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(54) **Title**: PHYSICAL VAPOR DEPOSITION USING ROTATIONAL SPEED SELECTED WITH RESPECT TO DEPOSITION RATE

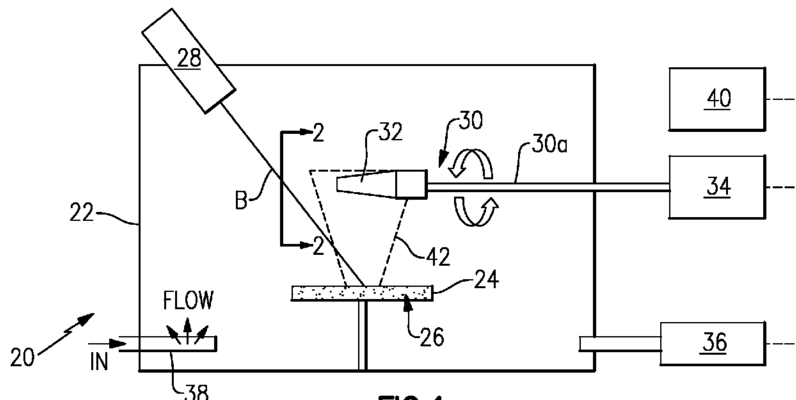

FIG.1

(57) **Abstract**: A method for use in a physical vapor deposition coating process includes depositing a ceramic coating material from a plume onto at least one substrate to form a ceramic coating thereon, and during the deposition, rotating the at least one substrate at a rotational speed selected with respect to deposition rate of the ceramic coating material onto the at least one substrate.

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PHYSICAL VAPOR DEPOSITION USING ROTATIONAL SPEED SELECTED WITH RESPECT TO DEPOSITION RATE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Application No. 61/929,178, filed January 20, 2014.

BACKGROUND

[0002] This disclosure relates to physical vapor deposition ("PVD"). PVD is one common method for depositing a coating, such as a metallic coating or a ceramic coating, on a substrate. One type of PVD process utilizes an electron beam gun to melt and evaporate a source coating material contained within a crucible. The evaporated source material condenses and deposits onto the substrate.

SUMMARY

[0003] A method for use in a physical vapor deposition coating process according to an example of the present disclosure includes depositing a ceramic coating material from a plume onto at least one substrate to form a ceramic coating thereon. During the deposition, rotating the at least one substrate at a rotational speed selected with respect to deposition rate of the ceramic coating material onto the at least one substrate.

[0004] A further embodiment of any of the foregoing embodiments include rotating the at least one substrate at the rotational speed selected with respect to deposition rate and also with respect to a resulting durability of the ceramic coating material.

[0005] In a further embodiment of any of the foregoing embodiments, the deposited ceramic coating has segmented columns extending outwardly from the at least one substrate, and including selecting the rotational speed with respect to deposition rate such that segments of the segmented columns have a thickness of 0.1-0.75 micrometers.

[0006] In a further embodiment of any of the foregoing embodiments, the deposited ceramic coating has segmented columns extending outwardly from the at least one substrate, and including selecting the rotational speed with respect to deposition rate such that segments of the segmented columns have a thickness of 0.3-0.5 micrometers.

[0007] In a further embodiment of any of the foregoing embodiments, the rotational speed is 12-120 revolutions per minute.

[0008] In a further embodiment of any of the foregoing embodiments, the rotational speed is 30-60 revolutions per minute.

[0009] In a further embodiment of any of the foregoing embodiments, the ceramic coating material is a zirconia-based material.

[0010] In a further embodiment of any of the foregoing embodiments, the at least one substrate includes an alumina scale, and the depositing includes depositing the ceramic coating material onto a surface of the alumina scale.

[0011] In a further embodiment of any of the foregoing embodiments, the deposited ceramic coating has a columnar microstructure with columns extending outwardly from the at least one substrate.

[0012] A further embodiment of any of the foregoing embodiments includes depositing the ceramic coating material in a chamber at an internal pressure in the chamber of $5x10^{-4}$ - $3x10^{-1}$ torr (0.067-40 pascals).

[0013] An apparatus for use in a physical vapor deposition coating process according to an example of the present disclosure includes a chamber, a crucible configured to hold a ceramic coating material in the chamber, an energy source operable to heat the interior of the chamber, a fixture for holding at least one substrate in the chamber, an actuator operable to rotate the fixture, and a controller. The controller is configured to establish a plume of the ceramic coating material in the chamber to deposit the ceramic coating material from the plume onto the at least one substrate and form a ceramic coating thereon, and during the deposition, rotate the at least one substrate at a rotational speed selected with respect to deposition rate of the ceramic coating material onto the at least one substrate.

