

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : F02B 75/08, B05D 1/36, 7/14, B22F 3/24, B32B 15/00, 18/00, C23C 8/10, 16/00, 16/22, 16/30	A1	(11) International Publication Number: WO 96/31687 (43) International Publication Date: 10 October 1996 (10.10.96)
(21) International Application Number: PCT/US96/03685 (22) International Filing Date: 18 March 1996 (18.03.96) (30) Priority Data: 08/417,578 6 April 1995 (06.04.95) US 08/417,580 6 April 1995 (06.04.95) US (71) Applicant: GENERAL ELECTRIC COMPANY [US/US]; 1 River Road, Schenectady, NY 12345 (US). (72) Inventors: HASZ, Wayne, Charles; R.D. #1, Box 376, Pownal, VT 05261 (US). BOROM, Marcus, Preston; Apartment B37, 1197 Hillside Avenue, Niskayuna, NY 12309 (US). JOHNSON, Curtis, Alan; 379 Vly Road, Schenectady, NY 12309 (US). (74) Agents: STECKLER, Henry, I. et al.; General Electric Company, 3135 Easton Turnpike W3C, Fairfield, CT 06431 (US).		(81) Designated States: CH, DE, JP, KR. Published <i>With international search report.</i>
(54) Title: METHOD AND COMPOSITE FOR PROTECTION OF THERMAL BARRIER COATING WITH AN IMPERMEABLE BARRIER COATING (57) Abstract A method and composite are provided for protecting thermal barrier coatings deposited on parts from the deleterious effects of environmental contaminants at operating temperatures. The method and composite use an impermeable barrier coating with the thermal barrier coating, where the impermeable barrier coating prevents environmental contaminants and resulting contaminant compositions from infiltrating openings in thermal barrier coatings during service at operating temperatures.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

- 1 -

METHOD AND COMPOSITE FOR
PROTECTION OF THERMAL BARRIER
COATING WITH AN IMPERMEABLE
BARRIER COATING

FIELD OF THE INVENTION

5 This invention relates to a method and
composite for protecting thermal barrier coatings at
operating temperatures from degradation caused by
environmental contaminants. More specifically, the
invention relates to the method and composite using an
10 impermeable coating on a thermal barrier coating,
where the impermeable coating reduces infiltration of
liquid contaminant compositions into the thermal
barrier coatings.

BACKGROUND OF THE INVENTION

15 Thermal barrier coatings are deposited onto
gas turbine and other heat engine parts to reduce heat
flow and to limit the operating temperature of metal
parts. These coatings generally are a ceramic
material, such as chemically stabilized zirconia.
Yttria-stabilized zirconia, scandia-stabilized
20 zirconia, calcia-stabilized zirconia, and magnesia-
stabilized zirconia are contemplated as thermal
barrier coatings. The thermal barrier coating of
choice is a yttria-stabilized zirconia ceramic
coating. A typical thermal barrier coating comprises
25 about 8 weight percent yttria-92 weight percent
zirconia. The thickness of a thermal barrier coating
depends on the application, but generally ranges
between about 5-60 mils thick for high temperature
engine parts.

- 2 -

Metal parts provided with thermal barrier coatings can be made from nickel, cobalt, and iron based superalloys. The process is especially suited for parts and hardware used in turbines. Examples of turbine parts would be turbine blades, buckets, nozzles, combustion liners, and the like.

Thermal barrier coatings are a key element in current and future gas turbine engine designs expected to operate at high temperatures which produce high thermal barrier coating surface temperatures. The ideal system for a hot high temperature engine part consists of a strain-tolerant thermal barrier ceramic layer deposited onto a bond coat which exhibits good corrosion resistance and closely matched thermal expansion coefficients.

Under service conditions, thermal barrier coated engine parts can be susceptible to various modes of damage, including erosion, oxidation, and attack from environmental contaminants. At temperatures of engine operation adherence of these environmental contaminants on the hot thermal barrier coated surface can lead to damage to the thermal barrier coating. Environmental contaminants form compositions, which are liquid at the surface temperatures of thermal barrier coatings.

Chemical and mechanical interactions occur between the contaminant compositions and the thermal barrier coatings. Molten contaminant compositions can dissolve the thermal barrier coating or can infiltrate its pores and openings, initiating and propagating cracks causing delamination and loss of thermal barrier coating material.

