Selected Abstracts of Thermal Spray Literature

Reprinted with permission from Elsevier Engineering Information, Inc., Hoboken, NJ, USA

Applications

Automotive and Mechanical Industry

Mechanical and microstructural characterization of cylinder liners. The automotive industry is seriously concerned with emission level control, vehicle weight reduction, and recycling. These are the purposes of introducing the all-aluminum cylinder blocks for the combustion engine. The spray forming process led to the fabrication of cylinder liners made of high aluminum silicon alloys. The aim of the present work was to evaluate and compare the microstructures and mechanical properties of three cylinder liners: gray cast iron and two aluminum silicon alloys. Their surface roughness and topology also have been investigated.

Keywords: aluminum alloys, automotive industry, metallographic microstructure, surface roughness, surface topography

H.O. Santos, I. Costa, and J.L. Rossi, IPEN, CEP 05422-970, Sao Paulo, Brazil. Cited: *Mater. Sci. Forum, 416-418*(1), 2003, pp. 407-412 [in English]. ISSN 0255-5476.

Ceramic coatings for cylinder liners in advanced combustion engines, manufacturing process and characterization. Recent automotive engineering developments concerning fuel consumption regulations and decreasing material and manufacturing cost result in an increasing utilization of light metal components for automotive applications. Significant weight savings are obtained by changing the engine block material from cast iron to aluminum. Since all parts of a combustion engine interact as a system, the individual components must sustain the combustion pressure and temperature as well as wear and friction effects of moving surfaces in different environmental and lubrication regimes. Approaches to increase combustion as well as operation efficiency and lifetime of light metal engines are ceramic and cermet coatings on the cylinder liners of die-cast aluminum crankcases. Such functional and protective thermally sprayed coatings on cylinder bores include material combinations with solid lubricant ability. The used thermal spray processes are high-energetic (atmospheric plasma spraying) and high-energetic hypersonic deposition methods (high-velocity oxygen fuel spraying). The knowledge of the mechanical and thermophysical properties of coatings is a key requirement for an optimized stable and repeatable manufacturing process, as well as for reproducible high-quality composites. This paper presents the actual trends in lightweight engine design and material engineering. In detail, a novel inside coating process by means of thermal spraying technologies is introduced and discussed. The obtained coating and composite quality is summarized and evaluated.

Keywords: crankcases, cylinders (containers), deposition, friction, internal combustion engines, machine design, manufacture, quality control, spraying, wear of materials

M. Buchmann and R. Gadow, Univ. Stuttgart, IMTCCC, D-70569 Stuttgart, Germany. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., A, 22*(3), 2001, pp. 75-86 [in English]. ISSN 0196-6219.

Biomedical Applications

Novel bioactive coatings for biomedical applications. There are thousands of implant operations every year that give significant pain relief to patients. Even small improvements can reduce the need for further revision surgery. Improving the bonding of an implant, by using a bioactive coating, increases the rate of fixture of the implant, reducing the healing time. The original artificial bioactive coatings, calcium phosphates and hydroxyapatite, were absorbed quickly by the body. This leaves the substrate bare, resulting in loosening of the implant. Hench developed bioactive glass ceramics in the 1970s that were longer lasting and bonded to bone. Due to the low fracture toughness of these glass-ceramics, these materials are used for nonload bearing components, or more commonly, as coatings. Many different methods of coating have been suggested with varying degrees of success. This paper compares coatings fabricated by plasma spraying and electrophoretic deposition and studies the effect of heat treatment on the coating quality, adhesion, phase distribution, and bioactivity of apatite-mullite glass-ceramic LG112 on Ti6Al4V.

Keywords: calcium compounds, hydroxyapatite, plasma spraying, surgery

J.K. Bibby, P.M. Mummery, N. Bubb, and D.J. Wood, Manchester Materials Science Centre, Manchester M1 7HS, U.K. Cited: Proc. 15th Int. Symposium on Ceramics in Medicine; The Annual Meeting of the International Society for Ceramics in Medicine, B. Ben-Nissan, D. Sher, and W. Walsh, Ed., 4-8 Dec 2002 (Sydney, Australia), *Key Eng. Mater., 240-242,* 2003, pp. 279-282 [in English]. ISSN 1013-9826.

Osteointegration of plasma spray, biomimetic octacalcium phosphate, and carbonate-apatite coatings on titanium implants. The biomimetic approach of producing calcium-phosphate (Ca-P) coating on metal implants offers the possibility to form Ca-P phases that cannot be produced by using the plasma spray (PS) technique. Furthermore, biomimetically produced coatings exhibit some important advantages in comparison to PS coatings, such as the ability to coat porous implants and to incorporate biologically active agents and the lack of delamination and particle release. In this study, PS coated Ti-6Al-4V implants are compared with biomimetic octacalcium phosphate (OCP) and carbonateapatite (CA) coated implants by implantation in muscles and bony sites of New Zealand White Rabbits. Previous reports have shown that coatings with high dissolution rate are highly bioactive and may ensure an early bone formation. However, the *in vivo* durability of the coating might be an important parameter for the long-term bone fixation of an implant. This study shows a complete dissolution of OCP and CA and no dissolution of PS coating after 12 weeks of intramuscular implantation. Implantation in bone shows a similar bone growth in the early period of time for different coatings, and a more positive effect of the soluble coatings in the bone remodeling process. This results in a higher amount of bone after 12 weeks of implantation for biomimetically coated implants than for PS coated implants.

Keywords: bone, calcium compounds, muscle, plasma spraying

P. Habibovic, C.M. Van der Valk, K. De Groot, and P. Layrolle, Biomaterial Research Group, Leiden Univ., Leiden, Netherlands. Cited: Proc. 15th Int. Symposium on Ceramics in Medicine; The Annual Meeting of the International Society for Ceramics in Medicine, B. Ben-Nissan, D. Sher, and W. Walsh, Ed., 4-8 Dec 2002 (Sydney, Australia), *Key Eng. Mater., 299-302,* 2003, pp. 387-390 [in English]. ISSN 1013-9826.

Coatings for Gas Turbine Components

Gas turbine research in the AGTSR program. The South Carolina Institute for Energy Studies (SCIES), administratively housed at Clemson Univ., has participated in the advancement of combustion turbine technology for nearly a decade. The Advanced Gas Turbine Systems Research (AGTSR) program has been administered by SCIES for the U.S. Dept. of Energy (DOE). Under the supervision of the DOE National Energy Technology Laboratory (NETL), the AGTSR has brought together the engineering departments at the leading U.S. universities and U.S. combustion turbine developers to assist in providing a solid base of knowledge for the future generations of gas turbines. In the AGTSR program, an Industrial Review Board (IRB) of gas turbine companies and related organizations defines needed gas turbine research. SCIES prepares yearly requests for university proposals that address the research needs identified by the IRB organizations. IRB technical representatives evaluate the Univ. proposals and review progress reports from the awarded university projects. Seventy-five (75) AGTSR university projects have been awarded in the areas of gas turbine combustion, aerodynamics/heat transfer, and materials. An overview of recent AGTSR university projects is given in this paper, and research results from several of the projects are described in greater detail.

Keywords: aerodynamics, algorithms, combustion, combustors, computer-aided design, cooling, engineering research, heat transfer, materials science, sensors, societies and institutions, thermal barrier coatings

R.A. Wenglarz and L.P. Golan, South Carolina Institute, Clemson Univ., Clemson, SC 29634, United States. Cited: *Proc. ASME Turbo Expo 2002: Aircraft Engine, Coal, Biomass and Alternative Fuels, Combustion and Fuels, Education, Electric Power, Vehicular, and Small Turbomachines,* Vol. 1, 3-6 June 2002 (Amsterdam), The International Gas Turbine Institute, American Society of Mechanical Engineers, 2002, pp. 975-985 [in English].

The evaluation of CFCC liners after field testing in a gas turbine—III Under the Ceramic Stationary Gas Turbine (CSGT) Program and the Advanced Materials Program, sponsored by the U.S. Dept. Energy (DOE), several silicon carbide/silicon carbide (SiC/SiC) combustor liners were field tested in a Solar Turbines Centaur 50S gas turbine, which accumulated approximately 40,000 h by the end of 2001. To date, five field tests were completed at Chevron, Bakersfield, CA, and one test at Malden Mills, Lawrence, MA. The evaluation of SiC/SiC liners with an environmental barrier coating (EBC) after the fifth field test at Bakersfield (13,937 h) and the first field test at Malden Mills (7238 h) is presented in this paper. The work at Oak Ridge National Laboratory (ORNL) in support of the field tests was supported by DOE's Continuous Fiber-Reinforced Ceramic Composite (CFCC) Program.

Keywords: carbon monoxide, combustors, gas turbines, high-temperature properties, nitrogen oxides, particulate emissions, protective coatings, quenching, silicon carbide

N. Miriyala, J. Kimmel, J. Price, K. More, P. Tortorelli, H. Eaton, G. Linsey, and

E. Sun, Solar Turbines Inc., San Diego, CA. Cited: *Proc. ASME TURBO EXPO 2002: Ceramics, Industrial and Cogeneration Structures and Dynamics,* Vol. 4A, 3-6 June 2002 (Amsterdam), The International Gas Turbine Institute, American Society of Mechanical Engineers, 2002, pp. 109-118 [in English].

Development and evaluation of ceramic components for gas turbine. An 8000 kW class hybrid gas turbine (HGT) project, administered by the New Energy and Industrial Technology Development Organization (NEDO), has been ongoing since July of 1999 in Japan. Targets of this project are improvement in thermal efficiency and output power by using ceramic components, and early commercialization of the gas turbine system. The ceramic components are used for stationary parts subjected to high temperature, such as combustor liners, transition ducts, and first-stage turbine nozzles. Development of the gas turbine is conducted by Kawasaki Heavy Industries, Ltd. (KHI) to achieve the turbine inlet temperature (TIT) of 1250 °C, thermal efficiency of 34%, NO_x emission less than standard regulation values, and 4000 h engine durability. Kyocera is in charge of the development and evaluation of the ceramic components. Recently, recession of the silicon-base ceramic materials under the combustion gas is the focus of attention to improve the reliability of ceramic components for gas turbine. For the HGT project, the silicon nitride material (SN282: silicon nitride material produced by Kyocera Corp.) is used for the components subjected to high temperature. The SN282 was evaluated under the combustion gas, and clear recession was observed. Our technology of the environmental barrier coating (EBC) is under development to obtain reliable heat resistive SN282 components, against the recession by combustion gas. Reliability of the SN282 with EBC has been evaluated by exposure and hydrothermal corrosion test. Ceramic components made of SN282 with EBC will be also evaluated by a proof engine test of 4000 h, which starts in the spring of 2002.

Keywords: ceramic materials, combustion, heat resistance, high-temperature effects, nitrogen oxides, regulatory compliance, reliability, silicon nitride, thermodynamic properties

T. Fukudome, S. Tsuruzono, W. Karasawa, and Y. Ichikawa, Yoshihiro, R&D Center Kagoshima, Kyocera Corp., Kokubu Kagoshima, Japan. Cited: *Proc. ASME TURBO EXPO 2002: Ceramics, Industrial and Cogeneration Structures and Dynamics,* Vol. 4A, 3-6 June 2002 (Amsterdam), The International Gas Turbine Institute, American Society of Mechanical Engineers, 2002, pp. 135-140 [in English].

Diagnostics and Control

In-Flight Particle Parameters

Effect of spray particle trajectory on the measurement signal of particle parameters based on thermal radiation. The influences of the dimensions of optical components and the trajectories of spray particles on the variations of the waveforms of the radiation signals from the spray particles were studied both theoretically and experimentally for correct simultaneous measurement of the particle parameters including particle velocity, surface temperature, size, and spatial distribution. Two types of filtering masks, including single-windowed and dual-windowed, were used as models in the current study. The evolution of the radiation pulse from a moving thermal spray particle was simulated through the change of the projected area of the particle image spot on the filtering mask window. The experimental detection of the thermal radiation pulses was performed for the high-velocity oxygen fuel (HVOF) process using an optoelectronic measurement system. The theoretical simulation clearly showed that the characteristic waveforms of the thermal radiation signals from the spray particles are varied with the distance and orientation of the trajectories of thermal spray particles with respect to the ideal image plane of the filtering window plane. The typical variations of the characteristic waveforms obtained theoretically have been observed experimentally with HVOF spraying. The waveforms expected theoretically were correlated well with those observed experimentally. The characteristic waveforms of the radiation signals from the spray particles in a trapezoid shape with a saturated top platform contain the information for spray particle parameters including velocity, surface temperature, size, and spatial distribution. With the dual-windowed filtering mask, the particle velocity can be correctly measured with the bipeak radiation signal in trianglelike shape, and the surface temperature may be estimated reasonably. However, the particle size cannot be estimated correctly. It was revealed that the characteristics of the waveforms were remarkably influenced by the image spot size. Therefore, the expansion of the image spot based on the relation between the image spot size of an in-flight particle and optical lens parameters obtained optically was discussed. The influence of the image spot size on the wave-form characteristics was examined.

Keywords: computer simulation, filtration, heat radiation, lenses, masks, optoelectronic devices, waveform analysis

C.-J. Li, T. Wu, C.-X. Li, and B. Sun, Welding Research Institute, Sch. of Mat. Science and Engineering, Xi'an Jiaotong Univ., Xi'an, Shaanxi 710049, China. Cited: *J. Therm. Spray Technol., 12*(1), March 2003, pp. 80-94 [in English]. ISSN 1059-9630.

In-flight characteristics of plasma sprayed alumina particles: measurements, modeling, and comparison. The key phenomena controlling the properties of sprayed coatings are the heat and momentum transfer between the plasma jet and the injected particles. Modern on-line particle monitoring systems provide an efficient tool to measure in-flight particle characteristics in such a way that factors that could affect the coating quality can be identified during the spray process. In this work, the optical sensing device, DPV-2000 from Tecnar, was used for monitoring the velocity, temperature, and diameter of in-flight particles during the spraying of alumina with a Sulzer-Metco F4 plasma torch. Evolution of particle velocity, temperature, diameter, and trajectory showed well-marked trends. Relationships between the position of the in-flight particles into the jet and their characteristics were pointed out, thus delivering valuable information about their thermal treatment. Moreover, a numerical model was developed, and predictions were compared with experimental results. A good agreement on particle characteristics was found between the two different approaches.

Keywords: alumina, heat treatment, numerical methods, sprayed coatings

M.P. Planche, R. Bolot, and C. Coddet, LERMPS, UTBM, 90010 Belfort, France. Cited: *J. Therm. Spray Technol., 12*(1), March 2003, pp. 101-111 [in English]. ISSN 1059-9630.

Study on atmospheric plasma spraying of Al_2O_3 using on-line particle monitoring. In recent years, the interest in on-line diagnostic methods for thermal spraying has been increasing. The particle in-flight properties can be determined using such methods. One of the methods is on-line particle monitoring. In this investigation, study of atmospheric plasma spraying of Al_2O_3 was done using a DPV-2000 system (TECNAR, Canada). The influence of some spray parameters and the noise factor "wear of electrodes" on the particle in-flight properties was investigated. It was found that the argon flow rate was the most influential factor for the particle velocity. The hydrogen flow rate influenced mainly the particle surface temperature. Increasing the electric current led to an increase in the particle velocity as well as in the particle surface temperature. The melting behavior of the powder was significantly influenced by the particle velocity. The higher particle velocity resulted in a worse melting behavior of the powder due to the shorter dwell time, leading to a lower deposition efficiency of the powder during spraying.

Keywords: argon, electrodes, melting, particles (particulate matter), plasma spraying, wear of materials

L. Zhao, K. Seemann, A. Fischer, and E. Lugscheider, Materials Science Institute, Aachen Univ. Technology, Aachen D-52070, Germany. Cited: *Surf. Coat. Technol., 168*(2-3), 22 May 2003, pp. 186-190 [in English]. ISSN 0257-8972.

Influence of plasma spray parameters on in-flight characteristics of ZrO_2-8 wt%Y_2O_3 ceramic particles. Yttria partially stabilized zirconia was atmospherically plasma sprayed by systematically varying the process conditions including carrier gas flow rate, torch power, standoff distance, and Ar/H_2 ratio in the plasma gas mixture. The in-flight particle parameters such as temperature, velocity, number, and size were determined using a commercially available diagnostic system. The particle parameters were controlled by the particle trajectory in the plume and plasma jet characteristics. The average temperature and the velocity of particles, which reached their maximum at an intermediate carrier gas flow rate of 3.5 L/min, varied as much as 6 and 25%, respectively, with a 75% variation in the carrier gas flow rate by going from the lowest to the intermediate rates. The average temperature and the velocity of particles were lower for a lower torch power, a higher Ar/H_2 ratio, and a larger standoff distance. It was necessary to obtain data on particle populations larger than 1000 for statistically reliable and reproducible information from the diagnostic system.

Keywords: argon, ceramic materials, flow of fluids, hydrogen, particle size analysis, plasma jets, plasma spraying, temperature, velocity, yttrium compounds

A. Kucuk, R.S. Lima, and C.C. Berndt, Karl Storz Endovision, Inc., Charlton, MA 01507. Cited: *J. Am. Ceram. Soc., 84*(4), April 2001, pp. 685-692 [in English]. ISSN 0002-7820.

Plasma Jets

Monitoring plasma jets containing microparticles with chromatic techniques. A description about the use of the chromatic methodology for monitoring an arc plasma jet utilized for heating microparticles for forming plasma sprayed coatings is given. It is shown that the behavior of both the plasma and heated microparticles are distinguishable from their different coordinates on an H-S polar map. Calibration with a standard ribbon lamp would appear feasible for tracking the temperature of the plasma heated microparticles.

Keywords: coating techniques, electric arcs, plasma spraying, sprayed coatings

P.C. Russell, B.E. Djakov, R. Enikov, D.H. Oliver, Y. Wen, and G.R. Jones, Dept. of Elec. Eng. and Electronics, Ctr. Intelligent Monitoring Syst., Univ. Liverpool, Liverpool, U.K. Cited: *Sensor Rev., 23*(1), 2003, pp. 60-65 [in English]. ISSN 0260-2288.

Swirl effects on flow dynamics and fuel spray structure in practical combustors. The effect of high shear in the flow on the spray flame characteristic

has been examined. The shear was provided using different swirl combination in the inner and outer swirlers in the double concentric swirl burner. The burner allowed independent control of swirl and combustion airflow in the inner and outer annulus of the burner. Particle image velocimetry (PIV) and phase Doppler particle analyzer (PDPA) laser diagnostic tools have been used to obtain comprehensive data related to droplet size, velocity, number density, vorticity in the flow for dispersed phase, and flow and strain rate in the axial direction in the carrier phase. A commercially available twin fluid nozzle has been used in this study. Results have been obtained for a swirl combination of 65° in inner swirler and 30° in outer swirler (referred to as 65°/30°). The results are compared with a swirl combination of 50°/30°. The results show secondary breakup of the droplets with high shear that was not present with low shear in the flow. They also show a new way to obtain smaller size of droplets from a spray. Smaller size of droplets allows one to easily control the size, shape, stability, and structure of the spray flames.

Keywords: drop formation, flame spraying, fuel burners, shear flow, strain rate, swirling flow, velocity measurement, vortex flow

B. Habibzadeh and A.K. Gupta, Combustion Laboratory, Dept. Mechanical Engineering, Univ. Maryland, College Park, MD 20742. Cited: *22nd Computers and Information in Engineering* (Conf. Proc.), Vol. 1, 29 Sept-2 Oct 2002 (Montreal, Quebec, Canada), American Society of Mechanical Engineers, 2002, pp. 317-329 [in English].

Thermal Spray Process Control

Investigation of optimal control system for arc spraying. An arc voltage feedback PID controller and arc current feedback PID controller with a control algorithm of discrete PID are designed separately to realize optimal control in computer controlling arc spraying system. In order to realize optimization and adaptation of the arc spraying process parameters as well as to reduce blindness in selecting process parameters, a serial communication interface between a PC for spraying data acquisition and a monolithic computer of the control system is designed so that on-time modification of the PID control parameters is implemented. At the same time, a genetic algorithm is adopted to optimize the control parameters of PID adjuster, where the difference between the actually sampled value and the setting value of spraying current is made as the judgment criterion to determine the adaptability. The given range of control parameters varies from 0-15 and is to be demoted by a coding of four-bit binary string. The chromosome code ought to be a 16-bit string. The optimal population of control parameters of the PID adjuster can be obtained through reproduction, crossing, and mutation, so that the optimal controlling in arc spraying is realized and to obtain an excellent layer of arc spraying.

Keywords: adaptive control systems, genetic algorithms, mathematical models, optimal control systems

H.-Q. Li, C.-X. Li, K.-X. Chen, and Z.-J. Zhang, Gansu Univ. of Technol., Lanzhou 730050, China. Cited: *Hanjie Xuebao/Trans. China Weld. Inst., 23*(6), Dec 2002, pp. 9-12 [in Chinese]. ISSN 0253-360X.

Thermal Spray Process Monitoring

CCD technology applied to noncontact diagnosis of plasma flame. Noncontact diagnosis of flame characteristics in plasma spraying forming has been realized by using CCD sensor to collect full flame data. The numerical model has been established through Abel transformation to analyze temperature field distribution of plasma flame by gray-scale values, which can investigate the regularity of temperature field distribution by fake color image. The collecting principle and method in the field of high temperature and flame shape affected by carrier gas flow rate are especially presented. The experimental system of dynamic collection is also very important to improve quality of ceramic cutting and to study further on flame characteristics of plasma-laser interaction in direct metal tooling by laser-plasma technology.

Keywords: charge coupled devices, color, flame spraying, laser applications, mathematical models, temperature distribution

J. Fang and W. Xu, School of Mechanical Engineering, Dalian Univ. Technology, Dalian, Liaoning, China. Cited: *Proc. Int. Conf. Energy Conversion and Application (ICECA'2001),* W. Liu, Ed., 17-20 June 2001 (Wuhan), Huazhong Univ. Science and Technology, 2001, pp. 1294-1297 [in English]. ISBN 7560924204.

Feedstock

Characterization of Hydroxyapatite Powders

Radio frequency (RF) suspension plasma sprayed ultrafine hydroxyapatite (HA)/zirconia composite powders. Ultrafine hydroxyapatite (HA)/ZrO_2 composite powders was synthesized by radio frequency (RF) induction suspension plasma spray. A wet suspension of HA/ZrO_2 was employed as feedstock. The suspension was injected axially into the RF plasma to produce the nanocomposite powders, which were subsequently accumulated in cyclone collectors. The particle size and morphology was resolved by using the zeta potential nanoparticle size analyzer, scanning electron microscopy, transmission electron microscopy, field emission microscopy techniques. The phase composition, phase concentration, and molecular structure of the powders were characterized using differential scanning calorimetry, Fourier transform infrared, and x-ray diffractometry with quantitative phase analysis empowered by the Rietveld method. Results indicated that nanosize, spherical HA/ZrO_2 composite powders were produced with varying morphological features that depend on the thermal treatment. Calcium zirconate ($CaZrO_3$) was produced as a by-product whose biocompatibility is not well documented. Results also showed that the HA decomposed into α- and β-TCP due to decreasing calcium/phosphorus ratio with the formation of $CaZrO_3$.

Keywords: composite materials, differential scanning calorimetry, field emission microscopes, Fourier transform infrared spectroscopy, hydroxyapatite, molecular structure, morphology, nanostructured materials, particle size analysis, plasma spraying, scanning electron microscopy, synthesis (chemical)

R. Kumar, P. Cheang, and K.A. Khor, Sch. of Mech./Production Engineering, Nanyang Technological Univ., Singapore 639798, Singapore. Cited: *Biomaterials, 24*(15), July 2003, pp. 2611-2621 [in English]. ISSN 0142-9612.

Nanopowders

Preparation of nanoparticles via spray route. Nanometer-sized particles (1-100 nm) are of considerable interest for a wide variety of applications, ranging from electronics via ceramics to catalysts, due to their unique or improved properties that are primarily determined by size, composition, and structure. In this study, we report a simple, rapid, and generalizable aerosol decomposition (spray pyrolysis) process for the continuous synthesis of nanoparticles with adjustable sizes, narrow size distribution, high crystallinity, and good stoichiometry. The production of spherical-shaped porous particles with nanoscale ordering porosity and the zinc oxide quantum dots in silica nanoparticles matrix by means of a spray drying method using a colloidal mixture as the precursor and by the combined sol-gel and spray drying method were also reported.

Keywords: catalysts, ceramic materials, electronic equipment, semiconductor quantum dots, sol-gels, spraying, structure (composition), synthesis (chemical), zinc oxide

K. Okuyama and W. Lenggoro, Dept. Chemical Engineering, Graduate School of Engineering, Hiroshima Univ., Higashi-Hiroshima 739-8527, Japan. Cited: *Chem. Eng. Sci., 58*(3-6), Feb/March 2003, pp. 537-547 [in English]. ISSN 0009-2509.

Flame spray pyrolysis of precursors as a route to nanomullite powder: powder characterization and sintering behavior. The flame spray pyrolysis of alcohol-soluble precursors allows the synthesis of mullite-composition nanopowders (average size of ~60-100 nm) that, when annealed carefully, provide processible nanomullite powders. The powders have been characterized using several spectroscopic and microscopy methods, including thermal gravimetric analysis, differential thermal analysis, diffuse reflectance infrared Fourier transform spectroscopy, and transmission electron microscopy. Preliminary studies on the pressureless-sintering behavior of these powders are presented. Without additives or any efforts to optimize the process, powder compacts could be sintered to relative densities of >90%, with grain sizes of $\leq$500 nm at 1600 °C.

Keywords: annealing, differential thermal analysis, flame spraying, Fourier transform infrared spectroscopy, nanostructured materials, powders, pyrolysis, sintering, synthesis (chemical), thermogravimetric analysis, transmission electron microscopy

R. Baranwal, M.P. Villar, R. Garcia, and R.M. Laine, Dept. of Materials Science and Eng., Univ. Michigan, Ann Arbor, MI 48109-2136. Cited: *J. Am. Ceram. Soc., 84*(5), May 2001, pp. 951-961 [in English]. ISSN 0002-7820.

Production/Preparation Technology

Submicron-sized $LiMn_2O_4$ prepared by a sol-gel, spray-drying method. Submicron-sized $LiMn_2O_4$ powders were produced by a sol-gel, spray-drying method in which a brown gel precursor was prepared via the reaction of LiOH alkaline solution with 1 *M* $Mn(CH_3COO)_2$. The gel precursor was then transferred into a dry precursor powder via a spray-dry process. After heating treatment the spinel $LiMn_2O_4$ powder was obtained. The composition and the crystal size of the samples were strongly affected by the spray speed in the drying process and the heating temperature. The structure and the morphology of $LiMn_2O_4$ powder were investigated by differential thermal analysis, thermogravimetric analysis, infrared, x-ray diffraction analysis, and scanning electron microscopy methods. It was discovered that submicron-sized $LiMn_2O_4$ powder could be formed under the conditions of rotating spray speed of 15,000 rpm and syntheses temperature of 700 °C. The electrochemical properties of $LiMn_2O_4$ samples in 1 *M* $LiPF_6$, EC:DMC = 1:1 solution were tested by measuring the voltammograms and charge-discharge curves. The submicron-sized $LiMn_2O_4$ sample made at 700 °C has a capacity of 128 mAh g^{-1} and good cycle stability for Li^+ intercalation reaction. This method may be applied to the industrial-scale production of superfine $LiMn_2O_4$ powder for use in lithium ion batteries.

