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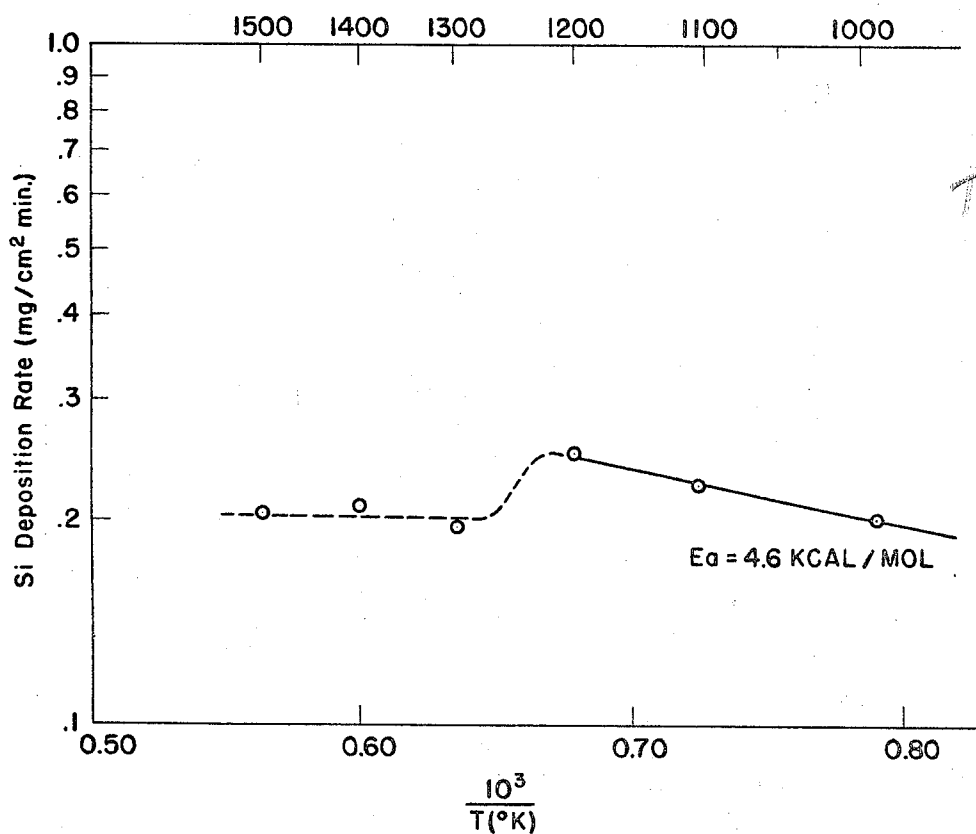
March 18, 1969

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3,433,682

SILICON COATED GRAPHITE

Filed July 6, 1965



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SILICON COATED GRAPHITE

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Filed July 6, 1965, Ser. No. 469,377

U.S. Cl. 148-6.3

13 Claims

Int. Cl. C23f 7/00

ABSTRACT OF THE DISCLOSURE

A process for coating graphite with silicon in which a preliminary coating is made of a material capable of forming a eutectic alloy with silicon and then the silicon coating is deposited at a temperature above the melting point of the eutectic alloy.

The present invention is directed to improvements in the production of coatings on articles having difficult-to-wet or irregular or defective surfaces. More particularly, the invention is concerned with an improved method for depositing a protective coating on a porous polycrystalline base article, such as one composed of graphite.

It is known that the deposition of a coating from the vapor phase onto a foreign polycrystalline body often produces non-uniform and porous deposits. Thus, the vapor phase deposition of silicon on graphite rods and mold inserts at constant temperature and flow increases up to a certain limit with an increase in the SiCl_4 concentration in the carrier gas. To increase the deposition rate it is the practice to increase the SiCl_4 concentration as much as possible. Initially, the rate of penetration of the silicon into the graphite is mainly dependent on the temperature and the porosity of the graphite. If the deposition rate of the silicon does not approximately equal the rate of its penetration, the deposited silicon will accumulate on the graphite surface in the form of peaked protrusions. Such a coating cannot be utilized without further machining or grinding which additional operations add considerably to the cost of production and lead to a high percentage of rejects owing to breakage during these operations.

