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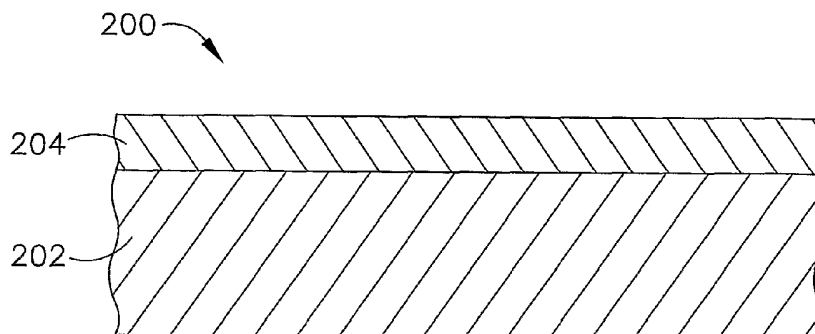
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(54) Title: ENVIRONMENTAL & THERMAL BARRIER COATING



(57) Abstract: An environmentally and thermally protected component comprising a silicon-based ceramic or composite substrate and an environmental and thermal barrier coating disposed on the substrate. The environmental and thermal barrier coating comprises at least about 50 mole %  $\text{AlTaO}_4$ . The composition of the environmental and thermal barrier coating may be adapted to provide excellent CTE (coefficient of thermal expansion) match with a substrate, such as a SiC-based ceramic or composite. Coating compositions of the invention have a stable crystalline structure at a temperature up to at least about  $1550^\circ\text{C}$ . Methods for preparing an environmentally and thermally protected component are also disclosed.

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## ENVIRONMENTAL & THERMAL BARRIER COATING

### BACKGROUND OF THE INVENTION

5   **[0001]**       The present invention generally relates to an environmental and thermal barrier coating, and to a component coated with such a coating. The present invention also relates to methods for preparing an environmental and thermal barrier coating, and for preparing a component coated with such a coating.

10   **[0002]**       Advanced turbomachines use silicon-based (Si-based) non-metallic materials such as silicon nitride, silicon carbide, molybdenum silicides, niobium silicides, and their composites for hot-section components. Due to the high temperature capability of Si-based ceramics, those ceramic turbomachines operate at higher temperatures with minimum cooling and higher engine  
15 performance. However, at operating temperatures above about 1200°C, Si-based ceramics can be adversely affected by oxidation and water vapor present in the flow stream. Such hostile engine environments result in rapid recession of Si-based ceramics parts. Recession refers to the wear of a substrate or component due to the effects of ablation and/or erosion due to particulate  
20 impact.

**[0003]**       In U.S. Patent No. 6,159,553 to Li *et al.*, discloses the use of tantalum oxide ( $Ta_2O_5$ ) as coating material on silicon nitride parts. A tantalum oxide coating of 2 to 500 microns in thickness can effectively protect the surface of silicon nitride parts from oxidation and reaction with water vapor at high  
25 temperatures. However, pure tantalum oxide coatings on Si-based parts have some limitations, including the following.

**[0004]**        $Ta_2O_5$  undergoes a phase transformation from a low temperature phase ( $\beta$ -phase) to a high temperature phase ( $\alpha$ -phase) at about 1350°C, which may cause cracking in the coating due to the change in volume which occurs  
30 during the phase transformation.

**[0005]** Ta<sub>2</sub>O<sub>5</sub> is susceptible to grain growth at temperatures above 1200°C. Pronounced grain growth results in a large grain microstructure of up to about 10 μ, which reduces the mechanical strength of the coating, induces high local residual stresses in the coating, and causes the coating to spall.

5 **[0006]** Ta<sub>2</sub>O<sub>5</sub> has a coefficient of thermal expansion (CTE) of about  $3 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , whereas silicon nitride has a CTE in the range of about  $3 - 4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  and silicon carbide (SiC) has a CTE in the range of  $4 - 5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ . Since there is about 10 to 30% CTE mismatch between Ta<sub>2</sub>O<sub>5</sub> and silicon nitride, and an even higher CTE mismatch between Ta<sub>2</sub>O<sub>5</sub> and SiC, residual stresses will  
10 develop in the Ta<sub>2</sub>O<sub>5</sub> coating on Si-based ceramics. These residual stresses can limit the service life of the coating.

**[0007]** Pure Ta<sub>2</sub>O<sub>5</sub> coatings have a relatively low fracture toughness (probably from <1 to <3 MPa.m<sup>0.5</sup>), which may adversely affect the mechanical integrity and the lifetime of the coating during service where there are foreign  
15 object impact and particulate erosion events.

**[0008]** Due to the above limitations, Ta<sub>2</sub>O<sub>5</sub> coatings on Si-based ceramics may not provide adequate protection for turbine engine applications at temperatures of about 1300°C or above, thousands of thermal cycles occur, and a coating lifetime greater than five thousand (5000) hours is required.  
20 Furthermore, the cost of Ta<sub>2</sub>O<sub>5</sub> raw powder material is relatively high compared with that of most other high temperature ceramic oxide powders. Still further, the density of Ta<sub>2</sub>O<sub>5</sub> is relatively high, so the weight of the coating may negatively affect the performance of the turbine machinery. It would be highly desirable to significantly improve the Ta<sub>2</sub>O<sub>5</sub> coating to meet the stringent  
25 demands of advanced ceramic turbine engine applications, and to reduce the cost and weight of the coating.

**[0009]** As can be seen, there is a need for an environmental and thermal barrier coating for coating Si-based substrates, e.g., comprising Si<sub>3</sub>N<sub>4</sub>, wherein the coating protects the substrate from recession and thermal cycling at  
30 temperatures in the range of from about 1300 to 1550°C. There is a further

need for an effective, low weight, and low cost environmental and thermal barrier coating for coating Si-based gas turbine engine components. There is also a need for a process for coating a silicon-based gas turbine engine component with an environmental and thermal barrier to provide an environmentally and thermally protected component. The present invention provides such coatings, components, and processes, as will be described in enabling detail hereinbelow.

### SUMMARY OF THE INVENTION

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**[0010]** In one aspect of the present invention, there is provided an environmental and thermal barrier coating comprising a layer of a composition which comprises at least about 50 mole %  $\text{AlTaO}_4$ , and the balance comprising at least one metal oxide selected from the group consisting of Ta, Al, Cr, Hf, Ti, Zr, Mo, Nb, Ni, Sr, Mg, Si, and the rare earth elements including Sc, Y, and the lanthanide series of elements. The composition may have a coefficient of thermal expansion (CTE) in the range of from about  $3.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , and a thickness in the range of from about 0.1 to 50 mils.

