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(54) Powder of plastic and treated mineral.

(57) A thermal spray powder is formed of a blend of particles of a polymeric powder and a mineral wherein the mineral particles, and preferably also the polymeric particles, each have a coating layer thereon approximately one monolayer thick. The layer is an organofunctional silane which includes an organofunctional group such as an amino propyltriethoxy. The silane is formed from a precursor silane having a hydrolyzable group bondable to the mineral constituent upon hydrolyzing of the hydrolyzable group. Desirably the mineral is silicon aluminum alloy and the polymeric powder is a poly-(para-oxybenzoyl)ester.

POWDER OF PLASTIC AND TREATED MINERAL

The present invention relates to a thermal spray powder formed of a plastic and a mineral, and particularly to such a powder characterized by improved cohesive strength and bonding when thermal sprayed onto plastic substrates.

BACKGROUND OF THE INVENTION

Many mechanical parts in automobiles and airplanes have special mineral coatings such as metal or ceramic for special properties such as hardness, wear resistance, etc. Such coatings are provided on parts such as gears, pulleys, shafts, and the like, made of metal. However, the metal part itself is often just a carrier for the coating and could be replaced by lighter weight, often easier to fabricate, plastic if it were possible suitably to coat the plastic.

A simple technique for coating surfaces with metal or ceramic is by thermal (flame) spraying, employing either powder or wire. When attempting to thermal spray onto plastic, however, special problems are encountered. Upon cooling, the sprayed metal contracts and may warp or distort the plastic. The coating sometimes fails to adhere uniformly. The plastic substrate may melt from the material being sprayed and lose its shape, or the plastic surface may burn or decompose.

As disclosed in U.S. Patent No. 4,388,373 (Longo et al) it has been found that plastic substrates can be flame sprayed with a mineral powder which has been admixed with small amounts of nylon and epoxy polymers in powder form. The powder particles in finely sub-divided form may be agglomerated with a binder or adhesive, mixed and dried, the agglomerates being composed of subarticles of the individual components and being screened to recover particles of a particular size. The resulting agglomerates, or a simple powder mixture itself, can be flame sprayed in conventional manner onto the substrate. The coating can range in thickness from about 25 um to 5 mm or greater.

A composite powder of austenitic stainless steel, epoxy and nylon according to the above-described patent (assigned to a predecessor of the present assignee) has been quite successful for producing a thermal spray coating on plastic substrates, either for bonding another thermal spray coating or for use as is. However, spray technique is somewhat critical causing variation in results, and further improvement in bonding and cohesive strengths has been in demand. Also, for certain applications a different plastic constituent for the coating material is necessary or desired, for example a high temperature plastic.

U.S. Patent No. 3,723,165 (Longo and Durmann) discloses thermal spray coating materials comprising a high temperature plastic and a metal. In particular a silicon aluminum powder blended with poly(para-oxybenzoyl)ester in accordance with Example 1 of the patent has been highly successful commercially as an abradable coating for turbine blade seals and the like in gas turbine engines. Again, however, the spraying is technique dependent and improved bonding and cohesiveness are desired.

Various binders have been used or suggested for forming composite thermal spray powders. For example, U.S. Patent No. 3,617,358 (Dittrich) discloses spray drying to produce thermal spray powders of fine particles agglomerated with any of a variety of binders. Usually the binder is burned off, but may not be in certain cases. For example, U.S. Patent No. 4,593,007 (Novinski) teaches silicon dioxide derived from ethyl silicate in the binder for producing an abradable and erosion resistant coating of an oxide and aluminum.

Silane coupling agents, such as described in a text book "Silane Coupling Agents" by E.P. Plueddemann (1982 Plenum Press, New York NY), for example Chapter 1(pp. 1-28) have been used traditionally in the fiber glass industry to improve the integrity and moisture resistance of composites reinforced with glass fibers. Organofunctional silanes are hybrid organic-inorganic compounds that are used as coupling agents. There exists more than one theory as to how silanes couple polymers and minerals, one of which is the formation of covalent bonds. The covalent bonds are formed during the curing cycle of the resin during the manufacture of the composite.

