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(54) **METHOD AND APPARATUS FOR DEPOSITING STABLE CRYSTALLINE PHASE COATINGS OF HIGH TEMPERATURE CERAMICS**

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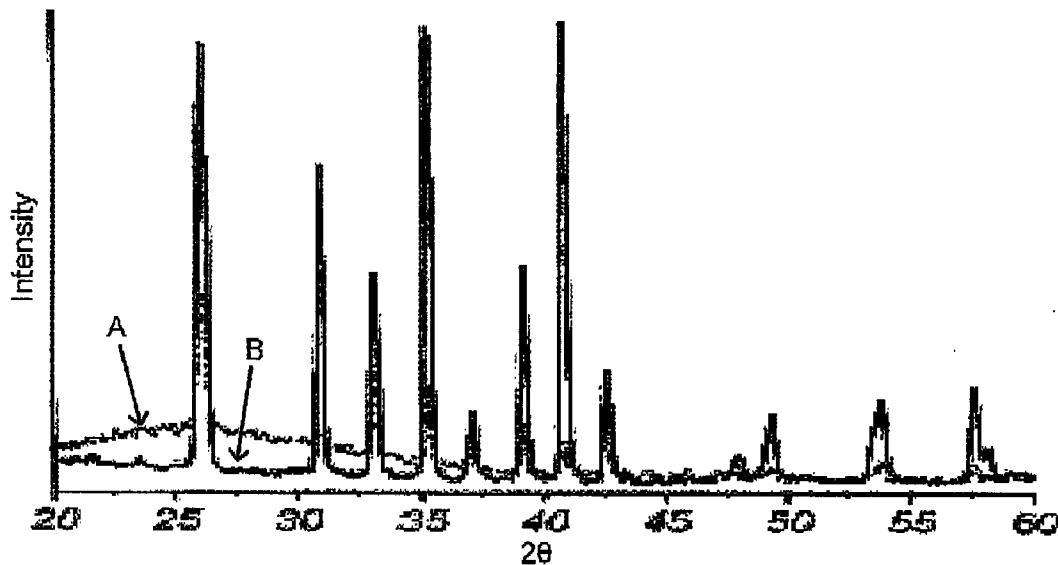
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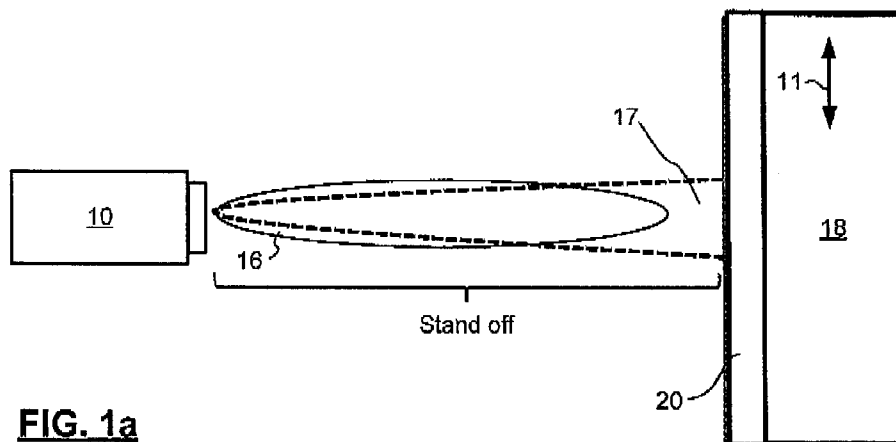
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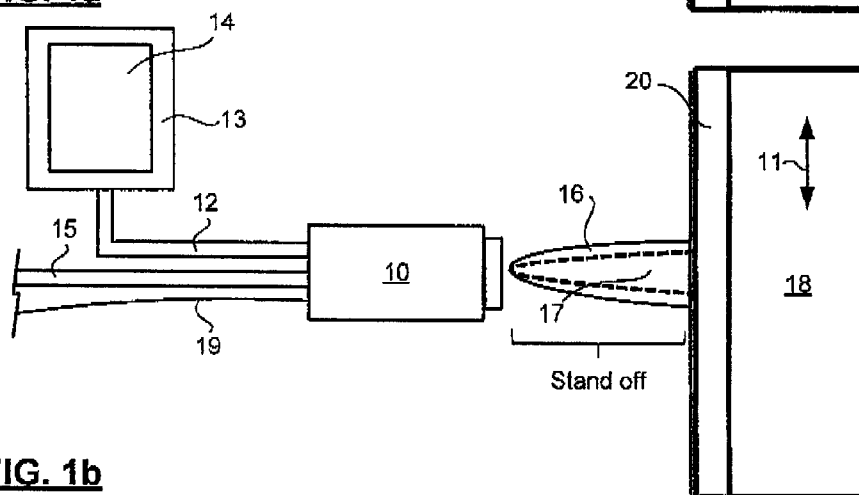
(57) **ABSTRACT**

Producing high temperature coatings on ceramics using a high enthalpy air plasma spray torch and supplying in at least 3 passes to deposit the coating is advantageous for spraying high temperature ceramics while avoiding formation of undesirable phases, if the stand off distance is chosen such that a width of a bead produced from a single spray pass on the substrate at ~800° C. is less than 70% of a diameter of a plume of the torch at the stand off, and neither assisted heating, nor forced cooling, nor subsequent heat treatment is used. The rapid cooling endemic to thermal spray that leads to amorphous, metastable and other undesirable phases of alkaline earth aluminosilicate (e.g., barium-strontium aluminosilicate (BSAS)), rare earth silicates (RESs), mullite, etc. can be mitigated sufficiently by the close stand off and high enthalpy torch to provide highly crystalline and stable phase coatings.