**[0011]** In another aspect of the present invention, an environmental and thermal barrier coating comprises a layer of a composition which comprises at least about 99 mole %  $\text{AlTaO}_4$ . The composition may be prepared by reacting a starting powder mixture comprising about 50 mole %  $\text{Ta}_2\text{O}_5$  and about 50 mole %  $\text{Al}_2\text{O}_3$ . Such an environmental and thermal barrier coating may have a coefficient of thermal expansion (CTE) in the range of from about  $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ .

**[0012]** In still another aspect of the present invention, there is provided a thermally protected component comprising a substrate having a surface, and an environmental and thermal barrier coating disposed on the substrate surface. The environmental and thermal barrier coating may comprise at least about 50 mole %  $\text{AlTaO}_4$ , and the balance may consist essentially of  $\text{Ta}_2\text{O}_5$  or  $\text{Al}_2\text{O}_3$ .

Such an environmental and thermal barrier coating may be characterized by a coefficient of thermal expansion (CTE) in the range of from about  $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ .

**[0013]** In yet another aspect of the present invention, a thermally protected component comprises a substrate having a surface, and an environmental and thermal barrier coating disposed on the substrate surface. The environmental and thermal barrier coating may comprise at least about 50 mole %  $\text{AlTaO}_4$ , and the balance may comprise at least one metal oxide including Ta, Al, Cr, Hf, Ti, Zr, Mo, Nb, Ni, Sr, Mg, Si, and the rare earth elements including Sc, Y, and the lanthanide series of elements.

**[0014]** In an additional aspect of the present invention, a method for preparing an environmentally and thermally protected component may include: providing a mixture of  $\text{Ta}_2\text{O}_5$  (or a precursor thereof), and  $\text{Al}_2\text{O}_3$  (or a precursor thereof); reacting the mixture to provide a reaction product comprising at least about 50 mole %  $\text{AlTaO}_4$ ; and depositing a layer of the reaction product on a component surface to form an environmental and thermal barrier coating on the component surface.

**[0015]** In a further aspect of the present invention, a method for making an environmentally and thermally protected component includes: providing a composition comprising at least about 90 mole %  $\text{AlTaO}_4$ , and the balance consisting predominantly of a metal oxide such as  $\text{Al}_2\text{O}_3$  or  $\text{Ta}_2\text{O}_5$ ; providing a substrate having a surface to be coated; and depositing a layer of the composition on the substrate surface to form an environmental and thermal barrier coating on the substrate. Such a coating may have a coefficient of thermal expansion (CTE) in the range of from about  $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , and a thickness in the range of from about 0.1 to 50 mils.

**[0016]** In another aspect of the present invention, there is provided a method for making an environmentally and thermally protected component including: providing a substrate to be coated with an environmental and thermal barrier coating. The substrate provided may comprise silicon carbide.

Thereafter, the method further includes providing a composition comprising at least about 90 mole %  $\text{AlTaO}_4$ , and the balance comprising an oxide of an element selected from the group consisting of Ta, Al, Cr, Hf, Ti, Zr, Mo, Nb, Ni, Sr, Mg, Si, and the rare earth elements including Sc, Y, and the lanthanide series of elements. Thereafter, the method still further includes depositing a layer of the composition on the substrate surface to form the environmental and thermal barrier coating. Each of the substrate and the environmental and thermal barrier coating may have a coefficient of thermal expansion (CTE) in the range of from about  $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ .

10 **[0017]** These and other features, aspects and advantages of the present invention will become better understood with reference to the following drawings, description and claims.

#### BRIEF DESCRIPTION OF THE DRAWINGS

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**[0018]** Figure 1 schematically represents a series of steps involved in a method for preparing an environmental and thermal barrier coating having an improved crystalline structure, according to one embodiment of the invention;

20 **[0019]** Figure 2 schematically represents a series of steps involved in a second method for preparing an environmental and thermal barrier coating having an improved crystalline structure, according to another embodiment of the invention;

**[0020]** Figure 3 schematically represents a component coated with an environmental and thermal barrier coating, according to the invention;

25 **[0021]** Figure 4 schematically represents a series of steps involved in a method for preparing an environmentally and thermally protected component having an environmental and thermal barrier coating thereon, according to another embodiment of the invention; and

**[0022]** Figure 5 is a scanning electron micrograph (SEM) showing the microstructure of an  $\text{AlTaO}_4$  environmental and thermal barrier coating prepared according to one aspect of the invention.

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### DETAILED DESCRIPTION OF THE INVENTION

**[0023]** The following detailed description is of the best currently contemplated modes of carrying out the invention. The description is not to be taken in a limiting sense, but is made merely for the purpose of illustrating the general principles of the invention, since the scope of the invention is best defined by the appended claims.

**[0024]** The present invention provides  $\text{AlTaO}_4$ -based coatings which can effectively protect substrates or components exposed to thermal cycling during service. Coatings of the invention are adapted to protect Si-based ceramic components from thermal damage during repeated thermal cycling to temperatures in the range of from about 1300 to 1550°C, and to protect such components from recession during service.

**[0025]** As an example, the present invention may be used to protect gas turbine engine components during exposure to service conditions. The environmental and thermal barrier coating compositions of the invention have a coefficient of thermal expansion (CTE) match with Si-based ceramic substrates, such as SiC- and  $\text{Si}_3\text{N}_4$ -based ceramics or composites. Coatings of the invention are therefore well adapted for coating Si-based substrates, e.g., gas turbine engine components comprising  $\text{Si}_3\text{N}_4$ , wherein the coating protects the substrate from recession and thermal cycling at temperatures in the range of from about 1300 to 1550°C.

**[0026]** The CTE of a 10 mole %  $\text{Al}_2\text{O}_3$ /90 mole %  $\text{Ta}_2\text{O}_5$  alloy is about  $3.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ . As the alloy composition increases to 25 mole %  $\text{Al}_2\text{O}_3$ /75 mole %  $\text{Ta}_2\text{O}_5$ , the microstructure includes a mixture of  $\text{Ta}_2\text{O}_5$ - $\text{Al}_2\text{O}_3$  solid solution and  $\text{AlTaO}_4$ , and the CTE is about  $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ . Coatings comprising from about 10

mole %  $\text{Al}_2\text{O}_3$ /90 mole %  $\text{Ta}_2\text{O}_5$  up to about 25 mole %  $\text{Al}_2\text{O}_3$ /75 mole %  $\text{Ta}_2\text{O}_5$ , having CTE values in the range of  $3.5 - 4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , may provide a suitable CTE match for coating  $\text{Si}_3\text{N}_4$ -based substrates. A starting mixture for forming a coating of the invention for coating SiC-based substrates (which may have a CTE in the range of  $4 - 5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ), may comprise from about 25 to 50 mole %  $\text{Al}_2\text{O}_3$ . For a starting mixture having about 50 mole %  $\text{Al}_2\text{O}_3$ /50 mole %  $\text{Ta}_2\text{O}_5$  the majority of the phase in the coating is  $\text{AlTaO}_4$ , and the CTE is about  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , thereby providing a good CTE match between the coating and the SiC-based substrate. In contrast, prior art coatings have CTE values too low to provide a good CTE match with SiC-based substrates.

