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DeBrunner et al.

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[54] METHOD OF PROTECTING CARBONACEOUS MATERIAL FROM OXIDATION AT HIGH TEMPERATURE

[76] Inventors: **Ralph E. DeBrunner**, 4717 Connel Dr., Raleigh; **Patricia C. Clements**, 1000 N. Duke St., Durham, both of N.C.

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[51] Int. Cl. **B44d 1/20**

[58] Field of Search.....117/123 A, 169 R, 228, DIG. 11,

117/116, 119; 148/6.15 R; 106/56, 65;
252/506; 310/252, 253; 314/60; 313/326

[56]

References Cited

UNITED STATES PATENTS

2,715,080	8/1955	Cashell.....	117/223
2,685,541	8/1954	Woodburn et al.....	117/228 X
2,685,540	8/1954	Woodburn et al.....	117/228 X

Primary Examiner—Ralph S. Kendall

Assistant Examiner—Caleb Weston

Attorney—Vance A. Smith, J. Bowen Ross and Neal E. Willis

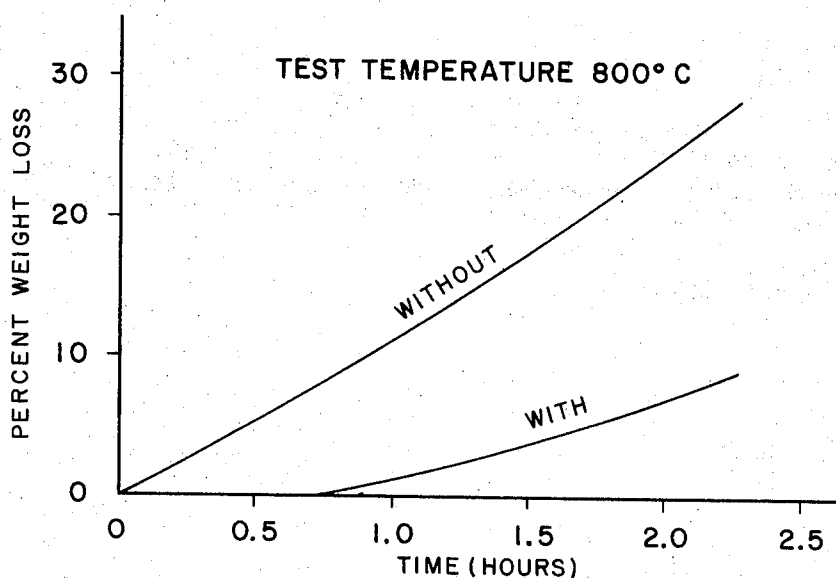
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ABSTRACT

Oxidation resistance is imparted to all-carbon bodies by applying a phosphoric acid solution of manganese pyrophosphate thereto and heating the coated body to a temperature of 500° C or greater for approximately 5–10 minutes.

2 Claims, 2 Drawing Figures

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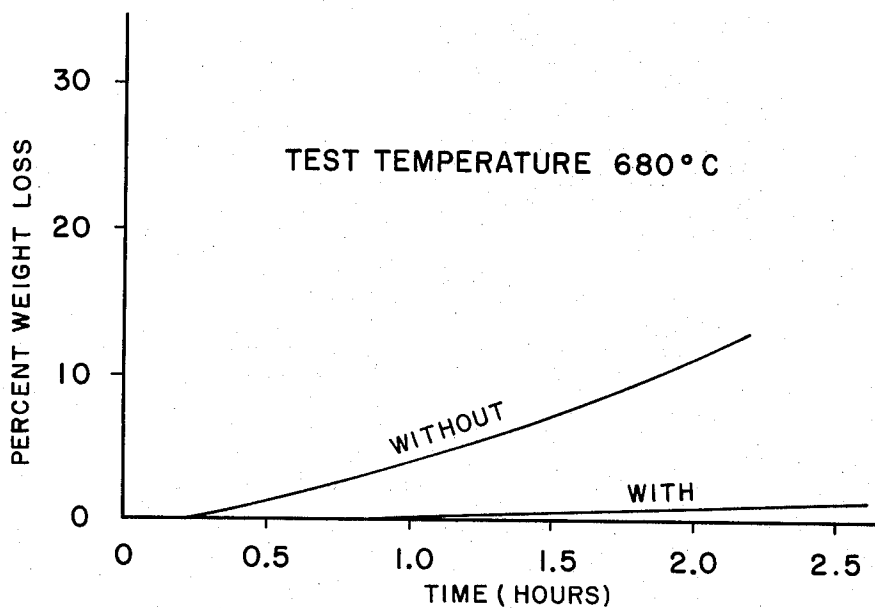


FIG. 1.

