

## Selected Patents Related to Thermal Spraying

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### Applications

**High-Performance Hardmetal Materials.** Hardmetal compositions each including hard particles having a first material and a binder matrix having a second, different material comprising rhenium or a Ni-based superalloy. Tungsten may also be used a binder matrix material. A two-step sintering process may be used to fabricate such hardmetals at relatively low sintering temperatures in the solid-state phase to produce substantially fully densified hardmetals. A hardmetal coating or structure may be formed on a surface by using a thermal spray method.

US 7645315: Shaiw-Rong S. Liu. Company: Worldwide Strategy Holdings Ltd. Issued/Filed: 2010-01-12/2005-03-15.

**Niobium-Based Compositions and Coatings, Niobium Oxides and Their Alloys Applied by Thermal Spraying, and Their Use as an Anticorrosive.** The novelty proposed herein describes the application of niobium-based compositions and coatings, niobium oxides and their alloys capable of associations with other oxides and alloys by means of the thermal spraying technique for the purpose of an anticorrosive protection in highly corrosive environments, mainly those which present high temperatures, show presence of gases such as  $H_2S$ ,  $SO_2$ ,  $CO_2$ , as well as organic and inorganic acids, commonly found in industrial centers.

US 7651731: Luiz R. Martins Miranda, Ladimir J. Carvalho, and Antonio C. Goncalves Pereira. Company: Universidade Federal do Rio de Janeiro. Issued/Filed: 2010-01-26/2002-11-13.

**Reactive Shaped Charges Comprising Thermal-Sprayed Reactive Composites.** Shaped charge liners are made of reactive materials formed by thermal spray techniques. The thermally sprayed reactive-shaped charge materials have low porosity and high structural integrity. Upon detonation, the reactive materials of the shaped charge liner undergo an exothermic reaction that raises the temperature and the effectiveness of the liner.

US 7658148: Timothy Langan, Michael A. Riley, and W. M. Buchta. Company: Surface Treatment Technologies, Inc. Issued/Filed: 2010-02-09/2007-10-05.

**Ceramic Fibers and Composites Comprising the Same.** Ceramic fibers comprising glass, and composites comprising such fibers. The glass comprises at least 35% by weight  $Al_2O_3$ , based on the total metal oxide content of the glass, a first metal oxide other than  $Al_2O_3$ , and a second, different metal oxide other than  $Al_2O_3$ . The glass contains not more than 10 wt.% collectively  $As_2O_3$ ,  $B_2O_3$ ,  $GeO_2$ ,  $P_2O_5$ ,  $SiO_2$ ,  $TeO_2$ , and  $V_2O_5$ , based on the total weight of the glass. The first and the second metal oxides are each selected from the group consisting of  $Y_2O_3$ , REO, MgO,  $TiO_2$ ,  $Cr_2O_3$ , CuO, NiO,  $Fe_2O_3$ ,  $ZrO_2$ ,  $HfO_2$ , and complex metal oxides thereof. At least a portion of the glass may be converted to crystals.

US 7662735: Anatoly Z. Rosenflanz, Ahmet Celikkaya, and Thomas J. Anderson. Company: 3M Innovative Properties Company. Issued/Filed: 2010-02-16/2007-06-26.

**Thermally Sprayed Bearing Layer, Which is Made of Copper Alloy.** The thermally sprayed bearing layer, which is made of copper alloy and is built with a filler material (2-60 wt.%) dispersed in the copper alloy, for a connecting-rod eye of a connecting rod, is claimed. The filler material is made of aluminum oxide powder, and has a maximum grain size of 50  $\mu m$ . The bearing layer has a gradient of aluminum oxide content, which decreases from the base of the thermally sprayed bearing layer to a surface. An independent claim is included for a method for producing a thermally sprayed bearing layer for a connecting-rod eye of a connecting rod.