**[0027]** According to one aspect of the present invention, there is provided an environmental and thermal barrier coating (e.g., Figure 3) comprising at least about 50 mole % of  $\text{AlTaO}_4$ . The balance in the coating may include at least one oxide of an element selected from the group consisting of Ta, Al, Cr, Hf, Ti, Zr, Mo, Nb, Ni, Sr, Mg, Si, and the rare earth elements including Sc, Y, and the lanthanide series of elements. In one embodiment, the invention provides a Si-based substrate or component coated with an environmental and thermal barrier coating (e.g., Figure 3), wherein the coating comprises at least about 50 mole % of  $\text{AlTaO}_4$ .

**[0028]** The  $\text{AlTaO}_4$ -based coatings of the present invention prevent the loss of silica oxidation product formed on the surface of the Si-based substrate. The close CTE match between  $\text{AlTaO}_4$  (ca.  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) and SiC-based substrates (ca.  $4 - 5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ) makes the  $\text{AlTaO}_4$ -based materials of the present invention suitable coatings for SiC-based materials and composites. Besides the benefit of CTE match,  $\text{AlTaO}_4$  further enjoys the benefits of having a stable crystalline structure at temperatures in the range of from about 1300 to 1550°C (e.g., does not undergo  $\beta$ - to  $\alpha$ -phase transformation at a temperature of 1550°C (see Example 5)), a relatively low weight (e.g., a weight which is about 30% less than that of prior art  $\text{Ta}_2\text{O}_5$  coatings), and a low production cost due to the low cost of  $\text{Al}_2\text{O}_3$  powder employed as starting material. Since,

coating compositions of the invention do not undergo  $\beta$ - to  $\alpha$ -phase transformation at temperatures as high as 1550°C, such coatings may protect components exposed to at least 1550°C.

**[0029]** Generally, the  $\text{AlTaO}_4$  in the coating of this invention may be prepared via the chemical reaction between  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  powders, or their precursors, provided in a starting mixture, or may be formed from a commercially available  $\text{AlTaO}_4$  powder. Various dopants or additives may be included in the starting mixture using either wet or dry mixing techniques in order to alter the CTE of the final product. Such dopants or additives may include one or more oxides, other compounds, or their precursors, of an element such as Hf, Ti, Zr, Mo, Nb, Ni, Sr, Mg, Si, Al, Cr, Ta, or the rare earth elements including Sc, Y, and the lanthanide series of elements. A coating composition prepared by firing such a mixture may be applied to a substrate to be coated using various deposition techniques well known in the art, such as plasma spray coating, dip coating, spray coating, sol-gel coating, chemical vapor deposition, physical vapor deposition, or electron beam physical vapor deposition.

**[0030]** The sintering property of  $\text{Ta}_2\text{O}_5$  is improved by the inclusion of  $\text{Al}_2\text{O}_3$  (alumina), as disclosed in commonly assigned co-pending U.S. Patent Application Publication No. 2002/0136835 A1, the disclosure of which is incorporated by reference herein in its entirety. Pressed pellets comprising alumina, e.g., containing from about 1.0 to 10 mole % of  $\text{Al}_2\text{O}_3$ , show higher density (e.g., as shown by less internal cracking of the  $\text{Al}_2\text{O}_3$  containing pellets) as compared with pure  $\text{Ta}_2\text{O}_5$  pellets sintered under the same conditions. For example, pure  $\text{Ta}_2\text{O}_5$  pellets tend to fracture and disintegrate at room temperature, whereas the  $\text{Al}_2\text{O}_3$  containing pellets remain intact. This improved sinterability is believed to be due to a reduction in the rate of  $\text{Ta}_2\text{O}_5$  grain coarsening by the addition of  $\text{Al}_2\text{O}_3$ , and/or the enhancement of Ta ion lattice diffusion as the number of cation vacancies is increased by the diffusion kinetics due to the presence of Al ions.

**[0031]** The solid solubility of  $\text{Al}_2\text{O}_3$  in  $\text{Ta}_2\text{O}_5$  may be about 10 mole % at about  $1500^\circ\text{C}$ . Since  $\alpha\text{-Al}_2\text{O}_3$  has a CTE of about  $8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , the CTE of a 10 mole %  $\text{Al}_2\text{O}_3$ /90 mole %  $\text{Ta}_2\text{O}_5$  alloy would be about  $3.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , which is 10% higher than the CTE of pure  $\text{Ta}_2\text{O}_5$  and closer to the CTE of silicon nitride.

5 When the amount of  $\text{Al}_2\text{O}_3$  in  $\text{Ta}_2\text{O}_5$  exceeds about 10 mole %, a second phase having the formula of  $\text{AlTaO}_4$  forms that has a CTE of about  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ . As the alloy composition increases to 25 mole %  $\text{Al}_2\text{O}_3$ /75 mole %  $\text{Ta}_2\text{O}_5$ , the microstructure includes a mixture of  $\text{Ta}_2\text{O}_5\text{-Al}_2\text{O}_3$  solid solution and  $\text{AlTaO}_4$ , and the CTE is about  $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , which provides a good CTE match with SiC. If

10 the  $\text{Al}_2\text{O}_3$  concentration exceeds 25 mole %, the CTE of the coating may become too high for application on  $\text{Si}_3\text{N}_4$  substrates. For SiC and its composites having a CTE in the range of  $4 - 5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , the starting mixture for forming the coating composition may comprise up to about 50 mole %  $\text{Al}_2\text{O}_3$ , so that the majority of the phase in the coating is  $\text{AlTaO}_4$ , and there is a good

15 CTE match between the coating and the substrate.

**[0032]** Coating compositions of the present invention exhibit low grain growth rate (e.g., having smaller grains, as shown by scanning electron microscopy, when  $\text{Al}_2\text{O}_3$  is present with  $\text{Ta}_2\text{O}_5$ , as compared to  $\text{Ta}_2\text{O}_5$  without  $\text{Al}_2\text{O}_3$ ), good CTE match with Si-based substrates (as described hereinbelow),

20 and high fracture toughness (e.g., as shown by difficulty in machining samples formed from the coating composition). The composition for forming the coating may comprise tantalum oxide ( $\text{Ta}_2\text{O}_5$ ), or a mixture of  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$ . Other oxides, compounds, or their precursors, of elements such as Cr, Hf, Si, Ln (rare earth elements including the entire lanthanum series and Y), Mg, Mo, Ni, Nb, Sr,

25 Ti, and Zr may be added as dopants or additives. Such dopants may have some effect on the CTE of the resultant coating composition, mostly shifting it higher.