[0014] In a further embodiment of any of the foregoing embodiments, the rotational speed is 12-120 revolutions per minute.

[0015] In a further embodiment of any of the foregoing embodiments, the rotational speed is 30-60 revolutions per minute.

[0016] In a further embodiment of any of the foregoing embodiments, the ceramic coating material is a zirconia-based material.

[0017] A coated article comprising according to an example of the present disclosure includes a substrate, and a ceramic coating on the substrate. The ceramic coating has a columnar microstructure with segmented columns having a thickness of 0.1-0.75 micrometers.

[0018] In a further embodiment of any of the foregoing embodiments, the segmented columns have a thickness of 0.3-0.5 micrometers.

[0019] In a further embodiment of any of the foregoing embodiments, at least a majority of the segmented columns have a uniform width.

[0020] In a further embodiment of any of the foregoing embodiments, at least a majority of the segmented columns are unbranched along at least half the total thickness of the ceramic coating distal from the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] The various features and advantages of the present disclosure will become apparent to those skilled in the art from the following detailed description. The drawings that accompany the detailed description can be briefly described as follows.

[0022] Figure 1 illustrates an example coating apparatus.

[0023] Figure 2 illustrates another view of a portion of the example coating apparatus of Figure 1 according to the view direction indicated in Figure 1.

[0024] Figure 3 illustrates an example article produced using the apparatus.

[0025] Figure 4 illustrates an image of a polished cross-section of a ceramic coating deposited at a rotational speed of 12 revolutions per minute in a low vacuum internal chamber pressure of 0.1 torr (13.4 pascals).

[0026] Figure 5 illustrates an image of a polished cross-section of a ceramic coating deposited at a rotational speed of 60 revolutions per minute in a low vacuum internal chamber pressure of 0.075 torr (10 pascals).

[0027] Figure 6 illustrates an image of a polished cross-section of an yttria-stabilized zirconia coating deposited at 60 revolutions per minute under a chamber pressure of 0.075 torr (10 pascals).

DETAILED DESCRIPTION

[0028] Figure 1 schematically illustrates an example apparatus 20 for use in a physical vapor deposition ("PVD") coating process, which will also be described with reference to the apparatus 20. The examples herein may be described with reference to the deposition of a ceramic coating onto a substrate, such as, but not limited to, gas turbine engine airfoils or airfoil multiplets of a plurality of airfoil vanes. It is to be understood, however, that the examples may also be applied to other coatings, other gas turbine engine components, and non-engine components.

[0029] The apparatus 20 in the illustrated example includes a chamber 22 and a crucible 24 that is configured to hold a coating material 26 in the chamber 22. For example,

the crucible 24 can be a tray that holds particulate of the coating material 26. Alternatively, the crucible 24 can be adapted to hold and present an ingot of the coating material 26.

[0030] The apparatus 20 further includes an energy source 28 that is operable to heat and vaporize the coating material 26. In one example, the energy source 28 includes one or more electron beam guns that are operable to emit electron beams, represented at B, onto the coating material 26.

[0031] The apparatus 20 also includes a fixture 30 for holding at least one substrate 32 in the chamber 22. In this example, the fixture 30 includes a shaft 30a that is connected to an actuator 34. The actuator 34 is operable to rotate the shaft 30a, and to thus also rotate the substrate 32.

[0032] Figure 2 illustrates schematically a view of a portion of the apparatus 20 according to the section line in Figure 1. In this example, the apparatus 20 includes a thermal hood 33, sometimes referred to as coater box. The walls of the thermal hood 33 extend partially around the substrate 32 and accommodate one or more gas manifolds 33a. The gas manifold(s) 33a is/are connected to one or more gas sources, such as an oxygen-containing gas, which can be pure, or substantially pure, oxygen. Arrows emanating from gas manifold(s) 33a schematically illustrate the direction of the gas flow.

[0033] Referring again to Figure 1, the apparatus 20 further includes a vacuum pump 36 that is operable to reduce the pressure inside of the chamber 22 and one or more additional gas manifolds 38 that can be connected to the same or different gas source (not shown) for providing process gas into the interior of the chamber 22. For example, the process gas can include oxygen, helium, neon, argon, krypton, xenon, or mixtures thereof. It is to be appreciated that this disclosure is not limited to the example configuration of the apparatus 20.

