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(54) **Plasma application of thermal barrier coatings with reduced thermal conductivity on combustor hardware**

(57) A process for forming a thermal barrier coating comprises the steps of providing a substrate, providing a gadolinia stabilized zirconia powder, and forming a thermal barrier coating having at least one of a porosity in a range of from 5 to 20% and a dense segmented

structure on said substrate by supplying the gadolinia stabilized powder to a spray gun and using an air plasma spray technique.

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## Description

### BACKGROUND

**[0001]** The present disclosure is directed to thermal barrier coatings with reduced thermal conductivity on combustor hardware, which coatings are applied using a plasma.

**[0002]** Ceramic thermal barrier coatings (TBCs) have been used for many years to extend the life of combustors and high turbine stationary and rotating parts in gas turbine engines. TBCs typically consist of a metallic bond coat and a ceramic top coat applied to a nickel or cobalt based alloy substrate which forms the part being coated. The coatings are typically applied to thicknesses between 5 and 40 mils and can provide up to 300 degrees F temperature reduction to the substrate metal. This temperature reduction translates into improved part durability, higher turbine operating temperatures, and improved turbine efficiency. Typically, the ceramic layer is a 7 wt% yttria stabilized zirconia applied by air plasma spray (APS). New low thermal conductivity coatings have been developed which can provide improved part performance.

**[0003]** One coating which has been used in the past for TBCs is gadolinia stabilized zirconia based thermal barrier coatings.

### SUMMARY OF THE INVENTION

**[0004]** It is desirable to form a thermal barrier coating which has a relatively low thermal conductivity.

**[0005]** As described herein, there is provided a process for forming a thermal barrier coating comprises the steps of providing a substrate, providing a gadolinia stabilized zirconia powder, and forming a thermal barrier coating having at least one of a porosity in a range of from 5 to 20% and a dense segmented structure on said substrate by supplying the gadolinia stabilized powder to a spray gun and using an air plasma spray technique.

**[0006]** Other details of the thermal barrier coatings applied using an air plasma spray technique, as well as advantages attendant thereto, are set forth in the following detailed description and the accompanying drawings.

### BRIEF DESCRIPTION OF THE DRAWINGS

#### **[0007]**

Figs. 1 and 2 are photomicrographs showing a low conductivity cracked coating formed using a F4 Plasma Spray Gun, which coating includes a ceramic layer consisting of 30 wt%  $Gd_2O_3$  and 70 wt%  $ZrO_2$  with a air plasma sprayed MCrAlY bond coat ;

Fig. 3 is a photomicrograph showing a coating system which includes a metallic bond coat, a ceramic bond coat, and a ceramic top coat formed by a low

conductivity coating in which the metallic bond coat is an air plasma-sprayed MCrAlY bond coat, the ceramic bond coat is a 7 YSZ interlayer, and the ceramic top coat is a 30 wt%  $Gd_2O_3$  - 70 wt%  $ZrO_2$  top layer.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

**[0008]** As described herein, a plasma spray technique is utilized to apply a gadolinia stabilized zirconia based thermal barrier coatings on combustor hardware such as panels, chambers, heat shields, transition ducts, augmenters, etc. The plasma spray technique may be an air plasma spray technique in which a desirable coating microstructure is produced.

**[0009]** In air plasma spray, the coating material is propelled toward the surface of the substrate to be coated. The coating material is in the form of a spray. The powder or powders forming the coating material are fed along with carrier gases into a high temperature plasma gas stream. In the plasma gas stream, the powder particles are melted and accelerated toward the surface of the substrate to be coated. The powder particles are fed to a spray gun at a desired feed rate. A carrier gas flow such as an argon gas flow is used to maintain the powder under pressure and facilitate powder feed. The carrier gas flow rate is described in standard cubic feet per hour. Standard conditions may be defined as about room temperature and about one atmosphere of pressure.

**[0010]** The gases that make up the plasma gas stream comprise a primary gas (such as an argon gas or nitrogen gas) and a secondary gas (such as a hydrogen gas). Helium gas may be used as the secondary gas if desired.

