature of the material deposited differs from that of the feedstock. Examples reported in the literature include the deposition of tungsten carbide using a feed of tungsten powder and methane as powder carrier gas. Titanium carbide is another example where the reaction between the titanium feed and methane used as powder carrier gas takes place in-flight in the plasma. Common to all these applications is the characteristic feature of induction plasmas, which is known to be a low-velocity plasma allowing for a long contact time between the feed material and the plasma. In the present investigation, induction plasma technology is taken one step further through the attachment of a supersonic laval type nozzle to a standard induction plasma torch. Materials processed in such a torch benefits from this added feature, which results in the tremendous acceleration of the particles at the exit of the torch prior to their impact on the substrate without sacrificing the inherent, above listed, features of induction plasma technology. Examples are given in this paper of different oxide ceramic coatings that were obtained using this technique. These exhibit excellent microstructural properties.

22. Improved Thermal Spray Processes for Production of Complex Multilayer Structures, by R.H. Henne, Institute für Technische Thermodynamik, DLR-Stuttgart, Stuttgart, Germany. One of the most challenging tasks for thermal spray technology represents the fabrication of the very complex multilayer structure of solid-oxide fuel cells (SOFC) by thermal spray processes. SOFCs can play an important role in future energy field as very efficient and environmentally friendly direct converters of chemical into electrical energy. The main precondition for a widespread application of SOFCs is high power density, high reliability, and long lifetime, and their economic production with low-cost materials and processes. The core of a SOFC is the membrane-electrode assembly (MEA), which consists of a material and porosity graded Ni-ZrO_2 cermet anode, a doped, thin, but gastight ZrO_2-electrolyte as oxygen-ion conductor, and an oxide cathode of perovskite material, again with graded porosity. Improved and specially adapted dc and rf plasma spraying shows a high potential to meet these demands and to be able to make such complex structures in an economic and consecutive multistep process. The presentation mainly concerns the required adaptation of the dc and rf plasma spraying processes, especially the modification of torch nozzles and of the parameters for improved and controlled plasma flow and plasma spray particle interaction and for the involvement of required plasma chemical effects in the spray process.

23. Synthesis and Characterization of Nanocrystalline Coatings by High-Velocity Oxyfuel Spray Processing for Biomedical Applications, by M.L. Lau, H.G. Jiang, and E.J. Lavernia, Department of Chemical Engineering and Materials Science, University of California-Irvine, Irvine, CA; C.J. Lavernia, Department of Orthopedics and Biomedical Engineering, University of Miami, School of Medicine, Miami, FL. In recent years, much research has been focused on various methods to produce coated implants for numerous biomedical applications. Thermal spray processing provides a potential means to rapidly deposit a coating onto an implant that facilitates the bonding between the implant surface and bone tissues. The present paper describes the synthesis and characterization of nanocrystalline coatings that may improve the quality of hip implants in the future. The feedstock powders were prepared by mechanical milling of micron-sized powders in methanol to produce flake-shaped agglomerates with the average grain size of less than 100 nm. The powders were HVOF-processed to produce nanocrystalline coatings. X-ray diffraction analysis was used for phase identification and to determine the average grain size of the milled powders as well as the coatings. Scanning electron microscopy and transmission electron microscopy were used to analyze the particle morphology as well as the microstructure of the coatings. In addition, coating properties of various materials were characterized by corrosion and hardness measurements. The results are compared to those of the micron-sized coatings.

24. Application of Thermal Spray Technology in Semiconductor Equipment Industry, by H. Wang, P. Ding, G. Yao, and S. Lai, Applied Materials Inc., Santa Clara, CA. Thermal spray technology has been used in the semiconductor equipment industry primarily for the purpose of particle reduction in the magnetron sputtering chambers, where metal interconnects of IC are built up on structured silicon wafers. During metal film deposition, the materials are not only deposited on the wafers, but also coated onto the process chamber kit components between the target and the wafer such as shields, clamp ring, and collimator. When the sputtered material is brittle or the chamber components have a complex shape, the sputtered films tend to dislodge from the component surfaces, even though the surfaces are usually roughened by bead blasting to improve adhesion. Pealing of the sputtered film from the component surfaces can lead to particles that significantly reduces die yield on the wafer. Thermal sprayed coatings can provide the controlled surface finish by choosing the proper spray techniques and optimizing spray parameters. Usually, a highly textured surface (rougher than the bead-blasted surface) is desired for providing mechanical bonding between the sprayed coating surface and the sputtered film. This leads to an increased kit lifetime and extended chamber service time. Experimental results have shown that particle performance and kit lifetime are significantly improved by applying the thermal sprayed coatings. The application of thermal spray technology can be extended to other areas. Another study has shown that with the application of a thermal sprayed coating on a component of an aluminum chamber, the aluminum films can be effectively deposited onto the bottom of the submicron contact via holes.

25. Microstructure and Properties of Plasma-Spray-Formed Ceramics, by E.H. Lutz, LWK-Plasmakeramik GmbH, D-51617 Gummersbach, Germany; U. Steinhauser and W. Braue, German Aerospace Research Establishment (DLR) Materials Research Institute, D-51147 Koln, Germany. Plasma spraying, originally a surfacing technology used for ceramic coating of metal substrates, is also an established technology suitable for producing bulk ceramic bodies such as plates and tubes of almost any size with characteristic anisotropic physical, mechanical, and thermomechanical properties. By plasma spray forming, components can be produced in situ and directly with the desired dimensions, posing an interesting alternative to conventional methods of shaping green bodies by molding and casting followed by sintering. These preferentially oxide and silicate "plasma ceramics" exhibit a porous laminar grain structure with porosities of 10 to 20%, low structural hardness (200 to 600 HV), low thermal conductivity (1 W/m · K and less) and heat capacity (1 J/g · K and less), extremely low Young's modulus of 4 to 20 GPa, low MOR with 20 to 40 MPa, but *R*-curve behavior and outstanding thermal shock properties. For example, mullite tubes of 3 mm wall thickness survive a ΔT quench of 1200 °C in 20 °C water without fracture. Subsequent firing at 1000 to 1800 °C results in a slight density increase of 1 to 5% and may cause a significant increase in MOR and a much greater increase in *E*-modulus. Accordingly, thermal shock resistance may be reduced considerably. There are many applications of plasma ceramics. They are used in hot corrosive environments of rapidly changing temperatures and where severe thermal gradients occur.