Some environmental contaminant compositions that deposit on thermal barrier coated surfaces

- 3 -

contain oxides of calcium, magnesium, aluminum, silicon, and mixtures thereof. These oxides combine to form contaminant compositions comprising calcium-magnesium-aluminum-silicon-oxide systems (Ca-Mg-Al-Si-O), herein referred to as CMAS. Damage to thermal barrier coatings occurs when the molten CMAS infiltrates the thermal barrier coating. After infiltration and upon cooling, the molten CMAS, or other molten contaminant composition, solidifies. The stress build up in the thermal barrier coating is sufficient to cause spallation of the coating material and loss of the thermal protection that it provides to the underlying part.

There is a need to reduce or prevent the damage to thermal barrier coatings caused by the reaction or infiltration of molten contaminant compositions at the operating temperature of the engine. This can be accomplished by covering the thermal barrier coating with an impermeable barrier that prevents liquid contaminant compositions when they form on the hot surfaces of thermal barrier coated parts from reacting or flowing into the thermal barrier coating.

SUMMARY OF THE INVENTION

The present invention satisfies this need by protecting a thermal barrier coating from degradation by environmental contaminant compositions which form on and adhere to a surface of a thermal barrier coated part. The method of the invention comprises depositing an impermeable coating on the surface of thermal barrier coating, in an effective amount, so that the impermeable coating inhibits liquid contaminant compositions formed from the

- 4 -

environmental contaminants from infiltrating into or reacting with the thermal barrier coating at the operating temperature of said thermal barrier coating. The impermeable barrier is a dense, non-cracked, non-porous layer comprising oxides, non-oxides, or
5 metallic coatings in conjunction with thermal barrier coatings.

The present invention also satisfies this need by providing a composite comprising a thermal
10 barrier coating on a part with a continuous impermeable barrier coating on the outer surface of the thermal barrier coating. The invention also includes a protected thermal barrier coated part comprising a part with a thermal barrier coating on
15 said part and a single protective layer of an impermeable barrier coating on an outer surface of said thermal barrier coating. The composite thermal barrier coating according to the present invention also comprises a substrate with a thermal barrier
20 coating, an impermeable barrier coating, and when needed a bond coat between the substrate and the thermal barrier coating.

Environmental contaminants are materials that exist in the environment and are ingested into
25 engines, from air and fuel sources, and impurities and oxidation products of engine components, such as iron oxide.

The term "operating temperature" means the surface temperature of the thermal barrier coating
30 during its operation in a given application, such as a gas turbine engine. Such temperatures are above room temperature, and generally are above 500°C. High temperature operation of thermal barrier coating parts is usually above about 1000°C.

- 5 -

DESCRIPTION OF THE INVENTION

It has been discovered that the degradation of thermal barrier coatings by environmental contaminants that form molten contaminant compositions can be prevented by depositing impermeable barrier coatings that are dense and non-cracked on surfaces of thermal barrier coatings. An impermeable barrier coating inhibits the degradation of the thermal barrier coating when in contact with the molten contaminant composition at operating temperatures of the thermal barrier coating.

Infiltration or viscous flow of the contaminant composition into thermal barrier coating cracks, openings, and pores is prevented. This invention also protects the thermal barrier coating from dissolution or spallation due to chemical and mechanical attack by the contaminant composition. The liquid contaminant composition is unable to penetrate the impermeable coating, and therefore can not attack the thermal barrier coating. The barrier coating enhances the life of the thermal barrier coated part and thus, reduces thermal barrier coated part failure.

Sources of environmental contaminants include, but are not limited to, sand, dirt, volcanic ash, fly ash, cement, runway dust, substrate impurities, fuel and air sources, oxidation products from engine components, and the like. The environmental contaminants adhere to the surfaces of thermal barrier coated parts. At the operating temperatures of the thermal barrier coating, the environmental contaminants then form contaminant compositions on surfaces of the thermal barrier coating which may have melting ranges or temperatures at or below the operating temperature.

- 6 -

In addition, the environmental contaminant may include magnesium, calcium, aluminum, silicon, chromium, iron, nickel, barium, titanium, alkali metals, and compounds thereof, to mention a few. The environmental contaminants may be oxides, phosphates, carbonates, salts, and mixtures thereof.

