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(54) **THERMAL SPRAY OF DOPED THERMAL BARRIER COATING MATERIAL**

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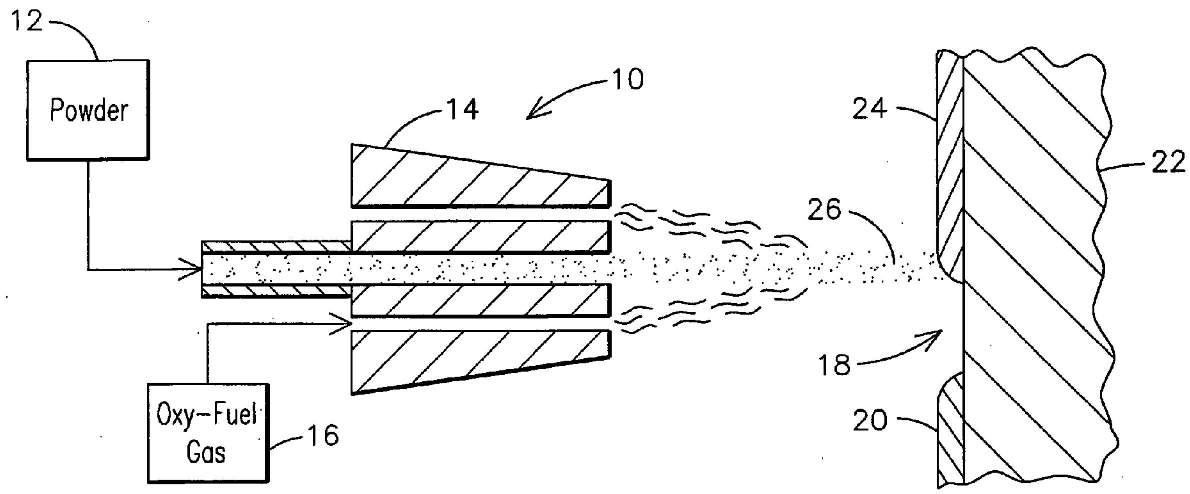
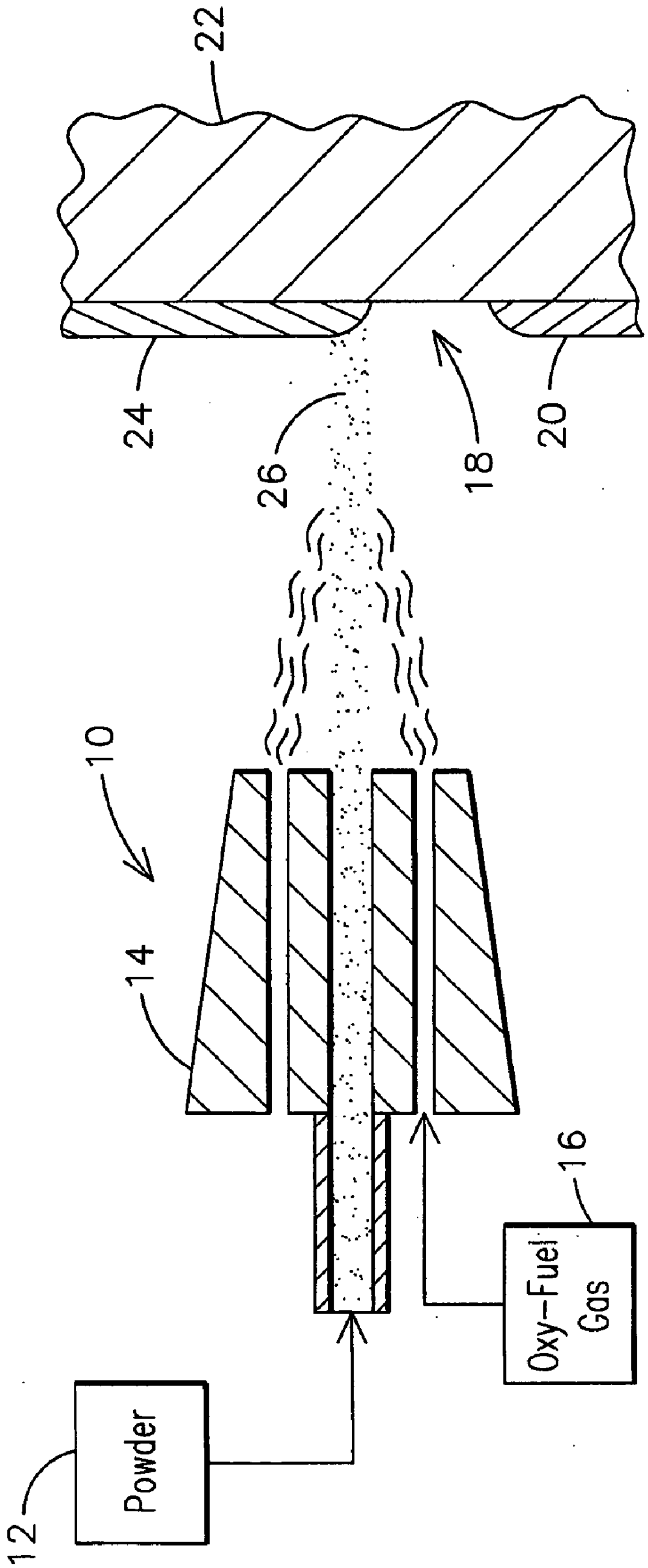
(57) **ABSTRACT**

