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(54) **Title:** HIGH TEMPERATURE CERAMIC COATINGS INCORPORATING NANOPARTICLES

(57) **Abstract:** Ceramic coatings are made from nanoparticles to improve heat resistance and bonding to a substrate. Composite materials made by coating a substrate with the nanoparticle ceramic coatings are less susceptible to delamination as compared to existing coatings. The nanoparticle ceramic coatings include metal nanoparticles. The metal nanoparticles absorb heat and migrate to the surface of the ceramic coating during exposure to extreme heat, thereby removing heat from the ceramic coating. The inventive coatings are particularly heat resistant and can withstand extreme temperatures such as 4000 °F. The nanoparticle ceramic coatings are particularly useful for coating ceramic tiles used to protect spacecraft on reentry to the earth's atmosphere. The coatings can also be applied underneath the tiles of a spacecraft as a safety measure in case a tile is damaged or lost during a flight.

HIGH TEMPERATURE CERAMIC COATINGS INCORPORATING NANOPARTICLES

BACKGROUND OF THE INVENTION

1. The Field of the Invention

The present invention relates to ceramic coatings suitable for use as thermal barriers on a substrate. More particularly, the present invention relates to ceramic coatings made from a matrix of ceramic nanoparticles and a binder.

2. Related Technology

Ceramic materials are well known for their heat and corrosion resistance. For example, many spacecraft such as NASA space shuttles have ceramic tiles that protect the spacecraft from heat generated during reentry to the earth's atmosphere. These tiles are typically designed to shield the spacecraft from temperatures of about 3000 °F.

High temperature ceramic materials are often brittle and difficult to machine. Many ceramic parts are molded and then adhered to a substrate. Many of the advantages of ceramics can be achieved while minimizing the disadvantages by applying a thin layer or coating of the ceramic material on a substrate. Ceramic coatings can be applied to almost any material, including metal, glass, wood, or even other ceramics. The substrate can provide strength, structure, workability or other bulk properties, and the ceramic coating can be applied to the surface of the substrate to protect the substrate from heat and/or corrosion.

One problem with ceramic coatings involves the bonding interface between the surface of the substrate and the ceramic coating. Poor bonding at the interface between the ceramic coating and the substrate can result in delamination. The process that leads to delamination often begins with a small defect in the coating that propagates to form a crack. Such a process is illustrated in Figures 1A and 1B. A material 10 includes a substrate 12 with a coating 14. A crack may form in coating 16 from a defect in the molecular structure of the coating material. Heat impinging on the surface of the coating will travel through the crack 16 until it reaches interface 18. The bonding between the substrate 12 and coating 14 at the interface is often weak, which allows a portion of the coating layer to break away as shown in Figure 1B. The heat impinging the surface of the substrate 12 where coating layer 14 has delaminated will have a tendency to wedge under the coating at substrate-coating interface 18, thereby causing further delamination. As coating 14 delaminates, surface 12 is exposed to the heat source and will eventually deteriorate and fail.

Another source of cracking can occur due to the lack of density of the coating material. Figure 2 is a schematic showing the substrate-coating interface on a molecular level. Particles 22 in the coating layer will pack in a particular configuration. The size of the particles and their packing arrangement determines the spacing between particles. Even tight spacing can allow heat energy represented by arrows 24 to penetrate between particles 22 of coating 16. Energy penetrating coating 16 between particles 22 can also be a source of cracking and delamination.

Cracking and delamination can also be caused by differential expansion and contraction of substrate 12 and ceramic coating 14. Differences in the coefficient of thermal expansion for the substrate and the coating cause one of the two materials to expand more than the other during heating. This differential expansion and/or contraction stresses the bond at the interface between the coating and the substrate, causing the bond to weaken and, eventually, delamination of the coating.

In addition to reducing or preventing delamination, there is a desire to improve the heat tolerance of ceramic coatings. While many ceramic coatings are capable of withstanding thousands of degrees Fahrenheit, there is still a need for coatings that can withstand higher temperatures. In some specialized applications such as spacecraft reentry, it is desirable to use ceramic materials that can withstand temperatures in excess of 4000 °F.

BRIEF SUMMARY OF THE INVENTION

The present invention relates to improved nanoparticle ceramic coatings, uncured coating compositions, and substrates coated with the ceramic coatings. The ceramic coatings of the present invention include nanoparticles that improve the heat resistance of the ceramic coating and improve bonding to a substrate, thereby making the coatings less susceptible to delamination as compared to existing coatings. The coatings can also include metal nanoparticles that migrate to the coating surface during exposure to extreme heat. These coatings are particularly heat resistant and can withstand extreme temperatures such as 4000 °F. The coatings of the present invention are particularly useful for coating ceramic tiles used to protect spacecraft on reentry, and can also be applied underneath the tiles of a spacecraft as a safety measure in case a tile is damaged or lost during a flight.

In an exemplary embodiment, the coatings of the present invention include (i) ceramic nanoparticles, (ii) metal nanoparticles, (iii) an organic or inorganic binder, and (iv) a solvent. The ceramic nanoparticles, metal nanoparticles, binder and solvent are combined to form a ceramic coating matrix. The solvent is included in the composition to make the coating composition initially flowable. The flowable coating composition can be applied as a thin layer to a substrate and/or molded or otherwise shaped as desired.