Objects of the present invention are to provide an improved plastic-containing thermal spray powder, to provide such a powder having improved bonding and cohesive strengths, to produce plastic-containing thermal spray coatings with reduced technique dependence, to provide a novel thermal spray material for bonding to plastic substrates, to provide a relatively high temperature plastic bonding powder, and to produce an improved abradable coating.

SUMMARY OF THE INVENTION

The foregoing and other objects are achieved by a thermal spray powder formed of a polymeric constituent and a mineral constituent, wherein at least the mineral constituent has a coating layer thereon comprising an organofunctional silane. The coating layer should be approximately one monolayer thick. Preferably the mineral constituent contains silicon and is, for example, a silicon aluminum alloy.

The silane preferably includes an organofunctional group of the amino or vinyl type. The silane should be formed from a precursor silane having a hydrolyzable group bondable to the mineral constituent upon hydrolyzing of the hydrolyzable group. Desirably the polymeric constituent also has a silane layer thereon and may comprise, for example, a poly(para-oxybenzoyl)ester or an epoxy.

The foregoing and other objects are further achieved by a process for manufacturing a thermal spray powder, comprising forming a slurry of a mineral powder with an aqueous solution of an organofunctional silane having a hydrolyzable group, drying the slurry to form silane coated powder particles, and blending the coated powder with a polymeric powder. Preferably and conveniently the polymeric powder is blended in the slurry such that the thermal spray powder also includes silane coated polymer powder particles. The objects are further achieved with a thermal spray powder formed by this manufacturing process, and by thermal spraying the powder formed thereby.

DETAILED DESCRIPTION OF THE INVENTION

Broadly a thermal spray powder of the present invention is formed of a mineral constituent and a polymeric constituent. The mineral constituent may be any conventional or desired inorganic material utilized for thermal spraying. Examples are listed extensively in the aforementioned U.S. Patent No. 4,388,373 and U.S. Patent No. 3,617,358, both of which are incorporated herein by reference. Preferably, for reasons presented below, the mineral contains silicon. Thus the mineral may be silicon itself; one or more silicides of titanium, zirconium, hafnium, vanadium, niobium, tantalum, molybdenum, tungsten, chromium, or boron; a silicate or glass such as $3Al_2O_32SiO_2$ (mullite), BaO_2SiO_2, $BaOAl_2O_3SiO_2$, $BaOTiO_2SiO_2$, $2CaOSiO_2$, $Cr_2O_3SiO_2$, $Er_2O_3SiO_2$, ZrO_2SiO_2 (zircon), $2MgOSiO_2$, $ZrOZrO_2SiO_2$; or a silicon alloy of aluminum, bronze, nickel, cobalt or iron.

The polymeric constituent may be any conventional or desired thermal sprayable plastic such as polyester, epoxy, nylon, polyimide, polyether-etherketone or combinations thereof; or a high temperature plastic such as disclosed in aforementioned U.S. Patent No. 3,723,165. Examples of these high temperature plastics include the well-known polyimide plastics, polyamide-imide plastics, the polyester-imide plastics and the aromatic polyester plastics. Particularly suitable are high temperature aromatic polyester plastics of the type formed from phenyl acetate, as for example the poly(para-oxybenzoly)ester or poly(para-oxybenzoylmethyl)ester, or a co-polyester of the type disclosed in U.S. Patent No. 3,784,405 (Economy et al).