Keywords: composition, crystals, differential thermal analysis, drying, electro-

chemistry, heating, morphology, powders, scanning electron microscopy, sol-gels, x-ray diffraction analysis

C. Wan, Y. Nuli, Q. Wu, M. Yan, and Z. Jiang, Dept. Chemistry, Fudan Univ., Shanghai 200433, China. Cited: *J. Appl. Electrochem., 33*(1), Jan 2003, pp. 107-112 [in English]. ISSN 0021-891X.

The influence of milling parameters on the properties of the milled powders and the resultant coatings. The high-energy ball-milling technique is an effective method for producing powders for metal-matrix composite (MMC) coatings. The properties of MMC coatings strongly depend on the amount, size, and distribution of hard phases in the metal matrix, which are influenced by properties and morphology of starting powders and milling parameters. In this study, Al_2O_3 dispersion-strengthened NiCr spray powders were produced using the high-energy ball-milling process with different milling parameters. Two of the milled powders and the unstrengthened matrix material were sprayed using a high-velocity oxyfuel spraying process. Both the milled powders and the coatings were studied in terms of their microstructure and microhardness. The abrasive wear resistance of the coatings was evaluated using pin-on-disk tests, during which a disk was covered by a 400 SiC grinding paper. It was found that better milling results were achieved using a longer milling time, a higher ball to powder ratio, and bigger milling balls. Premilling of the ceramic powder led to more homogeneous dispersion structure with finer Al_2O_3 particles. The harder the milled powder, the harder and the more wear resistant the coating.

Keywords: ball milling, nickel alloys, powders, strengthening (metal), wear resistance

L. Zhao, J. Zwick, and E. Lugscheider, Materials Science Institute, Aachen Univ. Technology, Aachen D-52070, Germany. Cited: *Surf. Coat. Technol., 168*(2-3), 22 May 2003, pp. 179-185 [in English]. ISSN 0257-8972.

Alumina slurry formulation intender for spray dried powder production. Ceramic powders are used to produce coatings using plasma spray processes. The powder granules are required to have a spherical shape, a mean diameter around 40 μm, and, moreover, different densities of the powder must be possible. Alumina powders are obtained by spray drying of concentrated aqueous suspensions of particles (slurries). The suspension must contain high solids loading, be stable during the process, and have a relatively low viscosity. The aim of this study was to determine how the properties of aqueous alumina slurries influence the characteristics of granules produced by spray drying. The effects of pH and additives (dispersant and binder) on settling and rheological properties of the alumina slurries were investigated. The curves recorded followed the Casson model in the observed range of shear rate. The Casson yield stress values, T_c, and the viscosity values, η were determined and used to evaluate particles interaction in the slurries. The dependence of the yield stress and viscosity was measured as a function of polyacrylate dispersant and binder concentration at pH 4 and 9. The corresponding powders have been characterized on a morphological basis.

Keywords: alumina, drying, rheology, slurries, spraying, suspensions (fluids), yield stress

C. Filiatre, G. Bertrand, C. Coddet, and A. Foissy, UFR des Sciences/Techniques, LCMI, Besancon 25030, France. Cited: *Polym. Int., 52*(4), April 2003, pp. 586-589 [in English]. ISSN 0959-8103.

Manufacturing

Rapid Tooling

Rapid tooling using plasma spraying and rapid prototyping. In the race to fabricate a product to market with increases in speed, cost, and quality, the drive to economically decrease tooling lead times becomes more important. Rapid tooling (RT) fabricated at Tsinghua Univ. uses a metal plasma spraying process and rapid prototyping (RP) to form a metal tool. The process uses plasma spraying as the heat pool to melt metal powder and then deposit molten metal on to the substrate made by RP. It provides a quick, accurate, simple, and relatively cost-effective route for producing metal parts or tools, especially for large tools. The process and key technologies are analyzed and described in detail. Applications illustrate that the total costs and lead times for new products can be reduced.

Keywords: cost effectiveness, manufacture, powder metals, quality control, rapid prototyping, tools

Z. Shan, Y. Yan, R. Zhang, and F. Qi, Centre for Laser Rapid Forming, Dept. Mechanical Engineering, Tsinghua Univ., Beijing 100084, China. Cited: *J. Mech. Eng. Sci., 217*(1), 2003, pp. 97-104 [in English]. ISSN 0954-4062.

Modeling

Fracture Behavior of Coatings

Effect of pre-existing surface crack morphology on the interfacial thermal fracture of thermal barrier coatings: a numerical study. The interfacial fracture of thermal barrier coatings (TBCs) at the ceramic-bond coat interface occurs during the cooling period following exposure to high temperatures. Previous studies showed that the presence of multiple vertical surface precracks that span over the entire coating thickness was beneficial in reducing the propagation of interface cracks. In this paper, the effect of different surface precrack morphologies, such as precrack length and precrack density, on an interface crack during a thermal shock caused by a high heat flux is presented. The results show that shorter surface precracks and a larger precrack density can delay the interfacial fracture. In particular, this behavior is shown to be more prominent in thicker TBCs.

Keywords: cooling, heat flux, interfaces (materials), morphology

B. Zhou and K. Kokini, School of Mechanical Engineering, Purdue Univ., West Lafayette IN, 47907-1288. Cited: *Mater. Sci. Eng. A, 348*(1-2), 15 May 2003, pp. 271-279 [in English]. ISSN 0921-5093.

Crack assessment in thermal barrier coating systems using finite-element method and taking mode mixity into account. Due to thermal expansion mismatch and bond coat (BC) oxidation, high residual stresses are induced in the thermal barrier coating (TBC), leading to failure by spalling and delamination. Using the finite-element method (FEM), a detailed analysis of the stress distributions in TBC systems, which is a prerequisite for the development of failure mechanisms, was performed. As cracking usually occurs at or near the interfaces between BC/thermally grown oxide (TGO) and TBC/TGO, depending on the processing mode of the TBC, cracks in the interface region were considered in the FE models in order to determine the loading conditions for their propagation and, thus, the failure criteria of the TBCs. Due to the mode mixity of these cracks, suitable methods are required for the determination of the fracture mechanics parameters needed for their assessment, such as strain-energy release rate (G), J-integral, and stress-intensity factor (K). The modified crack closure integral (MCCI) method was found to be a very efficient tool that can easily be combined with FE analysis and lead to highly accurate energy release rate values. Moreover, this method enables the determination of mode-dependent energy release rates. Using this tool and appropriate crack-propagation criteria, TBC failure models could be developed numerically and verified.

Keywords: bonding, crack propagation, finite-element method, fracture mechanics, interfaces (materials), oxidation, residual stresses, strain rate, stress-intensity factors, thermal expansion

K. Sfar, J. Aktaa, and D. Munz, Institute for Materials Research II, Forschungszentrum Karlsruhe GmbH, D-76021 Karlsruhe, Germany. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., B, 22*(4), 2001, pp. 397-406 [in English]. ISSN 0196-6219.

High-Velocity Oxyfuel Process

Modeling of particle in-flight and deposition during plasma and HVOF spraying. A multiphysics simulation tool has been developed for thermal spray application. A comprehensive multidimensional computational code (LAVA) that was originally developed at the INEEL and enhanced at Stony Brook is used to simulate plasma jet and injected particle behaviors. An in-house code for high-velocity oxyfuel (HVOF) process is developed to simulate transport phenomena for the formation of high-temperature and high-velocity (supersonic) jet and the interaction between jet and particle. A three-dimensional droplet spreading and rapid solidification model is developed based on multizone adaptive grid generation (MAGG) scheme tracking the moving boundaries and level set method capturing the free surface deformation. The multiphysics simulation provides a virtual environment for testing the processes, industrial design and control of spray coating processes.

Keywords: codes (symbols), computer simulation, high-energy physics, plasma jets, solidification

L. Zheng and H. Zhang, Dept. Mechanical Engineering, State Univ. New York at Stony Brook, Stony Brook, NY 11794-2300. Cited: *Proc. Int. Conf. Energy Conversion and Application (ICECA'2001),* W. Liu, Ed., 17-20 June 2001 (Wuhan), Huazhong Univ. Science and Technology, 2001, pp. 147-153 [in English]. ISBN 7560924204.

Properties of Coatings

Estimation of residual stresses from the simulation of the deposition process of ceramic coatings on light metal cylinder liners. Residual stresses induced by the manufacturing process influence significantly the ceramic coating quality and cylinder liner composite performance. The final residual stress state in thermally spray coated composites is superimposed by different stress mechanisms occurring during the manufacturing process. Because of different thermophysical properties of the composite materials and due to the local heat and mass transfer during the atmospheric plasma spraying process, residual stresses arise in the layer composite. By experimental measurement methods the residual stresses can be only locally defined after the manufacturing process. Also the development of stresses during thermal spraying and the distribution over the entire surface cannot be explained. To consider the formation of residual stresses during the spray process and to evaluate the influence of the different plasma spray parameters, a numerical

stress analysis of the coating process is indispensable. This paper describes an approach of a finite-element simulation for inside coating processes focused on heat development, component deformation, and residual stresses. The internal coating process is simulated in real time with several transitions of a heat and thermal spray torch. The simulated results are compared with experimentally measured stress results.

Keywords: computer simulation, engine cylinders, finite-element method, residual stresses, stress analysis, thermodynamic properties

M. Buchmann and R. Gadow, Univ. Stuttgart, IMTCCC, D-70569 Stuttgart, Germany. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., B, 22*(4), 2001, pp. 329-336 [in English]. ISSN 0196-6219.

Analytical modeling of stress evolution in air plasma sprayed thermal barrier coatings. Understanding stress evolution at rough interfaces in air plasma sprayed thermal barrier coatings due to thermal exposure in service is critical for failure prediction, This study analyzes stress evolution in these coatings by a concentric cylinder model. Contributions due to thermal mismatch, oxide growth, and microstructural changes in the coatings are discussed. Our analysis indicates an initial increase and a subsequent decrease in stress at the interface with exposure time.

Keywords: failure analysis, growth (materials), interfaces (materials), mathematical models, microstructure, plasma spraying, stress concentration, thermal effects, thermal expansion

B. Nair, J.P. Singh, and M. Grimsditch, Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., B, 22*(4), 2001, pp. 417-425 [in English]. ISSN 0196-6219.

Implementation of a viscoplastic model for a plasma sprayed ceramic thermal barrier coating. This paper describes the implementation and modification of a previously proposed unified viscoplastic constitutive model to simulate the behavior of a yttria-stabilized zirconia plasma sprayed thermal barrier coating. The model was recast for use in finite strain situations and modified to have a more physically acceptable nonassociated flow rule. Temperature-dependent material constants were found for a specific material using a novel approach based on genetic algorithms.

Keywords: computer simulation, genetic algorithms, mathematical models, plasma spraying, strain, thermal effects, viscoplasticity, zirconia

W. Xie, K.P. Walker, E.H. Jordan, and M. Gell, Univ. Connecticut, Storrs, CT 06268. Cited: *J. Eng. Mater. Technol., Trans. ASME, 125*(2), April 2003, pp. 200-207 [in English]. ISSN 0094-4289.

Spray Deposition Process

Process model of plasma enameling. A computational model has been developed to simulate the deposition of enamel on steel substrates by the use of plasma spraying. The model predicts the temperature profiles of the feedstock particles during their flight in the gas jet and the concurrent heating of the substrate. A process window is predicted for enamel deposition in terms of plasma gas composition and feedstock particle size. The model also predicts that the plasma jet produces a thermal shock at the surface of the coating and a high temperature gradient through its thickness during the scanning action. A series of experimental trials confirmed that plasma spraying could successfully produce dense coatings on steel. An inherent advantage of the process is that the enamel feedstock powder is fused separately in the plasma, while the substrate remains at a low temperature. This enables enameling to be carried out in a single-stage operation without the need for a furnace, which offers the potential of widening the applicability of enamel coatings.

Keywords: coating techniques, deposition, enameling, feedstocks, plasma spraying, steel, substrates, surface phenomena

T. Zhang, Y. Bao, and D.T. Gawne, School of Engineering, Kingston Univ., London, U.K. Cited: *J. Eur. Ceram. Soc., 23*(7), June 2003, pp. 1019-1026 [in English]. ISSN 0955-2219.

Numerical study on the characters of direct current plasma spraying in RPST. It is necessary to attain high deposition efficiency, a delicate duplication, and an easy coating-prototyping separation in rapid plasma spray tooling (RPST). Current problems with the plasma sprayed coatings involve the reliability and techniques of performance and the design of equipment, both of which need to study the characters of plasma spraying based on fundamental principles. A two-dimensional steady-state axisymmetric mathematical model has been set up in this paper for predicting temperature and velocity field of a free direct current plasma torch and the injected particles. According to the results of the computation, suggestions are proposed for the performance to obtain suitable coatings for RPST.

Keywords: computational methods, computer simulation, mathematical models, sprayed coatings, temperature measurement, velocity measurement

B. Fan, G. Wang, and H. Zhang, State Key Lab. Plast. F.S./D./M.T., Huazhong Univ. of Sci./Technology, Wuhan 430074, China. Cited: *Proc. Int. Conf. Energy Conversion and Application (ICECA'2001),* W. Liu, Ed., 17-20 June 2001 (Wuhan), Huazhong Univ. Science and Technology, 2001, pp. 266-269 [in English]. ISBN 7560924204.

Numerical modeling of motion and heating of particles during plasma spraying. A theoretical model based on a CFD (computational fluid dynamics) methodology has been developed to simulate the motion and heating of particles in a plasma jet during plasma spraying. The particle motion and heat transfer equations are solved semianalytically using a prediction-correction method, taking into account phase changes during heating. The computational model is verified by experimental measurements and by comparison with experimental data in the literature. The results show that the relative motion between particles and the plasma jet has a major influence on particle heating through its influence on the heat-transfer coefficient. The computational model can be used to predict the velocity, temperature, degree of melting, and trajectory of feedstock particles during practical plasma spraying.

Keywords: acceleration, computational fluid dynamics, computer simulation, deceleration, heat transfer, high-speed photography, Monte Carlo methods, particles (particulate matter), phase transitions, plasma jets, turbulent flow, velocity

B. Liu, T. Zhang, Y. Bao, and D.T. Gawne, School of Engineering, Kingston Univ., London SW15 3DW, U.K. Cited: *Surf. Eng., 18*(5), 2002, pp. 350-357 [in English]. ISSN 0267-0844.

Modeling of heat flow and solidification during atomization and spray deposition processing. A mathematical model of the spray deposition process, based on heat flow analysis during solidification of droplets, as well as that of the spray deposit, is presented. The heat flow during cooling of droplets is analyzed in five distinct stages. A one-dimensional heat-transfer model, using a finite difference method, is used to calculate the temperature of the deposit. The results indicate that the cooling rate of a wide size range of droplets of Al-4.5Cu alloy in the spray varies from 10^3 to 10^5 °C/s in contrast to a slow cooling rate of 1-10 °C/s of the spray deposit. The spray enthalpy on the deposition surface increases linearly with the melt superheat. In contrast, the atomization gas pressure does not have a significant influence on the enthalpy of the spray in this process. The cooling rate of the deposits predicted from the model compares well with those obtained by the measurements.

Keywords: atomization, computer simulation, cooling, deposition, enthalpy, solidification

P. Shukla, N.S. Mishra, and S.N. Ojha, Dept. of Metallurgical Engineering, Institute of Technology, Banaras Hindu Univ., Varanasi 221 005, India. Cited: *J. Therm. Spray Technol., 12*(1), March 2003, pp. 95-100 [in English]. ISSN 1059-9630.

A stochastic model to simulate the formation of a thermal spray coating. The authors present a three-dimensional, stochastic model of thermal spray coating. It is capable of predicting coating porosity, thickness, roughness, and the variation of these properties with spray parameters. The model assigns impact properties to molten droplets landing on the substrate by generating random values of process parameters, assuming that these properties follow normal distributions with user-specified means and standard deviations. The authors prescribed rules to calculate splat sizes after droplet impact and their interaction with each other. Porosity is assumed to be solely due to the curl-up of the splats as a result of thermal stresses. The authors use a Cartesian grid to define the computational domain and to track the shape and position of the deposited coating. The surface of the coating and the location of pores within it are specified using a variable known as the "volume fraction," defined as the fraction of the volume of a computational cell occupied by coating material. Results are given for the variation of coating porosity, thickness, and roughness with varying particle speed, size, and spraying gun speed. Predicted trends agree with experimental observation.

Keywords: computational methods, computer simulation, deposition, microstructure, porosity, random processes, spray guns, surface roughness, volume fraction

R. Ghafouri-Azar, J. Mostaghimi, S. Chandra, and M. Charmchi, Dept. Mechanical Engineering, Univ. Toronto, Toronto, Ont., Canada. Cited: *J. Therm. Spray Technol., 12*(1), March 2003, pp. 53-69 [in English]. ISSN 1059-9630.

An advanced model for plasma spraying of functionally graded materials. A comprehensive model for the simulation of the plasma spraying of functionally graded materials (FGMs) is developed based on the recently modified CFD code, LAVA-P, that incorporates a well-verified model for plasma gas flow and chemistry. The particle movement and its trajectory are described within a Lagrangian framework by considering the drag as the major driving force. Melting and evaporation of particles are considered using a recently developed model for particle-flame interaction that also accounts for the noncontinuum and variable property effects of high-temperature plasma on particle momentum and heat transfer. Calculations are performed for NiCrAlY (alloy) and Y_2O_3-stabilized ZrO_2 powders with a wide range of size distribution. The influence of the power levels and flow rate of H_2 on the plasma flow field, and hence, on the particle velocity and temperature are investigated numerically. The predicted velocity and temperature fields agree well with the measurements performed under similar spraying conditions. Segregation is inves-

tigated for two powder injection configurations. The model presented here can be used successfully for FGM deposition uniformity.

Keywords: evaporation, heat transfer, melting, plasma spraying

Y.P. Wan, S. Sampath, V. Prasad, R. Williamson, and J.R. Fincke, Center for Thermal Spray Research, Process Modeling Laboratory, State Univ. New York, Stony Brook, NY 11794-2275. Cited: *J. Mater. Process. Technol., 137*(1-3 SPEC), 30 June 2003, pp. 110-116 [in English]. ISSN 0924-0136.

Effects of velocity boundary layer on opposed flame spread over a thermally thin solid fuel in microgravity. Upstream (opposed) flame spread over a thermally thin cellulosic sheet in various imposed flow speed and ambient oxygen concentration under microgravity environment is studied numerically. Two-dimensional time-dependent phenomena, from spontaneous ignition to the flame spread in a fully developed velocity boundary layer formed over a flat cellulosic sheet, are simulated with a well-developed numerical model. The model predicts that the upstream flame spread in the boundary layer is essentially time-dependent phenomena, and the unsteadiness is pronounced when the imposed flow speed is very slow/high and lower oxygen concentration. This unsteady flame spread behavior is due to the boundary layer effect; when the flame spreads to upstream (i.e., thin boundary layer zone), local flow speed at the flame front is not constant but increased. The local flow speed has excellent correlation with the local flame spread rate. Plots of the flame temperature versus the local flame spread rate show their linear relationship for all conditions considered in the present study, indicating that classical deRis's theory still be valid for present unsteady (quasi-steady) flame spread mode.

Keywords: boundary layers, combustion, computer simulation, flame spraying, ignition, mathematical models, microgravity processing

Y. Nakamura, Y. Etoh, and H. Yamashita, Dept. of Mechanical Engineering, Nagoya Univ., Nagoya-shi, Aichi, 464-8603, Japan. Cited: *Nippon Kikai Gakkai Ronbunshu, B Hen/Trans. Jpn. Soc. Mech. Eng., B, 69*(677), Jan 2003, pp. 193-199 [in Japanese]. ISSN 0387-5016.

Postprocessing

Heat Treatment of Coatings

Structural evolution of thermally sprayed yttria-stabilized ZrO_2 thermal barrier coatings with annealing—a neutron diffraction study. The authors studied the influence of the annealing temperature on the atomic structure of yttria-stabilized tetragonal zirconia (YSZ) that was deposited as a 300 μm thick thermal barrier coating (TBC) on nickel superalloy substrates by plasma spraying. To obtain neutron powder diffraction patterns of the barrier coatings the authors used an experimental technique where the sample is randomly rotated in the neutron beam. The time-averaged neutron diffraction pattern was then analyzed using the Rietveld refinement technique without any need for corrections. This allowed the comparison of the average crystals structures from bulk tetragonal samples obtained via common ceramic routes and those of micrometer thick films deposited on substrates using plasma spray or other nonequilibrium techniques.

Keywords: annealing, crystal atomic structure, neutron beams, neutron diffraction, nickel alloys, plasma spraying, superalloys, thermal barrier coatings, thermal effects, thick films, yttrium compounds

T. Vogt, B.A. Hunter, and J. Thornton, Physics Dept., Brookhaven National Laboratory, Upton, NY 11973. Cited: *J. Am. Ceram. Soc., 84*(3), March 2001, pp. 678-680 [in English]. ISSN 0002-7820.

Influence of tetragonality on tetragonal-to-monoclinic phase transformation during hydrothermal aging in plasma sprayed yttria-stabilized zirconia coatings. The influence of tetragonality, which is defined as the lattice parameter ratio *c*/*a*, on the tetragonal-to-monoclinic phase transformation during hydrothermal aging was investigated in yttria-stabilized zirconia coatings. The yttria content was adjusted in the range of 4-8 mass% (denoted as *x*YZ, where *x* = 4-8 and YZ represents the yttria-stabilized zirconia). The tetragonality of the zirconia in the as-sprayed coatings was less than that in the powders. To change the tetragonality for each yttria content, the coatings were annealed at 1273 K before aging. Without annealing, the phase transformation was prevented only in 8YZ. When annealing was applied, an increase of the tetragonality (i.e., recovery of the tetragonality) was observed, and transformation during hydrothermal aging was also suppressed in 6YZ. It was concluded that the increase in tetragonality that occurred without a change in the yttria content was suggested to be caused by the lattice relaxation of the tetragonal phase, and this relaxation is believed to cause a reduction of the critical yttria concentration, thus preventing the phase transformation.

Keywords: aging of materials, annealing, lattice constants, phase transitions, plasma spraying, relaxation processes, sprayed coatings, stainless steel, substrates, yttrium compounds, zirconia

K. Yasuda, Y. Goto, and H. Takeda, Power Supply Mat. and Devices Lab., Corporate Res. and Development Ctr., Toshiba Corp., Kawasaki 210-8582, Japan. Cited: *J. Am. Ceram. Soc., 84*(5), May 2001, pp. 1037-1042 [in English]. ISSN 0002-7820.

High-Velocity Oxyfuel Coatings

Post-heat treatment microstructural changes in nickel-base HVOF coating. The effects of various heat treatments (oxyacetylene flame, argon atmosphere, vacuum) on the microstructure and hardness of thermal sprayed coatings has been studied. Commercial powder of the NiCrSiBW alloy known as Colmonoy 88 was sprayed using the HVOF (high-velocity oxyfuel) process. Coatings were deposited on AISI 1020 steel substrates using a JP5000 gun. The processing parameters recommended by the powder manufacturer were employed. The results indicate that post-heat treatments conducted in both vacuum and argon atmosphere produced significant changes in the morphology and distribution of the hard phases, but no noticeable changes were observed when the coatings were post-heat treated with an oxyacetylene flame. The measured microhardness values were correlated with the microstructural changes that took place during post-heat treatment.

Keywords: diffusion, energy-dispersive spectroscopy, microhardness, microstructure, morphology, nickel, phase transitions, porosity, powder coatings, x-ray diffraction analysis

M.A. Rodriguez, L. Gil, and M.H. Staia, School of Mechanical Engineering, Central Univ. Venezuela, Caracas 1041, A, Venezuela. Cited: *Surf. Eng., 18*(5), 2002, pp. 358-362 [in English]. ISSN 0267-0844.

Laser Surface Treatment

Raman spectroscopic and photoluminescence investigations on laser surface modified α-Al_2O_3 coatings. Laser surface modification of plasma sprayed alumina coatings were carried out for obtaining desired structural and microstructural transformations. Appearance of Raman modes was used to detect the transformation of Al_2O_3 from γ to α phase. Photoluminescence due to the natural occurrence of Cr^{3+} ions was used to probe the densification and enhancement of the surface quality of the coatings brought about by laser treatment.

Keywords: densification, inorganic coatings, laser beams, laser chemistry, microstructure, phase transitions, photoluminescence, plasma spraying, Raman spectroscopy, surface treatment

B. Raj, R. Krishnan, R. Kesavamoorthy, S. Dash, and A.K. Tyagi, Metallurgy and Materials Group, Indira Gandhi Ctr. for Atom. Res., Kalpakkam 603 102, India. Cited: *Scr. Mater., 48*(8), 14 April 2003, pp. 1099-1104 [in English]. ISSN 1359-6462.

Processing

Cold Gas Spraying

Deposition characteristics of titanium coating in cold spraying. Titanium coating was deposited by cold spraying using nitrogen and helium gases under different temperatures and pressures. The deposition characteristics of the particles in cold spray were studied by the examination of the microstructure evolution of the deposited spot and coating. The effects of the gas type and temperature on the deposition behavior were examined. The microstructure was examined using optical microscopy and scanning electron microscopy. It was found that the pattern of a sprayed spot in cold spray presents a conical shape. The deposition efficiency of spray particles increases with the increase in gas temperature. Two distinguishable top and inner regions exist in the spot deposit and coating, which are characterized by the porous and dense microstructures. The dense microstructure results from the accumulative effect of tamping on the top porous region by the successive impact of following particles. The tamping effect has great influence on the microstructure of the coating in cold spray.

Keywords: deposition, microstructure, spraying, titanium

C.-J. Li and W.-Y. Li, Welding Research Institute, Sch. of Materials Science/Eng., Xi'an Jiaotong Univ., Xi'an, Shaanxi 710049, China. Cited: *Surf. Coat. Technol., 167*(2-3), 22 April 2003, pp. 278-283 [in English]. ISSN 0257-8972.