The coating composition is cured to form the ceramic coatings of the present invention. Curing is typically carried out by heating the composition. During curing, the solvent is driven off and the binder and ceramic particles bond to form the ceramic coating. The coating composition typically cures at a temperature between about 100 °C and 700 °C. Depending on the type of binder used, the binder may be partially or completely burned out of the coating during curing. Organic binders are typically more likely to be burned out at the curing temperatures while inorganic binders are more likely to remain after curing.

The metal particles can participate in the curing process and/or act as a filler to give the coating material desired properties. Alternatively the metal particles can be a sacrificial component that is consumed at extreme temperatures such as 4000 °F.

The metal nanoparticles and/or the ceramic nanoparticles are selected to penetrate into the pores of the substrate and provide an exceptionally strong bond between the coating and a substrate. In a preferred embodiment, the nanoparticles have a size in a range from about 1 nm to about 300 nm, more preferably in a range from about 5 nm to about 200 nm and most preferably in a range from about 15 nm to about 60 nm. The smallness of the nanoparticles allows the nanoparticles to penetrate beneath the substrate surface into the pores to create a strong and irregular bond interface. Once the nanoparticles in the pore have cured, the nanoparticles in the pore can interlock with the pore cavity to provide an exceptionally good bond with the substrate.

Once cured, the diffused transition interface has an increased strength as compared to the interface between traditional ceramic coatings and substrates. The diffused transition interface is less likely to delaminate because the transition between the different materials is less abrupt. A crack is less able to propagate along an irregular amorphous bond interface. The penetration of the nanoparticles also changes the coefficient of thermal expansion of the substrate within the diffused transition interface. Even in coatings that have a significantly different thermal expansion as compared to the substrate, the expansion differential is spread out over the diffused irregular transition interface. Consequently, the shear forces caused by differential expansion are minimized and delamination is less likely to occur.

The nanoparticles of the present invention are also more effective at reflecting heat and preventing heat energy from penetrating the coating. The gaps between nanoparticles are much smaller than the gaps between larger particles. Heat energy is less likely to penetrate the coating of the present invention because the gaps in the nanoparticles are small and form many more layers for a given thickness of coating. Heat energy that cannot penetrate the coating is reflected or absorbed by the coating near the surface of the coating, thereby protecting the substrate underneath.

The combination of metal nanoparticles and ceramic nanoparticles within a matrix can be advantageous for withstanding extremely high temperatures. In one exemplary embodiment, the metal nanoparticles can be used as a sacrificial component that is burned out during high temperatures. At extreme temperatures (*e.g.*, 4000 °F) the material can become partially fluid and the metal particles will migrate to the surface of the coating. Typically, the metals will be oxidized as they reach the surface. The metal oxide layer formed on the surface of the ceramic coating during high temperature burn provides an additional thermal barrier for the substrate.

Metal nanoparticles migrating out of the ceramic coating are also advantageous because they absorb heat and take it with them, thereby protecting the underlying substrate. The use of small metal particles is advantageous because small particles can be more uniformly heated, thus allowing heat to penetrate to the center of the particle. Consequently, the metal nanoparticles of the present invention are more effective at absorbing and removing heat from the ceramic layer than larger particles.

In one embodiment, the presence of the sacrificial metal only delays the destruction of the ceramic coating. In some cases the delay may be only seconds or minutes; however, additional seconds can be extremely valuable in some circumstances, such as reentry into the earth's atmosphere by a spacecraft.

If the ceramic coating is exposed to extreme temperatures that begin to destroy the ceramic coating, the use of ceramic nanoparticles in the ceramic coatings can be advantageous. As the ceramic nanoparticles are burned off or removed, the ceramic coating loses a thinner layer of material because of the smallness of the particles. Thus, the rate at which the ceramic layer is wasted away is slower than for a coating having larger ceramic particles.

In addition, the ceramic nanoparticles are more likely to be uniformly heated throughout the particle as compared to larger particles. Thus, as the ceramic particles are removed from the surface of the coating, the ceramic nanoparticles remove a greater amount of heat for a given amount of material.

In another exemplary embodiment of the present invention the density of the coating is significantly improved by using nanoparticles of different sizes. The different-sized nanoparticles can be metal and/or ceramic. The increased density occurs because the small nanoparticles fill the spaces around the larger nanoparticles or micron-sized particles. The ceramic coating benefits from the strength and bulk properties provided by the larger particles while still achieving high density by packing the small particles in the spaces between the larger particles. In a preferred embodiment, larger diameter particles are larger by at least about 50% in diameter, more preferably at least about 100% larger in diameter, and most preferably at least about 200% larger in diameter.

