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1. A thermal barrier coating for substrates comprising zirconia partially stabilized by yttria and having a density greater than 88% of the theoretical density with a plurality of vertical macrocracks substantially homogeneously dispersed throughout the coating in which a cross-sectional area of the coating normal to the substrate exposes a plurality of vertical macrocracks with at least 70% of said vertical macrocrack extending at least 4 mils in length up to the thickness of the coating and having from 20 to 200 vertical macrocracks per linear inch measured in a line parallel to the surface of the substrate and in a plane perpendicular to the substrate.

13. A process for producing a thermal barrier coating having good thermal fatigue resistance comprising the steps:

a) thermally depositing zirconia-yttrium powder onto a substrate to form a monolayer having at least two superimposed splats of the deposited powders on the substrate in which the temperature of a subsequent deposited splat is higher than the temperature of a previously deposited splat;

b) cooling and solidifying said monolayer of step a) whereupon said monolayer has a density of at least 88% of the theoretical density and wherein a plurality of vertical cracks are produced in the monolayer due to shrinkage of the deposited splats;

c) repeating steps a) and b) at least once to produce an overall coated layer in which each monolayer has induced vertical cracks through the splats and wherein at least 70% of the vertical cracks in each monolayer are aligned with vertical cracks in an adjacent monolayer to form vertical macrocracks having a length of at least 4 mils up to the thickness of the coating and said coated layer having at least 20 vertical macrocracks per linear inch measured in a line parallel to the surface of the substrate and in a plane perpendicular to the substrate.

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(21) International Application Number: PCT/US90/06203 (22) International Filing Date: 22 October 1990 (22.10.90) (30) Priority data: 424,613 20 October 1989 (20.10.89) US (71) Applicant: UNION CARBIDE COATINGS SERVICE TECHNOLOGY CORPORATION [US/US]; 39 Old Ridgebury Road, Danbury, CT 06817 (US). (72) Inventor: TAYLOR, Thomas, Alan ; 5865 Winthrop Avenue, Indianapolis, IN 46220 (US). (74) Agent: BISHOP, Timothy, N.; Union Carbide Coatings Service Technology Corporation, Law Department - E134, 39 Old Ridgebury Road, Danbury, CT 06817 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 22 August 1991 (22.08.1991) 628 772
(54) Title: THERMAL BARRIER COATING FOR SUBSTRATES AND PROCESS FOR PRODUCING IT (57) Abstract A thermal barrier coating for substrates comprising zirconia partially stabilized by yttria and having a density greater than 88 % of the theoretical density with a plurality of vertical macrocracks homogeneously dispersed throughout the coating to improve its thermal fatigue resistance. The invention also discloses a process for producing the thermal barrier coating.		

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THERMAL BARRIER COATING FOR SUBSTRATES
AND PROCESS FOR PRODUCING IT

FIELD OF THE INVENTION

5 The invention relates to a thermal barrier coating and
process for producing such a coating for substrates intended
to operate in cyclic thermal environments, said coating
comprising zirconia partially stabilized by yttria and having
a substantial homogeneous dispersion of vertical macrocracks
throughout the coating to improve its thermal fatigue
10 resistance.

BACKGROUND OF THE INVENTION

Modern gas turbine engines operate in high temperature
environment in excess of 2000°F in which hot gases are
expanded across rows of turbine blades. Outer air seal or
15 shroud segments circumscribe the turbine blades to minimize
leakage of the gases over the tips of the blades. The use of
thermal barrier coatings on gas turbine blades and surfaces
such as such as shroud segments have been found to have
several advantages. Through the use of thermal barrier
20 coatings higher operating efficiency can be obtained because
less cooling air is required to maintain blade or shroud
temperatures. In addition, component life is extended since
the rate of change of metal temperature is reduced by the
insulating effect of the thermal barrier.

25 Zirconia based thermal barrier coatings, because of their
low thermal conductivity, are added to the surface of metal

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components to insulate them from the hot gas stream.