DE 102008053640: Karl Holdik, Thomas Kempe, Sven Kollinger, and Matthias Walther. Company: Daimler AG. Issued/Filed: 2010-02-18/2008-10-29.

**Thermally Sprayed Cylinder Bore Coating Useful in an Internal Combustion Engine.** The thermally sprayed cylinder bore coating useful in an internal combustion engine, comprises copper alloy containing manganese content (11-15 wt.%) and aluminum content (5-9 wt.%) or tin content (10-14 wt.%). An independent claim is included for a method for producing a thermally sprayed cylinder bore coating for an internal combustion engine.

DE 102008053641: Karl Holdik, Thomas Kempe, Sven Kollinger, and Matthias Walther. Company: Daimler AG. Issued/Filed: 2010-02-18/2008-10-29.

**Femoral Implant for Osteopathy Patient.** The implant has a spindle anchored by impaction in a bone area of a femur, and for fixing a connection head with a hip. The spindle is provided with a coating comprising a rough metallic layer and a bioactive layer based on hydroxyapatite, where thickness of the bio-active layer decreases from a proximal upper part to a distal part of the spindle. The bio-active layer is realized by depositing the hydroxyapatite through a plasma torch. An independent claim is also included for a method for fabricating a femoral implant.

FR 2925857: Massin Philippe, Galline Yves, Fariborg Sabri, Lazennec Jean Yves, Mauger Stephane, Robin Henri, Artieres Xavier, Soubrane Philippe, Ciampi Claudio, Deroche Philippe, Farizon Frederic, Chapuis Patrick, and Laine Marc. Company: Ceram Concept France SARL. Issued/Filed: 2010-03-05/2008-01-02.

**Susceptor Device.** A susceptor device comprises a base body, an electrostatic absorbing inner electrode which is disposed on a bottom surface of the base body, a power supplying terminal, an insulating-sprayed layer which coats the electrostatic absorbing inner electrode and a connecting section for the power supplying terminal and the electrostatic absorbing inner electrode, and a temperature controlling section. The insulating-sprayed layer and the

temperature controlling section are attached together unitarily via the bonding agent layer. The flange of the base body fits to a notched section of the temperature controlling section such that the electrostatic absorbing inner electrode, insulating-sprayed layer, and the bonding agent layer should be sealed from there outside. It is possible to form a thin supporting plate and improve controllability for temperature on the plate sample and transparency for the plasma.

US 7678197: Keigo Maki. Company: Sumitomo Osaka Cement Co. Ltd. Issued/Filed: 2010-03-16/2003-08-04.

**Connecting Rod With a Multilayered Thermally Sprayed Porous Bearing Layer.** Bearing shells are inserted into the connecting-rod eyes of connecting rods in internal combustion engines. The insertion of the bearing shells increases the complexity of the production process which can lead to errors being made. The aim of the invention is to provide a method for producing connecting-rod bearings which are easier to install. According to the invention, a microporous aluminum bronze plasma-coating is applied to the large connecting-rod eye. The connecting-rod eye is then opened by removing the bearing cover, thus breaking the plasma coating. The cover is subsequently screwed back on and the actual lining finished by fine spindling. The plasma coating has an annular groove to improve the oil retention volume. The invention is suitable for use in internal combustion engines.

EP 1000259: Udo Schlegel and Reinhard Vogelsang. Company: Volkswagen AG. Issued/Filed: 2010-03-17/1998-07-20.

**Proton Conducting Materials and Devices Incorporating Them.** Materials for use in proton transport characterized by several formulas are disclosed. Mixed ion and electron conductors may include metals and/or ceramic electron conductors and a proton conducting material. Hydrogen separation membranes may include porous layers and an electrolyte layer including a proton conducting material and an electron conductor. Hydrogen separation membranes may be formed by thermal spray techniques. Hydrogen separation membranes may include a catalyst layer. A method of separating hydrogen from a mixed gas stream

includes passing the mixed gas through a first porous layer to an electrolyte layer, dissociating protons and electrons, diffusing the protons and electrons through the electrolyte layer, recombining them, and passing molecular hydrogen through a second porous layer.