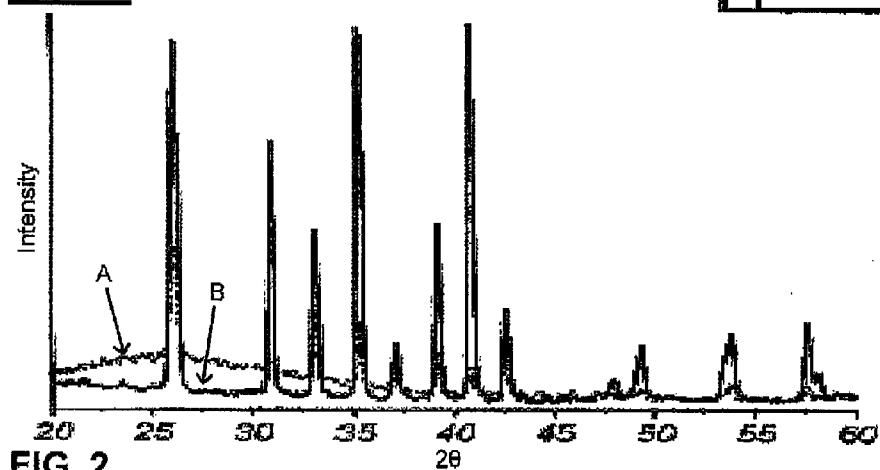




**FIG. 1a**



**FIG. 1b**



**FIG. 2**

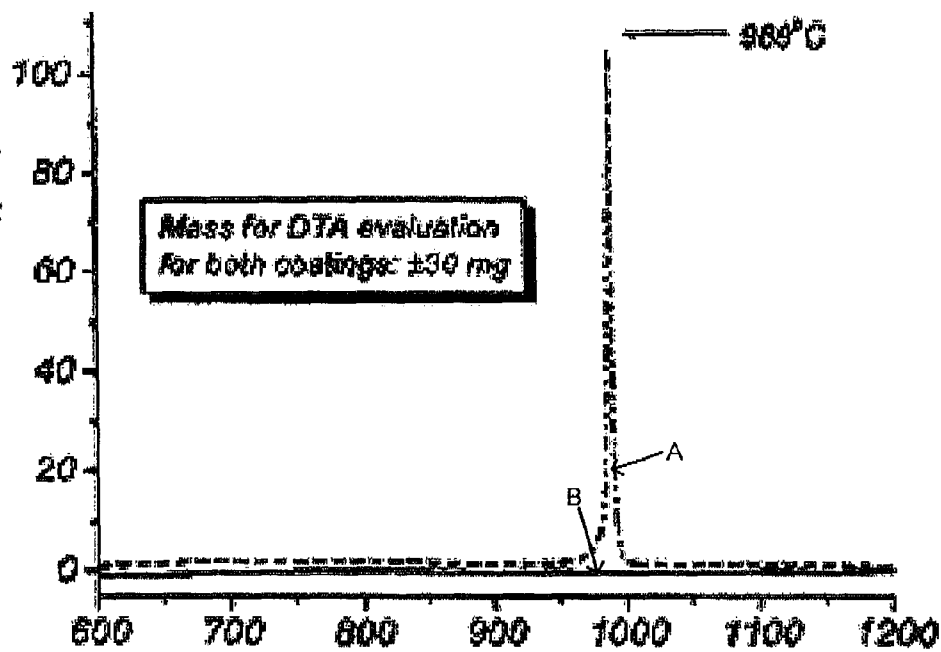


FIG. 3



FIG. 4



FIG. 5

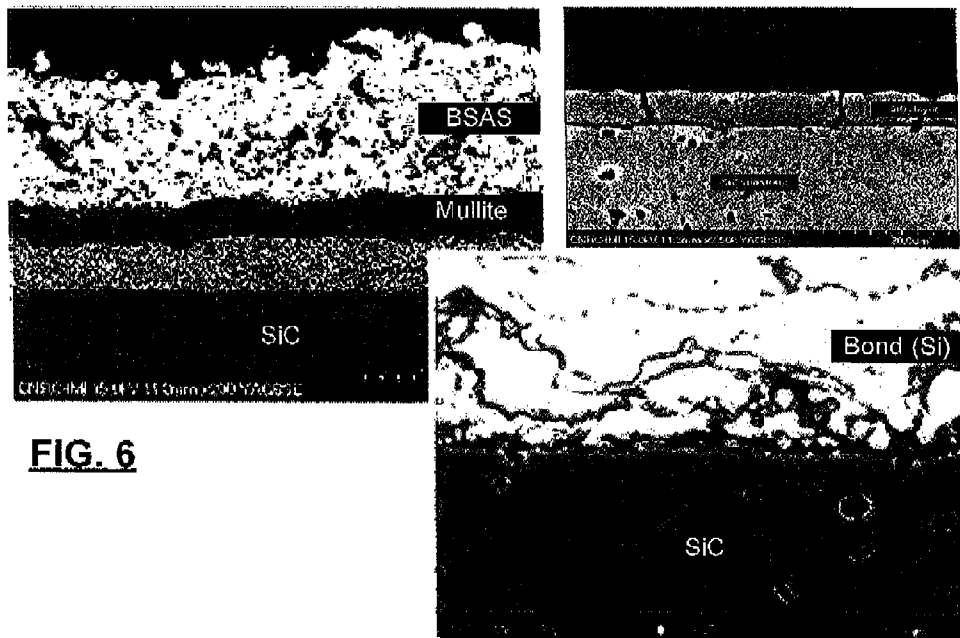


FIG. 6

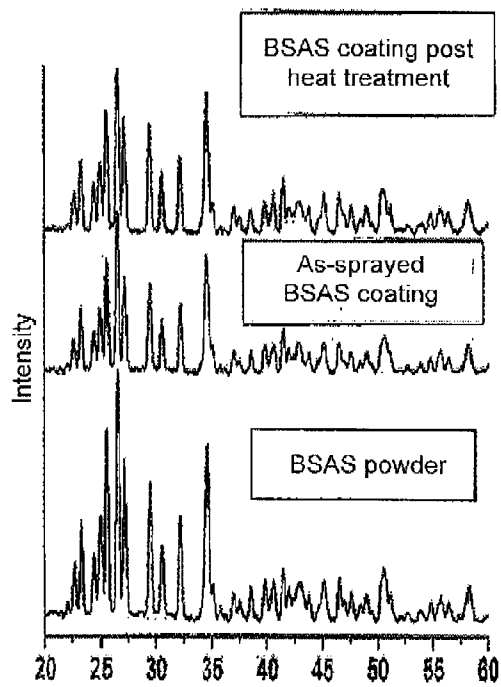


FIG. 7

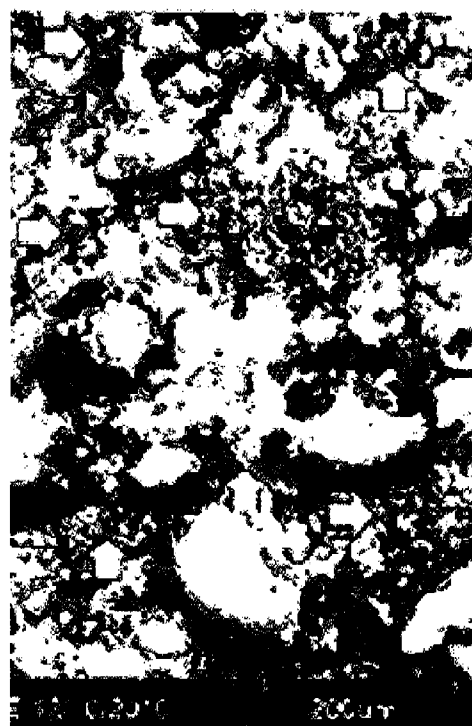
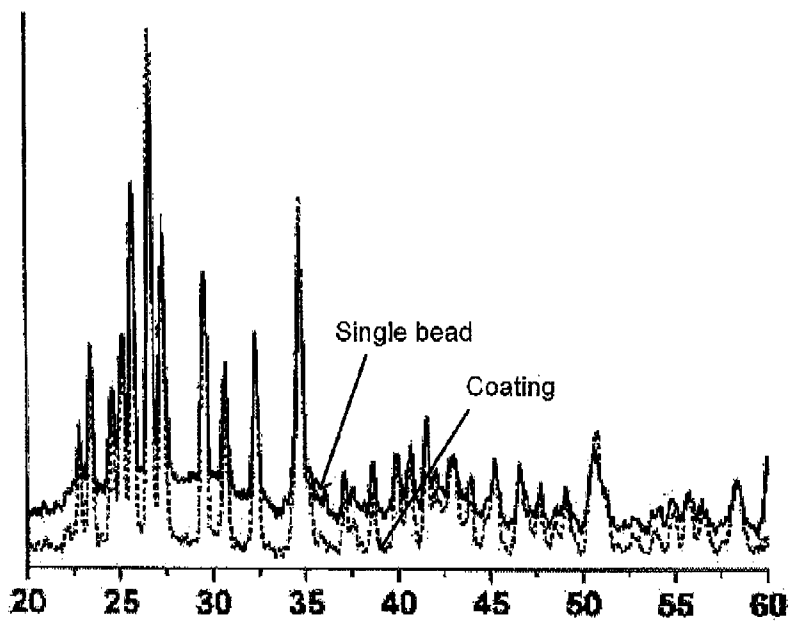
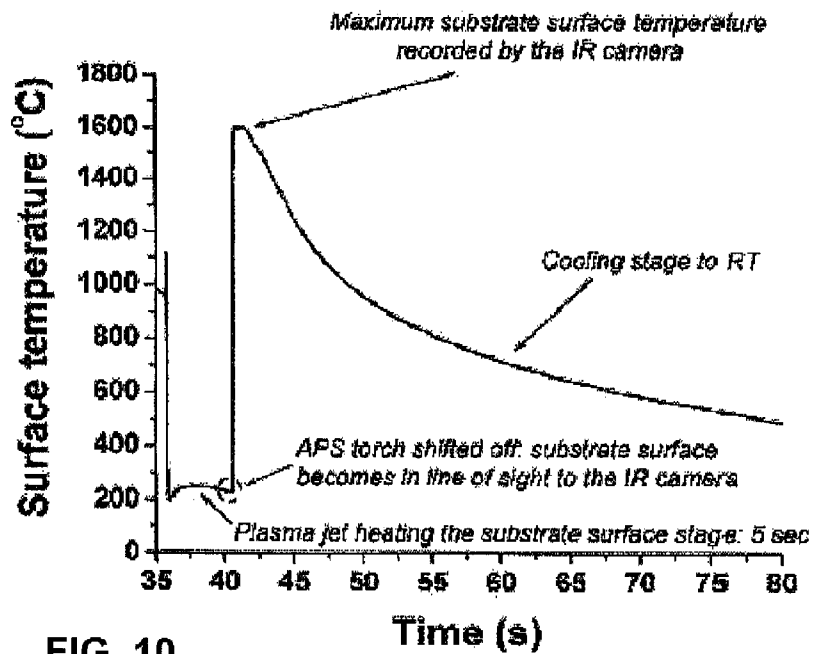


FIG. 8



**FIG. 9**



**FIG. 10**

**METHOD AND APPARATUS FOR  
DEPOSITING STABLE CRYSTALLINE PHASE  
COATINGS OF HIGH TEMPERATURE  
CERAMICS**

FIELD OF THE INVENTION

**[0001]** The present invention relates in general to thermal spray arts, and in particular to techniques for producing stable crystalline phase coatings of such materials as alkaline earth aluminosilicates (e.g., barium-strontium aluminosilicate (BSAS)), rare earth silicates (RESs), and mullites, and in particular to a low cost coating process that is phase pure, without assisted heating of a substrate.

BACKGROUND OF THE INVENTION

**[0002]** To increase the efficiency of a gas turbine engines for aerospace applications and power generation, higher operating temperatures are needed. In the same time the durability of the engine components must correspondingly sustain the temperature increase. While metal super alloys are widely used in the hot sections of gas turbines, there is currently a temperature limit ( $\sim 1200^\circ\text{C}$ .) for the usage of these metals. New materials, and in particular silicon (Si) based ceramics (e.g., SiC and  $\text{Si}_3\text{N}_4$ ) in the form of ceramic matrix composites (CMCs) have emerged for high temperature applications ( $200^\circ\text{C}$ .) due to their high mechanical strengths at high temperatures and density values in the order of  $\frac{1}{3}$  of those of metallic superalloys [1, 2, 3, 4, 5]. These same material characteristics can be applied to engineer the external structural body of the next generation of hypersonic vehicles.

**[0003]** For most of these applications (gas turbines and hypersonic aircraft) protective coatings are beneficial and even required. Layered refractory oxide coatings offering a suitable thermal-insulation reduce the thermal gradient through the structural component and increase its durability. A coating for components formed of Si-based materials (CMCs) must simultaneously fulfill a second role namely environmental protection, like for instance, in the high temperature environments containing water vapour in the hot sections of gas turbines (e.g., blades, vanes and combustion chambers) or in low  $\text{O}_2$  atmospheric pressures at high altitudes for hypersonic aircraft. Thus these coatings have been named environmental barrier coatings (EBCs), and they are expected to work at temperatures higher than  $1300^\circ\text{C}$ .

**[0004]** Regarding gas turbines, a low permeability for oxidant species is a critical feature for an EBC system so as to inhibit the major degradation mechanism of the Si-based substrate that is formation of silicon hydroxide ( $\text{Si}(\text{OH})_4$ ) gas by the reaction of the water vapour originating from the jet fuel combustion with the  $\text{SiO}_2$  scale formed on the Si-based substrate [1, 2, 3, 4, 5].

**[0005]** The future hypersonic vehicles flying in low Earth orbit will also employ Si-based materials on its external body structure. For this type of application, a silicon monoxide (SiO) scale will tend to be formed on the surface of these Si-based materials due to the low  $\text{O}_2$  atmospheric pressures at high altitudes and the high temperatures caused by the friction with the atmosphere during ascending and re-entry. The SiO scale will tend to sublime under these conditions. Therefore, EBCs will be needed to protect the exposed structure of hypersonic aircraft [6].