One prior art attempt to remedy the above-outlined problem has consisted in continuing the penetration of the silicon after the deposition process has been stopped. This technique, however, is not considered satisfactory as it often leads to non-uniform penetration. Furthermore, since this penetration is a slow process, an excessively long time would be required for the smoothing of the accumulated surface deposits.

With a view to overcoming the above-outlined deficiencies of the prior art techniques, the main object of this invention is to provide uniform protective coatings on graphite and similar polycrystalline articles.

Another object of this invention is to provide an improved method for coating graphite and similar materials.

A further object of this invention is to increase the formation rate of vapor-deposited coatings.

Yet, another important object of the invention is to provide a method for applying a protective coating on porous, uneven or otherwise defective substrates.

These and other related objects, features and advantages of the present invention will be more readily understood as the description thereof proceeds, particularly when taken together with the accompanying drawing wherein:

The figure is a hypothetical phase diagram showing the phase changes that take place when the silicon is vapor

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deposited on the precoat metal M according to this method.

Broadly stated, the claimed invention, whereby the foregoing objects are attained, comprises applying on the surface of a base material to be coated a thin layer of a precoat having a thickness of about 0.1 micron to about 100 microns of a metal or other material which forms an alloy with the material to be deposited at a temperature below the deposition temperature but which has little or no solubility in the base material when heated at the deposition temperature. The precoat material is then coated at a constant deposition temperature, high enough to permit the diffusion of the coating material into the precoat. As a result, alloying takes place and a liquid is formed on the base material for a period of time, depending on the thickness of the precoat. The liquid surface covers the nucleating centers of the original base substrate and takes over as the new substrate for further growth. As the deposition and the diffusion proceed, the liquidus resolidifies and provides a uniform base for the further deposition of a smooth coating to the desired thickness. In addition, the precoat causes a change in the deposition kinetics resulting in faster deposition at lower temperature than otherwise.

In the practice of the invention it is important that the precoat material does not react with the substrate nor evaporate readily. Similarly, the precoat and the protective coating to be deposited should have a eutectic or at least a peritectic point which lies below the deposition temperature. The deposition temperature which is employed should be high enough to permit rapid alloying by diffusion between the precoat and the coating. During the deposition the liquidus should wet the base material and should not ball up into droplets.

Among suitable precoat materials for graphite are gold and nickel which form a eutectic melt with the silicon below the deposition temperature between the deposited silicon and the original graphite substrate. The precoat can be applied by electroplating, painting, spraying or otherwise covering the substrate. The deposition of silicon from SiCl_4 then proceeds in accordance with the principles showing the hypothetical phase diagram appearing on FIG. 4. Other materials equivalent to gold and nickel for the purposes of the claimed invention include for example, but without limitation, manganese, iron, cobalt, palladium and platinum.

As indicated in the phase diagram, as the silicon deposits it dissolves in the precoat material ($T_D \approx \%T_M$), forming a mixture which melts when its composition has reached the liquidus temperature at T_D . T_D refers to the temperature at which silicon is deposited and the symbol T_M refers to that temperature at which the precoat material melts. In the molten state, the initial number of the active nucleation and growth centers, formed on the original surface, are eliminated. The deposition then proceeds for a time at the surface of the melt but as the melt becomes richer in vapor-deposited silicon it re-solidifies and from then on it is the pure silicon which deposits on the new solid surface which acts as a new substrate for further growth. The number of growth centers is now much greater because the growth centers are formed in the liquid phase where the concentration of nuclei is large, resulting in uniform growth of the silicon deposit. Since the deposition now takes place in effect on a new substrate, the rate of deposition and the activation energy are different. Thus an Arrhenius plot of the rate constant for silicon deposited on electroplated nickel precoat at various temperatures for 60 minutes shows a fourfold decrease in the activation energy. The

deposition rates for similar precoated and uncoated graphite substrates are compared in Table 1 below.