**[0033]** Additional additives (e.g., nitrides, carbides, borides, silicides) can be introduced to further inhibit grain growth, to modify the CTE, and reinforce

30 tantalum oxide. By selecting particular dopants or combinations of dopants and

additives, the above characteristics of grain growth rate, CTE/substrate match, and fracture toughness may be achieved.

**[0034]** A variety of ceramic processing methods can be used to introduce and incorporate various dopants and additives into coatings of the present invention. As shown by the method 100 in Figure 1, a process for forming a coating of the present invention may start with providing a commercially available powder, e.g., Ta<sub>2</sub>O<sub>5</sub> powder, (step 102), to which a suitable amount (e.g., from about 1 – 50 mole %) of other oxides, additives, or their precursors, may be added in a step 105. The additives or their precursors may be in the form of powders which may be mixed (step 106) with the powder provided in step 102 to form a mixture 104. The mixing step 106 may be preformed either wet or dry.

**[0035]** After mixing (and drying, if wet mixing in a liquid medium is used) the mixture 104 may be coated on a substrate during a coating operation or step 108. Alternatively, the mixture may be subjected to a calcination step 112 in which the mixture is heat-treated, e.g., at a temperature up to about 1600°C, before performing the coating step 108. Optionally, a milling or grinding step 110 may be preformed after the calcination step 112 and before the coating step 108.

**[0036]** Referring to Figure 2, an alternative method 113 of incorporating dopants or additives may use precursor compounds 114 (either solids or liquids) containing the dopant ions. The precursor compounds 114 may be dissolved in a solvent, such as water or an alcohol 116, mixed with Ta<sub>2</sub>O<sub>5</sub> powder 118, and then precipitated onto the surface of the Ta<sub>2</sub>O<sub>5</sub> particles 120. Alternatively, the Ta<sub>2</sub>O<sub>5</sub> powder can be dispersed in the solvent first, and added with the precursors. After drying and an optional calcination step 122 and/or grinding step 124, the mixture 120 is then ready for a coating operation 126. Drying the mixture (when wet mixing is used), as well as steps 122 and 124 may be performed essentially as described with reference to Figure 1.

**[0037]** The coating step 108 (Figure 1) or 126 (Figure 2) for applying the mixture (e.g., mixture 120, Figure 2) created by either of the methods 100 or 113 may include plasma spraying, dip or spray coating, sol gel coating, and chemical vapor deposition (CVD). Moreover, the coating can be formed by sintering pressed ingots or similar materials at about 1350° C for about 1 to 20 hours, and performing Physical Vapor Deposition, (PVD) or Electron Beam Physical Vapor Deposition (EB-PVD) methods (the latter method being well known in the field of thermal barrier coatings for super alloy turbine engine parts). Both PVD and EB-PVD coatings have the benefit of forming a uniform coating having a smooth surface, and allow strong bonding to the substrate, with uniform additive distribution.

**[0038]** Figure 3 shows a component 200 formed in accordance with the present invention. Component 200 can include a substrate 202 which may comprise a Si-based material such as a SiC-SiC composite material. A layer of an environmental and thermal barrier coating 204 may be disposed on the outer surface of substrate 202 as described above. Coating 204 may be deposited on substrate 202 using a deposition process, such as EB-PVD, which allows the thickness of coating 204 to be accurately controlled. Typically, the thickness of coating 204 is in the range of from about 0.1 to 50 mils, usually from about 0.1 to 20 mils, and often from about 0.5 to 10 mils.

**[0039]** The coating 204 typically comprises at least about 50 mole % AlTaO<sub>4</sub>. The coating 204 may be formed from a starting mixture comprising at least about 25 mole % Ta<sub>2</sub>O<sub>5</sub> and at least about 25 mole % Al<sub>2</sub>O<sub>3</sub>. One or more dopants or additives may be included in the starting mixture, as described hereinabove. In some embodiments, coating 204 may comprise at least about 90 mole % AlTaO<sub>4</sub>, and the balance may consist predominantly of Ta<sub>2</sub>O<sub>5</sub> or Al<sub>2</sub>O<sub>3</sub>. In other embodiments, coating 204 may comprise more than 99 mole % AlTaO<sub>4</sub>.

**[0040]** Figure 4 schematically represents a series of steps involved in a method for preparing an environmentally and thermally protected component

having an environmental and thermal barrier coating thereon, according to another embodiment of the invention. Step 300 involves providing a starting mixture. The starting mixture may comprise  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$ . For example, the starting mixture may comprise equimolar quantities of  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$ . The starting mixture may comprise equimolar quantities of  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$ . The  $\text{Ta}_2\text{O}_5$  ingredient of the starting mixture may be in the form of  $\beta$ -  $\text{Ta}_2\text{O}_5$  powder. Typically, the starting powder mixture comprises at least about 25 mole %  $\text{Al}_2\text{O}_3$  and at least about 25 mole %  $\text{Ta}_2\text{O}_5$ . In one embodiment, the starting mixture comprises at least about 45 mole %  $\text{Al}_2\text{O}_3$  and at least about 45 mole %  $\text{Ta}_2\text{O}_5$ .

**[0041]** Lesser amounts of dopants or additives may be added to the starting powder mix, according to the desired properties of the environmental and thermal barrier coating to be formed from the starting mix. Such dopants or additives may comprise oxides, or other compounds, or their precursors, of elements including Al, Ta, Cr, Hf, Ti, Zr, Mo, Nb, Ni, Sr, Mg, Si, and the rare earth elements including Sc, Y, and the lanthanide series of elements. In one embodiment, the starting mixture may comprise about 50 mole %  $\text{Al}_2\text{O}_3$  and about 50 mole %  $\text{Ta}_2\text{O}_5$ .

**[0042]** The composition of the starting mixture provided in step 300 may be selected in order to achieve a particular CTE for the environmental and thermal barrier coating product, to provide a CTE "match" with a particular substrate to be coated. That is to say, the composition of the starting mixture, and hence that of the environmental and thermal barrier coating, may be chosen according to the application, or the component to be coated to achieve a suitable CTE match between the component/substrate and the coating deposited thereon. For example, the substrate to be coated may have a CTE in the range of from about  $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , and the environmental and thermal barrier coating to be applied thereon may have a CTE in the same range.

**[0043]** The starting mixture may be mixed with a suitable solvent, e.g., an alcohol such as isopropanol. After mixing, the starting mixture may be dried to remove solvent (step 302) prior to firing.

**[0044]** Step 304 involves firing the starting mixture at an elevated temperature to form a reaction product. The firing step 304 may be performed in a furnace in the presence of air. Typically, the firing temperature is in excess of 1000°C, usually in the range of from about 1200 to 1600°C, and often in the range of about 1500°C. The firing step may be continued until reaction between Al<sub>2</sub>O<sub>3</sub> and Ta<sub>2</sub>O<sub>5</sub> in the starting mixture is complete.

