**ABSTRACT**

A scandia stabilized zirconia coating which is resistant to corrosion by sulfur and vanadium compounds at elevated temperatures. Scandia is present in the zirconia between about 4 to 8 mole percent. A composite formed from a coating of the stabilized zirconia on a substrate, such as a superalloy, is useful for turbine blades and engine pistons. Preferably, the coating is up to 10 mils thick.

17 Claims, 5 Drawing Sheets
OTHER PUBLICATIONS


FIG. 1

Temperature (deg. C)

Mol-% Sulfate Formation

50 m/o Y₂O₃ - Na₂SO₄

50 m/o Sc₂O₃ - Na₂SO₄
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SCANDIA-STABILIZED ZIRCONIA COATING FOR COMPOSITES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to vanadium and sulfur compound corrosion-resistant ceramic coatings. More particularly, this invention relates to scandia-stabilized zirconia coatings and composites formed with them.

2. Description of the Prior Art

As demands increase on fuel resources and as manufacturing techniques become more complex, industrial equipment is exposed to fuels and materials which contain corrosive contaminants. These corrosive contaminants can cause extensive damage to the surface and structure of industrial equipment, particularly to all types of motors, turbines, engines, furnaces, stacks, fluidized beds and the like.

In addition, it is often necessary to protect industrial parts from damage and fatigue caused by operation at high temperatures. Ceramic coatings have been used to protect exposed surfaces from heat deterioration and corrosion.

Vanadium and sulfur compounds are particularly virulent corrosive materials which are found in many fuels and raw materials. Sulfur and vanadium compounds react during combustion to produce high temperature vanadium and sulfur oxide gases within the machine or engine, and also react with sodium or sodium oxide (Na being a contaminant found in virtually all environments and ingested into the engine or machine) to deposit thin films of molten sodium vanadates and sulfates on the hot machine parts such as turbine blade or piston surfaces. It is believed that vanadium is oxidized to V₂O₅ in gas turbine combustion and that the sulfur compounds are present as oxides, acids and as free sulfur.

Because vanadium pentoxide (V₂O₅) is an acidic oxide, it reacts with Na₂O (a highly basic oxide) to form a series of compounds in which the acidic nature of the compounds decreases with the V₂O₅/Na₂O ratio from Na₂V₂O₆ (most acidic) to Na₂V₂O₅ (least acidic). Each of the acidic oxides can cause damage to machine parts. The oxides are formed as follows:

\[
\begin{align*}
\text{Na}_2\text{O} + 6\text{V}_2\text{O}_5 & \rightarrow \text{Na}_2\text{V}_2\text{O}_11 \quad (\text{vanadium bronze I}) \\
\text{Na}_2\text{O} + 3\text{V}_2\text{O}_5 & \rightarrow 2\text{Na}_2\text{V}_2\text{O}_7 \quad (\text{vanadium bronze II}) \\
\text{Na}_2\text{O} + \text{V}_2\text{O}_5 & \rightarrow \text{Na}_2\text{VO}_3 \quad (\text{sodium metavanadate}) \\
2\text{Na}_2\text{O} + 3\text{V}_2\text{O}_5 & \rightarrow 2\text{Na}_2\text{VO}_3 \quad (\text{sodium pyrovanadate}) \\
3\text{Na}_2\text{O} + 2\text{V}_2\text{O}_5 & \rightarrow 2\text{Na}_2\text{V}_3\text{O}_8 \quad (\text{sodium orthovanadate})
\end{align*}
\]

The combination of both vanadium and sulfur compounds is particularly destructive to machine parts. Rahmel, in the "Proceedings of International Conference on Ash Deposits and Corrosion Due to Impurities in Combustion Gases," Byers, Editor, p.185, Hemisphere, Washington, D.C. (1978), reports electrochemical studies of the corrosion of superalloys in molten sulfates containing different concentrations of the different vanadium compounds which indicate that the corrosiveness of the vanadium compounds decreases from V₂O₅ to Na₂V₂O₇ to Na₂V₂O₅.