The chemical composition of the contaminant composition corresponds to the composition of the environmental contaminants from which it is formed. For example, at operational temperatures of about 1000°C or higher, the contaminant composition corresponds to compositions of calcium-magnesium-aluminum-silicon oxide system or CMAS. Generally, the environmental contaminant compositions known as CMAS comprise primarily a mixture of magnesium oxide (MgO), calcium oxide (CaO), aluminum oxide (Al₂O₃), and silicon oxide (SiO₂). Other elements, such as nickel, iron, titanium, and chromium, may be present in the CMAS in minor amounts when these elements or their compounds are present in the environmental contaminants. A minor amount is an amount less than about ten weight percent of the total amount of contaminant composition present.

The protective coatings of this invention can be described as impermeable or impervious in that they prevent the liquid contaminant composition from contacting the thermal barrier coating so that chemical or physical changes of the thermal barrier coating do not occur due to infiltration or reaction with the contaminant composition. Thus, the character of the protective coating is dense and non-penetratable. The result is that infiltration of the contaminant composition, e.g., liquid CMAS, into the

- 7 -

thermal barrier coating at operating temperatures of engines is eliminated or decreased.

Such an impermeable or impervious coating is a ceramic or metal outer coating, deposited on the
5 outer surface of the thermal barrier coating. The impermeable coating acts as a barrier between the thermal barrier coating and the contaminant eutectic mixture; it is dense and non-porous.

Impermeable barrier coatings can be various
10 oxides; non-oxides such as carbides, silicides, and nitrides; and metals that form non-porous deposits. The metal oxide coating may be selected from the group consisting of silicon oxide, tantalum oxide, scandium oxide, aluminum oxide, hafnium oxide, zirconium oxide,
15 calcium zirconate, and spinels, such as magnesium aluminum oxide, and mixtures thereof. The metal carbide coating may be selected from the group consisting of silicon carbide, tantalum carbide, titanium carbide, tungsten carbide, silicon
20 oxycarbide, and mixtures thereof. The metal nitride coating may be selected from the group consisting of silicon nitride, zirconium nitride, tantalum nitride, boron nitride, and mixtures thereof. The metal silicide may be selected from the group consisting of
25 chromium silicide, molybdenum silicide, tantalum silicide, titanium silicide, tungsten silicide, zirconium silicide, and mixtures thereof. Noble metals that are suitable for coatings can include platinum, palladium, silver, gold, ruthenium, rhodium,
30 iridium, and alloys thereof, such as 80 weight percent palladium-20 weight percent silver.

Impermeable barrier coatings that are especially effective are a palladium-silver alloy, in particular about 80 weight % palladium-20 weight %

- 8 -

silver, palladium, platinum, silicon carbide, silicon oxide, tantalum oxide, calcium zirconate, magnesium aluminum oxide, silicon oxycarbide, and mixtures thereof.

5 An effective amount of an impermeable barrier coating is an amount needed to inhibit the contaminant composition from penetrating an opening in the thermal barrier coating. The thickness of the impermeable barrier coating is determined by such
10 considerations as: the application and design of the thermal barrier coated part, the amount and composition of the contaminant composition that is encountered during service, the operating temperature of the thermal barrier coating, and the locality and
15 geographical limitations where the thermal barrier coated part will be used.

 In selecting an impermeable barrier coating, the surface temperature of the thermal barrier coating during its operation needs to be
20 considered, as well as the type and composition of the environmental contaminants that will be encountered. It is contemplated that the impermeable barrier coating will have a melting temperature above the operating temperature of the thermal barrier coating.
25 For instance, if the surface of the thermal barrier coating is about 1200°C during operation, than the impermeable barrier coating needs to have a melting temperature above 1200°C.

 The impermeable barrier coating can be
30 deposited on the thermal barrier coating by coating methods known in the art, such as sol-gel, sputtering, air plasma spray, organo-metallic chemical vapor deposition, physical vapor deposition, chemical vapor deposition, and the like. The choice of the coating

- 9 -

method in part depends on where and how the thermal barrier coated part will be used and the desired thickness for such use. In selecting a method of deposition, a practitioner should look at the
5 criticality of the thickness requirement for the coating. Both thick and thin coatings should be dense and as pore-free as possible.