Detonation Spraying

Coatability and characterization of fly ash deposited on mild steel by detonation spraying. Recently, considerable emphasis has been placed on the processing of low-grade ore minerals through thermal spray techniques. In the present investigation, the suitability of detonation spray system for coating fly ash onto a mild steel substrate has been demonstrated. Resultant coatings are 2-3 times harder than the substrate material and also exhibit a three-fold reduction in coefficient of friction under sliding wear conditions. However, these coatings exhibit poor sliding wear resistance.

Keywords: carbon steel, detonation, fly ash, friction, wear resistance

L. Rama Krishna, D. Sen, D. Srinivasa Rao, and G. Sundararajan, Intl. Adv. Res. Ctr. Powder M.N.M., Hyderabad 500005, India. Cited: *J. Therm. Spray Technol., 12*(1), March 2003, pp. 77-79 [in English]. ISSN 1059-9630.

Evaluation of functionally graded thermal barrier coatings fabricated by detonation gun spray technique. In a new approach, an excellent function-

ally graded thermal barrier coating (FGM TBC) has been fabricated by the detonation gun spray process in conjunction with a newly proposed "shot-control method." FGM TBCs were sprayed in the form of multilayered coatings with a compositional gradient along the thickness direction. The gradient ranged from 100% NiCrAlY metal on the substrate to a 100%ZrO_2-8 wt.%Y_2O_3 ceramic for the topcoat and consisted of a finely mixed microstructure of metals and ceramics with no obvious interfaces between the layers. In the FGM layer of the FGM TBCs, the ceramics and metals maintained their individual properties without any phase transformation during the spraying process. Thermal shock properties of FGM TBCs were also investigated and the data obtained were compared with those for traditional duplex TBCs.

Keywords: ceramic materials, microstructure, nickel alloys, phase transitions, plasma spraying

J.H. Kim, M.C. Kim, and C.G. Park, Center for Advanced Aerospace Mat., Pohang Univ. of Sci. and Technology, Pohang 790784, South Korea. Cited: *Surf. Coat. Technol., 168*(2-3), 22 May 2003, pp. 275-280 [in English]. ISSN 0257-8972.

Electromagnetically Accelerated Plasma Spraying

Boron carbide coating by electromagnetically accelerated plasma spraying. A new system of electromagnetically accelerated plasma spraying (EMAPS) consisting of a pulsed high-current arc-plasma gun and a large flow rate pulsed powder injector has been developed to synthesize a hard and dense coating of boron carbide (B_4C) with a high adhesion. The plasma gun with a coaxial cylindrical electrode configuration generates electromagnetically accelerated arc plasma with a typical velocity and maximum pressure of 1.5-3.0 km/s and 1 MPa, respectively, by discharging a pulsed high current of about 100 kA in peak and about 300 ms of duration. The heating and accelerating of source powder are accomplished by injecting it into the interelectrode space of the gun prior to the plasma generation using a newly developed pulsed powder injector that enables a gram of powder to be injected within 1 ms with precisely controlled time delay. With this system, hard B_4C coatings with a high adhesion and crystallinity were successfully formed on mirror-polished stainless (SUS304) substrates without a binder.

Keywords: adhesion, boron carbide, coatings, crystalline materials, electrodes, heating, magnetoelectric effects, plasma guns

J. Kitamura, S. Usuba, Y. Kakudate, H. Yokoi, K. Yamamoto, A. Tanaka, and S. Fujiwara, Joint Research Consortium of FCT, Japan Fine Ceramics Center, c/o AIST, Tsukuba, Ibaraki 305-8565, Japan. Cited: *J. Therm. Spray Technol., 12*(1), March 2003, pp. 70-76 [in English]. ISSN 1059-9630.

High-Velocity Spray Parameters

Effect of a cylindrical shroud on particle conditions in high-velocity oxy-fuel (HVOF) spray process. Simulations of solid particles in a highly compressible gas flow in the high-velocity oxyfuel (HVOF) process are presented. The Eulerian formulation is used for the gas flow, and the particle phase is modeled by the Lagrangian method. Effects of attaching a cylindrical shroud to the end of the supersonic HVOF nozzle on gas and particle flows are analyzed. The authors found that the shroud significantly reduces the oxygen content in the field by protecting the supersonic jet from ambient air entrainment. The validation experiments were performed for the majority of process parameters such as shock formation, particle conditions, and coating oxygen content.

Keywords: coatings, compressible flow, fuels, nozzles, oxygen

A. Dolatabadi, J. Mostaghimi, and V. Pershin, Dept. Mechanical Engineering, Univ. Toronto, Toronto, Ont., M5S 3G8, Canada. Cited: *J. Mater. Process. Technol., 137*(1-3 SPEC), 30 June 2003, pp. 214-224 [in English]. ISSN 0924-0136.

Hydroxyapatite Biomaterials

Comparative study of bioceramic coatings in static and in simulated physiological conditions. Plasma sprayed HA coatings post-treated by two different methods were incubated in simulated body fluids (SBF). The soaking processes were conducted under both static and flowing conditions to study their effect on formation of hydroxyapatite (HA). In the static process of a closed system, the bonelike apatite deposited on the surface of the coating in a dissolution-precipitation process, the morphology of which was granular and without any orientation. The flowing system was open, the flow rate of which was 2 mL/100 mL · min. The bonelike apatite grew preferentially at the interstitial of coating. One on the 120 °C vapor treated coating behaved needlelike, and another on the 650 °C vacuum treated coating appeared grainy and somewhat fiberlike.

Keywords: body fluids, coatings, morphology, plasma spraying

Q. Zhang, Y. Cao, J. Chen, J. Feng, and X. Zhang, Xingdong, College of Chemical Engineering, Sichuan Univ., Chengdu 610065, China. Cited: Proc. 15th Int. Symposium on Ceramics in Medicine; The Annual Meeting of the International Society for Ceramics in Medicine, B. Ben-Nissan, D. Sher, and W. Walsh, Ed., 4-8 Dec 2002 (Sydney, Australia), *Key Eng. Mater., 299-302,* 2003, pp. 311-314 [in English]. ISSN 1013-9826.

Effects of bond coatings on plasma sprayed calcium phosphate coatings. In this study the effects of bond coatings on various calcium phosphate coatings were studied. From human teeth dentine (DFA) and enamel-derived fluorapatite (EFA) plasma powders were sprayed on titanium with and without a bond coating. As a control group, original hydroxyapatite (HA) powder for biomedical spraying purposes was also used on titanium with and without a bond coating. Tensile strength tests were performed according to ASTM F 633. It was observed that bond coatings had significantly increased the tensile strength values compared to nonbond coatings. It was interesting that the use of a bond coating did not influence any remarkable tensile strength values compared to original coating values, but that the percentage of microvoids has decreased from 1.11 to 0.29%. This means that a better plasma coating with fewer microvoids, which could affect the quality of the coating with continuous progress, has been provided. In other words, the use of bond coatings was found to be very useful. This phenomenon should be investigated in further studies to develop better implant coats.

Keywords: coatings, plasma spraying, tensile strength, trace elements

F.N. Oktar, G. Goller, M. Yetmez, and D. Toykan, Marmara Univ., Campus of Goztepe, New Technol. Res./Development Center, Ziverbey, Kadikoy, Istanbul, Turkey. Cited: Proc. 15th Int. Symposium on Ceramics in Medicine; The Annual Meeting of the International Society for Ceramics in Medicine, B. Ben-Nissan, D. Sher, and W. Walsh, Ed., 4-8 Dec 2002 (Sydney, Australia), *Key Eng. Mater., 299-302,* 2003, pp. 315-318 [in English]. ISSN 1013-9826.

Processing-microstructure-property relations in HVOF sprayed calcium phosphate based bioceramic coatings. Hydroxyapatite (HA) based bioceramic coatings were deposited onto titanium alloy substrates using the high-velocity oxyfuel (HVOF) spray technique. This study aimed to reveal the relations among processing parameters, microstructure, and properties of the bioceramic coatings. The processing conditions were altered through changing the starting HA powder size, content of bioinert ceramic additives, or composite powder preparation techniques. Coating structure was characterized through scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and the mechanical properties, Young's modulus, and fracture toughness of the coatings were evaluated through indentation techniques. Results demonstrated dominant influence of the melt state of HA powders on the phase composition of resultant coatings, and it was found that the HVOF HA coatings possess competitive mechanical properties. Furthermore, addition of titania or zirconia, as secondary phase in HA, showed promising effect on improving the mechanical properties of the HVOF HA-based coatings. Chemical reactions between HA and titania and between HA and zirconia during coating deposition were revealed and characterized. Incorporation modes of the additives into HA and their reinforcing mechanisms were elucidated. The relationship among the processing, microstructure, and mechanical properties of the HVOF sprayed bioceramic coatings was summarily examined.

Keywords: ceramic coatings, deposition, elastic moduli, fracture toughness, microstructure, scanning electron microscopy, spraying, transmission electron microscopy

K.A. Khor, H. Li, and P. Cheang, Sch. of Mech./Production Engineering, Nanyang Technological Univ., Singapore 639798, Singapore. Cited: *Biomaterials,* (13), June 2003, pp. 2233-2243 [in English]. ISSN 0142-9612.

Effect of spark plasma sintering on the microstructure and *in vitro* behavior of plasma sprayed HA coatings. The crystalline phases and degree of crystallinity in plasma sprayed calcium phosphate coatings on titanium substrates are crucial factors that influence the biological interactions of the materials *in vivo*. In this study, plasma sprayed hydroxyapatite (HA) coatings underwent postspray treatment by the spark plasma sintering (SPS) technique at 500, 600, and 700 °C for duration of 5 and 30 min. The activity of the HA coatings before and after SPS are evaluated *in vitro* in a simulated body fluid. The surface microstructure, crystallinity, and phase composition of each coating is characterized by scanning electron microscopy and x-ray diffractometry before and after *in vitro* incubation. Results show that the plasma sprayed coatings treated for 5 min in SPS demonstrated increased proportion of β-TCP phase with a preferred-orientation in the (214) plane, and the content of β-TCP phase corresponded to SPS temperature, up to 700 °C. SPS treatment at 700 °C for 30 min enhanced the HA content in the plasma spray coating as well. The HA coatings treated in SPS for 5 min revealed rapid surface morphological changes during in vitro incubation (up to 12 days), indicating that the surface activity is enhanced by the SPS treatment. The thickest apatite layer was found in the coating treated by SPS at 700 °C for 5 min.

Keywords: coatings, microstructure, scanning electron microscopy, sintering, x-ray diffraction analysis

L.-G. Yu, K.A. Khor, H. Li, and P. Cheang, Sch. of Mech./Production Engineering, Advanced Materials Research Centre, Nanyang Technological Univ., Singapore 639 798, Singapore. Cited: *Biomaterials, 24*(16), July 2003, pp. 2695-2705 [in English]. ISSN 0142-9612.

Plasma spraying of functionally graded hydroxyapatite/Ti-6Al-4V coatings. Functionally graded hydroxyapatite (HA)/Ti-6Al-4V coatings were produced by plasma spray process using specially developed HA-coated Ti-6Al-

4V composite powders as feedstock. The microstructure, density, porosity, microhardness, and Young's modulus (E) were found to change progressively through the three-layered functionally graded coating that composed of the layers 50 wt.% HA/50 wt.% Ti-6Al-4V; 80 wt.% HA/20 wt.% Ti-6Al-4V, and HA. No distinct interface between adjacent layers of different compositions was evident from scanning electron microscope observation. X-ray diffractometry showed that the coatings composed of HA and titanium phases. Microhardness, as measured through the indentation technique, and tensile adhesion strength decreased correspondingly with increasing HA content in the single-layered composite coatings. The application of HA/Ti-6Al-4V composite powders improved the tensile adhesion strength of the coatings significantly. The Young's modulus and fracture toughness results showed highly anisotropic elastic behavior with relatively higher E and K_{Ic} (fracture toughness) values parallel to the coating surface due to the intrinsic lamellar structure of the plasma sprayed coatings.

Keywords: composite materials, density (specific gravity), elastic moduli, functionally graded materials, microhardness, microstructure, plasma spraying, porosity, powders, scanning electron microscopy, titanium compounds, x-ray diffraction analysis

K.A. Khor, Y.W. Gu, C.H. Quek, and P. Cheang, P., Sch. of Mech. and Production Eng., Nanyang Technological Univ., Singapore 639798, Singapore. Cited: *Surf. Coat. Technol., 168*(2-3), 22 May 2003, pp. 195-201 [in English]. ISSN 0257-8972.

Nanobioceramics: synthesis, characterization, and applications. Nanobioceramics based on hydroxyapatite (HA) and its composites were synthesized using radio frequency (RF) induction suspension plasma spraying with a wet suspension as feedstock. The liquid suspension precursors were axially injected into the RF plasma at various plate powers (plasma energies), chamber pressures, probe distances, and plasma gas flow rates. The processed powders varied in size according to the cyclones designed to collect the powders from medium to ultrafine. The chamber collecting ultrafine powder contained particles ranging from 10 nm to 4 μm. This study suggests that the processing parameters associated with the production of the ultrafine powders interact in a complex manner, but can be rationalized by considering the overall thermal treatment experienced by the particulates during plasma treatment.

Keywords: heat treatment, plasma spraying, synthesis (chemical)

K.A. Khor, P. Cheang, H. Li, and R. Kumar, Advanced Materials Research Centre, Sch. of Mech./Production Engineering, Nanyang Technological Univ., Singapore 639798, Singapore. Cited: Nano- and Microtechnology: Materials, Processes, Packaging, and Systems, D.K. Sood, A.P. Malshe, and R. Maeda, Ed., 16-18 Dec 2002 (Melbourne, VIC, Australia), *Proc. SPIE, 4936,* 2002, pp. 35-42 [in English]. ISSN 0277-786X.

Influence of Spray Parameters

Development of process maps for plasma spray: case study for molybdenum. A schematic representation referred to as "process maps" examines the role of process variables on the properties of plasma sprayed coatings. Process maps have been developed for air plasma spraying of molybdenum. Experimental work was done to investigate the importance of such spray parameters as gun current, primary gas flow, auxiliary gas flow, and powder carrier gas flow. In-flight particle temperatures and velocities were measured and diameters estimated in various areas of the spray plume. Empirical models were developed relating the input parameters to the in-flight particle characteristics. Molybdenum splats and coatings were produced at three distinct process conditions identified from the first-order process map experiments. In addition, substrate surface temperature during deposition was treated as a variable. Within the tested range, modulus, hardness, and thermal conductivity increase with particle velocity, while oxygen content and porosity decrease. Increasing substrate deposition temperature resulted in dramatic improvement in coating thermal conductivity and modulus, while simultaneously increasing coating oxide content. Indentation reveals improved fracture resistance for the coatings prepared at higher substrate temperature. Residual stress was significantly affected by substrate temperature, although not to a great extent by particle conditions within the investigated parameter range. Coatings prepared at high substrate temperature with high-energy particles suffered considerably less damage in a wear test. The mechanisms behind these changes are discussed within the context relational maps, which have been proposed.

Keywords: coatings, flow of fluids, mathematical models, molybdenum, porosity

S. Sampath, X. Jiang, A. Kulkarni, J. Matejicek, D.L. Gilmore, and R.A. Neiser, Dept. of Materials Science and Eng., Center for Thermal Spray Research, State Univ. New York, Stony Brook, NY 11794-2275. Cited: *Mater. Sci. Eng. A, 348*(1-2), 15 May 2003, pp. 54-66 [in English]. ISSN 0921-5093.

Effect of plasma fluctuations on in-flight particle parameters. The influence of arc root fluctuations in direct current (d.c.) plasma spraying on the physical state of the particle jet is investigated by correlating individual in-flight particle temperature and velocity measurements with the instantaneous voltage difference between the electrodes. In-flight diagnostics with the DPV-2000 sensing device involve two-color pyrometry and time-of-flight technique for the determination of temperature and velocity. Synchronization of particle diagnostics with the torch voltage fluctuations are performed using an electronic circuit that generates a pulse when the voltage reaches some specific level; this pulse, which can be shifted by an arbitrary period of time, is used to trigger the acquisition of the pyrometric signals. Contrary to predictions obtained by numerical modeling, time-dependent variations in particle temperature and velocity due to power fluctuations induced by the arc movement can be very large. Periodic variations of the mean particle temperature and velocity, up to ΔT = 600 °C and Δv = 200 m/s, are recorded in the middle of the particle jet during a voltage cycle. To our knowledge, this is the first time that large time-dependent effects of the arc root fluctuations on the particle state (temperature and velocity) are experimentally demonstrated. Moreover, large fluctuations in the number of detected particles are observed throughout a voltage cycle; very few particles are detected during parts of the cycle. The existence of quiet periods suggests that particles injected at some specific moments in the plasma are not heated sufficiently to be detected.

Keywords: computer simulation, jets, networks (circuits), pyrometry, synchronization, velocity measurement

J.F. Bisson, B. Gauthier, and C. Moreau, National Research Council of Canada, Industrial Materials Institute, Boucherville, Quebec, J4B 6Y4, Canada. Cited: *J. Therm. Spray Technol., 12*(1), March 2003, pp. 38-43 [in English]. ISSN 1059-9630.

Control of thermal spray processes by means of process maps and process windows. A general method to map and control thermal spray processes, ensuring predefined levels of selected final coating properties, is presented. The method relies on monitoring and individually controlling particle velocity and particle temperature through selected spray gun parameters. Mapping of the process results in process maps describing the individual effect of particle velocity and particle temperature on each selected coating property of concern; in this case, different features of the microstructure and deposition efficiency. From the information provided by the process maps, a process window is constructed. This process window provides the limits within which particle velocity and particle temperature are allowed to vary to fulfill a predefined coating specification. To verify the method, two predefined thermal barrier top coatings—one porous and one dense—were produced by air plasma spray with satisfactory results.

Keywords: mapping, microstructure, plasma spraying, process control, thermal barrier coatings

M. Friis and C. Persson, Univ. Trollhattan/Uddevalla, S-461 29 Trollhattan, Sweden. Cited: *J. Therm. Spray Technol., 12*(1), March 2003, pp. 44-52 [in English]. ISSN 1059-9630.

Plasma chemistry during the deposition of a-C:H films and its influence on film properties. Plasma chemistry in an argon/acetylene expanding thermal plasma was studied by means of a residual gas analyzer (RGA) and cavity ring down spectroscopy (CRDS). With RGA, the consumption of acetylene in the plasma and the production of the C_4H_2 molecule was measured. CRDS was used for C, CH, and C_2 radical detection. It is demonstrated that C, CH, and C_2 are products of a secondary reaction chain of argon ions and electrons with radical products formed after the primary reaction of argon ions and electrons with acetylene. By increasing the acetylene injection the composition of the plasma, and consequently the film properties, can be controlled. The growth of the films was monitored using in situ real time single wavelength ellipsometry. Films were analyzed with Rutherford backscattering combined with elastic recoil detection analysis and with ex situ spectroscopic ellipsometry. The film properties reflect clearly the different plasma composition. Possible consequences for hydrogenated amorphous carbon films with good electronic properties are highlighted.

Keywords: gas fuel analysis, hydrogenation, plasma spraying, Rutherford backscattering spectroscopy

J. Benedikt, R.V. Woen, S.L.M. van Mensfoort, V. Perina, J. Hong, and M.C.M. van de Sanden, Dept. Applied Physics, Eindhoven Univ. Technology, Eindhoven, Netherlands. Cited: *Diam. Relat. Mater., 12*(2), Feb 2003, pp. 90-97 [in English]. ISSN 0925-9635.

Nanostructured Materials

Low-pressure plasma sprayed Al_2O_3 and Al_2O_3/SiC nanocomposite coatings from different feedstock powders. This paper describes a preliminary investigation of a nanocomposite ceramic coating system, based on Al_2O_3/SiC. Feedstock Al_2O_3/SiC nanocomposite powder has been manufactured using sol-gel and conventional freeze-drying processing techniques and then low-pressure plasma sprayed onto stainless steel substrates using a CoNiCrAlY bond coat. Coatings of a commercial Al_2O_3 powder have also been manufactured as a reference for phase transformations and microstructure. The different powder morphology and size distribution resulting from the different processing techniques and their effect on coating microstructure have been investigated. Phase analysis of the feedstock powders and of the as-sprayed coatings by x-ray diffractometry (XRD) and nuclear magnetic resonance (NMR) showed that the nanoscale SiC particles were retained in the composite coatings and that equilibrium α-Al_2O_3 transformed to metastable γ-

and δ-Al_2O_3 phases during plasma spraying. Other minority phases in the sol-gel Al_2O_3/SiC nanocomposite powder such as silica and aluminosilicate were removed by the plasma spraying process. Microstructure characterization by scanning electron microscopy (SEM) of the as-sprayed surface, polished cross section, and fracture surface of the coatings showed evidence of partially molten and unmolten particles Inc. into the predominantly lamella microstructure of the coating. The extent of feedstock particle melting and consequently the character of the coating microstructure were different in each coating because of the effects of particle morphology and particle size distribution on particle melting in the plasma.

Keywords: alumina, feedstocks, nanostructured materials, nuclear magnetic resonance, particle size analysis, phase transitions, plasma spraying, sol-gels, stainless steel, x-ray diffraction

S. Jiansirisomboon, K.J.D. MacKenzie, S.G. Roberts, and P.S. Grant, Dept. of Physics, Faculty of Science, Chiang Mai Univ., Chiang Mai, 50200, Thailand. Cited: *J. Eur. Ceram. Soc., 23*(6), May 2003, pp. 961-976 [in English]. ISSN 0955-2219.

Synthesis and characterization of nanocrystalline copper-aluminum coatings. Commercially pure copper and aluminum powders were blended in a 90:10 ratio by weight and then mechanically milled in methanol or in liquid nitrogen. The milled powders, as well as as-blended (nonmilled) powder, were deposited as coatings using high-velocity oxygen fuel thermal spraying. Scanning and transmission electron microscopy techniques were used to investigate the microstructure of the powders and coatings. The results showed that milling of the powders in methanol induced the conversion of most of the aluminum into amorphous Al_2O_3, precluding the desired mechanical alloying. This experimental observation was consistent with available thermodynamic data. In contrast, cryomilling exhibited no significant oxidation and induced mechanical alloying of the powders, albeit incomplete. The nonmilled powder generated a coating with a bimodal grain structure consisting of fine copper grains and coarse aluminum grains. Amorphous oxide regions and coarse aluminum grains were observed intermixed with the finer copper matrix in the coatings sprayed using the powders milled in methanol. Coatings based on cryomilled powders consisted primarily of equiaxed copper grains and twinned martensite regions, with occasional inclusion of elongated amorphous Al_2O_3 regions.

Keywords: martensite, mechanical alloying, methanol, powder metals, protective coatings, thermodynamics

M.L. Lau, J. He, R. Schweinfest, M. Ruhle, C.G. Levi, and E.J. Lavernia, Dept. of Chemical Eng./Mat. Science, Univ. California, Davis, CA 95616-5294. Cited: *Mater. Sci. Eng. A, 347*(1-2), 25 April 2003, pp. 231-242 [in English]. ISSN 0921-5093.

Formation of nanostructured TiO_2 by flame spraying with liquid feedstock. A liquid feedstock flame spraying system was developed to deposit the nanostructured TiO_2 coating using butyl titanate ($Ti(OC_4H_9)_4$) and ethanol solution as precursor. The resultant deposit was characterized by infrared spectrum (IR), x-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The results showed that during spraying, butyl titanate had been completely decomposed and converted into nanostructured anatase TiO_2, having a narrow size distribution from 10 to 20 nm.

Keywords: feedstocks, flame spraying, nanostructured materials, scanning electron microscopy, transmission electron microscopy, x-ray diffraction analysis

C.-J. Li, G.-J. Yang, and Z. Wang, Welding Research Institute, School of Mechanical Engineering, Xi'an Jiaotong Univ., Xi'an 710049, China. Cited: *Mater. Lett., 57*(13-14), April 2003, pp. 2130-2134 [in English]. ISSN 0167-577X.

Nanocrystalline nickel coatings strengthened with ultrafine particles. In this study, nanocrystalline nickel powders and thermally sprayed coatings, containing ultrafine AlN particles, were synthesized and characterized. The results indicated that the presence of AlN particles in the powders drastically decreased the dimension of agglomerates formed by cryomilling and increased the surface roughness of the agglomerates. The AlN phase was broken down into ultrafine particles of approximately 30 nm in size. These particles were dispersed in the nickel matrix and enhanced the development of a nanocrystalline structure in the nickel matrix during cryomilling. Selected-area diffraction patterns, obtained from transmission electron microscopy (TEM) and x-ray mapping with scanning electron microscopy (SEM), confirmed the presence of AlN particles in the coatings. The presence of AlN particles also led to an increase in the amount of NiO phase that was distributed in the coating, in the form of ultrafine, round particles. AlN particles increased the microhardness of the nickel coating by approximately 60%. Indentation-fracture results also indicated that the fine, dispersed AlN particles raised the apparent toughness of the nickel coating. The synthesized nickel coatings containing ultrafine AlN particles were characterized as equiaxed nanocrystalline grains with an average size of 24 nm, in which twins were observed. The increase in microhardness resulted from both grain refinement and the presence of ultrafine particles. The latter played the primary role in strengthening.

Keywords: fracture, grain size and shape, indentation, microhardness, nanostructured materials, particles (particulate matter), scanning electron microscopy, sprayed coatings, strengthening (metal), surface roughness, synthesis (chemical), transmission electron microscopy

J. He and J.M. Schoenung, Dept. of Chemical Eng. and Mat. Sci., Univ. California, Davis, Davis, CA 95616-5294. Cited: *Metall. Mater. Trans. A: Phys. Metall. Mater. Sci., 34A*(3), March 2003, pp. 673-683 [in English]. ISSN 1073-5623.

Nanostructures in thermal spray coatings. The nature of the nanograins formed by the high-velocity oxyfuel thermal spraying of (FeAl) milled powder was investigated. The size of the small nanocrystalline domains appeared to be less than 20 nm. The repeated fracturing and cold welding processes occurring during milling led to the formation of the disordered (bcc) FeAl phase.

Keywords: comminution, microstructure, nanostructured materials, recrystallization (metallurgy), solidification, transmission electron microscopy

J. Gang, J.-P. Morniroli, and T. Grosdidier, UMR CNRS 7078, ISGMP, Universite de Metz, 57045 Metz Cedex 01, France. Cited: *Scr. Mater., 48*(12), June 2003, pp. 1599-1604 [in English]. ISSN 1359-6462.

Perovskites

Novel synthesis and magnetocaloric assessment of functional oxide perovskites. The magnetic entropy change associated with the ferromagnetic Curie transition has been studied in $La_{0.85}Sr_{0.15}MnO_3$ (LSM) perovskites obtained by both the citrate-nitrate gel autoignition and combustion thermal spray techniques. A modest magnetic entropy change can be observed in $La_{0.85}Sr_{0.15}MnO_3$ by sintering the precursor-derived powder at 1200 °C for 16 h or by combustion spraying the solution precursor onto an aluminum substrate and annealing at 800 °C for 6 h. The combustion thermal spray process with rapid deposition rates and relatively low deposition temperature directly produces a microcrystalline perovskite phase. This microcrystalline powder can be processed more rapidly and at lower temperatures than that derived from the sol-gel syntheses process to produce material with fine crystallinity and an obvious magnetocaloric effect.