With the increasing threat of an energy crisis, pulverized coal is becoming more attractive as a fuel source, but coal also contains vanadium and sulfur compounds which can destroy the insides of furnaces, including incinerators, or other combustion equipment, stacks servicing that equipment or furnaces, and the containers of fluidized beds.

Ceramic coatings have been used to try and protect surfaces from corrosion and to provide, when appropriate, a thermal barrier. Zirconia is a ceramic with excellent heat insulating properties as well as excellent resistance to corrosion by vanadium and sulfur compounds. Zirconia appears well suited to act as a protective coating to materials exposed to an atmosphere containing corrosive vanadium and sulfur compounds, but pure zirconia undergoes a catastrophic tetragonal-to-monoclinic phase structure change at 1000°-1100° C. This change results in an approximately 4% change in volume of zirconia. Such a volume change in the working parts of a machine, such as an engine, as it cycles through that temperature range is likely to result in flaking or deterioration of coatings formed from zirconia. These flakes would be calamitous to the machine.

It is known that zirconia can be stabilized to the tetragonal crystal structure by the addition of stabilizer compounds such as 5-20 wt-% of calcia (CaO), magnesia (MgO), or yttria (Y₂O₃). Andreev et al., J Crystal Growth, V. 52, pp. 772-776 (1981), reports using zirconia crucibles stabilized with several different oxides, including scandia, to grow semiconductor crystals. Stabilized zirconia has also been used to form reaction vessels, electrodes, and electrolytes for electrochemical reactions.

NASA and others are developing zirconia "thermal barrier" coatings for use on gas turbine blades and diesel engine pistons. These coatings are expected to substantially increase engine thermal efficiency. Siemers et al., in U.S. Pat. No. 4,328,285, describes some of the prior art attempts to coat engine parts with ceramic base materials, and Siemens teaches using cerium oxide or ceria stabilized zirconia ceramic coatings to protect turbine and engine surfaces exposed to vanadium and sulfur compound corrosion.

The zirconia thermal barrier coatings have not been completely successful because stabilized zirconia has been found to react with, and be quickly degraded by traces of sulfur, and sulfur and vanadium compounds present in many commercial and industrial grade petroleum fuels. One of the inventors, together with colleagues, has reported in R. L. Jones, C. E. Williams, and S. R. Jones, J. Electrochem. Soc. 133, 227 (1986); R. L. Jones, S. R. Jones, and C. E. Williams, J. Electrochem. Soc. 132, 1498 (1985); and R. L. Jones and C. E. Williams, Surface and Coatings Tech. 32, Nr. 1-4, 349 (1987), that the instability of the zirconia is traceable to the leaching of the stabilizer from the coating and not to the zirconia itself. A stabilizer which will not be leached from the coating on high temperature exposure to vanadium and sulfur compounds is needed before zirconia can be successfully used as a corrosion resistant coating.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a ceramic coating which is resistant to reaction with molten vanadate and sulfate salts.

Also, it is an object of this invention to provide a stabilizer of the zirconia tetragonal structure which will not be leached at high temperatures.
In addition, it is an object of this invention to provide a stable, corrosion resistant thermal barrier for metals used in atmospheres containing molten vanadium and sulfur compounds. Yet another object of this invention is to form composites for use in engines and other machines or facilities which are resistant to corrosion by molten vanadium and sulfate compounds.

These and other objects of the invention are accomplished by a zirconia coating stabilized with from about 4 to 8 mole-percent of scandia. The objects are also accomplished by forming a composite of up to a 30 mil coating of the scandia stabilized zirconia coated on a substrate surface.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention will be readily obtained by reference to the following Detailed Description and the accompanying drawings in which like numerals in different figures represent the same structures or elements, wherein:

FIG. 1 is a graph comparing sulfation of Sc2O3 vs. Y2O3.

FIG. 2 is a photograph showing YVO4 crystals resulting from attack of NaVO3 on a yttria stabilized zirconia.

FIG. 3 is a photograph showing non-reaction of NaVO3 on a scandia stabilized zirconia.

FIG. 4 is a schematic drawing of a test apparatus for corrosive vapor testing.

FIG. 5 is a composite plot of the X-ray spectra comparing scandia stabilized zirconia to yttria stabilized zirconia after exposure to NaVO3 at 900° C.