Thicknesses of the impermeable barrier coating can vary from about 0.2 micrometers to about
10 250 micrometers. The preferred thickness is about 2-125 micrometers. The thickness of the impermeable coating is also in part, determined by the operating temperature of the thermal barrier coating and the amount and composition of the contaminant. If thick
15 impermeable barrier coatings are required, i.e., about 125 micrometers or more, a compositionally graded deposit can be used to keep internal stresses minimized in order that delamination of the impermeable coating does not occur.

20 For purposes of illustrating the use of a specific impermeable barrier coating, as well as imparting an understanding of the present invention, the reaction of CMAS composition with the impermeable coating on a thermal barrier coating is described at
25 operating temperatures of about 1200°C or higher.

The chemical composition of the CMAS composition was determined by electron microprobe analysis of infiltrated deposits found on thermal barrier coated engine parts where deposit-induced
30 damage to the thermal barrier coating had been observed. Analysis indicated that 127 micron (5 mils) of CMAS-like deposits ($\sim 34 \text{ mg/cm}^2$ assuming a density of 2.7 g/cm^3) can form on thermal barrier coating surfaces. The CMAS deposits evaluated were typically

- 10 -

in the compositional range (weight %): 5-35% CaO, 2-35% MgO, 5-15% Al₂O₃, 5-55% SiO₂, 0-5% NiO, 5-10% Fe₂O₃, however the content of the ubiquitous Fe₂O₃ can be as large as 75 wt%. An average composition for
5 such deposits (weight %: 28.7% CaO, 6.4% MgO, 11.1% Al₂O₃, 43.7% SiO₂, 1.9% NiO, 8.3% Fe₂O₃) was synthesized in the laboratory and used as a standard CMAS for the purpose of evaluating protective
10 coatings. Differential thermal analysis of actual CMAS deposits and the synthesized CMAS indicated that the onset of melting occurs at about 1190°C with the maximum of the melting peak occurring at about 1260°C. Thermal testing of candidate protective coatings for
15 thermal barrier coatings against the laboratory synthesized CMAS composition were carried out at about 1260°C.

The following examples further serve to describe the invention.

EXAMPLES

Impermeable barrier coatings on thermal
20 barrier coated components were investigated to prevent the infiltration of environmentally deposited mixtures of oxides of calcium, magnesium, aluminum, and silicon (CMAS).

Candidate impermeable barrier coating
25 compositions were deposited on thermal barrier coatings of 8 weight percent yttria-92 weight percent zirconia and assessed for CMAS infiltration resistance using metallography, SEM and electron microprobe chemical analysis. The above testing was conducted
30 under laboratory furnace test conditions (isothermal). Thermal barrier coated parts with impermeable barrier

- 11 -

coatings were found to minimize CMAS infiltration and damage under isothermal conditions.

Impermeable barrier coatings that were deposited by the sol-gel, air plasma spray, sputtering, and MOCVD methods were: an 80/20 weight percent palladium-silver film, palladium, platinum, silicon carbide, silicon oxide, scandia, silicon oxycarbide, tantalum oxide, calcium zirconate, and magnesium aluminum oxide.

The effectiveness of protective coatings in preventing CMAS-infiltration-induced thermal barrier coating damage was tested by comparing the infiltration resistance of protected and non-protected thermal barrier coated substrates which were thermally cycled in the presence of surface deposits of CMAS. In these experiments, 8mg/cm² of ground pre-reacted CMAS was deposited on masked areas of the thermal barrier coated substrates. A thermal cycle consisted of heating the samples to 1260°C in 10 minutes, holding it at 1260°C for 10 minutes, followed by cooling it to room temperature in 30 minutes. After each cycle the samples were inspected with the unaided eye and at 50x using a stereo microscope. This cycle was repeated several times. After completion of thermal testing, the samples were sectioned, metallographically polished, and inspected using bright field and dark field optical microscopy.

EXAMPLE 1

Example 1 demonstrates the effect of CMAS on a thermal barrier coated part without an impermeable barrier coating. Non-protected thermal barrier coating samples tested in the above-mentioned fashion exhibit visible CMAS induced thermal barrier

- 12 -

coating swelling and cracking (visible on sample edges under the stereomicroscope). Metallographic preparation and inspection of the non-protected samples shows CMAS induced thermal barrier coating densification, cracking and exfoliation.