US 7682494: Brian S. Berland, Sabina Gade, Ronald W. Schaller, and Michael Schwartz. Company: ITN Energy Systems, Inc. Issued/Filed: 2010-03-23/2008-05-16.

**Use of Metal Supported Copper Catalysts for Reforming Alcohols.** This invention is directed to a process for reforming an alcohol. The process comprises contacting an alcohol with a reforming catalyst comprising copper at the surface of a metal supporting structure, preferably a metal sponge supporting structure comprising nickel. In a certain preferred embodiment, hydrogen produced by the reforming process is used as a fuel source for a hydrogen fuel cell to generate electric power, particularly for driving a vehicle.

US 7682724: David A. Morgenstern. Company: Monsanto Technology LLC. Issued/Filed: 2010-03-23/2003-10-16.

**Heterogeneous Composite Bodies With Isolated Lenticular-Shaped Cermet Regions.** A heterogeneous body having ceramic-rich cermet regions in a more ductile metal matrix. The heterogeneous bodies are formed by thermal spray operations on metal substrates. The thermal spray operations apply heat to a cermet powder and project it onto a solid substrate. The cermet powder is composed of complex composite particles in which a ceramic-metallic core particle is coated with a matrix precursor. The cermet regions are generally comprised of complex ceramic-metallic composites that correspond approximately to the core particles. The cermet regions are approximately lenticular shaped with an average width that is at least approximately twice the average thickness. The cermet regions are imbedded within the matrix phase and generally isolated from one another. They have obverse and reverse surfaces. The matrix phase is formed from the matrix precursor coating on the core particles. The amount of heat applied during the formation of the heterogeneous body is controlled so that the core particles soften but do not

become so fluid that they disperse throughout the matrix phase. The force of the impact on the surface of the substrate tends to flatten them. The flattened cermet regions tend to be approximately aligned with one another in the body.

US 7681622: Andrew J. Sherman. Issued/Filed: 2010-03-23/2006-06-23.

**Method of Repairing a Stationary Shroud of a Gas Turbine Engine Using Plasma Transferred Arc Welding.** A stationary shroud of a gas turbine engine made of a base metal is repaired by removing any damaged material from a flow-path region of the stationary shroud to leave an initially exposed base-metal flow-path surface; and applying a base-metal restoration overlying the initially exposed flow-path surface. The base-metal restoration is applied by furnishing a source of a structural material that is compatible with the base metal, and depositing the source of the structural material overlying the initially exposed base-metal flow-path surface of the stationary shroud by plasma transferred arc welding to form a repaired base-metal flow-path surface. An environmentally resistant rub coating may be applied overlying the base-metal restoration.

CA 2445237: Grossklaus Warren Davis Jr and Miller Matthew Nicklus. Company: General Electric. Issued/Filed: 2010-03-30/2003-10-16.

**Plasma Arc Weld Repair of High Nickel Metal Alloys.** A method for weld repairing airfoils made from nickel-based super alloy material is provided. The method includes removing a damaged portion of the airfoil by machining the airfoil to a relatively smooth surface. Powdered alloy material, such as IN-100 material is then fed to a plasma arc welding device. A plurality of weld beads are deposited along the damaged portion of the airfoil in a continuous bi-directional pattern by the welding device to eliminate abrupt thermal transients at the ends of the weld, thereby reducing the thermal stresses that cause cracking in susceptible alloys such as IN-100.

SG 159514: Lin Wangen, Stone Richard A, Larson Gary J, and Matz John. Company: United Technologies Corp. Issued/Filed: 2010-03-30/2006-02-01.

