OXIDATION RESISTANT SLURRY COATING FOR CARBON-BASED MATERIALS

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ABSTRACT

An oxidation resistant coating is produced on carbon-base materials, and the same processing step effects an infiltration of the substrate with silicon containing material. The process comprises making a slurry of nickel and silicon powders in a nitrocellulose lacquer, spraying onto the graphite or carbon-carbon substrate, and sintering in vacuum to form a fused coating that wets and covers the surface as well as penetrates into the pores of the substrate.

Optimum wetting and infiltration occurs in the range of Ni-60 w/o Si to Ni-90 w/o Si with deposited thicknesses of 25–100 mg/cm². Sintering temperatures of about 1200° C. to about 1400° C. are used, depending on the melting point of the specific coating composition.

The sintered coating results in Ni-Si intermetallic phases and SiC, both of which are highly oxidation resistant. The final coating composition can be further controlled by the length of the sintering time.

5 Claims, 3 Drawing Figures
SiC + Si₃Ni - Si

C₆(Si) no Ni

Ni - Si

SiC

UNREACTED GRAPHITE

10 μm

20 μm

SiC

10 μm
OXIDATION RESISTANT SLURRY COATING FOR CARBON-BASED MATERIALS

ORIGIN OF THE INVENTION

The invention described herein was made by employees of the U.S. 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

This invention is directed to inhibiting the decomposition of carbon-base materials during high temperature exposure to air. The invention is particularly concerned with an improved coating for protecting these materials.

Coated carbon composite materials are used as heat shields for the space shuttle nose cap and wing leading edges. These carbon-carbon composites are also being considered for various high temperature components of aircraft turbine engines, such as turbine blades, vanes, and nozzle liners. The major advantage of these materials is their very high strength-to-weight ratios at temperatures between 1200° C. to 2000° C.

One major disadvantage of carbon-base materials is their extremely high oxidation rate. Conventional methods of protecting graphite and carbon-carbon composites generally consist of coating the material with a silicon carbide by chemical vapor deposition or pack cementation processes. A second step or series of steps may follow in which the coating cracks are infiltrated with an organic liquid containing silicon, such as tetraethylorthosilicate, and fired to form a crack sealing silica glass. Other processes, referred to as inhibition, are used to impregnate the carbon material with silicon containing materials and provide some measure of oxidation resistance to the base material itself prior to overcoating with SiC.

At high temperatures the silicon carbide coating reacts with oxygen in air to form a protective film of silicon dioxide. Therefore, the purpose of the overcoat is to provide silicon to take part in this reaction and protect the exterior of the engine component. Such coatings provide adequate protection above 1200° C. where a fluid SiO2 glass is formed as a protective oxide.

At lower temperatures, cracks are formed in the SiC graphite of the coupon substrates was about 73% dense and exhibited a substantial amount of large porosity. The coated coupons were placed in a furnace which utilized a slurry of nickel and silicon powders in a nitrocellulose lacquer. This slurry is applied to a carbon-carbon composite. The same processing step effects an infiltration of the substrate with silicon-containing material and provides a fused coating. The process utilizes a slurry of nickel and silicon powders in a nitrocellulose lacquer. This slurry is applied to a carbon-carbon or graphite substrate in a single spraying operation. After drying in air the coated substrate is fired in a single operation below 1400° C. Vacuum sintering between about 1200° C. and about 1400° C. at 10⁻⁵ torr has been successful in producing a coating which melted, wet, and infiltrated the substrate.

BRIEF DESCRIPTION OF THE DRAWING

The objects, advantages and novel features of the invention will be more fully apparent from the following detailed description when read in connection with the accompanying drawing wherein

FIG. 1 is a 500 magnification micrograph showing the distribution of phases in the cross section of an ATJ graphite substrate coated with a Ni-70 Si fused slurry;

FIG. 2 is a 3000 magnification micrograph from a scanning electron microscope showing SiC crystallites in a Ni-70 Si coating sintered by a two-step process of 1200° C. for one hour followed by 1325° C. for one hour; and

FIG. 3 is a graph showing compositional effects on 1200° C. cyclic oxidation behavior of coatings sintered by a two-step process of 1200° C. for one hour followed by 1325° C. for one hour.

BEST MODE FOR CARRYING OUT THE INVENTION

In order to illustrate the beneficial technical effect of the improved coating, a number of ATJ graphite coupons were coated in accordance with the present invention. Each coupon was 0.25 x 1.25 x 2.50 cm. The graphite of the coupon substrates was about 73% dense and exhibited a substantial amount of large porosity. A slurry of nickel and silicon powders in a nitrocellulose lacquer was prepared. The powders were about 325 mesh. The slurry was sprayed onto the surface of each coupon. Optimum coverage and infiltration occurred in the range of Ni-60 w/o Si to Ni-90 w/o Si. The coatings were deposited to thicknesses of about 25-100 mg/cm². The slurry was sprayed using a conventional paint sprayer in air, and the coated coupons were air dried.

