Selected Abstracts of Thermal Spray Literature

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

Applications

Automotive and Mechanical Industry

Low-friction coatings prepared by high-performance type spray gun. To produce low-friction coatings to be used as overlays for automobile journal bearings and to perform depositions with high rate, the authors prepared composite coatings of silver and graphite by using the new-type spray gun based on the forced constricted type plasma jet generator (i.e., the high-performance type spray gun). Characterization of the films showed the graphite phase dispersed into the silver matrix, analyzed by optical microscopy, electron probe microanalysis, and x-ray diffraction. The coefficient of friction of the silver/graphite overlay measured using ball-on-disk tribometer was reduced by a factor of five compared with that of bronze substrate and by factor of two compared with that of the silver/graphite overlay prepared by ECR sputtering.

Keywords: deposition, friction, journal bearings, plasma jets, spray guns, x-ray diffraction analysis

A.M. Lungu, O. Fukumasa, K. Osaki, S. Fujimoto, and C.P. Lungu, Dept. of Electrical/Electronic Eng., Faculty of Engineering, Yamaguchi Univ., Yamaguchi, Ube 755-8611, Japan. Cited: *Surf. Coat. Technol., 169-170*(1), 2 June 2003, Elsevier, pp. 415-418 [in English]. ISSN 0257-8972.

Coatings for Gas Turbine Components

Evaluation tests of 1700 °C class turbine cooled blades for a hydrogen fueled combustion turbine system. The development of 1700 °C class hydrogen-fueled combustion turbine system with output of 500 MW and thermal efficiency of more than 60% (HHV) has been conducted in the World Energy Network (WE-NET) program. This paper describes the development of the first-stage turbine cooled stator and rotor blades applied to the power-generation system. The conceptual design of these cooling blades, which were served in hot steam flow, was carried out. The hybrid cooling method combining recovery cooling with partial ejection cooling was chosen from several cooling systems from a viewpoint of plant efficiency, operational reliability, and durability of cooled blades. Also, the single-crystal (SC) superalloy as a blade substrate and thermal barrier coating (TBC) were applied. The experiments of the scale model turbine cooled blades were carried out using a hydrogen-oxygen combustion wind tunnel with practical steam conditions of 1700 °C and 2.5 MPa. The cooling effectiveness and metal temperature at rated condition and the soundness of TBC and blade substrate of the first-stage stator and rotor test blades were clarified.

Keywords: combustion, cooling, durability, hydrogen fuels, reliability, substrates, turbines, turbomachine blades

T. Okamura, H. Kawagishi, A. Koga, and S. Itoh, Department of Energy Engineering, Hachinohe Institute of Technology, Hachinohe 031-8501, Japan. Cited: *Heat Transf. Asian Res., 32*(3), May 2003 pp. 237-252 [in English]. ISSN 1099-2871.

Life prediction strategies for land-based gas turbine blades. A wide range of coatings including overlay, diffusion, duplex, and thermal barrier coatings, are used on the first-stage blades of land-based gas turbine machines. Life-limiting mechanisms of the first-stage blades include cyclic oxidation, thermo-mechanical fatigue, and among others, hot corrosion. In this overview paper, the development of a science-based methodology for lifing coated first-stage blades is presented. The potential failure mechanisms in coated gas turbine blades are summarized. The current status of a science-based life prediction methodology, which is implemented into a computer software named COATLIFE, for treating cyclic oxidation and thermomechanical fatigue is then highlighted. The scientific bases of COATLIFE are described. The technical capabilities and accuracy of COATLIFE are illustrated by comparisons against laboratory data and field experience. Extension of COATLIFE to predict the service life of TBC-coated blades is also discussed.

Keywords: computer simulation, corrosion protection, diffusion coatings, durability, fatigue of materials, gas turbines, oxidation resistance, performance, protective coatings, service life

K.S.Chan, N.S. Cheruvu, G.R. Leverant, and R. Viswanathan, Southwest Research Institute, San Antonio, TX 78238. Cited: TMS Annual Meeting, *Materials Lifetime: Science and Engineering,* P.K. Liaw, R.A. Buchanan, D.L. Klarstrom, R.P. Wei, D.G. Harlow, and P.F. Tortorelli, Ed., 2-6 March 2003 (San Diego, CA), Structural Materials Division of TMS Minerals, Metals, and Materials Society, pp. 191-209 [in English].

Materials for industrial gas turbines: Performance, problems and research. Gas turbines are nowadays the most effective machines for energy production from natural gas; their efficiency can be improved through the increase of the turbine inlet temperature (TIT), also through use of advanced materials. New materials are considered to be the technological barrier for the development of advanced gas turbines and are essential for the development of "clean" thermal cycles for electricity generation. In this paper are discussed: problems regarding applications of new materials in industrial gas turbines, requirements of new materials requested for specific components and the evolution of high-temperature materials in the last half century. The main differences between aeronautical and industrial gas turbines are shown. The requirements for the critical high-temperature components are then listed, i.e., for: combustion chambers and transition parts, vanes, blades and discs. Examples of alloys adopted for the different components are also reported. The characteristics of the most advanced industrial gas turbines are shown, such as TIT = 1430 °C, compression ratio ≈ 20, single cycle (SC) maximum power of 280 MW, SC efficiency ≈ 39%, and combined cycle (CC) efficiency ≈ 58%. The TIT and the thermal capability of the materials for critical high-temperature components of industrial gas turbines have increased continuously in the last 50 years. The article also shows the stress rupture increase of aeronautical and industrial gas turbines through production process innovation, i.e., forging, precision casting, directional solidification, and finally single-crystal large blade technology. Cooled components and thermal barrier coating technology contributed definitely to increase TIT and turbine efficiency. International projects on materials for industrial gas turbines are mentioned, such as the concerted actions COST 501 and 522, and the network CAME-GT in Europe, and the Advanced Turbine System project of DoE and specific EPRI research initiatives in the United States. The Italian contribution to research in this field is also mentioned.

Keywords: compaction, electric power generation, forging, precision casting, stresses, thermal barrier coatings, thermal cycling

C. Guardamagna, V. Lupinc, and G.C. Gualco. Cited: *Metall. Ital., 95*(6), 2003, pp. 45-51 [in Italian]. ISSN 0026-0843.

Coatings for Rocket Engine Components

RLV thrust cell liner coating analysis and design considerations. This study addresses the relative impact of cooling channel wall and protective thermal coating thickness on the deformation fields of reusable launch vehicle (RLV) thrust cell liners under in-service loading conditions. The ultimate objective is to identify an optimal liner and coating design that produces stress and deformation fields leading to improved life/durability. A reference case based on the work of previous studies is introduced, and subsequent changes in geometry and materials are investigated. Analyses are accomplished through the application of the cylindrical version of the higher-order theory for functionally graded materials/structural components. This theory provides a unique analytical tool for the design of advanced aircraft engine structural components with active cooling channels based on the concept of functionally graded material architectures through which improved deformation and life can be attained. The sensitivity of the cooling channel wall deformation to changes in the wall thickness is demonstrated, which is commensurate with the observed failure mode. Most importantly, the presence of a NiCrAlY thermal barrier coating is shown to substantially reduce the cooling channel wall distortion.

Keywords: boosters (rocket), boundary conditions, deformation, durability, finite-element method, functionally graded materials, protective coatings, thermal barrier coatings

D.T. Butler, Jr., J. Aboudi, S.M. Arnold, and M.-J. Pindera, Univ. Virginia, Charlottesville, VA 22903. Cited: Collection of Technical Papers—AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference, 7-10 April 2003 (Norfolk, VA), American Inst. Aeronautics and Astronautics Inc., pp. 2386-2396 [in English]. ISSN 0273-4508.

Fuel Cells

Materials synthesis and characterization of 8YSZ nanomaterials for the fabrication of electrolyte membranes in solid-oxide fuel cells. Two different nanosized materials were synthesized by two preparation methods, namely a sonochemical technique and a spray pyrolysis process. The powder properties, the sintering behavior and the resulting crystallinity with respect to their utilization for solid oxide fuel cell electrolytes were investigated. While the spray pyrolysis provides crystallized powder without any organic residue, the sonochemical powder is amorphous with some organic residue. Crystallization begins in the 400 to 500 °C temperature domain. The particle sizes vary between 10 and 50 nm for the sonochemical powder and between 50 nm and 1 μm for the spray pyrolysis powder, as determined by scanning electron microscopy (SEM) analyses. Crystal growth of both powders starts between

800 and 1000 °C. After heating and sintering at 1300 °C the resulting grain sizes of the spray pyrolysis powder are 5 times larger than those of the sonochemical powder (about 250 nm and 1.2 μm, respectively). Additionally, the maximum rate of grain growth for the spray-pyrolyzed material at 97 nm/h is even higher compared with 22 nm/h for the sonochemical powder.

Keywords: amorphous materials, crystal growth, crystallization, grain growth, grain size and shape, particle size analysis, powder coatings, pyrolysis, scanning electron microscopy, sintering, solid oxide fuel cells, sonochemistry, synthesis (chemical), yttrium compounds

N.H. Menzler, D. Lavergnat, F. Tietz, E. Sominski, E. Djurado, W. Fischer, G. Pang, A. Gedanken, and H.P. Buchkremer, Forschungszentrum Julich, Inst. Mat./Proc. Ener. Syst. IWV-1, 52425 Julich, Germany. Cited: *Ceram. Int., 29*(6), 2003, pp. 619-628 [in English]. ISSN 0272-8842.

Development of solid oxide fuel cells (SOFC) for stationary and mobile applications by applying plasma deposition processes. Solid oxide fuel cells convert directly the chemical energy of fuel gases into electrical energy with high overall efficiencies and low environmental impact, therefore gaining high interest for future energy supply systems. A planar SOFC concept has been developed at the German Aerospace Center (DLR) in Stuttgart using a metallic substrate support and thin-film ceramic layers that are deposited by plasma spray processes without any sintering steps or other thermal posttreatment. The paper gives an overview about the current state of development of this spray concept describing the fabrication technology by applying d.c. and rf plasma processes, cell and stack designs for stationary and mobile applications, recent developments with materials and components, as well as results on electrochemical performance.

Keywords: deposition, plasma spraying, plasmas, substrates, thin films

G. Schiller, R. Henne, M. Lang, and M. Muller, Deutsches Zentrum Luft-/Raumfahrt, Inst. fur Tech. Thermodynamik, D-70569 Stuttgart, Germany. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(3), 2003, pp. 2539-2544 [in English]. ISSN 0255-5476.

Diagnostics and Control

In-Flight Particle Parameters

Effect of direct-current plasma fluctuations on in-flight particle parameters: Part II. This paper is the continuation a previous work, in which plasma fluctuations were shown to produce significant time-dependent variations in the in-flight particle temperature and velocity, as well as in the number of detected particles. In this paper, the impact of the plasma fluctuations on the coating microstructure and deposition efficiency is demonstrated. Alumina coatings and deposition efficiencies, obtained with two sets of spray conditions showing similar in-flight particle conditions (velocity and temperature) with the DPV-2000 but displaying very different voltage fluctuations, are compared. The coating produced in the less stable plasma condition (C-I) is found to be more porous and to contain a larger number of unmelted particles than the other coating produced in more steady plasma conditions (C-II). Moreover, condition C-I yields a significantly lower deposition efficiency. Such large discrepancies must be traced back to the physical characteristics of the particle jet. Laser illumination of the particle jet is used to probe particles too cold to be detected by pyrometric means. Cold particles are found in a much larger proportion in C-I than in C-II. They are ascribed to particles that are injected when the plasma is in a low enthalpy state. Periodic time-dependent variations in the in-flight characteristics of cold and hot particles, synchronous with the voltage fluctuations, are revealed.

Keywords: enthalpy, flight dynamics, plasma applications, porosity, thermal effects

J.F. Bisson and C. Moreau, National Research Council of Canada, Industrial Materials Institute, Boucherville, Quebec, J4B 6Y4, Canada. Cited: *J. Therm. Spray Technol., 12*(2), June 2003, pp. 258-264 [in English]. ISSN 1059-9630.

Thermal Spray Process Monitoring

Understanding the formation of d.c. plasma sprayed coatings. A plasma sprayed coating is built by the impact of molten or semimolten particles on the substrate or previously deposited layers. The flattening droplets form splats that solidify in very short times (a few μs). Coatings result from the layering of successive splats. To achieve a better understanding of this complex process with timescales ranging between 0.1 μs and hundreds of seconds, it is a prerequisite to perform measurements and modelings of the plasma flow, particles in-flight and at impact as well as splats layering. This paper presents what is the actual state-of-the-art in these fields.

Keywords: molten materials, online systems, plasma flow, plasma spraying

P. Fauchais and M. Vardelle, Lab. Sci. des Procedes C.T.S., UMR CNRS 6638, Univ. of Limoges, Limoges, France. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(3), 2003, pp. 2459-2466 [in English]. ISSN 0255-5476.

Feedstock

Nanopowders

Nanoparticle synthesis at high production rates by flame spray pyrolysis. Scaling up of nanoparticle synthesis by the versatile flame spray pyrolysis process at production rates up to 1.1 kg/h is investigated. Product silica powder is collected continuously in a baghouse filter unit that is cleaned periodically by air-pressure shocks. The effect of powder production rate, dispersion gas flow rate, and precursor (hexamethyldisiloxane, HMDSO) concentration on product particle size, morphology and carbon content is investigated. Droplet size distributions of the cold spray are measured by laser diffraction, while N_2 adsorption (BET), transmission electron microscopy, and thermogravimetric analysis coupled with a mass spectrometer are employed to characterize the product powder. The product primary particle size was precisely controlled from 10 to 75 nm and compared to a well-established vapor-fed flame aerosol reactor.

Keywords: flame spraying, mass spectrometers, morphology, powders, pyrolysis, silica, thermogravimetric analysis, transmission electron microscopy

R. Mueller, L. Madler, and S.E. Pratsinis, Dept. of Mechanical/Process Eng., Particle Technology Laboratory, ETH Zurich, Zurich CH-8092, Switzerland. Cited: *Chem. Eng. Sci., 58*(10), May 2003, pp. 1969-1976 [in English]. ISSN 0009-2509.

Novel Materials and Processing Techniques

Processing of biocomposite Ti-6Al-4V/HA powder. A new powder processing technique that involves the processing of Ti-6Al-4V/HA biocomposite powder by a novel ceramic slurry approach was investigated. Thus, the processing powder can be used in various manufacturing methods such as powder metallurgy, powder injection molding, and hot/cold isostatic pressing to fabricate medical implants. The powder consists of an inner core of Ti-6Al-4V wrapped around by an outer layer of HA.

Keywords: biocompatibility, diffractometers, hydroxyapatite, implants (surgical), mechanical properties, particle size analysis, plasma spraying, prosthetics, scanning electron microscopy, synthesis (chemical), thermodynamic properties, titanium alloys

E.S. Thian, N.H. Loh, K.A. Khor, and S.B. Tor, School of Mechanical and Prod. Eng., Nanyang Technological Univ., Singapore 639798, Singapore. Cited: *J. Mater. Sci. Lett., 22*(10), 15 May 2003, pp. 775-778 [in English]. ISSN 0261-8028.

Production/Preparation Technology

Self-propagating combustion synthesis and plasma spraying deposition of TiC-Fe powders. The synthesis of titanium carbide/iron composite from elemental powders by means of self-propagating reactions to be subsequently employed for plasma spray deposition is investigated. The combustion temperature and velocity of propagating front are found to decrease as the amount of iron in the starting mixture increased. In addition, the maximum value of the iron content in the initial mixture allowable for guaranteeing the self-propagating character of the combustion synthesis process is identified. Below this threshold, i.e., 60 wt.%, independently of the iron content, the final products consisted of titanium carbide and iron, the latter found as a binder distributed around the carbide grains. In particular, a strong dependence of the grain size of the obtained titanium carbide on the iron content is observed. Once reduced in powder form, the obtained composite, specifically TiC-30 wt.% Fe, is subsequently used for thermal spraying coating deposition. Adhesion performance, hardness, and wear-resistance test results for the obtained coatings by vacuum plasma spraying are also reported.

Keywords: coatings, combustion, iron, plasma spraying

R. Licheri, R. Orru, G. Cao, A. Crippa, and R. Scholz, Dipartimento di Ingegneria Chimica, Ctro. Studi sulle Reazioni A., Univ. degli Studi di Cagliari, 09123 Cagliari, Italy. Cited: *Ceram. Int., 29*(5), 2003, pp. 519-526 [in English]. ISSN 0272-8842.

The synthesis of $(Y_{1-x}Gd_x)_2O_3$:Eu phosphor particles by flame spray pyrolysis with LiCl flux. $(Y_{1-x}Gd_x)_2O_3$:Eu phosphor particles with dense morphology were prepared by flame spray pyrolysis and the effect of LiCl flux on the crystallinity, morphology, and photoluminescence characteristics of the particles was investigated. All as-prepared particles had monoclinic phase regardless of flux and had different luminescence characteristics from those of commercial Y_2O_3:Eu particles of cubic phase. The addition of LiCl flux reduced the posttreatment temperature by 300 °C for phase transformation from the monoclinic phase to the cubic phase. The posttreatment temperature of $(Y_{1-x}Gd_x)_2O_3$:Eu particles for phase transformation decreased from 1100 to 700 °C when LiCl flux was used. The morphology of the particles was also influenced by the yttrium/gadolinium ratio and the LiCl flux. The as-prepared particles had spherical shape and nonaggregation characteristics regardless of yttrium/gadolinium ratio and flux. The sphericity of the as-prepared particles prepared without flux was maintained after post-treatment for phase transformation in all yttrium/gadolinium ratios. However, LiCl addition promoted the

aggregation between product particles. The prepared particles had high photoluminescence intensities comparable to that of the commercial product.

Keywords: agglomeration, europium, flame spraying, lithium compounds, morphology, phase transitions, photoluminescence, pyrolysis, synthesis (chemical), yttrium compounds

D.J. Seo, Y.C. Kang, and S.B. Park, Department of Chemical Engineering, Ctr. for Ultramicrochem. Proc. Syst., Korea Adv. Inst. of Sci./Technology, Yusonggu, Taejon 305-701, South Korea. Cited: *Appl. Phys. A, 77*(5), Oct 2003, pp. 659-663 [in English]. ISSN 0947-8396.

Production of nanocrystalline cermet thermal spray powders for wear resistant coatings by high-energy milling. TiC-Ni-based nanocrystalline cermet powders for thermal spraying were produced by high-energy milling. Milling experiments were performed in an attrition mill and a vibration mill in kilogram scale, and powder morphologies and microstructures were characterized using scanning electron microscopy, x-ray diffraction, and laser scattering for particle size analysis. Milling time and powder input were optimized with respect to the desired microstructure and particle sizes, and the results using both types of mill were compared. Powders with homogeneously dispersed hard-phase particles below 300 nm could be produced in both mills. Additional processes for the refinement of powder morphology and particle size distribution are discussed.

Keywords: comminution, microstructure, morphology, nanostructured materials, particle size analysis, scanning electron microscopy, x-ray diffraction

N. Eigen, T. Klassen, E. Aust, R. Bormann, and F. Gartner, GKSS Research Centre, Institut of Materials Research, Geesthacht 21502, Germany. Cited: *Mater. Sci. Eng. A, 356*(1-2), 15 Sept 2003, pp. 114-121 [in English]. ISSN 0921-5093.

Modeling

Fracture Behavior or Coatings

Computational analysis of thin coating layer failure using a cohesive model and gradient plasticity. Thermal barrier coatings (TBCs) are widely used to prevent transient high-temperature attack and allow components high durability. Due to strong inhomogeneous material properties, the TBC failure often initiates near the interface between the brittle oxide layer and the ductile substrate. A reliable prediction of the TBC failure requires detailed information about the crack tip field and the consequent fracture criteria. In this paper, both cohesive model and gradient plasticity are used to simulate the failure process and to study interdependence of the interface stress distribution with the specific fracture energies. Computations confirm that combination of the two models is able to simulate different failure mechanisms in the TBC system. The computational model has the potential to give a realistic prediction of the crack-propagation process.

Keywords: computational methods, computer simulation, crack propagation, ductility, durability, failure (mechanical), interfaces (materials), plasticity, stress concentration, thermal barrier coatings

H. Yuan and J. Chen, MTU Aero Engines GmbH, Munich D-80995, Germany. Cited: *Eng. Fract. Mech., 70*(14), Sept 2003, pp. 1929-1942 [in English]. ISSN 0013-7944.

Properties of Coatings

Barrier properties of SiO_x-coated polymers: Multilayer modeling and effects of mechanical folding. The oxygen permeability properties of polyethylene terephthalate, low- and high-density polyethylenes, and polypropylene coated with SiO_x using cold plasma were studied. A previously developed computer model for the calculation of transport properties in laminates containing very different layer thickness was fitted to experimental permeability data to obtain the oxygen transport properties of the SiO_x coating. For the first time, to the best of the authors' knowledge, it was possible to obtain the oxygen diffusivity and solubility of a SiO_x coating on a polymer substrate. The effects of folding the laminates through 90° on the permeability properties of the SiO_x coating were also investigated. The surface roughness of the substrates was obtained by atomic force microscopy, and the morphology of the laminate surfaces was analyzed by scanning electron microscopy. The oxygen diffusivity and solubility of a 45 nm thick SiO_x coating deposited on a 4000-fold thicker polypropylene substrate were 5×10^{-12} cm^2/s and 0.72 cm^3 (STP) cm^{-3}/atm, respectively. The diffusivity was approximately four orders of magnitude lower than that of the polymer substrate and, surprisingly, the solubility was higher than that of the polypropylene film. A hypothesis to explain these results is that the coating contained voids and, according to the permeability time lag, these were not continuous through the coating. The oxygen permeability of the coating increased with increasing substrate surface roughness, and was consequently lowest for polyethylene terephthalate). The folding operation initiated cracks in the coating, and the resulting increase in oxygen permeability was greater in the rougher substrates.

Keywords: atomic force microscopy, high-density polyethylenes, mechanical permeability, multilayers, plasma spraying, scanning electron microscopy, surface roughness, transport properties

M.S. Hedenqvist and K.S. Johansson, Department of Fibre/Polymer Tech., Royal Institute of Technology, Stockholm S-100 44, Sweden. Cited: *Surf. Coat. Technol., 172*(1), 15 July 2003, pp. 7-12 [in English]. ISSN 0257-8972.

Modeling of residual stresses in a plasma sprayed zirconia/alumina functionally graded-thermal barrier coating. Thermal barrier coating (TBC) structures composed of Al_2O_3 and ZrO_2 with different chemical compositions on the NiCoCrAlY bondcoat are proposed to improve the oxidation resistance of TBC systems. The concept of functionally graded materials is applied to manage residual stresses due to sharp interface between dissimilar materials that can lead to a premature failure of TBC system. A numerical study using finite-element analysis (FEA) was performed to investigate the effects of system architecture on the residual stresses developed in functionally graded thermal barrier coatings (FG-TBCs) and in a typical duplex TBC comprising NiCoCrAlY bondcoat and ZrO_2 topcoat. The effects of different cooling rates and substrate preheating process on the residual stress distribution were also evaluated. The results show that lower cooling rate and substrate preheating process reduce stresses within duplex coating. In addition, the incorporation of Al_2O_3 interlayer results in a manageable level of residual stress. Stresses at critical locations are reduced, and hence contributing to an increase in resistance to interfacial cracking. The probability of surface cracking is also reduced since the radial and tangential stresses within FG-TBC system are lower than in the duplex system. To provide adequate comparison to the computational results, x-ray diffraction was used to assess the residual stresses in the ZrO_2 coating surface. The measured residual stress was qualitatively in agreement with the numerical results obtained from FEA.

Keywords: alumina, composition, cooling, crack initiation, dissimilar materials, finite-element method, functionally graded materials, interfaces (materials), oxidation resistance, plasma spraying, preheating, residual stresses, thermal barrier coatings, x-ray diffraction

S. Widjaja, A.M. Limarga, and T.H. Yip, Science Division, Corning Inc., Corning, NY 14831. Cited: *Thin Solid Films, 434*(1-2), 23 June 2003, pp. 216-227 [in English]. ISSN 0040-6090.

