The object of the invention is to provide a thermal barrier coating system for protecting metal surfaces at high temperature in normally corrosive environments. The thermal barrier coating system includes a metal alloy bond coating, the alloy containing nickel, cobalt, iron, or a combination of these metals. The system further includes a corrosion resistant thermal barrier oxide coating containing at least one alkaline earth silicate. The preferred oxides are calcium silicate, barium silicate, magnesium silicate, or combinations of these silicates.

12 Claims, No Drawings
CORROSION RESISTANT THERMAL BARRIER COATING

ORIGIN OF THE INVENTION

The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

TECHNICAL FIELD

The invention relates to a thermal barrier coating system for metal surfaces that are subject to high temperature use in a normally corrosive environment. The invention is particularly directed to protecting the surfaces of metal components, gas turbines, and other heat engine parts that are exposed to fuels contaminated with metallic impurities which are normally corrosive to previously known metallic coatings.

Thermal barrier coatings for gas turbine service must be capable of withstanding exposure in contaminated hot corrosion or sulfidation causing fuels for at least 1000 hours and preferably much longer. Current zirconia-based thermal barrier coatings as well as coatings based on oxides with similar physical and chemical properties, such as ceria, hafnia, and thoria, do not have the requisite durability.

BACKGROUND ART

U.S. Pat. No. 4,055,705 to Stecura and Liebert discloses a thermal barrier coating system wherein a stabilized zirconia thermal barrier coating covers a NiCrAlY bond coating. Certain problems have been encountered when this system is used in an environment of contaminated fuels.

Tucker, Jr. U.S. Pat. No. 3,837,894 and Weatherly et al U.S. Pat. No. 4,095,003 disclose duplex coatings. Both patents are concerned with the porosity of prior art coatings. In the Tucker, Jr. patent the undercoat is metallurgically sealed by heat treating. Weatherly et al refers to the Tucker patent and points out that not all substrates can be heat treated without degrading the properties of the substrate. The Weatherly et al patent utilizes a bond coating that is formed in two layers and then heat treated prior to the application of the ceramic coating. Takabatake et al U.S. Pat. No. 3,927,223 is directed to refractory based oxide coated membrane on a substrate.

While satisfactory results for a limited time have been achieved with the coatings of the prior art, none are capable of withstanding the exposure of contaminated fuels for the time required for gas turbines and other heat engines.

DISCLOSURE OF INVENTION

A corrosion resistant thermal barrier coating system produced in accordance with the present invention has an outer layer of oxide 5 to 50 mils thick deposited on a bond coat. The thermal barrier oxide is one or a combination of alkaline earth silicates.

The preferred oxides are calcium silicate in the range CaO:SiO₂ to 3CaO:SiO₂, barium silicate in the range BaO:SiO₂ to 3BaO:SiO₂, magnesium silicate in the range MgO:SiO₂ to 3MgO:SiO₂, or combinations of these silicates. These oxides may also be used with additions of up to 50% by weight of excess free silica.
2.5 cm from the exit nozzle, and the measured substrate
temperature of 843° C.

The coated specimens were examined at intervals of
20 one-hour cycles. Any particular coated specimen
was removed from testing when the coating had spalled
over approximately one-fourth the hot zone on the
leading edge. The number of 1-hour cycles to spall is set
forth in the last column in the Table for each coating
system. This represents the total number of cycles that
the coating system had undergone at the end of the
inspection interval.

Metallographic examination of sections taken from the
hot zone and from a cool region near the base were
used to determine the extent of hot corrosion and the
mode of spalling. X-ray diffraction analysis was per-
formed on small samples of coating taken from locations
near cross-section cuts of the single fuel impurity sensi-
tivity specimens.

On the coatings shown in the Table, the one based on
1.8CaO:SiO2 reached 675 1-hour cycles before spalling.
Also, a cermet coating of 50 volume percent MgO-50
volume percent Ni-20 w/o Cr-17 w/o Al-1.0 w/o Y
survived 1000 one-hour cycles without spalling. These
two coatings proved to have significantly better high
corrosion resistance than the four standard thermal
barrier coatings which all spalled by 50 cycles.

The metal substrate temperature measured during the
same calibration run for both 1.8CaO:SiO2 and ZrO2-
12Y2O3 coated bars was 843° C. which indicates that the
1.8CaO:SiO2 and the ZrO2-12Y2O3 coatings are equivalent
in thermal insulating ability.