**[0011]** The process includes the step of translating a spray gun so that the nozzle is positioned at a desired distance from the surface to be coated. The substrate to be coated may be passed through the spray of powder particles emanating from the spray gun.

**[0012]** The spray gun to be used to form the coatings disclosed herein may include both internal feed and external feed spray guns. Suitable spray guns include the Plasmadyne SG-100, Sulzer Metco 3MB, 7 MB, or 9 MB, and the Plasma Technic F-4. The desired coating may also be applied with the high deposition rate Sulzer Metco Triplex gun and/or the Progressive HE100 gun.

**[0013]** Zirconia based powder with the additions of rare earth stabilizers, such as gadolinia, have been found to yield coatings having lower thermal conductivities than many current thermal barrier coatings. A useful zirconia based powder is one which consists of optionally 3.0 to 14 wt% of at least one of yttria and titania, 15 to 70 wt% gadolinia, and the balance zirconia. The yttria and/or titania, and the gadolinia, improve the thermal barrier coating's ceramic mechanical properties, while still achieving a reduced thermal conductivity ceramic coating. Coatings formed using these powders are shown in Figs. 1 and 2.

[0014] If desired, one could apply to a substrate, a coating which has a metallic bond coat, such as a MCrAlY type coating where M is Ni or Co, a ceramic interlayer, such as a 7 YSZ coating, deposited on the metallic bond coat and a ceramic top coat comprising from 15 to 70 wt% gadolinia and the balance zirconia. Such a coating system is illustrated in Fig. 3.

[0015] The air plasma spray parameters may be adjusted to produce a coating with a desired level of porosity or a coating with a dense segmented structure. For porous coatings, the coating may have a thermal conductivity which ranges from 3.0 to 10 BTU in/hr ft<sup>2</sup> F. For segmented coatings, the coating may have a thermal conductivity which ranges from 5.0 to 12.5 BTU in/hr ft<sup>2</sup> F.

[0016] A useful coating has a porosity in the range of 5.0 to 20%. The desired porosity for the coating may be obtained by altering the gun power settings, the standoff distance, the powder particle size, and the powder feed rate.

[0017] Segmented coatings provide the coating with strain tolerance during operation which leads to increased spallation life. For combustor panel applications, a coating system having a segmented microstructure top-coat layer with a ceramic interlayer provides a useful coating system.

[0018] If desired, one can obtain a coating with a dense segmented structure by increasing the power settings and shorten the standoff distance. One can do this by using the settings set forth in columns 6 - 8 of U.S. patent no. 5,879,753, which patent is incorporated by reference herein. The relevant disclosure of US patent no. 5,879,753 appears at the end of the description as Annex 1.

[0019] For example, a useful coating may be applied using the Plasmadyne SG-100 spray gun using an amperage range of 350 to 825 amps, a voltage of 35 to 50 volts applied to a cathode and anode within the plasma-gun body, an argon primary gas flow of 75 - 105 SCFH, a hydrogen secondary gas flow of 1.0 to 10 SCFH or a helium gas flow of 45 - 75 SCFH, a powder gas flow exiting the gun of 4.0 to 20 SCFH, a powder feed rate to the gun of 10 to 40 grams/min., and a gun distance from the surface being coated of from 3.0 to 5.0 inches. Alternatively, the coatings may be applied with the Plasma Technic F-4 spray gun using an amperage range of from 500 to 700 amps, a voltage of 55 to 65 volts, an argon primary gas flow of 65 to 90 SCFH, a hydrogen secondary gas flow of 8 - 22 SCFH, a powder gas flow from the spray gun of 6 to 12 SCFH, a powder feed rate to the spray gun of 35 - 55 grams/min. and a gun distance from the surface being coated of from 4.0 to 7.0 inches.

[0020] One of the benefits of the process of the present invention is the application of a thermal barrier coating having lower thermal conductivity than many current coatings resulting in longer coating life, performance improvements, and cost savings.