These and other advantages and features of the present invention will become more fully apparent from the following description and appended claims as set forth hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

To further clarify the above and other advantages and features of the present invention, a more particular description of the invention will be rendered by reference to specific embodiments thereof which are illustrated in the appended drawings. It is appreciated that these drawings depict only typical embodiments of the invention and are therefore not to be considered limiting of its scope. The invention will be described and explained with additional specificity and detail through the use of the accompanying drawings in which:

Figure 1A is a schematic drawing showing a substrate with a coating layer that has developed a crack;

Figure 1B is a schematic drawing showing the material of Figure 1A wherein a portion of the coating layer has delaminated;

Figure 2 is a schematic drawing of a substrate coated with a ceramic material that is susceptible to penetration of energy via gaps in the molecular structure of the coating material;

Figure 3A is a schematic representation of a ceramic coating, according to the present invention, bonded to a substrate and having a diffused transition layer;

Figure 3B is a schematic representation of the coating substrate interface of Figure 3A; and

Figure 4 is a schematic drawing of a ceramic coating, according to the present invention, having different-sized nanoparticles.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

I. INTRODUCTION

The present invention relates to high temperature ceramic coatings incorporating nanoparticles. The nanoparticles give the coating beneficial properties such as improved heat tolerance and improved resistance to delamination from a substrate.

For purposes of the present invention, “ceramic coating compositions” or “coating compositions” are uncured coating compositions that are flowable or moldable such that they can be applied to a substrate. The ceramic coating compositions are cured to form the ceramic coatings of the present invention.

The term “high temperature” coating refers to the property of the coating being able to protect a substrate from high temperatures, not that the coating itself has a high temperature.

II. COMPONENTS USED TO MAKE COATING COMPOSITIONS

The coating compositions of the present invention generally include the following components: (i) ceramic particles, (ii) metallic particles, (iii) a binder, and (iv) a solvent. The components are mixed to form a matrix with the ceramic particles and the metallic particles dispersed throughout the binder and solvent.

A. Ceramic Particles

Ceramic particles are included in the composition as the primary component. The ceramic particles are typically metal oxides that are corrosion resistant and relatively non-conductive to heat. Examples of suitable ceramic particles include oxides of silicon, zinc, zirconium, magnesium, manganese, chromium, titanium, iron, aluminum, noble metals, molybdenum, cobalt, nickel, tungsten and combinations thereof. Specific examples of suitable oxides include silica, calamine, zirconia, magnesia, titania, alumina, ceria, scandia, yttria, among others, used alone or in combination.

In an exemplary embodiment, at least a portion of the ceramic particles are nanometer sized (*i.e.*, have an average diameter of less than 1 micron). Nanometer-sized particles are particularly advantageous as they tend to be more reactive because of their large surface area. They can also better penetrate the surface of a substrate to improve bonding and prevent delamination.

In a preferred embodiment, at least a portion of the particles have an average diameter of about 1 nm to about 300 nm, more preferably about 5 nm to about 200 nm and most preferably about 15 nm to about 60 nm. Larger ceramic particles having average diameters of about 200 nm to about 3 microns, or about 2 microns to about 25 microns, can also be used for the ceramic particles either alone or in combination with ceramic particles having an average size of less than 300 nm.

B. Metal Particles

The coating compositions of the present invention can also include metal nanoparticles. The metal nanoparticles are typically included in the composition for their reactivity at high temperatures and/or the ability to migrate to the surface of the ceramic coating to be oxidized at high temperatures. Examples of suitable metals include silicon, zinc, zirconium, magnesium, manganese, chromium, titanium, iron, aluminum, noble metals, molybdenum, cobalt, nickel, tungsten, and the like.

In a preferred embodiment, at least a portion of the particles have an average diameter of about 1 nm to about 300 nm, more preferably about 5 nm to about 200 nm and most preferably about 15 nm to about 60 nm. The small size of the nanoparticles allows the particles to absorb heat uniformly throughout the particle and to migrate to the surface of the ceramic coating more rapidly thereby taking heat away from the substrate.

The metal nanoparticles can also be included in the coating as a filler material to improve the density of the ceramic coatings and/or to reduce the emissivity of the coating and/or to increase the coatings reflectivity.

Larger (including micron sized) metal particles can also be employed in addition to the metal nanoparticles (*e.g.*, about 200 nm to about 2 microns, or about 2 microns to about 25 microns in size).

C. Binders

The binders used in the coating compositions of the present invention are typically organic or inorganic materials that can react with the ceramic particles during curing. Examples of suitable organic binders include ethylene copolymers, polyurethanes, polyethylene oxides, various acrylics, paraffin waxes, polystyrenes, polyethylenes, celluslosic materials, polysaccharides, starch, proteins, “agar,” and other materials. Organic binders are typically burned out during the curing and/or during sintering. However, whether the organic binder is burned out will depend on the particular binder used and the curing temperature, sintering temperature, and/or the temperature during use of the composite.

In a preferred embodiment, the binder is an inorganic binder. Suitable inorganic binders include silicon-based binders such as soda silicate, kairome clay, titanium-based binders such as titania sol and other inorganic binders such as aluminum phosphate. Inorganic binders are preferred for their heat tolerance and reactivity to the ceramic materials. Inorganic binders that are reactive with the ceramic materials can form a matrix of ceramic material and binder during curing and/or sintering.

D. Solvents

Any solvent can be used to combine and/or deliver the metal particles, ceramic particles, and binder so long as the solvent is compatible with the particular metals and/or ceramics and binders being used. Examples of suitable solvents include polar solvents such as water, methanol, and ethanol, and non-polar organic solvents such as benzene and toluene.