**[0045]** Step 306 involves forming a particulate reaction product. For example, the reaction product may be broken up mechanically, e.g., by grinding and the like, to form particles of the reaction product. In one embodiment, a particular size range of the particulate reaction product is selected preparatory to depositing a layer of environmental and thermal barrier coating on the surface of a substrate/component. For example, a particulate reaction product formed in step 306 may be sieved to provide particles having a size range of from about 2 to 200 μ, and more typically in the range of from about 5 to 100 μ.

**[0046]** Step 308 involves depositing the reaction product on the substrate/component to form an environmentally and thermally protected component having an environmental and thermal barrier coating disposed on the surface of the substrate/component. Techniques for depositing solid coatings on a surface are well known in the art. For example, the environmental and thermal barrier coating may be applied to the surface of the substrate/component by a process such as plasma spray coating, dip coating, spray coating, sol-gel coating, chemical vapor deposition, physical vapor deposition, or electron beam physical vapor deposition.

**[0047]** The environmental and thermal barrier coating deposited in step 308 typically comprises at least 50 mole % AlTaO<sub>4</sub>, and may have a CTE in the range of  $3.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$  to  $5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ . In some embodiments, the environmental and thermal barrier coating may comprise at least about 50 mole % AlTaO<sub>4</sub> and the balance may consist essentially of Al<sub>2</sub>O<sub>3</sub> or Ta<sub>2</sub>O<sub>5</sub>.

**[0048]** In some embodiments, an environmental and thermal barrier coating of the invention may comprise at least about 90 mole % AlTaO<sub>4</sub>. Such

an environmental and thermal barrier coating may consist essentially of  $\text{AlTaO}_4$  and a metal oxide, such as  $\text{Al}_2\text{O}_3$  or  $\text{Ta}_2\text{O}_5$ . For example, an environmental and thermal barrier coating of the invention may comprise at least about 90 mole %  $\text{AlTaO}_4$  and the balance may consist predominantly of  $\text{Al}_2\text{O}_3$  or  $\text{Ta}_2\text{O}_5$ . In some  
5 embodiments, the  $\text{Al}_2\text{O}_3$  or  $\text{Ta}_2\text{O}_5$  component of the coating may be present in only trace amounts. An environmental and thermal barrier coating of the invention comprising about 90 mole %  $\text{AlTaO}_4$  may have a CTE in the range of from about  $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ . Such coatings typically provide a good CTE match between the coating and SiC-based substrates. In certain  
10 embodiments, an environmental and thermal barrier coating of the invention may comprise more than 99 mole %  $\text{AlTaO}_4$ .

**[0049]** The CTE of the environmental and thermal barrier coating varies according to the mole %  $\text{AlTaO}_4$  present therein. Thus, the mole %  $\text{AlTaO}_4$  present in the environmental and thermal barrier coating may be varied  
15 according to the intended application, e.g., to obtain a suitable match between the CTE of the environmental and thermal barrier coating and the CTE of a substrate to be coated with the environmental and thermal barrier coating.

**[0050]** In an alternative approach to the method described with reference to Figure 4, a mixture of  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  applied to a component may react to  
20 form a coating comprising  $\text{AlTaO}_4$  following exposure of the component to high temperatures during service conditions.

**[0051]** Figure 5 is a scanning electron micrograph (SEM) showing the microstructure of a fractured surface of an  $\text{AlTaO}_4$ -based environmental and thermal barrier coating prepared generally according to the method of Figure 4.  
25 The SEM of Figure 5 shows a dense, fine-grained microstructure indicative of the superior mechanical and protective properties of the  $\text{AlTaO}_4$ -based coating. Such a coating also exhibits the desirable properties of CTE match with silicon composite substrates, and effectively protects the substrate from recession and repeated thermal cycling.

## EXAMPLES

### Example 1

5 **[0052]** Three compositions were prepared from starting mixtures having 1, 10, and 25 mole %  $\text{Al}_2\text{O}_3$ , respectively, as the additive to  $\text{Ta}_2\text{O}_5$ . For each composition, about 1 Kg of a commercial  $\beta$ - $\text{Ta}_2\text{O}_5$  powder was mixed with commercial  $\text{Al}_2\text{O}_3$  powder in isopropanol in a milling jar for about 2 hours. After drying the mixture, the resultant powder was sieved to classify the particle size  
10 in the range of about 5 to 100 microns in preparation for plasma spray coating. If the particle size was too fine, a calcining process was included to coarsen the particles.

**[0053]** A coating of each of the above compositions was then applied to coupons of silicon nitride and SiC-SiC composite substrates by an air-plasma  
15 spraying process, as follows. The silicon nitride coupons had an as-sintered surface on which the plasma coating was applied. (Alternatively, a grit-blasted machine surface could have been utilized.) The coupons were degreased, and preheated to about  $1000^\circ\text{C}$  by either a torch or furnace. The powder was then fed into a high velocity, high temperature plasma air flow. The ceramic powder  
20 became molten and subsequently was quenched and solidified onto the coupons. The coating thickness varied from about 2 to 10 mils. (i.e., from about 50 to 250 microns).

**[0054]** The coated samples were then subjected to a thermal cycling regime wherein each sample was held in a furnace at about  $2400^\circ\text{F}$  ( $1315^\circ\text{C}$ )  
25 for about 30 minutes, and then quickly removed from the furnace and quenched to about  $200^\circ\text{C}$  in a stream of blowing air. The silicon nitride coupons coated with all three compositions survived about 100 hours and 200 cycles without spalling. X-ray diffraction showed the  $\text{Ta}_2\text{O}_5$  remained in the  $\beta$ - phase.

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### Example 2

**[0055]** Four compositions were prepared from starting mixtures having 3, 4, 6, and 10 mole %  $\text{La}_2\text{O}_3$ , respectively, as the additive to  $\text{Ta}_2\text{O}_5$ . In each batch, about 1 Kg of a commercial  $\beta$ - $\text{Ta}_2\text{O}_5$  powder was mixed with commercial  $\text{La}_2\text{O}_3$  powder in isopropanol in a milling jar for about 2 hours. After drying the mixture, the resultant powder was sieved to classify the particle size in the range of from about 5 to 100 microns preparatory to plasma spray coating.

**[0056]** Each composition was applied to coupons of silicon nitride and SiC-SiC composite substrates which were prepared and coated essentially as described in Example 1. The coating thickness varied from about 2 to 10 mils. The coated samples were then subjected to cyclic furnace testing essentially as described in Example 1.