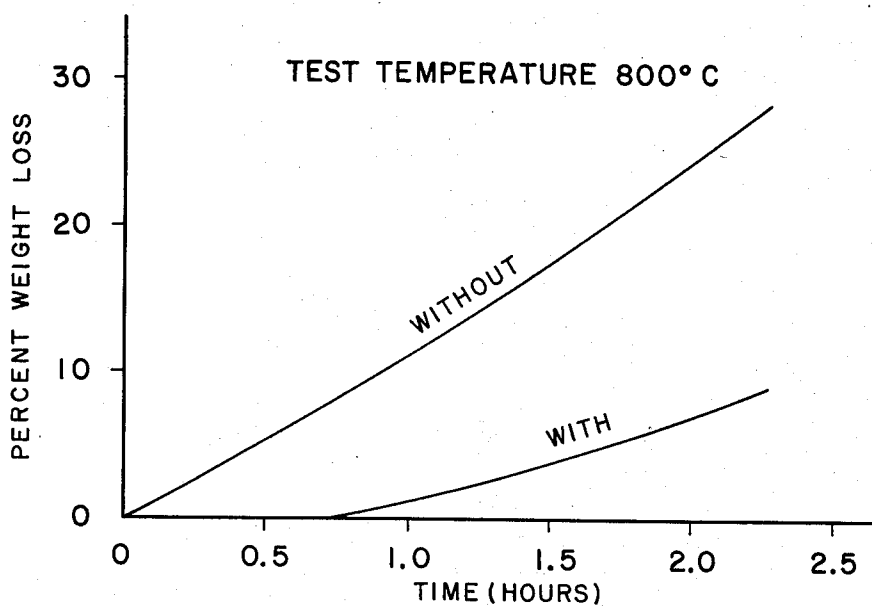


FIG. 2.

INVENTORS
 RALPH E. DeBRUNNER
 PATRICIA C. CLEMENTS,
 BY *Vance E. Smith*
 ATTORNEY

METHOD OF PROTECTING CARBONACEOUS MATERIAL FROM OXIDATION AT HIGH TEMPERATURE

CROSS-REFERENCE TO RELATED INVENTIONS

This application is related to copending application Ser. No. 866,116 filed Oct. 8, 1969, now U.S. Pat. No. 3,639,197, of Raymond G. Spain.

FIELD OF THE INVENTION

The present invention relates to improving the oxidation resistance of all-carbon bodies through application of an inorganic solution to the oxidatively exposed surfaces of all-carbon bodies.

BACKGROUND OF THE INVENTION

Carbonaceous items have found a wide range of industrial and aerospace applications due to combinations of generally desirable properties which include electrical conductivity, thermal conductivity, thermal heat capacity, resistance to thermal shock, high thermal stability, friction and wear characteristics, and chemical resistance to environments which are not strongly oxidative in nature.

Applications of such products include bearings, seals, electrodes, heating elements, electrical contacts of a wide variety and as materials for containing and conducting corrosive materials, such as in heat exchangers.

Essentially homogenous carbonaceous items are, however, highly susceptible to mechanical damage and are considered fragile in comparison to most structural materials. The strength of essentially all-carbon materials can be greatly increased if the items are fabricated as composites with strong carbonaceous filaments acting as reinforcements in a carbonaceous matrix. As an example, all-carbon composite aircraft brake discs survive the mechanical loads involved which would destroy essentially homogeneous carbonaceous disc. One example of such a composite is found in the commonly assigned referenced copending application Ser. No. 866,116 which describes and claims an all-carbon composite brake disc having increased strength in the lug areas due to a belt of carbon fibers which reinforce the disc.