While the preferred mode for carrying out the inven-
tion has been described, it will be appreciated that vari-
ous alternative modes may be utilized without departing
from the spirit of the invention or the scope of the sub-
joined claims. By way of example, it is contemplated that
the coating could be graded either continuously or
in several discrete steps from 100% bond coat at the
substrate surface to 100% oxide at the outer surface and
the total coating thickness would be 10 to 50 mils. Such
a coating could be applied by plasma spraying. In still
another embodiment the thermal barrier layer of alka-
line earth silicates may be deposited by physical vapor
deposition or by sputtering.

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COATING COMPOSITIONS OF THERMAL BARRIERS AND
BOND COATING

<table>
<thead>
<tr>
<th>Thermal Barrier</th>
<th>Bond Coating</th>
<th>Number of One-hour Cycles To Spall Coating From ca. 1 of the Hot Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO2-12 w/o Y2O3</td>
<td>Ni-16 w/o Cr-5 w/o Al-0.6 w/o Y</td>
<td>80</td>
</tr>
<tr>
<td>ZrO2-18 w/o Y2O3</td>
<td>Ni-16 w/o Cr-5 w/o Al-0.15 w/o Y</td>
<td>100</td>
</tr>
<tr>
<td>ZrO2-4 w/o Y2O3</td>
<td>Ni-16 w/o Cr-5 w/o Al-0.12 w/o Y</td>
<td>384</td>
</tr>
<tr>
<td>ZrO2-12 w/o Y2O3</td>
<td>Ni-16 w/o Cr-6 w/o Al-0.6 w/o Y</td>
<td>145</td>
</tr>
<tr>
<td>1.8CaO:SiO2</td>
<td>Ni-16 w/o Cr-6 w/o Al-0.6 w/o Y</td>
<td>178</td>
</tr>
<tr>
<td>30 Vol. % MgO</td>
<td>Ni-16 w/o Cr-6 w/o Al-0.6 w/o Y</td>
<td>675</td>
</tr>
<tr>
<td>20 Vol. % Ni</td>
<td>Ni-16 w/o Cr-6 w/o Al-0.6 w/o Y</td>
<td>20</td>
</tr>
<tr>
<td>1.0 w/o Y</td>
<td>Ni-16 w/o Cr-6 w/o Al-0.6 w/o Y</td>
<td>1000</td>
</tr>
</tbody>
</table>

We claim:
1. A thermal barrier coating system for protecting the
surface of a metal substrate in a hot corrosive gas comprising
a metal alloy bond coating containing a metal se-
lected from the group consisting of nickel, cobalt,
and iron covering said surface of said substrate, and
a corrosion resistant oxide thermal barrier coating
containing a combination of barium, magnesium,
and calcium silicates covering said bond coating.

We claim:
2. A thermal barrier coating system as claimed in
claim 1 wherein the substrate is a metal selected from
the group consisting of nickel-base and cobalt-base super-
alloys.

We claim:
3. A thermal barrier coating system as claimed in
claim 1 wherein the bond coating is an alloy which contains at
least one metal selected from the group consisting of chromium and aluminum.

4. A thermal barrier coating system as claimed in
claim 3 wherein the bond coating is an alloy selected from
the group consisting of NiCrAlY, CoCrAlY, and Ni-
CoCrAlY.

5. A thermal barrier coating system as claimed in
claim 4 wherein the bond coating has a thickness of
between about 0.005 centimeters and about 0.025 centi-
meters.

6. A thermal barrier coating system as claimed in
claim 1 wherein the oxide thermal barrier coating has a thickness between about 0.012 centimeters and 0.120 centimeters.

7. A thermal barrier coating system as claimed in
claim 6 wherein the oxide has a thickness of about 0.038 centimeters.

8. A thermal barrier coating system as claimed in
claim 1 wherein the corrosion-resistant oxide is calcium
silicate in the range of 1CaO:1SiO2 to 3CaO:1SiO2.

9. A thermal barrier coating system as claimed in
claim 1 wherein the corrosion-resistant oxide is magne-
sium silicate in the range between 1MgO:1SiO2 and
3MgO:1SiO2.

10. A thermal barrier coating system as claimed in
claim 1 wherein the corrosion-resistant oxide is barium
silicate in the range between 1BaO:1SiO2 and 3BaO:1-
SiO2.

11. A thermal barrier coating system for protecting the
surface of a metal substrate in a hot corrosive gas
comprising
a metal alloy bond coating containing a metal se-
lected from the group consisting of nickel, cobalt,