Stabilized zirconia was developed and used as a thermal barrier coating for turbine and shroud components. Coatings such as CaO stabilized zirconia, MgO stabilized zirconia and Y_2O_3 stabilized zirconia have been tested with Y_2O_3 partially stabilized zirconia providing the best results.

U.S. Patent 4,377,371 discloses an improved thermal shock resistance of a ceramic layer in which benign cracks are deliberately introduced to a plasma-sprayed ceramic layer.

The benign cracks are generated by scanning a laser beam over the plasma-sprayed ceramic surface where the ceramic material immediately beneath the beam melts to produce a thin fused layer. Shrinkage accompanying cooling and solidification of the fused layer produces a network of microcracks in the fused layer that resists the formation and growth of a catastrophic crack during thermal shock exposure. Another method disclosed for introducing fine cracks on the surface of a ceramic coating is to quench the surface of the ceramic while it is hot with an ethanol saturated paper pad.

An article published by the AIAA/SAE/ASME 16th Joint Propulsion Conference, June 30-July 2, 1980, Development of Improved-Durability Plasma Sprayed Ceramic Coatings for Gas Turbine Engines by I. E. Summer et al, discloses that the durability of plasma sprayed ceramic coatings subjected to cyclic thermal environment has been improved substantially by

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improving the strain tolerance of a ceramic structure and also by controlling the substrate temperature during the application of the coating. It further states that the improved strain tolerance was achieved by using ceramic structures with increased porosity, microcracking or segmentation.

In an article published by J. Vac. Sci. Technol. A3 (6) Nov/Dec 1985 titled Experience with MCrAl and Thermal Barrier Coatings Produced Via Inert Gas Shrouded Plasma Deposition, by T. A. Taylor et al, discloses the depositing of a ceramic oxide coating of ZrO_2 -7 wt% Y_2O_3 onto a coated substrate. The ceramic oxide coating is a thermal barrier coating which has intentionally imparted microcracks having an average spacing of about 15 microns and which are staggered from layer to layer of the coating.

It is an object of the present invention to provide a thermal barrier coating for components intended to be used in cyclic thermal environments in which the thermal barrier coating has deliberately produced macrocracks homogeneous dispersed throughout the coating to improve its thermal fatigue resistance.

It is another object of the present invention to provide a thermal barrier coating for components of turbine engines in which the coating is composed of zirconia partially stabilized by yttria and in which the coating has a density greater than

about 88% of theoretical.

It is another object of the present invention to provide a thermal barrier top coating over a bond coating of an alloy containing chromium, aluminum, yttrium with a metal selected from the group consisting of nickel, cobalt and iron.

It is another object of the present invention to provide a thermal barrier coating for gas turbine blades, vanes and seal surfaces exposed in the hot section of gas turbine engines.

It is another object of the present invention to provide a process for producing a thermal barrier coating having good thermal fatigue resistance.

SUMMARY OF THE INVENTION

The invention relates to a thermal barrier coating for protecting a substrate such as blades, vanes and seal surfaces of gas turbine engines, said coating comprising zirconia partially stabilized by yttria, having a density greater than 88% of the theoretical density, and having a plurality of vertical macrocracks substantially homogeneously dispersed throughout the coating in which a cross-section area of the coating normal to the surface of substrate exposes a plurality of vertical macrocracks with at least 70%, preferably at least 90%, of said macrocracks extending at least 4 mils, preferably 8 mils, in length up to the thickness of the coating and having 20 to 200 vertical macrocracks, preferably from 75 to 100 vertical macrocracks, per linear inch measured in a line

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parallel to the surface of the substrate and in a plane perpendicular to its substrate. The length of at least 70%, preferably 90%, of the vertical macrocracks should extend at least 4 mils so that they pass through at least 50 splats of the deposited powder.