**[0006]** Thermal spraying is the state-of-the-art processing method to deposit EBCs on Si-based materials. All ceramics

and cermets are not equally easy to apply by thermal spraying. Some are relatively simple: as long as the feedstock reaches a melting temperature during the spraying, and is accelerated to a speed within a given range, it can be deposited reasonably efficiently. Some are more complex in that overheating of the feedstock above a temperature far in excess of the melting point, leads to reactions between the feedstock and ambient gases that lead to impurities in the coating. But a large and growing class of materials that are desired to be thermally sprayed are quite challenging. Specifically the alkaline earth aluminosilicate Barium Strontium Aluminosilicate (BSAS), i.e.;  $\text{Ba}_{1-x}\text{Sr}_x\text{Al}_2\text{Si}_2\text{O}_8$ ,  $0 < x < 1$ , and the aluminosilicate mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ), which are highly regarded in the field of high temperature thermal coating industries, and solidify in various phases [1, 2, 5]. The phase constitution of such a coating is telling as to the thermal history of the coating, as each phase is formed preferentially at different temperatures and pressures. Only one phase of the BSAS or mullite, is desired. Other alkaline earth aluminosilicates, like barium aluminosilicate (SAS) and strontium aluminosilicate (SAS) can also be applied as EBCs. RESs have also been studied and considered as potential candidates for EBC applications, including but not limiting:  $\text{Y}_2\text{SiO}_5$ ,  $\text{Er}_2\text{SiO}_2$ ,  $\text{Yb}_2\text{SiO}_5$ ,  $\text{Lu}_2\text{SiO}_5$  and  $\text{Yb}_2\text{Si}_2\text{O}_7$  [7].

**[0007]** Currently BSAS and mullite are state-of-the-art materials thermal sprayed to produce EBCs. Thermal spraying is a group of processes wherein a feedstock material (usually in a powder, but also in the form of a wire or rod, or sometimes a precursor solution or suspension) is injected into a plume (typically a plasma or a combustion flame) of a thermal spray torch, where the feedstock is heated and propelled as a jet of individual molten or semi-molten particles, toward a substrate surface. At impact with the substrate/previous deposition, the at least semimolten particles flatten and form thin lamellae (splats) that conform and adhere to the irregular substrate/previous deposition, and/or to one another. At impact the splats cool down very rapidly ( $10^5$ - $10^7^\circ\text{C}/\text{s}$ ) and resolidify, generally before the arrival of the next splat, resulting in a distinctive lamellar structure.

**[0008]** Due to the high quenching (cooling/solidification) rates, the atoms of the molten particles may not have enough time and/or energy (nucleation kinetics) to achieve their most desired stable crystalline form. It is very common for thermal sprayed coatings to include multiple crystalline, metastable and/or amorphous zones.

**[0009]** The desire for pure Celsian (monoclinic) phase of BSAS is well known. The metastable Hexacelsian (hexagonal) phase is stable only within the temperature range of  $\sim 1600$ - $1760^\circ\text{C}$ ., whereas, the Celsian phase is stable from room temperature up to  $\sim 1600^\circ\text{C}$ . The coefficients of thermal expansion (CTEs) of the Hexacelsian phase ( $\sim 8 \times 10^{-6}^\circ\text{C}^{-1}$ ), the Celsian phase ( $\sim 5 \times 10^{-6}^\circ\text{C}^{-1}$ ), and a typical Si-based substrate (SiC, or  $\text{Si}_3\text{N}_4$ ) used in high temperature applications, is  $\sim 4$ - $5 \times 10^{-6}^\circ\text{C}^{-1}$ , attest to the compatibility of the Celsian phase with the substrate. This coupled with the fact that the Celsian phase provides a high resistance to water vapour attack [5, 7] explains why the Celsian phase is so valuable for high temperature applications. The matching of the expansion reduces stresses during thermal cycling (heating and cooling) increasing a lifetime and performance of the coating.

**[0010]** When BSAS is deposited under regular thermal spray conditions, i.e., when the substrate temperature is below  $\sim 500^\circ\text{C}$ ., the coating is amorphous and/or crystallizes

in the metastable Hexacelsian phase due to the rapid solidification of the BSAS particles. These two phases will transform into Celsian at temperatures  $\geq 1200^\circ\text{C}$ . Thus the inclusion of amorphous and hexacelsian phases occur to the detriment of high temperature coating performance in two ways. The difference in thermal expansion of the hexacelsian phase with respect to the Celsian phase and Si-based substrate will result in stress changes during heating, so that if enough Hexacelsian phase is present, the coating will crack and spall. Secondly, operation at temperatures of  $1300\text{--}1500^\circ\text{C}$ . will cause phase transformations that lead to stresses due to dimensional changes that result from the removal of amorphous/Hexacelsian phase in favour of the Celsian phase. If sufficient inclusions are present, the coating will likely crack and spall, as ceramics have very low plasticity. Therefore it is imperative that a pure Celsian phase is formed for like high temperature applications.

**[0011]** Given the control over the temperature that is required to selectively form the Celsian phase, and the transient nature of heating with thermal spray torches, conventional wisdom in the art dictates that BSAS is deposited at a relatively low temperature so that it includes substantial (or exclusively) amorphous phase on thermal spray deposition, followed by heating (annealing) the coating for an extended period at a temperature of over  $1200^\circ\text{C}$ . to effectively transform the amorphous and Hexacelsian phase into the Celsian phase [9]. Prior art references [10], [11], [12] teach methods of producing predominantly Celsian phase coatings, each requiring annealing at  $1250^\circ\text{C}$ . for 24 h, and none claims to produce an essentially pure Celsian phase. None of these teach use of a high enthalpy plasma thermal spray torch. One drawback to the teachings of [10], [11], is that the whole substrate has to be kept at high temperatures ( $>870^\circ\text{C}$ .). It is difficult to maintain these temperatures on large and complex turbine parts during thermal spraying. In any case, this generally requires that the thermal spraying be performed in a furnace.

**[0012]** Similarly, mullite is known to form a mixture of amorphous and crystalline phases during regular thermal spray deposition, i.e., when the substrate temperature is kept below  $\sim 500^\circ\text{C}$ . Mullite crystallizes at  $\sim 1000^\circ\text{C}$ ., leading to the cracking and failure of the coating (when operating at  $T \geq 1000^\circ\text{C}$ .) due to the lack of plasticity of this material. Therefore, it is known in the art to spray mullite in an oven at  $\sim 1000^\circ\text{C}$ . ([13][14]) which does provide highly crystalline mullite coatings, that exhibit excellent performance as intermediate layers in EBCs.

**[0013]** US patent application 2011/0033630 to Naik et al. teaches deposition of BSAS on a mullite interlayer with the substrate at a temperature of less than  $150^\circ\text{C}$ . when the BSAS is first deposited. This application teaches that the temperature of the substrate during deposition may be less than  $200^\circ\text{C}$ ., i.e., ( $15\text{--}200^\circ\text{C}$ . or  $20\text{--}150^\circ\text{C}$ .), presumably with forced cooling. The power of the torch, plasma gas flow rates, plasma constituents (especially the concentration of  $\text{N}_2$ ), and the stand-off between the plume is nowhere disclosed. As a result, it is impossible to reproduce, verify or compare coatings according to this invention.

**[0014]** All air plasma spray (APS) torches are not created equal. When not specified, a typical conventional plasma spray torch would be expected to have a power of 20-60 kW, and use  $\text{Ar}/\text{H}_2$  as plasma gases at total gas flow rates in the order of  $\sim 20\text{--}80$  standard litres per minute (slpm). Other possible combination of plasma gases for these types of equip-

ment operating at these ranges of power and total gas flow are  $\text{Ar}/\text{N}_2$ ,  $\text{Ar}/\text{He}$ ,  $\text{N}_2/\text{H}_2$ ,  $\text{N}_2/\text{He}$ , and on a lesser scale, a tertiary combination of thereof. In contrast, a high enthalpy APS torch for thermal spray processing, while generally providing the same mechanism, is typically designed for  $\sim 60\text{--}150$  kW power,  $\sim 100\text{--}400$  slpm total plasma gas flow delivery, and typically uses a tertiary plasma gas combination that includes  $\text{N}_2$ .

**[0015]** There is tremendous interest in next generation high temperature coatings such as EBCs, to contain high energy reactions, for aerospace turbines, power generation and hypersonic aircraft external structure. Several groups well versed in the art have tried to solve the problem of avoiding back-side heating or furnace-based deposition, but have failed to produce phase purity, have cracked the substrate, or have failed to produce optimized coatings. For example, according to NASA researchers (reported K. N. Lee et al. New Generation of Plasma-Sprayed Mullite Coatings on Silicon Carbide, *J Am, Ceram. Soc.* 78(3) (1995) 705-710): "Precipitation of amorphous mullite can be prevented by decreasing the cooling rate. One approach to decreasing the cooling rate is to heat the substrate during the spraying. A first attempt was made to heat the substrate with a plasma torch. However, it was not possible to attain a uniform and stable substrate temperature with the plasma torch heating. A severe cracking in the substrate was observed when mullite was sprayed on a plasma-torch-heated SiC. Amorphous mullite was still observed, indicating that substrate was heated below the crystallization temperature . . . . The reason for the substrate-cracking when underheated is not understood at this point." It is noted that the substrate used was the SiC "Hexoloy SA<sup>TM</sup>" from Saint-Gobain, Niagara Falls, N.Y., USA.

**[0016]** As mullite is a lower crystallization temperature material than BSAS and other RESs, as the prior art all teaches low temperature amorphous thermal spray deposition, it follows that all of the problems with mullite will be as great or greater for BSAS. More recently, a paper to Harder et al. entitled Chemical and Mechanical Consequences of Environmental Barrier Coating Exposure to Calcium-Magnesium-Aluminosilicate *J. Am. Ceram. Soc.* 94 [S1] S178-S185 (2011), teaches: "In room-temperature plasma-sprayed systems, BSAS is deposited as an amorphous phase and crystallizes in the metastable Hexacelsian phase (hexagonal) when heated. Heating the substrate to  $1200^\circ\text{C}$ . during the plasma-spray process is sufficient to deposit BSAS in the Hexacelsian phase. This Hexacelsian phase then undergoes a phase transformation at temperatures over  $1200^\circ\text{C}$ . into the stable Celsian phase (monoclinic). This transformation is accompanied by a 0.5% volume reduction and drastically changes the elastic modulus and coefficient of thermal expansion (GTE) of the topcoat . . ." Harder et al. does not disclose the details of the plasma spraying used, but does indicate that the coatings applied were sprayed in a furnace "where the substrate was heated to  $1200^\circ\text{C}$ . in order to avoid depositing amorphous material that would cause catastrophic failure upon crystallization."