26. Abrasive Wear Behavior of Quasicrystalline-Iron Aluminide Composite Coatings, by D. Sordelet and M. Besser, Ames Laboratory, Iowa State University, Ames, IA. Quasi-crystals are a new class of materials that exhibit previously forbidden rotational symmetries (e.g., five-fold) and long-range aperiodic translational order. Since their discovery in 1984, quasi-crystals have been studied not only because of their fascinating atomic structures, but as a result of their useful physical and mechanical properties, which include low surface energy, low coefficients of friction, high hardness, and low thermal and electrical conductivities. This research concerns developing Al-Cu-Fe-based quasi-crystalline surface coatings using conventional plasma and HVOF spraying techniques. High-density, crackfree coatings have been difficult to produce due to the low thermal conductivity and brittleness of the $Al_{65}Cu_{23}Fe_{12}$ quasi-crystalline phase. Therefore, experiments were performed to form composite coatings of the quasi-crystalline phase with an iron aluminide (*B*2 structure) phase. The latter was selected because separate work has shown that the material is easy to deposit as a dense, relatively ductile thermal spray coating. The objective of this study was to decrease the porosity, cracking, and brittleness of quasi-crystalline coatings through the addition of the iron aluminide phase. Quasi-crystalline powders were blended with iron aluminide (0, 1, 5, 10, 20, 100 vol%) powders and plasma sprayed in air and in argon at 300 torr. Fine (+25 μm, –45 μm) and coarse (+45 μm, –75 μm) size fractions were evaluated. Abrasive wear behavior was examined using a modification of the ASTM G-65 rubber wheel abrasion test. Results show that material removal during abrasion is decreased by the addition of iron aluminide. However, a particularly interesting observation is that the addition of only 1 vol% iron aluminide produced the most abrasive wear-resistant coatings. This effect was observed with all four coating conditions. A proposed explanation involving a change in wear mechanism from brittle fracture to plastic deformation along with maintaining coating hardness is presented.

27. Tribological Response of Plasma Sprayed Liquid Crystalline Polymers, by N. Wagner, D. Otterson, S. Usmani, and S. Sampath, SUNY—Stony Brook, Dept. of Materials Science and Engineering, Stony Brook, NY; J. Brogan, Poly Therm Corp, Stony Brook, NY. Liquid crystalline polymers display high-temperature resistance while maintaining excellent mechanical properties and chemical resistance. In addition, liquid crystalline polymers have intrinsically low oxygen and water vapor permeabilities. Such materials can often be used as barrier coatings at temperatures in excess of 200 °C. Thermotropic LCP coatings show strong potential for use in the chemical, pulp and paper, petrochemical, and aerospace industry as moistureproof seal liners, and other applications requiring high-temperature corrosion resistance. Thermotropic LCP coatings have been successfully produced using plasma spray technology onto metallic and organic substrate materials. Surface engineering by thermal spray represents a practical, efficient, and highly cost-effective means of protecting components from the effects of wear, corrosion, and other tribological aspects. In this study, thermotropic liquid crystalline polymer powder was introduced into a dc argon/hydrogen plasma to produce coatings on steel substrates. A design of experiments approach was used to systematically vary the process parameters to produce a range of coating microstructures. The coefficient of friction was determined during sliding wear against stainless steel balls in ball-on-flat tests. Relationships among plasma processing, particle melting, and friction are discussed in detail.

28. Abrasion and Sliding Friction of HVOF WC-Co Coatings, by S. Usmani, S. Sampath, and S. De Palo, Center for Thermal Spray Research, State University of New York, Stony Brook, NY; D.L. Houck, Osram Sylvania Inc., Towanda, PA. Thermal spray cermet coatings, such as WC-Co, TiC-Ni, and Cr_3C_2-NiCr, are widely applied for abrasion and friction control in a variety of industries. In this work, empirical relationships and mechanisms have been developed to explain the abrasion behavior of HVOF deposited WC-Co coatings. In addition, the friction behavior of the coatings has been examined as a function of carbide size distribution. It has been shown that indentation methods can be used to quantify the in-plane fracture behavior of WC-Co coatings. This method is a modification of the indentation fracture toughness measurement technique used for sintered WC-Co and was necessitated by short crack growth in the out-of-plane direction of coating cross sections. It has been also shown that carbide size distribution and cobalt content in the starting powders affect the resultant coatings W_2C content and their in-plane fracture behavior. Furthermore, it has been shown that there is a correlation between the normalized abrasion rate of the coatings and a combined microstructure/mechanical property parameter that includes their in-plane crack length, mean carbide size and distribution, the binder mean free path, and applied stress. In addition, it has been shown that the coefficient of friction of the coatings is independent of the carbide size for the test duration used in the study. This work highlights the influence of the anisotropic microstructure, lamellar and interlamellar strength, and nonequilibrium phases on the abrasion and friction behavior of thermal spray coatings. It is envisioned that this work will provide the framework for developments in coating reliability analysis and design.