## Thermal Barrier Coatings and Bondcoats

### *High-Temperature Strength Member.*

A high-temperature strength member comprises a substrate of Ni-based single crystal alloy or a Ni-based unidirectional solidified alloy and a coating of a B-containing alloy having a specified B content formed on the surface thereof by a spraying process or a vapor deposition process.

EP 1308535: Masakazu Okazaki, Yoshio Harada, and Tatsuo Suidzu. Company: Tocalo Co. Ltd. Issued/Filed: 2010-03-10/2002-10-31.

### *Method for Preparing an Article Protected by a Thermal Barrier Coating Having a Cerium (4+) Oxide-Enriched Surface.*

A protected article is prepared by depositing a bond coat onto an exposed surface of the article; and producing a thermal barrier coating on an exposed surface of the bond coat. The thermal barrier coating is produced by depositing a primary ceramic coating onto an exposed surface of the bond coat, depositing a cerium-oxide-precursor compound onto an exposed surface of the primary ceramic coating, and heating the cerium-oxide-precursor compound in an oxygen-containing atmosphere to form cerium-oxide adjacent to the exposed surface of the primary ceramic coating.

EP 1541711: John F. Ackerman, Ramgopal Darolia, Brett A. R. Boutwell, Venkat S. Venkataramani, and Irene Spitsberg. Company: General Electric Co. Issued/Filed: 2010-03-31/2004-12-06.

## Spraying Systems and Methods

### *Powder Port Blow-Off for Thermal Spray Processes.*

A powder port blow-off system for a plasma spray process includes a faceplate that includes a bore therein that is co-radially aligned with a nozzle of a plasma spray gun, which emits a plasma plume. A plurality of powder feed ports are arranged circumferentially around the nozzle for injecting a flow of powder particles toward the plasma plume. A plurality of powder port blow-offs are arranged circumferentially around the nozzle in order to direct blow-off gas across the powder feed ports. The powder port blow-offs are directed across the plasma

plume to create a vortex for carrying away powder particles unconsumed by the plasma plume.

US 7644872: Thomas E. Lang and Christopher W. Strock. Company: United Technologies Corporation. Issued/Filed: 2010-01-12/2006-03-23.

**Plasma Spraying Method.** A method of forming a thermally insulating layer system on a metallic substrate surface is disclosed. The method includes: forming a plasma beam; introducing a coating material in the form of a powder having particles in the range between 1 and 50  $\mu\text{m}$ , carried by a delivery gas into the plasma beam, so as to form a powder beam; defocusing the powder beam using the plasma beam with a sufficiently high specific enthalpy and by maintaining a process pressure between 50 and 2000 Pa for at least partially melting and vaporizing at least 5 wt.% of the powder, so as to form a vapor phase cloud; and forming from the vapor phase cloud onto the metallic substrate surface an insulating layer, being a part of the insulating layer system, having an anisotropic columnar microstructure having elongate particles; wherein the anisotropic columnar microstructure is aligned substantially perpendicular to the metallic substrate surface and low-density transition regions with little material delimit the elongate particles relative to one another.

US 7678428: Gerard Barbezat, Arno Refke, and Michael Loch. Company: Sulzer Metco AG. Issued/Filed: 2010-03-16/2003-03-18.

### *High Frequency Pulse Rate and High Productivity Detonation Spray Gun.*

A detonation gun for thermal spraying formed by a combustion chamber and a barrel, with entrances for fuel and for oxidizer, one or more spark plugs for detonating the fuel-oxidizer mixture and one or more injectors for the introduction of the product into the barrel, the gun in the invention centers its characteristics on the incorporation of a direct injection system of the fuel and oxidizer gases into the explosion chamber, producing explosive mixtures of different compositions according to the various zones in the explosion chamber, with a constrained volume existing in this explosion chamber in which only fuel is injected in such a way that it can generate high-energy

explosions, maintaining the cyclic operation of the gun. The gun also incorporates in the barrel (2-2'), one or more annular injectors, which allow the feeding of various products, and especially coating powder, so that it is possible to increase the number of kilograms deposited on the substrate per unit of time and, in consequence, the gun's productivity.