**[0017]** This crystallization issue also happens for RES materials during plasma spraying for EBC applications [7]. In this reference [7], Lee et al. state that "the details of the coating parameters are described elsewhere", which is another paper from Lee et al. [14]. In this reference [14], Lee et al. described that highly crystalline mullite was achieved

when the coatings were air plasma sprayed on SiC substrates that were kept inside a box furnace at 1050° C. during the deposition process.

**[0018]** A faster and lower cost solution for producing coatings of a stable crystalline phase are in demand for coating ceramics for high temperature application, such as EBCs, especially for alkaline earth aluminosilicates (e.g., BSAS), RESSs, and mullite. New and innovative solutions that reduce equipment requirements for producing the coatings are required.

#### SUMMARY OF THE INVENTION

**[0019]** Applicant has found, contrary to what has been established in the prior art, that by 1) employing a high enthalpy APS torch, 2) using a fairly short stand-off distance, and 3) applying the coating in at least 3 passes, as-sprayed coatings of BSAS, mullite, and the like, can be deposited without assisted heating or cooling, and without heat treatment, to produce coatings with levels of a high-temperature stable crystalline phase that are higher than that possible in accordance with the prior art.

**[0020]** In accordance with the present invention, a method of producing a high temperature coating on a ceramic substrate is provided. The method comprising: operating a high enthalpy plasma spray torch and supplying the torch with a feedstock powder comprising a high temperature ceramic with a melting point above 1600° C., forming undesirable solid phases when rapidly cooled below about 900° C.; and spraying the ceramic substrate with the torch in at least 3 passes to deposit the coating; wherein a stand off distance is maintained during the deposition such that a width of a bead produced from a single spray pass on the substrate at ~800° C. is less than 70% of a diameter of a plume of the torch at the stand off. Doing so, the coating contains less undesirable solid phase without requiring assisted heating, forced cooling or subsequent heat treatment.

**[0021]** The substrate surface temperature centred on the plume during deposition preferably exceeds 1000° C. because of the proximity of the torch, and the absence of assisted heating or forced cooling. Spraying the ceramic substrate with the torch in at least 3 passes may comprise moving a surface of the substrate to be coated in a direction perpendicular to the spray jet at a speed of 0.1-5 m/s. The stand-off distance may be chosen where the width of a single spray bead on a substrate at ~800° C. is 20-70%, more preferably 35-65%, more preferably 40-60% of the diameter of the plasma plume at the same stand-off distance, and the width of a single spray bead on a substrate at ~800° C. may be from ~0.5 cm to ~2.5 cm, and the plume diameter is from ~1 cm to ~5 cm.

**[0022]** Operating the high enthalpy torch may comprise supplying: electrical power of 60-200 kW, more preferably 80-150 kW, more preferably 110-140 kW; and plasma gas with a total flow rate of 100-500 slpm, more preferably 150-400 slpm; more preferably 250-310 slpm. The plasma gas may include N<sub>2</sub>, such as 10-90% N<sub>2</sub> and may consist of 10-80% Ar, 5-40% H<sub>2</sub>, and/or He, and 30-80% N<sub>2</sub>; or 10-25% H<sub>2</sub>, 25-45% Ar and 45-50% N<sub>2</sub>.

**[0023]** The feedstock powder may consist of 80% or more, or consist essentially of the high temperature ceramic with a melting point above 1600° C., such as a high temperature ceramic having a preferred phase preferentially formed only at a temperature above 900° C. such as at temperatures between 900-2000° C., or 900-1600° C.

**[0024]** The method may be applied to an alkaline earth aluminosilicate, or rare earth silicate, or mullite, as well as an alumina and a titania. In particular in deposition annealing of BSAS and mullite have been demonstrated.

**[0025]** Also accordingly a system for thermal spraying to produce a high temperature coating on a ceramic substrate is provided. The system comprises; a high enthalpy air plasma spray torch; a feed supply containing a feedstock powder comprising a high temperature ceramic that has a melting point above 1600° C., the feed supply operably coupled to the torch; a plasma gas supply operably coupled to the torch; an electrical power supply operably coupled to the torch; a ceramic substrate; and a support for controlling a stand-off distance between the ceramic substrate and torch, while permitting a spray jet of the torch to scan across a surface of the substrate to be coated. In such a system, the stand-off distance is chosen so that the width of a single bead on a substrate at ~800° C. is less than 70% of a diameter of a plume of the torch.

**[0026]** The support and torch are preferably operable so that a localized temperature of the substrate surface within the plasma plume spot during deposition exceeds 1000° C. because of the proximity of the torch, and because of an absence of assisted heating or forced cooling. The support permitting scanning may comprise a computer numerical controlled subsystem for spraying the ceramic substrate with the torch in at least 3 passes by moving a surface of the substrate to be coated in a direction perpendicular to the spray jet at a speed of 0.1-5 m/s. The stand-off distance is preferably where the width of a single bead on a substrate at ~800° C. is 20-70%, more preferably 35-65%, more preferably 40-60% of the diameter of the plume at the stand off, and the width of the bead at ~800° C. may be from ~0.5 cm to ~2.5 cm, and the plume diameter at the stand off may be from ~1 cm to ~5 cm.

**[0027]** The electrical supply applies a power of 60-200 kW, more preferably 80-150 kW, more preferably 110-140 kW. The plasma gas supply supplies a total plasma gas flow at 100-500 slpm, more preferably 150-400 slpm, more preferably 250-310 slpm. The plasma gas includes N<sub>2</sub>, for example, consisting of 10-90% N<sub>2</sub>. The plasma gas may consist of 10-80% Ar, 5-40% H<sub>2</sub>, and/or He, and 30-80% N<sub>2</sub>; or 10-25% H<sub>2</sub>, 25-45% Ar and 45-50% N<sub>2</sub>.

**[0028]** The feedstock powder may consist of 80% or more of, or substantially consist of an alkaline earth aluminosilicate or rare earth silicate, such as BSAS, or mullite.

**[0029]** Also accordingly, a method of producing a high temperature coating on a ceramic substrate is provided. The method comprising operating a high enthalpy air plasma spray torch and supplying the torch with a feedstock powder comprising a high temperature ceramic with a melting point above 1600° C., that forms undesirable solid phases when rapidly cooled below about 900° C., wherein a cumulative deviation from the following norms is less than 20%: |[N<sub>2</sub>]|=47.5±2.5%, |[H<sub>2</sub>]|=17.5±7.5%, |[Ar]|=35±10%, |TGF|=280±30 slpm, |P|=110±23 kW, |D|=8±2 cm, where [N<sub>2</sub>], [H<sub>2</sub>], and [Ar] are respectively the percentages of N<sub>2</sub>, H<sub>2</sub>, and Ar in the plasma plume, TGF is the total gas flow, P is the torch power, and D is the stand off distance measured in cm. The cumulative deviation may be less than 10%, more preferably less than 5% or 1%. Operating the torch may comprise spraying the ceramic substrate with at least 3 passes, by relative movement of a surface of the substrate to be coated perpendicular to the spray jet at a speed of 0.1-5



m/s. The feedstock powder may consist of 80% or more, or substantially consist of a ceramic with a melting point above 1600° C., such as a ceramic that preferentially forms a preferred phase only at a temperature above 900° C., such as at temperatures between 900-2000° C., or 900-1600° C.

**[0030]** Further features of the invention will be described or will become apparent in the course of the following detailed description.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0031]** In order that the invention may be more clearly understood, embodiments thereof will now be described in detail by way of example, with reference to the accompanying drawings, in which:

**[0032]** FIGS. 1a,b are schematic illustrations of a high enthalpy air plasma spray apparatus showing a typical suitable stand-off distance for thermal spraying in accordance with the prior art, and an embodiment of the invention, respectively;

**[0033]** FIG. 2 is a graph of X-ray diffraction (XRD) spectra of high enthalpy, and conventionally sprayed mullite coatings deposited on a ceramic substrate;

**[0034]** FIG. 3 schematically illustrates differential thermal analysis (DTA) of the mullite coatings of FIG. 2;

**[0035]** FIG. 4 is a scanning electron micrograph (SEM) image of BSAS powder particles for use as a feedstock in plasma spraying;

**[0036]** FIG. 5 is a scanning electron micrograph (SEM) image of a cross-section of a barrier system, including a silicon (Si) bond coat, a mullite interlayer and a BSAS top coat sprayed in accordance with an embodiment of the present invention;

**[0037]** FIG. 6 is a panel showing cross-sectional SEM image of the barrier system after high temperature exposure in water vapour environment, a high magnification image of the bond coat/substrate interface, and an unprotected substrate subjected to the same;

**[0038]** FIG. 7 plots X-ray diffraction spectra of BSAS powder, the as sprayed coating, and the coating after exposure to the heat treatment

**[0039]** FIG. 8 is an SEM top view image of a BSAS spray bead showing the importance of multiple passes of the spray torch;

**[0040]** FIG. 9 is an XRD spectrum of the bead shown in FIG. 8, confirming presence of an amorphous phase in the BSAS coating when only applied in a single pass; and

**[0041]** FIG. 10 is an image of the temperature profile of a SiC-based CMC substrate surface immediately after being heated by the air plasma spray torch for 5 seconds.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

**[0042]** The present invention was discovered with experiments using a high enthalpy APS torch. Given the problems reported in the prior art with cracking of substrates, it is surprising that using a much higher enthalpy torch, and a much shorter stand off distance, no substrate cracking is observed, and given the absence of any reproducible report of thermal sprayed coatings deposited without assisted heating, the very high purity observed was remarkable.