Finite-element method (FEM) simulations and optimization about residual stresses in coating structures with functionally graded materials layer. An elastoplastic finite-element method is developed to predict the residual stresses of thermal spraying coatings with functionally graded material layer. In numerical simulations, temperature sensitivity of various material constants is included, and mixture law is used to depict the constitutive behaviors of FGM layer. The optimized distribution form of the volume fractions of constituents in FGM is obtained by the first-order optimization method in the AL_2O_3-Ni system. At the same time, effects of geometry and materials behaviors on the optimization result are also investigated numerically. When the length of specimen, the width of FGM layer, and thermal expanding coefficient of the substrate material increase, the optimized distribution parameter p decreases obviously. It is found that the optimization of the constituent contents in FGM reduces the magnitude of residual stresses to a large degree and makes the maximum residual stresses to shun the weakest part of the coating structure.

Keywords: computer simulation, elastoplasticity, finite-element method, optimization, residual stresses, sprayed coatings, volume fraction

C. Huang, S. Chen, and Z. Duan, State Key Lab. of Nonlinear Mech., Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, China. Cited: Proc. Seventh International Symposium on Functionally Graded Materials, 15-18 Oct 2002 (Beijing), *Mater. Sci. Forum, 423-425,* 2003, pp. 659-664 [in English]. ISSN 0255-5476.

Effects of scanning path on the deposition process in rapid plasma spray tooling: Modeling by homogenization theory. Rapid plasma spray tooling (RPST) is a kind of process that can quickly make a mold from rapid prototyping or nature pattern without limitation of pattern's size or material. In a previous investigation of the authors, the process of coating growth, pore formation, and its effect on coating properties in RPST has been analyzed numerically. The objective of this work is to calculate temperature and stress field during plasma spray process when using a different kind of scanning path. In mesoanalysis, two-scale asymptotic homogenization theory is introduced to predict the effective properties of plasma sprayed coatings with porous. Based on this, in macroprocess simulation, a FEM software developed system has been used to analyze the effects of gun scanning path on the temperature and stress field. The numerical examples for the four kinds of gun scanning paths are presented. In the scanning paths of s-shape (perpendicular), spire in, spire out, and s-shape (parallel), characteristic of the temperature field under spire-out path is the best, and the maximum stress and deflection under spire-out path are the smallest after the model cools.

Keywords: computer simulation, protective coatings, rapid prototyping, scanning, software engineering, stress analysis

G. Wang, Y. Chen, and H. Zhang, Stt. Key Lab. Plast. F.S./D./M.T., Huazhong Univ. of Sci./Technology, Wuhan 430074, China. Cited: Proc. Joint International Plasma Symposium, 1-2 July 2003, *Thin Solid Films, 435*(1-2), pp. 124-130 [in English]. ISSN 0040-6090.

How creep properties influence the stress state of thermal barrier coatings. The stress state in thermal barrier coating systems is studied using the finite element method. It is shown that creep properties of the thermally grown oxide (TGO) layer strongly influence the resulting stress state. If the TGO is purely elastic, very large tensile stresses will occur due to the volume increase during TGO growth, allowing the propagation of cracks through the structure. If TGO creep is sufficiently rapid, these stresses are completely relaxed at high temperatures. In this case, failure is caused by the mismatch in the thermal expansion coefficients of the materials. It is shown that even in the case of complete stress relaxation at elevated temperatures, a TGO layer of several micrometer thickness will cause large cooling stresses in the thermal barrier coating that allow the coalescence of microcracks.

Keywords: crack propagation, creep, elasticity, stress relaxation, stresses, thermal expansion

M. Baker and J. Rosler, Institut fur Werkstoffe, Tech. Universitat Braunschweig, 38106 Braunschweig, Germany. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(3), 2003, pp. 2527-2532 [in English]. ISSN 0255-5476.

An assessment of the residual stresses in low-pressure plasma sprayed coatings on an advanced copper alloy. Modeling studies were conducted on low-pressure plasma sprayed (LPPS) NiAl topcoat applied to an advanced Cu-8(at.%)Cr-4%Nb alloy (GRCop-84) substrate using nickel as a bondcoat. A thermal analysis suggested that the NiAl and nickel top and bondcoats, respectively, would provide adequate thermal protection to the GRCop-84 substrate in a rocket engine operating under high heat flux conditions. Residual stress measurements were conducted at different depths from the free surface on coated and uncoated GRCop-84 specimens by x-ray diffraction. These data are compared with theoretically estimated values assessed by a finite-element analysis simulating the development of these stresses as the coated substrate cools down from the plasma spraying temperature to room temperature.

Keywords: coatings, computer simulation, finite-element method, heat flux, plasma spraying, residual stresses, substrates, thermoanalysis, x-ray diffraction analysis

S.V. Raj, L.J. Ghosn, A. Agarwal, and T.P. Lachtrupp, NASA Glenn Research Center, MS 24-1, Cleveland, OH 44135. Cited: *Surface Engineering in Materials Science II,* TMS Annual Meeting, 2-6 March 2003 (San Diego, CA), S. Seal, N.B. Dahotre, J. Moore, C. Suryanaryana, and A. Agarwal, Ed., The Surface Engineering Committee of the MPMD of TMS Minerals, Metals, and Materials Society, pp. 49-56 [in English].

Spray Deposition Process

Modeling of droplet dynamic and thermal behavior during spray deposition. Mathematical modeling of supersonic gas atomization for spray forming has been investigated. Influence of the droplet dynamic and thermal behavior on the resultant microstructure has been studied. Analytical models have been constructed, taking into account the higher Reynolds number owing to supersonic gas flow. The impact velocity profiles of the droplets lend credence to the evolution of equiaxed grain morphology through dendrite fragmentation. The thermal history profile along with the fraction solid plot could yield optimized standoff distance to obtain a mushy droplet. A comparison of secondary dendrite arm spacing obtained from the mathematical model showed good agreement with experimental observations.

Keywords: drop formation, gases, mathematical models, morphology, Reynolds number, spraying, supersonic flow, velocity

J. Mendonca, N.S. Mahesh, M.K. Muralidhara, B.K. Muralidhara, and C. Ramachandra, Department of Mechanical Engineering, M.S. Ramaiah Institute of Technology, Bangalore 560 054, India. Cited: *Bull. Mater. Sci., 26*(3), April 2003, pp. 355-364 [in English]. ISSN 0250-4707.

Postprocessing

Deposit Densification

Densification of a plasma sprayed YSZ coating by the penetration of liquid manganese. The microstructural change of YSZ plasma sprayed coating in penetration of manganese liquid metal, under a vacuum atmosphere, was investigated, and the densification mechanism was studied. During the process of penetration, it was found that the liquid manganese rapidly penetrated into the internal connected porosities of the coating, and dense coating was formed by liquid sintering of the stuffed manganese. With this treatment, the volume of YSZ solid phase increased to 99.3% from 85.0% of as-sprayed coating. By analyses of the microstructure and mechanism of densification, the following three steps were found to be involved: (1) quick densification associated with forming of partial dense areas, (2) spheroidizing of particles by shape accommodation, and (3) coalescence of particles. Additionally, the diffusion of manganese from liquid manganese to YSZ particles and the solution of YSZ particles to liquid manganese were also involved. The quick densification of the coating during the early step of penetration was mainly due to the great capillary attractive force generated in filling of liquid manganese in fine porosities among lamellae particles that are characteristic with sprayed coating. The sintering densification in the middle and latter steps was considered to be achieved by solution-reprecipitation of YSZ solid phase in liquid manganese.

Keywords: coalescence, densification, liquid metals, manganese, microstructure, plasma spraying, porosity, sintering, yttrium compounds

Z. Zhou, H. Shirasawa, and A. Ohmori, Third Research Department, Adv. Mat. Processing Institute Kinki, Amagasaki 660-0083, Japan. Cited: *Nippon Kinzoku Gakkaishi (J. Jpn. Inst. Met.), 67*(5), May 2003, pp. 239-246 [in Japanese]. ISSN 0021-4876.

Laser Cladding

Influence of laser cladding parameters on microstructure and wear-resistance of nickel-base alloy coatings. Nickel-base alloy coatings and nickel/tungsten carbide (Ni/WC) composite coatings were prepared on Q235 steel by thermal spray and larger cladding. The influences of the laser power on the properties of coatings were widely studied. The results showed that the high-quality coatings with uniform WC particles distribution, low dilution, and good combination with the substrate can be obtained under the optimized laser power. In the Ni/WC composite coatings, WC particles partly dissociated at the edge, and many needlelike dendrites grew epitaxially from the surface of the partially melted WC particles under the proper laser power. This can improve the microhardness of the coating and significantly combined the WC particles with the matrix alloy. When the laser power is too large, WC particles at the top of the coating were burned and remaining WC particles sank to the bottom of coating. Accordingly, there is a sharp transition in hardness at the interface between the coating and the substrate. It easily brings about cracks and fatigue failure and does not help to improve the wear resistance of the coating.

Keywords: cracks, hardness, microstructure, steel, wear resistance

P. Wu, E. Jiang, C. Zhao, C.-Z. Zhou, and X. Tang, Tianjin Univ., Tianjin 300072, China. Cited: *Hanjie Xuebao/Trans. China Weld. Inst., 24*(2), April 2003, pp. 44-46, 50 [in Chinese]. ISSN 0253-360X.

Laser or Electron Beam Remelting

Modification of ceramic thermal spray deposit microstructures implementing in situ laser remelting. Yttria partially stabilized zirconia thermal barrier coatings (TBCs) are widely used to protect components of gas turbines against deterioration at high temperatures. Air plasma spray and laser irradiation processes are combined to improve properties of TBCs. An in situ laser remelting plasma spraying technique, implementing in particular a diode laser, was performed. Results show that laser treatment may induce: (1) no phase transition: the metastable tetragonal phase still remains the predominant phase after laser treatment; (2) a decrease of the pore network connectivity level for a laser energy density ranging from 1.7 to 1.9 J/mm^2; (3) the growth of fine dendritic structures (due to the rapid solidification), which could be interesting with regard to the improvement of the thermomechanical properties of the coating.

Keywords: gas turbines, laser beam effects, microstructure, plasma spraying, rapid solidification, semiconductor lasers

G. Antou, G. Montavon, F. Hlawka, A. Cornet, C. Coddet, and F. Machi, LERMPS-Univ. Technol. Belfort-Montbel., Belfort Cedex 90 010, France. Cited: *Surf. Coat. Technol., 172*(2-3), 29 July 2003, pp. 279-290 [in English]. ISSN 0257-8972.

Processing

Cold Gas Spraying

On some aspects of gas dynamics of the cold spray process. This paper presents an overview of results of recent studies conducted at the Institute of Theoretical and Applied Mechanics of the Siberian Division of the Russian Academy of Science in the field of gas dynamics and heat transfer of the supersonic air jet under conditions typically used in the cold spray process. These studies are related to various aspects of the problem including a flow in the nozzle and the outflow of the jet, as well as effects of the interaction of the jet with a flat obstacle. They are conducted with a supersonic nozzle with a rectangular section at the exit with a Mach number M_0 between 2 and 3.5. The gas flow in the nozzle is theoretically and experimentally studied. It is shown that the boundary layer on the walls of the nozzle affects significantly the flow parameters (for example, Mach number M, pressure p, temperature T, and density ρ of the gas). A method of calculation of the gas parameters in the flow core of the nozzle is suggested, and it is shown that they depend mainly on the ratio of the nozzle width to its length. The results of the investigation of the supersonic air jets with stagnation temperature ranging from 300 to 600 K flowing in the atmosphere are presented. The corresponding dimensions of the jets, profiles, and axial distributions of the gas parameters are obtained. The interactions of the supersonic jet with the flat obstacle are studied. Self-similarity of the distribution of the pressure and of the Mach number on the obstacle surface is shown for the jets with various values of the Mach number and the angle of impingement. The oscillation regimen of the jet impingement, as well as a compressed layer structure is observed with the aid of a schlieren visualization technique. Some problems of heat exchange of the jets with the obstacle are considered. Distributions of stagnation temperature and heat-exchange coefficient in the near-wall jet are obtained. The temperature of the

obstacle for the stationary case is calculated, and it is shown that for heat conductive materials the surface temperature is lower than the stagnation temperature due to the redistribution of heat inside of the substrate.

Keywords: gases, heat transfer, spraying, thermal effects

V.F. Kosarev, S.V. Klinkov, A.P. Alkhimov, and A.N. Papyrin, Cited: *J. Therm. Spray Technol., 12*(2), June 2003, pp. 265-281 [in English]. ISSN 1059-9630.

Bonding mechanism in cold gas spraying. Cold gas spraying is a relatively new coating process by which coatings can be produced without significant heating of the sprayed powder. In contrast to the well-known thermal spray processes such as flame, arc, and plasma spraying, in cold spraying there is no melting of particles prior to impact on the substrate. The adhesion of particles in this process is due solely to their kinetic energy upon impact. Experimental investigations show that successful bonding is achieved only above a critical particle velocity, whose value depends on the temperature and the thermomechanical properties of the sprayed material. This paper supplies a hypothesis for the bonding of particles in cold gas spraying, by making use of numerical modeling of the deformation during particle impact. The results of modeling are assessed with respect to the experimentally evaluated critical velocities, impact morphologies, and strengths of coatings. The analysis demonstrates that bonding can be attributed to adiabatic shear instabilities that occur at the particle surface at or beyond the critical velocity. On the basis of this criterion, critical velocities can be predicted and used to optimize process parameters for various materials.

Keywords: bonding, heating, kinetic energy, morphology

H. Assadi, F. Gartner, T. Stoltenhoff, and H. Kreye, Department of Mechanical Engineering, Univ. the Fed. Armed Forces Hamburg, Hamburg D-22043, Germany. Cited: *Acta Mater., 51*(15), 3 Sept 2003, pp. 4379-4394 [in English]. ISSN 1359-6454.

Electromagnetically Accelerated Plasma Spray

Formation of boron carbide coating by electromagnetically accelerated plasma spraying. Boron carbide (B_4C) coating formation is investigated using an electromagnetically accelerated plasma spraying, which can generate a dense and a high-velocity plasma jet of 1 MPa and 2.0 to 2.5 km/s by applying a pulsed high-current arc discharge to accelerate and heat powders. Highly crystalline B_4C coatings with roughened coating/substrate interfaces were formed on mirror-polished stainless (SUS304) substrates without a binder material. The density and uniformity of the coating are improved by changing the source powder size from 30 to 10 μm, where the estimated porosity is decreased from 9 to 4%.

Keywords: boron carbide, plasma jets, plasma spraying, porosity, powders

J. Kitamura, S. Usuba, Y. Kakudate, H. Yokoi, K. Yamamoto, A. Tanaka, and S. Fujiwara, Joint Research Consortium of FCT, Japan Fine Ceramics Center, AIST, Tsukuba, Ibaraki 305-8565, Japan. Cited: *Surf. Coat. Technol., 169-170*(1), 2 June 2003, pp. 324-327 [in English]. ISSN 0257-8972.

Flame Spray Synthesis

Simultaneous deposition of gold nanoparticles during flame synthesis of TiO_2 and SiO_2. Nanostructured gold/titania and gold/silica particles with up to 4 wt.% Au were made by a single-step process in a spray flame reactor. Gold(III)-chloride hydrate and titania- or silica-based metalorganic precursors were mixed in a liquid fuel solution, keeping concentrations in the flame and overall combustion enthalpy constant. The powders were characterized by x-ray diffraction, transmission electron microscopy, Brunauer-Emmett-Teller, and ultraviolet-visible analysis. The titania or silica specific surface area and the crystalline structure of titania were not affected by the presence of gold in the flame. Furthermore the size of the gold deposits was independent of the metal oxide support (TiO_2 or SiO_2) and its specific surface area (100 and 320 m^2/g, respectively). The gold nanoparticles were nonagglomerated, spherical, mostly single crystalline, and well dispersed on the metal oxide support. Depending on the gold weight fraction (1, 2, and 4 wt.%) the Au nanoparticles' mass mean diameter was 3, 7, and 15 nm, respectively, on both titania and silica. The particles showed surface plasmon absorption bands in the ultraviolet-visible region, which is typical for nanosized gold. This absorption band was red shifted in the case of the titania support, while no shift occurred with the silica support.

Keywords: enthalpy, flame spraying, gold, liquid fuels, nanostructured materials, silica, surface plasmon resonance, transmission electron microscopy, x-ray diffraction analysis

L. Madler, W.J. Stark, and S.E. Pratsinis, Particle Technology Laboratory, Dept. of Mechanical Engineering, Eidgen. Tech. Hochsch. (ETH) Zurich, CH-8092 Zurich, Switzerland. Cited: *J. Mater. Res., 18*(1), Jan 2003, pp. 115-120 [in English]. ISSN 0884-2914.

High-Velocity Oxyfuel Spray Parameters

The effects of fuel chemistry and feedstock powder structure on the mechanical and tribological properties of high-velocity oxyfuel thermal sprayed WC-Co coatings with very fine structures. The authors have deposited a series of WC-Co coatings by the high-velocity oxyfuel (HVOF) process, using three different powders and different spray conditions. The powders are a nanocrystalline (Nanocarb), a near-nanostructured powder (Infralloy) containing a proprietary additive aimed at retarding grain growth, and multimodal (mixed micro and nano) powder (Nanomyte). HVOF spray conditions were stoichiometric, fuel rich, and oxygen rich. "In-flight" feedstock powder temperature and velocity were measured. The hardness and toughness of the coatings are found to depend on WC-binder adhesion and adhesion between splats. High flame temperatures increase WC-binder adhesion but increase decarburization. The latter is found to decrease adhesion between the splats. Decarburization is most pronounced for nanostructured powders because of their high specific surface. The additive in Infralloy decreases adhesion between WC grains and binder, but it also reduces decarburization. The wear resistance of the coatings increases with hardness and decreases with increasing decarburization. Sliding wear occurs by a attrition of the WC grains and the lifting of entire splats; abrasive wear occurs by ductile cutting, grain loss, and lifting of splats; the low wear rate in sliding leads to splat-boundary weakening by fatigue. The effect of decarburization predominates in sliding wear and is less pronounced in abrasion; the high abrasive wear removes material before fatigue becomes important. The coating deposited at high temperature, from the multimodal powder Nanomyte, presents outstanding sliding and abrasive wear resistance, but inflicts large wear on the opposing silicon nitride surface in sliding. Coatings deposited with the near nanostructured powder containing an additive present high sliding wear resistance, independent of the deposition parameters, and cause low wear of the opposing silicon nitride. Coatings deposited with spray-dried nanostructured powders offer comparatively low wear resistance, in agreement with previous reports.

Keywords: feedstocks, fuels, grain growth, nanostructured materials, powders

Y. Qiao, T.E. Fischer, and A. Dent, Dept. of Chem. Biochem./Mat. Eng., Stevens Institute of Technology, Hoboken, NJ 07030. Cited: *Surf. Coat. Technol., 172*(1), 15 July 2003, pp. 24-41 [in English]. ISSN 0257-8972.

Properties of aluminum deposited by a high-velocity oxyfuel process. Pure aluminum coatings deposited by a high-velocity oxyfuel (HVOF) process have been produced and studied. A simple design-of-experiment (DOE) was used to assess the effect of two deposition parameters, the spray distance and oxygen-to-fuel ratio, on relevant coating properties. Porosity, surface roughness, and microhardness of the coatings were measured as responses to changes in the DOE parameters. The results indicated that these three properties of the aluminum coatings were normally insensitive to spray distance. Oxygen-to-fuel ratio, by flow, did appear to affect the porosity level of the coatings. Some postcoat processing of the aluminum coatings and minimization of nozzle loading are discussed.

Keywords: aluminum, deposition, microhardness, oxygen, porosity, surface roughness

R. Chow, T.A. Decker, R.V. Gansert, D. Gansert, and D. Lee, Lawrence Livermore Natl. Laboratory, Livermore, CA 94550. Cited: *J. Therm. Spray Technol., 12*(2), June 2003, pp. 208-213 [in English]. ISSN 1059-9630.

High-velocity oxyfuel thermal spray deposited Y_2O_3-stabilized ZrO_2 coatings for thermal barrier applications. High-velocity oxyfuel (HVOF) thermal spray has been successfully used to deposit yttria-stabilized zirconia (YSZ) for thermal barrier coating (TBC) applications. Adherent coatings were obtained within a limited range of spray conditions using hydrogen as fuel gas. Spray parameters such as hydrogen-to-oxygen ratio, spray distance, and substrate cooling were investigated. Spray distance was found to have a pronounced effect on coating quality; adherent coatings were obtained for spray distances between 75 and 125 mm from the gun exit for the hydrogen-to-oxygen ratios explored. Compared to air plasma spray (APS) deposited YSZ coatings, the HVOF deposited coatings were more fully stabilized in the tetragonal phase, and of similar density, surface roughness, and cross-sectional microhardness. Notably, fracture surfaces of the HVOF coatings revealed a more homogeneous structure. Many theoretical models predict that it should not be possible to melt YSZ in an HVOF flame, and therefore it should not be possible to deposit viable YSZ coatings by this process. The experimental results in the present work clearly contradict those expectations. The present results can be explained by taking into account the effect of partial melting and sintering on particle cohesion, as follows. Combustion chamber pressures (P_0) of ~3.9 bar (58.8 psi) realized during HVOF gun operation allows adiabatic flame temperature values that are above the zirconia melting temperature. Under these conditions, the Ranz-Marshall heat transfer model predicts HVOF sprayed particle surface temperatures T_p that are high enough for partial melting of small (~10 μm) zirconia particles, T_p = (1.10 to 0.95)T_m. Further analysis shows that for larger particles (38 μm), adherent coatings are produced when the particle temperature, T_p = 0.59 to 0.60 T_m, suggesting that sintering may have a role in zirconia particle deposition during HVOF spray. These results suggest two different bonding mechanisms for powders having a broad particle size distribution.

Keywords: hydrogen, plasma spraying, thermal barrier coatings, yttrium compounds, zirconia

T.A. Dobbins, R. Knight, and M.J. Mayo, Stop 8520, Gaithersburg, MD 20899-

8520. Cited: *J. Therm. Spray Technol., 12*(2), June 2003, pp. 214-225 [in English]. ISSN 1059-9630.

Hydroxyapatite Biomaterial

Hydroxyapatite graded coatings made through subsonic thermal spraying. Bioactive graded coating of hydroxyapatite (HA) on Ti-6Al-4V substrate made through subsonic thermal spraying was investigated in the present study. Pure titanium powder was selected as material of bottom layer, Ti70%+HA30% powder as transitional layer and HA powder as working layer. To be compared, another coating (nongraded coating) was prepared by spraying HA on pure titanium bottom layer directly. The tensile test shows that the bond strength between bottom layer and substrate is higher than that between transitional layer and working layer, and the bond strength between bottom layer and working layer of the nongraded coatings is the lowest. This indicates that the graded structure leading to the changes of coefficient of thermal expansion (CTE) from bottom layer to working layer is beneficial to the bond strength. The cross section and surface morphology of the coatings were observed using optical microscope (OM) and scanning electron microscopy (SEM). The phases were determined using x-ray diffraction (XRD). The results show that the bottom layer is composed of TiN, TiO_2, TiO_2, Ti_2O_3, the working layer is composed of HA, $Ca_4P_2O_9$, and $Ca_3(PO4)_2$, and the transitional layer is composed of the composite of above two layers. From the implant point of view, microcracks and porosities formed in working layer surface are helpful to the growth of green bone and the bond strength between implant and bone.

Keywords: bond strength (chemical), coatings, morphology, optical microscopy, scanning electron microscopy, spraying, substrates, surfaces, tensile testing, thermal expansion, titanium alloys, x-ray diffraction analysis

M. Li, C. Ma, and D. Shang, Provincial Key Lab. for Biomaterials, Jiamusi Univ., Jiamusi 154007, Heilongjiang, China. Cited: Proc. Seventh International Symposium on Functionally Graded Materials, 15-18 Oct 2002 (Beijing), *Mater. Sci. Forum, 423-425,* 2003, pp. 327-330 [in English]. ISSN 0255-5476.