29. Effect of B_4C Addition on Cavitation Resistance of the HVOF Sprayed NiCrSi Alloy, by Y.T. Wu and T.S. Chin, National Tsing Hua University, Hsinchu, Taiwan. Cavitation resistance of metals is critically required in applications such as hydraulic turbines, ship propellers, etc. The effect of adding 6 to 18 wt% B_4C into the HVOF-sprayed NiCrBSi self-fluxing alloy on its cavitation resistance was studied. It was found that porosity of the as-sprayed layers increased linearly, while the hardness and adhesion decreased with the B_4C content. These led to lower cavitation resistance. After heat treatment at 1050 °C, the cavitation resistance was increased 9%, while the hardness of the coating was enhanced by 29% to 1035 HV for the 12 wt% B_4C added layer. The reasons for these variations were studied by DTA, SEM, and OM. The increase in porosity is due mainly to the release of CO gas from the reaction of B_4C with oxides in the alloy melt. The increase in hardness and cavitation resistance after heat treatment arise from the formation of borides, carbides, and borocarbides at around 890 to 980 °C during heat treatment.

30. Oxidation of Polyolefins during Flame Spraying, by J. Brogan, Poly Therm Corp, Stony Brook, NY; C.C. Berndt, SUNY Stony Brook, Dept. of Materials Science and Engineering, Stony Brook, NY; G.P. Simon, Monash University, Department of Materials Engineering, Australia; D. Hewitt, Monash University, Department of Chemistry, Australia. Thermal spraying of polymers represents an alternative method to process polymer powder to produce both polymeric coatings and free-standing forms of great complexity. Such alternative methods of applying barrier coatings are an environmentally attractive alternative to solvent-based paints due to their lack of hazardous chemicals. Despite the extensive utility of ethylene methacrylic acid copolymers in the field and in laboratory studies, most work has focused on the mechanical and adhesion properties. Much less work has been reported on the effect of rapid exposure of these organic molecules to a high-temperature flame. In this study, ethylene methacrylic acid copolymer (EMAA) was flame sprayed at different conditions and a range of physical and chemical properties were assessed. Fourier transform infrared spectroscopy (FTIR) was used to examine the chemistry of the starting powder with respect to the sprayed coatings. Differential scanning calorimetry (DSC) was used to determine crystallinity. Coatings were scanned using dielectric relaxation spectroscopy (DRS) with a frequency range from 100 Hz to 1 GHz over a temperature interval of –20 to 85 °C. The relaxation associated with the glass-transition temperature was dependent on the temperature of the deposited coating. The effects of thermal oxidation to EMAA copolymer in relation to the measured properties were discussed.

31. Physical Principles and Properties of Water-Stabilized Plasma Generators, by M. Hrabovsky, Institute of Plasma Physics, Prague, Czech Republic. Plasma torches with liquid-stabilized arcs provide an alternative to commonly used sources of thermal plasmas based on gas stabilized arcs or rf discharges. In the torches with liquid stabilization, the arc column is confined inside the vortex that is created in an arc chamber with tangential liquid injection. Evaporation from the inner wall of the vortex surrounding the arc column and heating and ionization of the vapor are basic mechanisms that produce an arc plasma. The relations between the power absorbed in the vapor sheath surrounding the arc column, the power absorbed in the boiling layer on the inner surface of the vortex, and the power transferred into the liquid are decisive for all arc and plasma parameters. Arc voltage and, thus, arc power are high for a water-stabilized torch. Typically the arc voltage is 300 V at an arc current of 300 to 600 A. The mean mass enthalpy of generated plasma is 160 to 270 MJ/kg. The centerline plasma temperature measured 2 mm downstream of the nozzle exit was 28,000 K for an arc current 600 A, plasma flow velocity at the same point was 7 km/s. The mean bulk plasma temperature was 16,200 K and the mean bulk plasma velocity was more than 4 km/s. High flow velocity and extremely low ratio of the jet density to ambient density lead to enhanced mixing between the jet fluid and ambient gas and to high level of turbulence. Consequently, the spread angle of the mixing zone is large, and fully turbulent flow was identified at short distances from the torch exit. The experimentally determined characteristic frequency for the production of vortex structures in the shear layer on the jet boundary was 60 to 100 kHz. High plasma temperature and velocity, high level of turbulence, very low characteristic time constants for mixing processes, and the large volume of mixing zone are the special characteristics in plasma spraying that enable high deposition rates.

32. Processing-Properties Relationship of Water-Stabilized Plasma Spray Coatings, by R. Gansert, Hardface Alloys Inc., Santa Fe Springs, CA; H. Herman, State Univ. of New York at Stony Brook, Dept. of Materials Sci. & Eng., NY; P. Chraska and J. Ilavsky, Institute of Plasma Physics, Czech Academy of Sciences, Prague, Czech Republic. Water-stabilized plasma (WSP) technology enables protective coatings to be applied to components at deposition rates significantly greater than conventional plasma spray technologies. Currently, limited studies examine the relationship between fundamental aspects of processing using WSP and the resultant microstructures and properties. This study examines the WSP spray process and coatings that are formed using process diagnostics, modeling, and materials characterization. Resulting microstructures are compared with microstructures obtained by other thermal spray processes. The particle velocity and temperature of molten particles are investigated, as well as the microstructures, phase composition, porosity, density, and strength of the materials. The results show the delicate relationship among processing, microstructure, and properties. The processing conditions play a major role in the formation of splats, deposit phases, microstructures, and strength. The morphology of the lamellae through the deposit thickness is substantially influenced by the processing temperatures. Subsequently, the deposit strength depends on the microstructure resulting from the processing. Quench stresses, differential thermal stresses, and phase transformation stresses that result from the deposition temperatures influence the strength. Industrial applications where the WSP can be applied are discussed and compared with areas of applications for other thermal spray processes.