The invention also relates to a process for producing a thermal barrier coating having good thermal fatigue resistance comprising the steps:

a) thermally depositing zirconia-yttria powders onto a substrate to form a monolayer having at least two superimposed splats of the deposited powders on the substrate in which the temperature of a subsequent deposited splat is higher than the temperature of a previously deposited splat;

b) cooling and solidifying said monolayer wherein said monolayer has a density of at least 88% of the theoretical density and wherein a plurality of vertical cracks are produced in the monolayer due to shrinkage of the deposited splats;

c) repeating steps a) and b) at least once to produce an overall coated layer in which each monolayer has induced vertical cracks through the splats and wherein at least 70% of the vertical cracks in each monolayer are aligned with vertical cracks in an adjacent monolayer to form vertical macrocracks having a length of at least 4 mils up to the thickness of the coating and said coated layer having at

least 20 vertical macrocracks per linear inch measured in a line parallel to the surface of the substrate.

As used herein, a splat shall mean a single molten powder particle impacted upon the surface of the substrate wherein it spreads out to form a thin platelet. Generally these platelets are from 5 to 100 microns in diameter and 1 to 5 microns thick, more generally about 2 microns thick.

As used herein, a vertical macrocrack is a crack in the coating if extended to contact the surface of the substrate will form an angle of from 30° to 0° with a line extended from said contact point normal to the surface of the substrate. Preferably, the vertical macrocracks will form an angle of 10° to 0° with the normal line. In addition to vertical macrocracks, one or more horizontal macrocracks may develop in the coating. Preferably, the coating should have no horizontal macrocracks. A horizontal macrocrack is a crack forming an angle of from 10° to 0° with a plane bisecting said crack and disposed parallel to the surface of the substrate. If present, the horizontal macrocracks preferably should not extend to contact more than one vertical macrocrack since to do so could weaken the coating and subject the coating to spalling. The length dimension of the vertical macrocrack and the length dimension of the horizontal macrocrack is the straight line distance from one end of the crack to the opposite end of the crack. The length of the horizontal macrocrack, if present, could be from about

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5 to 25 percent of the average length of the vertical macrocracks on both sides of the horizontal macrocrack.

For most applications, the density of the coating preferably should be between 90% and 98% of the theoretical density and most preferably about 92 percent of the theoretical density. The vertical macrocracks are formed in the coating by plasma depositing powders of the coating onto the surface of the substrate in discrete monolayers in which the thickness of each monolayer contains at least two superimposed splats of the deposited powder (about 0.16 mils) and preferably from about four to five splats of the deposited powder (from about 0.32 mils and 0.40 mils, respectively). Although not bound by theory, it is believed that the deposit of two or more superimposed splats of the powder will result in the second and subsequent splats being deposited at higher temperatures than the preceding splats. This is due to the fact that the first splat of the powder is deposited on a relatively colder substrate while the second and subsequent splats are deposited on preceding splats that are progressively hotter. Thus the overall deposit of two or more splats results in a temperature gradient with the higher temperature at the top surface. Upon cooling and solidification of the monolayer deposit, the second and subsequent splats shrink more than the preceding splats and form vertical microcracks through the deposited layer. Additional monolayers are

superimposed on the substrate with each monolayer forming vertical macrocracks which have a tendency to align with the previously formed macrocracks in the preceding monolayers. This effectively produces some macrocracks that extend
5 substantially through the thickness of the coating. The width of the vertical macrocracks, i.e., the distance between opposing faces defining the vertical macrocracks, is generally less than about 1 mil, preferably less than 1/2 mil.

It has been found that if the density of coating is less
10 than 88% of the theoretical density, the stress caused by the shrinkage of splats in the monolayer may be absorbed or compensated by the porosity of the coating. This will effectively prevent the formation of macrocracks throughout the coating as is required according to this invention and
15 prevent producing a coating with good thermal fatigue resistance. The substantial homogeneous distribution of vertical macrocracks throughout the coating as required by this invention will reduce the modulus of elasticity of the coating structure thereby reducing the local stresses. This results
20 in excellent thermal fatigue resistance for the coating that enables it to function without failure in cyclic thermal environments.