**[0057]** The silicon nitride samples coated with  $\text{La}_2\text{O}_3$  in the range of 3, 4, and 6 mole % survived more than 1000 hours and 2000 cycles at 1315°C. The SiC-SiC samples coated with compositions having  $\text{La}_2\text{O}_3$  at 4, 6, and 10 mole % survived more than 2,000 hours and 4,000 cycles. SEM examination showed needle-shaped  $\text{La}_2\text{O}_3 - \text{Ta}_2\text{O}_5$  precipitates on the surface of the coating. X-ray diffraction showed the existence of a second phase containing La, possibly the  $\text{La}_2\text{Ta}_{12}\text{O}_{33}$  phase according to the phase diagram. These needle-shaped second phases, which were distributed uniformly throughout the coating, increased the fracture toughness and mechanical strength of the coating. The second phase also increased the CTE of the coating, such that the CTE mismatch between the coating and the substrate was significantly reduced, resulting in improved coating life performance as shown by thermal cyclic testing.

### Example 3

**[0058]** A SiC-SiC coupon was coated with a composition prepared, from a starting mixture comprising about 50 mole %  $\text{Al}_2\text{O}_3$  and 50 mole %  $\text{Ta}_2\text{O}_5$ , by a process essentially as described for Example 1. The coating prepared in this manner survived the thermal cycling regime of Example 1 (i.e., 1315°C for about 30 minutes, and then quenched to about 200°C in a stream of blowing air) for over 3000 hours without spalling. After the thermal cyclic testing, the coating was found to have been transformed to the  $\text{AlTaO}_4$  phase, with some residual  $\text{Ta}_2\text{O}_5$ .

### Example 4

**[0059]** Coated silicon nitride coupons having coating compositions of 10 mole %  $\text{Al}_2\text{O}_3$ /90 mole %  $\text{Ta}_2\text{O}_5$  survived thermal cycling at 1315°C for 500 hours and 1000 cycles without spalling. X-ray diffraction of the thermally tested coating showed that the predominant phase in the coating was  $\beta\text{-Ta}_2\text{O}_5$  with some  $\text{AlTaO}_4$  phase.

### Example 5

**[0060]** Two coating compositions, 1 mole %  $\text{Al}_2\text{O}_3$ /99 mole %  $\text{Ta}_2\text{O}_5$  and 5 mole %  $\text{Al}_2\text{O}_3$ /95 mole %  $\text{Ta}_2\text{O}_5$ , were heat-treated at 1450°C for 2 hours. X-ray diffraction showed that the samples remained predominantly as  $\beta\text{-Ta}_2\text{O}_5$  after the heat treatment. In contrast, pure  $\beta\text{-Ta}_2\text{O}_5$  completely transformed to  $\alpha\text{-Ta}_2\text{O}_5$  after a heat treatment of 1 hour at 1450°C. Scanning electron microscopic (SEM) examination showed that the grain size for the 5 mole %  $\text{Al}_2\text{O}_3$  coating composition fired at 1450°C was significantly smaller than that of the pure  $\text{Ta}_2\text{O}_5$  sample fired at the same temperature. The coating composition of 5 mole %  $\text{Al}_2\text{O}_3$ /95 mole %  $\text{Ta}_2\text{O}_5$  was further heated at 1550°C for 15 hours,

and the  $Ta_2O_5$  remained as the  $\beta$ -phase after the heat treatment.

#### Example 6

5 **[0061]** Powders of two compositions, 7.5 mole %  $Al_2O_3$ /92.5 mole %  $Ta_2O_5$  and 4 mole %  $La_2O_3$ /96 mole %  $Ta_2O_5$ , respectively, were pressed into cylindrically-shaped green parts and sintered at 1350°C for 10 hours to form ingots for EB-PVD coating. Substrates of silicon nitride and SiC-SiC composites were loaded in a vacuum chamber and an electron beam was  
10 focused on an ingot of the material to be deposited. The substrate was preheated to 800-1200°C to improve bonding with the deposited material. The electron bombardment resulted in high local heating on the coating material, which evaporated atomistically and condensed onto the substrate. Oxygen gas was then fed into the system to compensate for the loss of oxygen from  $Ta_2O_5$   
15 during the evaporation. The coating was chemically bonded to the substrate. The coated silicon nitride and SiC-SiC parts having a 50 micron thick coating survived the above described thermal cycling regime at 1315°C for over 500 hours and 1000 cycles.

20

#### Example 7

**[0062]** An  $AlTaO_4$  powder compound was prepared by mixing 500 g of powder containing 50 mole %  $Al_2O_3$  and 50 mole %  $Ta_2O_5$  in isopropanol in a milling jar for about 2 hours, drying the mixture, and firing the resultant powder  
25 in a furnace in air at 1500°C for 1 hour. X-ray diffraction confirmed the complete reaction between  $Al_2O_3$  and  $Ta_2O_5$  powders to form  $AlTaO_4$ . The reacted powder was broken down mechanically and sieved to classify the particle size to about 5 to 100 micron range in preparation for plasma spray coating (Example 8).

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### Example 8

**[0063]** The resultant  $\text{AlTaO}_4$  powder prepared according to Example 7 was plasma-sprayed on a SiC-SiC composite substrate of about 2 cm x 2 cm x 5 1 mm to form a coating about 5 mils in thickness. The coated substrate was tested by thermal cycling at 1315 °C under the conditions described in Example 1. The coating survived 100 hours and 200 cycles without spallation and effectively protected the SiC-SiC substrate.

10

### Example 9

**[0064]** An  $\text{AlTaO}_4$  coating prepared according to the invention was examined by scanning electron microscopy to reveal a fined-grained microstructure (Figure 5). This coating survived the thermal cycling regime 15 described in Example 1 for more than 1600 cycles/800 hours at 1315°C.

**[0065]** It should be understood, of course, that the foregoing relates to preferred embodiments of the invention and that modifications may be made without departing from the spirit and scope of the invention as set forth in the 20 following claims.

WE CLAIM:

1. A thermally protected component (200), comprising:  
a substrate (202) having a surface; and  
an environmental and thermal barrier coating (204) disposed on said surface of said substrate (202), wherein said environmental and thermal barrier coating (204) comprises at least about 50 mole %  $\text{AlTaO}_4$ , and wherein said environmental and thermal barrier coating (204) is characterized by a coefficient of thermal expansion (CTE) in the range of from about  $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ .
2. The thermally protected component (200) of claim 1, wherein said substrate (202) comprises a silicon-based ceramic or a silicon-based composite, and said substrate (202) has a coefficient of thermal expansion (CTE) in the range of from about  $4 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ .
3. The thermally protected component (200) of any one or more of claims 1-2, wherein said environmental and thermal barrier coating (204) further comprises at least one metal oxide selected from the group consisting of Ta, Al, Hf, Ti, Zr, Mo, Nb, Ni, Sr, Mg, Si, and the rare earth elements including Sc, Y, and the lanthanide series of elements.
4. The thermally protected component (200) of any one or more of claims 1-2, wherein said environmental and thermal barrier coating (204) further comprises  $\text{Al}_2\text{O}_3$  or  $\text{Ta}_2\text{O}_5$ .
5. The thermally protected component (200) of any one or more of claims 1-4, wherein said environmental and thermal barrier coating (204) comprises at least about 90 mole %  $\text{AlTaO}_4$ .