Generally the powder is in the conventional size range, vis. -147 +5 microns, preferably -88 +44 microns or alternatively -44 +5 microns. Also, in a preferred embodiment the powder is a simple blend of a mineral powder and a polymeric powder, as distinguished from a composite powder. However, a composite powder wherein a fine powder of one constituent is clad onto core particles of the other constituent is an alternative. Yet another alternative is a composite powder formed of fine powder constituents with a binder and produced by spray drying as taught in aforementioned U.S. Patent No. 3,617,358 or by mixing and stirring as taught in aforementioned U.S. Patent No. 4,388,373. The proportion of plastic to mineral should generally be in the range of 5% to 95% by volume, and preferably 5% to 25%.

According to the present invention at least the mineral constituent is treated such that each powder particle has a coating layer thereon comprising an organofunctional silane. Preferably the polymeric constituent is also so treated. The coating layer should have a thickness between about one half and two monolayers of silane, i.e. approximately one monolayer.

Organofunctional silanes are composed of two functional groups attached to a silicon (Si) atom. The general formula is X_3SiRY. The (Y) is an organofunctional group which is chosen for reactivity or compatibility with a polymer, while the (X) is a hydrolyzable group which merely acts as an intermediate in the formation of silanol groups for bonding to mineral surfaces. In the presence of water, the (X) group hydrolyzes to form a radical OH^- group which then bonds to the electrophilic mineral (M^+). The (R) is a conventional silane radial.

The silane will yield optimum coupling if it has a monolayer coverage of the surface. The surface area of the powder needs to be determined to estimate the required concentration of the silane treatment. Surface area may be measured by the conventional B.E.T. analysis method.

Preferably the silane includes an organofunctional group of the amino type or the vinyl type. More specifically the organofunctional group should be an aminopropyltriethoxy or glycidoxypropyltrimethoxy.

The inorganic functional groups of the silane are believed to bond best to silica. Therefore it is quite desirable that the mineral powder contain silicon as described above. The requirement is fulfilled directly if the mineral contains silica for example as glass. However, silicon per se or as a silicide or in alloy form is suitable, because there is some normal oxidation of the silicon during the thermal spraying process. A particularly preferable mineral is based on aluminum metal which has a coefficient of thermal expansion similar to that of most plastics. Thus silicon aluminum alloy, for example containing about 12% silicon, balance aluminum, is most preferable.

A suitable method to manufacture a powder according to the present invention, the plastic and metallic constituents are blended in a steam heated pot. A silane solution diluted with 95% to 99% water is added to get the mixture to a homogeneous slurry. The steam is turned on to drive off the water. Once the powder is dry and free flowing it is removed and screened. Alternatively, only the mineral powder is so treated, and the plastic powder is blended in afterward.

The steam pot drying of the powder is at sufficiently low temperature so as not to cure the plastic constituent or the silane with respect to it. Thus it has been discovered that the thermal spraying step which melts or at least surface heat softens the powder constituents effects the appropriate heat treatment to achieve excellent bonding and coating cohesion, without a high degree of spray technique dependence. It is not yet understood how this occurs, e.g. whether the (X) group hydrolizes and reacts with the mineral powder during the manufacturing process while the (Y) remains unreacted until the thermal spray process.

Coatings from about 25 microns to several millimeters in thickness may be produced by any of the powder thermal spray processes such as with a combustion spray gun of the type described in U.S. Patent No. 3,455,510 (Rotolico) or a plasma spray gun of the type described in U.S. Patent No. 3,145,287 (Seibein et al) or a high velocity oxygen-fuel gun such as described in U.S. Patent No. 4,416,321 (Browning).

Example 1

A blend of 40% by weight (56% by volume) of a high temperature aromatic polyester plastic, poly-(para-oxybenzoly)ester, sold under the trade name of EKONOL by the Carborundum Company, Sanford, N.Y., having a size of -88 +44, microns is blended with 60% by weight (44% by volume) of a silicon-aluminium alloy containing 12 weight percent silicon and a size of -325 +10 microns. These plastic and metallic constituents were blended in a steam heated pot. A triaminopropyltriethoxysilane solution diluted with 99% water is added to form a homogeneous slurry. The steam is turned on to drive off the water and dry the powder. Once the powder is free flowing it is removed and screening to -88 +44 microns.