A yttria stabilized zirconia ceramic thermal barrier coating **(24)** is applied to a substrate **(22)** using an oxy-acetylene spraying process by including in the coating a eutectic phase having a melting temperature sufficiently low to cause melting of the eutectic phase during the oxy-acetylene spraying process. The eutectic phase may be present in the powder **(12)** used for the spraying process, or it may be formed during the spraying process by the oxidation of a layer of metal applied to yttria stabilized zirconia particles. The use of an oxy-acetylene spraying process facilitates the application of the coating during in-frame repair of a gas turbine component.




22
24
26
18
20
10
14
16
Oxy–Fuel Gas
Powder
12

THERMAL SPRAY OF DOPED THERMAL BARRIER COATING MATERIAL

[0001] This application claims benefit of the Jun. 18, 2003, filing date of United States provisional application number 60/479,266.

BACKGROUND OF THE INVENTION

[0002] Thermal barrier coatings (TBC) are ceramic insulating materials used to protect an underlying substrate material from a high temperature environment, such as the combustion gas of a gas turbine engine. TBC's may be applied by a variety of known processes, including plasma spray and vapor deposition techniques. TBC's are subject to service-induced damage, such as localized spalling of a TBC caused by bond coat oxidation, thermal stress due to excessive temperature and differential expansion, thermo-mechanical fatigue, erosion and impact by particulates, etc.

[0003] The prior art thermal spray processes used to apply zirconia coatings have included air plasma spray (APS) and physical vapor deposition (PVD). These processes are not useful for in-situ repairs of machines such as gas turbines due to the personnel safety concerns associated with the high temperature, high power requirements (150-200 amp, 440 volt, 3-phase power supply), and/or high sound energy levels produced. Plasma spray processes used to deposit a thermal barrier coating, such as a yttria stabilized zirconia (YSZ) coating, are particularly inappropriate for in-frame field repair of a gas turbine engine. The high temperatures [6,600° to 16,600° C.] and high velocities [50 to 100 m/sec] produced in a plasma spray process generate a high volume of hot material splatter and a high temperature within the immediate vicinity of the spraying area that can be hazardous for the operator. Lower temperature prior art processes such as oxy-acetylene flame spraying have not been used successfully to deposit zirconia due to the high melting point of zirconia.

[0004] Alternative approaches have been developed for in-situ repair applications. U.S. patent application Publication U.S. 2002/0164417 dated Nov. 7, 2002, describes a hydrated metallic halide paste that may be applied over a damaged region. U.S. Pat. No. 6,413,578 issued on Jul. 2, 2002, describes a paste comprising a ceramic powder in a binder. The paste is thermally reacted when the repaired component returns to service to yield a ceramic-containing repair coating. While such pastes avoid the problems associated with a high temperature plasma spray process, they often provide coatings having performance properties that are less than desired, especially under conditions of cyclic thermal exposures.

[0005] Accordingly, an improved repair technique for repairing service-induced damage in a thermal barrier coating is desired.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] The sole FIGURE is a schematic illustration of a portable oxy-acetylene flame spraying tool being used to deposit a ceramic coating doped with a melting point depressant onto a surface of a component that is in its operating position in a machine.

DESCRIPTION OF THE INVENTION

[0007] An oxy-acetylene flame spray process and a material deposited by the process are described herein for repairing a damaged ceramic thermal barrier coating or for otherwise depositing a ceramic coating in applications where relatively higher velocity/temperature plasma spray and high velocity oxy-fuel processes are undesirable.

[0008] Low velocity flame spray processes are used for depositing coatings of a variety of materials. However, such flame spray processes have not been used to deposit yttria stabilized zirconia coatings and other thermal barrier coating materials with similarly high melting temperature because the temperatures and dwell times achievable with oxy-acetylene [3000° C. to 3500° C.] are inadequate to melt YSZ feedstock material in a manner appropriate for spray deposition to obtain coatings. The incipient melting temperature of an 8YSZ material that may typically be used as a thermal barrier coating is about 2700° C.