III. MANUFACTURING COATING COMPOSITIONS

The coating compositions are made by selecting one or more types of ceramic particles, metal particles, binders, and solvents. The ceramic particles, metal particles, binders, and solvents are mixed together to form a matrix with the ceramic and metal particles dispersed throughout.

In an exemplary embodiment, the ceramic particles are the predominant component of the coating composition. The ceramic particles are typically included in an amount in a range from about 30% to about 70% by weight of the coating composition (*i.e.*, of the uncured composition).

Metal particles are typically included in the coating composition in smaller amounts than the ceramic particles. In a preferred embodiment, the amount of metal in the coating composition is in a range from about 0.5% to about 20% by weight of the coating composition. The metals can give the ceramic coating higher density and heat resistance and help with the curing process.

The binder is typically included in an amount from about 30% to about 70% by weight of the coating composition. The binder reacts with the metal nanoparticles and/or the ceramic particles during curing to form a ceramic material comprising a matrix of nanoparticles dispersed throughout the binder. For high temperature applications, an inorganic binder is preferred.

The solvent is mixed with binder, metal particles, and ceramic particles to facilitate mixing of the components. The consistency of the coating composition can be adjusted by adding greater or lesser amounts of solvent. The amount of solvent in the mixture is typically in a range from about 10% to about 30% by weight of the coating composition. If desired, the coating composition can be made into a slurry such that it can be applied by spray coating.

In an exemplary embodiment of the present invention, the coating compositions include ceramic particles and/or metal particles that are substantially different in size. The smaller particles are able to fill the voids between the larger particles. In a preferred embodiment, the larger particles are at least about 50% larger in diameter than the smaller particle, more preferably at least about 100% larger in diameter, and most preferably at least about 200% larger in diameter.

In an exemplary embodiment, the sizes of the particles (*i.e.*, ceramic and/or metal particles) in the coating can be categorized as small, medium, or large particles, where small particles have an average diameter between about 1 nm and 300 nm, medium particles have an average diameter between about 300 nm and 2 microns and large particles have an average particle size between about 2 microns and 25 microns.

Using two or more different sizes of particles can significantly improve the packing and density of the coating material. The smaller nanoparticles are able to fill voids where binder would otherwise be present. Using two or more different sizes of particles allows for thinner thicknesses of binder than in coatings that use substantially the same-sized particles. The larger-sized particles advantageously provide bulk and strength. The smaller particles increase the density of the coating and provide greater uniformity.

The two or more different sizes of particles can be selected from the group of ceramic particles, metal particles, or both. For example, ceramic particles with an average diameter of 300 nm can be combined with 30 nm metal particles or 30 nm ceramic particles or both. The exact size of the particles will depend on the particular application for the ceramic coating. Those skilled in the art will be able to select desired different particle sizes using the teachings herein to tailor the composition for a specific application.

In a preferred embodiment, ceramic particles are mixed with smaller metal particles. The smaller metal particles act as a sacrificial material during exposure to extreme heat. In this case, the metal particles will migrate to the surface and be oxidized on the surface. The oxidation of the sacrificial layer adds an additional thermal barrier that delays heating of the substrate for a period of time.

The metal oxides, metals, binders, and/or solvents can be selected to give the uncured coating composition a low emissivity such that the ceramic coating will reflect more heat. Ceramic coatings that have low emissivity are better at reflecting electromagnetic energy and thus can provide a better thermal barrier. In a preferred embodiment, the coating composition has an emissivity of less than about 0.6, more preferably less than about 0.4, and most preferably less than about 0.2. The emissivity of a material can depend on the temperature. For purposes of the present invention the emissivity is determined from the emissivity at about 200 °C to about 300 °C.

IV. APPLYING A COATING COMPOSITION TO A SUBSTRATE

The coating compositions of the present invention are applied to a substrate and then cured. The substrate can be almost any substrate with a hard surface. Examples of suitable substrates include carbon fiber, fiberglass, plastics, metals, glass, ceramic, wood, stone, or concrete. Optionally, the substrate surface can be roughened before the coating is applied to increase the surface area, improving the bonding of the coating to the substrate. However, even without roughening the surface, because the coating material includes nanoparticles, the coatings of the present invention can generally bond well to the substrate.

The coating composition can be applied to the substrate in any form so long as the coating can penetrate the surface of the substrate. Typically, the coating is applied as a flowable or liquid composition, such as a slurry. Examples of suitable forms for applying the coating composition include liquids (aqueous or non-aqueous), suspension, pastes, spray, foam, gels, and the like. The liquid compositions can be in a "concentrated" form. The coating can be applied to the substrate by dipping, brushing, spraying, vapor or the like.

The coating composition is applied to the substrate whereupon a portion of the coating composition penetrates the substrate’s surface pores. Figure 3 shows an exemplary material 100 according to the present invention that has a substrate 112 with a coating 114. The nanoparticles in coating layer 114 (illustrated as dots) are able to diffuse into the substrate beyond the surface 116 to form a diffused transition interface 118.

Once a portion of the coating composition has penetrated the surface of the substrate, the coating is cured. Typically, the coating is cured using heat. Any heat source can be used, such as conduction heating, convection heating or infrared radiation, among others. The curing process is preferably carried out at a temperature in a range from about 100 °C to about 650 °C, more preferably in a range from about 200 °C to about 550 °C, and most preferably in a range from about 250 °C to about 450 °C. In a preferred embodiment, the coating cures in less than about 0.5 hour, more preferably less than about 20 minutes, and most preferably in less than about 5 minutes.