DETAILED DESCRIPTION

The use of zirconia thermal barrier coatings has been severely limited because stabilized zirconia reacts with, and is quickly degraded by, traces of sulfur and vanadium contained in many commercial and industrial grade petroleum fuels and other combustion or high temperature environments. Zirconia itself is resistant to molten vanadium salts (Jones et al. J. Electrochem. Soc. 133, 227 (1986)) and molten sodium sulfate/sulfur trioxide (Jones et al., Metall. Trans. 16A, 303 (1985)). Principally, it is the stabilizer which is attacked. Jones et al. have shown, J. Electrochem. Soc. 133, 227 (1986), that the predominant cause of vanadate degradation of stabilized zirconia is a Lewis acid-base reaction between the yttria stabilizer and vanadium pentoxide (V2O5), the acidic component of vanadate compounds; i.e.,

\[ \text{Y}_2\text{O}_3 \text{(base)} + \text{V}_2\text{O}_5 \text{(acidic)} = 2 \text{YVO}_4 \text{("neutral salt")}. \]

On the basis of this understanding proposed in the literature by Jones et al., it would be expected that an oxide of the appropriate acidic nature would give reduced reaction with the acidic corrosives V2O5 and SO3. However, it has been found that the acidic nature of the stabilizing oxide is necessary but not the only condition for resistance to sulfur and vanadium compounds.

This is evidenced by the experience with ceria.

Although Ceria, CeO2, described by Siemens in U.S. Pat. No. 4,328,283, is in fact a more acidic oxide than yttria (J. Electrochem. Soc. 132, 1498 (1985)) and should withstand molten sulfate and vanadate attack better than yttria, it does not. As found by Jones et al., Surface and Coatings Tech. 32, Nr. 1-4, 349 (1987), CeO2 is readily leached from ceria-stabilized ZrO2 by NaVO3, and CeO2-stabilized zirconia is degraded by NaVO3 to an equal or greater extent than Y2O3-stabilized ZrO2 under the same test conditions. This degradation of CeO2-stabilized ZrO2 has been confirmed and reported by GE scientists B. Nagaraj and D. J. Wortman, “High Temperature Degradation of Ceramic Coatings in Environments Containing Sodium Sulfate and Sodium Vanadate,” presented at the 1988 International Conference on Metallurgical Coatings, 11-15 April, 1988, San Diego, Calif. (to be published).

Scandium (Sc2O3) is recognized as the most acidic rare earth oxide (“Comprehensive Inorganic Chemistry, Vol. Four”, p. 168, by M. C. Sneed and R. C. Bristed, Van Nostrand, New York (1955)). Also, R. Rub et al., reports, in Am. Ceram. Soc. 60, 399, (1977), that scandia is an effective stabilizer for zirconia in its different crystal structure forms.

Now, it has been found as part of this invention that zirconia stabilized with scandia maintains the alpha 2 prime tetragonal zirconia form and produces a ceramic coating which is resistant to corrosion from the combined or singular effects of vanadium and sulfur compounds at elevated temperatures. The required amount of scandia for this purpose is about 4 to 8 mole-percent preferably from about 4.5 to 7 mole-percent, and, most preferably, from 6 to 7 mole-percent.

Generally, the scandia stabilized zirconia ceramic is formed by combining acid solutions of scandia and a zirconium salt, neutralizing the solution to precipitate the mixed oxide ceramic precursor and recovering the precipitate. The precipitate is calcined, pressed and fired to form a dense ceramic material. The density of the ceramic can be created by isostatic pressing, hot pressing or any other means used to form ceramics.

Once formed, the stabilized zirconia ceramic is prepared in the usual manner for coating on to the substrate to be protected thus forming the composite of this invention. The support substrate can be any metal used in turbines, engines and other structures exposed to hot gases containing sulfur and vanadium compounds, or the substrate can be a ceramic such as is used in furnaces, incinerators, stacks, ceramic engines and the like. The surface of the composite is the scandia stabilized zirconia coating. The coating can be any practical thickness as is commonly used in constructing particular pieces of equipment. The coating can be as thick as 1 inch for thermal barrier use in large diesel engines. For the purpose of achieving corrosion resistance, coatings of up to 10 mils may be used in gas turbines, with 10 mils preferred and 5 mils most preferred. Coatings for corrosion resistance barriers in other engines or applications can be as thick as 50 mils or more.