33. Commercial Applications of Water-Stabilized Plasma Spraying, by K.R. Raab, Caterpillar Inc., Peoria, IL. The economics of the high spray rate capability of the water-stabilized plasma spray (WSP) technology makes this an attractive process for coating large components. Caterpillar has investigated the use of WSP technology with the support of the Advance Technology Program. Through this program, an advanced water-stabilized plasma system, the WSP 500, has been built and installed at Caterpillar's partner, St. Louis Metallizing Company, St. Louis, MO. Caterpillar's experience in operating this equipment in an industrial shop as well as several applications of the spray process are reviewed.

34. Alumina-Based Materials for Use with Water-Stabilized Plasma Spray System, by J. Ilavsky, P. Chraska, J. Dubsky, B. Kolman, and K. Neufuss, Institute of Plasma Physics, Prague, Czech Republic. Availability of a high-throughput water-stabilized plasma spray system with its significantly better economics brings about a number of emerging engineering applications, in which use of deposits becomes economically feasible. However, this reduction in cost of depositing a unit (kilogram) of material opens field for (new or old) materials with better economics. Such materials are alumina-based feedstock powders that have been used in plasma spraying for a long time. Alumina-based materials exhibit complex behavior, which has always limited their use especially at elevated temperatures. The processes occurring at temperatures above 1000 °C include complex phase transformations and sintering that may be accompanied by change in alumina density. Extensive work has been performed over the last few years on understanding and controlling the phase transformation temperatures by addition of other oxides. It was possible to control phase composition of the as-sprayed deposits by variations of feedstock chemistry and by manufacturing deposits in the stable α phase to avoid the phase transformations entirely. As-sprayed deposits are composed of metastable δ phase; if TiO_2 is present, γ phase, which transforms at temperatures below 1000 °C into δ phase. Stable α phase is formed between 1050 and 1200 °C, which is sometimes accompanied by an intermediate θ phase. Addition of TiO_2 into the alumina lowers the α-phase formation temperature and θ phase is not formed at all or its content is significantly reduced. Addition of Cr_2O_3 increases the α-phase formation temperature and also increases the amount of α phase present in as-sprayed deposits. Larger amounts of Cr_2O_3 stabilize the α phase in the as-sprayed deposits, thereby avoiding phase transformations entirely. The presentation reviews progress in understanding of temperatures of the phase transformations in plasma sprayed deposits, accompanying changes in microstructure and methods of controlling the temperatures.

35. Silicates and Other Natural Materials, by P. Chraska, K. Neufuss, B. Kolman, and J. Dubsky, Institute of Plasma Physics, Prague, Czech Republic. Materials that are inexpensive but have interesting properties have been extensively researched for use in the high throughput of WSP. In this regard, silicates and natural materials are promising materials; e.g., zircon, and various garnets and basalt. Zircon ($ZrSiO_4$) is a natural mineral used for various applications as a refractory bulk material. On plasma spraying, zircon decomposes into t-ZrO_2 and glassy SiO_2. Such a combination exhibits properties such as a high thermal shock resistance, very good corrosion resistivity, low wettability, etc. Garnets as a group are relatively common in highly metamorphosed rocks. The general formula for garnets is $A_3B_2(SiO_4)_3$, where A represents divalent elements such as iron, magnesium, calcium, etc., and B represents a trivalent metal. Regardless of the type of the feedstock garnet, all plasma sprayed deposits were in the amorphous (glassy) state. Two types of the amorphous character were observed—one with amorphous peaks and the other without, suggesting a certain redistribution and inhomogeneity of the chemical composition. Porosity of all the plasma sprayed deposits was very low, mostly below 4 to 5%. For one garnet type, almandine $Fe_3Al_2(SiO_4)_3$, the porosity reached a value below 2%. Adhesion to a steel substrate was similar to an alumina coating's adhesion—both without a bond coat. Excellent coatings were made of basalt. All the deposits, regardless of the spraying parameters, were in a glassy state with a very low porosity (2.5 to 3%), consisting of closed spherical pores. Practically no cracks were observed, thus offering a very low gas permeability of free-standing pipes, produced by spraying. Generally, it is evident that WSP, due to its very high temperature and energy dissipation, is capable of good melting and depositing of even large quantities of these materials with very interesting properties. Support of grant GACR 104/96/1353 is gratefully acknowledged.

36. Microstructure and Properties of Powders Consolidated by Laser Engineered Net Shaping (LENS), by J.E. Smugeresky, D.M Keicher, Optomec Design Company, Albuquerque, NM; M.L. Griffith, J.A. Romero, and L.D. Harwell, Sandia National Laboratories, Livermore, CA, and Albuquerque, NM. Laser engineered net shaping (LENS) is an advanced technology for consolidating metal powders into net-shaped structural components directly from computer-aided design files. This technology takes traditional polymer-based rapid prototyping processes one step further, where structural rather than surrogate or model materials are used. Considered to be a moldless direct fabrication technology, the LENS process produces shapes that provide rapid solidification microstructures, taking advantage of metastable conditions to enhance material properties. Critical to the success of this technology is the extent to which appropriate microstructure and mechanical properties can be achieved while simultaneously forming to net shape. Considerable promise has been demonstrated with extremely fine grain sizes resulting in yield strengths more than twice that of conventionally processed annealed stainless steels, with little or no reduction in ductility. Improvements in properties have also been obtained in Incoloy 625, although not as dramatic as in stainless steel. Tool steel materials, such as H13, have shown hardness values of 61 HRC, where the microstructure can be tailored by certain additions. This paper discusses the relation between the microstructure and properties of these materials as they are affected by processing conditions. Work supported by the U.S. Department of Energy under contract DE-AC04-94AL85000.