As the coating cures, the coating can mechanically and/or chemically bond to the substrate. The portion of the coating that has diffused into the substrate cures within the substrate (*i.e.*, within the diffused transition interface). Figure 3B shows nanoparticles diffused into pores 120a and 120b of substrate 112. The nanoparticles in coating 114 are able to penetrate into the pores because of their small size. Once the particles have cured and/or sintered, the particles within the pore form a shaped portion that interlocks with the substrate like a puzzle piece. The diffusion and interlocking of the coating 114 with the substrate 112 prevents delamination and allows the coating to protect the substrate from more stringent conditions.

During curing, the binder reacts with the metal and/or ceramic nanoparticles to form a rigid, strong, and lightweight material. The cured coating typically has a different weight percent of components than the uncured composition due to the loss of solvent and/or due to the loss of a portion of the binder (*e.g.*, an organic portion). In an exemplary embodiment, the weight percent of the components in the ceramic coating after curing is as follows: about 35% to about 85% by weight of a ceramic material; about 0.6% and about 25% by weight of a metal; and about 25% to about 70% by weight of a binder.

The ceramic coatings are preferably applied to the substrate with a thickness from about 0.5 thousandths of an inch to about 50 thousandths of an inch. The high density and high temperature resistance of the coatings of the present invention can be very thinly applied to a substrate while still achieving desired protection and performance against heat penetration and corrosion.

The use of nanoparticles allows the coating composition to penetrate into the substrate and form a diffused transition interface. The diffused transition interface is less susceptible to differential thermal expansion because the two materials (*i.e.*, the coating and the substrate) are blended over a transition area. In addition, the nanoparticles move more easily in the material as it is heated such that differential expansion is less likely to result in cracks and subsequent delamination.

The nanoparticles included in the coatings of the present invention also improve the heat tolerance of the ceramic coating. The smaller nanoparticles have smaller gaps between particles and more layers of particles, as compared to larger particles with the same coating thickness. The smaller gaps and increased number of layers makes it more difficult for heat energy to penetrate the coating. Consequently, the heat energy is reflected or absorbed by the coating closer to the surface of the coating.

The use of a combination of ceramic and/or metal nanoparticles in the coating compositions of the present invention can be particularly advantageous for providing superior performance. The metal nanoparticles tend to be highly reactive at high temperatures. The metal particles become fluid and migrate to the surface where they are oxidized and form an oxide layer. To migrate to the surface, the particles absorb energy and take that energy with them, thereby removing heat from the inside of the ceramic coating.

The use of particles of more than one size can also improve the density and thermal resistance of the ceramic coating. Figure 4 illustrates a coating composition wherein larger ceramic particles 220 have smaller ceramic and/or metal particles 222 that fill the spaces between larger particles 220. The different sizes of particles are better able to pack and fill voids thereby increasing density and forming a more uniform mix of particles and binder. The uniformity of the coating matrix can improve strength and occlude voids where gases and radiation would otherwise be able to penetrate the coating.

The ceramic coatings of the present invention can be used to create a thermal and/or corrosion barrier for any type of application. The ceramic coatings of the present invention are particularly beneficial for extreme temperatures such as above 3000 °F. The combination of ceramic particles and metal particles provides superior heat resistance for a period of time. The coatings of the present invention have been found to withstand temperatures as high as 4300 °F. Although the metal in the coating is typically leached out of the coating at extreme temperatures, sacrificing this metal allows the ceramic coating to reach extreme temperatures (*e.g.*, 4300 °F) without melting or disintegrating.

Because of the high temperature capabilities of the ceramic coatings of the present invention, the coatings can be used to coat the exterior of spacecraft to protect it from heat and friction upon reentry. For example, the coatings of the present invention can be used to coat the tiles on the underside of NASA space shuttles to add additional protection to the shuttles upon reentry. The ceramic coatings can also be placed under the tiles to provide protection in the event that the tile is damaged or lost during a flight. The coatings can even be applied to the spacecraft in orbit if it is found that the protective tiles have been compromised at any point during the flight.

Those skilled in the art will recognize that there are many applications where high temperature coatings can be particularly advantageous and not limited to use on spacecraft.

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

CLAIMS

1. A high temperature resistant composite article, comprising:

a substrate having a surface; and

a high temperature ceramic coating bonded together with a portion of the substrate surface and forming a substrate coating interface, the ceramic coating comprising:

a plurality of ceramic particles included in an amount in a range of about 35% to about 85% by weight of the ceramic coating, the ceramic particles having a diameter of in a range of about 1 nm to about 1 micron;

a plurality of metal nanoparticles included in an amount in a range of about 0.6% to about 25% by weight of the ceramic coating, the metal nanoparticles having a diameter in a range of about 1 nm to about 1 micron; and

a binder included in an amount in a range of about 25% to about 70% by weight of the ceramic coating,

wherein, the nanoparticles of the ceramic coating are diffused into pores in the substrate surface to form a substrate coating interface comprising material from the substrate and nanoparticles from the coating.

2. A composite article as in claim 1, wherein the ceramic nanoparticles have a diameter in a range of about 1 nm to about 300 nm.