[0034] A controller 40 is operably connected with at least the actuator 34 and the vacuum pump 36, and also optionally the gas manifolds 33a/38, to control rotation of the substrate 32 as well as gas flow and pressure within the chamber 22 during coating deposition. The controller 40 can include hardware, such as a microprocessor, software, or a combination thereof, that is configured to carry out the functions disclosed herein, individually or in any combination, and generally control operation of the apparatus 20.

[0035] In this example, the apparatus 20 and controller 40 are configured for a method of physical vapor deposition. For example, the method can include depositing the ceramic coating material 26 from a plume 42 onto the substrate 32 to form a ceramic coating thereon. Further, during the deposition, the controller 40 controls rotation of the substrate 32

and provides for rotation at a rotational speed selected with respect to deposition rate of the ceramic coating material 26 onto the at substrate 32. In further examples, the method may also include depositing at an internal pressure in the chamber 22 of $5x10^{-4}$ - $3x10^{-1}$ torr (0.067-40 pascals).

[0036] The controller 40 commands the actuator 34 to rotate the fixture 30, and thus the substrate 32, at a rotational speed that is selected with respect to deposition rate. One indicator of deposition rate can be coating flux per unit area, with units of weight per unit area. In the examples herein, coating flux is maintained to be constant or substantially constant during coating deposition. The selection of rotational speed with respect to deposition rate can be used to control, and improve, durability of the ceramic coating deposited at a given internal chamber pressure.

[0037] Durability can be evaluated by testing a durability parameter of one or more samples. Additionally, testing results can be used to estimate, at least qualitatively, the durability of one or more untested coatings, through microstructural analysis, for example. An example durability parameter useful for gas turbine engine components is spallation resistance in thermal cycling conditions, such as conditions found in, or that simulate, gas turbine engines. For example, for ceramic coatings deposited by physical vapor deposition as disclosed herein, durability, and the potential improvement thereof, can refer to spallation resistance in thermal cycling conditions for components or samples having a material difference in coefficient of thermal expansion ("CTE") between the substrate 32 and a ceramic coating 54 deposited thereon (see Figure 3). In one further example, durability refers to spallation resistance in thermal cycling conditions with a given difference in CTE between a nickel-based superalloy substrate 32 and a stabilized zirconia ceramic coating 54. As a further example, nickel-based superalloy can have a CTE of approximately 14 microinch/inch °C, and stabilized zirconia can have a CTE of approximately 9 microinch/inch °C. These values can vary in dependence on specific composition by approximately 10-15%. Thus, the present disclosure can be applied to control durability with respect to such nickel-based superalloy substrates and stabilized zirconia ceramic coatings, for example.

[0038] In one example, the rotational speed used during deposition can be as low as 12 revolutions per minute, and as high as 120 revolutions per minute. In further examples, the rotational speed is 30 revolutions per minute or greater, or 30 to 60 revolutions per minute.

[0039] In a further example, the coating material 26 is a zirconia-based material. Example zirconia-based materials can include yttria-stabilized zirconia and gadolinia-stabilized zirconia, but are not limited to these zirconia-based materials.

[0040] Figure 3 illustrates a representative portion of an example article 50 produced using the apparatus 20 and method described above. In this example, the substrate 32 includes an alumina scale 52 that was grown or prepared in a known manner prior to and/or during the deposition process. The ceramic coating is shown at 54 and has been deposited onto the top surface of the alumina scale 52. The ceramic coating 54 has a columnar microstructure 56 with columns that extend outwardly from the substrate 32.

[0041] During deposition, due to rotation of the substrate 32, the ceramic coating 54 deposits in sublayers. That is, for each rotation of the substrate 32, a single sublayer is deposited. When sectioned and polished for microstructural analysis, these sublayers are microstructurally distinguishable at magnification. The sublayers manifest as segments in the columnar microstructure 56. The thickness of the sublayers, or segments, in the vertical or substantially vertical direction from the substrate 32 can be used to assess the durability of a microstructure of a ceramic coating, and with a view to selecting rotational speed with respect to deposition rate to control durability of a deposited ceramic coating.