**[0043]** FIGS. 1a,b schematically illustrate a high enthalpy air plasma spray apparatus respectively showing a stand-off distance typically used for thermal spraying in accordance

with the prior art, and an embodiment of the invention. FIG. 1a, because of the larger stand off, illustrates less of the apparatus, however similar supply equipment is required for a high enthalpy torch 10, in either case, with the proviso that prior art systems typically do not spray the same ceramics that are an integral part of the spray system in FIG. 1b. As shown in FIG. 1b, the apparatus includes a hopper 13 connected to the torch by a feed supply 12. The hopper 13 contains a high temperature ceramic powder 14, composed of a ceramic that melts above ~1600° C., that is delivered to the torch 10 by the feed supply 12 in a manner known in the art. The ceramic used in accordance with the present invention tends to form amorphous, metastable, or otherwise undesirable phases if rapidly cooled below a temperature of about 900° C., and the invention mitigates the formation of the undesirable phases. For example, the ceramic may be an alkaline earth aluminosilicate (e.g., BSAS), RES, mullite, or an alumina or titania (doped or pure). A plasma gas supply 15 (partially shown) is coupled to the torch 10 to supply plasma gas. Preferably the plasma gas comprises a mix of plasma gasses that together provide 1) sufficient thermal conductivity to the ceramic particles, 2) sufficient enthalpy to heat the ceramic particles to a desired temperature, for example, above 2000° C., and 3) a low enough threshold for ionization to readily initiate plasma formation and low enough enthalpy to avoid melting the electrodes of the torch 10. Conveniently 1)-3) may be ensured by providing: sufficient concentrations of H<sub>2</sub> (e.g., 5-40%, more preferably 10-25%), N<sub>2</sub> (e.g., 30-80%, more preferably 45-50%), and Ar plasma gas (e.g., 10-80%, more preferably 25-45%), respectively, although other plasma gasses (e.g., He) could be added or substituted to some degree. The torch 10 includes an electrical power supply 19 (in partial view) for ionizing the gas to form the plasma, which defines a plume 16, which is typically relatively stable in shape and size during constant supply conditions. The particles of the ceramic powder 14, entrained in the plume 16, melt, at least at their surface, and are accelerated by the plume 16, to be ejected as a spray jet 17. The parameters of the spray jet 17 (velocity distribution, diameter, temperature distribution, size distribution, etc.) are not as uniform as the envelope of the plume 16, which can typically be maintained in a steady state, and keep a constant shape.

**[0044]** The spray jet 17 is rapidly cooling, and gradually decelerating in flight, until it strikes a coating surface of a substrate 18. Substrate 18 is formed of a ceramic, such as a Si-based ceramic matrix composite (including SiC, and Si<sub>3</sub>N<sub>4</sub>). In accordance with the present invention, the substrate 18 is positioned a relatively short stand off distance D from the torch 10. This obviates the need for assisted heating. The stand off distance D is chosen so that the diameter of the plume 16 at D is appreciably larger than the main core of spray jet 17, which forms the individual spray beads. The substrate 18 is typically supported by a sample holder 18 in a manner that permits the spray jet 17 to scan across the coating surface, either by motion of the torch 10 or of the sample holder 18 (i.e., the motion normal to the direction of spraying, such as shown by arrow 11).

**[0045]** For a stand off distance D shorter than the plume length 16, the shorter the stand off, the less dwell time the particles have within the plume 16, and accordingly the less energy is absorbed and the slower and colder spray jet 17 particles are, but the heat transfer from the plasma plume to the substrate is maximized. Conversely, the greater the stand off (until a distance beyond the plume's length), the greater

the temperature and speed imparted to the spray jet **17** (up to a critical point), and also a wider and less focused spray jet **17** is at contact with the surface. The greater the stand off, the lower the heat transfer from the plasma plume to the substrate. The less focused the spray jet **17**, results in a greater variability of the deposition conditions (particle angle, local surface temperature, particle temperature and velocity, etc.), leading to a less definite and compact deposition trace (continuous sequence of deposition produced by the scanning) known as a bead. Applicant postulates that if the stand-off distance *D* is chosen so that a width of a single bead on a substrate at  $\sim 800^\circ\text{C}$ . is less than 70% of a diameter of the plume **16** of the torch **10** at the same stand off distance, and the coating is produced with at least three passes of the spray jet **17**, substantially less of the undesired phase is produced, as sufficient substrate heating and dwell time of the particles are provided.

**[0046]** The bead width is a sensitive parameter, and may vary widely with changes in the spray jet conditions and deposition conditions. The stand off where the bead has a certain width may reliably be determined by providing stable feed conditions, and spraying the substrate while holding a temperature of the substrate constant, such as at  $800^\circ\text{C}$ . This not to be understood as a requirement for the substrate to be at  $800^\circ\text{C}$ . during coating deposition, but merely as one possible manner of reliably determining a bead width as a function of stand off. Coating deposition in accordance with the present invention is provided without assisted heating or cooling, and without post spray heat treatment or annealing.

**[0047]** In sum, it is believed that by providing a thin bead in a wide plume, the heat required for gradual enough cooling to provide favourable nucleation kinetics (e.g., sufficient duration at or above  $1000^\circ\text{C}$ .) is provided, to avoid deposition of undesirable phases. In all aspects of the invention, however, Applicant does not wish to be limited by the foregoing theory.

**[0048]** Alternatively viewed, the invention comprises operating the high enthalpy air plasma spray torch **10** with the ceramic powder **14** to produce a coating on substrate **18** using a set of deposition conditions that substantially conform with the following norms:  $|\text{[N}_2\text{]}|=47.5\pm 2.5\%$ ,  $|\text{[H}_2\text{]}|=17.5\pm 7.5\%$ ,  $|\text{[Ar]}|=35\pm 10\%$ ,  $|\text{TGF}|=280\pm 30$  slpm,  $|\text{P}|=110\pm 23$  kW,  $|\text{D}|=8\pm 2$  cm where  $[\text{N}_2]$ ,  $[\text{H}_2]$ , and  $[\text{Ar}]$  are respectively the percentages of  $\text{N}_2$ ,  $\text{H}_2$ , and Ar in the plasma plume, TGF is the total gas flow, P is the torch power, and D is the stand off distance measured in cm. Strict adherence to these limits are not believed to be required, as taking a slightly higher  $\text{N}_2$  or  $\text{H}_2$  fraction or lower Ar fraction may be mitigated by higher coolant rates, and/or slightly lower total gas flow rates, for example. Accordingly, a cumulative deviation from these norms of less than 20%, more preferably of less than 10%, and more preferably of less than 5%, or 1% are likely to be operable and provide the advantages of the present invention, subject to the limits on safe use of the high enthalpy air plasma spray torch, and an acceptable deposition efficiency.

**[0049]** Although not necessarily mandatory, pre-heating of the surface of the substrate using the torch can be employed. The typical pre-heating temperatures are above  $\sim 500^\circ\text{C}$ ., more preferably  $\sim 800\text{-}1000^\circ\text{C}$ .

#### EXAMPLE 1

##### Mullite

**[0050]** The same mullite powder (SG #1020,  $d_{10}=15$   $\mu\text{m}$ / $d_{50}=30$   $\mu\text{m}$ / $d_{90}=50$   $\mu\text{m}$ , Saint-Gobain, Worchester, Mass., USA) was sprayed using a conventional 40 kW APS torch

(F4-MB, Sulzer Metco, Westbury, N.Y., USA), and a high-enthalpy 120 kW APS torch (Axial III, Northwest Mettech, North Vancouver, BC, Canada). In the case of conventional spraying, a cooling system consisted of air jets was used to cool the front size of the substrate to limit the maximum coating surface temperature reached during deposition to  $\sim 100^\circ\text{C}$ . High-enthalpy spraying was performed without assisted heating or cooling, and the maximum coating surface temperature during deposition reached values of  $\sim 1000^\circ\text{C}$ .

**[0051]** A carrier gas (Ar at 9 slpm) was used to feed the mullite powder in a conventional manner, delivering the powder at a rate of approximately 4 g/min. Specifically, the high enthalpy torch spray parameters were as follows: torch plume gasses were:  $\text{N}_2$  45%, Ar 45%, and  $\text{H}_2$  10%, total gas flow 280 slpm, power  $\sim 120$  kW, and a stand off distance was 6 cm. The diameter of the torch nozzle was 0.5" (1.27 cm). The plume had a length greater than 6 cm. The substrate was SiC Hexaloy SA™ (Saint-Gobain, Niagara Falls, N.Y., USA). Pre-heating of the substrate with the torch was not employed in this specific case.

**[0052]** Both coatings were analyzed via XRD, and the results are shown in FIG. 2. The XRD technique was employed as an attempt to compare the degree of crystallinity of the coatings. The ratio of peak areas between  $20^\circ$  and  $40^\circ$  to the total integrated area in this region was measured and defined as a crystallinity index (CI). The CI value is proportional to the degree of crystallinity of the coating, at least on its surface. The high-enthalpy spraying produced highly crystalline mullite coatings (B: crystallinity index  $\text{CI}\geq 0.95$ ). These highly crystalline coatings also did not exhibit signs of debonding or delamination when deposited on SiC-based substrates. In comparison, the CI of the conventional sprayed mullite was about 0.25, and the XRD spectrum shows the typical amorphous hump across the  $20\text{-}40^\circ$  range (A).

**[0053]** Because X-rays used in regular XRD analysis penetrate the sample to a depth of few microns below its surface, and as the coating temperature was raised during deposition from room temperature, it might be hypothesized that some amorphous residual mullite phase may have been formed in the initial few layers (passes) of coating deposition. This residual amorphous mullite, if formed, is unlikely to be detected via regular XRD probing. In order to investigate whether amorphous mullite was present in the microstructure of the as-sprayed coatings, they were heat-treated at temperatures above the known crystallization point of mullite (i.e.,  $\sim 1000^\circ\text{C}$ .) and examined using differential thermal analysis (DTA). The temperature was raised at a rate of  $10^\circ\text{C}/\text{min}$  up to  $1200^\circ\text{C}$ . in an  $\text{N}_2$  atmosphere. The results of DTA are shown in FIG. 3. A shows a strong peak of the conventional APS sprayed coating, whereas B shows no peak at  $989^\circ$  for the high enthalpy APS sprayed coating.

**[0054]** In order to perform a valid comparison, the mass of each coating evaluated via DTA was similar ( $\pm 30$  mg). The DTA exhibited an exothermic phase transformation peak at  $989^\circ\text{C}$ . for the low crystallinity coating ( $\text{CI}=0.25$ ), very similar to that observed by Lee et al. [12] for a highly amorphous mullite thermal spray coating, which corresponds to the crystallization temperature of the mullite. The coating deposited with the high-enthalpy APS torch, did not exhibit any peaks at this region, confirming the mullite coating contained no amorphous phase through its overall microstructure.

