An article comprises a silicon-containing substrate and a zircon coating. The article can comprise a silicon carbide/silicon (SiC/Si) substrate, a zircon (ZrSiO₄) intermediate coating and an external environmental/thermal barrier coating.

13 Claims, 3 Drawing Sheets
**FIG. 1**
CERAMIC WITH ZIRCON COATING

This invention was made with government support under Contract No. NAS3-26385 awarded by NASA. The government may have certain rights in the invention.

BACKGROUND OF THE INVENTION

The invention relates to a composition that includes a silicon-containing substrate and a zircon coating.

Silicon-containing substrates are proposed for structures used in high temperature applications, such as in heat exchangers and advanced internal combustion engines. For example, silicon-based composite ceramics have been proposed as materials for applications in combustors for supersonic commercial airplanes. In many of these applications, the silicon-containing substrates are subjected to highly corrosive environments such as oxidizing or reducing atmospheres and environments containing salts, water vapor or hydrogen. Silicon-containing substrates exhibit poor oxidation resistance and may recede and lose mass under water-containing environments because of the formation of volatile species, such as silicon hydroxide [Si(OH)₄]. Hence, it is necessary to apply external environmental/thermal barrier coatings to these materials to provide protection from environmental attack at elevated temperatures.

Although an external environmental/thermal barrier coating is capable of preventing silicon-containing substrate materials from being in direct contact with the environment, typically the external coating is an oxide that has a high coefficient of thermal expansion (CTE). The difference between the coefficient of expansion (CTE) of the silicon-containing substrate and the coefficient of thermal expansion (CTE) of the external environmental/thermal barrier coating can result in high stress and lead to coating failure. Further, it has been shown that the performance characteristics of silicon carbide are a function of temperature. Mullite has a higher thermal expansion than either silicon carbide (SiC) or silicon (Si). Zircon has a thermal expansion closer to those of both silicon (Si) and silicon carbide (SiC). Therefore, the stress in mullite due to thermal expansion mismatch is lower than that in mullite.

SUMMARY OF THE INVENTION

The present invention provides a coating that reduces thermal expansion mismatch with a silicon-containing substrate and that can be applied as an intermediate layer or as an external coating in applications where water vapor is absent. The invention is an article that comprises a reinforcing fiber, particulate or whisker and a silicon-based composite processed by silicon melt infiltration coated with a zircon coating and yttria-stabilized zirconia external coating.

DETAILED DESCRIPTION OF THE INVENTION

According to the invention, a coating composition comprising zircon is applied to a silicon-containing substrate to provide a coating with a coefficient of thermal expansion that approaches the coefficient of thermal expansion of the silicon-containing substrate. For an infinite coating on a rigid substrate (very much thicker than the coating) stress in the coating due to thermal expansion mismatch is given by the formula:

$$\alpha = \frac{2G}{\gamma} \left( \sqrt{\alpha_1^2 - \alpha_2^2} \right)$$

where $\alpha$ is the shear modulus of the coating, $\gamma$ is the coefficient of thermal expansion (CTE) of a substrate designated $\alpha_1$, $\alpha_2$, $\Delta T$ is the temperature change, and $\nu$ is the Poisson's ratio of the coating. For a coating of zircon, the stress in the coating due to thermal expansion mismatch is lower than that in mullite. The lower coefficient of thermal expansion (CTE) of zircon than that of silicon carbide (SiC) results in a compressive stress in the zircon coating during cooling. The compressive stress decreases the likelihood of coating cracking as zircon has a higher compressive strength than tensile strength.

Zircon comprises $ZrSiO_4$ or $ZrO_2SiO_2$. It has an incongruent melting temperature of about 1680°C. Hence, it is adequate for most high temperature applications. Additionally, zircon has other advantages. A thin layer of silicon oxide ($SiO_2$) is formed on the surface of silicon (Si) and silicon-containing substrates due to the oxidation of silicon. Zirconia or one of various silicates can be used with the substrate as a water-resistant external coating. In these instances, a zircon intermediate coating has good chemical compatibility with both the underlying substrate and the external coating.

Suitable silicon-containing substrates include silicon carbide (SiC) and silicon nitride (Si₃N₄). The substrate can be a monolithic or composite. A composite can comprise reinforcing fiber, particulate or whisker and a silicon-based matrix. The matrix can be processed by melt infiltration (MI), chemical vapor infiltration (CVI) or other technique. Exemplary substrates include a monolithic silicon carbide (SiC) and silicon nitride (Si₃N₄), a silicon carbide (SiC) fiber-reinforced silicon carbide (SiC) matrix composite, carbon fiber-reinforced silicon carbide (SiC) matrix composite, and a silicon carbide (SiC) fiber-reinforced silicon nitride (Si₃N₄) composite. The preferred substrate comprises a silicon carbide (SiC) fiber-reinforced silicon carbide/silicon (SiC/Si) matrix composite processed by silicon melt infiltration.
Also suitable as silicon-containing substrates are silicon metal alloys. These alloys include niobium silicon alloys, molybdenum silicon alloys and the like.

The zircon coating can be applied by chemical vapor deposition (CVD), thermal spray, or sol-gel technique. Precipitation of the silicon-containing substrate may be employed to improve adhesion of the zircon layer. A zircon phase stabilizer, such as yttria (Y$_2$O$_3$), may be added to the coating starting composition to stabilize the cubic phase and prevent volumetric changes. A zircon phase stabilizer and/or modifier may be premixed through a vigorous mechanical process, such as ball milling, to provide interlocking of the powders and prevent segregation of phases due to density differences. For the same purpose, a sol-gel or colloidal process may be employed to coat the particles of one constituent with another.

The zircon coating of the invention can be used as an external coating in applications where water vapor is absent or as an intermediate layer with an external environmental/thermal barrier coating. The thickness of the zircon coating is determined by the application and the materials of the substrate and external coating. When the zircon coating is applied as an external barrier, it should completely cover the substrate. In this application, the coating is typically applied as a plasma deposited coating to a thickness between about 1 to about 20 mils (25 to 500 microns), preferably between about 2 to about 10 mils (50 to 250 microns). For applications where the zircon coating serves as a bond layer, its thickness can be determined by the CTE mismatch between the substrate and the external barrier coating and the magnitude of stresses generated as a result of the CTE mismatch. Typically for plasma deposited coatings, the thickness is between about 1 to 10 mils (25 to 250 microns), preferably about 2 to 5 mils (50 to 125 microns).

Suitable external barrier coatings in the zircon bond coat application comprise an oxide such as yttria-stabilized zirconia, scandia-stabilized zirconia, calcium-stabilized zirconia, magnesia-stabilized zirconia or magnesia-stabilized zirconia. Alumina and alumina silicates such as barium strontium aluminoisicate and calcium aluminoisicate are also typical external coating materials.

Preferably, a zircon coating is applied as an intermediate layer to a composite that comprises a silicon carbide/silicon (SiC/Si) substrate and a yttria-stabilized zirconia external environmental/thermal barrier coating. The following example is illustrative of the invention.