Keywords: annealing, plasma spraying, sintering, sol-gels, synthesis (chemical)

P.S. Devi, S. Sampath, M.H. Yu, L.H., Lewis, J.B. Parise, and R.J. Gambino, Materials Science Department, Brookhaven National Laboratory, Building 480, Upton, NY 11973. Cited: *Mater. Sci. Eng. B: Solid-State Mater. Adv. Technol., 97*(3), 15 Feb 2003, pp. 245-250 [in English]. ISSN 0921-5107.

Precursor Plasma Spraying

Yttrium aluminum garnet (YAG) films through a precursor plasma spraying technique. Coatings of yttrium garnet ($Y_3Al_5O_{12}$, YAG), which is a promising high-temperature ceramic, were developed for the first time using a novel precursor plasma spraying (PPS) technique. The precursor sol was sprayed using a radio-frequency induction plasma technique. X-ray diffraction analysis of the as-sprayed coatings confirmed that a metastable hexagonal yttrium aluminate (H-$YAlO_3$) was the major phase. The above-described specimen, on further treatment with plasma, was converted to cubic garnet (YAG) as the major phase, with a minor amount of orthorhombic $YAlO_3$ (O-YAP) phase. ^{27}Al magic-angle spinning nuclear magnetic resonance of the YAG coating corroborated the x-ray results and confirmed the presence of YAG and O-YAP phases. Formation of the garnet phase through the PPS technique is proof that the chemistry can be controlled in the plasma. This finding opens up new avenues for developing complex functional oxide deposits.

Keywords: coatings, garnets, nuclear magnetic resonance spectroscopy, phase diagrams, plasma spraying, sprayed coatings, x-ray diffraction analysis, yttrium compounds

S.D. Parukuttyamma, J. Margolis, H. Liu, C.P. Grey, S. Sampath, H. Herman, and J.B. Parise, Ctr. for Thermal Spray Research, Dept. of Materials Science and Eng., State Univ. New York, Stony Brook, NY 11794-2275. Cited: *J. Am. Ceram. Soc., 84*(8), Aug 2001, pp. 1906-1908 [in English]. ISSN 0002-7820.

Spray Forming

Effect of heat treatment on the microstructure of spray formed AISI M2 high-speed steel. The effect of heat treatment on the microstructure of spray formed AISI M2 high-speed steel is under evaluation. The objective of this work was to optimize the heat treatments aiming further mechanical working. The M2 steel used in the present work was obtained in a spray forming plant in Brazil, built for processing billets preforms of light alloys and steels. The typical microstructure of spray formed materials, that is, fine and equiaxial grains, allowed the optimization of the M2 spheroidization heat treatment. The heat treatment at 1160 ± 10 °C for 12 h was effective in producing microstructure and hardness suitable for further mechanical working.

Keywords: decomposition, hardness, heat treatment, metal forming, metal working, metallographic microstructure, optimization, solidification

R.M. Lima, E.R.B. Jesus, and J.L. Rossi, IPEN, CEP 05422-970, Sao Paulo, Brazil. Cited: *Mater. Sci. Forum, 416-418*(1), 2003, pp. 95-100 [in English]. ISSN 0255-5476.

Magnetic properties of spray formed Fe-3%Si, Fe-5%Si, and Fe-6.5%Si alloys. The aim of this work was to determine the influence of silicon content on the magnetic properties of spray formed iron-silicon alloys. The deposits presented interesting soft magnetic properties and random crystallographic texture. After annealing at 1250 °C for 1 h under vacuum, the samples presented the best magnetic properties for all compositions investigated and the power loss (P_T) decreased, while the maximum magnetic permeability (μ_{max}) increased. The best magnetic properties were: a power loss of 1.43 W/kg, maximum magnetic permeability of 14,000 and coercive force of 45 A/m, at B = 1 T, f = 60 Hz by using 0.60 mm thick rings, obtained with the Fe-6.5%Si alloy. The better magnetic properties after annealing were attributed to grain growth and defects elimination. The properties obtained for the Fe-5%Si and Fe-6.5%Si alloys were considerably better than those presented by commercial nonoriented Fe-3wt%Si steel sheets, and the deposits are isotropic, which make them attractive for applications in rotating devices and small power transformers.

Keywords: annealing, coercive force, composition effects, crystal defects, crystallography, grain growth, magnetic permeability, magnetic properties, metal forming, silicon, textures

C. Bolfarini, P.P. Gusson, M.C. Alves Silva, and C.S. Kiminami, UFSCar, DEMa, Sao Carlos, SP. CEP13.565-905, Brazil. Cited: *Mater. Sci. Forum, 416-418*(1), 2003, pp. 113-118 [in English]. ISSN 0255-5476.

Solidification of the nondendrite-forming Pb-16wt%Sn alloy during spray forming. The evolution of microstructure during spray forming (SF) have been extensively described on the basis of the solidification process of the droplets. On the other hand, the characteristics of the alloy such as temperature solidification range and the solute partitioning coefficient k_0 have not been focused. This work aimed to describe the microstructure evolution of spray formed Pb-16wt%Sn alloy into an equiaxed morphology instead of a dendrite structure. The microstructure of both atomized particles and deposited material was typically composed of equiaxial grains of lead phase with α-tin phase at the boundaries. It was shown that droplet solidification ruled the microstructure formation of the deposit in that the fine structure of presolidified droplets was extended to the deposit, despite the superheating prior to pouring and the low value of gas/metal flow rate (GMR) of processing. It was also shown that rapidly solidified structures can be produced by SF in a same way of containerless processing.

Keywords: metal forming, metallographic microstructure, morphology, porosity, rapid solidification

A. Florio, C. Bolfarini, and C.S. Kiminami, Depto. de Engenharia de Materiais, Univ. Federal de Sao Carlos Rodovia, CEP 13565-905 Sao Carlos, SP, Brazil. Cited: *Mater. Sci. Forum, 416-418*(1), 2003, pp. 401-406 [in English]. ISSN 0255-5476.

Particle size distribution in the radial direction of the spray cone and its influence on the formation of porosity in Fe-6%Si alloy processed by spray forming. The spray forming process consists of atomizing a molten metal flux by a high-velocity gas stream to generate small droplets. These are accelerated and simultaneously refrigerated/solidified by the atomization gas during their trajectory onto the substrate, upon which they consolidate, forming a coherent and dense preformed deposit. The present work consisted of investigating the behavior of particle size distribution in the radial direction of the spray cone and its influence on the porosity of the deposited material. It was found that the size distribution curves were dislocated to the region of the smallest particle size and increasing the distance was increased, leading to a decrease in the mean particle size and increasing the percentage of volumetric porosity in the material deposited in this direction.

Keywords: atomization, deposition, liquid metals, particle size analysis, porosity, substrates

V.S. Leal, W.M. Silva, C.S. Kiminami, and C. Bolfarini, DEMa, UFSCar, CEP 13565-905 Sao Carlos, SP, Brazil. Cited: *Mater. Sci. Forum, 416-418*(1), 2003, pp. 425-430 [in English]. ISSN 0255-5476.

Microstructure of spray formed 2.9%C-22%Cr high-chromium white cast iron. In the present work a 2.9%C-22%Cr white cast iron was processed by spray forming, aiming to investigate the potential of achieving novel microstructure by the high cooling rate involved in this process. Two gas flow rate to, metal flow rate ratios (0.12 and 0.23) were used. The microstructural characterization was performed by using x-ray diffractometry, optical and scanning electron microscopy. The conventional microstructure of this alloy shows M_7C_3 carbides (about 300 μm in length) embedded in a matrix of austenite and martensite dendrites; on the other hand the spray formed deposit showed a microstructure formed by fine M_7C_3 carbides (less than 10 μm in length) in a martensitic matrix. The overspray powders showed a microstructure composed mainly by carbides and austenite; the relatively rapid solidification of the droplets enhanced the chromium and carbon solubility in austenite changing the M_s temperature.

Keywords: cooling, metallographic microstructure, optical microscopy, rapid solidification, scanning electron microscopy, x-ray diffraction analysis

A.H. Kasama, R.D. Cava, A. Mourisco, C.S. Kiminami, and C. Bolfarini, UFSCar, DEMa, CEP 13.565-905 Sao Carlos-SP, Brazil. Cited: *Mater. Sci. Forum, 416-418*(1), 2003, pp. 419-424 [in English]. ISSN 0255-5476.

Influence of the process parameters in the microstructural evolution of Fe-6.5%Si alloy processed via spray forming. The microstructural evolution of spray formed materials depends on the thermal and dynamic behavior of the atomized droplets during their trajectory in direction of the substrate, which are governed by process parameters. In the present work, the influence of process parameters on the microstructural behavior of Fe-6.5%Si deposits was studied. The studied parameters were: gas/metal mass flow rate (GMR), the atomization nozzle-to-substrate distance and the substrate material. It was noticed that with the increase of nozzle-to-substrate distance or of the GMR, the porosity volumetric percentage increased, while grain size was reduced. Use of ceramic substrate resulted in porosity decrease and grain size increase when compared to results obtained with the use of water-cooled metallic substrate.

Keywords: atomization, grain size and shape, metallographic microstructure, nozzles, porosity, substrates

V.S. Leal, W.M. Silva, C. Kiminami, and C. Bolfarini, Depto. de Engenharia de Materiais, Univ. Fed. de Sao Carlos, Rodovia, CEP 13565-905, Brazil. Cited: *Mater. Sci. Forum, 416-418*(1), 2003, pp. 431-436 [in English]. ISSN 0255-5476.

Formation mechanism of the pressure zone at the tip of the melt delivery tube during the spray forming process. The gas pressures at the tip of the melt delivery tube in two typical atomizers are measured in this work. Gas dynamics is used to study the gas flow and pressure zone at the tip of the delivery tube, and a mechanism for the formation of pressurization and aspiration is proposed. The results show that the atomization efficiency of an atomizer with a Laval nozzle is superior to that of an atomizer with a converging nozzle. The gas jet expands strongly at the nozzle exit of a converging atomizer, while the Prandtl-Meyer angle of the jet is very small for a Laval nozzle. When the jet expands strongly, pressurization is likely to form at the tip of delivery tube. Aspiration is formed when the jet pressure at the exit of nozzle is equal to or smaller than the back pressure.

Keywords: gas dynamics, nozzles, pressurization, spraying, tubes (components)

C. Cui, F. Cao, and Q. Li, Harbin Institute of Technology, Heilongjiang Province, Harbin 150001, China. Cited: *J. Mater. Process. Technol., 137*(1-3 SPEC), 30 June 2003, pp. 5-9 [in English]. ISSN 0924-0136.

A high-strength and high-conductivity copper alloy prepared by spray forming. The use of spray forming process for preparing high-strength, high-conductivity copper alloy was discussed. Such an alloy has the advantages of high electrical and thermal conductivity and outstanding corrosion resistance. The microstructures of the alloy in various states were characterized by means of scanning electron microscopy and transmission electron microscopy.

Keywords: electric conductivity, hot rolling, microstructure, oxidation resistance, scanning electron microscopy, solid solutions, spraying, thermal conductivity, transmission electron microscopy

Z. Li, J. Shen, F. Cao, and Q. Li, Natl. Key Lab. Hot Prec. Proc. Met., Sch. of Mat. Sci. and Engineering, Harbin Institute of Technology, Harbin 150001, China. Cited: *J. Mater. Process. Technol., 137*(1-3 SPEC), 30 June 2003, pp. 60-64 [in English]. ISSN 0924-0136.

Microstructure and mechanical properties of spray formed Al-Si-Pb alloys. Liquid phase cospray forming (LPCSF) was employed to produce two Al-Si-Pb alloys. The preforms thus obtained were then subjected to hot extrusion at different extrusion ratios. Following extrusion, the materials were tensile tested at room temperature. The distribution of lead particles and the microstructural characterization in as-formed preforms and in the extruded rods were studied on the basis of scanning electron microscopy observation. The influence of the lead content on the mechanical properties was investigated.

Keywords: electrolytic polishing, grain boundaries, grain size and shape, heating furnaces, metal extrusion, microstructure, scanning electron microscopy, tensile properties

F. Yu, D.S. Dwarakadasa, and S. Ranganathan, Dept. Metal Forming, Northeastern Univ., Shenyang 110006, China. Cited: *J. Mater. Process. Technol., 137*(1-3 SPEC), 30 June 2003, pp. 164-167 [in English]. ISSN 0924-0136.

TiC particulate-reinforced Al-20Si-5Fe composite fabricated by melt in situ reaction spray forming. A novel technique in which TiC particulates are fabricated by an in situ reaction in molten aluminum is introduced for producing TiC/Al-20Si-5Fe composite. In order to reveal the characteristics of the technique, in this paper the formation mechanism of TiC particulates obtained by this method is studied. Both theoretical and experimental results have shown that the TiC particulates are formed by a diffusion mechanism when the molar fraction of aluminum in the preform is greater than 20.02%. Contrarily, the TiC particulates are formed by a solution-precipitation mechanism when the frac-

tion is less than 20.02%. An unwanted needlelike phase is always present in the spray formed alloys. Experimental results have shown that the amount of the brittle phase decreases in spray formed Al-20Si-5Fe preforms with increase in the TiC content, and that the brittle phase can be eliminated completely by adding more than 3 wt.% TiC particulates to the alloy. Moreover, another major problem of coarsened silicon particulates, often encountered in hypereutectic aluminum-silicon alloy has also been solved by using the technique.

Keywords: aluminum, diffusion, precipitation (chemical), titanium carbide

B. Yang, F. Wang, H. Cui, X.J. Duan, S.C. Hu, and J.S. Zhang, Stt. Key Lab. for Adv. Metallic Mat., Univ. of Sci. and Technology Beijing, Beijing 100083, China. Cited: *J. Mater. Process. Technol., 137*(1-3 SPEC), 30 June 2003, pp. 187-190 [in English]. ISSN 0924-0136.

Pseudoalloys for spray metal tooling. Spray formed high-carbon steel tools emerged in response to the challenge of finding spray formed materials with wear and abrasion properties between those of steel and zinc. These tools are designed to reduce lead time and costs in prototyping and production. This paper describes the process of fabricating spray formed tools, including the process of making tools of pseudoalloys, and describes their properties and applications.

Keywords: carbon steel, deformation, deposition, durability, hardness, injection molding, metal forming, sheet molding compounds, strength of materials, temperature, wear of materials, zinc

S. Wichmanowski, Praxair Surface Technologies, Indianapolis, IN 46224. Cited: *Adv. Mater. Process., 161*(4), April 2003, pp. 33-34 [in English]. ISSN 0882-7958.

Thermal Barrier Coatings

Lanthanum hexa-aluminate thermal barrier coatings. State-of-the-art thermal barrier coatings (TBC) consisting of yttria partially stabilized zirconia (Y-PSZ) are restricted to long-term application temperatures below 1100 °C. Exposed to higher temperatures, their thermally insulating properties decline due to densification. Moreover, Y-PSZ becomes an oxygen ion conductor at elevated temperatures. Lanthanum hexa-aluminate (LHA) is a novel thermal barrier material that is able to overcome these problems associated with the use of Y-PSZ at higher temperatures. LHA crystallizes in magnetoplumbite structure and shows an outstanding thermal stability up to 1600 °C and insulating properties comparable to Y-PSZ. The low thermal conductivity of LHA is caused by its microstructure—a random arrangement of LHA platelets that builds up a microporous coating—and the insulating properties of the material with its crystallographic features itself. This study describes the development of an optimized procedure for the processing, manufacturing, and application of LHA as TBC material. The plasma spray powders were produced by spray drying of aqueous ceramic slurries. The atmospheric plasma spray (APS) deposition process was optimized to yield an homogeneous coating with controlled microporosity and residual stresses. The crystalline phases were characterized by x-ray diffraction (XRD).

Keywords: crystallography, densification, high-temperature properties, lanthanum compounds, microporosity, plasma spraying, thermal conductivity, thermal insulation, thermodynamic stability, x-ray diffraction analysis, yttrium compounds, zirconia

C.J. Friedrich, R. Gadow, and M.H. Lischka, Univ. Stuttgart, IMTCCC, D-70569 Stuttgart, Germany. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., B, 22*(4), 2001, pp. 375-382 [in English]. ISSN 0196-6219.

Properties

Adhesion of Thermal Spray Coatings

Adhesion and residual stresses determination of thermally sprayed molybdenum on steel. Thermally sprayed molybdenum coatings are widely used to combat degradation of components and structures due to mechanical wear. However, the behavior and durability of these coatings are extremely dependent on their properties and on the spraying conditions. To date, efforts forwarded to develop thermal spray coatings technology have been focused on increasing the durability and integrity of the coating. Improvement of adherence of the deposit to the substrate, minimizing residual stress level, and reducing porosity are the main objectives of these works. The aim of this paper is to measure the adherence of flame sprayed molybdenum on steel substrate and to determine internal stress distribution at the interface of the obtained structure. The influence of a nickel-aluminum (80%, 20%) bond-coat and/or a post-annealing at 850 °C for 1 h in vacuum on the adherence and the residual stresses is also studied.

Keywords: adhesion, annealing, degradation, molybdenum, residual stresses, spraying, stress concentration, wear of materials

M. Laribi, N. Mesrati, A.B. Vannes, and D. Treheux, Ing. Fonctionalisation Surf., UMR CNRS 5621, Ecole Centrale de Lyon, Ecully Cedex 69 134, France. Cited: *Surf. Coat. Technol., 166*(2-3), 24 March 2003, pp. 206-212 [in English]. ISSN 0257-8972.

Evaluation for adhesion strength of coating and substrate by burying beforehand specimen. Adhesion strength is an important target in evaluating the quality of coating layers. The traditional way of adhesion strength test is bonding pull-off method for thick layers and scratch test for thin films. The drawbacks of these two methods are discussed in this paper, and an evaluating method for adhesion strength of coating by burying beforehand specimen is proposed. The adhesion strength of samples is measured with tico methods. The dispersity of testing data is lower than that in the ASTM C 663-79 standard.

Keywords: adhesion, fracture toughness, interfaces (materials), shear stress, strength of materials, substrates, thin films, viscosity

Y.-D. Liao, Z.-Y. Li, and G.-Q. Tang, Dept. of Mechanical Engineering, Wuhan Institute of Chem. Technol., Wuhan 430073, China. Cited: *J. Wuhan Univ. Technol., Mater. Sci. Ed., 18*(1), March 2003, pp. 31-32, 36 [in English]. ISSN 1000-2413.

Mechanical properties and platelet adhesion behavior of diamond-like carbon films synthesized by pulsed vacuum arc plasma deposition. Diamondlike carbon (DLC) is an attractive biomedical material due to its high inertness and excellent mechanical properties. In this study, DLC films were fabricated on Ti-6Al-4V and Si(100) substrates at room temperature by pulsed vacuum arc plasma deposition. By changing the argon flow from 0 to 13 sccm during deposition, the effects of argon flow on the characteristics of the DLC films were systematically examined to correlate to the blood compatibility. The microstructure and mechanical properties of the films were investigated using Raman spectroscopy, x-ray photoelectron spectroscopy (XPS) surface analysis, a nanoindenter, and pin-on-disk tribometer. The blood compatibility of the films was evaluated using *in vitro* platelet adhesion investigation, and the quantity and morphology of the adherent platelets was investigated employing optical microscopy and scanning electron microscopy. The Raman spectroscopy results showed a decreasing sp^3 fraction (an increasing trend in I_D/I_G ratio) with increasing argon flow from 0 to 13 sccm. The sp^3:sp^2 ratio of the films was evaluated from the deconvoluted XPS spectra. The authors found that the sp^3 fraction decreased as the argon flow was increased from 0 to 13 sccm, which is consistent with the results of the Raman spectra. The mechanical properties results confirmed the decreasing sp^3 content with increasing argon flow. The Raman D-band to G-band intensity ratio increased and the platelet adhesion behavior became better with higher flow. This implies that the blood compatibility of the DLC films is influenced by the sp^3:sp^2 ratio. DLC films deposited on titanium alloys have high wear resistance, low friction, and good adhesion.

Keywords: adhesion, inert gases, microstructure, optical microscopy, plasma spraying, Raman spectroscopy, scanning electron microscopy, substrates, surface chemistry, synthesis (chemical), vacuum deposited coatings, wear resistance, x-ray photoelectron spectroscopy

Y.X. Leng, J.Y. Chen, P. Yang, H. Sun, G.J. Wan, and N. Huang, Sch. of Mat. Science and Engineering, Southwest Jiaotong Univ., Sichuan, Chengdu 610031, China. Cited: *Surf. Sci., 531*(2), 20 May 2003, pp. 177-184 [in English], ISSN 0039-6028.

Alumina-Titania Coatings

Co-spraying of alumina-titania: correlation of coating composition and properties with particle behavior in the plasma jet. Plasma sprayed coatings of alumina-titania (60:40 by weight) have been prepared under different operating parameters. The coatings have been characterized with respect to chemical composition, phase composition, wear resistance, and microhardness. It was observed that the chemical composition of coatings prepared at low input power is significantly different from that of the feedstock powder. The coating composition progressively approaches that of the feedstock powder at higher power input. Numerical process simulation has been carried out using a one-dimensional model to illustrate the importance of plasma-particle interaction during cospraying of alumina-titania powder blend. Experimental results compare very well with the results predicted by the model. At lower power levels, titania particles are melted, whereas alumina particles remain unmelted. This is expected to give a coating composition quite different from that of the feedstock powder. With an increase in the plasma power, alumina particles are also heated to their melting point, and by choosing the proper combination of power and particle size, the spray process can be optimized to obtain a targeted coating composition.

Keywords: computer simulation, microhardness, phase composition, plasma jets, plasma spraying, titanium dioxide, wear resistance

P.V. Ananthapadmanabhan, T.K. Thiyagarajan, K.P. Sreekumar, R.U. Satpute, N. Venkatramani, and K. Ramachandran, Laser and Plasma Technology Div., Bhabha Atomic Research Centre, Bombay 400 085, India. Cited: *Surf. Coat. Technol., 168*(2-3), 22 May 2003, pp. 231-240 [in English]. ISSN 0257-8972.

Alumina Coatings

Hydrogen permeation resistance of plasma sprayed Al_2O_3 and Al_2O_3-13wt.%TiO_2 ceramic coatings on austenitic stainless steel. Al_2O_3 and Al_2O_3-13wt.%TiO_2 ceramic coatings were prepared on 21Cr-6Ni-9Mn austenitic stainless steel substrates by plasma spraying. The phase contents and microstructures of the plasma sprayed coatings were investigated by means of x-ray diffraction (XRD), electron probe microanalysis (EPMA), and scanning electron microscopy (SEM). Also, the hydrogen permeation resistance was measured by thermal hydrogen charging. The results showed that plasma sprayed Al_2O_3 and Al_2O_3-13wt.%TiO_2 ceramic coatings can improve the hydrogen permeation resistance of 21Cr-6Ni-9Mn austenitic stainless steel effectively, and the hydrogen resistance efficiency of Al_2O_3 coating was higher than that of Al_2O_3-13wt.%TiO_2 coating. Al_2O_3 coating displayed a denser structure than Al_2O_3-13wt.%TiO_2 coating. The phase content analysis revealed that the presence of the $Ni(Cr,Fe,Ti)_2O_4$ phase in the Al_2O_3-13wt.%TiO_2 coating in addition to γ-Al_2O_3 and α-Al_2O_3. It was found that the bonding between the plasma sprayed ceramic coatings and austenitic stainless steel substrates was mechanical rather than metallurgical.

Keywords: austenite, ceramic coatings, hydrogen, mechanical permeability, microstructure, plasma spraying, scanning electron microscopy, stainless steel, titanium dioxide, x-ray diffraction

R.G. Song, WZK, Center for Magnesium Technology, Institute of Materials Research, Geesthacht 21502, Germany. Cited: *Surf. Coat. Technol., 168*(2-3), 22 May 2003, pp. 191-194 [in English]. ISSN 0257-8972.

Aluminum Composites

Grain growth and mechanical properties of spray formed Al/SiC composites. The objective of this work was to evaluate the grain growth behavior and mechanical properties of metal-matrix composites. The material was produced elsewhere by spray forming of an aluminum alloy AA 7475 and codepositing silicon carbide particles (20 vol.%). The microstructure was evaluated in the as-received condition and after a series of heat treatments, annealing, aging, and overaging. Optical microscopy was used to characterize the composite microstructure. Hardness measurements and tensile testing assessed the mechanical properties. Accentuated grain growth occurred due to the solution heat treatment and subsequent aging and overaging did not produce further changes in grain size. The hardness peak was attained after heat treatment of the composite at 150 °C for 10 h. Aging the composite at 120 °C for 24 h led to higher tensile strength.

Keywords: aging of materials, aluminum alloys, annealing, grain growth, mechanical variables measurement, metallographic microstructure, optical microscopy, silicon carbide, tensile testing

E.G. Gomes and J.L. Rossi, IPEN, CEP 05422-970, Sao Paulo, Brazil. Cited: *Mater. Sci. Forum, 416-418*(1), 2003, pp. 413-418 [in English]. ISSN 0255-5476.

B_4C Coatings

Arcing at B_4C-covered limiters exposed to a SOL-plasma. Plasma sprayed B_4C-layers considered as wall coatings for the W7X stellarator have been studied during and after exposure to TEXTOR and after arcing experiments in vacuum. Arcing through the B_4C layer occurred favored by high power fluxes and not restricted to less stable phases. However, this arcing implies an especially noisy scrape-off layer (SOL). Instead of moving retrograde in the external magnetic field, the arc spot on the B_4C-layer sticks to the same location for its whole lifetime. Consequently, the arc erodes the entire B_4C layer, finally burning down to the copper substrate. In the neighborhood of craters, the surface contains copper originating from those craters. This material, hauled to the surface by the arc, is subject to subsequent erosion, transport, and redeposition by the SOL-plasma. The behavior of arcs on B_4C is most probably caused by the peculiar temperature dependences of the electrical and heat conductivity of B_4C.

Keywords: electric arcs, electric conductivity, erosion, limiters, magnetic fields, plasma confinement, plasma spraying, thermal conductivity

M. Laux, W. Schneider, P. Wienhold, B. Juttner, A. Huber, M. Balden, J. Linke, H. Kostial, M. Mayer, M. Rubel, A. Herrmann, A. Pospieszczyk, S. Jachmich, B. Schweer, D. Hildebrandt, and H. Bolt, Max-Planck-Inst. fur Plasmaphysik, Euratom Assoc., D-10117 Berlin, Germany. Cited: Plasma-Surface Interactions in Controlled Fusion Devices (Conf. Proc.), 26-31 May 2002, *J. Nucl. Mater., 313-316*(suppl.), March 2003, pp. 62-66 [in English]. ISSN 0022-3115.