[0042] As a general example, all else being equal, such as coating composition, temperature, pressure and deposition rate, relatively slow substrate rotation will result in thicker segments and relatively fast substrate rotation will result in thinner segments. Thus, for a given target coating thickness (overall thickness), a coating deposited at relatively slow substrate rotation will contain fewer segments in the vertical direction than a coating deposited at relatively fast substrate rotation. However, by comparison, coating processes typically focus on temperature control as a main control parameter with respect to durability, without regard to rotation speed and deposition rate. However, by selecting rotation speed with respect to deposition rate, the thickness of the segments can be controlled to, in turn, control durability. For example, the durability refers to spallation resistance in thermal cycling conditions with a given material difference in CTE between the substrate 32 and the ceramic coating 54, as discussed herein above.

[0043] In a further example, the selection of rotation speed with respect to deposition rate, and the resulting influence on durability, can be even more pronounced when using relatively low vacuum internal chamber pressures during deposition. For example, low vacuum internal chamber pressures can be deposition pressures in the range of 5×10^{-4} torr to 3×10^{-1} torr.

[0044] Deposition in a low vacuum internal chamber pressure range results in relatively high deposition rate of a ceramic coating material. Thus, rotation speeds that may yield good durability results at one pressure, may not yield good durability results at another, different pressure. For example, an increase in pressure from a given high vacuum internal chamber pressure to a given low vacuum internal chamber pressure by a factor of about 200 results in a higher deposition rate by a factor of about 4. At such high deposition rates, considerably thicker segments within the ceramic columns will be deposited, which reduces coating durability.

[0045] Figure 4 shows an image of a polished cross-section of a ceramic coating deposited at a rotational speed of 12 revolutions per minute in a low vacuum internal chamber pressure of 0.1 torr (13.4 pascals). The coating has a columnar microstructure (columns extending vertically in the image) with distinct deposition boundaries running substantially horizontally and defining column segments. In this example, the column segments are approximately 2.4 micrometers in thickness, in the vertical direction from the substrate at the bottom of the image. The coating of Figure 4 has a relatively low durability as a result of relatively low adherence between the segments, which reduces spallation resistance and strain tolerance of the coating as a whole. In addition, the gaps between the columns are relatively narrow, which can also contribute to reducing strain tolerance and spallation resistance.

[0046] As a comparison, Figure 5 shows a higher magnification image of a polished cross-section of a ceramic coating deposited at a rotational speed of 60 revolutions per minute in a low vacuum internal chamber pressure of 0.075 torr (10 pascals). In this example, the coating also has a columnar microstructure (columns extending vertically in the image) with distinct deposition boundaries running substantially horizontally and defining column segments. In this example, the column segments are approximately 0.29 micrometers in thickness, in the vertical direction from the substrate at the bottom of the image. The coating of Figure 5 has a relatively high durability as a result of good adherence between the segments, which increases spallation resistance and strain tolerance of the coating as a whole. The microstructure of the coating in Figure 5 is thus more favorable with respect to durability than the microstructure of the coating of Figure 4. In addition, the gaps between the columns are wider relative to the columnar gaps of the coating in Figure 4, which can also contribute to, comparatively, increasing strain tolerance and spallation resistance. In further examples, the rotational speed can be selected with respect to deposition rate to provide a segment

thickness of 0.1-0.75 micrometers to obtain good durability of a deposited ceramic coating, such as a zirconia-based ceramic coating.

[0047] Figure 6 illustrates another example image of a polished cross-section of a ceramic coating produced according to this disclosure. In this example, the ceramic coating is an yttria-stabilized zirconia coating deposited at 60 revolutions per minute under a chamber pressure of 0.075 torr (10 pascals). In this example, at least a majority of the columns of the columnar microstructure have a uniform width. Additionally, at least a majority of the columns are unbranched along at least half of the thickness of the ceramic coating that is distal from the substrate, which is at the bottom of the image.

[0048] Although a combination of features is shown in the illustrated examples, not all of them need to be combined to realize the benefits of various embodiments of this disclosure. In other words, a system designed according to an embodiment of this disclosure will not necessarily include all of the features shown in any one of the Figures or all of the portions schematically shown in the Figures. Moreover, selected features of one example embodiment may be combined with selected features of other example embodiments.

[0049] The preceding description is exemplary rather than limiting in nature. Variations and modifications to the disclosed examples may become apparent to those skilled in the art that do not necessarily depart from the essence of this disclosure. The scope of legal protection given to this disclosure can only be determined by studying the following claims.