[0009] The present inventors have discovered that a thermal barrier coating material that is intentionally doped with a melting point depressant material may be successfully applied with a low velocity oxygen fuel spray process. The present invention is especially useful for performing an in-situ repair of a damaged thermal barrier coating. The melting point depressing dopants are oxidized to form a eutectic phase within the material matrix, and the eutectic phase has a melting temperature that is sufficiently low to permit the material to be successfully applied with an oxy-fuel spray process.

[0010] In one embodiment of the present invention, the dopant phases are alloyed with a ceramic thermal barrier coating material such as 8YSZ to produce a low melting ceramic as a result of the formation of eutectics between the zirconia matrix and the dopant oxide phase. These eutectic phases melt at temperature significantly lower than that of 8YSZ, thereby allowing higher deposition rates and efficiency when used in flame spray processes. The compositions are selected so that the melting temperature of the lowest melting component of the alloy is higher than the operating temperature to which the coated component will be exposed during subsequent use, although lower than the undoped TBC material. The individual dopant phases do not have to possess a melting temperature that is significantly lower than that of 8YSZ. It is the eutectic phase formed by the diffusional mixing of the dopant phase with the zirconia parent lattice that has a low melting temperature. While the eutectic phase will melt at a temperature lower than the 8YSZ material to facilitate the deposition process, its melting temperature remains above the expected operating temperature to which the coating will be exposed during its subsequent use. For a gas turbine environment application, the melting temperature of the eutectic phase may be greater than 1,550 degrees Celsius, which is a typical gas turbine combustion temperature.

[0011] Specific examples of such two-phase eutectic and binary alloys are:

[0012] (i) a two-phase alloy of calcium zirconate ($CaZrO_2$) and zirconium oxide (Zr_2O_3) in the range of 50-35 mol % of calcium oxide (CaO) and 50-65 mol % of zirconium oxide (Zr_2O_3);

[0013] (ii) two phase alloy of cerium oxide (CeO_2) and zirconium oxide (Zr_2O_3) in the range of 50-10 mol % of CeO_2 and 50-90 mol % of Zr_2O_3.

[0014] Additionally, ternary alloys systems may also be used such as CaO, Al_2O_3 and Zr_2O_3; or CeO_2, Al_2O_3 and

Zr_2O_3. The amount of alumina in such ternary alloys may be limited in certain applications due to the relatively large difference in the coefficient of thermal expansion between alumina and zirconia. These compositions may be produced using standard powder processing techniques such as spray drying, slurry processing, sintering etc.

[0015] Another embodiment of the present invention involves coating particles of a thermal barrier coating material with a metal that will oxidize during an oxy-fuel flame spraying process to form a low-melting temperature eutectic phase. In one embodiment, elements such as yttrium, hafnium, calcium, aluminum and/or cerium are sputtered onto zirconia particles, such that during a subsequent oxy-acetylene spraying, will form oxides that combine with the 8YSZ matrix to form low-melting eutectics in the deposited coating. The amount of sputtered material deposited onto the TBC material particles may be selected to achieve a desired ratio of eutectic in the sprayed material. In one embodiment, a lower range of 1-5 mol % may be used for yttrium and hafnium, while a higher range of 45-65 mol % may be used for calcium, aluminum and cerium. The amount of sputtered material may be limited by the practical/economic limits of known sputtering techniques.

[0016] Other known lattice doping techniques such as molten slurry addition and wet chemical processing (sol-gel, co-precipitation) may be used to add the selected dopant to the YSZ material to be sprayed.

[0017] This invention involves alloys of compounds that form low melting eutectic phases. This is quite different from a physical mixture of two powders, i.e. a low-melting and high-melting powder. In the latter case only the low melting powder melts and forms a molten pool that binds the high-melting powders. In the present invention, there is only one powder type that has a specific composition as described; either a pre-alloyed material or a coated powder that alloys during the deposition process. The lowered melting temperature is due to a phase composition based on the formation of eutectics between the TBC material and a second ceramic.

[0018] The amount of melting point dopant added to the material to be sprayed may be selected to achieve a desired reduction in the incipient melting temperature and to minimize the residual effects of the dopant in the deposited coating. In one embodiment, the melting point of 8YSZ is depressed by about 700° C. (from a typical value of about 2,700° C.) in order to provide a sufficient amount of melting in a typical flame spray process to achieve desired coating properties using known flame spray processes and equipment. In one embodiment, a ceramic powder feedstock such as YSZ may be doped with one or more melting point depressants to a concentration in the range of 10-50 mol % in order to achieve a satisfactory reduction in overall melting characteristics of the powder. Other known thermal barrier coatings may be applied using appropriate dopant materials to form eutectics having melting temperatures that are sufficiently low to facilitate oxy-fuel flame spray deposition. In one such embodiment, mullite is doped with titania (TiO_2). Dopants such as sodium, silicon and phosphorous and compounds containing these elements may be used but may not be preferred in some embodiments due to other adverse properties exhibited by the deposited coating material as a result of the presence of these materials. When such materials are used, a diffusion heat treatment process may be performed on the deposited doped ceramic material in order to diffuse the melting point depressant.