EXAMPLE 2

A thick film (125 micrometers) of 80 weight percent palladium-20 weight percent silver was deposited by thick film screen printing of electrode paste on an 8 weight % yttria-stabilized 92 weight % zirconia coated coupon. The palladium-silver coating formed a dense, continuous film without voids after heat treatment. The palladium-silver coating partially melted and flowed into the top surface of the thermal barrier coating, providing good adhesion to the substrate. The palladium-silver film filled and bridged the thermal barrier coating microcracks.

Eight mg/cm² CMAS was deposited on the above impermeable coated samples and tested isothermally at 1260°C for ten minutes. The CMAS was retained on the top surface of the palladium/silver film. There were no apparent CMAS induced thermal barrier coating delamination cracks.

EXAMPLE 3

Microprobe analysis of a CMAS-spinel diffusion couple indicated that there was no reaction between the CMAS and a spinel coating, magnesium aluminum oxide. Therefore, magnesium aluminum oxide, was deposited on thermal barrier coated coupons using air plasma spray, sol-gel and metallic organic chemical vapor deposition techniques. Eight mg/cm² CMAS was deposited on the above impermeable coated

- 13 -

samples. Thermal cycling took place to 1260°C. The thermal barrier coating had no edge cracks in the CMAS application area at 20-50X view and limited CMAS infiltration in the cross-section.

EXAMPLE 4

5 Calcium zirconate was deposited on thermal barrier coated coupons by air plasma spray. The air plasma spray calcium zirconate coating was 125 micrometers thick and graded to accommodate an expansion mismatch. Eight mg/cm² CMAS was deposited
10 on the above impermeable coated samples. Heat cycling took place to 1260°C. Metallography showed that the CMAS was retained on top of impermeable barrier.

EXAMPLE 5

15 The above air plasma spray deposition of 125 micrometers (graded) of calcium zirconate on thermal barrier coated coupons was performed. An additional 125 micrometers of calcium zirconate was then air plasma sprayed on the previous graded calcium zirconate deposit. Eight mg/cm² CMAS was deposited on
20 the above impermeable coated samples. Heat cycling took place to 1260°C. Metallography showed that the CMAS was retained on top of impermeable barrier.

 The practice of this invention makes it possible to extend the effective life of gas turbine
25 engine thermal barrier coatings at a specific set of operating parameters including operating temperature and operating environment. It also provides a means to provide for engine designs which impose increased thermal burdens on thermal barrier coatings such as
30 reduced cooling of thermal barrier coated parts or exposure of such parts to higher temperature input,

- 14 -

i.e., effective increase of operating temperatures for the engine system. Accordingly, the practice of this invention provides for substantial enhancement of the functions of currently available thermal barrier
5 coatings under more rigorous thermal assault as demands for performance escalate.

- 15 -

What is claimed:

1. A method for protecting a thermal barrier coating at an operating temperature from degradation by environmental contaminants that form a liquid contaminant composition on a surface of a thermal barrier coating, where said contaminant composition infiltrates openings in the thermal barrier coating, said method comprises: depositing an impermeable barrier coating on the thermal barrier coating in an effective amount to decrease the contaminant composition from infiltrating openings in the thermal barrier coating at the operating temperatures of the thermal barrier coating.
2. A method according to claim 1 where the thermal barrier coating is a chemically stabilized zirconia selected from the group consisting of yttria-stabilized zirconia, scandia-stabilized zirconia, calcia-stabilized zirconia, and magnesia-stabilized zirconia.
3. A method according to claim 1 where the environmental contaminants comprise an oxide selected from the group consisting of magnesium oxide, calcium oxide, aluminum oxide, silicon oxide, iron oxide, nickel oxide, and mixtures thereof.
4. A method according to claim 3 where the environmental contaminants form a contaminant composition comprising compositions of calcium-magnesium-aluminum-silicon oxide (CMAS).
5. A method according to claim 1 where the impermeable barrier coating is selected from the group consisting of a metal oxide, a metal carbide, a metal nitride, a metal silicide, a noble metal, and mixtures thereof, where the metal oxide coating is selected from the group consisting of silicon oxide,

- 16 -

10 tantalum oxide, scandium oxide, aluminum oxide,
hafnium oxide, zirconium oxide, magnesium aluminum
oxide, calcium zirconate, and mixtures thereof, where
the metal carbide coating is selected from the group
consisting of silicon carbide, tantalum carbide,
titanium carbide, tungsten carbide, silicon
oxycarbide, and mixtures thereof, where the metal
nitride coating is selected from the group consisting
15 of silicon nitride, zirconium nitride, tantalum
nitride, boron nitride, and mixtures thereof, where
the metal silicide coating is selected from the group
consisting of chromium silicide, molybdenum silicide,
tantalum silicide, titanium silicide, tungsten
20 silicide, zirconium silicide, and mixtures thereof,
and where the noble metal coating is selected from the
group consisting of platinum, palladium, silver, gold,
ruthenium, rhodium, iridium, and mixtures thereof.