The blend is sprayed with a high velocity oxygen-fuel spray gun specifically a Metco Type DJ(TM) gun sold by The Perkin-Elmer Corporation, Westbury, New York, using a #3 insert, # 3 injector, "A" shell, #2 siphon plug and #2 air cap. Oxygen was 10.5 kg/cm^2 (150 psig) and 212 l/min (450 scfh), propylene gas at 7.0 kg/cm^2 (100 psig) and 47 l/min (100 scfh), and air at 5.3 kg/cm^2 (75 psig) and 290 l/min (615 scfh). A high pressure powder feeder sold as a Metco Type DJP powder feeder by Perkin-Elmer is used to feed the powder blend at 1.6 kg/hr in a nitrogen carrier at 8.8 kg/cm^2 (125 psig) and 7 l/min (15 scfh). Spray distance is 20 cm.

Coatings 2.54 mm thickness were produced on a polyimide PMR-15/carbon fiber composite sold by Hysol Composites, Cleveland Ohio and prepared by light grit blasting. The coatings had a bond strength of 1.28 kg/cm^2 (900 psi), compared with 0.28 kg/cm^2 (200 psi) for a coating of Example 1 of the aforementioned U.S. Patent No. 4,388,373 (Metco 625 powder) on a similar substrate. A 100 micron thick coating of the present example had a surface roughness of at least 12 microns (500 microinches) aa, so as to be ideal for subsequent application of a mineral overcoat. After deposition of the overcoat, the bond to the plastic substrate was so tenacious that in test fractures metal particles adhered to the plastic substrate, pointing up the strong adhesion of the undercoat-overcoat combination to the plastic. Overcoating with thermal sprayed coatings of aluminum-bronze, nickel chromium and austenitic stainless steel give strongly adherent overcoats. Photomicrographs clearly show the reason for the difference in the bond strengths. Cross sections at a magnification of 500X of coatings on a laminate using untreated powder in the blend reveal extensive microcracking between the coating and the substrate. Coatings produced with powder treated according the present example show no such cracking.

Example 2

Example 1 is repeated with a Metco Type 9MB plasma spray gun using a Metco Type 4MP powder feeder, using the following parameters: 733 nozzle, No. 2 feed port, argon plasma gas at 100 psi and 100 l/min (212 scfh) flow, hydrogen secondary gas at 3.5 kg/cm^2 (50 psi) and 9 l/min (19 scfh) flow, 500 amperes and 70 volts, cooling air jets at 5.25 kg/cm^2 (75 psi), 1.5 kg/hr powder feed rate in argon carrier gas, and 9 cm spray distance. Bond strength is again very good.

Example 3

Example 1 is repeated with a different polymer powder, namely a bisphenol a epoxy. The epoxy powder is about 8% by weight (15% by volume). Similar results are effected.

Example 4

Example 1 is repeated using a different silane, namely glycidoxypropyltrimethoxysilane, in 99% by weight (99% by volume) water. Similar results are effected.

Example 5

Example 1 is repeated except a coating 3.2 mm thick is produced on a turbine shroud of nickel alloy for the compressor section of a gas turbine engine. For this purpose of coating onto a metal surface, a bond coat of nickel aluminide is used. An excellent, abradable, cohesive coating results.

Example 6

Example 1 is repeated except that the polyester is replaced with a copolyester of recurring units of Formula I, III, and IV as disclosed in the aforementioned U.S. Patent No. 3,784,405 (incorporated herein by reference) and sold as Xydar$^{(TM)}$ by Dartco Manufacturing Inc., Augusta, Georgia. The blend contains about 25% by weight (61% by volume) of the polymer. Similar results are effected.

While the invention has been described above in detail with reference to specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to those skilled in this art. The invention is therefore only intended to be limited by the appended claims or their equivalents.