CLAIMS

What is claimed is:

1. A method for use in a physical vapor deposition coating process, the method comprising:

depositing a ceramic coating material from a plume onto at least one substrate to form a ceramic coating thereon; and

during the deposition, rotating the at least one substrate at a rotational speed selected with respect to deposition rate of the ceramic coating material onto the at least one substrate.

2. The method as recited in claim 1, including rotating the at least one substrate at the rotational speed selected with respect to deposition rate and also with respect to a resulting durability of the ceramic coating material.

3. The method as recited in claim 1, wherein the deposited ceramic coating has segmented columns extending outwardly from the at least one substrate, and including selecting the rotational speed with respect to deposition rate such that segments of the segmented columns have a thickness of 0.1-0.75 micrometers.

4. The method as recited in claim 1, wherein the deposited ceramic coating has segmented columns extending outwardly from the at least one substrate, and including selecting the rotational speed with respect to deposition rate such that segments of the segmented columns have a thickness of 0.3-0.5 micrometers.

5. The method as recited in claim 1, wherein the rotational speed is 12-120 revolutions per minute.

6. The method as recited in claim 1, wherein the rotational speed is 30-60 revolutions per minute.

7. The method as recited in claim 1, wherein the ceramic coating material is a zirconia-based material.

8. The method as recited in claim 1, wherein the at least one substrate includes an alumina scale, and the depositing includes depositing the ceramic coating material onto a surface of the alumina scale.

9. The method as recited in claim 1, wherein the deposited ceramic coating has a columnar microstructure with columns extending outwardly from the at least one substrate.

10. The method as recited in claim 1, including depositing the ceramic coating material in a chamber at an internal pressure in the chamber of $5x10^{-4}$ - $3x10^{-1}$ torr (0.067-40 pascals).

11. An apparatus for use in a physical vapor deposition coating process, comprising:

a chamber;

a crucible configured to hold a ceramic coating material in the chamber;

an energy source operable to heat the interior of the chamber;

a fixture for holding at least one substrate in the chamber;

an actuator operable to rotate the fixture; and

a controller configured to establish a plume of the ceramic coating material in the chamber to deposit the ceramic coating material from the plume onto the at least one substrate and form a ceramic coating thereon, and during the deposition, rotate the at least one substrate at a rotational speed selected with respect to deposition rate of the ceramic coating material onto the at least one substrate.

12. The apparatus as recited in claim 11, wherein the rotational speed is 12-120 revolutions per minute.

13. The apparatus as recited in claim 11, wherein the rotational speed is 30-60 revolutions per minute.

14. The apparatus as recited in claim 11, wherein the ceramic coating material is a zirconia-based material.

15. A coated article comprising:

a substrate; and

a ceramic coating on the substrate, the ceramic coating having a columnar microstructure with segmented columns having a thickness of 0.1-0.75 micrometers.

16. The coated article as recited in claim 15, wherein the segmented columns have a thickness of 0.3-0.5 micrometers.

17. The coated article as recited in claim 15, wherein at least a majority of the segmented columns have a uniform width.

18. The coated article as recited in claim 15, wherein at least a majority of the segmented columns are unbranched along at least half the total thickness of the ceramic coating distal from the substrate.