COST EFFECTIVENESS

Scandium is not a rare element, but, because it is found in very low concentration deposits, scandium is expensive. Scandium costs essentially the same as platinum (each costs approximately $20 per gram in industrial quantities at current market prices). However, despite its high cost, platinum is widely used as part of the commercially highly successful platinum-augmented aluminiue coating compositions for gas turbine blades.

In these augmented aluminiue coatings, a 0.2-0.4 mil thick layer of platinum is applied under an aluminiue outer layer. The materials cost for platinum in such a coating is about $0.32 per cm2 of coating. In contrast,
the cost for Sc₂O₃ in a 5 mil thick coating of 5 wt-% Sc₂O₃-ZrO₂ is about $0.07 per cm². Even for a 10 mil coating the cost would only be about $0.14 per cm². The additional cost of Sc₂O₃ is therefore not likely to be prohibitive for many gas turbine and other applications.

For example, the first stage blade from the Navy's LM2500 gas turbines requires approximately 10 square centimeters of coating, and the extra $1-$2 cost for Sc₂O₃ would be quite small in relation to the total cost of the blade. The benefit of substantially longer blade life while burning lower cost, vanadium-containing fuel far exceeds the minor cost differential.

This invention can lead to large money savings in gas turbines alone. Repair, replacement and fuel costs for the Navy and nation's industrial and marine gas turbines run to hundreds of millions of dollars per year, and even small percentage improvements correspond to large dollar savings. The following specific advantages can be gained by using a thermal barrier coating in engines burning low quality, sulfur and vanadium containing fuel: increased thermal efficiency from thermal barrier coatings; longer engine component life because of reduced corrosion attack; lower cost of fuel by virtue of using lower quality fuel; increased availability of fuel; and, especially for the Navy, insurance against crippling corrosion attack on engines when burning low quality fuel under emergency conditions. Advantages would also be expected in technologies such as coal conversion, waste incineration, fuel cells, and the like, where zirconia ceramics need to be protected against attack by acidic corrosives.

Now having generally described this invention, the following examples illustrate specific application of the invention.

### EXAMPLE 1

**Method of Preparation**

Sufficient commercial grade purity scandia (Sc₂O₃) to make the desired concentration (between 4 and 8 mole-%) of scandia in zirconia is dissolved in 12 molar HCl. Then, the solution is diluted to form a 3 molar HCl solution (about a 1-to-4 dilution). This solution is added to an appropriate quantity of ZrOCl₂ which is also dissolved in 3 Molar HCl. The acid solution is neutralized with a stoichiometric excess amount of 3 molar NH₄OH. The precipitate is collected by filtration, washed several times with deionized water and dried. The precipitate is calcined for 0.5 hours at 600°C.

Pellets are formed of the precipitate by pressing the material in a uniaxial die system to 4000 psi. The pellets thus formed are then isostatically pressed to 25,000 psi to obtain a dense ceramic structure. This dense pellet is fired at 2000°C for 3 hours. It is preferred that the pellets rest on a high purity Al₂O₃ substrate.

The scandia-stabilized zirconia formed by this method can be ground by known means and applied in a known manner to the substrate in need of protection. These application means include plasma spray and the like.

### EXAMPLE 2

**Comparison of Resistance of Scandia and Yttria to Sulfation**


A comparison was made by bringing 50 mole-% mixtures of Sc₂O₃-Na₂SO₄ and Y₂O₃-Na₂SO₄ to equilibrium under air containing 12.5 pa (125 ppm) of SO₃ (SO₃=SO₂+SO₃) at temperatures over a range of 700°-800°C. The partial pressure of 12.5 Pa of SO₃ (which corresponds to approximately 7 Pa of SO₃ at 700° C. and 5 Pa of SO₃ at 800° C.) was chosen as being representative of SO₃ concentrations that might be encountered in engines.