The density of the vertical macrocracks should be preferably 75 or more, most preferably 100 or more, vertical
25 macrocracks per linear inch taken in a cross-section plane

of the coating along a line parallel to the surface of the substrate. This will insure that sufficient vertical macrocracks are present in the coating to provide good thermal fatigue resistance. To obtain the necessary vertical macrocracks in this coating, the plasma apparatus should be of high efficiency and stable over the period of depositing the coating. The spray torch should be positioned at a fixed distance from the substrate and the relative speed between the torch and the substrate should be controlled to insure that the monolayer instantly put down by one sweep of the torch will be sufficient to produce overlap of the deposited splats of powder in which the second and subsequent deposited splats are hotter than the preceding deposited splats for the reason discussed above. The overall thickness of the coating can vary depending on the end use application. For components of gas turbine engines, the coating thickness can vary from 0.003 to 0.10 inch. The preferred zirconia partially stabilized by yttria would be 6 to 8 weight percent yttria with the balance zirconia and most preferably about 7 weight percent yttria with the balance substantially zirconia. The thermal barrier coating of this invention is ideally suited as a top coat for a metallic bond coated substrate such as blades, vanes and seals of gas turbine engines. The preferred metallic bond coating would comprise an alloy containing chromium, aluminum, yttrium with a metal selected from the group consisting of

nickel, cobalt and iron. This bond coating can be deposited using conventional plasma spray techniques or any other conventional technique. The substrate could be any suitable material such as a nickel-base, cobalt-base or iron-base alloy.

While the preferred embodiment of the invention has been described, it will be appreciated that various modifications may be made to the thermal barrier coating without departing from the spirit or scope of the invention.

Thermal Fatigue Test

Cyclic thermal exposure can help distinguish between a number of candidate thermal barrier coatings with regard to thermal fatigue resistance. A good thermal barrier coating must be able to survive a large number of thermal cycles to high temperature without spalling if it is to be useful in service.

To test the samples of this invention, a round metal alloy disc coated with a thermal barrier coating on one face was fabricated. The coated face was exposed to a high heat flux gas burner while the metal back face was allowed to cool by convection in air. The apparatus was automated with timers and a stepping motor which place the coated disc in the flame of a gas burner for a fixed time then move it out of the flame and to a second position where an air blast cools the coated face. The time at each position is adjustable, as well as the maximum temperature reached at the heating position. In the test work described herein the fixed variables of the test were as follows:

- 20 seconds heating to 2550°F (average maximum temperature measured on the thermal barrier coated face) wherein the back metal face reaches about 1400°F, followed by
- 20 seconds blast air cooling to about 1500°F, followed by

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- 40 seconds natural convection cooling to 850°F
(average minimum temperature measured on the
thermal barrier coated face)
--2000 heating/cooling cycles constitutes the full
test.

The thermal barrier coated layer thicknesses and
compositions were as follows:

- 6 to 8 mil thick bond coating of Co-32N-21Cr-8Al-0.5Y
composition and
--43 to 47 mil thick topcoat of a thermal barrier layer
of ZrO_2 -6 to 8 weight percent Y_2O_3 composition.

Before starting the thermal test, the edge of the coated
disk was polished so that the thermal barrier coating would
display any separation cracks that might be induced by the
thermal test. These separation cracks are horizontal cracks
within the thermal barrier layer that are visible at the
polished edge. Usually, if a coating is susceptible to this
cracking, a number of short horizontal crack segments are seen
to grow and link up around the edge circumference of the
thermal barrier layer. Usually the location of these cracks
is within 5 to 15 mils of the bond coat interface. The
lengths of these individual or linked cracks are measured
after the thermal test. A stereoscopic microscope at 30X
magnification is used to detect all such cracks. The total
length of edge cracks is expressed as a percentage of the