37. Laser Engineered Net Shaping (LENS): A CAD Solid Model Driven Direct Fabrication Spray and Beam Processing Technology, by D.M. Keicher, Optomec Design Company, Albuquerque, NM; M.L. Griffith, J.E. Smugeresky, J.A. Romero, and L.D. Harwell, Sandia National Laboratories, Albuquerque, NM, and Livermore, CA. The laser engineered net shaping (LENS) process, currently under development for direct fabrication, is a metal spray forming, laser-based technology that uses a high-power Nd:YAG laser to fuse metal particles together as they are injected into the deposition region. With the LENS process, designers use computer-aided design (CAD) solid models, in electronic format, to drive the motion, deposition, and power requirements for layered forming of functional metal parts. Using a highly localized laser beam, metal powders are used to produce near-net-shape, fully dense metallic parts with reasonably complex geometrical features. The results of current studies suggest that, with continued improvement, this process will indeed be feasible for direct fabrication applications. The current approach lends itself to produce components with a dimensional accuracy of 0.002 in. in the deposition plane and 0.015 in. in the growth direction. These results suggest that the LENS process will provide a viable means for direct fabrication of metallic hardware. With the continued development of faster, more powerful computers coupled with the existing level of the rapid prototyping techniques, this technology is beginning to be exploited to fabricate reasonably complex geometrical features with fine grain microstructures and enhanced mechanical properties in metallic materials. Efforts are currently underway to improve surface finish and understand the interactions between the various process parameters so that process control methodologies may be developed for closed-loop process control. This paper gives a brief description of the LENS process and the results that have been achieved to date. Work supported by the U.S. Department of Energy under contract DE-AC04-94AL85000.

38. Fabrication of 3-D Shapes by Laser-Aided Direct Deposition of Metals, by J. Mazumder, K. Nagarathnam, and J. Choi, Center for Laser Aided Intelligent Manufacturing, Univ. of Michigan, Ann Arbor, MI; J. Koch, Caterpillar Inc., Mossville, IL. Laser cladding by layers offers the possibility for fabrication of 100% dense metal components, even with a graded microstructure and composition. Present computer-controlled five-axis workstations integrated with lasers enable fabrication of various geometries. Initial work has demonstrated that components with mechanical properties similar to plate materials can be fabricated even from oxide formers such as aluminum in addition to copper, nickel, and ferrous alloys including H13. In other words one now can produce a 100% dense metal part in near-net-shape directly from the CAD drawing. H13 tool steel is one of the difficult alloys for deposition due to residual stress accumulation from martensitic transformation. However, it is the material of choice for the die and tool industry. A pair of functional dies have been fabricated with H13 alloy. Copper chill blocks and water-cooling channels were the integral part of the injection-molding dies. The as-deposited surface roughness was similar to that of a cast structure. The thinnest deposition of 25 μm has been achieved using a Nd-YAG laser. It has been demonstrated that a wide range of deposition rate and geometrical resolution may be possible with laser-based DMD as a function of the laser power and beam quality. This paper describes the properties and microstructure of materials produced by a laser-aided direct-metal-deposition technique.

39. Plasma Spray Forming of Structural Components, by T. McKechnie Plasma Processes Inc., Huntsville, AL. Near-net-shape spray forming of components significantly simplifies and reduces the cost of fabricating some structures. Material use is very high, and laborious machining can be avoided. As-spray-formed components have been tested and found to perform adequately. However, improvements in alloying, thermal treatment, and coating have been demonstrated to add increased performance to spray formed components. In fabricating tungsten components, alloying additions of rhenium, nickel, or iron have made significant increases in material strength and ductility. Thermal treatments such as heat treatment and HIP change and densify the microstructures. Coating the internal and external surfaces of spray formed components improves environmental compatibility. Functional gradients can be used to minimize thermal stress formed at bondlines between dissimilar materials. The plasma spray forming of superalloy, copper alloy, and refractory metal components is presented.

40. Low-Pressure Spray Forming of 2024 Aluminum Alloy, by W.D. Cai, J. Smugeresky, Sandia National Laboratories, Livermore, CA; E.J. Lavernia, Department of Chemical, Biochemical Engineering and Materials Science, University of California, Irvine, CA. In this paper, a newly developed low-pressure spray forming (LPSF) technique is described. The experimental results obtained with an as-deposited 2024 aluminum alloy are reported. It is shown that the application of reduced pressure significantly decreases porosity as compared to conventionally spray formed 2024 aluminum alloy. Moreover, the resultant microstructures are similar to those achieved with conventional spray forming. The mechanisms of porosity formation in deposited materials, obtained using both low-pressure and conventional spray forming, are discussed. Gas entrapment and interstitial porosity are proposed to be the two major sources of the porosity present in the as-deposited materials. On the basis of the present study, the controlled low-pressure environment during LPSF, appears to influence the droplet trajectories and the gas flow field, leading to flow straightening effects, which result in significant reduction of porosity in the deposited materials. Work supported by the Army Research Office (Grant No. DAAH04-95-1-0424), and U.S. Department of Energy (Contract No. DE-AC04-94AL85000.)

41. Thermo-Mechanical Response of Plasma-Sprayed Coatings, by S. Suresh, Massachusetts Institute of Technology, Dept. of Materials Science and Engineering, Cambridge, MA. The response of plasma sprayed coatings subjected to thermal and mechanical loads is examined. Particular attention is devoted to the arrest of surface flaws advanced through the coatings by fatigue. On the basis of critical experiments and detailed numerical analyses, strategies are presented for the enhancement of damage tolerance of thermal-barrier and wear-resistant plasma spray coatings. A case study that demonstrates the success of the proposed strategy for thermally sprayed wear-resistant coatings in an industrial application is also be discussed. New methods for the assessment of internal stresses in homogeneous as well as multilayered and graded coatings are also examined.