Biocompatible Coatings (Other Than HA)

A radiological follow-up study of plasma sprayed fluorapatite (FA) coatings. In this paper a radiologic follow-up study of plasma sprayed titanium implants in rams was performed. It is already known that, because of their properties, surface-active ceramics such as hydroxyapatite (HA) and bioglass have been used in orthopedic surgery. Because of their low toughness, their use on metal surfaces as coatings has proven more applicable. HA was produced from human teeth. Dentine and enamel fluorapatite (DFA and EFA) were separately plasma sprayed on 6.35 mm diam titanium implants. These produced implants sterilized and implanted in the metaphysis region of the tibia within the unsprayed control group. After ~2.5 months, x-rays were taken and it was noted that no radiolucent areas around the implants evidenced. The soft tissues above the tibias were healed. Thus no inflammation flow was observed. Osseointegration around the implants was verified.

Keywords: coatings, glass ceramics, implants (surgical), plasma spraying, titanium

F.N. Oktar, S. Ozsoy, and L.S. Ozyegin, Campus of Goztepe, New Technol. Res./Development Center, Marmara Univ., Ziverbey, Kadikoy, Istanbul, Turkey. Cited: Proc. 15th Int. Symposium on Ceramics in Medicine; The Annual Meeting of the International Society for Ceramics in Medicine, B. Ben-Nissan, D. Sher, and W. Walsh, Ed., 4-8 Dec 2002 (Sydney, Australia), *Key Eng. Mater., 299-302,* 2003, pp. 327-330 [in English]. ISSN 1013-9826.

Bioglass Coatings

Characterization of plasma sprayed bioglass coatings on titanium. Bioglass, 45S5 containing 45% SiO_2, 6% P_2O_5, 24.5% CaO, and 24.5% Na_2O (all in wt.%) was plasma sprayed onto a titanium substrate with and without 60 Al_2O_3 40 TiO_2 as a bond coating. Mechanical properties were evaluated by following the ASTM C 633 method, and the microstructural characterization has been carried out by using scanning electron microscope. Results indicate that the bonding strength of bond coatings is three times higher than of the coatings that are directly applied to the surface. It has been observed that there is a uniform coating layer with a thickness of 110 μm and that there was not any reaction observed at the coating-metal interface.

Keywords: organic coatings, plasma spraying, scanning electron microscopy, silica, titanium

G. Goller, F.N. Oktar, T. Yazici, S. Gurmen, and E.S. Kayali, Istanbul Technical Univ., Metallurgical Engineering Department, Maslak, Istanbul, Turkey. Cited: Proc. 15th Int. Symposium on Ceramics in Medicine; The Annual Meeting of the International Society for Ceramics in Medicine, B. Ben-Nissan, D. Sher, and W. Walsh, Ed., 4-8 Dec 2002 (Sydney, Australia), *Key Eng. Mater., 240-242,* 2003, pp. 283-286 [in English]. ISSN 1013-9826.

Composite Coatings

Structural characterization and strength evaluation of spray formed ceramic composite near-net shapes. This paper explores the characteristics of spray formed near-net-shaped ceramic composite. Alumina-titania composite (Al_2O_3 60 wt.%; TiO_2 40 wt.%) was spray formed using a plasma dyne atmospheric facility. Micrographs of as-sprayed samples are presented, along with micrographs of samples post-heat treated at different temperatures. Electron probe microanalysis profiles were determined, and x-ray diffraction phase analysis was carried out. Young's modulus, strength, and hardness of the samples was determined.

Keywords: characterization, elastic moduli, forming, hardness, heat treatment, plasma spraying, porosity, strength of materials, structural analysis, thermal effects, x-ray diffraction analysis

K. Metzgar, D. Rosetta, M.V. Gopalakrishnan, and R. Krishnamurthy, Superior Shot Peening Inc., Houston, TX 77039. Cited: *J. Mater. Process. Technol., 135*(2-3 SPEC.), 20 April 2003, pp. 228-234 [in English]. ISSN 0924-0136.

Improved oxidation resistance of titanium with a thermal sprayed $Ti_3Al(O)$-Al_2O_3 composite coating. A $Ti_3Al(O)$-Al_2O_3 in situ composite was explored as a coating system for titanium using thermal spray. Oxidation tests at 700-800 °C showed that this coating remarkably decreased the oxidation rate and increased the scale spallation resistance compared with titanium. The mechanisms for these improvements were then briefly discussed.

Keywords: intermetallics, oxidation resistance, spraying, titanium compounds

Z.-W. Li, W. Gao, D.-Y. Ying, D.-L. Zhang, Dept. Chemical Engineering, Univ. Auckland, Auckland, New Zealand. Cited: *Scr. Mater., 48*(12), June 2003, pp. 1649-1653 [in English]. ISSN 1359-6462.

Corrosion of High-Velocity Oxyfuel Coatings

High-temperature corrosion of coatings and boiler steels in oxidizing chlorine-containing atmosphere. High-temperature corrosion tests were performed on ferritic and austenitic boiler steels, five high-velocity oxyfuel (HVOF) coatings, laser-melted HVOF coating, and diffusion chromized steel. Synthetic atmosphere simulating biofuel combustion was created for the tests. The tests were performed in oxidizing atmosphere containing 500 vppm HCl, 20% H_2O, 3% O_2, and Ar as a balance. The test temperature was 550 °C, and the test duration was 1000 h. The corrosion resistance of steels was determined by alloy content. Homogeneous and dense coatings with high chromium content performed well and protected the substrate material. Corrosive species were able to penetrate through some of the HVOF coatings and attack the substrate via interconnected network of voids and oxides at splat boundaries.

Keywords: coatings, combustion, computer simulation, corrosion, oxidation

M.A. Uusitalo, P.M.J. Vouristo, and T.A. Mantyla, Institute of Materials Sci-

ence, Tampere Univ. of Technology, Tampere 33101, Finland. Cited: *Mater. Sci. Eng. A, 346*(1-2), 15 April 2003, pp. 168-177 [in English]. ISSN 0921-5093.

Corrosion resistance of Hastelloy C coatings formed by an improved HVOF thermal spraying process. The corrosion resistance of coatings obtained by an improved HVOF spraying method was evaluated by various electrochemical techniques. This spraying system could increase the flight velocity of sprayed particles and suppress their oxidation simultaneously by attachment of a gas shroud, employing nitrogen gas at a large flow rate. The process brought about attainment of both smaller porosity and lower oxide content of the resulting coatings. Consequently, the resistance of HVOF sprayed coatings against seawater corrosion was improved considerably.

Keywords: corrosion resistance, electrochemistry, oxidation, porosity, spraying

J. Kawakita, S. Kuroda, T. Fukushima, and T. Kodama, Natl. Inst. for Materials Science, Tsukuba 305-0047, Japan. Cited: *Mater. Trans., 44*(2), Feb 2003, pp. 253-258 [in English]. ISSN 1345-9678.

Cr_2O_3 Coatings

Stresses in plasma sprayed Cr_2O_3 coatings measured by neutron diffraction. Results of stress measurements in plasma sprayed coatings obtained by x-ray-diffraction measurements are often ambiguous and difficult to interpret. The neutron-diffraction method was used to determine the residual and applied stresses during four-point bending and compared with results obtained previously by x-ray diffraction. The volume-and lattice-effective Young's modulus was calculated from applied force and lattice deformation, respectively. The obtained results are discussed from the point of view of the behavior of cracks during tensile and compressive loading.

Keywords: bending strength, compressive strength, cracks, crystal lattices, elastic moduli, mechanical variables measurement, neutron diffraction, plasma spraying, stresses, tensile testing, x-ray diffraction analysis

J. Dubsky, H.J. Prask, J. Matejicek, and T. Gnaupel-Herold, Institute of Plasma Physics, 18600 Praha 8, Czech Republic. Cited: *Appl. Phys. A: Mater. Sci. Process., 74*(suppl. II), Dec 2002, pp. S1115-S1117 [in English]. ISSN 0947-8396.

The development of a thin Cr_2O_3 wear protective coating for the advanced digital recording system. In this paper the development of a 10 nm wear resistive Cr_2O_3 coating is reported. Results of extensive wear tests show that although the coating is susceptible to physical wear, the decrease in output seems to strive to a constant value over lifetime. This effect is linked to the protective action of the brown stains interacting with the 10 nm coating.

Keywords: chromium compounds, magnetic recording, sputter deposition, thin films, topology, wear resistance

M.D. Bijker, J.J.J. Bastiaens, E.A. Draaisma, L.A.M. De Jong, E. Sourty, S.O. Saied, and J.L. Sullivan, OnStream MST, Eindhoven 5652 AC, Netherlands. Cited: Tribology of Information Storage Devices 2001, J. Sullivan, Ed. (Senadai), 1 Dec 2001, *Tribol. Int., 36*(4-6), April/June 2003, pp. 227-233 [in English]. ISSN 0301-679X.

AEM study of aluminum phosphate sealed plasma sprayed Al_2O_3 and Cr_2O_3 coatings. The aluminum phosphate sealed plasma sprayed Al_2O_3 and Cr_2O_3 coatings was studied by using analytical transmission electron microscopes (AEM). The coatings were sprayed to the thickness of 800 μm for alumina coatings and 400 μm for chromia coatings onto Fe 52 substrates. The results showed that in the alumina coatings polycrystalline phosphate bonding phase was formed at the interface due to the chemical reaction between the coating lamellae and the sealants.

Keywords: alumina, chromium compounds, energy-dispersive spectroscopy, plasma spraying, polycrystalline materials, porosity

M. Vippola, P. Vuoristo, T. Lepisto, and T. Mantyla, Tampere Univ. Technology, Institute of Materials Science, FIN-33101 Tampere, Finland. Cited: *J. Mater. Sci. Lett., 22*(6), 15 March 2003, pp. 463-466 [in English]. ISSN 0261-8028.

Chromium Nitride Coatings

Mechanical property evaluation of cathodic arc plasma deposited CrN thin films on Fe-Mn-Al-C alloys. Chromium nitride is a promising hard coating applied in forming, drawing, and plastic molding industries due to its good thermal stability and excellent resistance to wear and corrosion. An austenitic Fe-30Mn-5.8Al-1C alloy was coated with a CrN film by a cathodic arc plasma deposition process. The mechanical and adhesion properties were evaluated by microhardness, scratch, nanoindentation, Daimler-Benz Rockwell C adhesion and pin-on-disk wear tests. The microhardness of CrN film reaches 2310 ± 100 HK under a 10 gf load. The elastic modulus of the CrN film is 290 GPa, measured with a nanoindenter under a 3000 μN load. The adhesion of CrN film deposited on Fe-Mn-Al-C substrate is observed to be better than HF1. The wear resistance of the Fe-Mn-Al-C substrate is also significantly improved by the presence of the CrN film.

Keywords: corrosion protection, elastic moduli, electric arcs, iron alloys, microhardness, thermodynamic stability, thin films

J.-W. Lee, J.-G. Duh, and J.-H. Wang, Dept. of Mechanical Engineering, Tung Nan Institute of Technology, Shenken, Taipei 222, Taiwan. Cited: *Surf. Coat. Technol., 168*(2-3), 22 May 2003, pp. 223-230 [in English]. ISSN 0257-8972.

Environmental Barrier Coatings

Development and evaluation of environmental barrier coatings for silicon nitride. Environmental barrier coatings (EBCs) are required for applications of silicon nitride (Si_3N_4) and silicon carbide (SiC) based materials in gas turbine engines because of the accelerated oxidation of Si_3N_4 and SiC and subsequent volatilization of silica in the high-temperature high-pressure steam environment. EBC systems for silicon carbide fiber reinforced silicon carbide ceramic-matrix composites (SiC/SiC CMCs) were first developed and have been demonstrated via long-term engine tests. Recently, studies have been carried out at United Technologies Research Center (UTRC) to understand the temperature capability of the current celsian-based EBC systems and its suitability for silicon nitride ceramics concerning thermal expansion mismatch between the EBC coating and silicon nitride substrates. This paper presents recent progress in improving the temperature capability of the celsian-based EBC systems and discuss their effectiveness for silicon nitride.

Keywords: ceramic-matrix composites, gas turbines, high-pressure effects, high-temperature effects, oxidation, silica, silicon carbide, silicon nitride, substrates, thermal expansion, vaporization

E.Y. Sun, H.E. Eaton, J.E. Holowczak, and G.D. Linsey, United Technologies Research Center, East Hartford, CT 06108. Cited: *Proc. ASME TURBO EXPO 2002: Ceramics, Industrial and Cogeneration Structures and Dynamics,* Vol. 4A, 3-6 June 2002 (Amsterdam), The International Gas Turbine Institute, American Society of Mechanical Engineers, 2002, pp. 141-146 [in English].

Environmental barrier coatings having a YSZ top coat. Environmental barrier coatings (EBCs) with a silicon bond coat, a yttria-stabilized zirconia (YSZ) top coat, and various intermediate coats were investigated. EBCs were processed by atmospheric pressure plasma spraying. The EBC durability was determined by thermal cycling tests in water vapor at 1300 and 1400 °C, and in air at 1400 and 1500 °C. EBCs with a mullite ($3Al_2O_3{\cdot}2SiO_2$) + BSAS ($1 - x$BaO·xSrO·$Al_2O_3{\cdot}2SiO_2$) intermediate coat were more durable than EBCs with a mullite intermediate coat, while EBCs with a mullite/BSAS duplex intermediate coat resulted in inferior durability. The improvement with a mullite + BSAS intermediate coat was attributed to enhanced compliance of the intermediate coat due to the addition of a low modulus BSAS second phase. Mullite + BSAS/YSZ and BSAS/YSZ interfaces produced a low melting (≤1400 °C) reaction product, which is expected to degrade the EBC performance by increasing the thermal conductivity. EBCs with a mullite + BSAS/graded mullite + YSZ intermediate coat showed the best durability among the EBCs investigated in this study. This improvement was attributed to diffused coefficient of thermal expansion mismatch stress and improved chemical stability due to the compositionally graded mullite + YSZ layer.

Keywords: aluminum compounds, interfaces (materials), melting, minerals, plasma spraying, silica, thermal conductivity, thermal cycling, vapors, yttrium compounds, zirconia

K.N. Lee, Cleveland State Univ., NASA Glenn Research Center, Cleveland, OH 44135. Cited: *Proc. ASME TURBO EXPO 2002: Ceramics, Industrial and Cogeneration Structures and Dynamics,* Vol. 4A, 3-6 June 2002 (Amsterdam), The International Gas Turbine Institute, American Society of Mechanical Engineers, 2002, pp. 127-133 [in English].

Evaluating environmental barrier coatings on ceramic-matrix composites after engine and laboratory exposures. SiC/SiC continuous fiber-reinforced ceramic-matrix composite (CFCC) combustor liners having protective environmental barrier coatings (EBCs) applied to the liner working surfaces have been field-tested in a Solar Turbines' Centaur 50S SoLoNOx engine at the Chevron, Bakersfield, CA, engine test site. This latest engine test ran for a total of 13,937 h. The EBCs significantly increased the lifetime of the in-service liners compared with uncoated CFCC liners used in previous field-tests. The engine test was concluded when a routine borescope inspection revealed the formation of a small hole in the inner liner. Extensive microstructural evaluation of both the inner and outer liners was conducted after removal from the engine. Post-test analysis indicated that numerous degradation mechanisms contributed to the EBC and CFCC damage observed on the liners, including EBC volatilization, subsurface CFCC oxidation and recession, and processing defects that resulted in localized EBC spallation and accelerated CFCC oxidation. The characterization results obtained from these field-tested liners have been compared with the analyses of similarly processed CFCC/EBCs that were laboratory tested in a high-pressure, high-temperature exposure facility (the ORNL "Keiser Rig") for >6000 h.

Keywords: ceramic-matrix composites, combustors, fiber-reinforced materials, gas engines, high-pressure effects, high-temperature effects, microstructure, oxidation, silicon carbide, vaporization

K.L. More, P.F. Tortorelli, L.R. Walker, J.B. Kimmel, N. Miriyala, J.R. Price, H.E. Eaton, E.Y. Sun, and G.D. Linsey, Oak Ridge National Laboratory, Oak

Ridge, TN. Cited: Cited: *Proc. ASME TURBO EXPO 2002: Ceramics, Industrial and Cogeneration Structures and Dynamics,* Vol. 4A, 3-6 June 2002 (Amsterdam), The International Gas Turbine Institute, American Society of Mechanical Engineers, 2002, pp. 155-162 [in English].

Phase evolution of BSAS in environmental barrier coatings. Barium strontium aluminosilicate (BSAS) has been demonstrated to be a beneficial constituent in coatings that prevent high-temperature environmental degradation of SiC. Promising plasma sprayed environmental barrier coatings (EBCs) have been produced using BSAS as a top layer above a mullite bottom layer that includes a significant BSAS second phase. Depending on deposition conditions and thermal treatments, BSAS can be present in the amorphous, hexagonal celsian, or monoclinic celsian phases. Because of differences in stability, volume, and coefficient of thermal expansion (CTE), the phase content is expected to significantly affect the EBC performance. While the monoclinic celsian phase is believed to be the most desirable due to its stability and low CTE, conversion of the hexagonal phase to the monoclinic can be very sluggish and difficult to achieve. In this study, Raman microscopy was applied to track the phase evolution of BSAS in these coatings with heat treatment. Striking differences were observed in the phase evolution occurring in the BSAS top layer compared to the evolution of the BSAS second phase in the mullite bottom layer. The implications of the observed BSAS phase evolution on stress development, and therefore coating lifetime, are discussed. A comparison is also made with EBCs incorporating strontium aluminosilicate (SAS) in place of BSAS, since the hexagonal phase is expected to convert more readily to monoclinic phase with SAS.

Keywords: barium compounds, degradation, heat treatment, phase transitions, plasma spraying, Raman spectroscopy, thermal barrier coatings, thermal expansion, thermodynamic stability

J.I. Eldridge and K.N. Lee, NASA Glenn Research Center, Cleveland, OH 44135. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., B, 22*(4), 2001, pp. 383-390 [in English]. ISSN 0196-6219.

Fatigue and Fracture

Indentation fracture behavior of plasma sprayed nanostructured Al_2O_3-13wt.%TiO_2 coatings. Indentation crack growth resistance of nanostructured Al_2O_3-13wt.%TiO_2 coatings plasma sprayed using nanosized powders was investigated. Comparisons were made between the nanocoatings and a commercial baseline coating of the same composition, Metco 130. In Metco 130 coatings that contain only the single-phase splat microstructure, long cracks initiate at the indent corners and propagate along splat boundaries. In contrast, the nanocoatings are composed of a bimodal microstructure (a fully melted splat structure and a partially melted particulate structure), and the partially melted particulate region serves to trap and deflect the splat boundary cracks. The interface between the fully melted region and the partially melted region also provides additional crack arrest mechanisms. At optimized conditions, these toughening mechanisms can produce an approximately 100% improvement in the crack growth resistance. The optimized microstructure for the nanocoatings is the microstructure containing 15-20% of the partially melted particulate region, which can be systematically controlled by changing the plasma flame temperature.

Keywords: alumina, coatings, composition, cracks, indentation, microstructure, plasma spraying, titanium dioxide

H. Lou, D. Goberman, L. Shaw, and M. Gell, Dept. of Metallurgy and Mat. Eng., Univ. Connections, Storrs, CT 06269 3136. Cited: *Mater. Sci. Eng. A, 346*(1-2), 15 April 2003, pp. 237-245 [in English]. ISSN 0921-5093.

High-temperature fatigue deformation behavior of ceramics thermally sprayed SUS304 steel measured with an ESPI system. In this paper, the surface strain of an Al_2O_3/Ni-Cr atmospheric plasma thermally sprayed SUS304 steel specimen during the fatigue test (σ_{max} = 173 MPa, R = 0, 873 K) was measured with an electronic speckle pattern interferometry (ESPI) system. The relationship between surface strain and crack initiation/delamination behavior was discussed. The strain value obtained from the ESPI system was confirmed to be almost the same as that obtained from a strain gage on an unsprayed specimen when tensile stress was loaded at 293 K. Thermal expansion deformation and stress deformation at high temperatures were easily measured with the ESPI system. The presence of cracks and delamination on a sprayed coating can be detected in sim, and the strain concentration or disappearing can be detected without damage. The sprayed specimen surface strain was almost the same as the unsprayed specimen at 873 K, which indicates that deformation of the sprayed coating is always associated with substrate surface deformation at high temperature. The maximum surface strain was lower after 1×10^5 cycles fatigue than after two cycles fatigue. Surface cracks occurred but stopped at the inner nickel-chromium layer after two fatigue cycles at 873 K. Many surface cracks and delaminations along the interface between the nickel-chromium layer and substrate were confirmed after 1×10^5 fatigue cycles.

Keywords: alumina, ceramic materials, crack initiation, fatigue testing, high-temperature applications, interferometry, plasma spraying, sprayed coatings, strain, tensile stress

M. Kido, R. Wang, S. Nakamura, M. Takeda, M. Yamazaki, and T. Tokuda, Dept. of Mech. Sys. Eng., Fac. of Tech., Hiroshima Inst. of Tech., Hiroshima 731-5193, Japan. Cited: *Zairyo/J. Soc. Mater. Sci., Jpn., 51*(12), Dec 2002, pp. 1417-1422 [in Japanese]. ISSN 0514-5163.

On the propagation and coalescence of delamination cracks in compressed coatings: with application to thermal barrier systems. Coatings subject to residual compression eventually fail by buckle-driven delamination. The phenomenon is most vivid in thermal barrier coatings (TBCs) used in gas turbines. The failure evolution commences with the formation of a large number of small cracks at geometric imperfections near the interface. These cracks spread upon thermal exposure, particularly upon thermal cycling, because of the formation of a thermally grown oxide (TGO) beneath the TBC, which introduces normal and shear stress near the interface. Experimental observations indicate that some of these cracks coalesce to form large-scale delaminations susceptible to buckling. The mechanics governing crack coalescence and the consequent failure are addressed in the present analysis. A model is introduced that simulates stresses induced in the TBC by spatial variations in TGO growth. Energy release rates for cracks evolving in this stress field are determined. Two related scenarios are considered, which differ in the way the TGO shape evolves. In both, contact between the crack faces and the consequent wedging action is responsible for ultimate coalescence. The wedging force induces a mode I stress intensity that becomes infinite as the cracks coalesce. The consequence is that, for some TGO shapes, the energy release rate is always nonzero, with a minimum at a characteristic crack length. This minimum establishes a criterion for crack coalescence and failure. Based on these insights, finite-element simulations have been used to predict cyclic crack growth rates in a TBC system that correlate well with experimental observations.

Keywords: coalescence, compaction, computer simulation, cracks, delamination, interfaces (materials), shear stress, toughness

X. Chen, J.W. Hutchinson, M.Y. He, and A.G. Evans, Div. of Eng. and Applied Sciences, Harvard Univ., Cambridge, MA 02138. Cited: *Acta Mater., 51*(7), 18 April 2003, pp. 2017-2030 [in English]. ISSN 1359-6454.

Deformation and tensile cyclic fatigue of plasma sprayed ZrO_2-8wt.%Y_2O_3 thermal barrier coatings. Deformation (constitutive relations) of free-standing, thick thermal barrier coatings of plasma sprayed ZrO_2-8wt.%Y_2O_3 was determined at ambient temperature in both pure tension and pure compression using cylindrical bar test specimens. The material exhibited both significant nonlinearity and hysteresis in its load-strain curves. The load-strain relations in four-point uniaxial flexure were determined from tension and compression sides and were compared with individual pure tension and compression constitutive data. Effect of sintering on deformation behavior was significant, resulting in a dramatic change in constitutive relation. Cyclic fatigue testing of the coating material in tension-tension at room temperature showed an insignificant susceptibility to fatigue, similar to the slow crack growth behavior of the material in flexure in 800 °C air.

Keywords: compression testing, crack propagation, deformation, fatigue testing, hysteresis, plasma spraying, sintering, strain, tensile strength, tensile testing, thermal effects, zirconia

S.R. Choi, D. Zhu, and R.A. Miller, Ohio Aerospace Institute, Cleveland, OH. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., B, 22*(4), 2001, pp. 427-434 [in English]. ISSN 0196-6219.

Thermal fatigue and fracture behavior of ceramic thermal barrier coatings. Thermal fatigue and fracture behavior of plasma sprayed ceramic thermal barrier coatings has been investigated under high heat flux and thermal cyclic conditions. The coating crack propagation is studied under laser heat flux cyclic thermal loading, and is correlated with dynamic fatigue and strength test results. The coating stress response and inelasticity, fatigue and creep interactions, and interface damage mechanisms during dynamic thermal fatigue processes are emphasized.

Keywords: crack propagation, creep, elasticity, fatigue of materials, fracture, heat flux, interfaces (materials), plasma spraying, strength of materials, stresses, thermal cycling, thermal load

D. Zhu, S.R. Choi, and R.A. Miller, NASA Glenn Res. Ctr. at Lewis Field, Cleveland, OH 44135. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., B, 22*(4), 2001, pp. 453-461 [in English]. ISSN 0196-6219.

Multiple surface cracking and its effect on interface cracks in functionally graded thermal barrier coatings under thermal shock. The thermal fracture behavior in functionally graded yttria-stabilized zirconia-NiCoCrAlY bond coat alloy thermal barrier coatings was studied using analytical models. The response of three coating architectures of similar thermal resistance to laser thermal shock tests was considered. Mean field micromechanics models were used to predict the effective thermoelastic and time-dependent (viscoplastic) properties of the individual layers of the graded thermal barrier coatings (TBCs). These effective properties were then utilized in fracture mechanics analyses to study the role of coating architecture on the initiation of surface cracks. The effect of the surface crack morphology and coating architecture on

the propensity for propagation of horizontal delamination cracks was then assessed. The results of the analyses are correlated with previously reported experimental results. Potential implications of the findings on architectural design of these material systems for enhanced thermal fracture resistance are discussed.

Keywords: crack initiation, fracture, heat resistance, morphology, surfaces, zirconium alloys

S. Rangaraj and K. Kokini, School of Mechanical Engineering, Purdue Univ., West Lafayette, IN 47907-1288. Cited: *J. Appl. Mech., Trans. ASME, 70*(2), March 2003, pp. 234-245 [in English]. ISSN 0021-8936.