Influence of deposition temperature on mechanical properties of plasma sprayed hydroxyapatite coating on titanium alloy with ZrO_2 intermediate layer. Hydroxyapatite (HA) coatings were plasma sprayed on the Ti-6Al-4V substrate with and without an intermediate ZrO_2 layer; meanwhile the temperatures of substrates were varied at 90, 140, and 200 °C. The coatings were subjected to the standard adhesion test per ASTM C 633-79. The purpose of the investigation was to study the effects of those processing variables on the bonding strength and failure behavior of the system. It is found that the bonding strengths of HA/ZrO_2 and HA coatings generally decrease with increasing substrate temperature, except for the HA/ZrO_2 coating deposited at 200 °C. The rationale of the results is attributed to the residual stress reported in the literature. Introducing ZrO_2 bondcoat is found to significantly promote the bonding strength of HA coating. The possible strengthening mechanism is the rougher surface of ZrO_2 bondcoat and the higher toughness of ZrO_2, which provide the mechanical strengthening effects. The slightly denser HA in 200 °C deposited HA coating cannot explain the high bonding strength of the HA/ZrO_2 coating, nor the mechanical strengthening effect of ZrO_2 intermediate layer should apply. It is believed that a stronger diffusion bonding is formed at the interface of HA and ZrO_2, which increases the bonding between them chemically. The bonding strengths of HA/ZrO_2 and HA coatings are correlated with the area fraction of adhesive failure of the coatings. The correlation explains the findings in this study.

Keywords: deposition, hydroxyapatite, plasma spraying, titanium alloys, zirconia

B.-Y. Chou and E. Chang, Dept. of Mat. Sci. and Engineering, National Cheng Kung Univ., Tainan 701, Taiwan. Cited: *J. Therm. Spray Technol., 12*(2), June 2003, pp. 199-207 [in English]. ISSN 1059-9630.

Improvement of bond strength of plasma sprayed hydroxyapatite/titanium composite coatings on titanium: Partial nitriding of titanium deposits by rf thermal plasma. The influence of partial nitriding of the titanium splats in hydroxyapatite/titanium (HA/Ti) composite coatings on the adhesion of those coatings to a titanium substrate was determined in terms of the microstructure of the coating and the phases formed. Both the interface between two nitrided titanium splats and the internal structure of the nitrided titanium splats were also investigated in detail using transmission electron microscopy. Results show that the partial nitriding of titanium splats in HA/Ti composite coatings improved the bond strength of the coatings on a titanium substrate.

Keywords: bond strength (materials), composition effects, crystal lattices, electron diffraction, hydroxyapatite, interfaces (materials), nitriding, scanning electron microscopy, sprayed coatings, titanium compounds, transmission electron microscopy, x-ray diffraction analysis

M. Inagaki, Y. Yokogawa, and T. Kameyama, Bio-functional Ceramics Res. Group, Ceramic Research Institute, National Institute of AIST, Moriyama-ku, Nagoya 463-8560, Japan. Cited: *J. Vac. Sci. Technol. A, Vac. Surf. Films, 21*(40), July/August 2003, pp. 1225-1229 [in English]. ISSN 0734-2101.

Magnetic Materials

Plasma sprayed Nd-Fe-B permanent magnets. Plasma sprayed Nd-Fe-B permanent magnets were discussed. Two other processes such as the powder metallurgy process for producing sintered Nd-Fe-B magnets and the melt spinning process for bonded Nd-Fe-B magnets were studied. Results showed that controlled atmosphere plasma spray (CAPS) chamber produces $Nd_{15}Dy_1Fe_{77}B_7$ magnets with commercially useful magnetic properties.

Keywords: crystal structure, magnetic anisotropy, melt spinning, plasma spraying, powder metallurgy, sintering

M. Willson, S. Bauser, S. Liu, and M. Huang, APS Materials, Inc., Dayton, OH 45405. Cited: *J. Appl. Phys., 93*(10), 15 May 2003, pp. 7987-7989 [in English]. ISSN 0021-8979.

Structural and magnetic properties of nanostructured $Ni_{0.5}Zn_{0.5}Fe_2O_4$ films fabricated by thermal spray. The fabrication of nanostructured $Ni_{0.5}Zn_{0.5}Fe_2O_4$ thick films by a high-velocity oxygen fuel (HVOF) thermal spray approach was reported. The study of microstructural, crystallographic, and static and dynamic magnetic properties of the films by x-ray diffraction, high-resolution transmission electron microscopy, superconducting quantum interference device magnetometer, and high-frequency impedance analyzer was also presented. It was found that for the fabrication of nanostructures ferrite films, HVOF is an effective approach.

Keywords: crystallography, electric impedance measurement, gas fuels, heat treating furnaces, magnetic properties, magnetic thick films, microstructure, nanostructured materials, oxygen, SQUIDs, structure (composition), transmission electron microscopy, x-ray diffraction

S. Ge, X. Ma, T. Zhang, M. Wu, H. Zhang, Y.D. Zhang, J. Ings, and J. Yacaman, Inframat Corporation, Willington, CT 06279. Cited: *J. Appl. Phys., 93*(10), 15 May 2003, pp. 7498-7500 [in English]. ISSN 0021-8979.

Perovskites

Dielectric properties of plasma spray deposited $BaTiO_3$ and $Ba_{0.68}Sr_{0.32}TiO_3$ thick films. The dielectric properties of high-k dielectric $BaTiO_3$ and $Ba_{0.68}Sr_{0.32}TiO_3$ thick films deposited on alumina substrates using a plasma spray process were investigated. The as-deposited films were predominantly crystalline, but contained an amorphous second phase, the amount of which depended on spray conditions. The effect of the spray conditions on crystallinity was studied and related to the dielectric properties of the films. The presence of a low dielectric constant interfacial layer in plasma spray deposited films was determined from the dependence of the dielectric constant on film thickness. After annealing at 500 °C for 20 h in air, the crystallinity and dielectric constant increased. Annealing was also found to affect the interfacial layer properties.

Keywords: alumina, annealing, crystalline materials, deposition, interfaces (materials), permittivity, plasma spraying, thick films

K. Ahn, B.W. Wessels, and S. Sampath, Department of Materials Science, Northwestern Univ., Evanston, IL 60208. Cited: *J. Mater. Res., 18*(5), May 2003, pp. 1227-1231 [in English]. ISSN 0884-2914.

Spark Plasma Sintering

Densification of plasma sprayed YSZ electrolytes by spark plasma sintering (SPS). Solid oxide fuel cells (SOFC) are promising candidates for alternative power-generation systems due to their high-energy conversion efficiencies, and low emissions of environmentally hazardous by-products. Plasma spray (PS) is an effective and relatively inexpensive process for fabricating high-performance yttria-stabilized zirconia (YSZ) electrolyte for SOFC. Yet, because of the numerous intergranular defects introduced to the electrolyte by the plasma spray process, the electrolyte is not gastight, and consequently the energy efficiency of the cell is severely curtailed. In order to improve the performance of the SOFC, spark plasma sintering (SPS) is introduced as a postspray treatment to enhance the density of the PS YSZ electrolyte rapidly and effectively. In this study, spark plasma sintering (SPS) was performed at 1200, 1400, and 1500 °C. Each sintering cycle had a holding time of 3 min. Single and multiple SPS cycles (3 min at preset temperature per cycle) were used to treat the PS YSZ electrolytes. The microstructure of as-received and SPS treated electrolytes as examined by scanning electron microscopy (SEM) demonstrated a microstructure transition above 1200 °C, where the typical plasma sprayed lamella structure transformed to a granular-type structure. The porosity of as-received and SPS posttreated electrolytes, which were determined by a mercury intrusion porosimeter (MIP), revealed a significant reduction in pores at 1500 °C. Average pore size reduced from 0.2 to 0.08 μm. The ionic conductivity of the electrolytes is evaluated by a.c. impedance spectroscopy to characterize the effect of SPS on enhancing the ionic conductivity of the electrolytes.

Keywords: densification, electric power generation, microstructure, plasma spraying, porosity, scanning electron microscopy, sintering, solid oxide fuel cells, zirconia

K.A. Khor, L.-G. Yu, S.H. Chan, and X.J. Chen, School of Mechanical/Production Eng., Nanyang Technological Univ., Singapore 639798, Sin-

gapore. Cited: *J. Eur. Ceram. Soc., 23*(11), Oct 2003, pp. 1855-1863 [in English]. ISSN 0955-2219.

Spray Forming

Research in spray forming technology and its applications in metallurgy. The processing, materials characterization, and applications of spray formed Cu-15Ni-8Sn, Cr12MoV steel, and GCr15 steel are reported in this paper. Spinodal decomposed phase, metastable γ' preprecipitates, and discontinuous precipitates exist during aging treatment of spray formed Cu-15Ni-8Sn alloy. The as-sprayed Cr12MoV steel shows the depressed martensite start temperature (M_s) and the reduced hardenability in comparison with the conventionally processed one. Transmission electron micrographs of the spray formed GCr15 steel reveal the fine pearlite with interlamellar spacing of 85 nm and the martensite of the width of 0.35 μm.

Keywords: copper alloys, metallurgy, precipitation (chemical), steel, transmission electron microscopy

J.G. Zhang, H.S. Shi, and D.S. Sun, Institute of Advanced Materials, Shanghai Baosteel Research Institute, Shanghai 201900, China. Cited: *J. Mater. Process. Technol., 138*(1-3), 20 July 2003, pp. 357-360 [in English]. ISSN 0924-0136.

Metal spray tooling for composite forming. Thermal spraying methods have been mooted as a method of manufacturing tooling for many years, and yet they have not made a significant in-road into this market. Generally, recent metal spraying research has focused on the manufacture of small, high-pressure tools (for example, for automotive injection molding tools). However, the metal spray process really lends itself to the manufacture of large tooling where it can compete more effectively against alternatives such as machining. The three-year, 750k, IMI Spray Mould Programme, funded jointly by EPSRC (IMI) and the industrial partners: Airbus, BAE SYSTEMS, Bombardier Aerospace Shorts, A.T. Poeton, Rover Group, and Sulzer Metco, commenced in June 1997. The aim of this research is to develop a method of manufacturing tooling for composite aerospace components, particularly large primary structures more than 15 m in length. This paper presents the results of this research program, including technical data comparing both the technical and economic advantages of this novel approach to tool construction.

Keywords: aerospace applications, autoclaves, carbon fibers, composite materials, economics, forming, manufacture, metals, nickel alloys, spraying, thermal expansion

D.I. Wimpenny and G.J. Gibbons, Rapid Prototyping and Tooling, Warwick Manufacturing Group, Univ. of Warwick, Coventry CV4 7AL, U.K. Cited: *J. Mater. Process. Technol., 138*(1-3), 20 July 2003, pp. 443-448 [in English]. ISSN 0924-0136.

Superplastic ultrahigh carbon steels processed by spray forming. The superplasticity and microstructure of the spray formed 1.25C-3.0Si-1.5Cr ultrahigh carbon steels (UHCS) are described. The 1.25C-3.0Si-1.5Cr steel processed by spray forming to break up carbide network had microstructure consisting of fine pearlite with average interlamellar spacing of 0.20 μdm and revealed superplastic characteristics at elevated temperature. The dramatic change of microstructure from a fine lamellar mixture to equiaxed grains stabilized by spheroidized particles during superplastic deformation has been observed. The ultimate tensile strength and the pearlite spacing in the 1.25C-3.0Si-1.5Cr steel can be related by the Hall-Petch equation. The estimation on the basis of thermodynamics shows that the content of chromium of 1.6 wt.% is needed to inhibit graphite formation in the 1.25C-3.0Si-l.5Cr UHCS.

Keywords: graphitization, metal forming, microstructure, pearlite, spraying, superplasticity, tensile strength, thermodynamics

J.-G. Zhang, B. Yan, H. Zhang, C.-D. Zhou, Y.-J. Lin, H.-S. Shi, J.-S. Yao, and D.-S. Sun, Baosteel Adv. Technology Institute, Shanghai Baosteel Research Institute, Baoshan, Shanghai 201900, China. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(2), 2003, pp. 919-924 [in English]. ISSN 0255-5476.

Spray forming: An energy saving and process efficient technique. Spray forming technique has attracted considerable attention, not only from the standpoint of metallurgical advantages, but also as a potential for near-net-shape fabrication with energy and cost savings. In this paper, principles, processes, and industrial practices of spray forming to manufacture different geometry parts (i.e., plates/strips/sheets, billets/rods, tubes/rings, etc.) are reviewed and compared with those of conventional ingot metallurgy (I/M) or continuous casting and powder metallurgy (P/M) techniques. The factors related to energy efficiency (i.e., reduction of operation steps, deposition yield, and inert gas consumption) are overall analyzed, and equipment investments are evaluated in spray forming. They are compared with those in conventional I/M or continuous casting and P/M techniques. The results reveal that energy consumption and capital and labor costs can be significantly saved using spray forming technique as a result of reduction in operation steps. In order to improve the competitiveness of spray forming technique with conventional I/M or continuous casting and P/M techniques, the approaches to continuously spray form different geometry parts (i.e., plates/strips/sheets, billets/rods, tubes, etc.) are introduced. In addition, the principle of spray forming for the fabrication of complex molds/dies is reviewed. Similarly, production cost and time can be significantly reduced, compared with the conventional fabrication procedures for molds/dies.

Keywords: deposition, ingots, metal castings, spraying

Y. Lin, Y. Zhou, and E.J. Lavernia, Department of Chemical Engineering, Univ. of California Irvine, Irvine, CA 92697-2575. Cited: *Proc. Technical Sessions,* presented by the Materials Processing and Manufacturing Division of TMS, I. Anderson, T. Marechaux, and C. Cockrill, Ed., 2-6 March 2003 (San Diego, CA), Minerals, Metals, and Materials Society, pp. 63-78 [in English].

Thermal Barrier Coatings

Pt and Hf additions to NiAl bondcoats and their effect on the lifetime of thermal barrier coatings. The lifetimes of thermal barrier coatings (TBCs) with various NiAlPt(HfZr) bondcoats were determined by cyclic oxidation testing at 1163 °C (2125 °F). The bondcoats were sprayed from powders by low-pressure plasma spraying onto René N5 superalloy substrates. Yttria-stabilized zirconia (8YSZ) topcoats were applied by air plasma spraying. Surprisingly, there was not a strong correlation between TBC lifetime and platinum or hafnium content, although zirconium additions decreased lifetimes. TBC failure morphologies and bondcoat microstructures were examined and are discussed with respect to the bondcoat compositions.

Keywords: composition, hafnium, microstructure, oxidation, plasma spraying, platinum, thermal barrier coatings

J.A. Nesbitt, B. Gleeson, D. Sordelet, and C.A. Barrett, NASA Glenn Research Center, Cleveland, OH 44135. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(1), 2003, pp. 209-214 [in English]. ISSN 0255-5476.

Nanocharacterization of ceramic topcoat/metallic bondcoat interface for thermal barrier coating systems by plasma spraying. Characterization at the ceramic topcoat/metallic bondcoat interfacial region was conducted for several kinds of the plasma sprayed thermal barrier coating (TBC) systems by means of a transmission electron microscope (TEM), an electron probe microanalysis (EPMA), and so forth, in order to find out the optimal compositional and structural conditions of the coating components together with the optimal coating processing condition for designing advanced TBC systems. Specimens with different coating features were prepared systematically by using different coating parameters such as the topcoat spraying conditions and reheat-treatment conditions. Especially, the reheat treatment was applied to the TBC specimen with different temperature either in air or in inert argon gas atmosphere. It was found that in the case of reheat treatment in air the thermally grown oxide (TGO) was developed at the interface as multiple oxide layers; one is Al_2O_3 layer developed discontinuously at directly above the bondcoat, and another is the mixed oxides layer consisting of the aluminum, chromium, cobalt, and nickel oxide particles on the Al_2O_3 layer. Such a TGO layer was heterogeneous and an imperfect layer with containing many kinds of defects. On the contrary, the TGO layer formed by the reheat treatment in argon was composed dominantly of the continuous and fairly purified Al_2O_3 layer with large grain size and homogeneous layer thickness. The growth mechanism and influencing factors for TGO were discussed in some detail on the basis of the nanocharacterization and quantitative evaluation of TGO.

Keywords: ceramic materials, composition, grain size and shape, heat treatment, interfaces (materials), metals, nanostructured materials, plasma spraying, structure (composition), thermal effects, thickness measurement, transmission electron microscopy

S. Takahashi, M. Yoshiba, and Y. Harada, Department of Mechanical Engineering, Graduate School of Engineering, Tokyo Metropolitan Univ., Tokyo 192-0397, Japan. Cited: *Mater. Trans., 44*(6), June 2003, pp. 1181-1189 [in English]. ISSN 1345-9678.

Ultrahigh-Temperature Ceramics

High-temperature characterization of an UHTC candidate materials for RLVs. Nose and wing leading edges of the future generations reentry vehicles will withstand very high temperature in an oxidizing environment. Ultrahigh temperature ceramics (UHTC) materials are very promising candidate materials for such applications. An innovative, proprietary methodology was developed to produce, by plasma spray deposition, a ceramic composite containing SiC particles (25 wt.%) dispersed in a ZrB_2 matrix. With such a technique, both coatings and self-standing parts were fabricated. In spite of the well-known difficulty to obtain plasma sprayed coatings containing SiC, characterization results evidenced that the used process did not affect the phase composition. The high-temperature behavior of such a composite was characterized and the formation of a passivation layer, composed by mixed oxides of silicon and zirconium, was assessed, thus confirming that the developed material can withstand high temperatures in oxidizing atmosphere, as requested by the envisaged application.

Keywords: deposition, oxidation, phase composition, plasma spraying, silicon carbide, thermal conductivity of solids, vehicles

M. Tului, G. Marino, and T. Valente, Centra Sviluppo Materials S.p.A., 00128

Rome, Italy. Cited: *Hot Structures and Thermal Protection Systems for Space Vehicles,* Fourth European Workshop, 26-29 Nov 2002 (Palermo), Special Publication No. 521, A. Wilson, Ed., European Space Agency, April 2003, pp. 161-165 [in English]. ISSN 0379-6566.

Properties

Alumina-Titania Coatings

Influence of additive silica on the laser melting of the ceramic coatings. The influence of additive silica on the microstructure of plasma sprayed Al_2O_3 and Al_2O_3 + 13 wt.% TiO_2 ceramic coatings at laser melting has been investigated in this study. At the laser melting, the addition of silica in the Al_2O_3 ceramic coating can reduce the stress of cooling shrinkage generated during the solidification. Moreover, silica can render finer size of grains of the melting layer and form the continuous glassy matter around to grain boundaries so as to reduce further the cooling stress and to suppress the formation and spreading of cracks. On the other hand, at the laser melting, TiO_2 reacts with Al_2O_3 and transforms into $TiAl_2O_5$. The latter new phase has great and anisotropic coefficients of thermal expansion, which lead to big and asymmetrical stresses and thus form cracks in the melting layer of Al_2O_3 + 13 wt.% TiO_2 coating. Due to the fact that the influence of additive silica on the suppression of the formation of cracks is rather limited and cannot counterbalance the negative effect of $TiAl_2O_5$, thus in the melting layer of Al_2O_3 + 13 wt.% TiO_2 coating doped with 3 wt.% SiO_2, cracks occur also. Nevertheless, TiO_2 can greatly improve the wear resistance of the ceramic coating as sprayed or laser melted.

Keywords: coatings, cooling, cracks, microstructure, shrinkage, silica, stresses

Y. Yang, X. Bai, Z. Xie, T. Kuang, Z. Liu, Y. Zhuang, B. Tong, and Y. Liang, Faculty of Mat. and Energy, Guangdong Univ. of Technol., Guangzhou 510643, China. Cited: *J. Mater. Sci. Technol., 19*(1), Jan 2003, pp. 33-36 [in English]. ISSN 1005-0302.

Cermet Coatings

M_3B_2 boride cermet coating by sintered powder. The boride cermet composed with M_3B_2 (M: metal)-system complex borides and metals have attained superiority over carbide cermets in various mechanical properties. However, their sintered materials have put into only the limited uses due to the cost. Therefore, two sorts of the boride cermet coating have been developed. Thermal spray coating of the boride cermet was investigated. The sprayed powder was prepared by low-temperature sintering, and the spraying was performed by high-velocity oxyfuel (HVOF) spraying. Microstructure of the sprayed layer was finer, and its hardness was superior to sintered body in vacuum having same compositions. Overlay of the boride cermet was investigated using sintered powder. Plasma transfer arc was selected as welding method. The suitable compositions were not same between overlay and thermal spraying owing to the deference of provided heat in process.

Keywords: cermets, composition, powders, protective coatings, sintering, spraying

K. Hamashima, Asahi Glass Co., Ltd., Research Center, Yokohama City, Japan. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(3), 2003, pp. 2545-2550 [in English]. ISSN 0255-5476.

Corrosion and erosion damage mechanisms during erosion-corrosion of WC-Co-Cr cermet coatings. Experiments were performed in order to evaluate the behavior of WC-Co-Cr coatings applied by the Super D-Gun thermal spray process in erosion-corrosion environments. The experiments were performed in 3.5% NaCl with different silica sand loadings (200 and 500 mg/L). The results were compared with UNS S31603 and UNS S32760 stainless steels. Measurements of the total material loss showed that the coating applied by Super D-Gun presented higher resistance to erosion-corrosion compared to both stainless steel materials as expected. The connection between the erosion-corrosion behavior of the Super D-Gun coating and the microstructure is assessed. Scanning electron microscopy (SEM) images enabled the different mechanisms of tribocorrosion to be understood. With cermet materials, there has been much discussion relating to the role of corrosion in removing the hard phase particles that can breach tribological performance. The corrosion rate (i_{corr}) of the coating was determined under erosion conditions and an evaluation of the influence of corrosion and synergistic processes on the erosion process was made using applied cathodic protection.

Keywords: cathodes, corrosion resistance, microstructure, scanning electron microscopy, silica, stainless steel

V.A. de Souza and A. Neville, School of Eng. and Physical Sciences, Corrosion/Surface Eng. Res. Group, Heriot-Watt Univ.-Edinburgh, Edinburgh EH14 4AS. Cited: *Wear, 255*(1-6), Aug/Sept 2003, pp. 146-156 [in English]. ISSN 0043-1648.

Composite Coatings

Processing-microstructure-property predictions for short fiber reinforced composite structures based on a spray deposition process. Manufacturing of composite preforms by use of a programmed and controlled reinforcement spray-deposition process presents itself as an attractive approach to produce short-fiber reinforced composite structures. To predict properties of the final composite structure, simulations of the reinforcement deposition process are conducted to obtain the reinforcement orientation distribution. A micromechanics analysis incorporating the Mori-Tanaka method and texture tensors is used to predict the properties of the final consolidated composite parts. This processing-microstructure-property prediction scheme is applied to the analysis of composite structures in the carbon-carbon system. The effects of variations in reinforcement length in the spray deposited preform, and boundary effects as occurring in a near-net-shape composite disk are discussed.

Keywords: computer simulation, deposition, microstructure

J. Liakus, B. Wang, R. Cipra, and T. Siegmund, School of Mechanical Engineering, Purdue Univ., West Lafayette, IN 47907-1288. Cited: *Compos. Struct., 61*(4), Sept 2003, pp. 363-374 [in English]. ISSN 0263-8223.

Investigating feasibility of incorporating diamond into metal-matrix composites using thermal spraying. Diamond is seeing increasing use in surface engineering applications because it can offer extremely desirable properties, such as high strength, high hardness, and good thermal properties. However, in terms of practical use, pure diamond has limitations due to brittleness, difficulty in processing, and, importantly, cost. The incorporation of diamond into the metal matrix of a thermal spray coating to produce a composite hardfacing coating is investigated in this work. In this preliminary study, the feasibility of spraying a diamond-metal composite, the ability to retain the diamond without excessive degradation, and the associated properties of the coating in terms of hardness are reported. Synthetic and natural diamond grits were used in conjunction with nickel-base hardfacing powders as the matrix to produce the composite coatings. Spraying was carried out using a standard oxyacetylene spraying torch. The coating microstructures were then investigated using light and scanning electron microscopy, and their elemental composition was probed using energy dispersive x-ray analysis. X-ray diffraction was used to identify whether diamond was retained without phase transformation to graphite and to characterize the other phases in the coatings. Macrohardness testing was also used as a preliminary measure of the quality of the coating. Preliminary results show that it is possible to produce a hardfacing diamond composite coating and that there is scope to optimize the coating for the ultimate application, which, in this case, is for an oilfield drilling tool, where the coating would be subjected to extreme conditions of wear and wear corrosion.