3. A composite article as in claim 1, wherein the ceramic nanoparticles have a diameter in a range of about 5 nm to about 200 nm.

4. A composite article as in claim 1, wherein the ceramic nanoparticles have a diameter in a range of about 15 nm to about 60 nm.

5. A composite article as in claim 1, wherein the metal nanoparticles have a diameter in a range of about 1 nm to about 300 nm.

6. A composite article as in claim 1, wherein the metal nanoparticles have a diameter in a range of about 5 nm to about 200 nm.

7. A composite article as in claim 1, wherein the metal nanoparticles have a diameter in a range of about 15 nm to about 60 nm.

8. A composite material as in claim 1, wherein the substrate is selected from the group consisting of carbon fiber, fiberglass, plastic, metal, glass, ceramic, wood, stone, concrete, and combinations thereof.

9. A composite material as in claim 1, wherein the binder is selected from the group consisting of ethylene copolymers, polyurethanes, polyethylene oxides, acrylics, paraffin waxes, polystyrenes, polyethylenes, celluslosic materials, polysaccharides, starches, proteins, agars, silicates, kairome clay, titanates, titania sol, aluminum phosphate, and combinations thereof.

10. A composite material as in claim 1, wherein the ceramic particles are selected from the group consisting of an oxide of silicon, zinc, zirconium, magnesium, manganese, chromium, titanium, iron, aluminum, noble metals, molybdenum, cobalt, nickel, or tungsten, and combinations thereof.

11. A composite material as in claim 1, wherein the metal nanoparticles are selected from the group consisting of silicon, zinc, zirconium, magnesium, manganese, chromium, titanium, iron, aluminum, noble metals, molybdenum, cobalt, nickel, tungsten, and combinations thereof.

12. A method of manufacturing a high temperature resistant composite article, comprising:

providing a substrate having a surface with pores greater than about 1 micron;

coating at least a portion of the surface of the substrate with a coating composition comprising:

a plurality of ceramic particles included in an amount in a range of about 30% to about 70% by weight of the coating composition;

a plurality of metal particles included in an amount in a range of about 0.5% to about 20% by weight of the coating composition;

a binder included in an amount in range of about 30% to about 70% by weight of the coating composition;

a solvent included in an amount in a range of about 10% to about 30% by weight of the coating composition,

wherein at least a portion of the metal or ceramic particles are nanoparticles having a diameter of less than about 1 micron and at least a portion of the nanoparticles diffuse into the pores of the substrate; and

curing the coating composition and allowing or causing at least a portion of the solvent to be removed.

13. A method as in claim 12, wherein at least a portion of the nanoparticles have a diameter in a range from about 1 nm to about 300 nm.

14. A method as in claim 12, where at least a portion of the nanoparticles are ceramic nanoparticles.

15. A method as in claim 12 wherein the nanoparticles include ceramic nanoparticles and metal nanoparticles.

16. A method as in claim 12, wherein at least a portion of the ceramic particles have a diameter in a range from about 200 nm to about 2 microns.

17. A method as in claim 12, wherein at least a portion of the ceramic particles have a diameter in a range from about 2 microns to about 25 microns.

18. A method as in claim 12, wherein the coating composition is cured at a temperature in a range from about 100 °C to about 650 °C.

19. A method as in claim 12, wherein the protective coating composition is applied as a slurry.

20. A method as in claim 12, wherein the solvent comprises water.

21. A method as in claim 12, wherein the binder comprises an inorganic compound.

22. A high temperature resistant composite article manufactured according to the method of claim 12.

23. A ceramic coating composition, comprising:

a plurality of ceramic and metal particles, the ceramic particles being included in an amount in a range of about 30% to about 70% by weight of the coating composition and the metal particles being included in an amount in a range of about 0.5% to about 20% by weight of the coating composition, wherein a first portion of the ceramic and/or metal particles have a diameter that is at least about 50% larger than a second portion of the ceramic and/or metal particles;

a binder included in an amount in a range of about 30% to about 70% by weight of the coating composition; and

a solvent included in an amount in a range of about 10% to about 30% by weight of the coating composition;

24. A ceramic coating composition as in claim 23, wherein the first portion of ceramic and/or metal particles has a diameter in a range of about 1 nm and about 300 nm.

25. A ceramic coating composition as in claim 23, wherein the second portion of ceramic or metal particles ceramic nanoparticles has a diameter in a range of about 1 to about 300 nm.

26. A ceramic coating composition as in claim 23, wherein the second portion of ceramic or metal particles ceramic nanoparticles has a diameter in a range of about 200 nm to about 2 microns.

27. A ceramic coating composition as in claim 23, wherein the second portion of ceramic or metal particles ceramic nanoparticles has a diameter in a range of of about 2 microns to about 25 microns.

28. A coating composition comprising:

a plurality of metal nanoparticles included in an amount in a range of about 0.5% to about 20% by weight of the coating composition, the metal nanoparticles having a diameter in a range of about 1 nm to about 300 nm;

a plurality of ceramic particles included in an amount in a range of about 30% to about 70% by weight of the coating composition;

a binder comprising an organic material and/or an inorganic material and included in an amount in a range of about 30% to about 70% by weight of the coating composition; and

a solvent included in a range of about 10% to about 30% by weight of the coating composition.