Influence of corrosion resistant coating on thermomechanical fatigue life of gas turbine blade material IN738LC. The purpose of this study is to clarify the effect of CoCrAlY coating on biaxial thermomechanical fatigue (TMF) life property of Inconel 738LC. In-phase and out-of-phase TMF tests at temperature between 450 and 850 °C were carried out by using a tension/torsion and compression TMF testing machine. In addition to these fundamental TMF tests, a complicated temperature and strain history tests, so called a blade waveform that simulates temperature and strain histories of actual gas turbine blade, were performed. Failure life of coated specimens under the in-phase condition is longer than that of the substrate and the main crack propagated from boundary between the coating and substrate to inside of the substrate. Therefore, the coating plays a positive role for the substrate life due to suppression of crack initiation and propagation in the coating. On the other hand, failure life of the coated material under out-of-phase and blade waveform tests is approximately ½ of the substrate life indicating negative effect. It was suggested from failure surface observation that crack initiation period in the coating is shortened by the difference of deformation behavior between the substrate and coating and that crack propagation rate in the substrate of the coated specimen is accelerated by the cracking of the coating compared with the crack propagation rate of substrate itself.

Keywords: cobalt alloys, computer simulation, corrosion protection, crack initiation, crack propagation, fatigue of materials, gas turbines, iron alloys, mechanical testing, plastic deformation, protective coatings, thermomechanical treatment

T. Ogata and A. Nomoto, Ctrl. Res. Inst. Elec. Power Indust., Chiyoda-ku, Tokyo 100-8126, Japan. Cited: *Zairyo/J. Soc. Mater. Sci/, Jpn., 52*(2), Feb 2003, pp. 139-145 [in Japanese]. ISSN 0514-5163.

Hardness and (Visco)elastic Properties of Thermal Barrier Coatings

Mesoscopic nonlinear elastic modulus of thermal barrier coatings determined by cylindrical punch indentation. Cylindrical punch indentations are performed to determine the effective modulus of a plasma sprayed ZrO_2-8 wt.%Y_2O_3 thermal barrier coating (TBC) as a function of coating depth. Cylindrical punch indentations offer significant advantages over pointed (Vickers, Berkovich, or Knoop) indentations for materials that do not exhibit linear elastic behavior. Cyclic loading with a cylindrical punch clearly shows the TBCs to exhibit nonlinear elastic behavior with significant hysteresis that is related to the compaction and internal sliding within the plasma spray splat microstructure. Also, the effect of a high-heat-flux laser treatment is shown to produce a gradient both in the effective TBC modulus and degree of loading/unloading hysteresis with depth.

Keywords: elastic moduli, heat flux, indentation, microstructure, plasma spraying, thermal barrier coatings

J.I. Eldridge, D. Zhu, and R.A. Miller, NASA Glenn Research Center, Cleveland, OH 44135. Cited: *J. Am. Ceram. Soc., 84*(11), Nov 2001, pp. 2737-2739 [in English]. ISSN 0002-7820.

High-Velocity/Electric Arc Sprayed Coatings

Microstructure of alloyed layer and nitriding process in foreign metals under arc sprayed titanium composite coating. The authors investigated the nitriding process and the microstructure of the alloyed layer between foreign metals under composite arc spraying using two different wire materials, titanium and the paired metal (molybdenum, nickel, copper, and aluminum). The titanium element in the composite coatings (Ti-Mo, Ti-Ni, Ti-Cu, and Ti-Al) was of TiN and/or $TiN_{0.3}$, and the oxide or nitride of the paired metal was not found in the coatings. An intermetallic compound (Ti_2Al) in the titanium-aluminum coating was detected in the x-ray diffraction pattern, but none was detected in the other coatings. It is considered that the reaction of titanium with foreign metal occurs only in the solidification process at the moment of droplet impact. The composite coatings were of very dense packing and had the diffusion layer in the interface region between the foreign metals. The solute element, titanium in the composite coating titanium-molybdenum, reacted with nitrogen to form many micrograins of $TiN_{0.3}$ within molten molybdenum during thermal spraying. In the other coatings (Ti-Ni, Ti-Cu, and Ti-Al), eutectics were mainly identified, and the titanium nitride in the alloyed layer between foreign metals was only $TiN_{0.3}$. In addition, the intermetallic compounds, which were not detected in the XRD pattern, were identified in the TEM observation.

Keywords: diffusion in solids, interfaces (materials), intermetallics, metallographic microstructure, metals, nitriding, solidification, sprayed coatings, transmission electron microscopy, x-ray diffraction analysis

N. Sakoda, M. Hida, Y. Takemoto, A. Sakakibara, and T. Tajiri, Okayama Univ., Grad. Sch. Natural Sci. and Technol., Okayama 700-8530, Japan. Cited: *Nippon Kinzoku Gakkaishi/J. Jpn. Inst. Met., 66*(12), Dec 2002, pp. 1304-1310 [in Japanese]. ISSN 0021-4876.

Correlations between operating conditions, microstructure, and mechanical properties of twin wire arc sprayed steel coatings. An experimental design matrix was set up in which carbon steel coatings were deposited with a twin wire arc spray gun (TAFA 9000), using either compressed air or nitrogen as spraying gas. The coating mechanical properties were studied. Some correlations were made among these properties, spraying conditions, and the microstructure of the deposits. Young's modulus was estimated by the single-beam method using finite-element modeling. Results show that direct relationships do exist among spray conditions, oxide content in the coating, and microhardness. Young's modulus of the coatings depends on the lamella thickness and the oxide content. When increasing the compressed air flow rate, Young's modulus increase at first because smaller particles and finer lamellae were made and it decreases later because of a higher oxide content. The increase of nitrogen flow rate lowers the oxide content and increases Young's modulus.

Keywords: deposition, elastic moduli, microhardness, microstructure, sprayed coatings

G. Jandin, H. Liao, Z.Q. Feng, and C. Coddet, LERMPS, Universite de Technologie Belfort, Belfort Cedex 90010, France. Cited: *Mater. Sci. Eng. A, 349*(1-2), 25 May 2003, pp. 298-305 [in English]. ISSN 0921-5093.

High-Velocity Oxyfuel Microstructures

Microstructure and corrosion resistance of HVOF sprayed 316L stainless steel and Hastelloy C coatings. In order to develop dense corrosion-resistant coatings by thermal spraying, 316L stainless steel and Hastelloy C alloy powders were sprayed by an HVOF thermal spraying apparatus onto a mild steel substrate. The microstructure, pore size distribution, composition, and corrosion resistance of the obtained coatings were evaluated experimentally. Corrosion resistance in seawater was examined by monitoring the impedance and corrosion potential of samples immersed in artificial seawater at 300 K over a period of more than 3 months and also by polarization measurement. It was found that the stainless steel coatings composed mainly of plastically deformed particles and some splats that were molten at the impact. By increasing the combustion pressure, the porosity measured by a mercury porosimeter was reduced to below 1%. In comparison, Hastelloy C deposits sprayed under a standard condition were so dense that their porosity could not be measured by the porosimeter. The polarization curves and the results of impedance monitoring exemplified that the Hastelloy C coatings possess much superior corrosion resistance to the stainless steel coatings in seawater, which was attributed mainly to the higher density and better adhesion of the nickel-base alloy coatings.

Keywords: adhesion, composition, electrochemistry, metallographic microstructure, plastic deformation, porosity, protective coatings, seawater corrosion, spraying, stainless steel

S. Kuroda, T. Fukushima, M. Sasaki, and T. Kodama, National Inst. Materials Science, Tsukuba 305-0047, Japan. Cited: *Mater. Trans., 43*(12), Dec 2002, pp. 3177-3183 [in English]. ISSN 1345-9678.

Comparison of HVOF and plasma sprayed alumina/titania coatings—microstructure, mechanical properties, and abrasion behavior. The authors have evaluated the microstructure, mechanical properties, and abrasion wear resistance of alumina/titania ceramic coatings deposited with nanostructured and microstructured powders by high-velocity oxygen fuel (HVOF) and plasma spray (PS) processes. The deposition guns have a strong influence on the mechanical properties and abrasive wear resistance of the coatings, but the powders do not. The coatings deposited by HVOF are significantly harder and tougher, and their abrasion resistance is two- to three-fold higher. Plastic microcutting plays the predominant role in abrasion wear of the coating deposited by HVOF. A combination of brittleness and porosity results in fracture that dominates the abrasion wear of plasma sprayed coatings. The abrasion resistance measured follows an Evans-Marshall equation modified to account for the effects of porosity.

Keywords: abrasion, alumina, microstructure, plasma spraying, porosity, wear resistance

Y. Liu, T.E. Fischer, and A. Dent, Dept. of Chem. Biochem./Mat. Eng., Stevens Institute of Technology, Hoboken, NJ 07030. Cited: *Surf. Coat. Technol., 167*(1), 1 April 2003, pp. 68-76 [in English]. ISSN 0257-8972.

Effect of particle size on microstructure of high-velocity oxyfuel (HVOF) sprayed hydroxyapatite coatings. Hydroxyapatite (HA) coatings were deposited on Ti-6Al-4V substrates using high-velocity oxyfuel (HVOF) spray process, with the aim of achieving high degree of crystallinity and limited phase decomposition of HA during coating development. The starting HA powders with particle size range, 50 ± 10 μm, 40 ± 10 μm, and 30 ± 10 μm, were

sprayed to obtain an eclectic mix of melt states in the sprayed powders. Microstructure of the coatings and sprayed powders was characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Furthermore, x-ray diffraction analysis, differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR) were conducted to characterize the coatings and powders. Results showed that the melted portion of sprayed HA particles was responsible essentially for the HA phase transformation and decomposition. Crystalline HA coatings (>90% crystallinity) can be deposited by HVOF spraying large HA powders, >50 μm. The phase composition of the as sprayed HA coatings can be controlled through controlling the melt state of the powders. It also stated that phase transformation of HA during coating formation mostly occurred within the melted portion of the particles.

Keywords: coatings, differential scanning calorimetry, Fourier transform infrared spectroscopy, microstructure, particle size analysis, phase transitions, scanning electron microscopy, x-ray diffraction analysis

K.A. Khor, H. Li, and P. Cheang, Sch. of Mech./Production Engineering, Nanyang Technological Univ., Singapore. Cited: Proc. 15th Int. Symposium on Ceramics in Medicine; The Annual Meeting of the International Society for Ceramics in Medicine, B. Ben-Nissan, D. Sher, and W. Walsh, Ed., 4-8 Dec 2002 (Sydney, Australia), *Key Eng. Mater., 299-302,* 2003, pp. 311-314 [in English]. ISSN 1013-9826.

Interlamellar boundary characterization in nickel-base alloy thermally sprayed coating. The use of thermal spraying process for corrosion protection requires a high level of knowledge concerning the material modifications during coating deposition. The effect of the high-velocity oxygen fuel process on Inconel 718 thermally sprayed coating microstructure was studied by x-ray diffraction, transmission electron microscopy, and scanning transmission electron microscopy analyses. Thermally sprayed coating exhibits an interlamellar oxidation related to the in-flight and cooling particles. The in-flight oxidation is characterized by a globular oxide that results from convective motion in the liquid phase of the molten particles before impact on the substrate. The oxide was identified as $CrNbO_4$. The cooling step on the substrate induces a duplex oxide with an outer layer composed of columnar spinel oxide $(Ni,Fe)Cr_2O_4$ and an inner oxide corresponding to a nanocrystalline $CrNbO_4$ oxide, which is related to the rapid cooling of the flattened particles.

Keywords: corrosion protection, microstructure, nanostructured materials, oxidation, scanning electron microscopy, sprayed coatings, transmission electron microscopy, x-ray diffraction

R. Molins, B. Normand, G. Rannou, B. Hannoyer, and H. Liao, UPR15-CNRS, LPLE, Univ. Pierre et Marie Curie Paris VI, Paris Cedex 05 F-75 252, France. Cited: *Mater. Sci. Eng. A, 351*(1-2), 25 June 2003, pp. 325-333 [in English]. ISSN 0921-5093.

Microstructural characterization of thermally sprayed quasi-crystalline Al-Co-Fe-Cr coatings. A microstructural characterization was carried out for Al-Co-Fe-Cr feed powder and the coatings sprayed with a high-velocity oxyfuel method using different operation conditions. The aims of the study were to explore the structural development of thick Al-Co-Fe-Cr coatings and the influence of the spraying parameters on the microstructure of produced Al-Co-Fe-Cr coatings. X-ray diffractometry, scanning electron microscopy, and analytical transmission electron microscopy were the techniques used in the phase identification and in the microstructural exploration of the study. The results show that Al-Co-Fe-Cr feed powder and the coatings sprayed with low and high operation temperature are composed of a dodecagonal quasi-crystalline phase. The composition of this new dodecagonal phase approximately corresponds to that of the feed powder, being $Al_{70.6}Co_{12.5}Fe_{9.4}Cr_{7.5}$. The dodecagonal phase does not decompose during the spraying process. Instead, it orientates to form a lamellar coating structure. When a lower spraying temperature is used, the incomplete melting of powder particles introduces a partly orientated coating structure. Due to this incomplete melting of powder particles, porosity is also involved in these coatings. Higher spraying temperature, in turn, promotes oxidation, leading to the incorporation of an oxygen-containing film on the splat boundaries. While the feed powder and the coating deposited with a lower spraying temperature are one-phase quasi-crystalline structures, the coating sprayed with a higher operation temperature is composed of a dodecagonal phase and an oxygen-containing phase. This oxygen-containing phase is not pure aluminum oxide, but contains all the elements present in the alloy.

Keywords: microstructure, porosity, scanning electron microscopy, sprayed coatings, spraying, transition metal alloys, transmission electron microscopy, x-ray diffraction analysis

E. Huttunen-Saarivirta, E. Turunen, and M. Kallio, Tampere Univ. Technology, Institute of Materials Science, Fin-33101, Tampere, Finland. Cited: *J. Alloy. Compd., 354*(1-2), 12 May 2003, pp. 269-280 [in English]. ISSN 0925-8388.

Hydroxyapatite Biomaterial

Dental implants: surface modification of commercially pure titanium (cp-Ti) using plasma spraying and the deposition of hydroxyapatite. Commercially pure titanium (cp-Ti) is currently being used with great success in dental implants. In this work, the authors investigate how the cp-Ti implants can be improved by modifying the metal surface morphology on which a synthetic material with properties similar to that of the inorganic part of the bone is deposited to facilitate the bone/implant bonding. This synthetic material is the hydroxyapatite (HA) a calcium-phosphate ceramic. The surface modification consists in the application of a titanium oxide (TiO_2) layer, using the thermal aspersion plasma spray technique, with posterior deposition of HA, using the biomimetic method. The x-ray diffraction (XRD), scanning electron microscopy (SEM) with energy-dispersive x-ray (EDX) and diffuse reflectance infrared Fourier transform (DRIFT) techniques have been used for characterizing phases, microstructures, and morphologies of the coatings. The TiO_2 deposit shows a mixture of anatase, rutilo, and TiO_{2-x} phases, and a porous and laminar morphology, which facilitate the HA deposition. After the thermal treatment, the previously amorphous structured HA coating, shows a porous homogeneous morphology with particle size of about 2-2.5 μm, with crystallinity and composition similar to that of the biological HA.

Keywords: bone, deposition, energy-dispersive spectroscopy, Fourier transform infrared spectroscopy, hydroxyapatite, morphology, plasma spraying, scanning electron microscopy, surface treatment, titanium, titanium dioxide, x-ray diffraction analysis

V.L.C. Oliveira, A.C. Alencar, I. Ramires, and A.C. Guastaldi, Departamento de Fisico-Quimica, Instituto de Quimica de Araraquara, UNESP, Araraquara, SP, Brazil. Cited: *Mater. Sci. Forum, 416-418*(1), 2003, pp. 669-674 [in English]. ISSN 0255-5476.

Laser ablation rate of hydroxylapatite in different atmospheres. Hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$) is a calcium phosphate used as coating for dental and orthopedic implants, because its composition and structure are similar to the mineral part of bone. Pulsed laser deposition has been applied as an alternative to the commercial technique for the production of hydroxylapatite coatings: plasma spraying. Hydroxylapatite targets were ablated at 0.9 J/cm^2 using an ArF excimer laser (193 nm) at 20 Hz in order to investigate the ablation rate of hydroxylapatite in different atmospheres: water vapor, Ar and O_2. The ablation rate was measured by profilometry for different pressures in a range of 15-80 Pa. The ablation rate depends on the backscattering of the ablated particles by the molecules of the gas, which produces different amounts of redeposited material on the target surface for each gas. The ablation rate in a water vapor atmosphere presents a particular behavior due to the formation of different calcium phosphate phases from the original hydroxylapatite under ArF excimer laser irradiation as compared those formed in other ambient gases.

Keywords: calcium compounds, dental prostheses, electromagnetic wave backscattering, excimer lasers, orthopedics, plasma spraying, pulsed laser deposition

J.L. Arias, M.B. Mayor, J. Pou, B. Leon, and M. Perez-Amor, Depto. de Fisica Aplicada, Universidade de Vigo, E-36200 Vigo, Spain. Cited: *Appl. Surf. Sci., 208-209*(1), 15 March 2003, pp. 57-60 [in English]. ISSN 0169-4332.

Hydroxyapatite coatings on sulfuric acid treated type 316L SS and its electrochemical behavior in Ringer's solution. The corrosion behavior of various concentrations of sulfuric acid immersion on 316L SS is studied using cyclic anodic polarization experiments. The results from the experiments showed that 20% sulfuric acid treated stainless steels showed better resistance to pitting attack compared to the pristine 316L SS. Similarly, the hydroxyapatite (HAP) coatings carried on 20% H_2SO_4 treated 316L SS exhibited excellent resistance to localized attack than the HAP coatings on pristine 316L SS.

Keywords: anodic polarization, corrosion, electrochemistry, Fourier transform infrared spectroscopy, hydroxyapatite, protective coatings, stainless steel, sulfuric acid, x-ray diffraction analysis

S. Kannan, A. Balamurugan, and S. Rajeswari, Dept. Analytical Chemistry, Univ. Madras, Guindy Campus, Chennai 600 025, India. Cited: *Mater. Lett., 57*(16-17), May 2003, pp. 2382-2389 [in English]. ISSN 0167-577X.

Bond strength and microstructure of radio frequency thermal plasma sprayed hydroxyapatite/titanium composite coatings. The influences of plasma gas composition on the bond strength and on the microstructures of hydroxyapatite/titanium (HA/Ti) composite coatings were investigated. HA/Ti composite coatings were deposited on titanium substrates by a radio frequency thermal plasma spraying (RF-TPS) method with RF input powers of 11-27 kW. The ratio of hydroxyapatite and titanium powders supplied into the plasma was precisely controlled by two microfeeders so as to change the composition from titanium-rich to hydroxyapatite-rich toward the upper layer of the coating. When sprayed in argon plasma with a small amount of N_2 added, the bond (tensile) strength of the obtained HA/Ti composite coatings was 40-65 MPa. However, the HA/Ti composite prepared with a pure argon plasma or plasma gas containing some O_2, gave significantly lower bond strength (under 33 MPa), regardless of the other processing parameters such as RF input, substrate temperature and working distance. X-ray diffraction patterns of titanium coatings without hydroxyapatite showed that titanium nitride and titanium dioxide formed at the surface of the titanium deposits sprayed with plasma gas containing N_2 and O_2, respectively. Scanning electron microscopic

observation showed that the microstructures of interface between titanium particles were drastically changed by the plasma gas composition during RF-TPS.

Keywords: bond strength (materials), microstructure, plasma spraying, scanning electron microscopy, titanium, x-ray diffraction analysis

M. Inagaki, Y. Yokogawa, and T. Kameyama, Ceramic Research Institute, Natl. Inst. Adv. Indust. Sci./T., Nagoya, Japan. Cited: Proc. 15th Int. Symposium on Ceramics in Medicine; The Annual Meeting of the International Society for Ceramics in Medicine, B. Ben-Nissan, D. Sher, and W. Walsh, Ed., 4-8 Dec 2002 (Sydney, Australia), *Key Eng. Mater., 299-302,* 2003, pp. 283-286 [in English]. ISSN 1013-9826.

Torsional fatigue resistance of plasma sprayed HA coating on Ti-6Al-4V. The torsional strength of plasma sprayed hydroxyapatite (HA) coatings was studied under static and cyclic loading. The torsional shear tests were conducted in a frustum test device developed in this laboratory, which adapted to various coating thicknesses. The interfacial fatigue resistance was measured in terms of interfacial fatigue strength defined as the average maximum stress (τ_{fmax}). A staircase fatigue method was employed to determine the interfacial fatigue strength; this method resolved the uncertainty in detecting coating failure during torsion fatigue. The values for coating shear strength and shear fatigue strength obtained from the torsional tests did not differ from those obtained by previous tensional shear tests in this laboratory. The fatigue strength of one million cycles was about 35% lower than static shear strength. This finding might be used for estimating fatigue life span without cyclic loading tests.

Keywords: coatings, cyclic loads, fatigue testing, plasma spraying, shear stress, torsional stress

L. Yan, Y. Leng, and J. Chen, Jiyong, Dept. Mechanical Engineering, Hong Kong Univ. of Sci. and Technol., Hong Kong. Cited: *J. Mater. Sci.: Mater. Med., 14*(4), 1 April 2003, pp. 291-295 [in English]. ISSN 0957-4530.

Characterization of chemical inhomogeneity in plasma sprayed hydroxyapatite coatings. Successful applications of plasma sprayed hydroxyapatite (HA) coating for implants rely on understanding characteristics of the coating microstructure, particularly its inhomogeneity. The authors explored three new techniques for characterizing the chemical inhomogeneity of sprayed HA coatings on titanium substrate: micro-Raman spectroscopy (MRS), positive and negative ion ratios of time-of-flight secondary ion mass spectrometry (ToF-SIMS), and the energy loss peaks of x-ray photoelectron spectroscopy (XPS). The results showed that MRS effectively revealed a chemical gradient in the direction of the coating thickness and a decrease in crystallinity from the surface to interface within the as-sprayed coatings. The postspray treatment effectively promoted homogeneity between surface and the coating/titanium interfaces. Elucidating the chemistry of the sprayed HA coatings using the ion ratios of ToF-SIMS and the energy loss peaks of XPS remains a challenge, even though such techniques can be used to identify certain calcium phosphate phases in pure powder form.

Keywords: calcium compounds, hydroxyapatite, implants (surgical), microstructure, plasmas, Raman spectroscopy, secondary ion mass spectrometry, x-ray photoelectron spectroscopy

L. Yan, Y. Leng, and L.-T. Weng, Dept. Mechanical Engineering, Hong Kong Univ. of Sci./Technology, Kowloon, Hong Kong. Cited: *Biomaterials, 24*(15), July 2003, pp. 2585-2592 [in English]. ISSN 0142-9612.

Low-Temperature Oxidation

Effect of spray coated SiO_2 layers on the low-temperature oxidation of Si_3N_4. Si_3N_4 using Y_2O_3 as a sintering additive provides good mechanical properties and high-temperature oxidation resistance, but can suffer from crack formation when oxidized at 1000 °C. In order to minimize this problem, a SiO_2 layer was deposited onto Si_3N_4 by the spray coating method. The dispersion of the SiO_2 slurry for the spray coating process was optimized, and dense silicate layers were formed by the spray coating and heat treatment in nitrogen atmosphere. Penetration of the coating layer into the sample was observed when the heat treatment temperature was higher than 1400 °C. The crystallization behavior of silicate coatings is similar to that of native oxide layers, but the formation of cristobalite is suppressed. The SiO_2 coating inhibits the rapid oxidation of Si_3N_4 at 1000 °C effectively.

Keywords: crack initiation, low-temperature effects, silica, silicon nitride, sprayed coatings

S.-H. Lee, G. Rixecker, F. Aldinger, S.-C. Choi, and K.-H. Auh, Max-Planck-Institut Metallforschung, Inst. Nichtmetallische Anorganische, Universitat Stuttgart, Stuttgart 70569, Germany. Cited: *J. Eur. Ceram. Soc., 23*(8), July 2003, pp. 1199-1206 [in English]. ISSN 0955-2219.

Microstructure of NiCrAlY

Characterization of thermally sprayed metallic NiCrAlY deposits by multiple small-angle scattering. The technique of multiple small-angle neutron scattering (MSANS) was applied to thermally sprayed metallic deposits. The samples are technologically relevant nickel-base NiCrAlY coatings manufactured by different spray techniques (atmospheric and water-stabilized plasma spraying, flame spraying). MSANS measurements were made in directions parallel and perpendicular to the surface plane. Based on empirical considerations and on the analysis of SEM micrographs of coating cross sections, the complex microstructures were modeled in terms of three distinct void systems. Employing a recent MSANS formalism, the experimental beam-broadening as a function of incident wavelength was used to derive the model parameters under the constraints of MSANS anisotropy, total measured porosity, and total internal surface area. The surface area was obtained from small-angle neutron-scattering analysis in the Porod regime.

Keywords: anisotropy, microstructure, neutron scattering, nickel alloys, porosity, scanning electron microscopy

T. Keller, W. Wagner, A. Allen, J. Ilavsky, N. Margadant, S. Siegmann, and G. Kostorz, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland. Cited: *Appl. Phys. A: Mater. Sci. Process., 74*(suppl. II), Dec 2002, pp. S975-S977 [in English]. ISSN 0947-8396.

Microstructure of Thermal Barrier Coatings

Intrinsic and extrinsic variable effects on thermal barrier coatings life. Thermal barrier coating (TBC) life is dependent on many intrinsic and extrinsic variables within the environment that they operate within. Intrinsic variables include material composition, mechanical and thermal properties, microstructure, and ceramic coating thickness. On the other hand, extrinsic variables include cycle time, interface and top surface temperatures, and the gaseous environment, among others. Laboratory testing was conducted to determine the effects of these variables on TBC life. This paper addresses TBC life as a function of microstructure, thickness, and interface temperature.

Keywords: ceramic coatings, composition, interfaces (materials), mechanical properties, microstructure, thermal effects, thermodynamic properties

Z. Mutasim, Solar Turbines Inc., San Diego, CA. Cited: *Proc. ASME Turbo Expo 2002: Heat Transfer, Manufacturing Materials and Metallurgy,* Vol. 3B, 3-6 June 2002 (Amsterdam), The International Gas Turbine Institute, American Society of Mechanical Engineers, 2002, pp. 1135-1140 [in English].

Multiple small-angle neutron-scattering studies of anisotropic materials. Building on previous work that considered spherical scatterers and randomly oriented spheroidal scatterers, the authors describe a multiple small-angle neutron-scattering (MSANS) analysis for nonrandomly oriented spheroids. The authors illustrate this with studies of the multicomponent void morphologies found in plasma spray thermal barrier coatings.

Keywords: anisotropy, crystal orientation, morphology, optical devices, plasma spraying, thermal insulating materials

A.J. Allen, N.F. Berk, J. Ilavsky, and G.G. Long, NIST, Gaithersburg, MD 20899. Cited: *Appl. Phys. A: Mater. Sci. Process., 74*(suppl. II), Dec 2002, pp. S937-S939 [in English]. ISSN 0947-8396.