Keywords: diamonds, hardness, microstructure, scanning electron microscopy, sprayed coatings, thermal effects, x-ray diffraction analysis

A.F. Richardson, A. Neville, and J.I.B. Wilson, Corros./Surf. Eng. Research Group, Department of Mechanical Engineering, Heriot-Watt Univ., Edinburgh, U.K. Cited: *Surf. Eng., 19*(2), April 2003, pp. 114-120 [in English]. ISSN 0267-0844.

The microstructure and erosive-corrosive wear performance of laser-clad Ni-Cr_3C_2 composite coating. The microstructure and erosive-corrosive wear (ECW) performance of laser-clad Ni-Cr_3C_2 composite coating with overlapping clad tracks on a 0.2% C martensitic stainless steel have been investigated by means of scanning electron microscopy (SEM), x-ray diffraction (XRD), energy-dispersive x-ray analysis, microhardness testing, and ECW testing. The average microhardness of the composite coating is increased with increasing amounts of added carbide in the considered range. The complete dissolution of Cr_3C_2 particles in the melted pool leads to carbon and chromium enrichment in the matrix and hence causes the formation of M_7C_3 (M:Fe,Cr) in the solidifying structures. The clad layer consists of dense austenite (γ) dendrites surrounded by a γ-M_7C_3 eutectic. The ECW rate of the Ni-Cr_3C_2 coating decreased by about 50% compared to the stainless steel substrate under the condition of acid slurry contained quartz sand. It is suggested that the improvement in ECW resistance is closely related to the formation of a more ductile austenite structure and the clad layer being strengthened due to the increase of coating hardness.

Keywords: carbon, chromium, corrosion, laser applications, martensite, microstructure, nickel compounds, scanning electron microscopy, stainless steel, x-ray diffraction analysis

D.-W. Zhang and T.C. Lei, College of Industrial Engineering, Wenzhou Univ., Wenzhou, Zhejiang Province 325035, China. Cited: *Wear, 255*(1-6), Aug/Sept 2003, pp. 129-133 [in English]. ISSN 0043-1648.

Copper Coatings

Effect of spray conditions on the microstructure and properties of microplasma sprayed copper coating. Copper coating is deposited by microplasma spraying system under a low power of 2.8 to 4.2 kW. The effects of the main processing parameters, including plasma arc power, operating gas flow, and spray distance, on the particle velocity during spraying, the microstructure, and the hardness of the coating are investigated. The experimental results show that the particle velocity is nearly independent of plasma arc power and spray distance, but is significantly influenced by operating gas flow. Moreover, the microhardness of the coating was influenced significantly by plasma arc

power and spray distance and is influenced weakly by operating gas flow. The analysis suggests that the microhardness of the coating is strongly affected by particle temperature. The comparison shows that the microhardness of copper coating deposited by microplasma spray is comparable to that of the coating deposited by the conventional plasma spray system at a power level of 30 kW.

Keywords: copper, microhardness, plasma arc melting, velocity

C. Li, B. Sun, M. Wang, F. Feng, and T. Wu, Sch. of Mech. Eng., Xi'an Jiaotong Univ., Xi'an 710049, China. Cited: *Hsi-An Chiao Tung Ta Hsueh/J. Xi'an Jiaotong Univ., 36*(11), Nov 2002, pp. 1182-1186 [in Chinese]. ISSN 0253-987X.

Microstructural and macroscopic properties of cold sprayed copper coatings. Macroscopic and microstructural properties of cold sprayed copper coatings were investigated. Mechanical and conductive behavior of cold sprayed copper coatings were also analyzed to explain the possible bonding mechanisms. It was found that the microstructural property is influenced by high local stress and fast temperature rises.

Keywords: cold rolling, conductive materials, copper, kinetic energy, microstructure, phase composition, stress analysis, thermal effects

C. Borchers, F. Gartner, T. Stoltenhoff, H. Assadi, and H. Kreye, Department of Mechanical Engineering, Univ. of the Federal Armed Forces, D-22043 Hamburg, Germany. Cited: *J. Appl. Phys., 93*(12), 15 June 2003, pp. 10064-10070 [in English]. ISSN 0021-8979.

Copper-Iron Microstructures

Influence of chromium alloying on the microstructure of thermally sprayed quasi-crystalline Al-Cu-Fe coatings. The present work reports the structural development of Al-Cu-Fe and Al-Cu-Fe-Cr coatings deposited by the high-velocity oxyfuel thermal spraying process and the influence of chromium alloying on the phase selection of Al-Cu-Fe coatings at various deposition temperatures. The porosity levels of the Al-Cu-Fe and Al-Cu-Fe-Cr coatings of the study are demonstrated to be lower than those reported for corresponding plasma sprayed coatings. The results show that high-velocity oxyfuel spraying technique produces Al-Cu-Fe coatings that are phase structurally similar to plasma sprayed Al-Cu-Fe coatings reported in literature. Al-Cu-Fe coatings are composed of a crystalline β-AlFe phase and a quasi-crystalline i-$Al_{65}Cu_{20}Fe_{15}$ phase as well as an oxidized form of either or both of these phases. Addition of chromium to Al-Cu-Fe alloys introduces coatings that are made up of the crystalline θ-Al_2Cu phase and two quasi-crystalline phases, the i_1-$Al_{80}Cr_{13.5}Fe_{6.5}$ and i_2-$Al_{13}Cr_3Cu_4$ phases. The formation of these icosahedral phases in Al-Cu-Fe-Cr alloys has not been reported before, although the occurrence of quasi-crystal approximants with compositions close to those of the i_1-$Al_{80}Cr_{13.5}Fe_{6.5}$ and i_2-$Al_{13}Cr_3Cu_4$ phases has been demonstrated. On the basis of the authors' results they propose that the icosahedral phase structure is greatly stabilized by the chromium addition to Al-Cu-Fe alloys.

Keywords: alloying, chromium, composition, microstructure, porosity, protective coatings, spraying

E. Huttunen-Saarivirta, E. Turunen, and M. Kallio, Tampere Univ. of Technology, Institute of Materials Science, Fin-33101 Tampere, Finland. Cited: *Intermet., 11*(9), Sept 2003, pp. 879-891 [in English]. ISSN 0966-9795.

Corrosion and Electrochemical Behavior

High-temperature erosion and corrosion measurement of thermally sprayed materials. The high-temperature erosion and corrosion measurement of thermally sprayed materials was presented. Numerous materials like unalloyed, low-alloyed, alloyed, high-alloyed, and superalloy steels were studied under the operation conditions of waste incinerators at 530 to 640 °C. It was found that nickel- or cobalt-base alloys have higher corrosion resistance than high-alloyed steels.

Keywords: abrasion, corrosion resistance, erosion, refuse incinerators, sintering, steel, superalloys

S.C. Cha and P. Wolpert, Max-Planck-Inst. Eisenforsch. GmbH, D-40237 Düsseldorf, Germany. Cited: *Adv. Eng. Mater., 5*(4), 1 April 2003, pp. 213-217 [in English]. ISSN 1438-1656.

Linking electrochemical corrosion behavior and corrosion mechanisms of thermal spray cermet coatings (WC-CrNi and WC/CrC-CoCr). In this experimental study, the corrosion characteristics (rates and mechanisms) of two thermally sprayed cermet (ceramic/metal composite) coatings have been examined in a static saline environment. The coatings have complex microstructures where the ceramic hard-phase constituents are embedded in a metallic matrix. Their electrochemical response during accelerated corrosion d.c. polarization tests reflects this complexity. A test protocol involving potentiostatic and potentiodynamic tests has been devised that enables the mechanisms of corrosion occurring on the WC/CrC-CoCr cermet and the WC-CrNi cermet to be compared and contrasted. A "critical" temperature has been defined for the WC-CrNi coating similar to the critical pitting temperature defined for stainless steels. Electrochemical behavior, which cannot be simply described as truly "passive" behavior, is displayed by the WC/CrC-CoCr coating, and such a well-defined "critical" temperature is not apparent. The contrasting mechanisms of corrosion on the two coatings, identified during post-test examination, can be correlated to the contrasting electrochemical response.

Keywords: electrochemical corrosion, microstructure, phase composition, spraying, stainless steel, thermal effects, tungsten carbide

V.A.D. Souza and A. Neville, Corrosion/Surface Eng. Res. Grp., Dept. of Mechanical/Chemical Eng., Heriot-Watt Univ., Edinburgh EH 14 4AS, U.K. Cited: *Mater. Sci. Eng. A, 352*(1-2), 15 July 2003, pp. 202-211 [in English]. ISSN 0921-5093.

Microstructure and oxidation resistance of a plasma sprayed Mo-Si-B multiphase alloy coating. A multiphase Mo-Si-B alloy coating can be successfully deposited onto the Mo-ZrC composite using a low-pressure plasma spraying method. Microstructure of the plasma sprayed Mo-Si-B coating consists of Mo_5Si_3, Mo_3Si, and Mo_5SiB_2 phases, which are the same constituents as Mo-Si-B alloy powder. Nanostructure is formed in the Mo-Si-B coating with the eutectic composition owing to the rapid quenching effect by plasma spraying. The oxidation behavior of the Mo-Si-B coating shows rapid mass loss followed by slow mass gain at 1673 K in Ar-20%O_2. Dense and adherent borosilicate glass formation passivates the coating against further oxidation at 1673 K.

Keywords: borosilicate glass, composite materials, eutectics, intermetallics, microstructure, nanostructured materials, oxidation, plasma spraying, quenching, sprayed coatings

N. Nomura, T. Suzuki, K. Yoshimi, and S. Hanada, Institute for Materials Research, Tohoku Univ., Sendai 980-8577, Japan. Cited: *Intermet., 11*(7), July 2003, pp. 735-742 [in English]. ISSN 0966-9795.

Oxidation behavior of chromium-doped $Nb(Si,Al)_2$ and coating niobium substrates with chromium-doped $Nb(Si,Al)_2$. Powder compacts with some different compositions of Nb-Si-Al-Cr system were prepared by spark plasma sintering (SPS), and oxidation behavior of each compact was examined by a thermobalance. In addition, some niobium substrates were coated with chromium-doped $Nb(Si,Al)_2$ by SPS and low-pressure plasma spraying (LPPS), and then their microstructure was observed. Chromium-doped $Nb(Si,Al)_2$ matrix compacts with a composition of Nb-56Si-11Al-3Cr (at.%) showed extremely good oxidation resistance in the temperature range of 773 to 1673 K. The chromium-doped $Nb(Si,Al)_2$ layer adhesively stuck to niobium substrate when thin aluminum foil was inserted between chromium-doped $Nb(Si,Al)_2$ powder and the substrate before the SPS. Moreover, chromium-doped $Nb(Si,Al)_2$ layer adhesively stuck to niobium substrate when the substrate was SPSed under conditions of pseudo hot isostatic pressing after the LPPS.

Keywords: chromium, composition, doping (additives), hot isostatic pressing, microstructure, oxidation, protective coatings, substrates

T. Murakami, S. Sasaki, K. Ito, H. Inui, and M. Yamaguchi, Inst. of Mech. Systems Engineering, Natl. Inst. Adv. Indust. Sci./T., Tsukuba, Ibaraki 305-8564, Japan. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(3), 2003, pp. 2557-2562 [in English]. ISSN 0255-5476.

Oxidation resistance coating for niobium-base structural composites. Oxidation behavior of aluminum-rich $Mo(Si,Al)_2$-base alloys, which is a candidate material for the oxidation-resistant coating on niobium-base structural composites, were investigated by thermogravimetry. The $Mo(Si,Al)_2$-base alloys containing $Mo_5(Si,Al)_3$ up to about 10 vol.% exhibits excellent oxidation resistance at temperatures ranging from 780 to 1580 K, particularly at 1580 K due to continuous Al_2O_3 layer development. To evaluate the applicability of the $Mo(Si,Al)_2$-base coating, plasma spraying on niobium-base composites were undertaken. However, interface reaction layer was found to form during the following heat treatment. Preparation of $Mo(Si,Al)_2/Al_2O_3$/Nb layered structures via powder metallurgical process was attempted to preclude diffusion reaction between coating and substrate.

Keywords: coatings, diffusion, heat treatment, oxidation resistance, plasma spraying, powder metallurgy, thermogravimetric analysis

T. Tabaru, K. Shobu, J.H. Kim, H. Hirai, and S. Hanada, Inst. for Struct./Eng. Materials, Natl. Inst. Adv. Indust. Sci./T., Tosu, Saga 841-0052, Japan. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(3), 2003, pp. 2581-2586 [in English]. ISSN 0255-5476.

Structure and electrochemical behavior of plasma sprayed LSGM electrolyte films. An intermediate temperature solid oxide fuel cell (SOFC) electrolyte film of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ (LSGM) was fabricated using a plasma spray process. The microstructure and phase were investigated using x-ray diffraction (XRD) and scanning electron microscopy (SEM). The electrochemical behavior of the thermal sprayed LSGM film was investigated using electrochemical impedance spectroscopy (EIS). The study indicates that thermal spray can deposit a dense LSGM layer. It was found that the rapid cooling in the thermal process led to an amorphous or poor crystalline LSGM deposited layer. This amorphous structure has a significant effect on the performance of the cell. Crystallization of the deposited LSGM layer was observed during annealing between 500 and 600 °C. After annealing at 800 °C, the ionic

conductivity of the sprayed LSGM layer can reach the same level as that of the sintered LSGM.

Keywords: annealing, conductive films, crystal microstructure, crystallization, ionic conduction in solids, lanthanum compounds, phase composition, plasma applications, scanning electron microscopy, solid oxide fuel cells, spectroscopic analysis, x-ray diffraction analysis

H. Zhang, X. Ma, J. Dai, S. Hui, J. Roth, T.D. Xiao, and D.E. Reisner, U.S. Nanocorp, Inc., Farmington, CT 06032. Cited: *Solid State Ionics 2002* (Conf. Proc.), P. Knauth, J.M. Tarascon, E. Traversa, and H. Tuller, Ed., 2-5 Dec 2002 (Boston, MA), Materials Research Society, pp. 491-496 [in English]. ISSN 0272-9172.

***In vivo* corrosion behavior of bioceramic, metallic, and bioceramic-metallic coated stainless steel dental implants.** Objectives: The most common metals and alloys used in dentistry may be exposed to a process of corrosion *in vivo* that make them cytotoxic. The biocompatibility of dental alloys is primarily related to their corrosion behavior. The aim of this work was to evaluate the corrosion behavior and thus the biocompatibility of the uncoated and coated stainless steels and compare the effect of type of coatings on corrosion behavior. Methods: Three types of coatings, hydroxyapatite (HA), titanium (Ti), and a double-layer HA/Ti on AISI 316L stainless steel were made. HA coating was produced using plasma spraying technique and Ti coating was made using physical vapor deposition process. In order to perform a novel double-layer composite coating, a top layer of HA was plasma sprayed over a physical vapor deposited Ti layer on AISI 316L stainless steel. Structural characterization techniques including XRD, SEM, and EDX were used to investigate the microstructure, morphology and crystallinity of the coatings. Electrochemical potentiodynamic tests were performed in physiological solutions in order to determine and compare the corrosion behavior of the coated and uncoated specimens as an indication of biocompatibility. Results: Double-layer HA/Ti coating on AISI 316L stainless steel had a positive effect on improvement of corrosion behavior. The decrease in corrosion current densities was significant for these coated specimens and was much lower than the values obtained for uncoated and single HA coated specimens. Ti coating on AISI 316L stainless steel also has a beneficial effect on corrosion behavior. The results were compared with the results of corrosion behavior of HA coated commercially pure titanium (cpTi) and uncoated cpTi. Significance: These results demonstrated that the double-layer HA/Ti coated 316L stainless steel can be used as an endodontic implant, and two goals including improvement of corrosion resistance and bone osteointegration can be obtained simultaneously.

Keywords: biocompatibility, ceramic materials, coating techniques, corrosion, dentistry, hydroxyapatite, metals, physical vapor deposition, plasma spraying, stainless steel

M.H. Fathi, M. Salehi, A. Saatchi, V. Mortazavi, and S.B. Moosavi, Department of Materials Engineering, Isfahan Univ. of Technology, Isfahan 84154, Iran. Cited: *Dent. Mater., 19*(3), May 2003, pp. 188-198 [in English]. ISSN 0109-5641.

Evaluation of corrosion on plasma sprayed and anodized titanium implants, both with and without bone cement. The corrosion behavior of titanium with vacuum plasma sprayed titanium coatings and with anodized surfaces, both with and without polymeric bone cement were evaluated. Electrochemical extraction tests were carried out with subsequent analysis of the electrolyte by ICP-MS in order to verify the authors' hypothesis of the ionic permeability of the polymer cement. The complexity of the situation resides in the existence of two interfaces: electrolyte/polymer and polymer/metal. The surface preparation (treatment of the surface) plays an important role in the corrosion resistance of titanium. The electrochemical magnitudes that were examined reveal that the plasma spray surfaces have the lowest corrosion resistance. The cement, in spite of having reduced electrical conductivity in comparison to metal, is an ionic transporter, and therefore capable of participating in the corrosion process. In the present study, the authors observed in fact crevice corrosion at the metal/cement interface. In the case of plasma spray surfaces, a process of diffusion of titanium particles in the electrolyte could accompany the crevice corrosion. In this study, the authors have shown that there is a corrosion process at the surface of the titanium through the cement that has as a consequence on the one hand the formation of titanium cations and on the other hand the growth of a passive layer on the titanium. In conclusion, the authors identified two principal factors that influence the corrosion process: the type of surface treatment for the titanium the ionic conductivity of the cement. There is indeed ionic transport through the cement, as evidenced by the presence of titanium in the electrolyte solution (ICP-MS analysis) and chloride at the surface of the titanium sample (EDX analysis). The authors show that the polymer cement is an ionic conductor and participates in the corrosion of the embedded titanium. The authors cannot deduce from their results, however, whether the polymer itself possesses corrosive properties. Long-term experiments will be necessary to study the degradation behavior of the polymer cement.

Keywords: anodic oxidation, bone cement, corrosive effects, extraction, inductively coupled plasma, mass spectrometry, plasma spraying, titanium

L. Reclaru, R. Lerf, P.-Y. Eschler, A. Blatter, and J.-M. Meyer, Groupe PX, PX Tech., La Chaux-de-Fonds 2304, Switzerland. Cited: *Biomaterials, 24*(18), Aug 2003, pp. 3027-3038 [in English]. ISSN 0142-9612.

Corrosion and Oxidation of Thermal Barrier Coatings

High-temperature oxidation and corrosion-resistant nanocrystalline coatings. Traditional high-temperature oxidation-resistant coatings are divided into three types: aluminide or modified aluminide coatings such as Cr-Al, Si-Al, and Pt-Al; MCrAlY (M = Fe, Co, and/or Ni) overlayer coatings and MCrAlY + Y_2O_3/ZrO_2 thermal barrier coatings. Characteristic of these coatings is that their compositions are very different from their substrate alloys. Protection comes from the higher aluminum content in the coating to form Al_2O_3 at high temperature. However, these coatings may be harmful to the mechanical properties of the alloys as a result of the interdiffusion or thermal mismatch between the coating and substrate. Recently, a new kind of coating has been developed: high-temperature oxidation-resistant and hot corrosion resistant nanocrystalline coating, the composition of which is the same as the substrate. The only difference is that the grain size of the coating is several orders of magnitude smaller than that of the substrate. The formation of protective Al_2O_3 scale is not from the high aluminum content, but from the grain-boundary diffusion. The main advantages of this kind of coating are that neither interdiffusion nor thermal mismatch exist between coating and substrate. The present paper reviews the high-temperature oxidation and hot corrosion resistant nanocrystalline coating with particular reference to the authors' own results.

Keywords: alumina, corrosion resistance, grain boundaries, grain size and shape, high-temperature operations, interdiffusion (solids), nanostructured materials, oxidation, thermal effects

F. Wang and S. Geng, State Key Lab. for Corrosion Protect, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China. Cited: *Surf. Eng., 19*(1), Feb 2003, pp. 32-36 [in English]. ISSN 0267-0844.

Hot corrosion behavior of yttria- and ceria-stabilized ZrO_2 thermal barrier coatings. Yttria-stabilized zirconia (YSZ; ZrO_2-8 wt.%Y_2O_3) and ceria-stabilized zirconia (CSZ; ZrO_2-25 wt.%CeO_2-2.5 wt.%Y_2O_3) thermal barrier coatings (TBCs) were fabricated by detonation gun spraying and tested hot corrosion by $NaVO_3$ at 900 °C. Hot corrosion properties of both TBCs and stabilizer behavior during the tests were compared. The microscopic degradation mechanism of zirconia-base TBCs by hot corrosion were discussed.

Keywords: corrosion, detonation, thermal barrier coatings, yttrium compounds

S.Y. Park, J.H. Kim, C.G. Park, M.C. Kim, and H.S. Song, Dept. of Mat. Sci. and Engineering, Pohang Univ. of Sci./Technol., Pohang 790-784, South Korea. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(3), 2003, pp. 2593-2598 [in English]. ISSN 0255-5476.

Etude par cartographies spectrales EDX de l'oxydation d'un systeme barriere thermique (Study by EDX spectral cartography of the oxidation of a thermal barrier coating). The degradation of a thermal barrier coating is closely linked to the microstructural and chemical stability of the complex system and of its interfaces. The coating in the as-received condition as well as the modifications during isothermal oxidation at 1100 °C were characterized using transmission electron microscopy and spectral mapping. Significant modifications (precipitation, phase transformations) occurred as a consequence of the oxidation process and interdiffusion phenomena.

Keywords: microstructure, transmission electron microscopy, turbomachine blades, zirconia

R. Molins, C. Guerre, and L. Remy, Ecl. Natl. Sup. des Mines de Paris, Centre des Materiaux, UMR CNRS 7633, Evry, France. Cited: *Rev. Metall., 100*(5), May 2003, pp. 507-512+v-viii [in French]. ISSN 0035-1563.

Evaluation of the corrosion resistance of thermal spray coatings under oxidant atmosphere in a fluid catalytic-cracking unit. The effectiveness of several thermal spray coatings for improving the corrosion resistance of a low-alloy steel was evaluated at 650 °C under two conditions: an oxidizing atmosphere in a fluid catalytic-cracking regenerator of a petrochemical unit and a simulated laboratory atmosphere. The high porosity present in all coatings studied in the present work, inherent to the thermal spray technique, allowed the penetration of gaseous species from the atmosphere into the substrate, leading to the formation of nonprotective oxides and sulfides, as well as internal oxidation, sulfidation, and nitridation. A protective alumina and/or chromia layer did not form, probably due to the relatively low temperature used in both the real and simulated conditions. Characterization of the phases present in the oxidized layer was carried out by x-ray diffraction (XRD), optical microscopy (OM), and scanning electron microscopy (SEM) with x-ray energy-dispersive analysis (EDS).

Keywords: coatings, energy dispersive spectroscopy, fluid catalytic cracking, optical microscopy, scanning electron microscopy, x-ray diffraction analysis

F. Rizzo, M. Monteiro, M.F. Lopes, I. Caminha, C. Zeng, and M. Piza Paes, Pont. Univ. Catolica Rio de Janeiro, Depto. de Cie. dos Materiais, Gavea, RJ, CEP 22 453-900, Brazil. Cited: *Oxid. Met., 57*(3-4), April 2002, pp. 323-338 [in English]. ISSN 0030-770X.

Corrosion of High-Velocity Oxyfuel Coatings

Importance of the adhesion of HVOF sprayed coatings for aqueous corrosion resistance. Importance of coating adhesion in an aqueous corrosion environment was studied experimentally. Tensile adhesion strength of HVOF sprayed 316L stainless steel and Hastelloy C coatings were tested in as-sprayed condition as well as after immersion in seawater. It was found that the adhesion strength of the stainless steel coatings degraded rapidly, whereas that of the Hastelloy coatings remained almost intact. Specimens with an artificial defect were also immersed in seawater. The cross-sectional observation after the test revealed that the corrosion at the coating/substrate interface proceeded much faster with the stainless steel coating as compared to the nickel-base alloy coating. A model experiment to simulate the galvanic corrosion of a coating/substrate couple was carried out, and no significant difference in the galvanic current density was found between the two coatings when coupled with the steel substrate. The tightness of the coating-substrate interface was then tested with a fluorescent dye penetration test. The dye could penetrate the boundary between the stainless steel coating and the substrate, whereas the boundary between the nickel-base alloy coating and the substrate was so tight that no penetration occurred. The penetration behavior of the dye into the microgaps at the coating/substrate boundary was discussed from the viewpoint of classical Washburn-Rideal theory applied to a model of capillary flow between a pair of parallel circular disks. It was concluded that such microgaps between the coating and substrate must be eliminated for these barrier-type coatings to be used in corrosive environments. Heat treatment was highly effective for suppressing the preferential corrosion at the coating/substrate boundary.