42. Mechanism-Based Failure Prediction for Thermal Barrier Coatings, by A. Evans, Harvard University, Cambridge, MA. The evolution of cracks that lead to the eventual spalling of thermal barrier coatings is discussed. Mechanic solutions that characterize each step in this evolution are presented and compared with experimental findings. Particular emphasis is given to the initial formation of separation at the bond coat/oxide interface, inclusion of the effect of segregation. Preliminary life models are presented.

43. Residual Stress Generation in Thermal Barrier Coatings, by W.J. Brindley, NASA Lewis Research Center, Cleveland, OH; A.M. Freborg and B.L. Ferguson, DCT, Inc., Cleveland, OH. The mechanisms by which oxidation and thermal cycling cause thermal barrier coating (TBC) failure are not well understood. A very general explanation is that oxidation and thermal cycling cause increasing residual stresses and/or decreasing coating strength. However, this explanation provides no mechanistic basis from which to predict TBC behavior. A finite element study has been conducted to examine thermal cycle residual stress generation in a TBC as a function of materials properties, with an emphasis on bond coat properties. The results indicate that oxidation of the bond coat, bond coat creep, top coat creep, and bond coat thermal expansion coefficient can all have a strong influence on stresses in the ceramic layer, both individually as well as through property interactions. Results of an investigation of oxide growth stress effects and thermal cycle hot time effects on TBC stresses are also presented.

44. Mechanical Properties of Thermal Barrier Coatings: Effects of Fracture, Residual Stresses, and Void Distributions, by T. Nakamura and G. Qian, Dept. of Mechanical Engineering; C.C. Berndt, Dept. of Materials Science and Engineering, SUNY at Stony Brook, NY. Driving mechanisms that lead to internal crack growth and failure in thermally sprayed coatings are identified using detailed finite element models. Coatings are assumed to contain embedded cracks, and they are thermally loaded according to a typical high-temperature environment. In order to determine the accurate stress state, the thermal gradient within the coating is calculated from the steady-state heat transfer analysis. The models take into account various locations of cracks, temperature-dependent, and -independent plasticity, thermal conductivities of different layers, and thermal insulation across crack surfaces. The results indicate that the energy release rate of large cracks can reach close to the fracture toughness of ceramic coatings. The effect of residual stresses has also been studied. For a penny-shaped crack located parallel to the coating layers, a limited influence of residual stresses is observed. The effect is more pronounced when the crack orientation is perpendicular to the coating layers where it has shown a beneficial influence. The implications of this work to internal crack initiation and growth, which can lead to coating failure, are addressed. In addition, ceramic coating containing many microvoids have been modeled. Initially, the effects of void distribution as well as their morphologies on the overall elastic moduli are investigated. In this analysis, voids are randomly distributed to simulated pores and cracks observed in actual TBCs. The results show that if the distribution is sufficiently random, the elastic moduli can be approximated as a function of void volume fraction. Furthermore, random models have been used to study the residual stress field within multilayered TBCs. Here, a bond coat is modeled as elastic-plastic material, and the influence of void size and distribution on the magnitude of residual stresses are studied.

45. Determination of Process-Induced Residual Stress in Plasma Sprayed Layered and Graded Coatings, by O. Kesler and S. Suresh, Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA; S. Sampath, Center for Thermal Spray Research, State University of New York, Stony Brook, NY. All processing methods used to deposit surface coatings on substrates invariably generate "intrinsic" or "quench" stresses. These internal stresses, which strongly depend on the specific deposition conditions and processing methods employed, arise from factors such as: rapid quenching of a molten-droplet, nonuniform sintering of the material across the thickness of the coating, nonequilibrium cooling of different phases, etc. In addition, temperature excursions cause "thermal stresses" to develop due to expansion/contraction mismatch between the constituent phases in the same layer or between layers. An experimental method has been developed that enables the determination of process-induced residual stresses, the elastic modulus, and coefficients of thermal expansion of surface coatings of homogeneous or graded compositions. In this method, the substrate curvature change is monitored ex situ before and after deposition. When combined with four-point bend tests, the magnitude of intrinsic stresses through the thickness of the coating can be obtained. In addition, the in-plane Young's modulus and the coefficient of thermal expansion coefficient can also be determined. Results are presented for plasma sprayed nickel-alumina graded coating and plasma sprayed molybdenum of different thickness.