circumference length; i.e., 100% edge cracking would have a visible crack fully around the entire edge circumference. In some cases where 100% edge cracking would occur, the thermalbarrier layer could spall off. In other cases, it remains bonded by uncracked areas deeper into the coating. In either case, 100% or other high percentage edge cracking results are taken as indicative of poor thermal fatigue resistance of that particular thermal barrier specimen. Thermal barrier coatings that have a low percentage of edge cracking at the conclusion of the test are considered to have good thermal fatigue resistance. Thermal barrier coatings that have zero percent edge cracking at the end of the test are considered to have outstanding thermal fatigue resistance.

EXAMPLE 1

In this example, three different zirconium-yttrium oxide thermal barrier coatings (Samples A, B, and C) were prepared to have different macrocrack structures and then subjected to the thermal cycle test. All coatings were made from the same starting powder having the following characteristics shown in Table 1.

TABLE 1Powder Characteristics

Composition: 7.11 wt.% Y_2O_3 , 0.23 SiO_2 ,
0.15 TiO_2 , 0.07 Al_2O_3 , 0.09 Fe_2O_3 ,
balance ZrO_2

Type powder: fused and crushed

Size analysis:	+ 200 mesh	0.0 wt. percent
	+ 230 mesh	0.0 wt. percent
	+ 325 mesh	18.55 wt. percent
	- 325 mesh	81.45 wt. percent

Using Microtrac^e analysis, the mean particle diameter size was found to be 40.95 microns.

^eMicrotrac powder size analysis instrument, Model 7995-11 by Leeds and Northrup Co.

All three coatings were deposited on 1 inch diameter x 1/8 inch thick Inconel 718 discs. All sample discs had a 6 mil bond undercoat of a plasma sprayed alloy of Co-32Ni-21Cr-8Al-0.5Y.

A number of specimens were made for each sample. A specimen of each sample was mounted on edge in epoxy resin, cured under pressure, then polished in cross-section so that the structure could be quantitatively analyzed. The high pressure epoxy cure

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allows penetration of epoxy into the somewhat porous zirconium-yttrium oxide layer which then better preserves the nature of the structure during abrasive polishing. The specimens were examined at 100X using a Leitz Orthoplan microscope, for an analysis of the microcrack structure. Separate specimens of the thermal barrier layer samples were carefully removed from the substrates and measured for their density. The density procedure using the water immersion method is described in ASTM B-328. All were sprayed with the same Union Carbide plasma torch, Model 1108. Certain torch operating parameters, standoff distance from torch to substrate and substrate velocity past the torch spray were changed in this example, to show how superior thermal fatigue resistance can be achieved. The properties and test data for each sample specimen are shown in Tables 2, 3, and 4.

TABLE 2Plasma Spray Conditions⁺

Sample	Total coating thickness, mils	Powder* Feedrate	Torch Current, (amps)	Standoff (in)	Substrate** velocity	Monolayer Height (mils)	Final Coating Temperature
A	45	90	150	0.75	6,000	0.16	317°F
B	45	90	150	0.75	12,000	0.07	341°F
C	45	50	170	0.87	2,750	0.34	472°F

* grams/minute

** inches/minute

⁺The primary torch gas flows for each sample was:

90 cfh torch gas, 90 cfh powder carrier (both argon), and 40 cfh auxiliary (hydrogen).

TABLE 3Thermal Barrier Layer Properties

<u>Sample</u>	<u>Density (gm/cm³)</u>	<u>% of Theoretical Density*</u>	<u>Vertical cracks length, (mils)</u>	<u>Vertical Macrocracks per Inch laterally</u>	<u>Horizontal Branch cracks length, (mils)</u>
A	5.471	90.29	4 - 10	77.6	1 - 2
B	5.485	90.53	0	0.0	0
C	5.539	91.42	20 - 40	86.4	2 - 4

*** Theoretical density is the density of the pore-free materials, 6.059 gm/cm³ for ZrO₂ - 7.11 wt. % Y₂O₃, as derived from Ingel and Lewis, "Lattice Parameters and Density for Y₂O₃ - Stabilized ZrO₂", J. Am. Ceramic Society, Vol. 69, No. 4, p. 325, April, 1986.