Keywords: adhesion, capillary flow, corrosion resistance, heat treatment, interfaces (materials), mathematical models, nickel alloys, stainless steel, substrates, tensile strength

S. Kuroda, J. Kawakita, T. Fukushima, and S. Tobe, Natl. Institute for Materials Sci., Tsukuba 305-0047, Japan. Cited: *Mater. Trans., 44*(3), March 2003, pp. 381-388 [in English]. ISSN 1345-9678.

Effect of an enamel coating on the oxidation and hot corrosion behavior of an HVOF-sprayed Co-Ni-Cr-Al-Y coating. The oxidation and hot corrosion behavior of a Co-Ni-Cr-Al-Y coating produced by high-velocity oxygen fuel (HVOF) with and without an enamel coating were investigated in air at 900 °C and in molten 75 wt.% NaCl + 25 wt.% Na_2SO_4 at 850 °C. The results show that the enamel coating possesses excellent hot corrosion resistance in the molten salt, in comparison with the HVOF sprayed Co-Ni-Cr-Al-Y coating alone. In the hot corrosion test, breakaway corrosion did not occur on the samples with the enamel coating, and the composition of the enamel did not significantly change. The oxidation resistance of the Co-Ni-Cr-Al-Y coating, which had good adhesion, was also improved by the enamel coating.

Keywords: adhesion, cobalt compounds, composition, corrosion, fuels, oxidation, sodium chloride

D. Xie, Y. Xiong, and F. Wang, Stt. Key Lab. for Corros./Protection, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China. Cited: *Oxid. Met., 59*(5-6), June 2003, pp. 503-516 [in English]. ISSN 0030-770X.

Erosion and Abrasion Resistance

Effect of ceria on the erosion resistance of HVOF thermal sprayed NiAl intermetallic coatings. The influence of rare earth ceria on the mechanical and erosion properties of nickel aluminides (NiAl) intermetallic coatings was investigated. It was found that addition of ceria reduced the tendency of brittle peeling of NiAl intermetallic coatings during thermal spraying. The NiAl intermetallic coatings containing ceria exhibited increase in their erosion resistance as compared with pure NiAl coatings due to improved mechanical properties and physical integrity.

Keywords: brittleness, cerium compounds, elastic moduli, energy dispersive spectroscopy, erosion, microstructure, nickel compounds, protective coatings, scanning electron microscopy, spraying, x-ray diffraction

Y. Wang and W. Chen, Department of Chemical Engineering, Univ. of Alberta, Edmonton, Alta., T6G 2G6, Canada. Cited: *J. Mater. Sci. Lett., 22*(11), 1 June 2003, pp. 845-848 [in English]. ISSN 0261-8028.

HVOF fuel coating and surface treatment for enhancing droplet erosion resistance of steam turbine blades. This paper describes the water droplet erosion characteristics of high-velocity oxygen fuel sprayed (HVOF) coated and laser-hardened 12Cr steels along with steels and titanium alloys used in steam turbine blades at two different energy fluxes. For droplet erosion study, round samples as per ASTM G73-98 were used. At low energy flux, the HVOF coated 12Cr steel performed much better than 12Cr and 13Cr-4Ni steels. This is due to integrity of hard carbide particles in cobalt chrome matrix and its ability to absorb shocks due to high hardness of the carbide particles. During incubation as well as in the long run, laser-hardened 12Cr steel performed exceptionally well followed by 17Cr-4Ni "PH" and heat treated 12Cr steel. From the experimental study, it appears that ultimate and modified resilience of materials play significant role to combat droplet erosion. Droplet erosion test results of all these materials and HVOF coating along with their properties and scanning electron micrographs are reported and discussed in this paper.

Keywords: erosion, hardening, laser applications, steam turbines, steel, surface treatment, turbomachine blades

V. Arya and B.S. Mann, Surface Coatings and Treatment Lab., BHEL, Corporate R and D Division, Vikasnagar, Hyderabad 500093, India. Cited: *Wear, 254*(7-8), April 2003, pp. 652-667 [in English]. ISSN 0043-1648.

Hot erosion behavior of two new iron-base coatings sprayed by HVCC process. The hot erosion resistance of two new iron-based coatings sprayed by high velocity continuous-combustion (HVCC) process was studied using a nozzle-type elevated-temperature erosion tester. The coating samples were prepared under as-deposited, post heat treated, and sealed plus heat treated conditions. For comparison, AISI 1018 low-carbon steel, two existing HVCC iron-base coatings, and two high-velocity oxygen fuel (HVOF) sprayed carbide-cermet coatings were also tested. The morphology of samples was examined by light microscopy and scanning electron microscopy (SEM) with energy-dispersive spectroscopy (EDS). It was found that these two new iron-base coatings exhibited better erosion behavior than the two existing iron-base coatings. One of the new coatings showed the same level of erosion resistance as the HVOF chromium carbide-cermet coating, but with much lower cost. In addition, heat treatment at 500 °C and sealing treatment can improve erosion resistance of these two new coatings remarkably. The erosion mechanism of coatings was also discussed and compared.

Keywords: coatings, energy-dispersive spectroscopy, erosion, gas fuels, heat treatment, iron, nozzles, scanning electron microscopy

B.Q. Wang, FBE Technology Center, Metalspray United, Midlothian, VA 23112. Cited: *Wear, 255*(1-6), Aug/Sept 2003, pp. 102-109 [in English]. ISSN 0043-1648.

Fatigue and Fracture

Fretting fatigue properties of WC-Co thermal sprayed NiCrMo steel. Fretting fatigue tests of NiCrMo steel (JIS SNCM439) sprayed with tungsten carbide with additive of 12% Co (WC-Co) by high-velocity oxygen fuel (HVOF) were carried out to study the effect of WC-Co coating on fretting fatigue behavior. Since the fatigue strength of the present alloy steel was reduced to about 27% by the effect of fretting, fretting fatigue strength was improved by approximately 30% by WC-Co spraying onto the specimen. The tangential force coefficient, which is tangential force measured during the fretting fatigue tests divided by contact load, behaviors of WC-Co sprayed specimen were different from those of the nonsprayed specimen. Especially, the tangential force of WC-Co specimen in an early stage of the test indicated significant low value compared with that of nonsprayed specimen, and this resulted from good wear resistance of WC-Co layer. Therefore, the initiation of a fretting crack in case of WC-Co sprayed specimen delayed, and crack propagation rate was lower than that of nonsprayed specimen. These were main reasons for the improvement of fretting fatigue strength by WC-Co spray.

Keywords: additives, crack propagation, fretting corrosion, nickel alloys, spray steelmaking, steel, strength of materials, thermal effects, tungsten carbide, wear resistance

M. Okane, K. Shiozawa, M. Hiki, and K. Suzuki, Department of Mechanical Engineering, Faculty of Engineering, Toyama Univ., Toyama 930-8555, Japan. Cited: *Fretting Fatigue: Advances in Basic Understanding and Applications,* STP 1425, S.E. Kinyon, D.W. Hoeppner, and Y. Mutoh, Ed., 15-18 May 2001 (Nagaoka), American Society for Testing and Materials, pp. 385-399 [in English]. ISSN 1040-3094.

The influence of bondcoat and oxide layer on the debonding of graded coatings. In this study, the axisymmetric interface crack problem in a layered medium that consists of a substrate, bondcoat, thermally grown oxide, and a graded topcoat is considered. The topcoat is assumed to be under thermally or mechanically induced compressive stresses. By using a nonlinear continuum theory the instability and postbuckling problems are solved, the crack opening displacement, the strain energy release rate, and the stress-intensity factors are calculated, and the results are compared with that obtained from the von Karman plate theory.

Keywords: approximation theory, buckling, compressive stress, crack propagation, debonding, interfaces (materials), nonlinear systems, oxides, strain rate, stress-intensity factors, substrates, thermal expansion

F. Erdogan and T.-C. Chiu, Mechanical Eng. and Mechanics, Lehigh Univ., Bethlehem, PA 18015. Cited: China. Cited: Proc. Seventh International Symposium on Functionally Graded Materials, 15-18 Oct 2002 (Beijing), *Mater. Sci. Forum, 423-425,* 2003, pp. 523-528 [in English]. ISSN 0255-5476.

Fatigue behavior of a 4140 steel coated with a Colmonoy 88 alloy applied by HVOF. The fatigue behavior of a quenched-and-tempered AISI 4140 steel has been investigated, both uncoated and after coating with a deposit of NiCrBSiW alloy (Colmonoy 88) of approximately 240 to 250 μm in thickness, applied by high-velocity oxyfuel (HVOF) thermal spraying. Previous to the deposition of the Colmonoy 88 alloy, an intermediate layer of a NiMoAl alloy known commercially as Metco 447 of approximately 60-70 μm was also applied by means of HVOF thermal spraying in order to avoid grit blasting of the

steel substrate with alumina particles. It has been determined that coating this steel substrate with such a deposit leads to a significant reduction in fatigue properties in comparison with the uncoated substrate. The reduction in fatigue life, evaluated in the alternating stress range of 544 to 598 MPa has been found to achieve up to 99.8%, whereas, the decrease in fatigue limit was approximately 43%, that is, 220 MPa below the fatigue limit of the uncoated substrate. It has been shown that such a decrease in fatigue properties can be attributed almost entirely to the presence of both the intermediate bonding layer and coating, rather than to the inclusion of the coating thickness in the computation of the alternating stress applied to the material. The correction of the specimen diameter by subtracting the coating thickness indicates that the drop in fatigue life is still of approximately 99.2%, whereas, the fatigue limit is decreased by 37%. The interpretation of the stress-life curves, together with fractographic analyses conducted on selected samples tested at both low and elevated alternating stresses indicates that the fatigue cracks are nucleated at the surface of the coating and subsequently transferred to the intermediate bonding layer and the substrate. It is believed that at the substrate/bonding-layer interface such cracks bifurcate and propagate both along the interface and toward the substrate. The intersection of the cracks that run along the interface with other circumferential cracks leads to extensive delamination, fracture, and complete separation of the coating from the substrate in some sections of the samples.

Keywords: alumina, fatigue of materials, fractography, fracture, inorganic coatings, interfaces (materials), quenching, stress analysis, tempering

E.S. Puchi Cabrera, J.A. Berrios-Ortiz, J. Da-Silva, and J. Nunes, Sch. of Metallurgical Eng./Mat. Sci., Faculty of Engineering, Universidad Central de Venezuela, Los Chaguaramos, Caracas 1045, Venezuela. Cited: *Surf. Coat. Technol., 172*(2-3), 29 July 2003, pp. 128-138 [in English]. ISSN 0257-8972.

Contact fatigue failure modes in hot isostatically pressed WC-12%Co coatings. The objective of this experimental study was to investigate the influence of the posttreatment, hot isostatic pressing (HIP), on the rolling contact fatigue (RCF) performance of thermal spray (WC-12%Co) coatings. Thermal spray coatings were deposited using a JP5000 high-velocity oxyfuel (HVOF) system in three different thicknesses on the surface of 440-C steel substrate cones to vary the depth of the shear stress within the Hertzian stress field. The furnace temperature during the HIP process was varied at 850 and 1200 °C. RCF tests were conducted using a modified four-ball machine under identical tribological conditions of contact stress, configuration, and lubrication. Surface observations were made using scanning electron microscopy (SEM) and light microscopy. Results of this preliminary study, which is the first of its kind in published literature to evaluate the RCF of HIP cermet coatings, indicate that variation in HIP temperature can have a significant influence on the delamination resistance of a coating. These results are discussed to comprehend the performance and ascertain the fatigue failure modes in HIP HVOF coated rolling elements. Apart from comparing the failure modes between HIP and as-sprayed coatings, results indicate that by increasing the HIP temperature to 1200 °C and maintaining full-film lubrication, it is possible to achieve a fatigue life in excess of 70 million stress cycles without failure in relatively thin (50 μm) cermet coatings. Coating failure was attributed to maximum shear stress occurring either at the coating/substrate interface or within the coating microstructure, resulting in delamination due to cyclic loading.

Keywords: cyclic loads, electric conductivity, fatigue of materials, optical microscopy, scanning electron microscopy, sprayed coatings, tribology

S. Stewart and R. Ahmed, Heriot-Watt Univ., Sch.of Eng./Physical Sciences, Ricarton, Edinburgh EH14 4AS, U.K. Cited: *Surf. Coat. Technol., 172*(2-3), 29 July 2003, pp. 204-216 [in English]. ISSN 0257-8972.

Tensile damage evolution behavior in plasma sprayed thermal barrier coating system. Cracking and fracture behavior in a plasma sprayed thermal barrier coating system were evaluated using a sandwiched specimen under uniaxial tensile stress combined with an in situ microscope observation. It was found that initial crack initiation and transverse crack propagation occurred in the topcoat layer. The number of transverse cracks increased rapidly and then saturated with an increase in tensile strain. After the saturation of the multiple cracks, the cracks passed through the interface between the topcoat and bondcoat, and propagated in the bondcoat. Finally, decohesion occurred at the bondcoat/substrate interface when the transverse cracks reached the interface. A model was proposed to describe the fracture processes.

Keywords: crack propagation, interfaces (materials), plasma spraying, stress analysis, thermal barrier coatings

L. Qian, S. Zhu, Y. Kagawa, and T. Kubo, Institute of Industrial Science, The Univ. of Tokyo, Meguro-ku, Tokyo 153-8505, Japan. Cited: *Surf. Coat. Technol., 173*(2-3), 22 Aug 2003, pp. 178-184 [in English]. ISSN 0257-8972.

Evolution of fatigue crack corrosion from surface irregularities. A moving boundary model is presented for crack nucleation and growth from surface flaws. It concerns chemical attack that results in material dissolution. A controlling mechanism for evolution is the rupture of a brittle corrosion-protective film that is built up along the corroding surface. The evolution rate is a function of the degree of protective film damage caused by the surface straining. The problem is formulated for an elastic body containing a single and double pits. Low-frequency cyclic loading is considered. Numerical solution is proposed. The behavior of a growing crack and of two competing cracks are described. Stages of incubation, blunting, and steady-state growth characterize a single crack evolution. The steady-state growth rate is found independent of the initial geometry. Stages of independent growth, interactive growth, and arrest of one crack characterize the evolution of two competing cracks. The lengths of the arrested cracks are presented as functions of the ratio between the pit depth for a series of different distances between the pits. It is emphasized that the solutions correspond to a homogeneous material. Further work is required to account for the material microstructure.

Keywords: brittleness, crack propagation, cyclic loads, microstructure, nucleation, protective coatings, strain, surface structure

A.P. Jivkov, Malmo Univ., Division of Solid Mechanics, Malmo SE-205 06, Sweden. Cited: *Theor. Appl. Fract. Mech., 40*(1), July/Aug 2003, pp. 45-54 [in English]. ISSN 0167-8442.

Foreign Object Damage

Foreign object damage in a thermal barrier system: Mechanisms and simulations. Experimental studies have been performed of foreign object damage (FOD) imparted to a thermal barrier system under conditions representative of those found in a turbine engine. The subsurface damage has been characterized by using the focused ion beam (FIB) imaging system. The characterization reveals changes in the thermal barrier coating (TBC), caused by particle impact, that confirm and elaborate previous observations of FOD. These features include a permanent impression, a zone of densification, shear bands penetrating from the impact site to the interface with the bondcoat, and delamination cracks extending away from the impact in the TBC adjacent to the interface. The dimensions of these features have been reported. A simulation procedure has been devised and implemented. The simulations have been performed in conjunction with a new nondimensional analysis that allows the impact and material variables to be grouped into the smallest possible parameter set needed to characterize the stresses and projectile velocities, as well as the impression and densification zone dimensions. This parameterization provides explicit results for the stresses and displacements that arise as the projectile characteristics and material properties are varied over a range applicable to FOD in gas turbines. A scaling relation has been derived from the stress field and the penetration that relates the length of the interface delamination to the impact and material variables. A comparison of the simulations with the measurements indicates that the unknown impact velocity of the projectile can be ascertained from the penetration depth if the yield strength is known and vice versa. With this information, the scaling relation for the size of the interface delamination indicates consistency with the measured cracks. The implication is that delamination can be suppressed by lowering the high-temperature hardness of the TBC and by increasing its toughness.

Keywords: computer simulation, cracks, delamination, densification, gas turbines, hardness, interfaces (materials), ion beams, stresses, surface phenomena, toughness, yield stress

X. Chen, R. Wang, N. Yao, A.G. Evans, J.W. Hutchinson, and R.W. Bruce, Division of Eng./Applied Sci., Harvard Univ., Cambridge, MA 02138. Cited: *Mater. Sci. Eng. A, 352*(1-2), 15 July 2003, pp. 221-231 [in English]. ISSN 0921-5093.

Friction and Wear

Effect of iron content on wear resistance of thermal sprayed Al-17Si-XFe alloy coating on A6063 aluminum alloy substrate. To improve the wear resistance of aluminum alloy, Al-17 mass% Si- X mass% Fe aluminum alloy powders with different iron content from 5 to 30 mass% and Al-50 mass% Fe alloy powders were thermal sprayed on aluminum alloy A6063 substrate by a low-pressure plasma spraying. Microstructure and wear property of the coatings were evaluated. The most beneficial coating can be obtained with Al-17 mass% Si-10 to 15 mass% Fe alloy powders, showing good wear resistance, four times of the substrate and low friction coefficient, approximately 0.4 without cracking and peeling in the coating and the interface between the substrate.

Keywords: aluminum alloys, crack initiation, friction, iron, peeling, plasma spraying, wear resistance

K. Nakata and M. Ushio, Joining and Welding Research Inst., Osaka Univ., Ibaraki, Osaka 567-0047, Japan. Cited: *Surf. Coat. Technol., 169-170*(1), 2 June 2003, pp. 443-446 [in English]. ISSN 0257-8972.

Assessment of wear performance of flame sprayed and fused nickel-base coatings. Characterization of the flame sprayed and furnace fused NiCrBSiC alloy coatings with two different carbon contents and 15-45 wt.% WC-Co addition is described in terms of microstructure, microhardness, and differential thermal analysis. Microstructural development of these coatings before and after fusing treatment is discussed to identify the precipitates in the coatings. Optimal fusing conditions (time and temperature) for wear testing sample were investigated in terms of microhardness and porosity of the coatings. Wear performance of these coatings was also investigated by two- and three-body abrasive and dry sliding wear experiments. The coating of 35% WC

with NiCrBSiC is showing the best quality (the highest hardness and the lowest porosity). However, 25% WC addition is showing the best wear resistance for Sugaru abrasive wear test, while 40% WC addition is showing the best wear resistance for DSRW (dry sand rubber wheel) abrasive wear test. It is also shown that the dry sliding wear resistance of the 20% (and/or 30%) WC-NiCrBSiC composite coating is almost 10 times better than that of the quenched and tempered JIS SUJ2 bearing steel.

Keywords: differential thermal analysis, flame spraying, hardness, microstructure, nickel alloys, porosity, precipitation (chemical), quenching, tempering, wear of materials

H.-J. Kim, S.-Y. Hwang, C.-H. Lee, and P. Juvanon, Res. Inst. of Indust. Sci./Technol., Welding Research Center, Pohang 790-600, South Korea. Cited: *Surf. Coat. Technol., 172*(2-3), 29 July 2003, pp. 262-269 [in English]. ISSN 0257-8972.

Wear of plasma sprayed nanostructured zirconia coatings against stainless steel under distilled-water conditions. The friction and wear properties of plasma sprayed nanostructured and traditional zirconia coatings against stainless steel were investigated with a sliding, reciprocating, and vibrating test machine under water-lubricated conditions. The counterface was a 10 mm diameter AISI 316 stainless steel ball. It was found that the plasma sprayed nanostructured zirconia coating possessed better wear resistance than traditional zirconia coating. The wear rates of the nanostructured zirconia coatings are in the range from one-fourth to four-fifths of the traditional zirconia coating under loads ranging from 20 to 50 N. The plasma sprayed nanostructured zirconia coating also reduces wear rate of the friction pair materials. The higher wear resistance of the plasma sprayed nanostructured zirconia coating is attributed to its enhanced cohesion, improved microhardness and homogenous microstructure. The wear mechanisms of nanostructured and traditional zirconia coatings under water-lubricated conditions are discussed.

Keywords: friction, hardness, microstructure, nanostructured materials, plasma spraying, stainless steel, wear resistance, zirconia

H. Chen, C. Ding, P. Zhang, P. La, and S.W. Lee, Plasma Spray Laboratory, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China. Cited: *Surf. Coat. Technol., 173*(2-3), 22 Aug 2003, pp. 144-149 [in English]. ISSN 0257-8972.

Comparison of the tribological properties of an ion sulfurized coating and a plasma sprayed FeS coating. The microstructures and tribological behaviors of ferrous sulfide solid lubrication coatings prepared by low-temperature ion sulfuration and plasma sprayed techniques were investigated against the 52 100 steel balls. The friction and wear tests were performed with different parameters of the time and velocity under oil lubrication. The results demonstrated the influence of the coating microstructures on the frictional and wear behaviors. The friction reduction and wear resistance of ion sulfurized coating were better than that of plasma sprayed FeS coating; however, the antiscuffing behavior of the latter coating was better than that of the former. The difference of the tribological properties of two coatings can be attributed to their different forming mechanisms and microstructures. A SEM equipped with EDX and XRD were employed to analyze the morphologies and phase structures. The scratching apparatus was utilized to measure the bonding strength between coatings and substrate.

Keywords: energy dispersive spectroscopy, friction, low-temperature effects, microstructure, morphology, plasma spraying, scanning electron microscopy, sprayed coatings, substrates, tribology, wear of materials, x-ray diffraction analysis

H.-D. Wang, D.-M. Zhuang, K.-L. Wang; and J.-J. Liu, Department of Mechanical Engineering, Tsinghua Univ., Beijing 100084, China. Cited: *Mater. Sci. Eng. A, 357*(1-2), 25 Sept 2003, pp. 321-327 [in English]. ISSN 0921-5093.

An experimental study of the wear performance of NiCrBSi thermal spray coatings. The increasingly extreme conditions in which components are required to work have led to the use of thermal coatings in a lot of industrial applications. Special attention has been paid to NiCrBSi alloys since they provide a high wear and corrosion resistance at high temperatures. In this communication, an experimental program has been carried out to analyze the influence of several factors such as load, temperature, presence of reinforcement particles, and the type of thermal spray technique on the wear behavior of a NiCrBSi alloy. Specimens were tested in a reciprocating pin-on-plate wear machine able to select loads ranging from 50 to 200 N and temperatures up to 500 °C. Four sets of specimens were tested varying the composition (with the presence or not of WC in the powders) and the type of thermal spraying technique (plasma or flame + fusion). A statistical analysis based on the design of experiments methodology was applied to identify the main significant effects and interactions.

Keywords: corrosion resistance, nickel alloys, reinforcement, thermal effects

J. Rodriguez, A. Martin, R. Fernandez, and J.E. Fernandez, High Sch. of Exp. Sciences/Technol., Universidad Rey Juan Carlos, Madrid E28933, Spain. Cited: *Wear, 255*(7-12), Aug/Sept 2003, pp. 950-955 [in English]. ISSN 0043-1648.

Hardness and (Visco)elastic Properties of Thermal Barrier Coatings

Effect of uniaxial pressure on ultrasound velocities and elastic moduli in plasma sprayed ceramics. Microcracks and thin voids in plasma sprayed ceramics are known to be responsible for elastic anisotropy and for small values of elastic stiffness constants (measured at small stresses), compared with well-sintered materials. The increase of ultrasound velocities with increasing uniaxial pressure up to 300 MPa in three types of plasma sprayed ceramics was measured in two directions. The corresponding elastic stiffnesses increased from 1.4 to 4.7 times. The experimental results were explained by closing of intrasplat microcracks and intersplat thin voids by uniaxial pressure.

Keywords: elastic moduli, plasma spraying, stiffness, ultrasonic applications

M. Landa, F. Kroupa, K. Neufuss, and P. Urbanek, Institute of Thermomechanics, ASCR, 182 00 Prague 8, Czech Republic. Cited: *J. Therm. Spray Technol., 12*(2), June 2003, pp. 226-233 [in English]. ISSN 1059-9630.