[0021] Burner rig testing of a low conductivity coating formed in accordance with the present disclosure with a

ceramic interlayer was found to be 1.6 to 1.9 times better in spallation resistance than without the interlayer. In addition, low conductivity coatings with an interlayer are 1.3 to 1.5 times better in spallation than current coatings.

[0022] In accordance with the foregoing disclosure, there has been provided a plasma application of thermal barrier coatings with reduced thermal conductivity on combustor hardware. While the plasma application of thermal barrier coatings has been described in the context of specific embodiments thereof, other unforeseeable alternatives, modifications, and variations may become apparent to those skilled in the art having read the foregoing description. Accordingly, it is intended to embrace those alternatives, modifications, and variations as fall within the broad scope of the appended claims. In particular, it is possible to use in the process the various process parameters set forth in Annex 1 hereinbelow.

#### ANNEX 1

[0023] The processing steps include the selection of certain parameters. These parameters include rotating the fixture at a preselected speed, angling the gun with respect to the substrate, moving the gun at a preselected traverse speed, heating the substrate to a preselected temperature, injecting the coating powder at a preselected rate, and flowing the carrier gas and plasma gases at preselected flow rates. These parameters all influence the structure of the coating and as such should be adjusted to provide uniform coating of compressor blades, or other substrates. In general, it has been found that a close gun-to-substrate spray distance coupled with relatively high spray gun power results in the desired vertical segmentation or microcracking of the coating structure. The parameters described herein were tailored for use with an F-4 model air plasma spray gun purchased from Plasma Technics, Inc., now supplied by Sulzer Metco having facilities in Westbury, N.Y., and various diameter cylindrical fixtures depending on substrate configuration. As will be realized, the parameters may vary with the use of a different spray gun and/or fixture. Accordingly, the parameters set forth herein may be used as a guide for selecting other suitable parameters for different operating conditions.

[0024] The process for controllably applying spray coating as flow charted in FIG. 1, includes a number of interrelated steps beginning with providing blades having clean, exposed blade tips and protected airfoil and root surfaces typically provided by masking. Conventional cleaning and preparation of the blade tip prior to application of the abrasive layer should be conducted. In the practice of the present invention, for example with a blade tip as shown in the figures, the surface of the blade tip is cleaned and roughened to enhance adherence of subsequently applied coating materials. Such cleaning can include mechanical abrasion such as through a vapor or air blast type process employing dry or liquid carried abrasive particles impacting the surface.

**[0025]** Prior to cleaning the surface, blades are suitably masked as shown in U.S. Application Number EH-10117, U.S. Ser. No. 08/994,676, filed Dec. 19, 1997, entitled "Shield and Method for Protecting an Airfoil Surface", by Zajchowski and Diaz, herein incorporated by reference.

**[0026]** The process includes propelling a spray of particles of softened bond coating medium toward the blade tips. The step of propelling the coating medium includes the step of forming a spray of particles of softened bond coating medium in the spray coating apparatus. This step includes flowing bond coat powder and carrier gases into a high-temperature plasma gas stream. In the plasma gas stream, the powder particles are melted and accelerated toward the substrate. Generally, the powder feed rate should be adjusted to provide adequate consistency and amount of bond coating. The bond coat powder feed rate ranges from thirty to fifty-five grams per minute (30 to 55 grams/min). Carrier gas flow (argon gas) is used to maintain the powder under pressure and facilitate powder feed. The carrier gas flow rate ranges from four to eight standard cubic feet per hour (4 to 8 scfh) (1.9 to 3.8 standard liters per minute (SLM)). Standard conditions are herein defined as about room temperature (77 DEG F.) and about one atmosphere of pressure (760 mmHg) (101 kPa).

**[0027]** The gases that make up the plasma gas stream comprise of a primary gas (argon gas) and a secondary gas (hydrogen gas). Helium gas may also be used as a secondary gas. The primary gas flow rate in the gun ranges from seventy-five to one hundred and fifteen standard cubic feet per hour (75 to 115 scfh) (35 to 54 SLM), while the secondary gas flow rate ranges from ten to twenty-five standard cubic feet per hour (10 to 25 scfh) (4.7 to 12 SLM). Spray gun power generally ranges from thirty to fifty kilowatts (30 to 50 KW).