## EXAMPLE 2

## BSAS

[0055] FIG. 4 is a SEM image of a spray-dried BSAS powder (Amperit 870.084,  $d_{10}=20 \mu\text{m}/d_{50}=53 \mu\text{m}/d_{90}=86 \mu\text{m}$ , H. C. Starck, Newton, Mass., USA) employed in this invention.

[0056] This powder was fed to a high enthalpy APS torch. The coating was applied overtop of an interlayer of mullite (deposited as described above). The powder feed was assisted by a carrier gas (Ar at 9 slpm) at a powder feed rate of ~4 g/min.

[0057] Table 1 lists spray parameters used to produce BSAS coatings and mullite coatings with the Axial III APS torch (torch nozzle diameter 0.5" (1.27 cm)). The first three rows are better suited to BSAS deposition, and the last two sets are better suited to mullite deposition. Specifically, the density of BSAS coating produced with the deposition conditions according to bottom two rows were found to be too dense, precluding the easy formation of vertical cracks, and the deposition conditions according to the first 3 rows produce mullite with lower density than is desired. Many other thermal spray conditions could be varied that would have an expected effect on the thermal spray conditions resulting in similar coatings, as is well known in the art, and thus features such as feedstock characteristics (e.g. morphology and porosity), feedstock particle size distribution, and feedstock powder feed rate, inter alia can have some impact on the optimal settings.

TABLE 1

N2 %	Ar %	H2 %	Total gas flow (slpm)	Power (kW)	Stand off distance (cm)
45	45	10	280	87	6
45	45	10	280	113	6
45	45	10	280	118	6
50	25	25	280	127	10
50	25	25	280	133	10

[0058] The BSAS powder was sprayed using a high-enthalpy APS torch (Axial III, Northwest Mettech, North Vancouver, BC, Canada). The coating deposition occurs via a scan pattern of the APS torch on the substrate surface, which sprays successive layers. The temperature of the surface of the coating was monitored with a pyrometer, which is placed behind the APS torch. It is important to point out that the pyrometer measures the temperature aimed over a specific point (target) on the coating surface, i.e., the overall surface coating temperature and the substrate temperature are not measured.

[0059] The maximum measured coating surface temperature at the target of the pyrometer was at least ~1000° C. when the high-enthalpy torch was operated at ~113-118 kW, and at least 800° C. when operated at ~87 kW both at a stand off distance of 6 cm. The coating surface temperature is challenging to measure, due to the fact that this event occurs when the high energetic plasma plume and spray jet is over the specific pyrometer target. Thus there is a spatial and/or temporal lag between when the surface is maximally heated and when the temperature is measured. Therefore, the real maximum coating (or substrate) surface temperature is higher than measured via a pyrometer or infra-red camera.

[0060] FIG. 5 is a SEM image showing an as-sprayed barrier system on the SiC substrate, the barrier system having the Si bond coat, the mullite interlayer and a BSAS top coat deposited on a SiC Hexoloy SA™ substrate. The microstructure in FIG. 5 shows that the Si bond coat appears as a dense and crack-free layer showing good adhesion to the substrate (i.e., no gaps or spallation). Likewise good adhesion is shown between the interfaces of the Si bond coat, the mullite interlayer and the near-crack free BSAS top coat. This appears to be the first report of an as-sprayed crystalline BSAS coating (Celsian phase) produced without assisted heating or post spray annealing, and the first report of an as-sprayed crystalline mullite coating produced without assisted heating or cooling or post spray annealing.

[0061] As the standard attempt to simulate the lean environment of a gas turbine [2], the barrier system was subjected to a thermal treatment at 1300° C. (1 atm) in a continuous flow (~3.5 cm/s) of water vapour (90% H<sub>2</sub>O, 10% air) inside a tube furnace for up to 500 h. FIG. 6 includes an image of the same barrier system, showing the effects of heat treatment at 1300° C. for 500 h in a water vapour environment (left). An enlargement of the SiC substrate/bond coat interface (bottom right) shows no appreciable difference before and after the heat treatment. An image of an unprotected SiC Hexoloy SA™ substrate after the same type of heat treatment is shown at the top right. After 1300° C./500 h in water vapour, a SiO<sub>2</sub> scale loosely adhered to the substrate was formed over the SiC surface. Severe through-cracks were formed throughout this silica layer. Therefore, the mullite and BSAS coatings deposited in accordance with an embodiment of the present invention effectively protected the Si-based ceramics substrate against oxidation and water vapour attack.

[0062] The BSAS coating composition was analyzed in several manners. FIG. 7 shows X-ray diffraction (XRD) spectra of BSAS powder (Amperit 870.084, H. C. Starck, Newton, Mass., USA), the as-sprayed coating, and the coating after exposure to a high temperature, aggressive heat treatment. Both which substantially consist of the Celsian monoclinic phase (Ba<sub>0.75</sub>Sr<sub>0.25</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), as identified based on the JCPDF #38-1451. The as-sprayed coating basically exhibits the same crystalline structure, i.e., the diffraction peaks overlap those of the powder. No evident amorphous hump is observed. Therefore, this as sprayed coating appears to be highly crystalline, exhibiting predominantly the celsian phase. After heat treatment at 1300° C. for 500 h, substantially the same XRD pattern is produced.

[0063] Harder and Faber [8] studied the amorphous/Hexacelsian-to-Celsian phase transformation kinetics of BSAS. They subjected samples to heat treatments between 1100 and 1400° C. from 30 min to 40 h. At 1100° C., there was no discernable transformation up to 40 h of heat treatment. Phase transformation to Celsian began to be observed at temperatures of 1200° C. This explains why the prior art typically requires annealing at temperatures above 1250° C.

[0064] The exclusivity of the Celsian phase in the as-sprayed coating can be explained by positing that the real maximum coating surface temperature at the plasma jet spot was higher than 1200° C. By using a spray jet diameter that is smaller than the plume diameter at the surface, the region under the spot is subjected to an intense heat provided by the plume, providing for annealing in real time of the coating during its deposition.

[0065] FIG. 8 is a scanning electron micrograph showing in plan view, a single bead of BSAS sprayed at ~120 kW (SiC

Hexoloy SA™ substrate surface pre-heated with the torch at ~800° C.). Arrows point to inclusions that were partially molten in deposition. About half of the surface of the bead is covered by such semi-molten regions. This considerable amount of semi-molten particles will likely influence the energy necessary to nucleate Celsian from amorphous and metastable Hexacelsian (Harder and Faber [8]) during the concurrent annealing and deposition performed by the high enthalpy APS torch.

**[0066]** FIG. 9 is a XRD spectrum of the single BSAS bead of FIG. 8 and the XRD spectrum of a BSAS coating (~180 μm thick/SiC substrate surface pre-heated with the torch at ~700° C.) sprayed at ~85 kW (maximum coating temperature ~800° C.), using the same APS torch, plasma gas composition and spray distance (6 cm). The XRD spectrum shows that in spite of being deposited at similar surface temperature conditions, the bead exhibits a significant amount of amorphous phase, characterized by the amorphous hump between the angles of 20° and 40°. On the contrary, the coating exhibits a highly crystalline Celsian phase. Based on this information, it is advisable to deposit the BSAS in at least 3 and preferably in at least 5 passes to perform annealing in real time. The conditions employed in high-enthalpy APS torches, such as, higher torch power and total gas flow than those of conventional ones, help to explain the fact that other inventions had to employ holding time and/or post-spray annealing to produce BSAS coatings exhibiting at least 50 vol % of celsian phase. The higher power levels and total gas flows, in addition to the high enthalpy N<sub>2</sub> gas, provided by the high enthalpy APS torch create the conditions for annealing the sample in real time during spraying, thereby inducing the formation of the celsian phase in as-sprayed coatings, without the necessity of a holding time and/or post-spray annealing. This annealing in real time is carried out throughout the successive deposit of spray beads, layers and torch passes over the substrate surface, because one single pass forming a single bead does not promote the formation of a highly crystalline celsian phase.

**[0067]** Harder and Faber [8] studied the transformation kinetics of BSAS coatings produced via APS from a fully crystalline celsian powder. As-sprayed coatings exhibited a mixture of amorphous, metastable Hexacelsian and Celsian BSAS phases. The presence of the Celsian phase was attributed to the presence of semi-molten particles embedded in the coating microstructure, which was estimated to be ~10 wt %. By employing electron backscattered diffraction (EBSD) it was observed that the transformations from amorphous/metastable Hexacelsian phase to the Celsian phase at high temperatures were strongly influenced by the Celsian phase. The semi-molten BSAS celsian particles embedded in the as-sprayed coating acted as seeds for the nucleation of the Celsian phase transformation from the amorphous and metastable hexacelsian, upon annealing. Harder and Faber concluded that the energy necessary to transform APS BSAS coatings will be heavily influenced by the semi-molten particles [8], i.e., the higher the amount of semi-molten BSAS Celsian particles embedded in the coating microstructure, the lower the amount of energy required to nucleate the amorphous/Hexacelsian BSAS into stable crystalline Celsian.

**[0068]** Based on the equations determined by Harder and Faber [8], it is possible to calculate that it is necessary to reach a temperature of 1850° C. for ~8 seconds to induce the phase transformation of 50% of Celsian phase from metastable Hexacelsian. Over a 4 cm×4 cm substrate area, the ~2.5 cm diameter plasma plume spot stays ~8 seconds over the surface

of the coating during one complete set of torch passes (single beads) to produce a single layer.

**[0069]** In order to obtain an approximate effect of the substrate surface heating by the spray torch, the following experiment was carried out. The high enthalpy APS torch was set up at the same conditions to deposit a BSAS coating and placed standing still in front of a SiC-based CMC substrate for 5 seconds, but no BSAS powder was fed. After this interval, the torch was set aside in a rapid thrust to open a line of sight for the infra-red (IR) camera to immediately measure the substrate surface temperature. The temperature profile can be seen in FIG. 10.

**[0070]** The IR camera used can measure temperatures from 200° C. to 1600° C. When the torch is shifted off the substrate surface, and the IR camera comes in line of sight with the substrate surface, the measured temperature increases abruptly to values higher than 1600° C. (i.e., the limit of the equipment). The temperature is not registered for ~1.5 s, until it cools down to 1600° C. and below. Therefore, during a continuous deposition when multiple torch scans are employed to build the coating on the substrate surface, using the conditions described in this invention, the coating surface temperature levels under the plasma plume spot likely reach values higher than 1600° C. When the BSAS coating surface is exposed to these temperature levels for some seconds, the thermodynamic conditions required to induce the amorphous/Hexacelsian phase transformation to stable crystalline Celsian seem to occur.