High-Velocity/Electric Arc Sprayed Coatings

Microstructure and properties of high-velocity arc spraying coatings. The high-velocity arc spray (HVAS) coating is investigated and compared with regular arc spray coatings. The wear properties of three HVAS coatings are also tested. Results show that HVAS coatings have better comprehensive mechanical properties and quality. For the HVAS coating, the adhesion strength and the relative wear resistance increase respectively by 40% and more than two times than those of regular arc spray coatings.

Keywords: adhesion, mechanical properties, microstructure, wear resistance

X. Liang, B. Xu, and S. Ma, Acad. of Armored Forces Eng., Beijing 100072, China. Cited: *Jixie Gongcheng Xuebao/Chin. J. Mech. Eng., 39*(2), Feb 2003, pp. 119-122 [in Chinese]. ISSN 0577-6686.

Hydroxyapatite Biomaterials

Plasma sprayed graded titanium-hydroxyapatite coatings. A series of graded titanium-hydroxyapatite (HA) coatings have been produced by single gun plasma spray technology, and their performance was compared with that of pure HA coating. The results show that deformed HA and titanium particles exhibit an alternate distribution in respective networks formed within the coatings. In comparison with a pure HA coating, fewer cracks appeared on the surface of the graded coatings, and the shear bond strength was increased by 50 to 80%. The graded coating with two interlayers and a thin outer HA layer contained crystalline HA, an amorphous phase, α-tricalcium phosphate (TCP), β-TCP, tetracalcium phosphate (TTCP), TiO_2, and TiN; while no Ti-HA compounds were formed. As compared with pure HA coating, the graded coating contained more decomposed phases TCP and TTCP, resulting from titanium catalyzing HA decomposition.

Keywords: coatings, cracks, crystalline materials, decomposition, deformation, plasma spraying

Y.P. Lu, R.F. Zhu, S.T. Li, Y.J. Song, M.S. Li, and T.Q. Lei, Sch. of Mat. Science and Engineering, Shandong Univ., Jinan 250061, China. Cited: *Mater. Sci. Technol., 19*(2), 1 Feb 2003, pp. 260-263 [in English]. ISSN 0267-0836.

Investigation on the bonding behavior of hydroxyapatite coating to hard tissue. Hydroxyapatite coating was applied to the surface of titanium alloy employing plasma spray technology. An animal model was employed to investigate the biocompatibility of the hydroxyapatite coating. It is revealed by push-out test that the hydroxyapatite coating greatly prompts the bonding strength between implant and surrounding hard tissues. Scanning electron microscopy observation shows that a biological fixation is created between bone and hydroxyapatite, while a layer of fiber is formed between noncoated titanium implant and surrounding bone. The different interfacial fixation is the main factor, which causes great difference in interfacial strength.

Keywords: bonding, hydroxyapatite, sprayed coatings

D.-L. Mao, H.-P. Cao, C.-K. Chang, and Y.-F. Gu, Sch. of Mat. Sci. and Eng., Shanghai Jiaotong Univ., Shanghai 200030, China. Cited: *Shanghai Jiaotong Daxue Xuebao/J. Shanghai Jiaotong Univ., 37*(2), Feb 2003, pp. 264-268 [in Chinese]. ISSN 1006-2467.

Bioceramic hydroxyapatite at high pressures. A bioceramic hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ polycrystalline sample was studied. The study was performed under high pressures in a diamond anvil cell to investigate its structural, electrical, and mechanical properties under compression. The study demonstrated that a fully dense and translucent hydroxyapatite sample was attained above 10 GPa at 300 K.

Keywords: anisotropy, ceramic materials, compaction, diamonds, high-pressure effects, plasma spraying, polycrystalline materials, x-ray diffraction analysis

N. Velisavljevic and Y.K. Vohra, Department of Physics, Univ. of Alabama at Birmingham (UAB), Birmingham, AL 35294-1170. Cited: *Appl. Phys. Lett., 82*(24), 16 June 2003, pp. 4271-4273 [in English]. ISSN 0003-6951.

Microstructure of Thermal Barrier Coatings

Failure aspects of thermal barrier coatings. The paper describes aspects of thermal barrier coating (TBC) microstructure and the physical and mechanical properties that they influence. The stress-strain behavior of air plasma sprayed (APS) TBCs is discussed, including the role of residual stresses. Failure phenomena as well as the TMF behavior of TBC coated nickel-base superalloys are described. The role of bondcoat oxidation on TBC life is discussed as well as some mechanical properties of vacuum plasma sprayed MCrAlY-bondcoatings. Finally, life-prediction methodologies are addressed and discussed in terms of a critical strain accumulation concept. From this is derived an equation that covers time-dependent effects such as bondcoat oxidation and sintering. The paper concludes with a brief summary of the evolution of TBCs in aero and industrial gas turbines, and the failure modes in each. In particular the increased importance of erosion, in industrial gas turbines, due to water injection is highlighted.

Keywords: chromium alloys, failure (mechanical), gas turbines, microstructure, oxidation, plasma spraying, residual stresses, sintering, strain, stresses, superalloys

L. Singheiser, R. Steinbrech, W.J. Quadakkers, and R. Herzog, Forschungszentrum Julich GmbH, D-52425 Julich, Germany. Cited: *Mater. High Temp., 18*(4), 2001, pp. 249-259 [in English]. ISSN 0960-3409.

Microstructural features of mechanical failure in thermal barrier coating systems under static loadings. In order to clarify qualitatively and quantitatively the failure mechanism of plasma sprayed thermal barrier coating (TBC) systems from the microstructural viewpoint, in situ observation of the mechanical failure behavior was conducted for TBC systems under the static loadings at ambient temperature; as the most fundamental aspect, by means of an optical microscopy. Several kinds of TBC systems were prepared by using different sorts of ceramic coating materials. Mechanical tensile loading or compressive loading was gradually applied to the plate shape of TBC specimen using a four-point bending test methodology. It was found that the tensile failure behavior of TBC systems depends strongly on the topcoat microstructures as well as heat treatment after the plasma spraying. The compressive failures were also found rather incidental and depended on the strength of topcoat at the interfacial region. Among different TBC systems, those with the finely segmented topcoat exhibited a good spalling resistance.

Keywords: ceramic coatings, compression testing, crack initiation, crack propagation, crystal microstructure, failure analysis, optical microscopy, plasma spraying, temperature, tensile testing

S. Takahashi, M. Yoshiba, and Y. Harada, Department of Mechanical Engineering, Graduate School of Engineering, Tokyo Metropolitan Univ., Tokyo 192-0397, Japan. Cited: *Mater. High Temp., 18*(2), 2001, pp. 125-130 [in English]. ISSN 0960-3409.

Nanostructured Coatings

Improved interfacial mechanical properties of Al_2O_3-13wt.%TiO_2 plasma sprayed coatings derived from nanocrystalline powders. The interfacial toughness of two types of Al_2O_3-13wt.%TiO_2 plasma sprayed ceramic coatings on steel substrates—"conventional" and "nano"—has been measured using the Rockwell indentation method. The interfacial toughness of the "conventional" coating and the "nano" coating is found to be 22 and 45 J/m^2, respectively. The "conventional" coating, which was prepared using a fused feedstock powder available commercially, has a microstructure consisting primarily of fully molten (FM) and solidified "splats." The feedstock powder for the "nano" coating comprised reconstituted agglomerates of nanocrystalline Al_2O_3 and TiO_2 powders. The microstructure of the "nano" coating, as characterized using scanning and transmission electron microscopy techniques, consists of regions of FM "splats" interspersed with partially molten (PM) rounded microstructural features. The substructure in these PM features (20-50 μm diameter) consists of α-Al_2O_3 grains (0.5-1 μm) surrounded by a TiO_2-rich amorphous phase. The FM/steel interfaces in both the "conventional" and the "nano" coatings are found to be cracked (before mechanical testing), whereas the PM/steel interfaces in the "nano" coating are found to be adherent. It is believed that the unique bimodal microstructure, together with the presence of the TiO_2-rich amorphous phase at the PM/steel interface, is responsible for the significantly improved interfacial toughness of the "nano" coating. The key differences in the failure modes in the two types coatings are also discussed, with reference to a simple model.

Keywords: amorphous materials, feedstocks, metallographic microstructure, nanostructured materials, plasma spraying, powders, transmission electron microscopy

P. Bansal, N.P. Padture, and A. Vasiliev, Department of Metallurgy Engineering, Institute of Materials Science, Univ. of Connecticut, Storrs, CT 06269-3136. Cited: *Acta Mater., 51*(10), 11 June 2003, pp. 2959-2970 [in English]. ISSN 1359-6454.

Microgrinding of nanostructured material coatings. This study is aimed at experimentally investigating the effect of microgrinding process on the surface finish, subsurface damage, and residual stresses of thermally sprayed nanostructured WC/12Co (n-WC/12Co), and Al_2O_3/13TiO_2 (n-Al_2O_3/13TiO_2) coatings. The material removal mechanisms are discussed. Surface textures are measured with stylus profilometry, scanning electronic microscopy (SEM), and atomic force microscopy (AFM) and analyzed using conventional methods and scale-sensitive fractal analysis. Residual stresses are measured with glancing incident x-ray diffraction (GIXD) technique that is capable of providing the depth profiles of residual stresses. Investigated is also grinding damage to the coatings.

Keywords: grinding (comminution), nanostructured materials, residual stresses, spraying, x-ray diffraction analysis

B. Zhang, X. Liu, C.A. Brown, and T.S. Bergstrom, Department of Mechanical Engineering, Univ. of Connecticut, Storrs, CT. Cited: *CIRP Ann. Manuf. Technol., 51*(1), 2002, pp. 251-254 [in English]. ISSN 0007-8506.

Adhesion of HVOF sprayed diamond-containing nanostructured composite coating. In the present paper, mechanical properties of HVOF sprayed diamonds containing aluminum oxide composite coating have been investigated. Crystallographic and morphologic texture was measured. Diamonds nanoparticles may improve fracture resistance of aluminum oxide based coating. Investigations of thermally sprayed coatings by the test revealed high accuracy, speed, and reliability of the test. It is also thought that the composite coatings will have better thermal conductivity and thermal shock resistance than that of aluminum oxide based coatings.

Keywords: adhesion, coatings, composite materials, deuterium, textures, thermal conductivity

M.V. Kireitseu and I. Nemerenco, Department of Mechanics, Inst. Mech./Mach. Reliability, Natl. Academy of Sciences of Belarus, Minsk 223052, Belarus. Cited: *Nanomaterials for Structural Applications* (Conf. Proc.), 2-6 Dec 2002 (Boston, MA), C.C. Berndt, T.E. Fischer, I. Ovid'ko, G. Skandan, and T. Tsakalakos, Ed., Materials Research Society, pp. 223-228 [in English]. ISSN 0272-9172.

Wear behavior of spray coatings based on nanocrystalline cermet powders. Wear behavior of spray coatings based on nanocrystalline cermet powders was studied. The microstructures of composite coatings containing nanocrystalline ceramic phases can be tailored with respect to optimal performance for particular applications. The results suggested that the homogeneous microstructure of nanostructured coatings with less priority should show good corrosion resistance.

Keywords: cermets, comminution, microstructure, nanostructured materials, tribology, wear of materials

T. Klassen, N. Eigen, X. Qi, F. Gartner, E. Aust, R. Bormann, and H. Kreye, GKSS Research Center Geesthacht GmbH, 21502 Geesthacht, Germany. Cited: *Surface Engineering in Materials Science II,* TMS Annual Meeting, 2-6 March 2003 (San Diego, CA), S. Seal, N.B. Dahotre, J. Moore, C. Suryanaryana, and A. Agarwal, Ed., The Surface Engineering Committee of the MPMD of TMS Minerals, Metals, and Materials Society, pp. 99-110 [in English].

Microstructure of alumina-3wt.% titania coatings by plasma spraying with nanostructured powders. The microstructure of plasma sprayed alumina-3wt.% titania coatings with the nanostructured powders was investigated by x-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The results showed that the nanostructured coating exhibited a bimodal microstructure: splat lamellae similar to the conventional coating and equiaxed grains originating from the starting feedstock. The splat lamellae consisted of γ-Al_2O_3 grains, and most of them were less than 200 nm in diameter. Equiaxed grains took the modification of α-Al_2O_3 and ranged from 150 to 800 nm in size. In addition, the modifications of TiO_2 disappeared and titanium element was dissolved in γ-Al_2O_3 grains. The bimodal microstructure contributed to the improvement in mechanical properties of the nanostructured coating.

Keywords: microstructure, nanostructured materials, plasma spraying, scanning electron microscopy, titanium dioxide, transmission electron microscopy, x-ray diffraction

X. Lin, Y. Zeng, X. Zhou, and C. Ding, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China. Cited: *Mater. Sci. Eng. A, 357*(1-2), 25 Sept 2003, pp. 228-234 [in English]. ISSN 0921-5093.

Polymer Coatings

Potentiodynamic study of the corrosion protection of aluminum by plasma-polymerized coatings. The corrosion-protective performance of plasma-polymerized (PP) coatings on aluminum substrates has been investigated by potentiodynamic (cathodic) polarization curve measurement, x-ray photoelectron spectroscopy (XPS), and temperature-programmed photoelectron emission (TPPE) measurement. PP films from tetraethoxysilane (TEOS)/O_2, hexamethyldisiloxane/O_2, and cyclohexane were deposited on previously argon plasma treated aluminum substrates by a 13.56 MHz radiofrequency generator. The weight loss rate obtained from the cathodic polarization curve for the PP film samples utilized as the working electrode was employed to evaluate the corrosion-protective performance. The PP films of TEOS/O_2 mixtures gave the best protective performance. The corrosion potential for all the PP films became more negative than that for the substrate only. The XPS

analysis indicated that TEOS films have a chemical structure like SiO_2. The TPPE analysis revealed that the argon plasma pretreatment of the metal substrate enhances greatly the ability of the surface to emit electrons.

Keywords: corrosion resistance, electrons, protective coatings, x-ray photoelectron spectroscopy

Y. Momose, M. Tomii, T. Maruyama, T. Shimoda, and Y. Motohashi, Department of Materials Science, Ibaraki Univ., Hitachi, Ibaraki 316-8511, Japan. Cited: *Surf. Coat. Technol., 169-170*(1), 2 June 2003, pp. 682-685 [in English]. ISSN 0257-8972.

Residual Stress and Oxidation of Thermal Barrier Coatings

Analysis and measurement of thermal residual stresses in ceramic/metal gradient thermal barrier coatings. Ceramic/metal gradient coatings with two substrate materials (i.e., 1Cr18Ni9Ti and 2Cr13), two substrate structures (i.e., convex top and concave top), and four coating schemes are considered and compared in the numerical analysis and the experiment study. Four coating schemes include: 1) two-layer coating, 2) three-layer coating, 3) four-layer coating, and 4) gradient coating. The numerical results obtained by finite-element method show that gradient coating with 2Cr13 concave top substrate is an optimal coating scheme. The measurement results by the hole-drilling method show that compressional stresses present in the coatings on 1Cr18Ni9Ti substrate and tensile stresses present in the coatings on 2Cr13 substrate, which agrees with the numerical analysis results.

Keywords: chromium alloys, compressive stress, finite-element method, residual stresses, stress analysis, substrates, tensile stress, thermal stress, zirconia

J. Xiao, C. Liu, Z. Zhao, and W. Fu, Sch. of Energy and Power Engineering, Wuhan Univ. of Technology, Hubei 430063, China. Cited: Proc. Seventh International Symposium on Functionally Graded Materials, 15-18 Oct 2002 (Beijing), *Mater. Sci. Forum, 423-425,* 2003, pp. 555-560 [in English]. ISSN 0255-5476.

Spray Formed Alloys

Auswirkungen des spruhkompaktierens auf bearbeitung und eigenschaften einer Al-Cu-knetlegierung (Effects of spray forming on formability and properties of an Al-Cu wrought alloy). Aluminum-copper alloys are one of the first developed light metal alloys showing precipitation hardening. They became more and more important for industrial applications because of their good properties. Besides the usual process route consisting of casting, high-temperature annealing, hot working, solution heat treatment, quenching, and subsequent aging, other techniques have been developed to produce aluminum alloys of high quality capable for forming. Spray forming has been established as one of these techniques. As one of the essential advantages in comparison to the as-cast state, spray formed materials do not show distinct dendrite structures. To investigate the properties and the formability of aluminum-copper alloys produced by spray forming, a study was carried out within the Collaborative Research Centre SFB 372 "Spray forming." As one result, it has been shown that the cold forming behavior was improved by spray forming comparing to the cast alloy. A further comparison between the spray formed material without secondary high-temperature processing and the alloy after casting and subsequent high-temperature annealing proved the equivalence of the finally obtained microstructure and resulting mechanical properties. This suggested the possibility of shortening the process line by means of spray forming.

Keywords: age hardening, annealing, formability, forming, metallographic microstructure

K. Schimanski, A. Schulz, H. Vetters, and P. Mayr, Inst. fur Werkstofftechnik, Universitat Bremen, Bremen, Germany. Cited: *HTM Härt.-Tech. Mitt., 58*(3), 2003, pp. 170-176 [in German]. ISSN 0341-101X.

Microstructures and workability of spray formed and cast AZ91 magnesium alloys. Spray forming was employed to refine the microstructures to improve the workability of AZ91 magnesium alloys. The process parameters of spray forming were varied to reduce the porosity level and improve the morphology of the billet preforms. As-spray-formed microstructures were characterized, which were compared with as-cast microstructures. In the workability study, cylinder specimens were extruded by simple direct extrusion with various ram speeds at various temperatures. Surface conditions and microstructures of extruded materials, and extrusion pressure versus ram displacement were analyzed. The effects of extrusion temperatures and ram speeds on the workability of spray formed and cast materials were studied and compared. The extrusion operating conditions of spray formed and cast materials were determined.

Keywords: casting, extrusion, metallographic microstructure, morphology, spraying

C.Y.A. Tsao and C.Y. Chen, Department of Materials Science, National Cheng Kung Univ., Tainan 701, Taiwan. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(1), 2003, pp. 429-434 [in English]. ISSN 0255-5476.

Steel and Cast Iron Coatings

Plasma sprayed coatings with water and gas-atomized bearing steel powders. The present paper investigates the characteristics of plasma sprayed coatings with water-atomized bearing steel powder in comparison with gas-atomized powder particularly focusing on oxidation during the spray process. As yet, there has been no research on the use of water-atomized powders (characterized by nonspherical irregular appearance and high oxygen content) in plasma spraying on aluminum alloy substrate. The oxygen content increases beyond 10 wt.% in sprayed particles after fusion and resolidification in air, although oxygen is only 0 to 20 wt.% of the as-received water-atomized powder. Sprayed particles are composed of αFe, γFe, $Fe_{1-x}O$, and Fe_3O_4 after their heavy surface oxidation in flight. Coating examination shows wavy oxide phases at the interfaces between layered splats. Water-atomized powder at a spray distance of 150 mm form coatings with an average oxygen content of 3 to 9 wt.%. At shorter spray distances, in both water- and gas-atomized powder coatings, the formed oxides almost disappear. The oxygen content of powder sprayed in an argon atmosphere does not increase, and therefore the oxidation mainly occurs during the droplet flight and is caused by oxygen captured in the plasma flame. If a shroud with argon shielding is installed in front of the gun tip to reduce oxygen mixed with the flame, it significantly reduces the oxidation during the droplet flight, especially at a longer spray distance.

Keywords: aluminum alloys, atomization, interfaces (materials), oxidation, plasma spraying, powder metals, solidification, steel, substrates

Y. Tsunekawa, T. Ueno, M. Okumiya, and T. Yashiro, Cited: *Surf. Eng., 19*(1), Feb 2003, pp. 17-22 [in English]. ISSN 0267-0844.

High-temperature fatigue deformation measurement of ceramics thermally sprayed SUS304 steel using an ESPI system. Surface strains of Al_2O_3/NiCr thermally sprayed SUS304 steel specimens during the fatigue test (σ_{max} = 173 MPa, R = 0, T = 873 K) were measured using an electronic speckle pattern interferometry (ESPI) system. The relationships between surface strain and crack-initiation/delamination behavior are discussed. The strain values obtained from the ESPI system were confirmed to be almost the same as those from strain gages on unsprayed specimens when tensile stresses were 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 the sprayed coatings can be nondestructively detected by analyzing the strain concentration or decrease. The surface strains of sprayed specimens were almost the same as those of unsprayed specimens at 873 K, indicating that the deformation of the sprayed coatings are always associated with that of the substrate surfaces at high temperature. The maximum surface strain after 1×10^5 cycles test was a little lower than after two cycles test. Surface cracks occurred, but stopped at the inner NiCr layer after two cycles test at 873 K. Many surface cracks and delamination along the interface between the NiCr layer and substrate interface were confirmed after 1×10^5 cycles test.

Keywords: alumina, fatigue of materials, fatigue testing, high-temperature effects, interferometry, nickel compounds, plastic deformation, speckle, sprayed coatings, steel, strain, thermal expansion

R. Wang, T. Tokuda, and M. Kido, Dept. of Mech. Sys. Eng., Fac. of Tech., Hiroshima Institute of Technology, Saeki-ku, Hiroshima, 731-5193, Japan. Cited: *Mater. Sci. Res. Int., 9*(1), March 2003, pp. 69-74 [in English]. ISSN 1341-1683.

Microstructure of plasma sprayed cast iron splats with different particle sizes. The superior wear-resistant property of cast irons is closely linked with their microstructure, in which graphite formation in plasma sprayed cast iron coatings causes distinct characteristics owing to its self-lubricating property. Since the solidification rate generally affects graphite formation, the optimum in spray parameters such as substrate temperature, ambient pressure, particle size, and spray distance is required to slow down the solidification rate, as well as to improve the adhesive strength of splats. In this study, cast iron splats were induced on an aluminum alloy substrate by plasma spraying using alloyed cast iron powder high in silicon and aluminum in a low-pressure argon atmosphere. Then, the effects of particle size on the microstructure and adhesive strength of splats were investigated by introducing the correlation between the solidification rate and the microstructure. Spraying with large particles leads to an increase in the number fraction of disk splats and a slight decrease in their adhesive strength. Cross-sectional observations reveal fine graphite growing in splats nearly perpendicular to the substrate surface.

Keywords: adhesion, aluminum alloys, graphite, metallographic microstructure, morphology, particle size analysis, plasma spraying, pressure, silicon, solidification, temperature, wear resistance

M.F. Morks, Y. Tsunekawa, M. Okumiya, and M.A. Shoeib, Toyota Technological Institute, Nagoya 468-8511, Japan. Cited: *Mater. Trans., 44*(4), April 2003, pp. 743-748 [in English]. ISSN 1345-9678.

Splat microstructure of plasma sprayed cast iron with different chamber pressures. Achieving a plasma sprayed cast iron coating containing graphite requires stringent control on spray parameters that synergistically influence the coating properties and thus the performance. The microstructure of cast

iron splats greatly depends on spray parameters such as substrate temperature, chamber pressure, and spray distance. This paper presents the effect of chamber pressure on the splat microstructure, including oxides and graphite. At low chamber pressures, most splats exhibit a disk shape with high flattening ratios, whereas star-shaped splats extensively appear at high chamber pressures. Spraying at high chamber pressures causes the formation of pores and thick oxide zones at the splat/substrate interface, mainly due to the atmospheric gases, which are responsible for a decrease in splat adhesion. Spraying in argon atmosphere reduces the splat oxidation due to a decrease in the oxygen partial pressure. Small deformed substrate ridges are observed adjacent to the periphery of splats sprayed at low chamber pressures, whereas no ridges are detected at high chamber pressures. Ridge formation generates a kind of mechanical bond, which increases the adhesive strength. Since the molten droplets impinge with high velocity and thus high flattening ratio at low chamber pressures, the solidification rate becomes faster, and graphite formation is resultantly hindered.

Keywords: microstructure, oxidation, oxides, plasma spraying, pressure effects

M.F. Morks, Y. Tsunekawa, M. Okumiya, and M.A. Shoeib, Toyota Technological Institute, Nagoya, Japan. Cited: *J. Therm. Spray Technol., 12*(2), June 2003, pp. 282-289 [in English]. ISSN 1059-9630.