[0019] It may be possible to perform in-frame repair of a coated component, such as a hot combustion gas portion of a gas turbine engine, without complete disassembly of the component by spraying YSZ material doped with a melting point depressant using a hand-held oxy-acetylene flame spray gun. The FIGURE illustrates a low velocity flame spray system **10** being used to spray a doped YSZ powder **12**. The powder may be alloyed with the dopant or the dopant may be applied in elemental form as a coating over the TBC material particles. The powder **12** is accelerated through a spray gun **14** wherein it is heated by the combustion of an oxy-fuel gas **16** such as oxy-acetylene to form a spray **26** containing a eutectic phase exhibiting a melting temperature sufficiently low such that the eutectic phase material is melted during the spraying process. Normal particle sizes may be selected to ensure the proper operation of the LVOF system **10**, such as in the range from −120+325 mesh, from −140+325 mesh, or from −150+325 mesh for example. The eutectic phase is either present in the powder **12** or it is formed when the powder is heated by the oxidation of a metallic coating on a ceramic powder.

[0020] The FIGURE illustrates a damaged region **18** of an existing coating **20** on a component **22** being repaired by the deposition of a layer of a repair coating material **24** with the component **22** in place in its operating position within a machine of which it forms a part. Access is provided to the damaged region **18** without removing the component **22** from the machine. The damaged region may be cleaned prior to the coating operation with any known cleaning process, such as by grit blasting or chemical cleaning. The repair coating **24** may be applied onto a surface such as the substrate **22**, a bond coat layer (not shown) covering the substrate **22**, and/or over a portion of the existing coating **20**. Repair coating **24** may be applied to any desired thickness, such as in the range of 8-35 mils, for example. The spray **26** is directed onto the surface where the eutectic phase solidifies to form a layer **24** of thermal barrier coating material.

[0021] Other types of coatings that are not normally applied with a low velocity flame spray process may be applied when the material to be applied is intentionally doped in order to depress its melting point to a temperature sufficiently low to achieve adequate deposition properties. Other potential applications wherein this concept may be applied include the deposition of abradable ceramic systems such as zirconia or titania.

[0022] While the preferred embodiments of the present invention have been shown and described herein, it will be obvious that such embodiments are provided by way of example only. Numerous variations, changes and substitutions will occur to those of skill in the art without departing from the invention herein.

We claim as our invention:

1. A method of depositing a ceramic thermal barrier coating material, the method comprising:

heating a powdered ceramic material in an oxy-fuel spraying process to produce a spray comprising eutectic phase material exhibiting a melting temperature sufficiently low such that the eutectic phase material is melted during the spraying process; and

directing the spray onto a surface where the eutectic phase solidifies to form a layer of thermal barrier coating material.

2. The method of claim 1, further comprising forming the eutectic phase during the spraying process by oxidizing a metallic coating applied to the powdered ceramic material.

3. The method of claim 1, further comprising forming the powdered ceramic material to comprise yttria stabilized zirconia particles coated with a layer of one of yttrium, hafnium, calcium, aluminum and cerium.

4. The method of claim 1, further comprising forming the powdered ceramic material to contain the eutectic phase material prior to the step of heating.

5. The method of claim 4, further comprising forming the powdered ceramic material to comprise a two-phase alloy of calcium zirconate and zirconium oxide.

6. The method of claim 5, further comprising forming the two-phase alloy to comprise the range of 50-35 mol % of calcium oxide and 50-65 mol% of zirconium oxide.

7. The method of claim 4, further comprising forming the powdered ceramic material to comprise a two-phase alloy of cerium oxide and zirconium oxide.

8. The method of claim 7, further comprising forming the two-phase alloy to comprise the range of 50-10 mol % of cerium oxide and 50-90 mol % of zirconium oxide.

9. The method of claim 4, further comprising forming the powdered ceramic material to comprise a ternary alloy comprising calcium oxide, alumina and zirconium oxide.

10. The method of claim 4, further comprising forming the powdered ceramic material to comprise a ternary alloy comprising cerium oxide, alumina and zirconium oxide.

11. The method of claim 1, further comprising using an oxy-acetylene spraying process to produce a spray comprising yttria stabilized zirconia and a melted eutectic phase.

12. The method of claim 11, further comprising using the oxy-acetylene spraying process to heat particles of yttria stabilized zirconia coated with a metal.

13. The method of claim 12, further comprising using the oxy-acetylene spraying process to heat particles of yttria stabilized zirconia coated with one of yttrium, hafnium, calcium, aluminum and cerium.

14. The method of claim 1 applied to an in-frame component of a gas turbine engine.

15. A product formed by the process of claim 1.

16. A product formed by the process of claim 11.

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