**[0028]** The process then includes the step of translating the spray of softened bond coating medium at a distance ranging between about four to six inches (4 to 6") (102 to 152 mm) from the blade tips, between a first and second position. In one embodiment, the spray gun is moved in a direction substantially parallel to the surface of rotation of the holding fixture. Spray gun traverse speed during bond coat deposition ranges from six to twelve inches per minute (6 to 12 in/min) (152 to 305 mm/min).

**[0029]** Further, the process includes passing the blades through the spray of particles of softened bond coating medium by rotating the fixture about its axis of rotation. This step includes heating the blades to a temperature of two hundred to four hundred and fifty degrees Fahrenheit (200 DEG to 450 DEG F.) by passing the blades in front of the spray gun and hot plasma gas stream. The step of passing the blades through the spray of particles of softened bond coating medium also includes cooling the blades and the coating layer deposited by rotating them away from the spray gun. Additional cooling of the blades can be provided by directing a cooling air stream or cooling jet on the blades or the fixture.

Independent sources of heating can also be provided to heat the blades prior to the blades entering the spray of particles of coating medium. The independent heating source would allow for control of blade temperature without adjusting the spray gun to provide heating. Specifically, during bond coat deposition, the cylindrical fixture rotates at a speed which ranges from twenty to seventy-five revolutions per minute (20 to 75 rpm), depending on substrate diameter. The surface speed of the blades ranges typically from one hundred and twenty-five to three hundred surface feet per minute (125 to 300 sfpm).

**[0030]** The coating process then includes the step of forming a spray of particles of softened top coating medium. This step includes flowing top coat powder and carrier gases into the high-temperature plasma gas stream. Generally, the powder feed rate should be adjusted to provide adequate mix to cover the substrate, yet not be so great as to reduce melting and crack formation. Top coat powder feed rate ranges from fifteen to forty grams per minute (15 to 40 grams/min). Carrier gas flow (argon gas) is used to maintain the powder under pressure and facilitate powder feed. The flow rate ranges from four to eight standard cubic feet per hour (4 to 8 scfh) (1.9 to 3.8 SLM). As described hereinabove, standard conditions are herein defined as about room temperature (77 DEG F.) and about one atmosphere of pressure (760 mmHg) (101 kPa).

**[0031]** The step of forming a spray of particles of softened top coating medium includes the injection of the top coat powder angled such that it imparts a component of velocity to the powder which is opposite to the direction of flow of the plasma toward the rotating fixture. The projection of the injection angle in a plane perpendicular to the axis of rotation of the holding fixture lies in a range from sixtyfive to eighty-five degrees (65 DEG to 85 DEG). This injection angle serves to introduce the top coat powder further back into the plasma plume, thus increasing the residence time of the powder in the plasma gas stream. The increased residence time in the plasma gas stream provides for better melting of the powder particles.

**[0032]** Primary gas flow (argon gas) in the gun ranges from fifty to ninety standard cubic feet per hour (50 to 90 scfh) (24 to 43 SLM). Similarly, secondary gas flow (hydrogen gas) in the gun ranges from ten to thirty scfh (10 to 30 scfh) (4.7 to 14 SLM). Spray gun power generally ranges from thirty to fifty kilowatts (30 to 50 KW).

**[0033]** The process further includes the step of translating a spray of softened top coating medium at a distance ranging from three to four inches (3 to 4") (76 to 102 mm) from the blade tips, between a first and second position in a direction substantially normal to the plane of rotation of the holding fixture. Spray gun traverse speed across each part during deposition ranges from two to ten inches per minute (2 to 10 in/min) (50.8 to 254 mm/min). The gun-to-substrate distance may be varied with the intent of maintaining the appropriate temperature level at the substrate surface. A close gun-to-substrate

distance is necessary for satisfactory vertical microcracking.