Thermal and Phase Stability of Coatings

Zeit- und temperaturabhangige entwicklung von physikalischen defekten in warmedammschichtsystemen (Time- and temperature-dependent development of physical defects in thermal barrier coating systems). A study was performed on the time- and temperature-dependent development of physical defects of thermal barrier coating (TBC) systems. Pulsed vapor deposited and atmospheric plasma sprayed (APS) coated specimens with TBC coatings of partially yttria-stabilized zirconia were aged in air for a maximum of 5000 h at 950, 1000, and 1050 °C. The oxidation behavior of the TBC systems was characterized.

Keywords: cracks, electron beams, interfaces (materials), metallographic microstructure, oxidation resistance, physical vapor deposition, plasma spraying, scanning electron microscopy, single crystals, zirconia

E. Berghof-Hasselbacher, H. Echsler, P. Gawenda, M. Schorr, and M. Schutze, Karl-Winnacker-Inst. Dechema e.V., D-60061 Frankfurt, Germany. Cited: *Prakt. Metallogr., 40*(5), May 2003, pp. 219-231 [in German, English]. ISSN 0032-678X.

TEM studies of nonequilibrium microstructure evolution and phase transformation of Fe-Cr-B-Ni-Mo spray coatings. The nonequilibrium microstructure evolution has been investigated by using transmission electron microscopy (TEM) in thermally sprayed Fe-Cr-B-Ni-Mo coatings. The spray coated layer was seen to be composed of $(Cr,Fe)_2B$ boride particles and α-(Fe,Cr) matrix phase. The dissolution of $(Cr,Fe)_2B$ boride followed by the supersaturation of boron within the matrix, during the thermal spraying, could result in a brick-wall type matrix structure through the homogeneous volume nucleation of nanocrystalline α-(Fe,Cr) phase inside the sprayed splats. Thermal stability of these metastable phases and consequent microstructure development has also been investigated by in situ TEM heating experiments. The sequences of thermal decomposition of the nanocrystalline matrix phase, upon exposure to high temperature above 670 K, to the final intragranular precipitation of Cr_2B borides within the coarsened α-(Fe,Cr) grains will be presented.

Keywords: dissolution, microstructure, nanostructured materials, nucleation, phase transitions, pyrolysis, supersaturation, thermodynamic stability, transmission electron microscopy

H.W. Jin, M.C. Kim, and C.G. Park, ExxonMobil Res. and Engineering Co., Corporate Strategic Research, Annandale, NJ. Cited: TMS Annual Meeting, *Electron Microscopy: Its Role in Materials Science,* J.R. Weertman, M. Fine, K. Faber, W. King, and P. Liaw, Ed., 2-6 March 2003 (San Diego, CA), ASM-MSCTS of SMD Minerals, Metals, and Materials Society, pp. 235-242 [in English].

Long-term behavior and application limits of plasma sprayed zirconia thermal barrier coatings. Investigations of changes in phase composition, mechanical properties, and microstructure of ZrO_2-based plasma sprayed thermal barrier coatings (TBCs) with 8 mol% CeO_2, 19.5 mol% CeO_2/1.5 mol% Y_2O_3, 35 mol% CeO_2, and 4.5 mol% Y_2O_3 after long-term heat treatments at typical operating temperatures (1000-1400°C) are presented. Experimental studies include x-ray diffractometry, mechanical testing, and scanning electron microscopy. Thermal cycling experiments also have been performed. TBCs with 8 mol% CeO_2 contain mainly the tetragonal equilibrium phase and, therefore, show rapid failure because of the high amount of tetragonal τ monoclinic phase transformation, even after relatively short heat treatments (1250 °C/1 h). In the case of the other systems that consist mainly of the tetragonal or cubic nonequilibrium phases, TBCs with 19.5 mol% CeO_2/1.5 mol% Y_2O_3 or 35 mol% CeO_2 reveal a smaller amount of monoclinic phase after long-term heat treatments (1250°C/1000 h) compared with TBCs containing 4.5 mol% Y_2O_3. TBCs containing 35 mol% CeO_2 show a higher degree of sintering than the TBCs with 19.5 mol% CeO_2/1.5 mol% Y_2O_3 and, therefore, a greater increase of the elastic modulus. Among the systems investigated, TBCs containing 4.5 mol% Y_2O_3 exhibit the highest resistance to failure in thermal-cycling experiments.

Keywords: elastic moduli, microstructure, phase transitions, plasma spraying, scanning electron microscopy, sintering, thermal barrier coatings, thermal cycling, x-ray diffraction analysis

P.A. Langjahr, R. Oberacker, and M.J. Hoffmann, Inst. for Ceram. in Mech. Eng., Univ. of Karlsruhe, D-76131 Karlsruhe, Germany. Cited: *J. Am. Ceram. Soc., 84*(6), June 2001, pp. 1301-1308 [in English]. ISSN 0002-7820.

Thermal Cycling and Thermal Shock Resistance

Effect of the composition profile and density of LPPS sprayed functionally graded coating on the thermal shock resistance. Low-pressure plasma spraying (LPPS) is a promising coating method for functionally graded material (FGM) expected to be able to reduce the thermal stress in high-temperature environments such as a gas turbine. In this paper, we report the effect of the composition profile and coating density of LPPS sprayed FGM, consisting of ZrO_2-8wt.%Y_2O_3 (YSZ) topcoating, YSZ-Ni-20wt.%Cr (NiCr) FGM coating, NiCr under coating and copper substrate, on the thermal shock resistance evaluated by a modified temperature difference test. The density of YSZ and NiCr coating was successfully controlled by the chamber pressure and initial particle size in the range from 5.43 to 5.79 g/cm^3 and from 7.89 to 8.09 g/cm^3, respectively. For an YSZ composition profile from NiCr under coating to YSZ topcoating (in FGM), the highest thermal shock resistance was obtained when the fraction of YSZ increased with gentle slope just over NiCr coating and acute slope just under YSZ coating. Also, the higher-density coatings tended to perform the higher thermal shock resistance. Initial cracks formed in the YSZ topcoating propagated into YSZ parts in FGM coating through the grain boundary of YSZ and/or the interface between flattened NiCr and YSZ particles. After the cracks connected, the coupled cracks caused the coating spallation.

Keywords: gas turbines, particle size analysis, plasma spraying, pressure effects

H. Hamatani, N. Shimoda, and S. Kitaguchi, Welding and Joining Laboratory, Nippon Steel Corporation, Futtsu-city, Chiba 293-8511, Japan. Cited: *Sci. Technol. Adv. Mater., 4*(2), 2003, pp. 197-203 [in English]. ISSN 1468-6996.

Thermal shock resistance of ceramic/metal gradient thermal barrier coating. The thermal shock experiment is an important measure to evaluate the thermal shock resistance of ceramic/metal gradient thermal barrier coatings. Two substrate materials and four coating schemes were adopted to make the specimens. Before and after the thermal shock experiments, the microstructure of specimens was observed. The heat transfer and the associated thermal stresses produced in the thermal shock procedure were simulated by finite element software ANSYS. The simulation results showed that the gradient coating scheme is much better than layered coating schemes and 2Cr13 is more suitable than 1Cr18Ni9Ti as substrate material. The experiment results demonstrated that the large thermal shock stresses and the large thermal stress gradient are the main reasons of crack initiation and propagation. The finite-element simulation results agree with the thermal shock experiment results.

Keywords: ceramic materials, chromium alloys, computer simulation, crack initiation, crack propagation, finite-element method, heat resistance, microstructure, substrates, thermal gradients, thermal stress, zirconia

J. Xiao, J. Liu, W. Zhao, and W. Fu, Sch. of Energy and Power Engineering, Wuhan Univ. of Technology, Hubei 430063, China. Cited: Proc. Seventh International Symposium on Functionally Graded Materials, 15-18 Oct 2002 (Beijing), *Mater. Sci. Forum, 423-425,* 2003, pp. 551-554 [in English]. ISSN 0255-5476.

Durability of TBCs with a surface environmental barrier layer under thermal cycling in air and in molten salt. In order to protect the thermal barrier coatings (TBCs) from oxidation and hot corrosion attack, several barrier coatings on top of the yttria-stabilized zirconia (YSZ) TBC have been evaluated. Thermal cycling tests in air and hot corrosion resistance tests in molten Na_2SO_4 were used to determine the durability of these coatings. Barrier layers investigated include mullite ($3Al_2O_3{\cdot}2SiO_2$), BAS ($BaO{\cdot}Al_2O_3{\cdot}2SiO_2$) and calcium silicate ($1.8CaO{\cdot}SiO_2$). Mullite and BAS barrier coatings showed the best promise as potential hot corrosion barriers. TBCs with mullite or BAS barrier showed life similar to that of standard YSZ TBC under thermal cycling in air, while demonstrating the ability to limit seepage of salt into YSZ in hot corrosion test. In order to avoid the coating damage due to seepage of salt through the edge, there is a need to examine the hot corrosion resistance on coupons that are completely enclosed by the coating.

Keywords: corrosion resistance, oxidation, salts, thermal cycling, yttrium compounds

C. Ramachandra, K.N. Lee, and S.N. Tewari, Chemical Engineering Department, Cleveland State Univ., Cleveland, OH 44115. Cited: *Surf. Coat. Technol., 172*(2-3), 29 July 2003, pp. 150-157 [in English]. ISSN 0257-8972.

Evaluation of interfacial fracture toughness of thermal barrier coating under heat cycles. Thermal barrier coating (TBC) has been developed to

protect gas turbine components from oxidation. However, the delamination of coating sometimes occurs, and the underlying component is exposed to hot gas environment that may cause premature failure of the components. In the present research, the method to estimate the delamination life of coating was proposed from the viewpoint of fracture mechanics. During the heat cycle tests, two types of delamination mode were observed. One was the partial delamination from the edge of the coating, and another was the delamination by buckling in the center of coating. In order to express the delamination life of coating, the interfacial thermal strain energy release rate was introduced for both cases as a function of temperature difference at heat cycles, strain of specimen, thickness of coating, and materials and thermal constants.

Keywords: delamination, fracture mechanics, fracture toughness, gas turbines, strain

L. Gao, K. Nakasa, M. Kato, and H. Nishida, Hiroshima Univ., Higashi-Hiroshima 739-8527, Japan. Cited: Proc. Int. Conf. Experimental and Computational Mechanics in Engineering, 24-27 Aug 2002, *Key Eng. Mater., 243-244,* 2003, pp. 267-272 [in English]. ISSN 1013-9826.

Estimating the fracture resistance of functionally graded thermal barrier coatings from thermal shock tests. Characterizing the fracture resistance of thermal barrier coatings (TBCs) is of technological importance in TBC design. It can enable coating designers predict the expected thermal fracture response under various thermomechanical loading conditions. A methodology is presented wherein results from previously reported laser thermal shock experiments are utilized in conjunction with principles of crack arrest to estimate the resistance to crack growth in a functionally graded yttria-stabilized zirconia (YSZ) -bondcoat (BC) alloy (NiCoCrAlY) TBC. Fracture resistance curves for cracks initiating at the TBC surface and propagating through its thickness are presented. The results show that fracture resistance increases with crack extension for the single-layer YSZ TBC as well as for the YSZ-BC alloy graded TBCs. Furthermore, the addition of BC alloy to the TBC layers (in the graded coatings) results in a substantial increase to their fracture resistance. The approach used provides a means of estimating the fracture resistance of such coatings at elevated temperatures.

Keywords: crack propagation, fracture, laser applications, thermomechanical treatment, zirconia

S. Rangaraj and K. Kokini, School of Mechanical Engineering, Purdue Univ., West Lafayette, IN 47907-2088. Cited: *Surf. Coat. Technol., 173*(2-3), 22 Aug 2003, pp. 201-212 [in English]. ISSN 0257-8972.

Thermally Grown Oxide Instability in Thermal Barrier Coatings

Relation of microstructural and compositional features to the electrical properties in degraded thermal barrier coating systems. Degraded thermal barrier coating samples cut from different afterservice gas turbine components are examined by both electron microscopy and impedance spectroscopy. There is a relationship between the microstructural and compositional features of the thermally grown oxide (TGO) and its electrical properties. The resistance of the TGO decreases with the TGO evolution from alumina to porous mixed oxides composed probably of NiO, spinel, Cr_2O_3, and Al_2O_3, while the relaxation frequency corresponding to the TGO increases. For seriously degraded TBCs, there is an additional semicircle in the impedance spectra in the extremely low frequency range, possibly arising from cracking in the vicinity of YSZ/TGO interface regions.

Keywords: composition, crack initiation, degradation, electric properties, electron microscopy, energy dispersive spectroscopy, film growth, interfaces (materials), microstructure, relaxation processes

S.-H. Song and P. Xiao, Department of Mechanical Engineering, Brunel Univ., Uxbridge, Middlesex UB8 3PH, U.K. Cited: *J. Mater. Sci., 38*(8), 15 April 2003, pp. 1661-1665 [in English]. ISSN 0022-2461.

Interface oxidation process of 8wt.%Y_2O_3-ZrO_2/CoNiCrAlY thermal barrier coating under variation of temperature. When a thermal barrier coating (TBC) is subjected to a high-temperature environment, a thermally grown oxidation (TGO) layer is grown at interface between the topcoat and the bondcoat. The existence of oxidation will bring reduction of coating cohesion. The aim of this study is to clarify TGO growth process under variation of temperature condition. For this purpose, one-stage variation of temperature tests, which is one that after heating TBC specimen at constant temperature 973 K during a constant period 500 h, specimen is heated additionally at 1173 K, for instance, was conducted. TGO growth process was examined by SEM observation of a cross section of the aged specimen. As some results obtained: (1) TGO growth process had no effect of difference in a kind of substrate material. (2) TGO layer was not formed at aged temperature below 973 K. In aging temperature range between 1073 and 1173 K, Al_2O_3 as TGO layer was formed at interface between topcoat and bondcoat layers. (3) TGO grew under post-aged temperature, which is higher than preaged temperature. TGO growth law at a constant temperature is also effective to complicated condition as a variation of temperature focused in this study.

Keywords: aging of materials, cobalt compounds, delamination, gas turbines, growth kinetics, heating, high-temperature effects, interfaces (materials), scanning electron microscopy, thermooxidation, yttrium compounds, zirconia

M. Arai and U. Iwata, Materials Science Department, Ctrl. Res. Inst. Elec. Power Indust., Komae-shi, Tokyo, 201-8511, Japan. Cited: *Nippon Kikai Gakkai Ronbunshu, A Hen/Trans. Jpn. Soc. Mech. Eng., Part A, 69*(4), April 2003, pp. 800-804 [in Japanese]. ISSN 0387-5008.

Nanocrystalline MCrAlY bondcoat for thermal barrier coating applications. This work describes recent progress in improving the oxidation behavior of the bondcoat using HVOF nanostructured MCrAlY coatings. NiCrAlY powder was cryomilled and HVOF sprayed onto a nickel-base alloy. Oxidation experiments were performed on the coating to form the thermally grown oxide layer (TGO). The formation of the oxide phases on top of the bondcoat after heat treatment at 1000 °C was analyzed (morphology and composition) for different heat treatment times. In the nanostructured coatings, the presence of a homogeneous α-Al_2O_3 layer was observed. The nanostructured characteristic of the coating and the presence of Al_2O_3 within the cryomilled powders enhance the nucleation of the TGO alumina layer that protects the coating from further oxidation and avoids the formation of mixed oxide protrusions presented on the coating sprayed using the as-received powder. The cryomilling process of the MCrAlY powders has shown to be effective in improving the oxidation behavior of the coatings used in turbine engines applications.

Keywords: heat treatment, morphology, nickel alloys, nucleation, oxidation, thermal barrier coatings

L. Ajdelsztajn, J. He, G.E. Kim, V. Provenzano, E.J. Lavernia, and J.M. Schoenung, Department of Chemical Eng., Univ. of California, Davis, CA 95616. Cited: *Surface Engineering in Materials Science II,* TMS Annual Meeting, 2-6 March 2003 (San Diego, CA), S. Seal, N.B. Dahotre, J. Moore, C. Suryanaryana, and A. Agarwal, Ed., The Surface Engineering Committee of the MPMD of TMS Minerals, Metals, and Materials Society, pp. 71-80 [in English].

The effect of sulfur segregation on the adherence of the thermally grown oxide on NiAl-I: Sulfur segregation on the metallic surface of NiAl(001) single crystals and at NiAl(001)/Al_2O_3 interfaces. The aim of this study was to improve the understanding of the deleterious effect of sulfur impurities on the adherence of the thermally grown oxide on the boundary layer in thermal-barrier-coating systems. In part I, the sulfur segregation on the free surface of NiAl(001) and at different interfaces between metal and transient alumina scales has been characterized by AES, XPS, and LEED. The sulfur diffusion coefficient in the alloy has been determined ($D = 0.15 \exp(-218{,}000/\mathrm{RT})$ cm^2/s). It is by three orders of magnitude larger than the nickel and aluminum self-diffusion coefficients. It has also been observed that the sulfur desegregates upon aluminum enrichment of the metallic surface. The saturation of the metallic surface with an amorphous alumina layer formed at room temperature blocks the segregation of sulfur. However, in the initial stages of oxidation where the transient θ-alumina grows by cationic transport and inject vacancies at the interface. Sulfur segregates at the interface between the alumina thin films and the metallic substrate.

Keywords: alumina, Auger electron spectroscopy, diffusion, interfaces (materials), low-energy electron diffraction, oxidation, segregation (metallography), single crystals, sulfur, temperature, thermal barrier coatings, x-ray photoelectron spectroscopy

L. Rivoaland, V. Maurice, P. Josso, M.-P. Bacos, and M. Marcus, LPCS, CNRS (UMR 7045), Universite Pierre et Marie Curie, Ecole Nationale Sup. Chim. de Paris, 75231 Paris Cedex 05, France. Cited: *Oxid. Met., 60*(1-2), Aug 2003, pp. 137-157 [in English]. ISSN 0030-770X.

Titania Coatings

Photocatalytic properties of nanostructured TiO_2 plasma sprayed coating. Nano-TiO_2 photocatalytic coatings were deposited on stainless steel 304 ($50 \times 55 \times 3$ mm^3) by the atmospheric plasma spraying process. To apply nano-TiO_2 powder to thermal spraying, the starting nano-TiO_2 powder with 100% anatase phase was agglomerated by the spray drying process. The plasma second gas (H_2) flow rate and spraying distance were used as principal process parameters that controlled the heat enthalpy (heat input). When the plasma spraying was completed, the relationship among the process parameters, the characteristics of microstructure such as the anatase phase fraction and grain size of the TiO_2 coatings and the photodecomposition efficiency were investigated. The photodecomposition efficiency of the TiO_2 coatings was evaluated by the kinetics of the methylene blue aqueous solution decomposition after irradiation using an ultraviolet ray lamp, which excites electrons and forms holes in TiO_2 coatings. It was found that TiO_2 coating applied under a lower heat input, resulting in a higher anatase phase fraction and smaller anatase grain size showed the best photodecomposition efficiency.

Keywords: decomposition, enthalpy, nanostructured materials, photocatalysis, plasma spraying, titanium dioxide

C. Lee, H. Choi, C. Lee, and H. Kim, Res. Inst. of Indust. Sci./Technol., Pohang 790-600, South Korea. Cited: *Surf. Coat. Technol., 173*(2-3), 22 Aug 2003, pp. 192-200 [in English]. ISSN 0257-8972.

High Weibull modulus HVOF titania coatings. The mechanical behavior of high-velocity oxyfuel (HVOF) sprayed titania (TiO_2) coatings was evaluated using Vickers hardness measurements on the cross section and top surface. The distribution of hardness values for the cross section and top surface under 25, 50, 100, 300, 500, and 1000 g loads was analyzed via Weibull statistics. The coating microstructure was evaluated using scanning electron microscopy (SEM). It was observed that the microstructural features were similar in the top surface and cross section, different from the lamellar structure commonly found in thermal spray coatings. X-ray diffraction (XRD) analysis identified rutile as the major coating phase. The in-flight sprayed particle parameters such as temperature and velocity were determined using a commercial diagnostic system based on pyrometry and time-of-flight measurements. The uniformity of the microstructure resulted in a near-isotropic behavior of the mechanical properties, such as hardness, in the coating cross section and top surface. High Weibull modulus values were observed when compared with results of other thermal spray coatings available in the literature. These initial results should contribute to a more general understanding of the conditions necessary to achieve coatings with high uniformity and assist in the engineering of coating microstructures for specific applications.

Keywords: microstructure, scanning electron microscopy, titanium compounds, Vickers hardness testing, Weibull distribution, x-ray diffraction analysis

R.S. Lima and B.R. Marple, National Research Council of Canada, Boucherville, Quebec J4B 6Y4, Canada. Cited: *J. Therm. Spray Technol., 12*(2), June 2003, pp. 240-249 [in English]. ISSN 1059-9630.

Wear and Adhesion of High-Velocity Oxyfuel Coatings

Wear behavior of HVOF thermal sprayed WC-Co and CrC-NiCr coatings. One of the most important uses of HVOF thermal sprayed coatings is for wear resistance. The present study describes and compares the mechanical and tribological properties of the thermal sprayed CrC75 (NiCr20) 25, CrC60 (NiCr20) 40, WC Co 88 12, and WC Co Cr 86 10 4 coatings, obtained by high-velocity oxyfuel (HVOF) technology. These coatings are required to provide protection against sliding, abrasive, erosive, and fretting wear, and they are candidates for replacement of hazardous hard chromium plating coatings used today in the industry on several applications. The coating microstructures were characterized by SEM microscopy. Differences in roughness have been determined by profilometry. The ultramicroindentation technique was applied to measure the hardness and the elastoplastic properties of the coating. Experiments using a tribometer (pin-on-disk configuration) under lubricated and dry conditions have been performed in order to evaluate the friction and wear properties of the different coatings. It was found that the coatings with a higher carbide particle percentage presented poorer abrasive wear resistance than coatings with higher metallic binder phase, under all the conditions examined. This fact could be explained in terms of differences of cohesion between the carbide particles and the binder phase.

Keywords: fretting corrosion, microstructure, tribology, wear resistance

A. Forn, J.A. Picas, and G. Matthaus, Dept. de Ciencia de Materials, Univ. Politecnica de Catalunya, 08800 Vilanova i la Geltru, Spain. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(3), 2003, pp. 2623-2628 [in English]. ISSN 0255-5476.

Structure and wear behavior of HVOF sprayed Cr_3C_2-NiCr and WC-Co coatings. Hard chrome plating is used to restore the original dimensions to worn surfaces of gas turbine shafts. However, its use is about to decrease due to some intrinsic limitations of its deposits and the toxic and carcinogenic characteristics of the hexavalent chromium. During the last decade, high-velocity oxyfuel (HVOF) thermal sprayed cermet coatings have played an important role in industrial applications where exceptional friction and wear resistance are required. The purpose of this study is to investigate and to compare the microstructure, wear resistance, and potentials of HVOF sprayed Cr_3C_2-NiCr and WC-Co coatings for a possible replacement of hard chromium plating in gas turbine components repair. It has been shown that coatings exhibit high hardness with a high volume fraction of carbides being preserved during the spraying and have different wear behavior.

Keywords: carbides, cermets, gas turbines, hardness, microstructure, sprayed coatings, surface structure, toxicity, wear resistance

T. Sahraoui, N.-E. Fenineche, G. Montavon, and C. Coddet, Lab. d'Etudes/deRech. sur Mat. Plasmas, Univ. de Technol. de Belfort-Montbeliard, Belfort 90 010, France. Cited: *Mater. Des., 24*(5), August 2003, pp. 309-313 [in English]. ISSN 0264-1275.

The slurry erosion behavior of high-velocity oxyfuel (HVOF) sprayed aluminum bronze coatings. This paper investigates the erosion aspects of a novel high-velocity oxyfuel (HVOF) sprayed aluminum bronze coating under sand particle impingement conditions, using a free-jet impingement erosion rig. Erodents at various kinetic energies (0.1-0.8 μJ) and impingement angles (30, 60, and 90°) were used to simulate actual service conditions. Gravimetric measurements, surface profilometry and microscopy techniques were utilized to determine both the erosion rate and the mechanisms of coating failure. The erosion rate of the coating was found to be comparable to bulk 90/10 cupronickel (C70600) and about twice that of Marinel and AISI 316L stainless steel. These results suggest that HVOF aluminum bronze coatings are suitable candidates for marine applications. Analysis of the erosion scars suggest that coating erosion occurred by a combination of cutting wear, plastic deformation, and crack propagation at splat boundaries (brittle oxides) leading to the detachment of coating splats, cutting wear was found to be the most dominant. The cutting process was dominated by smaller particle impacts. The number of these particles that cause damage appears to be a function of kinetic energy.