TABLE 4Thermal Fatigue Test Results

<u>Sample</u>	<u>% Edge Cracks after 2000 Cycles</u>
A1	32
A2	0
B1	100*
B2	100
C1	0

* Failed early, after approximately 900 cycles.

The test results showed Sample C had the best thermal fatigue resistance with no edge cracking after the test. Sample A was intermediate with specimen A1 having 32% edge cracking and

specimen A2 having 0%. Sample B was the worst having 100% edge cracking, and specimen B1 failing even before the end of the test.

5 Samples A and B can be compared to see the effect of the macrocracks in the coating structure. The densities of A and B are essentially the same. The torch operating parameters were the same, and the final coating temperatures were essentially the same. The substantial difference was that Sample A was coated with a 6,000 in/min substrate velocity and Sample B with 10 12,000 in/min. This was done to provide different buildup rates of the thermal barrier layers on the samples. The monolayer height of Sample A was 0.16 mils while that of Sample B was only 0.07 mils. The higher monolayer height on Sample A created sufficient stress in the $ZrO_2-Y_2O_3$ coating layer to 15 produce macrocracks throughout the coating of Sample A. Sample A had about 77.6 cracks/inch on average, while Sample B, coated at the lower monolayer height had no cracks. With all other coating properties the same, the presence of the high number of macrocracks in Sample A is responsible for the much better 20 thermal fatigue resistance, compared to Sample B which had no macrocracks.

25 Sample C is a case where the results of Samples A and B were applied to further control the macrocrack structure. In this case slightly higher torch current was used in order to increase deposition efficiency so that a lower powder feedrate to the

torch would produce about the same coating volume deposited per minute on the sample specimen. A substantial change was also made to substrate velocity in order to produce an even higher monolayer height which induced even more macrocracking in the coating. Sample C was coated at 2750 inches/minute substrate velocity. Sample C had a 0.34 mil monolayer height and 86.4 vertical macrocracks per inch on average. After the 2000 cycle thermal test no edge cracking was found upon examination. This study showed that macrocracks can be inducted into the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ coating by proper control of the coating parameters and that macrocracks are critical to the success of the coating in a thermal fatigue environment.

EXAMPLE 2

In this example, the coating parameters of Sample C of Example 1 were repeated with an entirely new setup. The powder characteristics of that coating material are shown in Table 5.

TABLE 5Powder Characteristics

Composition: 7.03 wt% Y_2O_3 , 0.33 SiO_2 ,
0.15 TiO_2 , 0.093 Al_2O_3 ,
0.09 Fe_2O_3 , balance ZrO_2

Type Powder: Fused and crushed

Size Analysis: +200 mesh 0.0 wt percent
+230 mesh 0.0 wt percent
+325 mesh 19.09 wt percent
-325 mesh 80.87 wt percent

Using Microtrac analysis, the mean particle diameter size was found to be 39.61 microns.

Two of the same type 1-inch diameter disc substrates were coated, again with the same undercoat as in Example 1. The torch parameters were the same as for Sample C, Example 1. One sample was coated with a slight variation on the standoff distance from torch to substrate as shown in Table 6.

TABLE 6Plasma Spray Conditions

<u>Sample</u>	<u>Powder Feed Rate (gm/min)</u>	<u>Torch Current (amps)</u>	<u>Standoff (inches)</u>	<u>Substrate Velocity (in/min)</u>
D	50	170	0.87	2750
E	50	170	1.0	2800

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Cross-sectioned polished areas of each sample prior to thermal testing were examined using the optical microscope. Coating density was measured on separate samples as before. The data obtained are shown in Table 7. The coating characteristics of Samples D and E are comparable to Sample C, Example 1, and show that the macrocracks homogeneously produced throughout the coating can be reproducibly obtained.