46. The Influence of Temperature and Stress State on the Young's Modulus of Plasma Sprayed Yttria-Stabilized Zirconia Thermal Barrier Coatings, by F. Szuecs and H.-J. Fecht, Technical University of Berlin, Dept. of Materials Science and Engineering, Germany; T. Cosack, J. Bamberg, and C. Schwarminger, Daimler-Benz Aerospace, MTU Munich, Germany. Thermal barrier coatings (TBCs) become an important structural element in the design of modern flight and land-based gas turbine engines. Yttria-stabilized zirconia is a common material for thermal barriers, because it combines a low thermal conductivity with a relative high thermal expansion and fracture toughness. TBCs need to be highly strain tolerant to avoid delamination. It is reported in literature that TBCs with superior lifetimes have a low apparent Young's modulus. The thermoplastic behavior of plasma sprayed 8 wt% yttria-stabilized zirconia TBCs with an underlying low-pressure plasma sprayed M-CrAlY bond coat on superalloy substrates is analyzed between room temperature and 1000 °C by dynamic three-point-bending experiments performed on free-standing and composite beams. The measurements on the composite beams are analyzed with respect to the apparent Young's modulus of the TBC using a composite beam deflection model, which also allows calculation of inner stresses. The as-sprayed TBC has an apparent Young's modulus between 20 and 24 GPa. This strongly reduced stiffness compared to sintered zirconia is discussed in relation to the TBC defect structure. Above 700 °C, an irreversible increase in apparent Young's modulus can be observed. Isothermal measurements at 1000 °C show a parabolic time-law dependency. We explain this effect with a change in the defect structure due to surface diffusion. After heat treatments the apparent Young's modulus of free-standing zirconia coatings is nearly temperature independent. Zirconia coatings attached to a substrate show a different behavior. The apparent Young's modulus is now strongly temperature dependent, which can be explained by the influence of the stress state on the elastic behavior. Compressive stresses arise on cooling as a result of relaxation of tensile stresses above 650 °C, when the bond coat becomes ductile. The observed stiffening can be explained by a reversible closure of microcracks under compressive stresses. The irreversible change in the defect structure of plasma sprayed zirconia coatings has to be interpreted as a degradation phenomena and a life-limiting factor. Whenever simulating the thermomechanical behavior of TBC composite systems, time-dependent behavior as well as the observed eigenstress-dependency of the elastic properties has to be considered.

47. Processing Effects on Residual Stress in Plasma Sprayed Molybdenum Deposits, by J. Matejicek and S. Sampath, Center for Thermal Spray Research, State University of New York, Stony Brook, NY; P.C. Brand and H.J. Prask, National Institute of Standards and Technology, Gaithersburg, MD. Plasma sprayed molybdenum coatings find many applications in the automotive industry. Their performance and lifetime can be significantly affected by residual stresses, originating from the manufacturing process. This process involves numerous variables that affect the deposit formation dynamics, microstructure, and properties; including residual stress. This study is mainly concerned with the deposition temperature, which has a significant effect on the splat formation, coating buildup, oxidation, strength, and stress. Residual stress is particularly influenced by the temperature drop during the particle impact, its adhesion to the substrate and the difference in contraction during the cooling of the coating/substrate couple from deposition to ambient temperature. In this investigation, molybdenum powder was sprayed onto steel, aluminum, and copper substrates at three different temperatures, all other parameters being kept constant. Coatings microstructure were examined, and a complex characterization of their properties was conducted. Residual stresses in thin and thick coatings were measured using x-ray and neutron diffraction, respectively. Based on the results, the relative magnitude of quenching and thermal mismatch stress can be assessed and correlated to the processing and microstructure.

48. Determination of Creep Behavior of Thermal Barrier Coatings under Laser Imposed Temperature and Stress Gradients, by D. Zhu and R.A. Miller, NASA Lewis Research Center, Cleveland, OH. In the present study, a laser-sintering and creep technique has been established to quantitatively determine the creep behavior of TBCs under high heat flux conditions. An approach is proposed to separate the stress relaxation effect, based on the variable strain rate changes with respect to time and temperature during testing. For a plasma sprayed zirconia-8wt% yttria ceramic coating, a large primary creep strain and low creep activation energy were observed. The significant primary creep stage and low apparent creep activation energy for the coating are attributed to stress-induced mechanical sliding, and temperature- and stress-enhanced cation diffusion through the splat and grain boundaries. The possible creep mechanisms for the ceramic coating are also discussed. The elastic modulus evolution, the stress response, and the total accumulated creep strain variation across the ceramic coating under laser-imposed temperature and stress conditions are simulated using a finite difference approach, based on the measured creep data. The modeled creep response is consistent with experimental observations.

49. Microstructural Characterization of Plasma Sprayed Deposits by Means of Small-Angle Neutron Scattering, by G.G. Long, J. Ilavsky(current address: Institute of Plasma Physics, Prague, Czech Republic), and A.J. Allen, National Institute of Standards and Technology, Materials Science and Engineering Laboratory, Gaithersburg, MD. Despite the fact that the porous microstructure of plasma sprayed deposits directly determines their physical and mechanical properties, the complexity of the deposit microstructure has long impeded quantitative assessment as a function of powder feedstock and processing parameters. At NIST, small-angle neutron scattering (SANS) techniques and instruments have been developed to measure microstructural features from 1 nm to 3 μm in size to follow ceramic microstructural parameters in situ as a function of thermal treatment and to measure anisotropic as well as isotropic materials. Porod scattering studies have been used to measure, independently, the specific surface areas of interlamellar pores and intralamellar cracks. Multiple SANS (MSANS) measurements have been able to add relative volume fractions and mean sizes of the void systems and have led to the quantification of a third (globular) population of voids. Studies of plasma sprayed deposits include investigations of processing/microstructure relationships and of the evolution of microstructure as a function of in-service heat treatment. The results offer the first proof that the quantity and the character of the porosity can be controlled independently by means of processing protocols, and that the in-service thermal environment plays a distinct role in the evolution of the microstructure and properties of product coatings.

50. Thermal Conductivity of Low-Pressure Plasma Sprayed Metal Coatings, by K.J. Hollis and R.G. Castro, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM. The effect of plasma spray processing conditions on the thermal conductivity of metallic coatings was investigated. Conditions varied were the starting powder impurity concentration, powder atomization method, plasma torch secondary gas additions, and the deposit substrate temperature. Flash thermal diffusivity measurements of coatings sprayed under various conditions were collected. Powder impurity, secondary gas addition, and substrate temperature have significant effects on the coating thermal diffusivity. Chemical analysis, optical microscopy, SEM, TEM, mechanical properties testing, and finite element heat transfer modeling were used to explain the changes in thermal properties. Porosity and impurity content were largely responsible for the losses in coating thermal conductivity. The coatings investigated had from 60 to 98% of the theoretical thermal conductivity of the bulk material.