Keywords: aluminum coated steel, erosion, gas fuels, kinetic energy, spraying

K.S. Tan, R.J.K. Wood, and K.R. Stokes, Surface Eng. and Tribology Group, School of Engineering Sciences, Univ. of Southampton, Highfield, Southampton SO17 1BJ, U.K. Cited: *Wear, 255*(1-6), Aug/Sept 2003, pp. 195-205 [in English]. ISSN 0043-1648.

Sliding wear behavior of HVOF sprayed WC-Co coatings deposited with both gas-fueled and liquid-fueled systems. WC-Co thermally sprayed coatings are now widely used in a range of industries to combat wear. During spraying of WC-Co coatings, there is a decomposition involving dissolution of the hard phase into the molten binder; as such, the coatings are often made up of WC along with other carbides in a matrix consisting of tungsten and carbon dissolved in the cobalt. High-velocity oxyfuel (HVOF) spraying is seen as the preeminent process for deposition of such coatings. There have been moves in the industry to spray coatings with liquid-fueled systems rather than gas-fueled guns, since the former lead to shorter residence times of the particles in the flame and lower temperatures, both of which lead to less dissolution of WC and decomposition of the coating. This paper presents work concerning the sliding wear behavior of WC-Co coatings HVOF sprayed with both liquid-fueled (HVOLF) and gas-fueled (HVOGF) systems and demonstrates that with a dense powder feedstock, the HVOGF deposited coating is superior to the HVOLF deposited coating. The poorer performance of the HVOLF-sprayed coating is associated with mechanical damage to the WC-Co powder particles as they impact with the substrate resulting in carbide cracking and a reduction in the integrity of the bond between the carbide particles and the matrix phase.

Keywords: binders, chemical bonds, cobalt, dissolution, gas fuel analysis, liquid fuels, molten materials, tungsten carbide, wear of materials

T. Sudaprasert, P.H. Shipway, and D.G. McCartney, Advanced Materials Group, Sch. of Mech., Mat., Mfg. Eng./Mgmt., Univ. of Nottingham, Univ. Park, Nottingham NG7 2RD, U.K. Cited: *Wear, 255*(7-12), Aug/Sept 2003, pp. 943-949 [in English]. ISSN 0043-1648.

Wear and Corrosion/Oxidation

Plasma sprayed yttrium silicates for oxidation/erosion protection of C/C-SiC components. An effective two-layer coating system for C/C-SiC has been developed in order to improve both oxidation protection and erosion resistance. The base layer consists of CVD-SiC, and the outer erosion protection layer is composed of yttrium silicate with inlays of amorphous silica, which is applied by low-pressure plasma spraying (LPPS). While thermogravimetric measurements showed adequate oxidation protection, the thermal shock resistance was proofed by tests in a solar furnace between 400 and 1600 °C with the result of a very good adhesion to the bonding layer. Finally, the coating system was successfully qualified on C/C-SiC specimens by several test campaigns within plasma wind tunnels at temperatures up to 1650 °C. After a test duration of more than 20 min at 1500 °C the surface of the coating did not show any visible degradation.

Keywords: erosion, oxidation, silicon carbide, thermogravimetric analysis, yttrium compounds

T. Ullmann, M. Schmucker, H. Hald, R. Henne, and H. Schneider, DLR, German Aerospace Center, Institute of Structures and Design, D-70469 Stuttgart, Germany. Cited: *Hot Structures and Thermal Protection Systems for Space Vehicles,* Fourth European Workshop, 26-29 Nov 2002 (Palermo), Special Publication No. 521, A. Wilson, Ed., European Space Agency, April 2003, pp. 147-153 [in English]. ISSN 0379-6566.

Corrosion and wear behaviors of ferrous powder thermal spray coatings on aluminum alloy. Atmospheric plasma spray coating was performed on a cast AA383 aluminum alloy plate, and this process formed a 170 μm thick spray coating layer by using tentative Fe-C powders with nickel added (up to 14 mass%) or without supplementary nickel. Hardness test, microstructure observation, corrosion test, and wear tests in engine oil with or without sulfuric acid water solutions added were performed as well. The corrosion performance was dependent on the nickel content. On the contrary, the wear resistance testing under two engine oil lubrication conditions (with or without sulfuric acid water solution) showed the different tendency instead.

Keywords: corrosion, hardness, lubrication, microstructure, wear of materials, wear resistance

S. Uozato, K. Nakata, and M. Ushio, Manufacturing Engineering Office, Isuzu Motors Ltd., Fujisawa, Kanagawa 252-8501, Japan. Cited: *Surf. Coat. Technol., 169-170*(1), 2 June 2003, pp. 691-694 [in English]. ISSN 0257-8972.

Wear Mechanisms

Nanoscale fatigue wear of carbon nitride coatings: Part II—Wear mechanisms. This is the second part of two companion papers, the first of which reported the empirical data on wear properties in carbon nitride coatings by a spherical diamond counterface in repeated sliding contacts through in situ examination, with an emphasis on the effect of friction cycles and normal load. The second part will concentrate on wear mechanisms for the transition from "No observable wear particles" to "Wear particle generation." The relationship between the critical number of friction cycles, N_c, and the representative plastic strain, $\Delta\varepsilon_p$, at asperity contact region was confirmed to follow the Manson-Coffin equation with two empirical constants, β and C. The observed generation of wear particles in carbon nitride coatings is therefore concluded to be a low-cycle fatigue wear by surface flow and surface delamination in the plowing mode. For further predicting lifespan, a simplified theoretical expression, combining the Manson-Coffin equation with the analytical solution of a proposed elastic perfectly-plastic indentation model, gives the relation between the critical number of friction cycles, N_c, and the coating thickness h, with respect to the contact pressure P, and the radius R of the asperity on the tip of the diamond pin.

Keywords: carbon nitride, elasticity, fatigue of materials, friction, loads (forces), strain

D.F. Wang and K. Kato, Lab. of Biometrical Engineering, Dept. of Mechatronics/Precision Eng., Faculty of Engineering, Sendai 980-8579, Japan. Cited: *J. Tribol., 125*(2), April 2003, pp. 437-444 [in English]. ISSN 0742-4787.

Wollastonite Coatings

Bioactivity of plasma sprayed Wollastonite coatings in simulated body fluid. Wollastonite coatings were deposited by plasma spraying and incubated in simulated body fluids to investigate the nucleation and growth of apatite on their surface. Surface structural of the coatings were analyzed by x-ray diffraction (XRD) and infrared (IR) technologies. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to observe surface and cross-section morphologies and determine the composition of wollastonite coatings before and after immersion in simulated body fluid. The changes in the concentrations of calcium, silicon, and phosphorus in the simulated body fluids due to the immersion of the coatings were measured by inductively coupled plasma atomic emission spectroscopy. The cytocompatibility of wollastonite coatings was examined by osteoblasts culturing test. The carbonate-containing hydroxyapatite (CHA) layer was formed on the surface of plasma sprayed wollastonite coating soaked in SBF solution. Prior to the formation of the CHA layer, silica-rich layer appeared on the surface of plasma sprayed wollastonite coating soaked in SBF solution. The formation of CHA layer on coating surface indicates wollastonite coating had a good bioactivity. Osteoblasts survive and proliferate on the surface of wollastonite coating, which showed plasma sprayed wollastonite coatings possess good cytocompatibility.

Keywords: coatings, composition, energy dispersive spectroscopy, hydroxyapatite, morphology, nucleation, plasma spraying, scanning electron microscopy, surfaces, x-ray diffraction analysis

X. Liu, L. Deng, and C. Ding, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China. Cited: Proc. Seventh International Symposium on Functionally Graded Materials, 15-18 Oct 2002 (Beijing), *Mater. Sci. Forum, 423-425,* 2003, pp. 331-334 [in English]. ISSN 0255-5476.

Plasma sprayed wollastonite 2M/ZrO_2 composite coating. Wollastonite 2M/ZrO_2 composite coatings in different proportions were deposited onto Ti-6Al-4V substrates using plasma spraying. The tensile adhesion test (TAT) specified by ASTM C 633-79 was used to measure the tensile bonding strength of the coating. The bioactivity of coatings was evaluated using a simulated body-fluid soaking test. The results obtained showed that the composite coatings have a lamellar structure with alternating wollastonite 2M and ZrO_2 phases. The Vickers microhardness of composite coatings increases with increasing ZrO_2 content. Carbonate-containing hydroxyapatite (CHA) was formed on the surface of the wollastonite 2M and wollastonite 2M/ZrO_2 composite coatings soaked in simulated body fluid, but was not formed on the surface of the ZrO_2 coatings after immersion. This indicates that wollastonite 2M and W7Z3 and W3Z7 coatings have very good bioactivity. In addition, a silica-rich layer appeared at the interface of CHA and wollastonite 2M and W7Z3 coatings, but is absent in the case of the W3Z7 coating. The ZrO_2 in the composite coatings may decrease the dissolution rate of the coating in simulated body fluid compared to pure wollastonite 2M coatings.

Keywords: body fluids, bond strength (materials), composite materials, dissolution, plasma spraying, Vickers hardness testing

X. Liu and C. Ding, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China. Cited: *Surf. Coat. Technol., 172*(2-3), 29 July 2003, pp. 270-278 [in English]. ISSN 0257-8972.

Review

Advantages of Thermal Spray

High properties metallic alloys obtained through the thermal spray route. For a long time now, atmospheric thermal spray has been used to produce a variety of protective coatings and even free-standing shapes based particularly on ceramic materials using tailored powders. Although spraying metallic powders suffer from drawbacks arising from the oxidizing environment, it has also a number of applications. Unfortunately, the mechanical properties of the deposits are often lower than those of the corresponding bulk materials. With the development of "vacuum" or "low-pressure" plasma spraying in the past two decades, new achievements have been obtained concerning the production of high mechanical properties metallic free-standing parts. Meanwhile, this production route, which necessitates the initial production of high-grade alloyed feedstock powders, remains expensive. The aim of this paper is to demonstrate that an alternative route, using blends of elemental powders, is promising both from the economical and metallurgical points of view. Such a process allows the production of metastable phases that are normally not obtained using the traditional metallurgical routes. These phases may lead to outstanding mechanical properties. Examples are given for titanium- and copper-base alloys.

Keywords: ceramic materials, copper alloys, powder metals, protective coatings, titanium alloys

C. Coddet, C. Verdy, L. Dembinski, T. Grosdidier, D. Cornu, and J.C. Garcia, LERMPS, Univ. of Belfort-Montbeliard, 90010 Belfort Cedex, France. Cited: Thermec 2003 Processing and Manufacturing of Advanced Materials, 7-11 July 2003, *Mater. Sci. Forum, 426-432*(3), 2003, pp. 2467-2472 [in English]. ISSN 0255-5476.

Testing

Hardness

Indentation responses of plasma sprayed ceramic coatings. This investigation aims at finding the Vickers and Knoop indentation responses of a few plasma sprayed ceramic coatings, namely Indian alumina, imported alumina, zircon, plasma dissociated zircon (PDZ), and zircon-20 wt.% CaO. Some of the sprayed coatings under Vickers indentation show typical indentation size effect (ISE), while others exhibit reverse indentation size effect (RISE). Such coating behavior may be attributed to the heterogeneous phase composition and microstructure of the coatings. "True hardness" and "elastic modulus" of the ceramic coatings have been calculated. Also the ISE phenomenon observed for all the coatings undergoing Knoop indentation are explained using models such as Meyer's law, Normalized Meyer's law, Hays' Kendall Approach, and Proportional Resistance models. These models have so far been used for explaining the ISE behavior of only the sintered crystalline ceramics. In this paper, it has been shown that these models hold good to an appreciable extent for plasma sprayed ceramic coatings as well.

Keywords: alumina, composition effects, elastic moduli, indentation, lime, mathematical models, plasma spraying, sintering, sprayed coatings, Vickers hardness testing

S. Ghosh, S. Das, T.K. Bandyopadhyay, P.P. Bandyopadhyay, and A.B. Chattopadhyay, Metallurgical and Materials Eng., Indian Institute of Technology, Kharagpur 721 302, India. Cited: *J. Mater. Sci., 38*(7), 1 April 2003, pp. 1565-1572 [in English]. ISSN 0022-2461.

Microhardness variation in relation to carbide development in heat treated Cr_3C_2-NiCr thermal spray coatings. Cr_3C_2-NiCr thermal spray coatings have been extensively used to mitigate high-temperature wear. During deposition, compositional degradation occurs through dissolution of the carbide phase into the matrix. High-temperature exposure leads to transformations in the microstructure, which influences the coating microhardness. While such developments have been investigated in short-term trials, no systematic long-term investigations of the microhardness variation as a function of microstructural development have been presented. In this work, high-velocity sprayed Cr_3C_2-NiCr coatings were heat treated at 900 °C for up to 60 days in air and argon. With treatment, matrix phase supersaturation was reduced, while widespread carbide nucleation and growth generated an expansive carbide skeletal network. An initial softening of the coatings occurred through matrix phase refinement, the subsequent hardness recovery was a function of

carbide development. Treatment in air generated further hardness increases as a result of internal oxidation.

Keywords: carbides, cermets, composition, degradation, microhardness, sprayed coatings

S. Matthews, M. Hyland, and B. James, Department of Chemical Engineering, Univ. of Auckland, Auckland, New Zealand. Cited: *Acta Mater., 51*(14), 15 Aug 2003, pp. 4267-4277 [in English]. ISSN 1359-6454.

Nondestructive Testing

Acoustic emission study on WC-Co thermal sprayed coatings. Thermally sprayed coatings contain residual stresses that are produced in the spraying process. These may reduce the coating lifetime. In order to determine the optimum spraying conditions with respect to the residual stress level present, the acoustic emission (AE) during four-point bend tests on tungsten carbide-cobalt coatings sprayed onto mild steel substrates was investigated. Samples tested at different levels of deformation were studied by means of scanning electron microscopy and AE in order to understand the cracking mechanisms. Relationships between the number and amplitude of AE events detected and the type of cracking processes occurring were established. It has been possible to compare the residual stresses caused by the effect of different spraying parameters, such as coating thickness, spraying distance, and high-velocity oxyfuel gun.

Keywords: acoustic emission testing, carbon steel, cobalt, crack initiation, deformation, residual stresses, scanning electron microscopy, spraying, tungsten carbide

J.M. Miguel, J.M. Guilemany, B.G. Mellor, and Y.M. Xu, CPT (Thermal Spray Centre), Materials Engineering, Dept.d'Enginyeria Quimica i Metall., Barcelona E-08028, Spain. Cited: *Mater. Sci. Eng. A, 352*(1-2), 15 July 2003, pp. 55-63 [in English]. ISSN 0921-5093.

Quantitative infrared thermographic nondestructive testing of thermal barrier coatings. In power production and aviation, thermal barrier coatings are widely used to improve performance of turbine blades. During deposition of plasma sprayed coatings, some discontinuities might appear to affect the ability of turbine blades to withstand high temperatures and protect primary parts. Thermal testing systems are increasingly used in the testing of thermal barrier coatings due to large surface, rapid and noncontact testing capabilities. In this work, the features of the thermal nondestructive testing (NDT) of thermal barrier coatings are summarized and current problems, such as residual heating, spurious reflections, and coating transparency, are addressed. The experimental data are presented along with advanced processing results obtained by using pulse phase thermography and principal component analysis. The comparison of the processing techniques is done in the detection of delaminations between the coating and substrate. The problem of the discrimination between the coating thickness variations and delaminations, as well as the sensitivity of thermal NDT, is discussed.

Keywords: coating techniques, delamination, infrared radiation, nondestructive examination, principal component analysis, surface properties, thermal effects, thermography (temperature measurement), turbomachine blades

S. Marinetti, V. Vavilov, P.G. Bison, E. Grinzato, and F. Cernuschi, Ist. Tecnologie della Costruzione, Padova 4-35127, Italy. Cited: *Mater. Eval., 61*(6), June 2003, pp. 773-780 [in English]. ISSN 0025-5327.

Nondestructive measurement of fatigue damage of thermally sprayed Al_2O_3/NiCr using ESPI method under high temperature. High-temperature fatigue ($R = 0$) damage and deformation behaviors of SUS304 steel thermally sprayed with an Al_2O_3/NiCr coating were investigated using a servopulse fatigue-testing machine, scanning electron microscopy (SEM), and an electronic speckle pattern interferometry (ESPI) method. The relation between crack/delamination and strain variation is discussed. Surface cracks occurred at the outer Al_2O_3 coating, but stopped at the inner NiCr coating after one fatigue cycle when the tensile stress was 202 MPa at 873 K. They propagated into the NiCr coating but stopped at the substrate, and local delamination occurred along the NiCr/substrate interface after 1×10^5 cycles test in condition (σ_{max} = 202 MPa, T = 873 K). Cracks and delamination largely decreased when σ_{max} = 115 MPa or T = 573 K. No influence of cycle frequencies (6.7 or 14 Hz) was detected. The strain value measured by ESPI method was confirmed to be almost the same as that obtained with strain gauges at 293 K. Strain values along cracks measured with the ESPI method were much larger than other areas as a result of crack opening under the tensile load, referred to as the strain concentration zone in this work. Positions of strain concentration zones on strain distribution figures by the ESPI method corresponded well to positions of cracks on sprayed coatings. Moreover, strain values largely decreased where local delamination occurred.

Keywords: aluminum coated steel, deformation, delamination, fatigue of materials, high-temperature effects, interfaces (materials), interferometry, nickel compounds, nondestructive examination, strain

R. Wang and M. Kido, Dept. of Mech. Systems Engineering, Faculty of Engineering, Hiroshima Univ., Higashi-Hiroshima 739-8527, Japan. Cited: *J. Nondestr. Eval., 21*(4), Dec 2002, pp. 117-126 [in English]. ISSN 0195-9298.

Residual Stress Determination

Analysis for residual stress and deformation of coated member using inherent strain method. The characteristics of residual stress and deformation of thermal sprayed plates, that are the most important property from the viewpoint of production technique for preventing the cracking and delaminating of coatings, have not always been made clear. In this paper, the residual stress and deformation behaviors of rectangular plate, induced by the inherent strain of coating layer due to thermal spraying, was analyzed using the finite-element method. It was confirmed that the dimensionless parameters of $\sigma \cdot (1 - V_c)/(E_c \cdot \varepsilon_I)$ and $u \cdot T/(L^2 \cdot \varepsilon_I)$ was useful for presenting the residual stress and deformation characteristics of thermal sprayed plates. (σ = residual stress, ν_c = Poisson's ratio of coating, E_c = Young's modulus of coating, ε_I = inherent strain of coating layer, u = displacement. T = thickness of substrate, and L = length of substrate) It was found that the inherent strain of coating layer, which was calculated by the deformation of thermal sprayed plates, was almost constant in case of the atmospheric plasma sprayed CoNiCrAlY over IN 738 LS substrate.

Keywords: coatings, crack initiation, delamination, elastic moduli, finite-element method, plasma spraying, plastic deformation, Poisson ratio, residual stresses, strain, thickness measurement

Y. Itoh, A. Tanaka, K. Saitoh, and R. Takaku, Power and Indust. Syst. R and D Ctr., Toshiba Corporation, Tsurumu-ku, Yokohama-shi, Kanagawa, Japan. Cited: *Nippon Kikai Gakkai Ronbunshu, A Hen/Trans. Jpn. Soc. Mech. Eng., Part A, 69*(4), April 2003, pp. 727-732 [in Japanese]. ISSN 0387-5008.

Metallurgical characterization and determination of residual stresses of coatings formed by thermal spraying. This work presents an experimental determination of residual stresses in 35CrMo4 (Euronorm) low-alloy steel substrates with thermally sprayed coatings. Two different materials were separately deposited. The first one consisted of a blend of two superalloys: chromium-nickel steel and chromium-manganese steel, designated 55E and 65E, respectively. The second material was molybdenum. In a first part, basic characteristics of the deposited layers (metallographic analysis, hardness, and adhesion) are presented. In a second part, the determination of the residual stresses, in both substrate and thermal sprayed layers is performed using an extensometric method in combination with a simultaneous progressive electrolytic polishing. The influence of a nickel-aluminum (80:20%) bondcoat and/or a post-annealing at 850 °C in air for 1 h is studied.

Keywords: adhesion, residual stresses, spraying, steel, superalloys

M. Laribi, A.B. Vannes, N. Mesrati, and D. Treheux, Dpt. de Metallurgie, Ecole Nationale Polytechnique, El Harrach, Algiers, Algeria. Cited: *J. Therm. Spray Technol., 12*(2), June 2003, pp. 234-239 [in English]. ISSN 1059-9630.

Residual stress in plasma sprayed hydroxyapatite coating measured by the material removal method. Plasma sprayed hydroxyapatite (HA) on titanium alloy implants was used for orthopedics and dentistry. The HA coating was able to form a chemical bond to bone. As such, a study was conducted on the residual stress of HA coating on titanium alloy using x-ray diffractometry and found that the stress was compressive. The residual stress state in the coating does explain the findings that the bonding strength of the system decreases with increasing compressive residual stress, which was supported by mechanics of coated surfaces.

Keywords: bending (deformation), chemical bonds, mechanical variables measurement, melting, plasma spraying, protective coatings, residual stresses, scanning electron microscopy, shear strength, thickness measurement, x-ray diffraction analysis

Y.C. Yang and E. Chang, Dept. of Materials Science and Eng., National Cheng Kung Univ., Tainan 701, Taiwan. Cited: *J. Mater. Sci. Lett., 22*(13), 1 July 2003, pp. 919-922 [in English]. ISSN 0261-8028.

Small-Angle Neutron Scattering

Small-angle neutron scattering study of the role of feedstock particle size on the microstructural behavior of plasma sprayed yttria-stabilized zirconia deposits. The microstructures of thick plasma sprayed yttria-stabilized zirconia deposits were discussed. The deposits were studied in a series of Porod small-angle neutron scattering (SANS) and multiple small-angle neutron scattering (MSANS) experiments. The study was focused on gaining a better understanding of the effects of initial feedstock particle size and annealing temperatures on the microstructure of deposits.

Keywords: annealing, elastic moduli, microstructure, neutron scattering, particle size analysis, plasma spraying, scanning electron microscopy, volume fraction

H. Boukari, A.J. Allen, G.G. Long, J. Ilavsky, J.S. Wallace, C.C. Berndt, and H. Herman, Natl. Inst. of Std. and Technology, Gaithersburg, MD 20899. Cited: *J. Mater. Res., 18*(3), March 2003, pp. 624-634 [in English]. ISSN 0884-2914.

Stiffness and Fracture Toughness

Toughness evaluation of HVOF WC-Co coatings using nonlinear regression analysis. The models for predicting indentation toughness of materials are usually functions of both indenter and induced crack (i.e., Palmqvist or Half-Penny) geometries. Palmqvist cracks have already been identified in sintered WC-Co cermets. In the present work, the indentation toughness of high-velocity oxyfuel thermally sprayed WC-12%Co coatings has been evaluated using a standard metallographic procedure. Two crack regimes were found to occur in such coatings, depending on the indentation load: at low indentation loads, Palmqvist cracks appeared, while Half-Penny cracks were detected at high indentation loads. A statistical methodology was developed in order to determine the indentation toughness of WC-12%Co coatings, which were heat treated at 1173 and 1463 K, from induced crack sizes measured at different loads. The nonlinear regression analysis statistically confirmed the existence of two regimes for crack propagation and two distinct toughness values were recorded for the same material under different load conditions. The present results indicate that adequate postheat treatments can lead to an increase in coating toughness.

Keywords: crack propagation, cracks, heat treatment, indentation, regression analysis, toughness

M.M. Lima, C. Godoy, J.C. Avelar-Batista, and P.J. Modenesi, Res. Centre in Surface Engineering, Univ. of Hull, Hull HU6 7RX, U.K. Cited: *Mater. Sci. Eng. A, 357*(1-2), 25 Sept 2003, pp. 337-345 [in English]. ISSN 0921-5093.