Theoretical analysis and experimental investigation of structure-formation principles during the application of thermally sprayed metallic coatings. A parametric study is reported of crystallographic texture, internal stress, and coating defects such as pores, in coatings formed with plasma or flame spraying techniques, and factors affecting the incidence of these. Theoretical assumption were tested with molybdenum coatings and a range of alloy powders (with the metals nickel, copper, iron, cobalt) on steel substrates. Correlations between thermophysical and mechanical properties of these coatings and their structural features, are presented.

Keywords: crystal lattices, crystallography, grain size and shape, mechanical properties, metals, microstructure, morphology, plasma spraying, porosity, positron annihilation spectroscopy, residual stresses, sprayed coatings, textures, thermodynamic properties

I. Iordanova and V. Antonov, Dept. Solid State Phys./M., Univ. Sofia, Sofia, Bulgaria. Cited: *Galvanotechnik, 94*(3), March 2003, pp. 682-691+VII [in English]. ISSN 0016-4232.

Influence of plasma spray parameters on formation and morphology of ZrO_2-8wt% Y_2O_3 deposits. Spray prints of thermal spray coatings were created on glass slides for air plasma sprayed 8 wt.% yttria partially stabilized zirconia (YSZ) deposits. The spray parameters such as carrier gas flow rate, standoff distance, and torch power were systematically changed to investigate the influence of these parameters on the YSZ deposit characteristics. The deposit properties such as deposition efficiency (DE), substrate coverage, deposit thickness, and roughness were measured. The deposits sprayed with a 3.5-4.0 L/min carrier gas flow rate at an 80 mm standoff distance exhibited higher values of DE within the range of studied process parameters. The DE increased as much as 25% by varying the carrier gas flow rate from 2.0 to 4.0 L/min. The deposits sprayed at a higher standoff distance and low torch power gave poor deposit characteristics. The deposit characteristics were compared with the in-flight particle parameters and revealed that the deposit characteristics strongly depended on the in-flight particle temperature. Using the in-flight particle properties, the flattening ratio and the splat thickness were calculated. The average size of particles adhering to the substrate was found to drastically change with a change of process conditions, being much less than the average size of the starting powder.

Keywords: calculations, flow of fluids, morphology, plasma spraying, substrates, surface roughness, yttrium compounds, zirconia

A. Kucuk, R.S. Lima, and C.C. Berndt, Karl Storz Endovision, Inc., Charlton, MA 01507. Cited: *J. Am. Ceram. Soc., 84*(4), April 2001, pp. 693-700 [in English]. ISSN 0002-7820.

Microstructure and heat transfer phenomena in ceramic thermal barrier coatings. Comparably thick Y_2O_3-partially stabilized ZrO_2 thermal barrier coatings were deposited by two different techniques, air plasma spray (APS) and electron beam physical vapor deposition (EB-PVD), on the same type of substrate. Microstructure and grain texture, as studied by SEM and XRD, were markedly different. The complex microstructure of the APS coatings, made of curled lamellar grains, was replaced in EB-PVD coatings by long columnar grains, aligned along the growth axis, with strong grain texture. Average porosity and other average or intrinsic properties, such as density and specific heat, were nearly the same for all studied coatings; phase composition ranged between 0 and 6 wt.% of the *m* phase in a prevalent *t*′-phase matrix. The main difference was in the shape and orientation of porosity with respect to the thermal flux direction, which was responsible for the different thermal diffusivity that was three times higher in EB-PVD than in APS coatings. An appropriate modeling of the heat diffusion process, including open and closed porosity with orientation and shape factors, could explain the observed diffusivity values.

Keywords: crystal microstructure, grain size and shape, physical vapor deposition, plasma spraying, porosity, scanning electron microscopy, textures, thermal barrier coatings, thermal diffusion, x-ray diffraction analysis, yttrium compounds, zirconia

P. Scardi, M. Leoni, F. Cernuschi, and A. Figari, Dipto. di Ingegneria dei Materiali, Universita di Trento, Trento 38050, Italy. Cited: *J. Am. Ceram. Soc., 84*(4), April 2001, pp. 827-835 [in English]. ISSN 0002-7820.

Nanostructured Coatings

Investigation of the thermomechanical properties of a plasma sprayed nanostructured zirconia coating. Yttria partially stabilized nanostructured zirconia coatings were deposited by atmospherical plasma spraying (APS). The microstructure of the as-sprayed nanostructured coating was characterized with scanning electronic microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), and Raman spectroscopy (RS). The laser-flash diffusivity method and push-rod method were used to examine the thermomechanical properties of the nanostructured zirconia coatings. The results obtained indicated that the plasma sprayed zirconia coating possessed nanostructure, and its average grain size was about 73 nm. The average thermal expansion coefficients of the nanostructured coating at the first thermal cycle and second thermal cycle from room temperature to 1200 °C are 11.0 and 11.6 × 10^{-6}/°C, respectively. The thermal diffusivity of the nanostructured zirconia coating was 1.80-2.54 × 10^{-3} cm^2/s between 200 and 1200 °C. The microhardness of the nanostructured zirconia coating was 8.6 GPa, which was 1.6 times as large as that of traditional zirconia coating.

Keywords: coatings, grain size and shape, microhardness, microstructure, nanostructured materials, Raman scattering, scanning electron microscopy, thermal cycling, thermal diffusion, thermal expansion, transmission electron microscopy, x-ray diffraction, zirconia

H. Chen, X. Zhou, and C. Ding, Chuanxian, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China. Cited: *J. Eur. Ceram. Soc., 23*(9), Aug 2003, pp. 1449-1455 [in English]. ISSN 0955-2219.

NiAl Coatings

Microindentation and erosion properties of thermal sprayed NiAl intermetallic-base alloy coatings. This investigation reports the effect of CeO_2 and chromium additives on the microstructures, microindentation, and erosion properties of the high-velocity oxyfuel (HVOF) thermal sprayed NiAl intermetallic coatings. It has been found that the addition of CeO_2 and chromium reduces the tendency of brittle peeling of NiAl intermetallic coatings during thermal spraying, presumably due to the improved wetness and bond strength of the sprayed intermetallic materials. The NiAl intermetallic coatings containing CeO_2 and chromium are also featured with fewer cracks, less porosity, higher hardness, and higher elastic modulus than the pure NiAl coatings. Due to the improvement in mechanical properties and physical integrity, the NiAl intermetallic coatings containing CeO_2 and chromium have exhibited significant increase in their erosion resistance compared with that of pure NiAl coatings. The possible mechanisms related to the improved microstructures, mechanical properties, and erosion resistance of the NiAl intermetallic coatings containing CeO_2 and Cr additives are also discussed.

Keywords: cerium compounds, chromium, coatings, cracks, elastic moduli, erosion, hardness, indentation, intermetallics, microstructure, porosity

Y. Wang, W. Chen, and L. Wang, Dept. of Chemical and Materials Eng., Univ. Alberta, Edmonton, Alta. T6G 2G6, Canada. Cited: *Wear, 254*(3-4), Feb 2003, pp. 350-355 [in English]. ISSN 0043-1648.

Ni-Co-Cr-Al Microstructures

Eutectic structures in the Ni-Co-Cr-Al system obtained by plasma spraying and by Bridgman growth. Formation of a regular fibrous two-phase microstructure was found in low-pressure plasma spray (LPPS) deposited Ni-Co-Cr-Al-Y coatings by transmission electron microscopy and analyzed by energy-dispersive spectroscopy. The structure is compared to aligned lamellar three-phase structures of an Ni-Co-Cr-Al alloy obtained on Bridgman growth under slow unidirectional solidification (UDS) conditions. The composition of the Ni-Co-Cr-Al alloy for UDS experiments has been identified by DTA. The conditions for the formation of both the LPPS and the UDS structures are discussed.

Keywords: Bridgman growth, differential thermal analysis, energy-dispersive spectroscopy, eutectics, microstructure, nickel compounds, plasma spraying, solidification, transmission electron microscopy

K. Fritscher, DLR German Aerospace Center, Institute of Materials Research, D-51170 Koln, Germany. Cited: *J. Cryst. Growth, 250*(3-4), April 2003, pp. 546-557 [in English]. ISSN 0022-0248.

Ni-Cr Coatings

Steam oxidation resistance of nickel-chromium thermal spray coatings on 9Cr-1Mo steel. Part 1: 80Ni-20Cr. The steam oxidation resistance of 80%Ni-20%Cr metallic coatings has been evaluated at four different steam temperatures in the range of 600-750 °C. Substrate used for the study was 9Cr-1Mo type steel. The thermal spray coatings were carried out using two different processes: atmospheric plasma spray (APS) and high-velocity oxyfuel (HVOF) spray. Thickness of the coatings was about 40 and 60 μm respectively. The results show that the thick and dense HVOF coating showed a better steam oxidation resistance than the thin porous APS coatings. At prolonged aging (1000 h), the HVOF coating showed the best protection up to 650 °C. Beyond this temperature, the presence of Fe_2O_3 was noticed at the coating surface. The reason for the protectiveness and failure at higher temperatures (above 650 °C) are discussed in detail.

Keywords: nickel alloys, oxidation resistance, plasma spraying, sprayed coatings, temperature

T. Sundararajan, S. Kuroda, T. Itagaki, and F. Abe, National Inst. for Materials Science, Sengen, Tsukuba 305-0047, Japan. Cited: *ISIJ Int., 43*(1), 2003, pp. 95-103 [in English]. ISSN 0915-1559.

Steam oxidation resistance of nickel-chromium thermal spray coatings on 9Cr-1Mo steel. Part 2: 50Ni-50Cr. The present work focuses on the steam oxidation resistance of 50%Ni-50%Cr metallic coatings produced using atmospheric plasma spray (APS) and high-velocity oxyfuel (HVOF) spray processes on 9Cr-1Mo type steel substrate. Thickness of the coatings obtained in the HVOF and APS processes were about 60 and 40 μm respectively. The steam oxidation resistance of the coatings was evaluated at four different temperatures: 600, 650, 700, and 750 °C. The results showed that the thick and denser HVOF coating yielded a better steam oxidation resistance than the thin and porous APS coatings. At prolonged aging (1000 h), the HVOF coating showed the best protection in all tested steam temperatures. APS coating performed satisfactorily well till the 100 h of test duration. However, it started the scale initiation at the coating interface, and incorporation of scales occurred at 1000 h of steam oxidation test. The reason for the protectiveness by HVOF coating and failure of APS coatings at prolonged aging are discussed in detail.

Keywords: aging of materials, interfaces (materials), oxidation resistance, plasma spraying, porous materials, powder coatings, steel, substrates, thermal effects

T. Sundararajan, S. Kuroda, T. Itagaki, and F. Abe, National Inst. for Materials Science, Sengen, Tsukuba 305-0047, Japan. Cited: *ISIJ Int., 43*(1), 2003, pp. 104-111 [in English]. ISSN 0915-1559.

Polymer Coatings

Peel-strength behavior of bilayer thermal sprayed polymer coatings. The authors prepared various bilayer polymer coatings of ethylene methacrylic acid (EMAA) copolymer and ionomer by the thermal spray process under a range of preheat temperatures (PTs) to investigate their ability to be repaired. The thermal properties, crystallinity, microstructure, and interface strength of the coatings were investigated with differential scanning calorimetry, x-ray diffraction, scanning electron microscopy, and mechanical testing. Processing parameters influenced the final morphological structure of the coatings. The crystallinity of the coatings increased with a higher final temperature, whereas the coating density decreased. The decrease in density was attributed to the appearance of bubbles, 250 μm in size, formed in the coatings during the spray process. For the monolayer coating of polymer on a metal substrate, a higher PT produced a greater contact area of the coating to the substrate. The adhesion of EMAA ionomer to steel was always lower than that of EMAA copolymer to steel. This may have been largely due to the interfacial adhesion between the polymer and steel being dominated by strong secondary bond interactions. Experimental results also indicate that the peel strength between

polymers was at least twofold stronger than that between the polymer and the steel substrate for PTs greater than 100 °C. The mixed bilayer coating of ionomer on copolymer produced the highest peel strength. The interface between the plastic layers was clearly visible under the scanning electron microscope at lower PTs, becoming more diffuse with an increase in PT. On the basis of these observations, the adhesion mechanism between polymers was explained by the formation of welding points.

Keywords: adhesion, copolymers, crystal microstructure, differential scanning calorimetry, ionomers, mechanical testing, scanning electron microscopy, sprayed coatings, strength of materials, thermodynamic properties, x-ray diffraction analysis

F.Y. Yan, K.A. Gross, G.P. Simon, and C.C. Berndt, Sch. of Physics and Materials Eng., Monash Univ., Parkville, Vic. 3800, Australia. Cited: *J. Appl. Polym. Sci., 88*(1), 4 April 2003, pp. 214-226 [in English]. ISSN 0021-8995.

Porosity and Thermal Conductivity of Coatings

Development of operating temperature prediction method using thermophysical properties change of TBC. The relations between the decrease of the noncontact area and the exposure conditions, by measuring the thermal conductivity and the porosity of thermal barrier coatings (TBCs) exposed to the temperatures that exist in an actual gas turbine and derives the correlation with exposure conditions. As a result, very high correlations were found between the thermal conductivity and exposure conditions of TBCs and between the porosity and exposure conditions. In addition, very high correlation were found between the thermal conductivity and porosity of TBCs.

Keywords: combustors, deterioration, porosity, sintering, thermal barrier coatings, thermal conductivity, thermal effects

T. Fujii and T. Takahashi, Ctrl. Res. Inst. Elec. Power Indust., Yokosuka, Kanagawa, Japan. Cited: *Proc. ASME Turbo Expo 2002: Heat Transfer, Manufacturing Materials and Metallurgy,* Vol. 3B, 3-6 June 2002 (Amsterdam), The International Gas Turbine Institute, American Society of Mechanical Engineers, 2002, pp. 1141-1146 [in English].

Radiative Properties and Thermal Conductivity of Thermal Barrier Coatings

Improvement of new thermal barrier coating systems using a layered or graded structure. Oxides with a pyrochlore structure have been identified as promising candidates for new thermal barrier coatings. Several of these oxides possess an improved high-temperature capability and a reduced thermal conductivity compared to yttria-stabilized zirconia (YSZ). One of these candidates, $La_2Zr_2O_7$, has been characterized in detail. Besides very promising results, a relatively poor thermal cycling behavior of plasma sprayed $La_2Zr_2O_7$ coatings was found. A successful way to overcome this problem was the use of layered or graded coatings with a YSZ layer as the first ceramic coating of the TBC system. The final topcoat, which will be exposed to the highest temperature during operation, consists of $La_2Zr_2O_7$. Detailed results of thermal cycling experiments performed at intermediate and elevated surface temperatures (>1300 °C) are presented.

Keywords: ceramic coatings, high-temperature properties, lanthanum compounds, structure (composition), surface properties, thermal conductivity, thermal cycling, zirconia

R. Vassen, X. Cao, and D. Stover, Inst. for Mat. Proc. in Energy Syst., Forschungszentrum Julich GmbH, D-52425 Julich, Germany. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., B, 22*(4), 2001, pp. 435-442 [in English]. ISSN 0196-6219.

Residual Stress and Oxidation of Thermal Barrier Coatings

Study by x-ray diffraction and mechanical analysis of the residual stress generation during thermal spraying. Thermally sprayed coatings are formed by the deposition of molten or partially molten particles, propelled onto a substrate where they impact, spread, and solidify rapidly. Residual stresses are expected within the sprayed deposit as a consequence of the release of thermal and kinetic energies. A wide range of materials and two spraying techniques are considered in this study, namely atmospheric plasma spraying (APS) and high-velocity oxygen fuel. Stresses were determined by the x-ray diffraction (XRD) method. The results were compared with those calculated by mechanical analysis of stress relief in coatings detached from the substrate. Comparison of the results for adherent and free-standing coatings shows that the residual stress state can be resolved in terms of the components suggested by models that propose two stages of stress generation: quenching stresses and secondary cooling stresses. The in-depth distribution of residual stresses, through the coating thickness, is discussed in terms of the nature of the coating system.

Keywords: kinetic energy, molten materials, plasma spraying, residual stresses, sprayed coatings, x-ray diffraction analysis

J. Pina, A. Dias, and J.L. Lebrun, Dept. Physics, Univ. Coimbra, Coimbra P-3004-516, Portugal. Cited: *Mater. Sci. Eng. A, 347*(1-2), 25 April 2003, pp. 21-31 [in English]. ISSN 0921-5093.

Influence of water vapor on the high-temperature oxidation behavior of thermal barrier coatings. The oxidation of thermal barrier coating (TBC) specimens consisting of nickel-base superalloy, low-pressure plasma sprayed Ni-28Cr-6Al-0.4Y (wt.%) bond coatings and air plasma sprayed 7.5 wt.% yttria-stabilized zirconia top coatings was studied at 1050 °C in flows of O_2, and mixture of O_2 and 5% H_2O under atmospheric pressure. The TBC exhibits very low oxidation rate at 1050 °C in pure O_2, and the oxidation kinetics accords with parabolic law. The oxidation kinetics of TBC obeys almost linear law after long exposure times in the presence of 5% water vapor. Oxide formed along the bond coat and top coat interface after oxidation at 1050 °C in pure O_2 consisted of Al_2O_3, whereas interfacial scales formed after oxidation at 1050 °C in a mixture of O_2 and 5% H_2O were mainly composed of $Ni(Al,Cr)_2O_4$, NiO, Cr_2O_3, and Al_2O_3. It is suggested that the effect of water vapor on the oxidation of the NiCrAlY coating may be attributed to the increase in nickel and chromium ions transport.

Keywords: plasma spraying, reaction kinetics, superalloys, thermo-oxidation, zirconia

C. Zhou, J. Yu, S. Gong, and H. Xu, Huibin, Dept. of Materials Sci./Engineering, Beijing Univ. of Aeronautics, Beijing 100083, China. Cited: *Mater. Sci. Eng. A, 348*(1-2), 15 May 2003, pp. 327-332 [in English]. ISSN 0921-5093.

Residual stress in plasma sprayed zirconia on cylindrical components. This paper presents a finite-element model able to predict the residual stress in a plasma sprayed cylindrical components, as used in foundry applications. The studied coating is a zirconia (ZrO_2) stabilized with 25% ceria (CeO) and 2-3% yttria (Y_2O_3), deposited by plasma spraying on a Cr-Mo-V tool steel. The main problem in stress-field measurement for ceramic coatings results from their typical morphology, characterized by voids and microcracks. This type of morphology leads to great scatter in residual stress measurement in almost any kind of plasma deposited ceramic coating. Analytical methods can be used to evaluate the residual stresses field, but these methods fail also to predict the effect of discontinuities, and, moreover, this approach does not take into account the specific morphology of the coating. The residual stresses values calculated by the numerical simulation are in very good agreement with the experimental results obtained by neutron diffraction in the substrate and satisfactory for measurements in the ceramic layer. Therefore, the presented model can be used to predict the residual stress distribution in ceramic plasma coated cylindrical components.

Keywords: ceramic coatings, computer simulation, finite-element method, mathematical models, microcracks, morphology, plasma spraying, residual stresses

P. Fogarassy, F. Turquier, and A. Lodini, CCTT, 1900 Timisoara, Romania. Cited: *Mech. Mater., 35*(7), July 2003, pp. 633-640 [in English]. ISSN 0167-6636.

Effect of residual stresses on air plasma sprayed thermal barrier coatings. Thermal barrier coating with a CoNiCrAlY bond coating and a 0.3 mm thick zirconia, (7% yttria stabilized) top coating were air plasma sprayed onto a Hastelloy-X nickel-base superalloy substrate coupons. Substrate preparation is a key initial step in the production of quality thermal sprayed coatings. Grit blasting is usually used to roughen the substrate surface so that better adhesion of the coating to the substrate is achieved. The effects of different grit-blasting variables on the substrate surface roughness were examined by using the Taguchi designed experimentation. The residual stress profiles were determined for a different set of conditions by hole drill method. The Anstis et al. model was modified for the determination of indent toughness of the substrate and bond coat interface. The results showed that the combination of grit size with distance and pressure during the grit blasting were the most influential parameters. The adhesion of the coatings increases with increase of substrate roughness up to certain limits and then decreases. It was observed that the residual stresses have an impact over the adhesion of the coatings. The indentation toughness results showed that with increase of substrate roughness there is an increase in interfacial toughness due to high compressive stresses associated with high rough surfaces. Further, the final deposition temperature and heat treatment effect the residual stress profile and subsequently the interfacial toughness of the coatings.

Keywords: adhesion, blasting, compressive strength, drilling, plasma spraying, residual stresses

A. Nusair Khan, J. Lu, and H. Liao, LASMIS, Universite de Technologie de Troyes, Troyes, France. Cited: *Surf. Coat. Technol., 168*(2-3), 22 May 2003, pp. 291-299 [in English]. ISSN 0257-8972.

Microanalysis on the oxidation and sulfate attack of partially stabilized zirconia thermal barrier coating. This aim of this investigation is to study the effect of the presence of Na_2SO_4 deposits and water vapor on the oxidation of an air plasma sprayed TBC composed of a partially stabilized ZrO_2 top coat with an underlying NiCoCrAlY bond coat. X-ray diffraction and SEM/EDX were used to analyze the changes in the coatings after oxidation at 1000 °C for 72 h in dry or humidified (containing 50% H_2O) O_2 atmosphere, with or without

Na_2SO_4 deposited on the top coat. When oxidized in oxygen, bond coat oxide regions, consisting of almost pure aluminum oxide, were formed at the top coat/bond coat and bond coat/substrate interfaces and in the bond coat around the splat lines. When water vapor was present, the top coat/bond coat interface oxide was marginally thicker and included small regions with more chromium, cobalt, and nickel. The addition of the salt deposits resulted in some destabilization in the outermost regions of the top coat. The salt deposits also caused the formation of thicker oxide comprising two regions, though this formation was observed only at the top coat/bond coat interface. The first type was a thin inner (i.e., bordering the bond coat) oxide that was mostly aluminum oxide. The other was a much thicker oxide containing higher levels of chromium, cobalt, and nickel along with aluminum. In this oxide region, the aluminum level was higher when the chromium level was lower and vice versa.

Keywords: composition effects, energy-dispersive spectroscopy, interfaces (materials), microanalysis, oxidation, plasma spraying, scanning electron microscopy, sodium compounds, x-ray diffraction analysis, zirconia

J.E. Tang, M. Halvarsson, K. Hansson, and J.-E. Svensson, X.-H. Li, and R. Pompe, Dept. of Experimental Physics, Chalmers Univ. Technology, Goteborg Univ., SE-412 96, Goteborg, Sweden. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., B, 22*(4), 2001, pp. 463-470 [in English]. ISSN 0196-6219.

Thermally Grown Oxide Instability in Thermal Barrier Coatings

Observations and analysis of the influence of phase transformations on the instability of the thermally grown oxide in a thermal barrier system. Observations and measurements have been performed on a thermal barrier system comprising a platinum-aluminide bond coat and a thermal barrier coating deposited by electron beam evaporation. Past research has highlighted a displacement instability in the thermally grown oxide (TGO), as it affects the failure mechanism in the thermal barrier coating (TBC). Phase transformations in the bond coat have also been identified, with a proposed role in the TGO instability. The present study assesses this influence by characterizing the transformations as well as their spatial correlation with the instability sites. Both the isothermal transformation from $\beta \geq \gamma'$ and the martensite transformation in the β have been addressed. Toward the end of life, the instabilities are preferentially located in the β phase, between neighboring domains of γ'. After cycling, the composition of the β grains is spatially uniform. Within the γ', there are nickel and aluminum composition gradients in narrow layers near the interfaces with the β phase and the TGO. An evaluation suggests that the primary influence of transformation on the cyclic displacement of the TGO is to create a local misfit between the growing γ' domains and the volume strain accompanying the martensite transformation in the intervening β phase, upon cooling and reheating.

Keywords: cooling, electron beams, evaporation, heating, interfaces (materials), isotherms, martensitic transformations, oxides, phase transitions, thermodynamic stability

S. Darzens, D.R. Mumm, D.R. Clarke, and A.G. Evans, Princeton Materials Institute, Princeton Univ., Princeton, NJ 08540-5211. Cited: *Metall. Mater. Trans. A: Phys. Metall. Mater. Sci., 34A*(3), March 2003, pp. 511-522 [in English]. ISSN 1073-5623.

The displacement of the thermally grown oxide in thermal barrier systems upon temperature cycling. Models that characterize the displacement instability of the thermally grown oxide (TGO) found in some thermal barrier systems are reviewed, consolidated, and extended. It is demonstrated that the simulations are only consistent with the observations whenever the bond coat and TGO both undergo plastic deformation. The TGO yields at the peak temperature, during growth, while the bond coat yields on thermal cycling. The trends oppose. Namely, the TGO displacement is diminished by increasing the high-temperature strength of the bond coat, but is increased upon increasing the TGO strength. The model rationalizes certain experimental trends, particularly the decrease in durability as the hot time per cycle decreases. Interactions between the instability and cracks in the thermal barrier layer are discussed.

Keywords: computer simulation, cracks, plastic deformation, thermal cycling

A.M. Karlsson, J.W. Hutchinson, and A.G. Evans, Dept. of Mechanical Eng., Univ. Delaware, Newark, DE 19716. Cited: *Mater. Sci. Eng. A, 351*(1-2), 25 June 2003, pp. 244-257 [in English]. ISSN 0921-5093.

On interface oxidation process of 8wt.%Y_2O_3-ZrO_2/CoNiCrAlY thermal barrier coating. Thermal barrier coating (TBC) is used to protect hot parts of gas turbine from a high-temperature environment. Recently, TBC delamination damage was also reported in some Japanese electric power plants. It is important to establish a TBC delamination evaluation method for preventing such damage. It is known that the delamination is due to a reduction of interface cohesion between coating layer and substrate, and then the reduction is caused by a formation of thermally growth oxidation (TGO) layer at the interface. Thus, it is necessary to understand TGO layer growth behavior and the growth mechanism. The aim of this study is to examine effect of an aging temperature and an aging time on TGO layer growth under various aging temperature conditions and then to discuss a TGO growth mechanism through SEM observation of a cross section of aged TBC specimen. As some results obtained, TGO layer was not formed at the aged temperature below 973 K. In aging temperature range between 1073 K and 1173 K, Al_2O_3 as TGO layer was formed at the interface between top coating and bond coating layer. At aging temperature 1273 K, (Co, Cr, Al) complex oxidation in addition to Al_2O_3 at the interface was observed. It was shown from TGO growth curve that the growth exponent n was 0.3 in aging temperature range 1073 K to 1173 K, and then 0.1 at 1273 K in contrast with 0.5 for a metal oxidation process. Then, TGO layer grew by diffusion of oxidizing species on grain boundary in coating layer. Additionally, the reason that the growth exponent at 1273 K was reduced was due to what the complex oxidation layer was acted as barrier to the species diffusion.