The coated coupons were placed in a furnace which was evacuated to 10⁻⁵ torr. The coupons were then vacuum-sintered between about 1200° C. to about 1400° C. for a time period of up to three hours. The coupons were sintered either while resting on an aluminum oxide plate or while suspended from aluminum oxide hangar rods.

The sintered coatings produced Ni-Si intermetallic phases and SiC, both of which are highly oxidation resistant. A cross section of a SiC+Si reaction zone of

BACKGROUND ART

The present invention is directed to an improved method of producing an oxidation resistant coating on a carbon-based substrate. The same processing step effects an infiltration of the substrate with silicon-containing material and provides a fused coating. The process utilizes a slurry of nickel and silicon powders in a nitrocellulose lacquer. This slurry is applied to a carbon-carbon or graphite substrate in a single spraying operation. After drying in air the coated substrate is fired in a single operation below 1400° C. Vacuum sintering between about 1200° C. and about 1400° C. at 10⁻⁵ torr has been successful in producing a coating which melted, wet, and infiltrated the substrate.

DISCLOSURE OF INVENTION

The invention described herein was made by employees of the U.S. Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.
a coating that was processed at 1325° C. for five minutes is shown in FIG. 1. This micrograph shows an intact area of the coating after oxidation at 1200° C. for five hours. The coating has penetrated pores, and the outer layer has protected the unreacted graphite. FIG. 1 illustrates the assintered coating structure and phases as well.

Referring to FIG. 1 in greater detail, an outer 10 μm layer of substantially continuous and uniform SiC, Ni-Si, and Si coating is apparent. The pores near the surface have been filled with a liquid Ni-Si phase to a depth of about 180 μm. The external layer and the filled pores of both these areas show some internal structures which are probably SiC precipitates. A microprobe study of these areas showed high levels of Ni in the penetrated pores with amounts of Si consistent with the formula for Ni2Si. In this phase the carbon content was very low. In adjacent phases the Si and C contents were more consistent with SiC, and the Ni content was low. The dark areas between the filled pores showed only C with a trace of Si and no Ni.

A two-step sintering process produced optimum results in terms of wetting, flow, and uniformity. A 1200° C./1 hr + 1200° C./1 hr sample contained a relatively large amount of the Ni-Si compounds compared to coatings sintered in a single step. A 1200° C./hr + 1325° C./1 hr sample indicated a major decrease in the amount of the metallic phase, and a corresponding increase in the Sic phase. A 1200° C./1 hr + 1450° C./1 hr sample indicated again a large amount of Ni-Si compounds which is consistent with the observed remelting and lack of SiC crystallites at the surface.

The improved results obtained by the coating of the present invention have the potential for greater protection from oxidation. While the preferred embodiment of the invention has been disclosed it will be appreciated that various modifications may be made to the invention without departing from the spirit thereof or the scope of the subjoined claims. For example, glass powders may be easily incorporated into the slurry. These powders have the potential for melting and sealing any cracks subsequently formed in the coating. Other transition elements besides Ni and Si can be used to form eutectic melts with Si to produce fused coatings on carbon-base materials. Examples would be Fe, Cr, Co, etc. which could operate according to the same principles described above for Ni-Si coatings.

It is contemplated that the process may also be altered to include other metallic elements, such as chromium and aluminum, which together have been found to form protective Al2O3 scales on NiCrAl alloys. Therefore, by the application of a fused NiCrAlSi alloy slurry coating, a carbon substrate may be protected by other oxide films, even though the low melting Ni-Si eutectic temperature is still utilized.

We claim:

1. A method of inhibiting the decomposition of a carbon-base material during high temperature exposure to air comprising the steps of:
   - preparing a slurry of nickel powders and silicon powders containing about 60 w/o to about 90 w/o silicon in a nitrocellulose lacquer,
   - spraying said slurry onto a surface of the carbon-base material to a thickness between about 25 mg/cm2 to about 100 mg/cm2 in an air environment to coat the same,
   - drying the coated carbon-base material in air, and
   - vacuum-sintering the coated carbon-base material at 1200° C. for one hour and then vacuum-sintering at 1325° C. for one hour.

2. A method of coating a carbon-base material comprising the steps of:
   - preparing a slurry containing nickel powders and silicon powders onto said carbon-base material in an air environment,
   - placing said slurry covered carbon-base material in a vacuum, and
   - sintering said slurry covered carbon-base material in said vacuum by heating the same to 1200° C. for one hour and then heating said slurry covered carbon-base material to 1325° C. for one hour.

3. A method as claimed in claim 2 wherein the slurry contains about 60 w/o to about 90 w/o silicon in a nitrocellulose lacquer.

4. A method as claimed in claim 2 wherein the carbon-base material is covered with the nickel-silicon slurry to a thickness between about 25 mg/cm2 to about 100 mg/cm2.

5. A carbon-base material coated in accordance with the method of claim 2.