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- [0085] Other advantages that are inherent to the structure are obvious to one skilled in the art. The embodiments are described herein illustratively and are not meant to limit the scope of the invention as claimed. Variations of the foregoing embodiments will be evident to a person of ordinary skill and are intended by the inventor to be encompassed by the following claims.
1. A method of producing a high temperature coating on a ceramic substrate, the method comprising:
    - operating a high enthalpy plasma spray torch and supplying the torch with a feedstock powder comprising a high temperature ceramic with a melting point above 1600° C., forming undesirable solid phases when rapidly cooled below about 900° C.;
    - spraying the ceramic substrate with the torch in at least 3 passes to deposit the coating;
    - wherein a stand-off distance is maintained during the deposition such that a width of a bead produced from a single spray pass on the substrate at ~800° C. is less than 70% of a diameter of a plume of the torch at the stand-off,
    - whereby the coating contains less undesirable solid phase without requiring assisted heating, forced cooling or subsequent heat treatment.
  2. The method according to claim 1 wherein the substrate surface temperature centred on the plume during deposition exceeds 1000° C. because of the proximity of the torch, and the absence of assisted heating and forced cooling.
  3. The method according to claim 1 wherein the substrate surface temperature is raised prior to deposition by scanning with the torch over the substrate, immediately prior to deposition, to raise the surface temperature above ~500° C., more preferably from ~800-1000° C.
  4. The method according to claim 1 wherein spraying the ceramic substrate with the torch in at least 3 passes; comprises moving a surface of the substrate to be coated in a direction perpendicular to the spray jet at a speed of 0.1-5 m/s; or exposes each region of the substrate to the plume for about 8 s per coating.
  5. (canceled)
  6. The method according to claim 1 wherein the stand-off distance is:
    - chosen where the width of a single spray bead on a substrate at ~800° C. is 20-70% of the diameter of the plasma plume at the same stand-off distance;
    - chosen where the width of a single spray bead on a substrate at ~800° C. is 35-65% of the diameter of the plasma plume at the same stand-off distance;
    - chosen where the width of a single spray bead on a substrate at ~800° C. is 40-60% of the diameter of the plasma plume at the same stand-off distance;
    - chosen where the width of a single spray bead on a substrate at ~800° C. is from ~0.5 cm to ~2.5 cm, and the plume diameter is from ~1 cm to ~5 cm, the former being at most 70% of the latter; or
    - chosen where the width of a single spray bead on a substrate at 800° C. is from ~0.5 cm to ~2.5 cm, and the plume diameter is from ~1 cm to ~5 cm, the former being at most 40-60% of the latter.
  7. The method according to claim 1 wherein operating the high enthalpy torch comprises:
    - supplying a power of 60-200 kW;
    - supplying a power of 80-150 kW;
    - supplying a power of 10-140 kW;
    - supplying a total plasma gas flow at 100-500 slpm;
    - supplying a total plasma gas flow at 150-400 slpm;
    - supplying a total plasma gas flow at 250-310 slpm;
    - supplying plasma gas including N<sub>2</sub>;
    - supplying plasma gas including 10-90% N<sub>2</sub>;
    - supplying plasma gas consisting of 10-80% Ar, 5-40% H<sub>2</sub>, and/or He, and 30-80% N<sub>2</sub>; or
    - supplying plasma gas consisting of 0-25% H<sub>2</sub>, 25-45% Ar and 45-50% N<sub>2</sub>.
  8. The method according to claim 1 wherein the feedstock powder:
    - consists of 80% or more of the high temperature ceramic with a melting point above 1600° C.;
    - consists essentially of the high temperature ceramic with a melting point above 1600° C.;
    - consists of 80% or more of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at a temperature above 900° C.;
    - consists essentially of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at a temperature above 900° C.;
    - consists of 80% or more of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between 900-2000° C.;
    - consists essentially of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between 900-2000° C.;
    - consists of 80% or more of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between 900-1600° C.; or

consists essentially of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between 900-1600° C.

9. A method of producing a coating of an alkaline earth aluminosilicate or rare earth silicate (RES) on a ceramic substrate, the method comprising:

providing a feedstock of an alkaline earth aluminosilicate or RES powder and the ceramic substrate;

plasma spraying the feedstock onto the ceramic substrate with a high enthalpy plasma spray torch to deposit the coating in at least 3 passes;

wherein a stand-off distance is maintained during the deposition such that the width of a bead produced from single spray pass on the substrate at ~800° C. is less than 70% of a diameter of a plume of the torch at the stand-off, whereby the coating consists essentially of a desirable stable crystalline phase without assisted heating, forced cooling, or subsequent heat treatment.

10. The method according to claim 9 wherein the substrate surface temperature centred on the plume during deposition exceeds 1000° C. because of the proximity of the torch, and because of the absence of assisted heating and forced cooling.

11. The method according to claim 9 wherein the substrate surface temperature is raised prior to deposition by scanning with the torch over the substrate, immediately prior to deposition, to raise the surface temperature above ~500° C., more preferably from ~800-1000° C.

12. The method according to claim 9 wherein depositing the coating in at least 3 passes comprises moving a surface of the substrate to be coated in a direction perpendicular to the spray jet at a speed of 0.1-5 m/s.

13. The method according to claim 9 wherein the stand-off distance is:

chosen where the width of a single spray bead on a substrate at ~800° C. is 20-70% of the diameter of the plume at the stand-off distance,

chosen where the width of a single spray bead on a substrate at ~800° C. is 35-65% of the diameter of the plume of the plume at the stand-off distance, chosen where the width of a single spray bead on a substrate at ~800° C. is 40-60% of the diameter of the plume at the stand-off distance,

chosen where the width of a single spray bead on a substrate at ~800° C. is from ~0.5 cm to ~2.5 cm, and the plume diameter at the stand-off distance is from ~1 cm to ~5 cm, the former being at most 70% of the latter, or

chosen where the width of a single spray bead on a substrate at ~800° C. is from ~0.5 cm to ~2.5 cm, and the plume diameter at the stand-off distance is from ~1 cm to ~5 cm, the former being 40-60% of the latter.

14. The method according to claim 9 wherein plasma spraying comprises:

supplying a power of 60-200 kW;

supplying a power of 80-150 kW;

supplying a power of 110-140 kW;

supplying a total plasma gas flow at 100-500 slpm;

supplying a total plasma gas flow at 150-400 slpm;

supplying a total plasma gas flow at 250-310 slpm;

supplying plasma gas including N<sub>2</sub>;

supplying plasma gas including 10-90% N<sub>2</sub>;

supplying plasma gas consisting of 10-80% Ar, 5-40% H<sub>2</sub>, and/or He, and 30-80% H<sub>2</sub>; or

supplying plasma gas consisting of 10-25% H<sub>2</sub>, 25-45% Ar and 45-50% N<sub>2</sub>.

15. The method according to claim 9 wherein the alkaline earth aluminosilicate or RES powders:

consists of 80% or more of the alkaline earth aluminosilicate or RES and has a melting point above 1600° C.;

consists essentially of the alkaline earth aluminosilicate or RES and has a melting point above 1600° C.;

consists of 80% or more of the RES and has a melting point above 1600° C., the alkaline earth aluminosilicate or RES having a preferred phase preferentially formed only at a temperature above 1000° C.;

consists essentially of the alkaline earth aluminosilicate or RES and has a melting point above 1600° C., the alkaline earth aluminosilicate or RES having a preferred phase preferentially formed only at a temperature above 1000° C.;

consists of 80% or more of the alkaline earth aluminosilicate or RES and has a melting point above 1600° C., the RES having a preferred phase preferentially formed only at temperatures between 1000-2000° C.;

consists essentially of the alkaline earth aluminosilicate or RES and has a melting point above 1600° C., the alkaline earth aluminosilicate or RES having a preferred phase preferentially formed only at temperatures between 1000-2000° C.; consists of 80% or more of the alkaline earth aluminosilicate or RES and has a melting point above 1600° C., the alkaline earth aluminosilicate or RES having a preferred phase preferentially formed only at temperatures between 1200-1600° C.;

consists of the alkaline earth aluminosilicate or RES and has a melting point above 1600° C., the alkaline earth aluminosilicate or RES having a preferred phase preferentially formed only at temperatures between 1200-1600° C.;

consists of 80% or more of BSAS; or

consists essentially of BSAS.

16. A method of producing a mullite coating on a ceramic substrate, the method comprising:

providing a feedstock of mullite powder and the ceramic substrate; and plasma spraying the feedstock onto the ceramic substrate with a high enthalpy plasma spray torch to deposit the coating in at least 3 passes;

wherein a stand-off distance is maintained during the deposition such that a width of a bead produced from a single spray pass on the substrate at ~800° C. is less than 70% of a diameter of a plume of the torch at the stand-off,

whereby the desirable stable crystalline phase of the coating is maintained without requiring assisted heating, forced cooling or subsequent heat treatment.

17. The method according to claim 16 wherein the localized temperature of the substrate surface within the plasma plume spot during deposition exceeds 1000° C. because of the proximity of the torch in the absence of assisted heating and forced cooling.

18. The method according to claim 16 wherein the substrate surface temperature is raised prior to deposition by scanning with the torch over the substrate, immediately prior to deposition, to raise the surface temperature above ~500° C., more preferably from ~800-1000° C.

19. The method according to claim 16 wherein depositing the coating in at least 3 passes comprises moving a surface of the substrate to be coated in a direction perpendicular to the spray jet at a speed of 0.1-5 m/s.