As shown in FIG. 1, Y₂O₃ is essentially converted completely to sulfate even at 800°C. (46.3 mole-% sulfate formation, 93% conversion), while Sc₂O₃ gives only 9.9 mole-% sulfate formation (20% conversion) at 700° C., which diminishes to 0.3 mole-% (0.6% conversion) at 800°C. These results confirm that Sc₂O₃ is a significantly more acidic oxide than Y₂O₃, and that Sc₂O₃-stabilized ZrO₂ is more resistant to degradation via a sulfation mechanism than Y₂O₃-stabilized ZrO₂, especially above 800°C. (gas turbine blades are usually above this temperature except in low power running) where Sc₂O₃ sulfation would not be expected.

### EXAMPLE 3

**Comparison of Scandia and Yttria to Vanadium Compounds**

Vanadate Reaction. Experimentally we have demonstrated that Y₂O₃ reacts with NaVO₃ at both 700° C. and 900° C., forming YVO₃ in each case. On the other hand, Sc₂O₃ does not react with NaVO₃ at 900° C., but did form some ScVO₄ at 700° C. These results indicate that Sc₂O₃ is less reactive with NaVO₃ than Y₂O₃, and while there is some reaction at 700° C., the compound produced, ScVO₄, is unstable at higher temperatures and will break down to the original components. Scandia-stabilized zirconia is therefore less likely to undergo vanadic attack by a vanadate formation mechanism, especially at the high temperatures of an operating turbine blade, than is yttria-stabilized zirconia, where yttrium vanadate forms readily to 900°C and beyond.

### EXAMPLE 4

**Molten NaVO₃**

Reaction of NaVO₃ with 5 wt-% Sc₂O₃-ZrO₂ vs 8 wt-% Y₂O₃-ZrO₂.

A ceramic pellet of 5 wt-% (4.5 mole-%) Sc₂O₃ in ZrO₂, and a ceramic pellet of 8 wt-% (4.5 mole-%) Y₂O₃ in ZrO₂, were prepared using the methods of preparation described in Example 1. Each of these pellets was deposited together with 5-10 mg of NaVO₃ (corresponding to 10-20 mg/cm²) in a vessel and exposed in furnaces at both 700° C. and 900° C. Results from a 475 hour test conducted at 700° C. are shown in
FIG. 2 for 8 wt-% Y$_2$O$_3$-ZrO$_2$. Results for 5 wt-% Sc$_2$O$_3$-ZrO$_2$ are shown in FIG. 3.

The photograph, FIG. 2, shows that the NaVO$_3$ has quickly and completely reacted with the Y$_2$O$_3$-ZrO$_2$ leaving numerous acicular YVO$_3$ crystals on the zirconia surface. The surface is depleted of Y$_2$O$_3$ and destabilized to the monoclinic structure.

In contrast, as is seen in FIG. 3, even after exposure for 475 hours, the NaVO$_3$ phase exists on the Sc$_2$O$_3$-ZrO$_2$ surface with little reaction appearing to have occurred between NaVO$_3$ and Sc$_2$O$_3$-ZrO$_2$. However, detailed analysis shows that some reaction has taken place forming, within the NaVO$_3$ film, a limited amount of a phase which contains scandium, calcium (an impurity from either the ceramic or NaVO$_3$), zirconium, and vanadium. If the NaVO$_3$ film is washed off, x-ray diffraction reveals that the outer surface now contains some monoclinic phase; i.e., that sufficient Sc$_2$O$_3$ has been removed to allow partial destabilization of the outermost region of the ceramic. However, the amount of reaction and destabilization is significantly less than observed with Y$_2$O$_3$-ZrO$_2$. Thus, the experiment at 700° C. clearly demonstrates the superiority of Sc$_2$O$_3$-ZrO$_2$ over Y$_2$O$_3$-ZrO$_2$ in resistance to molten vanadate corrosion.

The experiments with molten NaVO$_3$ deposits at 900° C. gave similar results, except that the NaVO$_3$ film, although still much less reactive with Sc$_2$O$_3$-ZrO$_2$ than with Y$_2$O$_3$-ZrO$_2$, did not persist as long on the Sc$_2$O$_3$-ZrO$_2$ surface at 900° C. as at 700° C.