29. A coating composition as in claim 28, wherein the binder is selected from the group consisting of ethylene copolymers, polyurethanes, polyethylene oxides, acrylics, paraffin waxes, polystyrenes, polyethylenes, celluslosic materials, polysaccharides, starches, proteins, agars, silicates, kairome clay, titanates, titania sol, aluminum phosphate, and combinations thereof.

30. A coating composition as in claim 28, wherein the ceramic nanoparticles are selected from the group consisting of an oxide of silicon, zinc, zirconium, magnesium, manganese, chromium, titanium, iron, aluminum, noble metals, molybdenum, cobalt, nickel, or tungsten, and combinations thereof.

31. A composite material as in claim 28, wherein the solvent comprises water, methanol, ethanol, benzene, toluene, or combinations thereof.

32. A coating composition as in claim 28, wherein the metal particles are selected from the group consisting of silicon, zinc, zirconium, magnesium, manganese, chromium, titanium, iron, aluminum, noble metals, molybdenum, cobalt, nickel, tungsten, and combinations thereof.

33. A coating composition as in claim 28, wherein at least a portion of the ceramic particles are nanoparticles having a diameter of less than 1 micron.

34. A green composite material comprising a substrate coated with the coating composition of claim 28.

35. A composite material manufactured by curing the green composite composition of claim 34.

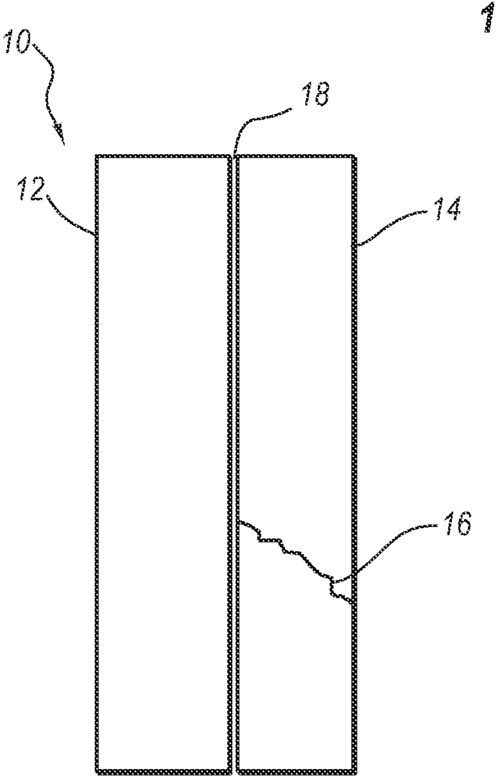

Fig. 1A
(Prior Art)

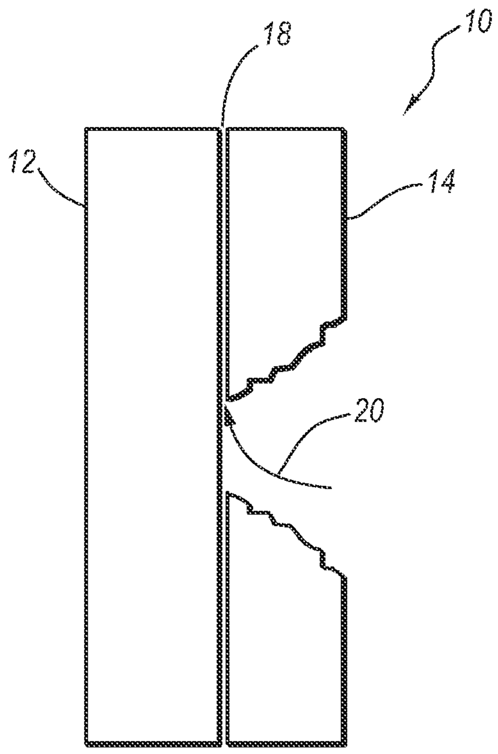

Fig. 1B
(Prior Art)