TABLE 7Coating Characteristics

<u>Sample</u>	<u>Density (gm/cm³)</u>	<u>Density percent of Theoretical</u>	<u>Vertical macrocracks per inch</u>	<u>Vertical macrocrack length (mils)</u>	<u>Horizontal branch crack length (mils)</u>
D**	5.55	91.6	79.7	23.7	4
E	5.52	91.1	73.1	29.0	3

*Crack length and spacing values are an average of 30 or more measurements.

**Sample D also had several examples of horizontal branching cracks extending to contact two adjacent vertical macrocracks.

As shown in Table 7, Sample D, coated at slightly closer standoff, obtained a slightly higher density, slightly more vertical macrocracks per inch, but also had slightly longer

horizontal branching cracks connected to the vertical macrocracks. In fact, Sample D had several examples of horizontal branching cracks extending to contact two adjacent vertical macrocracks.

5 The disc specimens were tested the same as in Example 1 using the thermal cycle test for 2000 cycles. The data obtained are shown in Table 8.

TABLE 8

Thermal Fatigue Test Results

10

<u>Sample</u>	<u>% Edge Cracks after 2000 Cycles</u>
D	12
E	1

15

The results were again good for these samples prepared under thermal spraying conditions that would produce macrocracks. Any result of less than 15% edge cracking is considered excellent in this very severe thermal cycle test.

20

The results for Sample D in the thermal cycle test are good but not as outstanding as for Sample E. Table 7 shows that Sample D and E are very similar in characteristics, except that Sample D had instances where it had horizontal branching cracks that extended to contact two adjacent vertical macrocracks. This observation leads to the conclusion that it is preferable to minimize the extent of the horizontal cracks, in order to obtain excellent thermal fatigue resistance.

25

What Is Claimed

1. A thermal barrier coating for substrates comprising zirconia partially stabilized by yttria and having a density greater than 88% of the theoretical density with a plurality of vertical macrocracks substantially homogeneously dispersed throughout the coating in which a cross-sectional area of the coating normal to the substrate exposes a plurality of vertical macrocracks with at least 70% of said vertical macrocrack extending at least 4 mils in length up to the thickness of the coating and having from 20 to 200 vertical macrocracks per linear inch measured in a line parallel to the surface of the substrate and in a plane perpendicular to the substrate.

2. The thermal barrier coating of Claim 1 wherein the density is from 90% to 98% of the theoretical density and wherein at least 90% of said vertical macrocracks extend at least 8 mils in length.

3. The thermal barrier coating of Claim 1 or 2 wherein said coating has about 75 vertical macrocracks per linear inch measure in a line parallel to the surface of the substrate and in a plane perpendicular to the substrate.

4. The thermal barrier coating of Claim 3 wherein said coating has about 100 vertical macrocracks per linear inch measured in a line parallel to the surface of the substrate and in a plane perpendicular to the substrate.

5. The thermal barrier coating of Claim 1 or 2 wherein said coating contains one or more horizontal macrocracks extending within the coating parallel to the surface of the substrate.

6. The thermal barrier coating of Claim 5 wherein the horizontal macrocracks do not contact more than one vertical macrocrack.

7. The thermal barrier coating of Claim 1 or 2 wherein the width of the vertical macrocracks is less than 1 mil.

8. The thermal barrier coating of Claim 1 or 2 wherein the density is greater than 90% of the theoretical density and the coating has at least 75 vertical macrocracks per linear inch measured in a line parallel to the surface of the substrate and in a plane perpendicular to the substrate.

9. The thermal barrier coating of Claim 1 or 2 wherein the coating comprises 6 to 8 weight percent yttria balance substantially zirconia.