6. A method according to claim 5 where
the impermeable barrier coating is selected from the
group consisting of 80 weight % palladium-20 weight %
silver, palladium, platinum, silicon carbide, silicon
5 oxide, tantalum oxide, calcium zirconate, magnesium
aluminum oxide, silicon oxycarbide, and mixtures
thereof.

7. A method according to claim 1 where
the effective amount of the impermeable barrier
coating is about 0.2-250 micrometers.

- 17 -

8. A method to protect a thermal barrier coating, where a thermal barrier coating comprises about 8 weight percent yttria and about 92 weight percent zirconia from degradation by a contaminant composition, where said contaminant composition comprises compositions of calcium-magnesium-aluminum-silicon oxide, said method comprises: depositing an impermeable barrier coating selected from the group consisting of 80 weight % palladium-20 weight % silver, palladium, platinum, silicon carbide, silicon oxide, tantalum oxide, calcium zirconate, magnesium aluminum oxide, silicon oxycarbide, and mixtures thereof, on the thermal barrier coating in an amount between about 0.2-250 micrometers to prevent said contaminant composition from infiltrating openings in the thermal barrier coating.

9. A composite comprising a thermal barrier coating on a part with a continuous impermeable barrier coating adjacent to an outer surface of the thermal barrier coating.

10. A composite according to claim 9 where the impermeable barrier coating is selected from the group consisting of a metal oxide, a metal carbide, a metal nitride, a metal silicide, a noble metal, and mixtures thereof, where the metal oxide coating is selected from the group consisting of silicon oxide, tantalum oxide, scandium oxide, aluminum oxide, hafnium oxide, zirconium oxide, magnesium aluminum oxide, calcium zirconate, and mixtures thereof, where the metal carbide coating is selected from the group consisting of silicon carbide, tantalum carbide, titanium carbide, tungsten carbide, silicon oxycarbide, and mixtures thereof, where the metal nitride coating is selected from the group consisting

- 18 -

15 of silicon nitride, zirconium nitride, tantalum
nitride, boron nitride, and mixtures thereof, where
the metal silicide coating is selected from the group
consisting of chromium silicide, molybdenum silicide,
tantalum silicide, titanium silicide, tungsten
20 silicide, zirconium silicide, and mixtures thereof,
and where the noble metal coating is selected from the
group consisting of platinum, palladium, silver, gold,
ruthenium, rhodium, iridium, and mixtures thereof.

11. A composite according to claim 10
where the impermeable barrier coating is selected from
the group consisting of 80 weight % palladium-20
weight % silver, palladium, platinum, silicon carbide,
5 silicon oxide, tantalum oxide, calcium zirconate,
magnesium aluminum oxide, silicon oxycarbide, and
mixtures thereof.

12. A composite according to claim 9 where
the impermeable barrier coating is about 0.2-250
micrometers thick.

13. A composite according to claim 9 where
the thermal barrier coating is a chemically stabilized
zirconia selected from the group consisting of yttria-
stabilized zirconia, scandia-stabilized zirconia,
5 calcia-stabilized zirconia, and magnesia-stabilized
zirconia.

14. A composite according to claim 9 where
the part is an alloy selected from the group
consisting of nickel based alloys, cobalt based
alloys, iron based alloys, and mixtures thereof.