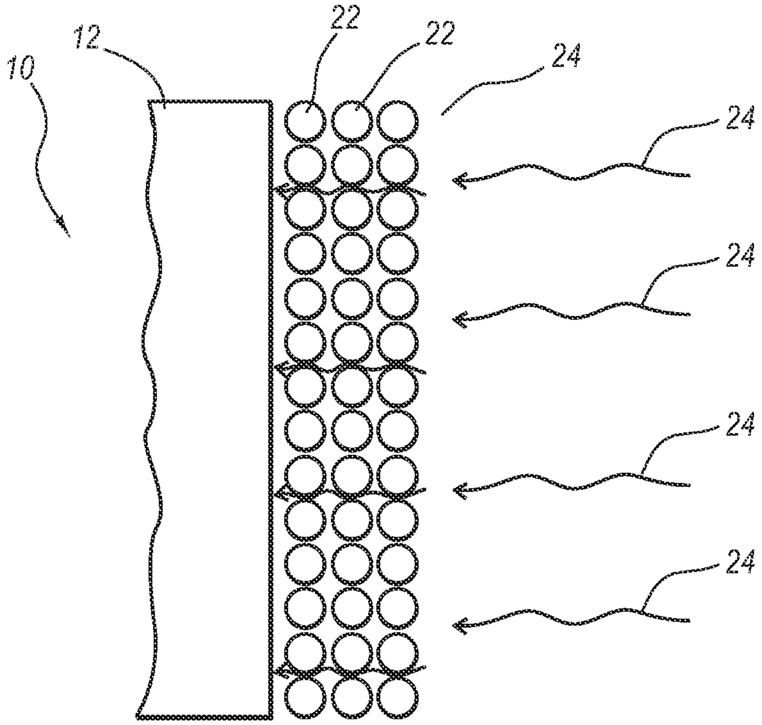

Fig. 2

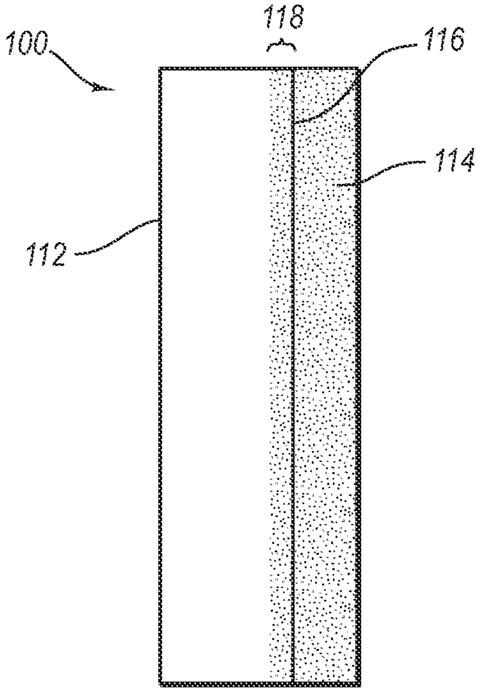

Fig. 3A

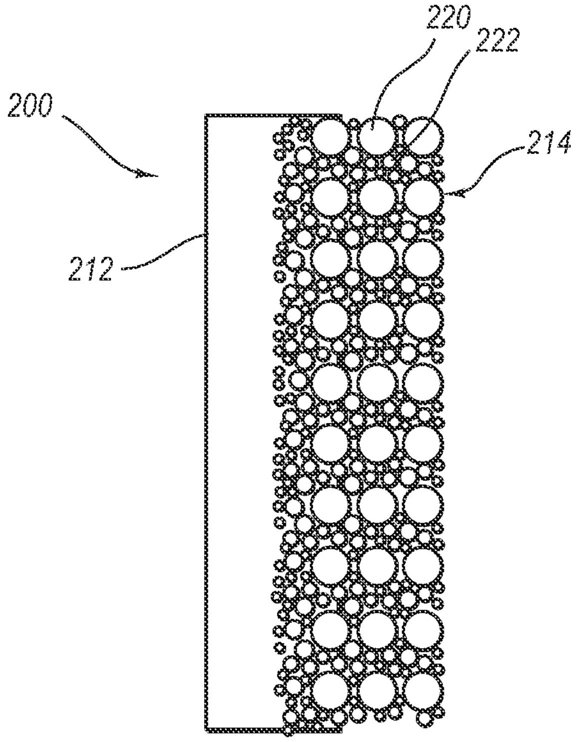

Fig. 4

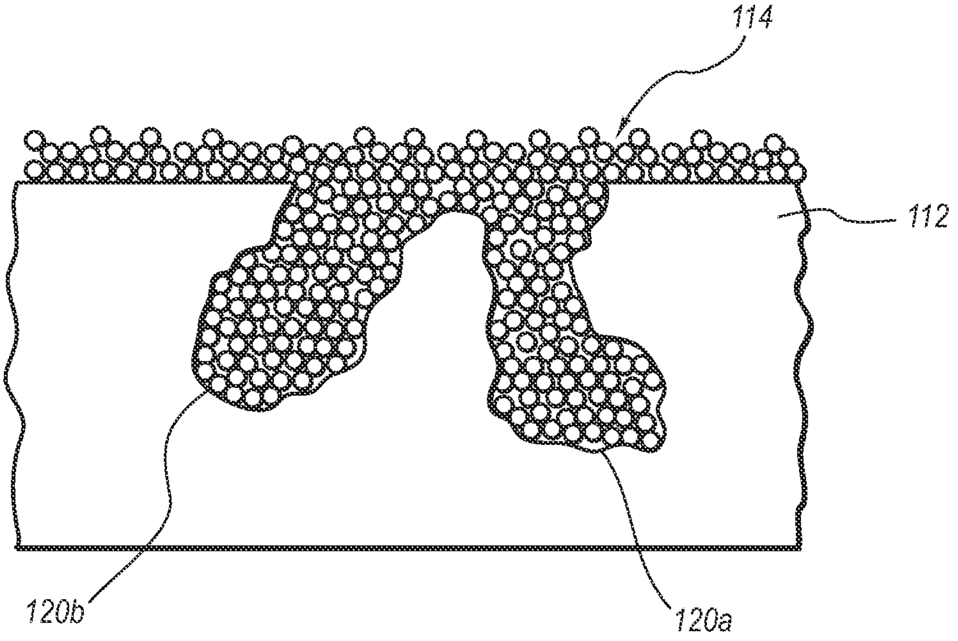

Fig. 3B