**20.** The method according to claim **16** wherein the stand-off distance is:

chosen where the width of a single spray bead on a substrate at  $\sim 800^{\circ}\text{C}$ . is 20-70% of the diameter of the plume at the stand-off distance,

chosen where the width of a single spray bead on a substrate at  $\sim 800^{\circ}\text{C}$ . is 35-65% of the diameter of the plume at the stand-off distance,

chosen where the width of a spray bead on a substrate at  $\sim 800^{\circ}\text{C}$ . is 40-60% of the diameter of the plume at the stand-off distance,

chosen where the width of a spray bead on a substrate at  $\sim 800^{\circ}\text{C}$ . is from  $\sim 0.5\text{ cm}$  to  $\sim 2.5\text{ cm}$ , and the plume diameter at the stand-off is from  $\sim 1\text{ cm}$  to  $\sim 5\text{ cm}$ , the former being at most 70% of the latter, or

chosen where the width of a spray bead on a substrate at  $\sim 800^{\circ}\text{C}$ . is from  $\sim 0.5\text{ cm}$  to  $\sim 2.5\text{ cm}$ , and the plume diameter at the stand-off is from  $\sim 1\text{ cm}$  to  $\sim 5\text{ cm}$ , the former being 40-60% of the latter.

**21.** The method according to claim **16** wherein plasma spraying comprises:

supplying a power of 60-200 kW;

supplying a power of 80-150 kW;

supplying a power of 110-140 kW;

supplying a total plasma gas flow at 100-500 slpm;

supplying a total plasma gas flow at 150-400 slpm;

supplying a total plasma gas flow at 250-310 slpm;

supplying plasma gas including  $\text{N}_2$ ;

supplying plasma gas including 10-90%  $\text{Ar}$ ;

supplying plasma gas consisting of 10-80%  $\text{Ar}$ , 5-40%  $\text{H}_2$ , and/or  $\text{He}$ , and 30-80%  $\text{N}_2$ ; or

supplying plasma gas consisting of 10-25%  $\text{H}_2$ , 25-45%  $\text{Ar}$  and 45-50%  $\text{N}_2$ .

**22.** The method according to claim **16** wherein the mullite powder:

consists of 80% or more of the mullite; or

consists essentially of the mullite.

**23.** A system for thermal spraying to produce a high temperature coating on a ceramic substrate, the system comprising:

a high enthalpy air plasma spray torch;

a feed supply containing a feedstock powder comprising a high temperature ceramic that has a melting point above  $1600^{\circ}\text{C}$ ., the feed supply operably coupled to the torch;

a plasma gas supply operably coupled to the torch;

an electrical power supply operably coupled to the torch;

a ceramic substrate; and

a support for controlling a stand-off distance between the ceramic substrate and torch, while permitting a spray jet of the torch to scan across a surface of the substrate to be coated,

wherein the stand-off distance is chosen so that the width of a single bead on a substrate at  $\sim 800^{\circ}\text{C}$ . is less than 70% of a diameter of a plume of the torch.

**24.** The system according to claim **23** wherein the localized temperature of the substrate surface within the plasma plume spot during deposition exceeds  $1000^{\circ}\text{C}$ . because of the proximity of the torch, and because of an absence of assisted heating or forced cooling.

**25.** The system according to claim **23** wherein the support permitting scanning comprises a computer numerical controlled subsystem for spraying the ceramic substrate with the

torch in at least 3 passes by moving a surface of the substrate to be coated in a direction perpendicular to the spray jet at a speed of 0.1-5 m/s.

**26.** The system according to claim **23** wherein the stand-off distance is:

where the width of a single bead on a substrate at  $\sim 800^{\circ}\text{C}$  is 20-70% of the diameter of the plume at the stand-off,

where the width of a single bead on a substrate at  $\sim 800^{\circ}\text{C}$ . is 35-65% of the diameter of the plume at the stand-off,

where the width of a single bead on a substrate at  $\sim 800^{\circ}\text{C}$ . is 40-60% of the diameter of the plume at the stand-off,

where the width of a single bead on a substrate at  $\sim 800^{\circ}\text{C}$ . is from  $\sim 0.5\text{ cm}$  to  $\sim 2.5\text{ cm}$ , and the plume diameter is from  $\sim 1\text{ cm}$  to  $\sim 5\text{ cm}$  at the stand-off, or where the width of a single bead on a substrate at  $\sim 800^{\circ}\text{C}$  is from  $\sim 0.5\text{ cm}$  to  $\sim 2.5\text{ cm}$ , and the plume diameter is from  $\sim 1\text{ cm}$  to  $\sim 5\text{ cm}$  at the stand-off, the former being 40-60% of the latter.

where the width of a single bead on a substrate at  $\sim 800^{\circ}\text{C}$ . is from  $\sim 0.5\text{ cm}$  to  $\sim 2.5\text{ cm}$ , and the plume diameter is from  $\sim 1\text{ cm}$  to  $\sim 5\text{ cm}$  at the stand-off, or where the width of a single bead on a substrate at  $\sim 800^{\circ}\text{C}$  is from  $\sim 0.5\text{ cm}$  to  $\sim 2.5\text{ cm}$ , and the plume diameter is from  $\sim 1\text{ cm}$  to  $\sim 5\text{ cm}$  at the stand-off, the former being 40-60% of the latter.

**27.** The system according to claim **23** wherein:

the electrical supply applies a power of 60-200 kW;

the electrical supply applies a power of 80-150 kW;

the electrical supply applies a power of 110-140 kW;

the plasma gas supply supplies a total plasma gas flow at 100-500 slpm;

the plasma gas supply supplies a total plasma gas flow at 150-400 slpm;

the plasma gas supply supplies a total plasma gas flow at 250-310 slpm;

the plasma gas supply supplies plasma gas including  $\text{N}_2$ ;

the plasma gas supply supplies plasma gas including 10-90%  $\text{N}_2$ ;

the plasma gas supply supplies plasma gas consisting of 10-80%  $\text{Ar}$ , 5-40%  $\text{H}_2$ , and/or  $\text{He}$ , and 30-80%  $\text{N}_2$ ; or

the plasma gas supply supplies plasma gas consisting of 10-25%  $\text{H}_2$ , 25-45%  $\text{Ar}$  and 45-50%  $\text{N}_2$ .

**28.** The system according to claim **23** wherein the feedstock powder:

consists of 80% or more of an alkaline earth aluminosilicate or rare earth silicate; consists essentially of an alkaline earth aluminosilicate or rare earth silicate; consists of 80% or more of BSAS;

consists essentially of BSAS;

consists of 80% or more of mullite;

consists essentially of mullite;

consists of 80% or more of the high temperature ceramic with a melting point above  $1600^{\circ}\text{C}$ .;

consists essentially of the high temperature ceramic with a melting point above  $1600^{\circ}\text{C}$ .;

consists of 80% or more of the high temperature ceramic with a melting point above  $1600^{\circ}\text{C}$ ., the high temperature ceramic having a preferred phase preferentially formed only at a temperature above  $900^{\circ}\text{C}$ .;

consists of 80% or more of the high temperature ceramic with a melting point above  $1600^{\circ}\text{C}$ ., the high temperature ceramic having a preferred phase preferentially formed only at a temperature above  $900^{\circ}\text{C}$ .;

consists of 80% or more of the high temperature ceramic with a melting point above  $1600^{\circ}\text{C}$ ., the high temperature ceramic having a preferred phase preferentially formed only at a temperature above  $900^{\circ}\text{C}$ .;

consists of 80% or more of the high temperature ceramic with a melting point above  $1600^{\circ}\text{C}$ ., the high temperature ceramic having a preferred phase preferentially formed only at a temperature above  $900^{\circ}\text{C}$ .;

consists of 80% or more of the high temperature ceramic with a melting point above  $1600^{\circ}\text{C}$ ., the high temperature ceramic having a preferred phase preferentially formed only at a temperature above  $900^{\circ}\text{C}$ .;

consists of 80% or more of the high temperature ceramic with a melting point above  $1600^{\circ}\text{C}$ ., the high temperature ceramic having a preferred phase preferentially formed only at a temperature above  $900^{\circ}\text{C}$ .;

consists of 80% or more of the high temperature ceramic with a melting point above  $1600^{\circ}\text{C}$ ., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between  $900^{\circ}\text{C}$  and  $2000^{\circ}\text{C}$ .;

consists essentially of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between 900-2000° C.;

consists of 80% or more of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between 900-1600° C., or consists essentially of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between 900-1600° C.

**29.** A method of producing a high temperature coating on a ceramic substrate, the method comprising operating a high enthalpy air plasma spray torch and supplying the torch with a feedstock powder comprising a high temperature ceramic with a melting point above 1600° C., that forms undesirable solid phases when rapidly cooled below about 900° C., wherein a cumulative deviation from the following norms is less than 20%: |[N<sub>2</sub>]|=47.5±2.5%, |[H<sub>2</sub>]|=17.5±7.5%, |[Ar]|=35±10%, |TGF|=280±30 slpm, |P|=110±23 kW, |D|=8±2 cm, where [N<sub>2</sub>], [H<sub>2</sub>], and [Ar] are respectively the percentages of N<sub>2</sub>, H<sub>2</sub>, and Ar in the plasma plume, TGF is the total gas flow, P is the torch power, and D is the stand-off distance measured in cm.

**30.** The method according to claim **29** wherein the cumulative deviation is less than 10%.

**31.** (canceled)

**32.** The method according to claim **29** wherein the cumulative deviation is less than 1%.

**33.** The method according to claim **29** wherein:

operating the torch comprises spraying the ceramic substrate with at least 3 passes, by relative movement of a surface of the substrate to be coated perpendicular to the spray jet at a speed of 0.1-5 m/s:

spraying the ceramic substrate with the torch in at least 3 passes exposes each region of the substrate to the plume for about 8 s per coating; or

the substrate surface temperature is raised prior to deposition by scanning with the torch over the substrate, immediately prior to deposition, to raise the surface temperature above ~500° C., more preferably from ~800-1000°C.

**34.** (canceled)

**35.** (canceled)

**36.** The method according to claim **29** wherein the feedstock powder:

consists of 80% or more of the high temperature ceramic with a melting point above 1600° C.;

consists essentially of the high temperature ceramic with a melting point above 1600° C.;

consists of 80% or more of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at a temperature above 900° C.;

consists essentially of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at a temperature above 900° C.;

consists of 80% or more of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between 900-2000° C.;

consists essentially of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between 900-200 Q° C.;

consists of 80% or more of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between 900-1600° C.; or

consists essentially of the high temperature ceramic with a melting point above 1600° C., the high temperature ceramic having a preferred phase preferentially formed only at temperatures between 900-1600° C.

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