Claims

1. A thermal spray powder formed of a polymeric constituent and a mineral constituent, wherein the mineral constituent has a coating layer thereon comprising an organofunctional silane.

2. A thermal spray powder according to Claim 1, wherein the mineral constituent is selected from the group consisting of metals, silicon and alloys thereof.

3. A thermal spray powder according to Claim 2, wherein the mineral constituent is a metallic alloy containing silicon.

4. A thermal spray powder according to Claim 3, wherein the metallic alloy is silicon aluminum.

5. A thermal spray powder according to Claim 2, wherein the mineral constituent comprises aluminum.

6. A thermal spray powder according to Claim 1, wherein the coating layer is approximately one monolayer thick.

7. A thermal spray powder according to Claim 1, wherein the silane includes an organofunctional group of the amino type or the vinyl type.

8. A thermal spray powder according to Claim 7, wherein the organofunctional group is amino propyltriethoxy or glyidoxypropyltrimethoxy.

9. A thermal spray powder according to Claim 1, wherein the silane is formed from a hydrolyzable silane group bondable to the mineral constituent upon hydrolyzing of the hydrolyzable group.

10. A thermal spray powder according to Claim 1, wherein the powder is formed as a simple blend of a first powder consisting essentially of the polymeric constituent and a second powder consisting essentially of the silane coated mineral constituent.

11. A thermal spray powder according to Claim 1, wherein the polymeric constituent is a modified polyester.

12. A thermal spray powder according to Claim 1, wherein the polymeric constituent is a poly(paraoxybenzoyl)ester.

13. A thermal spray powder according to Claim 1, wherein the polymeric constituent has a coating layer thereon comprising the organofunctional silane.

14. A thermal spray powder formed of a blend of particles of a polymeric powder and a silicon aluminum alloy, wherein the polymeric particles and the alloy particles each have a coating layer thereon approximately one monolayer thick comprising an organofunctional silane, the silane including a amino propyl triethoxy organofunctional group and being formed from a precursor silane having a hydrolyzable group bondable to the mineral constituent upon hydrolyzing of the hydrolyzable group.

15. A thermal spray powder according to Claim 14, wherein the polymeric powder is a poly(para-

oxybenzoyl) ester.

16. A process of manufacturing a thermal spray powder, comprising forming a slurry of a mineral powder with an aqueous solution of hydrolyzable organofunctional silane, drying the slurry to form a silane coated powder, and blending the coated powder with a polymeric powder.

17. A process according to Claim 16, wherein the polymeric powder is blended with the mineral powder in the slurry prior to drying.

18. A thermal spray powder formed by the process of Claim 16

19. A thermal spray powder formed by the process of Claim 17.

20. A process for producing a well bonded and coherent polymer-containing coating comprising thermal spraying the thermal spray powder of Claim 18.

21. A process for producing a well bonded and coherent polymer-containing coating comprising thermal spraying the thermal spray powder of Claim 19.

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EUROPEAN SEARCH REPORT

Application Number

EP 90 10 1100

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 279 769 (ROGERS CORP.) ---		C 23 C 4/04
A	PATENT ABSTRACTS OF JAPAN, vol. 8, no. 116 (M-299)[1553], 30th May 1984; & JP-A-59 23 801 (CHISSO K.K.) 07-02-1984 ---		
A	PATENT ABSTRACTS OF JAPAN, vol. 2, no. 74 (C-273)[1797], 3rd April 1985; & JP-A-59 208 064 (MITSUBISHI DENKI K.K.) 26-11-1984 ---		
A	FR-A-2 388 776 (SHERRITT GORDON MINES) ---		
A	GB-A-1 520 184 (METCO) ---		
A	GB-A-1 305 778 (STATNI VYZKUMNY USTAV MATERIALU) -----		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 23 C
B 22 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20-04-1990	ELSEN D.B.A.

CATEGORY OF CITED DOCUMENTS

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