**[0034]** The process further includes the step of passing blades through the spray of particles of softened top coating medium by rotating the fixture about its axis of rotation, wherein the step includes heating the blades by passing the blades in front of the spray gun. The temperature of top coat application is the temperature measured at the substrate at the time of applying the top coating. The temperature of application may vary from three hundred to eight hundred and fifty degrees Fahrenheit (300 DEG F. to 850 DEG F.). The actual temperature of application is preferably maintained at a relatively constant level varying from about +/- five to ten percent (+/- 5% to 10%) of a predetermined temperature, depending upon the size of engine element coated, and the substrate on which the top coating is sprayed.

**[0035]** The step of passing the blades through the spray of softened particles includes the step of cooling the blades. Additionally, external cooling may be used to control deposition temperature.

**[0036]** This process results in layers of bond and top coating being sequentially deposited onto the blade tips in a surface of rotation substantially parallel to the surface of rotation which the blades describe when rotating in operating conditions. While the phenomenon is not well understood, it is believed that by depositing coating layers one at a time in an orientation substantially parallel to the surface of rotation that the coating layers will experience in an operating engine, the process confers an advantage as it provides relatively uniform microcracking of the coating in a radial direction. This results in relatively uniform stresses in the coating structure during operative conditions.

## Claims

1. A process for forming a thermal barrier coating comprising the steps of:

providing a substrate;  
providing a gadolinia stabilized zirconia powder;  
and  
forming a thermal barrier coating having at least one of a porosity in a range of from 5 to 20% and a dense segmented structure on said substrate by supplying the gadolinia stabilized powder to a spray gun and using an air plasma spray technique.

2. The process according to claim 1, wherein said substrate providing step comprises providing a combustor component.

3. The process according to claim 1, wherein said substrate providing step comprises providing one of a combustor panel, a combustor chamber, a combustor

tor heat shield, a combustor transition duct, and a combustor augmentor.

4. The process according to any preceding claim, wherein said powder providing step comprises providing a powder consisting of optionally from 3.0 to 14 wt% of at least one of yttria and titania, from 15 to 70 wt% gadolinia, and the balance zirconia.

5. The process according to claim 1, 2 or 3 wherein said powder providing step comprises providing a powder consisting of from 3.0 to 14 wt% of at least one of yttria and titanium, from 15 to 70 wt% gadolinia, and the balance zirconia.

6. The process according to any preceding claim, wherein said thermal barrier coating forming step comprises using an amperage range of 350 to 825 amps, a voltage of 35 to 50 volts, an argon primary gas flow of 75 to 105 SCFH, at least one of a hydrogen secondary gas flow of 1.0 to 10 SCFH and a helium secondary gas flow of 45 to 75 SCFH, a powder gas flow exiting a spray gun of 4.0 to 20 SCFH, a powder feed rate to the spray gun of 10 to 40 grams/min., and a gun distance from a surface of the substrate being coated of from 3.0 to 5.0 inches.

7. The process according to any one of claims 1 to 5, wherein said thermal barrier coating forming step comprises using an amperage range of from 500 to 700 amps, a voltage of 55 to 65 volts, an argon primary gas flow of 65 to 90 SCFH, a hydrogen secondary gas flow of 8 to 22 SCFH, a powder gas flow from a spray gun of 6 to 12 SCFH, a powder feed rate to the spray gun of 35 to 55 grams/min. and a gun distance from a surface of a substrate being coated of from 4.0 to 7.0 inches.

8. The process according to any preceding claim, further comprising depositing a ceramic interlayer on said substrate prior to said thermal barrier coating step.

9. The process according to claim 8, wherein said ceramic interlayer depositing step comprises depositing a layer of 7.0 wt% yttria stabilized zirconia.

10. The process according to claim 8 or 9, further comprising depositing a bondcoat layer on said substrate prior to said ceramic interlayer depositing step.

11. The process according to claim 10, wherein said bondcoat layer depositing step comprises depositing a metallic bondcoat layer.

12. The process according to any preceding claim, wherein said thermal barrier coating forming step comprises forming a segmented coating having a

thermal conductivity in the range of from 5.0 to 12.5  
BTU in/hr ft<sup>2</sup> F.