CA 2388618: Barykin Georgy Yur'evich and Fagoaga Altuna Inaki. Company: Aerostar Coatings S L. Issued/Filed: 2010-03-23/1999-10-28.

## Pre- and Post-Treatment

### *Method of Thermal Spraying.*

An adhesion strength of spray coating comparable to that obtained in a conventional combination of blast treatment and gas flame spraying can be realized even if roughening is conducted with the use of simple tools by performing in advance such a roughening treatment that the average roughness ( $R_a$ ) of the surface of the thermal spray subject falls within the range of 2-10  $\mu\text{m}$  with the use of a grinding tool, and thereafter carrying out thermal spraying under such conditions that the average area of each of molten particles when molten particles of a thermal spray material have stuck to the surface of thermal spray subject falls within the range of 10,000 to 100,000  $\mu\text{m}^2$ . In the roughening by grinding tools, a large-scale apparatus is not needed as different from the blast treatment, and portable small tools can be used in overhead location work at field repair. The scattering of powder resulting from grinding is slight so that the danger of environmental pollution is low.

US 7682667: Yukio Imaizumi, Hiroki Kamakura, Toshio Sakurada, Kenichi Yamada, and Katsuhiko Ishibashi. Company: Nishinippon Plant Engineering and Construction Co. Ltd., Yamada Corrosion Protection Co. Ltd., Kyushu Electric Power Co. Inc. Issued/Filed: 2010-03-23/2004-10-15.

### *Thermal Spraying Device and Method.*

A high-velocity oxygen-fuel (HVOF) thermal spray assembly applies a protective coating of, e.g., MCrAlX to a workpiece, e.g., gas turbine engine blade as it rotates about an axis. The spray jet directed at an angle to the axis of rotation and varies during the spray application procedure by part alteration

of the axis of rotation. The change in axis of rotation is synchronized with the shift in angle of spray discharge. The axis of rotation varies between 0° and 30° and passes through the work piece. The assembly has a work piece holder that rotates about an axis, a spray jet, a swivel-action motion driver, and a movable spray jet. Also claimed is a commensurate process.

EP 1816229: Katharina Bergander, Thomas Berndt, and Francis-Jurjen Dr. Ladru. Company: Siemens AG. Issued/Filed: 2010-03-24/2006-01-31.

#### ***Thermal Deposition Coating Method.***

A process for the thermal deposition coating of a workpiece, said process comprising the steps of: (a) thermally depositing a coating on a metallic surface of a workpiece from a deposition head wherein at least one condition selected from the group of: coating deposition rate onto said surface, relative motion between the surface and said deposition head, and cryogenic coolant application rate onto said workpiece is controllable; (b) substantially simultaneously measuring temperatures at a plurality of locations over the metallic surface of the workpiece; (c) determining an average temperature of the temperatures measured in step (b); (d) comparing the average temperature to a preselected minimum temperature and a preselected maximum temperature for the workpiece; and (e) adjusting at least one of the controllable conditions if said average temperature is not between the preselected minimum temperature and the preselected maximum temperature for the workpiece. Standard deviations of all temperature readings and controlling the relative motion speed between the thermal coating deposition head and the workpiece provide another improvement for obtaining temperature uniformity over the workpiece surface.

CA 2542013: Zurecki Zbigniew. Company: Air Products & Chemicals, Inc. Issued/Filed: 2010-03-30/2006-04-05.

#### **Feedstock**

***Composite Wires for Coating Substrates and Methods of Use.*** A composite wire for producing a wear-resistant and corrosion-resistant coating on a substrate by thermal spraying,

spray and fuse, or welding techniques are disclosed. The physical properties of the coating are particularly suited for high-temperature erosion-corrosion environments. The resultant coating exhibits good hardness, toughness, and bonding characteristics. The composite wire comprises a metallic outer sheath and an inner core containing boron carbide and chrome carbide.