10. The thermal barrier coating of Claim 9 wherein a bond coating is deposited between the substrate and the thermal barrier coating, said bond coating comprising an alloy containing chromium, aluminum, yttrium with a metal selected from the group consisting of nickel, cobalt and iron.

11. The thermal barrier coating of Claim 10 wherein the density is at least 90% of the theoretical density and the coating has at least 100 vertical macrocracks per linear inch

measured in a line parallel to the surface of the substrate and in a plane perpendicular to the substrate.

12. The thermal barrier coating of Claim 11 wherein said thermal barrier coating thickness is from 0.003 to 0.10 inch.

13. A process for producing a thermal barrier coating having good thermal fatigue resistance comprising the steps:

a) thermally depositing zirconia-yttrium powder onto a substrate to form a monolayer having at least two superimposed splats of the deposited powders on the substrate in which the temperature of a subsequent deposited splat is higher than the temperature of a previously deposited splat;

b) cooling and solidifying said monolayer of step a) whereupon said monolayer has a density of at least 88% of the theoretical density and wherein a plurality of vertical cracks are produced in the monolayer due to shrinkage of the deposited splats;

c) repeating steps a) and b) at least once to produce an overall coated layer in which each monolayer has induced vertical cracks through the splats and wherein at least 70% of the vertical cracks in each monolayer are aligned with vertical cracks in an adjacent monolayer to form vertical macrocracks having a length of at least 4 mils up to the thickness of the coating and said coated layer having at least 20 vertical macrocracks per linear inch measured in a line parallel to the surface of the substrate and in a plane perpendicular to the substrate.

14. The process of Claim 13 wherein in step a) said powder comprises 6 to 8 weight percent yttria balance substantially zirconia.

15. The process of Claim 13 wherein in step a) the monolayer comprises at least 5 superimposed splats.

16. The process of Claim 13 wherein in step b) the density is at least 90% of the theoretical density.

17. The process of Claim 15 or 16 wherein the coating in step c) has from 20 to 200 vertical macrocracks per linear inch measured in a line parallel to the surface of the substrate and in a plane perpendicular to the substrate.

18. The process of Claim 15 or 16 wherein the substrate in step a) comprises a bond coated substrate wherein the bond coating comprises an alloy containing chromium, aluminum, yttrium with a metal selected from the group consisting of nickel, cobalt, and iron.

19. The process of Claim 18 wherein in step c) the length of the vertical macrocracks is at least 8 mils up to the thickness of the coating.

20. The process of Claim 19 wherein in step c) the thickness of the coating is from 0.003 to 0.10 inch.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/06203

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 23 C 4/10, C 23 C 4/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 23 C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US, A, 4457948 (DUANE L. RUCKLE) 3 July 1984 see claims 1-6; column 4, lines 50-54; column 6, lines 34-65; column 8, lines 6-16 ---	1-4,7-12
A	GB, A, 2100621 (UNITED TECHNOLOGIES CORP.) 6 January 1983 see claims 1-8; page 2, left-hand column, lines 15-19 ---	1,9,10
A	DE, A, 2028050 (METALLGESELLSCHAFT) 16 December 1971 see claims 1,8 ---	13
A	FR, A, 1049255 (PECHINEY) 29 December 1953 ---	
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¹⁰ Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
10th June 1991	24. 07. 91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	Mme Dagmar FRANK	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	Patent Abstracts of Japan, volume 13, no. 42 (C-564)(3390), 30 January 1989 & JP, A, 63241153 (TOSHIBA CORP.) 6 October 1988 -----	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9006203
SA 44062

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 18/07/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4457948	03-07-84	None	
GB-A- 2100621	06-01-83	DE-A, C 3224305	03-02-83
		FR-A- 2508493	31-12-82
		JP-B- 1001551	11-01-89
		JP-C- 1527481	30-10-89
		JP-A- 58016094	29-01-83
DE-A- 2028050	16-12-71	None	
FR-A- 1049255		None	