13. The process according to any preceding claim,  
wherein said thermal barrier coating forming step 5  
comprises forming a porous coating having a thermal  
conductivity in the range of from 3.0 to 10 BTU in/hr  
ft<sup>2</sup> F.

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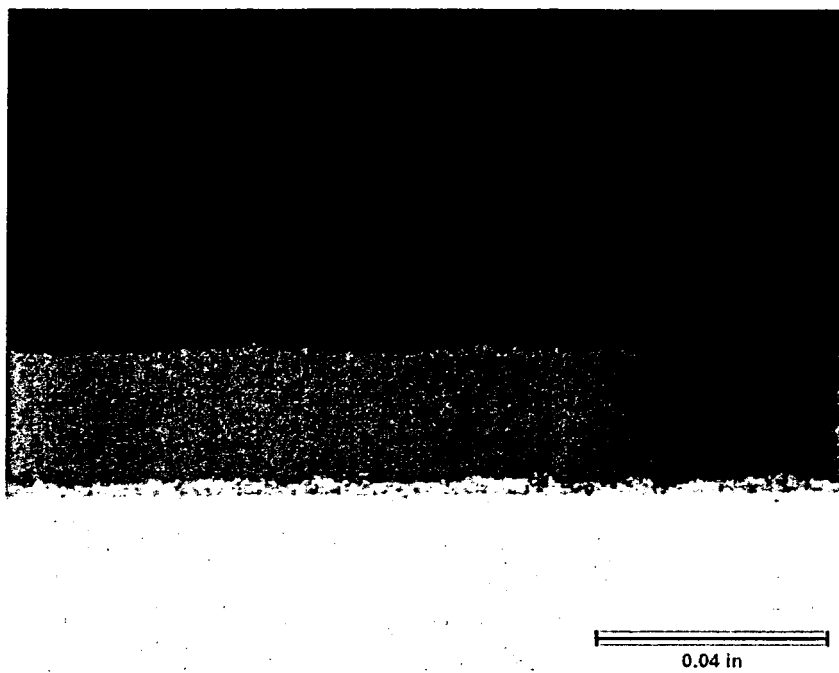
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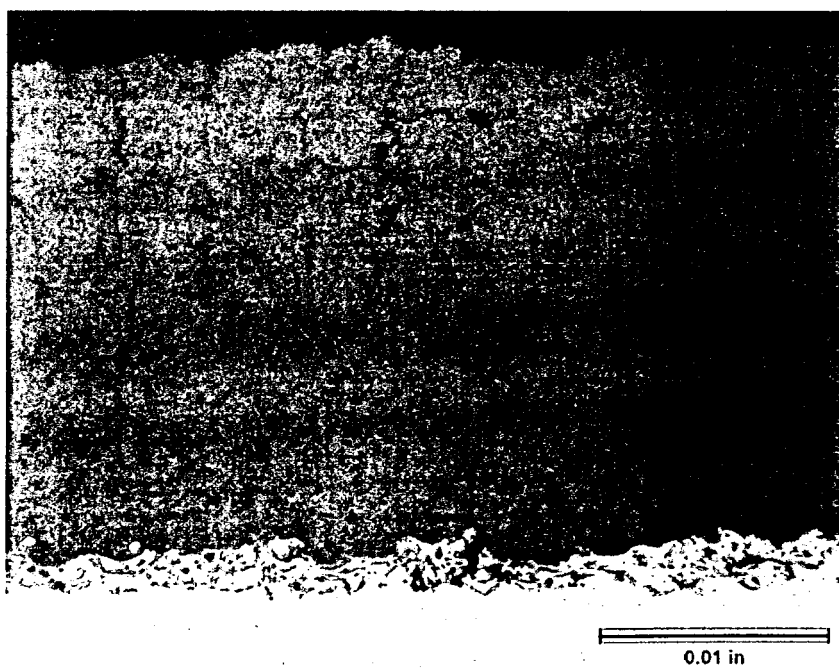