51. Processing Effects on Microstructure Development during Thermal Spraying, by S. Sampath, Center for Thermal Spray Research, State University of New York, Stony Brook, NY. Thermal spraying is a highly dynamic process resulting from rapid heating/melting/accelerating of powder particles or wire in a flame, followed by impact and rapid solidification of the droplet (splat). The particles experience large thermal gradients in the flame during its heating/melting, which can lead to phase decomposition, species volatilization and oxidation of metallic components. Due to the rapid solidification nature of the process, deposit evolution is complex, commonly leading to ultrafine-grained and metastable microstructures. Thus, the nonequilibrium phenomena are common in the microstructure, with important implications for properties and performance. A splat resulting from the flattening of an individual droplet is the basic building block of the thermal spray microstructure. The phase and microstructure of the splats and the integration of the splats are both affected by processing. Furthermore, particle size and deposition temperature have been shown to influence the microstructure development. Thus, understanding and prediction of phase/microstructure evolution by examining rapid solidification provide insight into structure-property-performance triad. This presentation covers the deposit formation dynamics and the evolution of the rapidly solidified microstructure and provides case studies to illustrate the relationships between processing and microstructure. Implications of the effects on properties are also discussed for select systems.

52. Microstructural Changes In Plasma Sprayed Deposits during Annealing, by J. Ilavsky (current address: Institute of Plasma Physics, Prague, Czech Republic), A.J. Allen, and G.G. Long, National Institute of Standards and Technology, Materials Science and Engineering Laboratory, Gaithersburg, MD; C.C. Berndt and H. Herman, SUNY at Stony Brook, Dept. Materials Science and Engineering, Stony Brook, NY. The anisotropic microstructure of plasma sprayed yttria-stabilized-zirconia deposits was investigated as a function of temperature by means of small-angle neutron scattering (SANS). SANS Porod scattering measurements, as applied to anisotropic structures, can be used to determine the surface characteristics of the void systems. The experiments were performed in situ in a ceramic furnace built for use on the SANS instrument. The evolution of the microstructure was followed (1) with the temperature increasing from 600 to 1400 °C at a heating rate of 50 °C/h, and (2) at 1100 °C over the course of 23 h. The microstructure of plasma sprayed coatings is sufficiently anisotropic for the interlamellar pores and the intralamellar cracks to be characterized independently. During the furnace experiments, the specific surface areas of the interlamellar pores decreased at higher temperatures. The anisotropy of the microstructure increased below 1000 °C due to decreasing specific surface area of the intralamellar cracks. At 1100 °C, the anisotropy decreased roughly exponentially with time. These results suggest that significant microstructural changes in ceramic deposits may occur at operating temperatures and that these are a complex function of temperature and time.

53. Microstructure and Deformation Characteristics of Plasma Spray Formed 2/1 Mullite Ceramics upon Annealing, by U. Steinhauser, W. Braue, J. Goering, B. Kanka, and H. Schneider, German Aerospace Research Establishment (DLR), Materials Research Institute, Cologne, Germany; E.H. Lutz, LWK Plasmakeramik GmbH., Gummersbach, Germany. Mullite-based plasma spray formed ceramics (MPC) exhibit both a marked property anisotropy and a nonlinear stress-strain behavior due to their typical porous laminar grain structure. The effects of annealing on the microstructure-property anisotropy and the macroscopic deformation behavior of a 2/1 mullite composition has been addressed through the combined approach of mechanical testing and SEM, TEM, XRD, and DSC investigations. Upon heat treatments between 1000 and 1700 °C the rather low MOR (20 MPa) and Young's modulus (35 GPa) levels in the as-sprayed state show a significant increase by an order of 2, which is even more pronounced in other plasma ceramics. Simultaneously, the load-displacement characteristics gradually change from a nonlinear, damage-tolerant response for as-sprayed mullite to a linear behavior emphasizing the effects of a more rigid microstructure after sintering of adjoining mullite lamellae upon the heat treatment. Despite their brittleness, however, the structural integrity of annealed MPCs upon thermal shock is maintained due to substantial microcrack formation. Burner rig and combustion chamber tests employing bulk MPCs as well as thin MPC-based protective layers on ceramic substrates confirm that the excellent thermal stability of MPCs is retained upon annealing in reducing and oxidizing atmospheres employing different flame compositions.

54. Quantitative Studies of the Three Void Systems in Plasma-Spray Deposits by Anisotropic Multiple Small-Angle Neutron Scattering, by A.J. Allen, G.G. Long, and J. Ilavsky (current address: Institute of Plasma Physics, Prague, Czech Republic), National Institute of Standards and Technology, Materials Science and Engineering Laboratory, Gaithersburg, MD. In plasma sprayed ceramic deposits, three void component morphologies can be identified: intrasplat cracks, intersplat planar pores, and a broad size distribution of globular pores or bubbles. Small-angle neutron scattering (SANS) Porod studies have made an important contribution in characterizing the anisotropies in the surface area distributions of the intrasplat cracks and intersplat pores, but there is a need to quantify the relative volume fractions and mean sizes of all three void systems, as well as the orientation distributions of the cracks and intersplat pores, because these are major factors in determining the mechanical and thermal properties of the coatings. Multiple SANS (MSANS) measurements of neutron beam broadening, as a function of wavelength, can provide much of this additional information. The dependence of MSANS on the microstructural anisotropy is different to that of Porod scattering, and while the globular pores contribute only slightly to the overall surface area (without orientational dependence), they represent a significant volume fraction that has a strong effect on the MSANS broadening. Quantitative results will be presented for the microstructural evolution during heat treatment for two yttria-stabilized zirconia thick-deposit systems sprayed using different feedstock materials.