US 7645493: Michael Seitz. Issued/Filed: 2010-01-12/2007-06-05.

#### ***Thermal Spray Powder of Dicalcium Silicate and Coating Thereof and Manufacture Thereof.***

A powder of dicalcium silicate is made by spray drying calcia and silica with incorporation of sodium and phosphorus or stabilized zirconia. The spray dried powder is sintered to form a thermal spray powder. Sprayed coatings have a web of interconnected, randomly oriented microcracks substantially perpendicular to the coating surface. The coatings are stable in thermal cycling and a hot corrosive environment.

CA 2308921: Wei Xiaohan, Dorfman Mitchell R, Correa Luis F., Jansen Franz, and Peters John. Company: Sulzer Metco US Inc. Issued/Filed: 2010-02-09/2000-05-18.

#### ***Wire-Like Spray Material, Useful for Arc Wire Spraying, and Coating Substrate.***

Wire-like spray material comprises iron, where the spray material is formed together with carbon as a microalloy, so that bainite and martensite are developed during hardening of the spray material, and the alloy contains carbon (0.23-0.4 wt.%); silicon (0.7-0.98 wt.%); manganese (1.4-1.9 wt.%); chromium (0.75-0.95 wt.%); copper (0.2-0.25 wt.%); molybdenum (0.07-0.095 wt.%); nickel (0.15-0.25 wt.%); aluminum (greater than 0.05 wt.%); vanadium (0.17-0.2 wt.%); nitrogen (0.005-0.013 wt.%); boron (0.0015-0.0025 wt.%); and titanium (0.02-0.035 wt.%).

DE 102008034547: Christian M. Erdmann, Patrick Izquierdo, Eyuep A. Oezdeniz, and Franz Rueckert. Company: Daimler AG. Issued/Filed: 2010-02-25/2008-07-24.

***Sprayable Compositions.*** The present invention provides a sprayable composition comprising a ceramic particulate including albite, illite, and quartz, and a

metallic composition, including nickel, chromium, iron, and silicon. The sprayable composition may be a composite particle, a blend, or a cored wire. The present invention further provides an abrasible coating formed on a metal substrate according to a method comprising the step of depositing a bond coat on the metal substrate by thermal spraying of a bond coat composition comprising nickel, chromium and optionally aluminum and yttrium on the metal substrate and depositing the abrasible coating on the bond coat by thermal spraying of a sprayable composition comprising a ceramic particulate including albite, illite, and quartz, and a metallic composition, including nickel, chromium, iron, and silicon. The sprayable composition may be a composite particle, a blend, or a cored wire. The abrasible coating may be applied to the top of the bond coat that is applied to a metal substrate such as steel, nickel-based alloys, and titanium.

CA 2639732: Hajmrle Karel, Chilkowich Anthony Peter, and Fiala Petr. Issued/Filed: 2010-03-19/2008-09-19.

#### **Diagnostics and Characterization**

##### ***Arrangement for Monitoring Thermal Spray Processes.***

An arrangement for measuring characteristic properties of a plasma beam in a thermal spray process, including a device for introducing spray materials into the plasma, a one-dimensional or two-dimensional array including first optical waveguides for receiving the light radiation emitted by the plasma, and other optical waveguides for distributing the light radiation emitted by the plasma. A device is provided for splitting the light guided in the first optical waveguides into the other optical waveguides, one optical waveguide being connected to the opening diaphragm of a particle flow arrangement, and the other optical waveguide being connected to the opening diaphragm of a spectrometer. A device is also provided for determining the current state of the spray process.

US 7688441: Manuel Hertter, Joerg Hoeschele, Stefan Schneiderbanger, and Juergen Steinwandl. Company: MTU Aero Engines GmbH. Issued/Filed: 2010-03-30/2006-03-30.