6. The thermally protected component (200) of any one or more of claims 1-4, wherein said environmental and thermal barrier coating (204) comprises greater than 99 mole %  $AlTaO_4$ .

7. The thermally protected component (200) of any one or more of claims 1-6, wherein said substrate (202) comprises a SiC-SiC composite or a  $Si_3N_4$  composite.

8. The thermally protected component (200) of any one or more of claims 1-7, wherein said environmental and thermal barrier coating (204) has a stable crystalline structure at a temperature of about 1550°C.

9. The thermally protected component (200) of any one or more of claims 1-8, wherein said environmental and thermal barrier coating (204) has a thickness in the range of from about 0.1 to 20 mils.

10. The thermally protected component (200) of any one or more of claims 1-9, wherein said substrate (202) comprises a component of a gas turbine engine.

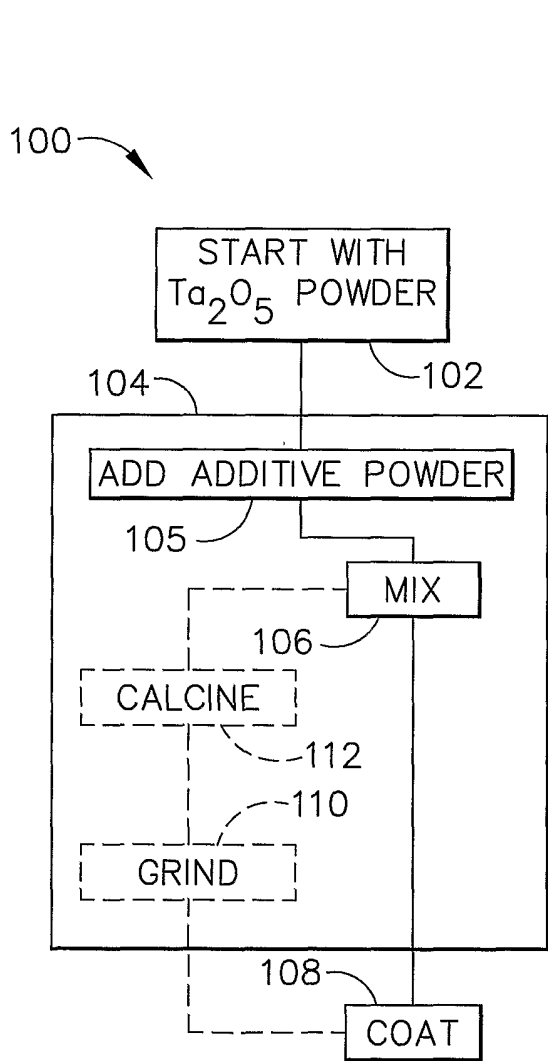


FIG. 1

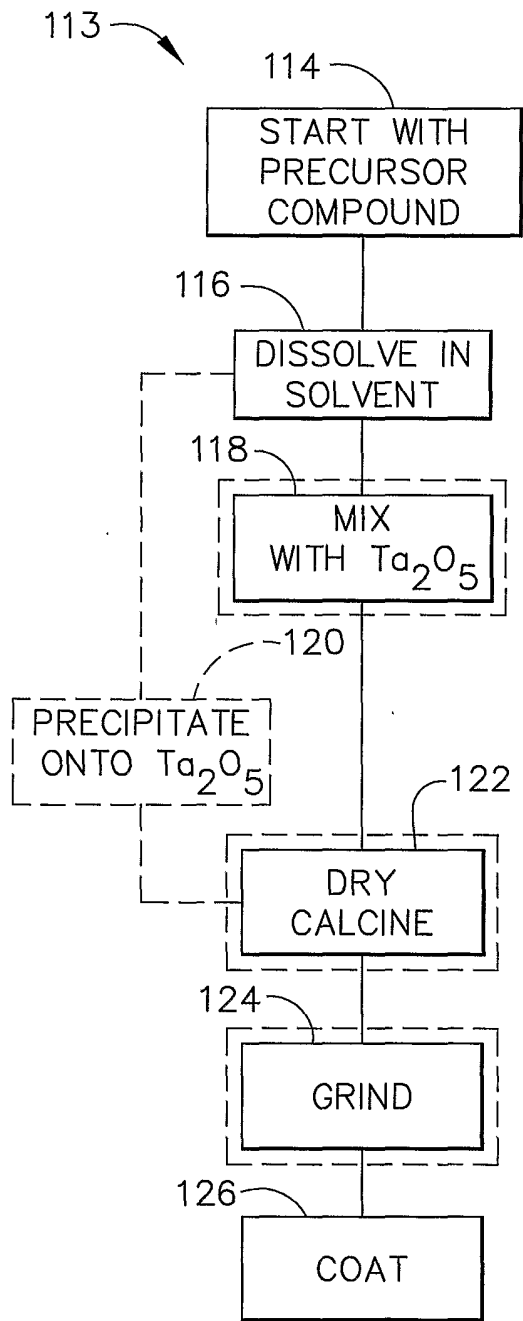


FIG. 2

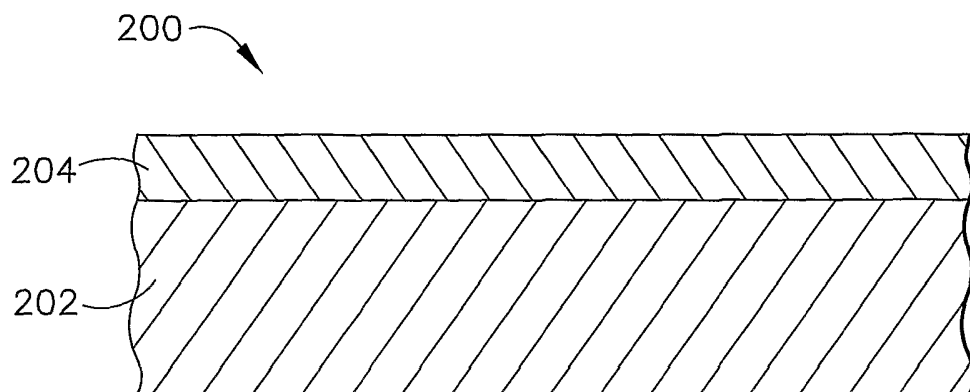


FIG. 3

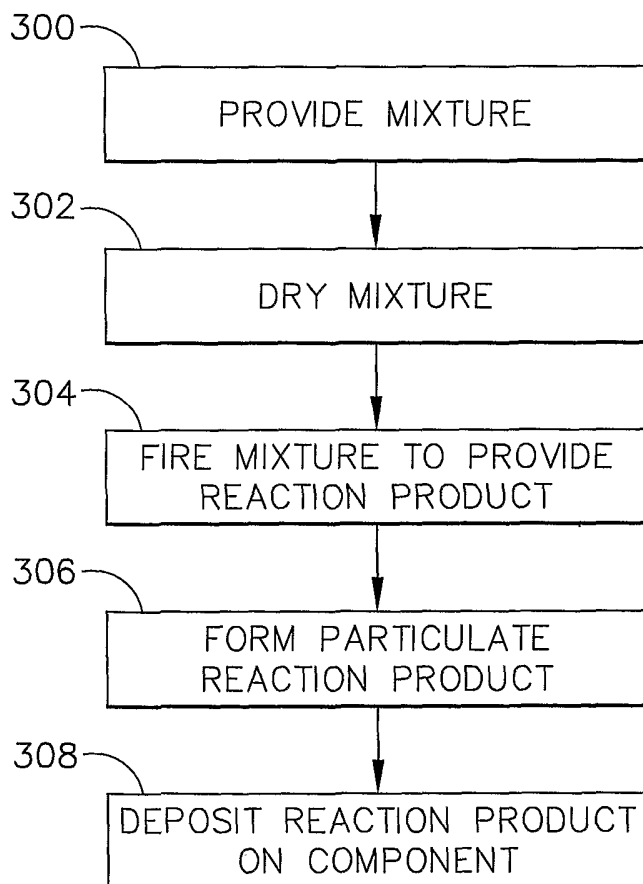


FIG. 4

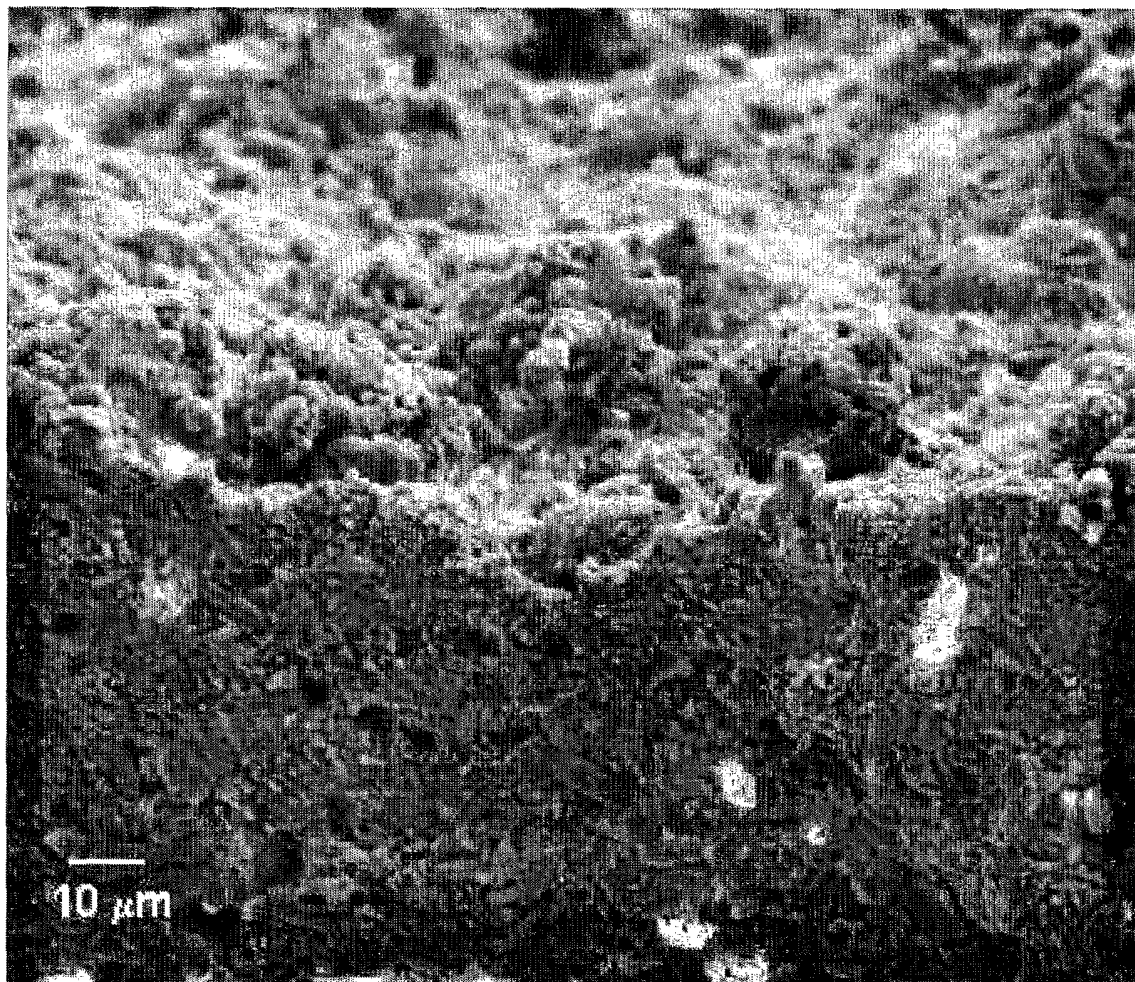


FIG. 5

**INTERNATIONAL SEARCH REPORT**

International Application No  
PCT/US2004/022940

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC 7	C23C30/00	F01D5/28 C04B41/50 C09C3/06 C23C28/00