The problem of oxidative susceptibility, however, is severe for all-carbon composites when employed at elevated temperatures such as the levels present when aircraft brake discs are operated. While it is well known that the oxidative resistance of homogeneous and composite carbonaceous materials can be significantly enhanced by the addition or in situ formation of selected borides, nitrides, and carbides, these added or formed modifiers detract from the performance of such items as otherwise all-carbon composite brake discs due to undesirably altered thermal, frictional, or wear characteristics.

It is therefore the primary object of this invention to provide a carbonaceous body, including an all-carbon composite body which will resist oxidation at high temperatures by modifying the formed carbonaceous body by a coating of the exterior of the body.

SUMMARY

An all-carbon body is provided with oxidation resistance to temperatures of 760° C or above by applying a phosphoric acid solution of manganese pyrophosphate thereto and heating the coated body to a temperature of 500° C or greater for approximately 5-10 minutes. Resulting measurements show little weight loss due to oxidation after prolonged exposure to air at temperatures of 760° C and higher.

BRIEF DESCRIPTION OF THE DRAWINGS

The features of the invention desired to be protected are pointed out in particularity in the appended claims. The invention itself may be best understood by reference to the following description and accompanying drawings in which:

FIG. 1 is a comparison graph of the weight loss of a carbon body with the oxide inhibitor of the present invention to one without the inhibitor when exposed to air at a temperature of 680° C.

FIG. 2 is a comparison graph of the weight loss of a carbon body with the oxide inhibitor of the present invention to one without the inhibitor when exposed to air at a temperature of 800° C.

Examples 1 and 2 below disclose preferred techniques by which the oxide inhibitor of the present invention is made.

EXAMPLE 1

An all-carbon composite test specimen identical to the compositions described in the referenced application was soaked for approximately 10 minutes in a phosphoric acid solution of manganese pyrophosphate of the following weight ratios: 28% H₂O/50% H₃PO₄/2 2% MnP₂O₇ · 7H₂O. The coated specimen then was heated in air for approximately 5-10 minutes at a temperature of about 760° C.

Coated and uncoated specimens were next subjected to oxidation in air at various temperatures for about 60 minutes. The "oxidation resistance index," i.e., (% wt. loss of coated specimen)/(% wt. loss of uncoated specimen) × 100, was then determined and recorded in Table 1.

TABLE 1

Oxidation Temperature	ORI
760°C (1400°F)	0
870°C (1600°F)	25
980°C (1800°F)	65

EXAMPLE 2

It is often desirable to protect only particular regions of an all-carbon composite. Because the technique of Example 1 employs air during the heat treatment, uncoated regions would undergo oxidation. In this example, a nitrogen atmosphere was used during heat treatment since nitrogen is unreactive either with the solution or all-carbon composite specimen. The solution employed was identical to that used in Example 1. The specimen was heated at a temperature of about 500° C for approximately 5-10 minutes. Representative data is found in Table 2 below. The data again indicated a significant increase in oxidation resistance as compared to uncoated all-carbon specimens.

TABLE 2

Oxidation Temperature	ORI
760°C	0
870°C	25
980°C	60

EXAMPLE 3

To further illustrate the oxidation resistance provided all-carbon composites, reference is made to FIGS. 1 and 2. Prolonged exposure of all-carbon composite specimens to air were made at temperatures of 680° C and 800° C, respectively. The results are very evident since the plots of specimens without the coating described herein graph as a line with a much sharper slope.

The weight ratios described in the examples are

limited to the preferred percentages in deference to the best technique of making the oxidation resistant article.

It should be noted, however, that other percentages may also be used as limited by the following ranges:

5 25-30% H₂O/45-55% H₃PO₄/20-25% MnP₂O₇ · 7H₂O.

What we claim is:

1. An all-carbon oxidation resistant body having a coating formed by applying a phosphoric acid solution of manganese pyrophosphate in the weight ratios of 10 25-30% H₂O/45-55% H₃PO₄/20-25% Mn₂P₂O₇ · 7H₂O and heating the coated body to a temperature of at least 500° C for approximately 5-10 minutes.

2. The oxidation resistant body of claim 1 wherein the phosphoric acid solution of manganese pyrophosphate is in the weight ratio of 28% H₂O/50% 15 H₃PO₄/22% Mn₂P₂O₇.

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