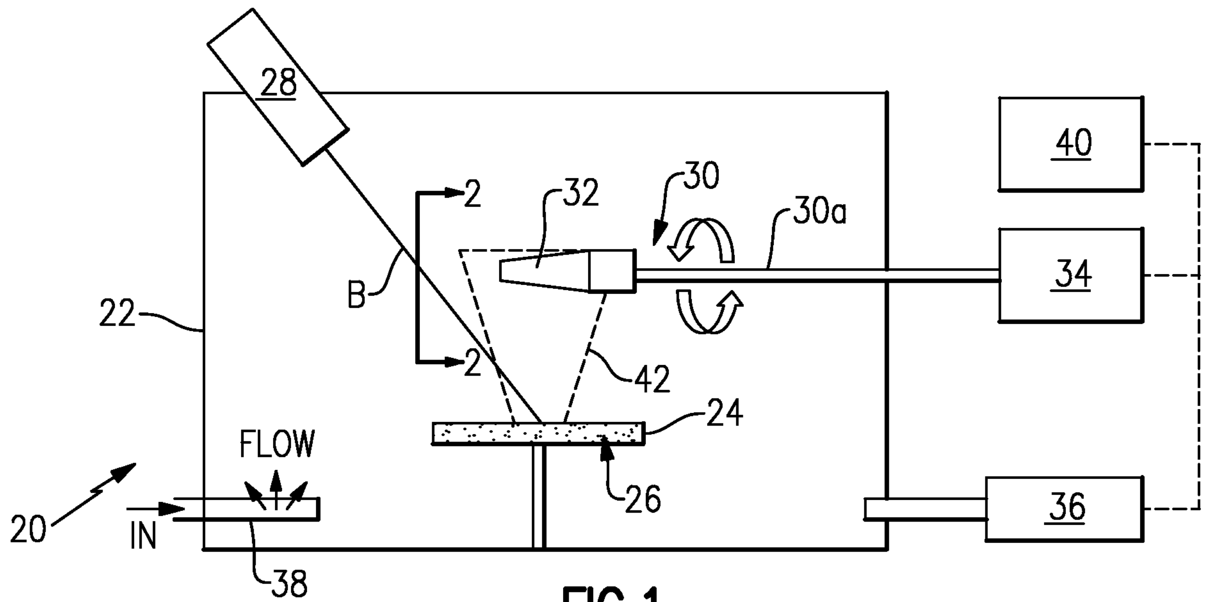

FIG.1

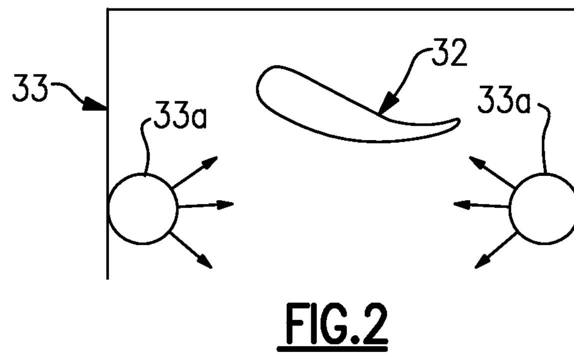

FIG.2

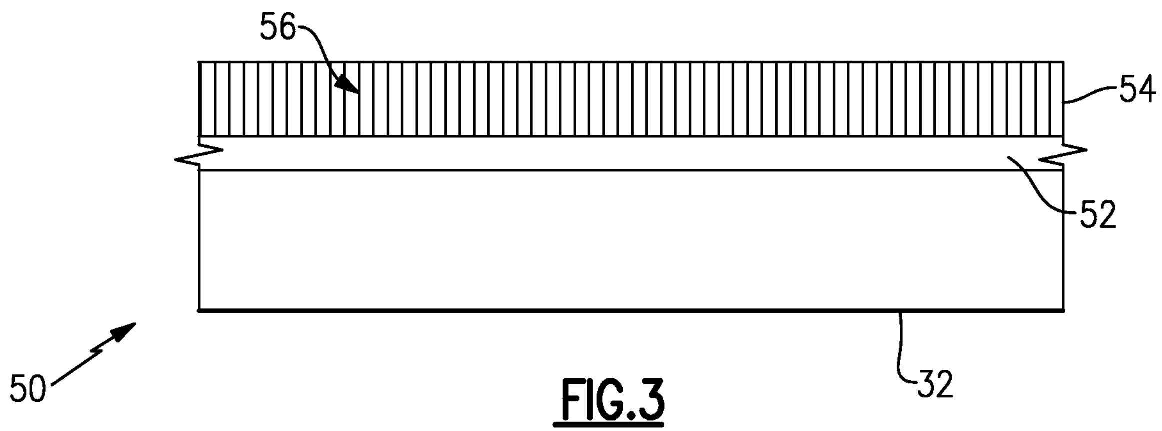

FIG.3

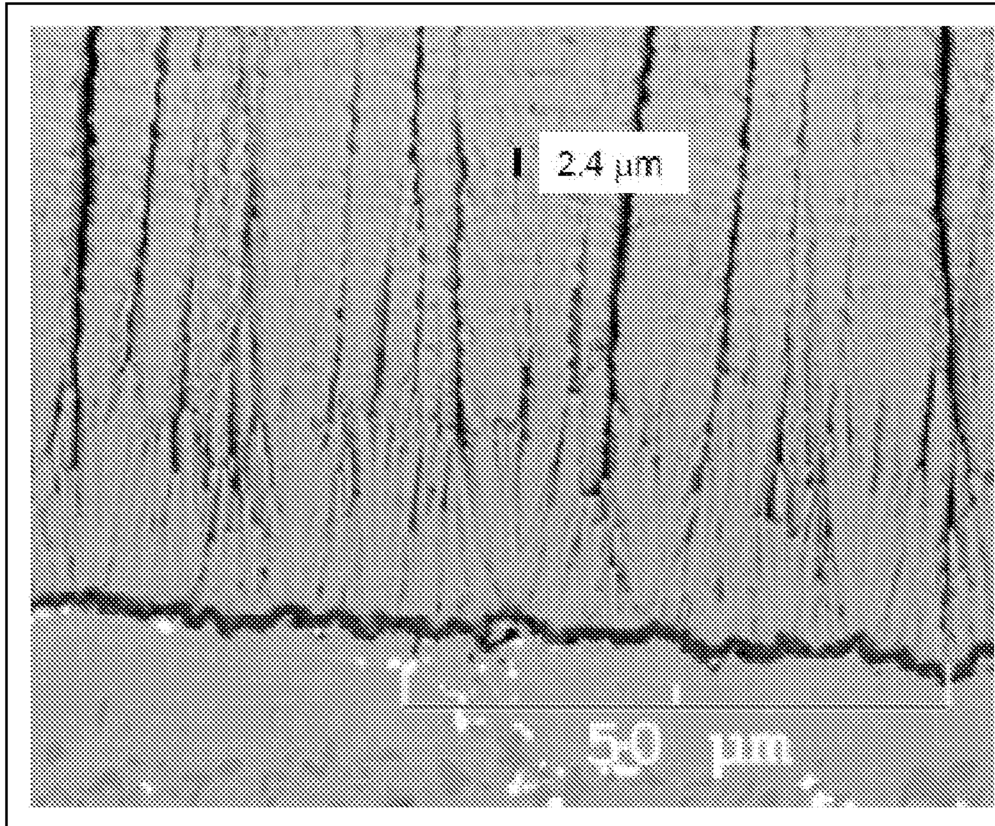

FIG.4

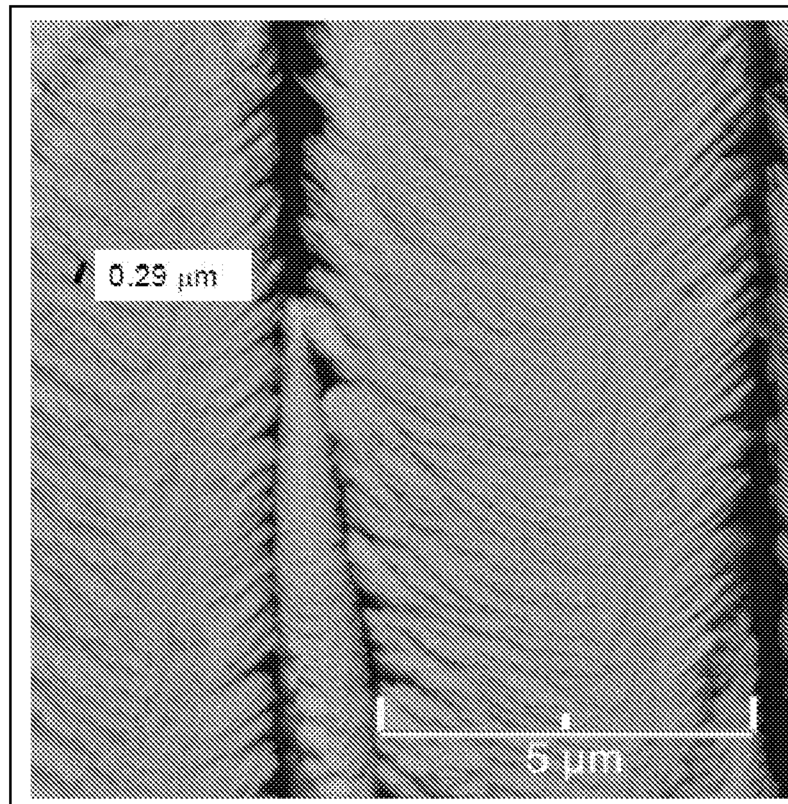

FIG.5

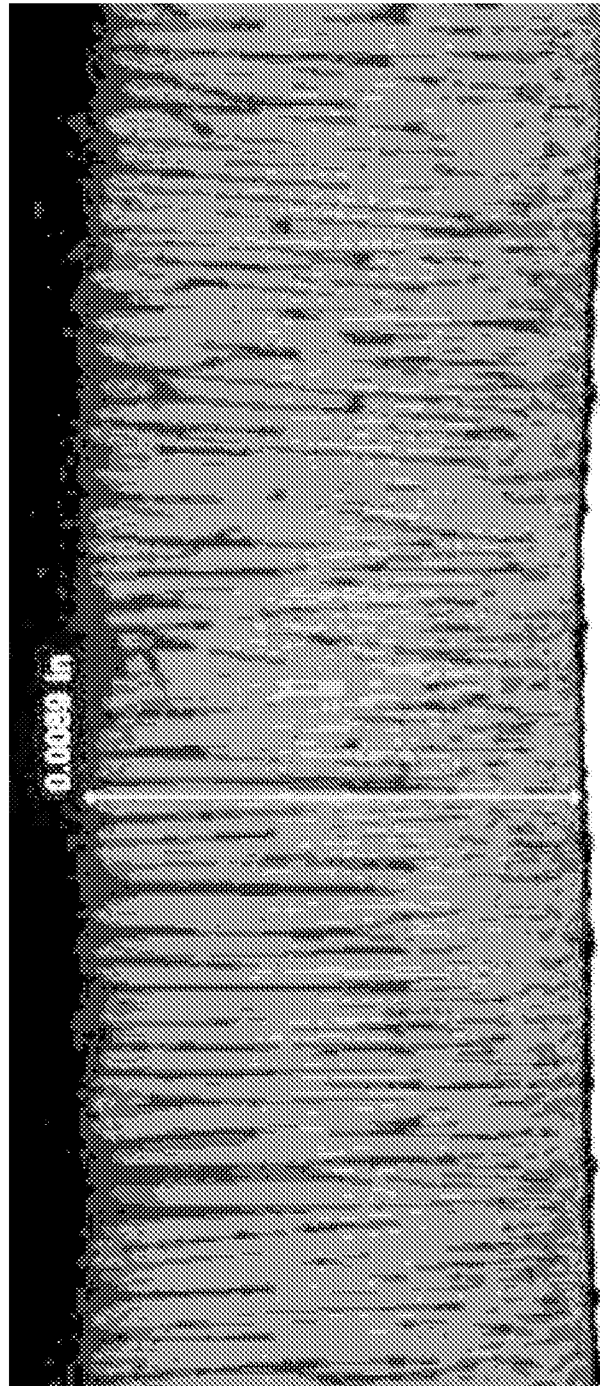

FIG.6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/010589

A. CLASSIFICATION OF SUBJECT MATTER

C23C 14/06(2006.01)i, C23C 14/22(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C 14/06; B05D 5/12; B32B 9/00; B32B 15/04; C23C 14/30; B32B 15/00; C23C 28/00; B05D 3/06; C23C 14/08; C23C 16/00; C23C 14/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: physical vapor