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
IPC 7 C23C C04B C09C F01D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
EPO-Internal, WPI Data, PAJ		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/136835 A1 (XUE LIANG A ET AL) 26 September 2002 (2002-09-26) page 1, paragraph 17 page 2, paragraph 21 - paragraph 23; claims 1,4-7,11-13; example 3	1-10
A	EP 1 205 574 A (APPLIED MATERIALS INC) 15 May 2002 (2002-05-15) column 6, line 36 - line 40 column 7, line 50 - column 8, line 3; claims 1,12,13	1,2,5,6
A	US 6 552 403 B1 (LUCOVSKY GERALD) 22 April 2003 (2003-04-22) column 7, line 45 - line 63; claims 1,4,8-10,13; example 1	1,2
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
° Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
8 October 2004		14/10/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  Elsen, D

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US2004/022940

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002136835	A1	26-09-2002	EP 1373684 A1 02-01-2004
			WO 02077418 A1 03-10-2002
			US 2004157062 A1 12-08-2004
EP 1205574	A	15-05-2002	EP 1205574 A2 15-05-2002
			JP 2002164348 A 07-06-2002
			SG 90269 A1 23-07-2002
US 6552403	B1	22-04-2003	AU 2619401 A 14-05-2001
			EP 1236224 A1 04-09-2002
			TW 541600 B 11-07-2003
			WO 0133619 A1 10-05-2001
			US 2003139026 A1 24-07-2003