Keywords: aging of materials, alumina, cobalt alloys, delamination, gas turbines, grain boundaries, growth (materials), interfaces (materials), oxidation, scanning electron microscopy, yttrium compounds, zirconia

M. Arai, U. Iwata, H. Satoh, and K. Kishimoto, Material Science Dept., Ctrl. Res. Inst. Elec. Power Indust., Komae-shi, Tokyo, 201-8511, Japan. Cited: *Nippon Kikai Gakkai Ronbunshu, A Hen/Trans. Jpn. Soc. Mech. Eng., A, 69*(2), Feb 2003, pp. 245-250 [in Japanese]. ISSN 0387-5008.

Thermal and Phase Stability of Coatings

Phase stability of thermal barrier coatings made from 8 wt.% yttria-stabilized zirconia: a technical note. The phase stability of thermal barrier coatings is discussed. It is made from 8 wt.% yttria-stabilized zirconia. The two coatings behaved similarly and exhibited minimal change in the monoclinic content at exposures of 982 °C. Exposures at 1204 and 1315 °C resulted in increasing amounts of monoclinic phase versus time; the monoclinic phase reached a maximum of 40% at longer time exposures at the highest temperature as predicted by the phase diagram.

Keywords: composition, cracks, diffraction, fatigue of materials, melting, microstructure, thermal barrier coatings

J.D. Ballard, J. Davenport, C. Lewis, W. Nelson, R.H. Doremus, and L.S. Schadler, Dept. Materials Science, Rensselaer Polytechnic Institute, Troy, NY 12180-3590. Cited: *J. Therm. Spray Technol., 12*(1), March 2003, pp. 34-37 [in English]. ISSN 1059-9630.

Thermal stability of lanthanum zirconate plasma sprayed coating. Lanthanum zirconate ($La_2Zr_2O_7$, LZ) is a newly proposed material for thermal barrier coatings (TBCs). The thermal stability of LZ coating was studied in this work by long-term annealing and thermal cycling. After long-term annealing at 1400 °C or thermal cycling, both LZ powder and plasma sprayed coating still kept the pyrochlore structure, and a preferred crystal growth direction in the coating was observed by x-ray diffraction. A considerable amount of La_2O_3 in the powder was evaporated in the plasma flame, resulting in a nonstoichiometric coating. Additionally, compared with the standard TBC material yttria-stabilized zirconia (YSZ), LZ coating has a lower thermal expansion coefficient, which leads to higher stress levels in a TBC system.

Keywords: annealing, crystal growth, plasma spraying, plasmas, sprayed coatings, stresses, thermal barrier coatings, thermal cycling, thermal expansion, thermodynamic stability, x-ray diffraction, zirconia

X.Q. Cao, R. Vassen, W. Jungen, S. Schwartz, F. Tietz, and D. Stover, Institut Werkstoffe Energie Technik, Forschungszentrum Julich GmbH, D-52425 Julich, Germany. Cited: *J. Am. Ceram. Soc., 84*(9), Sept 2001, pp. 2086-2090 [in English]. ISSN 0002-7820.

Thermal Cycling

Thermal gradient cyclic behavior of a thermal/environmental barrier coating system on SIC/SIC ceramic-matrix composites. Thermal barrier and environmental barrier coatings (TBCs and EBCs) will play a crucial role in future advanced gas turbine engines because of their ability to significantly extend the temperature capability of the ceramic-matrix composite (CMC) engine components in harsh combustion environments. In order to develop high performance, robust coating systems for effective thermal and environmental protections of the engine components, appropriate test approaches for evaluating the critical coating properties must be established. In this paper, a laser high-heat-flux, thermal gradient approach for testing the coatings is described. Thermal cyclic behavior of plasma sprayed coating systems, consisting of ZrO_2-8wt%Y_2O_3 thermal barrier and NASA Enabling Propulsion Materials (EPM) Program developed mullite + BSAS/Si type environmental barrier coatings on SiC/SiC ceramic-matrix composites, was investigated under thermal gradients using the laser heat-flux rig in conjunction with the furnace thermal cyclic tests in water-vapor environments. The coating sintering and interface damage were assessed by monitoring the real-time thermal conductivity changes during the laser heat-flux tests and by examining the microstructural changes after the tests. The coating failure mechanisms are discussed based on the cyclic test results and are correlated to the sintering, creep, and thermal stress behavior under simulated engine temperature and heat flux conditions.

Keywords: ceramic-matrix composites, gas turbines, heat flux, microstructure,

plasma spraying, sintering, thermal conductivity, thermal cycling, thermal gradients, yttrium compounds, zirconia

D. Zhu, K.N. Lee, and R.A. Miller, NASA Glenn Research Center, Cleveland, OH 44135. Cited: *Proc. ASME TURBO EXPO 2002: Ceramics, Industrial and Cogeneration Structures and Dynamics,* Vol. 4A, 3-6 June 2002 (Amsterdam), The International Gas Turbine Institute, American Society of Mechanical Engineers, 2002, pp. 171-178 [in English].

Evolution of a diffusion aluminide bond coat for thermal barrier coatings during thermal cycling. The thermal cyclic durability of a TBC is thought to be strongly dependent on the physical and mechanical properties of the bond coat layer. A novel high-temperature microsample tensile testing technique has been employed to characterize the mechanical behavior of a platinum-modified nickel aluminide bond coat at 0 and 28% of cyclic life in the temperature range of 25-1150 °C. Values for the coefficient of thermal expansion and the Young's modulus are reported. The bond coat exhibits a ductile-to-brittle transition temperature at approximately 600 °C, and above this temperature the yield and creep strengths decrease rapidly with temperature. A power-law description of elevated-temperature stress relaxation is developed. The intermediate temperature strength was found to increase with thermal cycling, while the high-temperature strength remained the same. This evolution in properties has been related to the development of a martensitic transformation that occurs during each thermal cycle.

Keywords: creep, diffusion, durability, elastic moduli, martensitic transformations, platinum, stress relaxation, tensile testing, thermal cycling

D. Pan, M.W. Chen, P.K. Wright, and K.J. Hemker, Dept. Mechanical Engineering, Johns Hopkins Univ., Baltimore, MD 21218. Cited: *Acta Mater., 51*(8), 7 May 2003, pp. 2205-2217 [in English]. ISSN 1359-6454.

Thermal cycling behaviors of thermal barrier coatings on intermetallic Ni_3Al-base superalloy. Ni_3Al base alloy IC6, a high-performance cast alloy with approximately 14 wt.% Mo addition, has been developed for turbine blades and vanes of advanced aeroengines and other high-temperature structural components. However, because of the high molybdenum content, during high-temperature use, molybdenum will diffuse into the protective coating layer, which will affect the thermal cycling performance directly. In order to block the diffusion and improve the thermal cycling behavior of thermal barrier coatings (TBCs), a silicon chemical gradient MCrAlY-Si bond coat was prepared by changing the silicon content from 0.35 wt.% at the interface of substrate and bond coat to almost 0 near to the surface of the bond coat. For comparison, conventional two-layered structural TBCs with MCrAlY as bond coat were also prepared. The fabricated coatings were evaluated for the microstructures and the composition distribution properties, such as thermal stability and resistance to oxidation. For the bond coat without silicon addition, molybdenum content near the surface was higher than 7 wt.% after isothermal oxidation at 1373 K for 60 h and 12.5 wt.% after thermal cycling tested at 1373 K for 300 h (600 cycles). However, in the silicon chemical gradient bond coat, only 0.4 wt.% Mo was detectable after isothermal oxidation at 1373 K for 100 h and approximately 0.66 wt.% after thermal cycling tested at 1373 K for 340 h (680 cycles).

Keywords: coatings, composition, interfaces (materials), microstructure, nickel alloys, oxidation resistance, superalloys, thermal barrier coatings, thermal cycling, thermodynamic stability

D. Zhang, S. Gong, H. Xu, H. Zhang, and Y. Han, Dept. of Materials Sci. and Eng., Beihang Univ., Beijing 100083, China. Cited: *Surf. Coat. Technol., 168*(2-3), 22 May 2003, pp. 77-83 [in English]. ISSN 0257-8972.

Thermal conductivity and thermal gradient cyclic behavior of refractory silicate coatings on SiC/SiC ceramic-matrix composites. Plasma sprayed mullite and BSAS coatings have been developed to protect SiC/SiC ceramic-matrix composites from high-temperature environmental attack. In this study, thermal conductivity and thermal barrier functions of these coating systems are evaluated using a laser high-heat-flux test rig. The effects of water vapor on coating thermal conductivity and durability are studied by using alternating furnace and laser thermal gradient cyclic tests. The influence of laser high-thermal-gradient cycling on coating failure modes is also investigated.

Keywords: ceramic-matrix composites, composition effects, durability, laser applications, materials testing, refractory materials, silicates, silicon carbide, thermal conductivity, thermal cycling, thermal gradients, vapors

D. Zhu, K.N. Lee, and R.A. Miller, NASA John H. Glenn Research Center, Cleveland, OH 44135. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., B, 22*(4), 2001, pp. 443-452 [in English]. ISSN 0196-6219.

Damage evolution and stress analysis in zirconia thermal barrier coatings during cyclic and isothermal oxidation. The failure mechanisms of air plasma sprayed ZrO_2 thermal barrier coatings with various microstructures were studied by microscopic techniques after thermal cycling. The elastic modulus (E) and hardness (H) of the coatings were measured as functions of the number of thermal cycles. Initially, both E and H increased by ~60% with thermal cycling because of sintering effects. However, after ~80 cycles (0.5 h at 980 °C), the accumulated damage in the coatings led to a significant decrease of ~20% of the maximum value in both E and H. These results were correlated with stresses measured by a spectroscopic technique to understand specific damage mechanisms. Stress measurement and analysis revealed that the stress distribution in the scale was a complex function of local interface geometry and damage in the top coat. Localized variations in geometry could lead to variations in measured hydrostatic stresses from –0.25 to –2.0 GPa in the oxide scale. Protrusions of the top ZrO_2 coat into the bond coat were localized areas of high stress concentration and acted as damage-nucleation sites during thermal and mechanical cycling. The net compressive hydrostatic stress in the oxide scale increased significantly as the scale spalled during thermal cycling.

Keywords: elastic moduli, failure (mechanical), hardness, microscopic examination, microstructure, nucleation, oxidation, spectroscopy, stress analysis, stress concentration, thermal cycling, zirconia

J.P. Singh, B.G. Nair, D.P. Renusch, M.P. Sutaria, and M.H. Grimsditch, Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439. Cited: *J. Am. Ceram. Soc., 84*(10), Oct 2001, pp. 2385-2393 [in English]. ISSN 0002-7820.

Titania Coatings

Microstructure of plasma sprayed titania coatings deposited from spray-dried powder. TiO_2 coatings were prepared by plasma spraying using a spray-dried powder as feedstock material. A systematic study has been performed to determine how the titania slurry formulation (e.g., dispersant level, pH, binder addition) affects the granule characteristics. Aqueous slurries consisting of 50 wt.% of TiO_2 particles, 0-1.2 wt.% ammonium polyacrylate as a dispersant and up to 15 wt.% styrene-ester acrylic copolymer as a binder were investigated using settling experiments. It was shown that when the relative sedimentation height (RSH) value is below 0.45 the fully dispersed slurry leads to the fabrication of a hollow powder, whereas when the RSH is over 0.50 the flocculated slurry leads to a dense powder. TiO_2 coatings were prepared from a batch of hollow granules of anatase. The microstructure and crystallographic phases of these deposits were characterized using scanning electron microscopy, three porosimetry methods (image analysis, Archimedean and calculation from thickness, and x-ray diffraction, XRD) and quantitative XRD. The results showed that the TiO_2 coatings consist of a mixture of anatase and rutile. The content of anatase was varied from 35 to 50 vol.%, depending on the operating conditions (mainly plasma power and cooling rate). These great amounts of anatase phase were obtained along with rather high percentage of porosity (between 13 and 25%).

Keywords: copolymers, crystallography, feedstocks, microstructure, plasma spraying, powders, slurries, sprayed coatings, x-ray diffraction analysis

N. Berger-Keller, G. Bertrand, C. Filiatre, C. Meunier, and C. Coddet, LERMPS-UTBM, Belfort Cedex 90010, France. Cited: *Surf. Coat. Technol., 168*(2-3), 22 May 2003, pp. 281-290 [in English]. ISSN 0257-8972.

Tungsten Carbide (WC) Coatings

Structure and mechanical properties of tungsten carbide films deposited by off-plane double bend filtered cathodic vacuum arc. The deposition of nanocrystalline tungsten carbide films was reported. The surface morphology, crystalline structure, internal stress, hardness, and Young's modulus of the films were strongly dependent on the substrate bias. The high density and strain caused by the lattice mismatch between the different phases contributed to the highest internal stress, hardness and Young's modulus for the films deposited at a substrate bias of 200 V.

Keywords: atomic force microscopy, crystal structure, nanostructured materials, substrates, tungsten carbide, vacuum applications, x-ray diffraction analysis

Y.H. Cheng and B.K. Tay, Institut fur Physik, TU Chemnitz, D-09107 Chemnitz, Germany. Cited: *J. Vac. Sci. Technol. A: Vac., Surf. Films, 21*(2), March/April 2003, pp. 411-415 [in English]. ISSN 0734-2101.

Characterization of thermal sprayed nanostructured WC-Co coatings derived from nanocrystalline WC-18wt.%Co powders. Nanostructured WC-Co coatings were synthesized using high-velocity oxygen fuel (HVOF) thermal spray. The nanocrystalline feedstock powder with a nominal composition of WC-18wt.%Co was prepared using the novel integrated mechanical and thermal activation (IMTA) process. The effects of HVOF thermal spray conditions and powder characteristics on the microstructure and mechanical properties of the as-sprayed WC-Co coatings were studied. It was found that the ratio of oxygen-to-hydrogen flow rate (ROHFR) and the starting powder microstructures had strong effects on decarburization of the nanocoatings. Decarburization was significantly suppressed at low ROHFR and with the presence of free carbon in the powder. The level of porosity in the coatings was correlated with the powder microstructure and spray process conditions. The coating sprayed at ROHFR = 0.5 exhibited the highest microhardness value (HV_{300g} = 1077), which is comparable to that of conventional coarse-grained coatings.

Keywords: composition, decarburization, microhardness, microstructure, nanostructured materials, porosity, tungsten carbide

Z.-G. Ban and L.L. Shaw, Dept. Metallurgy Engineering, Institute of Materials

Science, Univ. Connecticut, Storrs, CT 06269. Cited: *J. Therm. Spray Technol., 12*(1), March 2003, pp. 112-119 [in English]. ISSN 1059-9630.

Vacuum Plasma Sprayed MCrAlY Coatings

Aluminizing behaviors of vacuum plasma sprayed MCrAlY coatings. The objective of this study is aluminide overlay coatings of MCrAlY sprayed by a vacuum plasma spraying (VPS) process for the protection against high-temperature corrosion and oxidation of gas turbine components. Diffusion coating processes have been applied for many years to improve similarly the environmental resistance by enriching the surface of nickel-base superalloys with chromium, aluminum, or silicon element. Recently, aluminizing of MCrAlY coatings is used for improving further the high-temperature oxidation resistance. However, the aluminizing properties of plasma sprayed MCrAlY coatings, which have an important effect on the coating performance, have not been clarified. In this study, five kinds of plasma sprayed MCrAlY (CoCrAlY, CoNiCrAlY, CoNiCrAlY + Ta, NiCrAlY, and NiCoCrAlY) coating were selected for pack-aluminizing tests. The as sprayed and the heat treated (1393 K, 2 h, argon cooled and 1116 K, 24 h, argon cooled) MCrAlY specimens were Al-Cr-Al_2O_3-NH_4Cl pack aluminized at 1173, 1223, and 1273 K for 5, 10, and 20 h, respectively. The experimental results showed that the aluminizing process formed the aluminum-rich layers of NiAl or CoAl phase. It also indicated that the thickness of the aluminum rich layer showed a parabolic time-dependence in all MCrAlY coatings. The order of reaction diffusion rate was NiCoCrAlY = NiCrAlY > CoNiCrAlY > CoNiCrAlY + Ta > CoCrAlY. There was a tendency that the reaction diffusion rate by aluminizing increased with increasing nickel content in the MCrAlY coatings and the reaction diffusion rate of as sprayed MCrAlY coatings is faster than that of the heat treated MCrAlY coating.

Keywords: aluminum compounds, corrosion protection, diffusion, oxidation, plasma spraying, rate constants, sprayed coatings, vacuum applications

Y. Itoh, M. Saitoh, and Y. Ishiwata, Metal and Ceramics Technology, R&D Department, Toshiba Corp. Tsurumi-ku, Yokohama 230-0045, Japan. Cited: *J. Eng Gas Turbines Power, 124*(2), April 2002, pp. 270-275 [in English]. ISSN 0742-4795.

Wear and Adhesion of High-Velocity Oxyfuel Coatings

Abrasive wear behavior of Ni(Cr)-TiB_2 coatings deposited by HVOF spraying of SHS-derived cermet powders. Self-propagating high-temperature synthesis (SHS) was used to generate cermets consisting of TiB_2 hard particles in a Ni(Cr) binder phase. Three cermets were prepared with the following target compositions, namely Ni(Cr)-65wt.% TiB_2, Ni(Cr)-40wt.%TiB_2, and Ni(Cr)-40wt.% TiB_2 with 5 at.% excess boron in order to promote matrix amorphization. The size of the TiB_2 particles within the cermet depended critically on the initial composition; large particles were favored by low binder fractions and the presence of the excess boron. The SHS products were milled, and the resulting powder classified, from which coatings were deposited onto steel substrates by high-velocity oxyfuel (HVOF) thermal spraying. Coatings consisted primarily of TiB_2 particles in a nickel-base binder phase. Abrasive wear behavior was examined with both alumina and silica abradents. All the coatings had similar, low wear rates with silica abrasive while with alumina abrasive, significantly different wear rates were observed. Although the Ni(Cr)-65 wt.%TiB_2 coating had the lowest indentation fracture toughness and the lowest hardness of all the coatings, it exhibited the greatest resistance to abrasive wear with alumina abrasive. Also, the Ni(Cr)-40 wt.%TiB_2 coating with excess boron had a higher wear resistance than its stoichiometric counterpart. In light of this, it is proposed that in these coatings, the presence of the larger boride particles imparts wear resistance.

Keywords: abrasion, cermets, coatings, composition, fracture toughness, high-temperature effects, stoichiometry, synthesis (chemical)

B. Lotfi, P.H. Shipway, D.G. McCartney, and H. Edris, Advanced Materials Group, Sch. of Mech. Mat. Mftg. Eng./Mgmt., Univ. Nottingham, Univ. Park, Nottingham NG7 2RD, U.K. Cited: *Wear, 254*(3-4), Feb 2003, pp. 340-349 [in English]. ISSN 0043-1648.

The effect of WC-17Co thermal spray coating by HVOF and hard chromium electroplating on the fatigue life and abrasive wear resistance of AISI 4340 high-strength steel. One of the most interesting alternatives for replacement of hard chrome plating is tungsten carbide thermal spray coating applied by the high-velocity oxyfuel (HVOF) process which presents a safer, cleaner, and less expensive alternative to chromium plating. The objective of this research is to compare the influence of the tungsten carbide-17cobalt (WC-17Co) coating applied by high-velocity oxyfuel (HVOF) process with that of hard-chromium electroplating on the fatigue strength and abrasive wear of AISI 4340 steel.

Keywords: electroplating, fatigue of materials, protective coatings, strength of materials, tungsten alloys, wear resistance

R.C. Souza, M.P. Nascimento, H.J.C. Voorwald, and W.L. Pigatin, FAENQUIL/DEMAR, Dept. Materials Engineering, CP 116 Lorena/SP/BR - CEP: 12600-000, Brazil. Cited: *Corros. Rev., 21*(1), 2003, pp. 75-96 [in English]. ISSN 0048-7538.

Review

Advantages of Thermal Spray

The advantages of thermal spray. The advantages of thermal spray technology, which is a cost-effective means to repair worn-out components and incorrectly machined parts, are discussed. With relatively low particle velocities, the flame spray process can provide thicker buildup for a given material of any of the thermal spray processes. Thermal sprayed surfaces, with a variety of application methods and coating selections, offer solutions for parts renewal, wear prevention, and corrosion resistance.

Keywords: chromium plating, cost effectiveness, machine components, maintenance, welding

K. Dobler, St. Louis Metallizing Company, St Louis, MO. Cited: *Prod. Finish. (Cincinnati), 68*(7), April 2003, pp. 47-51 [in English]. ISSN 0032-9940.

Grinding

Grinding and thermal spraying. The importance of grinding and thermal spraying are discussed. Portable grinders come electrically or pneumatically powered in horizontal, right-angle, or vertical design. Industry has no standards for grinder design and performance. Users should select the tool based on severity of the grinding operation. Grinders come equipped with wheel guards to shield workers from particles of base material, wheel shatter, and sparks.

Keywords: bevel gears, ergonomics, flame spraying, plasma spraying, pneumatic tools, portable equipment, shafts (machine components), shielding

Cited: *Weld. Des. Fabr., 75*(12), Dec 2002, pp. 43-45 [in English]. ISSN 0043-2253.

Testing

Nondestructive Testing

Nondestructive characterization of environmental barrier coatings applied to monolithic ceramics. Full-size silicon nitride gas turbine vanes coated with an environmental barrier coating (EBC) were evaluated in an exploratory way by two nondestructive methods: polarized elastic optical scattering and infrared thermal imaging. Initial test results indicate that the laser scatter data correlate with EBC thickness. A description of the methods and results of recent tests are presented.

Keywords: ceramic materials, gas turbines, infrared imaging, light scattering, nondestructive examination, oxidation resistance, silicon nitride

W.A. Ellingson, C. Deemer, S. Erdman, and A. Parikh, Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439. Cited: *Proc. ASME TURBO EXPO 2002: Ceramics, Industrial and Cogeneration Structures and Dynamics,* Vol. 4A, 3-6 June 2002 (Amsterdam), The International Gas Turbine Institute, American Society of Mechanical Engineers, 2002, pp. 179-185 [in English].

Residual Stress Determination

Residual stress in sprayed Ni + 5% Al coatings determined by neutron diffraction. Coatings of nickel-base alloys are used in numerous high-performance applications. Their properties and lifetimes are influenced by factors such as residual stress. Neutron diffraction is a powerful tool for nondestructive residual stress determination. In this study, through-thickness residual stress profiles in Ni + 5% Al coatings on steel substrates were determined. Two examples of significantly different spraying techniques—plasma spraying and cold spraying—are highlighted. Different stress-generation mechanisms are discussed with respect to process parameters and material properties.

Keywords: aluminum alloys, neutron diffraction, nickel alloys, particle size analysis, particles (particulate matter), plasma spraying, residual stresses, steel, substrates

J. Matejicek, S. Sampath, T. Gnaupel-Herold, and H.J. Prask, Institute of Plasma Physics, 18221 Praha 8, Czech Republic. Cited: *Appl. Phys. A: Mater. Sci. Process., 74*(suppl. II), Dec 2002, pp. S1692-S1694 [in English]. ISSN 0947-8396.

Rig Testing

Simulated engine test of combustor minisegments using a high power CO_2 laser. A laser test rig has been developed for durability studies of ceramic thermal barrier coatings for combustor applications. By using a high-power laser-optic system, the test rig is capable of achieving temperature gradients across the coating thickness, as well as tailored temperature distributions on the coated combustor minisegment surface. Realistic engine combustor high-temperature, and moderately high-pressure, conditions are achieved with a 6 atm, high-pressure chamber system and by controlling appropriate backside cooling gas temperatures and flow rates. Thermal barrier coating sintering/

creep, thermal conductivity, and stress/strain data have been obtained from laser heat flux simulated engine component tests.

Keywords: ceramic materials, coatings, combustors, durability, engines, high-power lasers, high-pressure effects, laser applications, materials testing, temperature distribution, thermal gradients, thickness measurement

D.S. Fox, D. Zhu, and R.A. Miller, NASA John H. Glenn Research Center, Cleveland, OH 44135. Cited: 25th Annual Conference on Composites, M. Singh and T. Jessen, Ed., 21-27 Jan 2001 (Cocoa Beach, FL), *Adv. Ceram. Mater. Struct., B, 22*(4), 2001, pp. 409-416 [in English]. ISSN 0196-6219.

Stiffness and Fracture Toughness

Determination of interface fracture toughness in thermal barrier coating system by blister tests. The theoretical model for the blister test method was used to analyze the interface fracture toughness of zirconia coating deposited on an SUS304 stainless steel substrate by a plasma spraying method. The elastic parameters of the debonded coating were determined by testing the oil pressure q and maximum deflection $w(0)$. Scanning electron microscopy observation, compliance method, and ultrasonic detection were used to determine the radius of the debonded coating. The three methods gave the same results for the debonded coating radius. Micro-observations showed that the interfacial crack propagates by the growth of voids or microcracks ahead of the main crack and coalescence with the main crack. The energy release rate G_o with phase angle $\Upsilon = 0$ for type A coating and type B coating was, respectively, 14.54-25.88 J/m^2 and 11.88-16.21 J/m^2. The corresponding interface fracture toughness for type A TBC coating and for type B TBC coating is, respectively, 0.77-1.02 MPa $\cdot$ m$^{1/2}$ and 0.52-0.61 MPa $\cdot$ m$^{1/2}$. The stable phase angle was approximately –31.5° and –30.2° for coating A and coating B, respectively.

Keywords: crack propagation, elastic moduli, fracture toughness, interfaces (materials), materials testing, mathematical models, microcracks, plasma spraying, scanning electron microscopy, stainless steel, thermal barrier coatings, ultrasonic applications

Y.C. Zhou, T. Hashida, and C.Y. Jian, Fracture Research Institute, Tohoku Univ., Sendai 980-8579, Japan. Cited: *J. Eng. Mater. Technol., Trans. ASME, 125*(2), April 2003, pp. 176-182 [in English]. ISSN 0094-4289.

Thermal Wave Interferometry

Sensitivity of thermal-wave interferometry to thermal properties of coatings: application to thermal barrier coatings. Thermal-wave interferometry is used as a means for measuring the thermal properties of coatings. The characterization procedure is influenced by the magnitude of the signal-to-noise ratio and also by the amount of experimental data available. These issues are analyzed using a sensitivity study, and the factors that determine the accuracy of the technique are described. Results obtained from experiments on plasma sprayed yttrium-stabilized zirconia coatings illustrate the accuracy and the limitations of TWI for the evaluation of the thermal properties.

Keywords: interferometry, plasma spraying, sensitivity analysis, signal-to-noise ratio, sprayed coatings

A. Bendada, National Research Council Canada, Industrial Materials Institute, Boucherville, QC J4B 6Y4, Canada. Cited: *Meas. Sci. Technol., 13*(12), Dec 2002, pp. 1946-1951 [in English]. ISSN 0957-0233.