**EXAMPLE 5**

**Exposure to Vanadate Vapor**

Vaporous NaVO$_3$ Reaction with 5 wt-% Sc$_2$O$_3$-ZrO$_2$ vs 8 wt-% Y$_2$O$_3$-ZrO$_2$. Molten salt deposits occurring in engines are normally very thin containing on the order of 1 mg/cm$^2$ or less of material rather than the 10-20 mg/cm$^2$ of material used in the preceding examples.

In engines, incinerators, furnaces or the like much of the corrosion will involve vaporous corrosives. To test reaction to corrosive vapor, experiments were conducted at 900° C. using the arrangement illustrated in FIG. 4. The NaVO$_3$ melt was contained in a porcelain crucible, and the Sc$_2$O$_3$-ZrO$_2$ and Y$_2$O$_3$-ZrO$_2$ pellets were placed in a platinum pan upnext resting on top of the boat but not touching the NaVO$_3$ melt so that only predominantly vaporous species of NaVO$_3$ (and possibly some ZrO$_2$ resulting from NaVO$_3$ reaction with the porcelain boat) came in contact with the ceramic pellets. In addition to-providing a more realistic test, this arrangement helps avoid artifacts involved with the use of thick molten phase deposits, such as the suspected calcium contamination problem and the possibility that stabilizer depletion may occur by simple physical dissolution into the molten vanadate layer, rather than actual chemical reaction between NaVO$_3$ and stabilizer.

The 900° C. vapor phase experiments proved to be excellent discriminatory tests, and provide further clear evidence that Sc$_2$O$_3$-ZrO$_2$ is more resistant to vanadic attack than Y$_2$O$_3$-ZrO$_2$. As shown by the solid line in FIG. 5, X-ray diffraction of the Y$_2$O$_3$-ZrO$_2$ surface of pellets exposed 119 hours shows conclusively that YVO$_3$ has been formed and that substantial destabilization to the monoclinic phase has occurred. In FIG. 5, "Y" denotes the YVO$_3$ peaks, "M" denotes monoclinic zirconia peaks, and "T" denotes tetragonal zirconia peaks. FIG. 5 also shows by a dashed line the X-ray diffraction of Sc$_2$O$_3$-ZrO$_2$ exposed in the same test. It is clear that the scandia stabilized zirconia remains entirely in the tetragonal structure. There is no indication at all of vanadic reaction.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

What we claim is:

1. A composite structure comprising a substrate and a protective coating of scandia stabilized zirconia on said substrate, said coating of scandia stabilized zirconia having an outer surface which is exposed to, and resistant to corrosion by, sodium vanadates and sodium sulfates under combustion conditions.

2. A composite structure according to claim 1 wherein the substrate is a metal.

3. A composite structure according to claim 1 wherein the substrate is a ceramic.

4. A composite structure according to claim 1 wherein the substrate is a ceramic.

5. A composite structure according to claim 1, further comprising deposits of a sodium vanadate upon said exposed outer surface.

6. A composite structure according to claim 1, further comprising deposits of a sodium vanadate upon said exposed outer surface, said deposits having been formed from a molten sodium vanadate.

7. A composite structure according to claim 6 wherein the layer is up to about 50 mils thick.

8. A composite structure according to claim 7 wherein the layer is about 5 mils thick.

9. A composite structure according to claim 1 wherein the layer contains about 4 to 8 mole-percent scandia.

10. A composite structure according to claim 9 wherein the layer contains about 4.5 to 7 mole-percent scandia.

11. A composite structure according to claim 10 wherein the layer contains about 6 to 7 mole-percent scandia.

12. A composite structure according to claim 11 wherein the substrate is a metal.

13. A composite structure according to claim 12 wherein the substrate is a metal.

14. A composite structure according to claim 13 wherein the layer is up to about 10 mils thick.

15. A composite structure according to claim 14 wherein the substrate is a metal.

16. A composite structure according to claim 15 wherein the substrate is a metal.
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