15. A protected thermal barrier coated
part comprising a part selected from the group
consisting of nickel based alloys, cobalt based
alloys, iron based alloys, and mixtures thereof, with
5 a thermal barrier coating selected from the group
consisting of a chemically stabilized zirconia

- 19 -

selected from the group consisting of yttria-stabilized zirconia, scandia-stabilized zirconia, calcia-stabilized zirconia, and magnesia-stabilized zirconia, on said part and an impermeable barrier coating selected from the group consisting of a metal oxide, a metal carbide, a metal nitride, a metal silicide, a noble metal, and mixtures thereof, where the metal oxide coating is selected from the group consisting of silicon oxide, tantalum oxide, scandium oxide, aluminum oxide, hafnium oxide, zirconium oxide, magnesium aluminum oxide, calcium zirconate, and mixtures thereof, where the metal carbide coating is selected from the group consisting of silicon carbide, tantalum carbide, titanium carbide, tungsten carbide, silicon oxycarbide, and mixtures thereof, where the metal nitride coating is selected from the group consisting of silicon nitride, zirconium nitride, tantalum nitride, boron nitride, and mixtures thereof, where the metal silicide coating is selected from the group consisting of chromium silicide, molybdenum silicide, tantalum silicide, titanium silicide, tungsten silicide, zirconium silicide, and mixtures thereof, and where the noble metal coating is selected from the group consisting of platinum, palladium, silver, gold, ruthenium, rhodium, iridium, and mixtures thereof, in an amount of about 0.2-250 micrometers thick on an outer surface of said thermal barrier coating.

16. A composite comprising a substrate with a first layer that includes a thermal barrier coating, and a second layer on the outer surface of the thermal barrier coating that includes a continuous impermeable barrier coating.

- 20 -

17. An article of manufacture for use in gas turbine engines comprising a part having a surface covered with a thermal barrier coating, where the thermal barrier coating is selected from the group
5 consisting of yttria-stabilized zirconia, scandia-stabilized zirconia, calcia-stabilized zirconia, and magnesia-stabilized zirconia, and said thermal barrier coating having an outer surface covered with a impermeable barrier coating in an amount of about 0.2-
10 250 micrometers, where the impermeable barrier coating is selected from the group consisting of a metal oxide, a metal carbide, a metal nitride, a metal silicide, a noble metal, and mixtures thereof, where the metal oxide coating is selected from the group
15 consisting of silicon oxide, tantalum oxide, scandium oxide, aluminum oxide, hafnium oxide, zirconium oxide, magnesium aluminum oxide, calcium zirconate, and mixtures thereof, where the metal carbide coating is selected from the group consisting of silicon carbide,
20 tantalum carbide, titanium carbide, tungsten carbide, silicon oxycarbide, and mixtures thereof, where the metal nitride coating is selected from the group consisting of silicon nitride, zirconium nitride, tantalum nitride, boron nitride, and mixtures thereof,
25 where the metal silicide coating is selected from the group consisting of chromium silicide, molybdenum silicide, tantalum silicide, titanium silicide, tungsten silicide, zirconium silicide, and mixtures thereof, and where the noble metal coating is selected
30 from the group consisting of platinum, palladium, silver, gold, ruthenium, rhodium, iridium, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/03685**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

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)

U.S. : 427/419.2, 419.3, 419.7, 405, 383.7; 148/272, 277, 284, 285, 668, 672; 428/ 627, 628, 629, 630

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

search terms: thermal barrier, engine zirconia, carbide, nitride, contaminant, oxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,399,199 (McGILL ET AL.) 16 August 1983; col.2, line 24-col.3, line 31.	1-17
X	US, A, 5,338,577 (BURDETTE, II) 16 August 1994, col.2, line 15-col.4, line 46, 51-68; col.5, line 18-col.6, line 50; col.7, line 38-col.8, line 65.	1-7, 9-17
Y	US, A, 5,223,045 (PRICEMAN) 29 June 1993, col.2, line 45-col.3, line 38; col.5, lines 5-60.	8
A	US, A, 5,350,599 (RIGNEY ET AL.) 27 September 1994.	1-17
A	US, A, 5,382,347 (YAHALOM) 17 January 1995	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*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
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*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
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)	* & * document member of the same patent family
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	

Date of the actual completion of the international search

21 MAY 1996

Date of mailing of the international search report

18 JUL 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

fr. DIANA DUDASH

Telephone No. (703)-308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/03685

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,715,902 (ALLAM ET AL.) 29 December 1987	1-17

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/03685

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

F 02 B 75/08; B 05 D 1/36, 7/14; B 22 F 3/24; B 32 B 15/00, 18/00; C 23 C 8/10, 16/00, 16/22, 16/30

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

427/419.2, 419.3, 419.7, 405, 383.7; 148/272, 277, 284, 285, 668, 672; 428/ 627, 628, 629, 630