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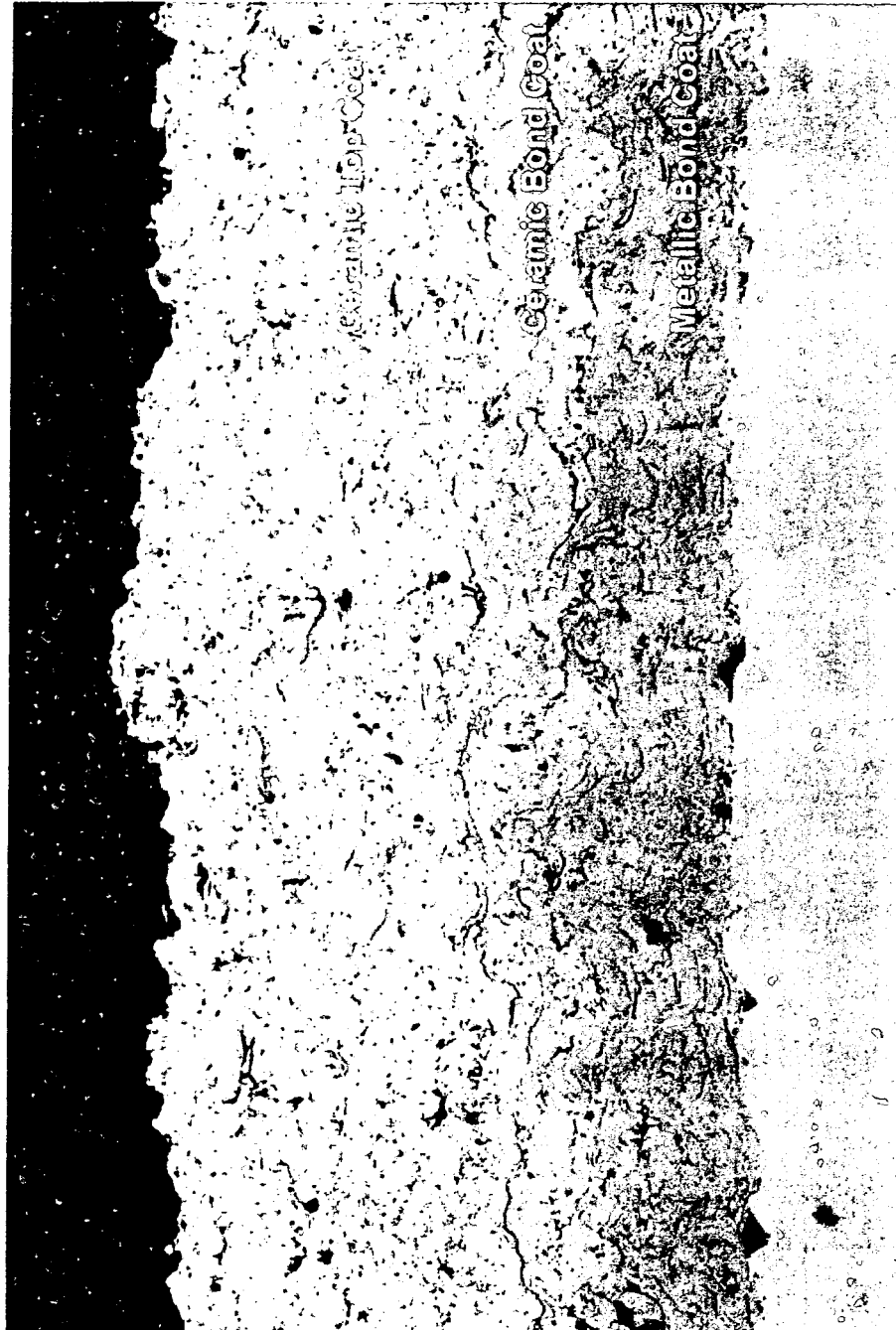
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*FIG. 1*



*FIG. 2*



*FIG. 3*





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Place of search The Hague		Date of completion of the search 7 December 2010	Examiner Chalaftris, Georgios
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