deposition, ceramic coating, rotation, speed, deposition rate, columnar microstructure, segmented columns

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003-0180571 A1 (SINGH, J.) 25 September 2003 See abstract; paragraphs [0014], [0046], [0048], [0050], [0065] and [0066]; claims 1, 3 and 19; figures 4 and 8.	1-18
A	US 2003-0203127 A1 (BRUCE, R. W. et al.) 30 October 2003 See abstract; paragraph [0024]; claims 1-11; figure 1.	1-18
A	US 5087477 A (GIGGINS, JR., C. S. et al.) 11 February 1992 See abstract; column 4, line 65-column 5, line 5; claims 1-3; figures 1 and 2.	1-18
A	EP 0972853 A1 (UNITED TECHNOLOGIES CORPORATION) 19 January 2000 See abstract; paragraphs [0030]-[0032]; figure 2.	1-18
A	US 6221512 B1 (RICKERBY, D. S.) 24 April 2001 See abstract; column 3, lines 16-23; claim 1; figures 2-5.	1-18

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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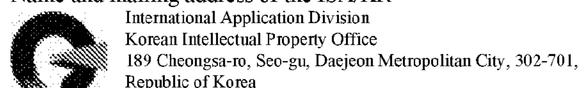
Date of the actual completion of the international search	Date of mailing of the international search report
29 April 2015 (29.04.2015)	**29 April 2015 (29.04.2015)**

Name and mailing address of the ISA/KR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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/010589

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