TABLE I

[The Si deposition rate constants for nickel precoated and uncoated AUC graphite substrates, k_p and k_u . The symbol k_p refers to the deposition rate constant of silicon onto a precoat substrate while the symbol k_u refers to the deposition rate constant of silicon into an uncoated graphite substrate]

Temperature (° C.)	k_p (mg./min. cm. ²)	k_u (mg./min. cm. ²)	k_p/k_u
1,000-----	0.200	0.032	6.25
1,100-----	0.225	0.050	4.50
1,200-----	0.250	0.075	3.33
1,300-----	0.195	0.105	1.86
1,400-----	0.210	0.150	1.40
1,500-----	0.205	0.190	1.08

The following examples illustrate the practice of the claimed invention.

EXAMPLE 1

A cylinder of AUC grade graphite having a diameter of 19.3 mm. and a height of 51.2 mm. weighing 24.54235 g. precoated with gold as follows. The specimen was washed with distilled water, degreased with acetone solvent and immersed in a gold cyanide plating bath of the well-known composition: potassium gold cyanide 8 g./l., potassium cyanide 4 g./l., potassium carbonate 8 g./l., potassium hydrogen phosphate 8 g./l. and electroplated at 60° C. and current density of 5 amp./ft.² for 15 minutes. The cylinder weight after electroplating was 25.11232 g. indicating the weight gain of gold as 659.97 mg.

After precoating the cylinder was inserted in a quartz reaction chamber. Hydrogen gas and a nitrogen gas purge were passed over the cylinder. The reaction chamber was heated with a radio frequency heat source to 1300° C. for 10 minutes. Then silicon tetrachloride gas in a nitrogen gas carrier was passed through the chamber at atmospheric pressure at 1300° C. for 60 minutes. The cylinder was weighed and found to have increased in weight by 0.40368 g. The appearance of its external surfaces was excellent as is apparent from FIG. 2.

EXAMPLE 2

A cylinder similar to that used in Example 1 and weighing 24.27353 g. was coated with nickel by electroplating from a conventional aqueous electroplating bath containing 200 g./l. of nickel sulphate, 50 g./l. of nickel chloride and 30 g./l. of boric acid for five minutes under an amperage of 10 amp./ft.² and solution temperature of 40° C. The cylinder was weighed after electroplating and had picked up 0.18121 g. The cylinder was then preheated at 700° C. for 5 minutes under vacuum and then at 1000° C. for another 5 minutes. It was then coated with silicon in a quartz reaction chamber at 1000° C. using SiCl₄ in a nitrogen carrier for 60 minutes. The coated cylinder was weighed and found to have picked up 430 mg. in weight. The external appearance of the cylinder was free from flaws.

EXAMPLE 3

A cylinder similar to that used in Example 1 and weighing 24.40151 g. was coated with nickel by electroplating for 5 minutes under an amperage of 1 amp. at a solution temperature of 40° C. The cylinder picked up 0.54886 g. The cylinder was then preheated under vacuum at 700° C. for 5 minutes and then at 1000° C. for 5 minutes. Nitrogen was introduced in the reaction chamber then hydrogen and the temperature was raised from 1000° C. to 1200° C. as the silicon tetrachloride gas was introduced and passed through for 60 minutes until 0.5489 g. of silicon had been picked up. The coated sample presented a uniform surface as is apparent from FIG. 3 of the drawing.

EXAMPLE 4

A cylinder similar to that used in the preceding examples and weighing 24.4000 g. was pre-coated with nickel

as in Example 3 until it had picked up 0.46522 g. of nickel. It was then siliconized as in Example 3 but at 1400° C. until it had picked up 465.2 mg of silicon. The external surfaces of the cylinder were uniform.

EXAMPLE 5

An AUC graphite rod was precoated with nickel as in Example 3 until it had picked up 0.43358 gram. The rod was then siliconized as in the above examples at 1300° C. until it had picked up 433.6 mg. of silicon. The external surfaces of the rod were all uniformly coated.

EXAMPLE 6

A rod similar to that used in Example 5 was processed as in that example except that it was siliconized at 1500° C. for 36 minutes, until it had picked up 266.8 mg. of silicon. It was noted that its external surfaces were all uniform.

EXAMPLE 7

Pre-coat applied by evaporation

(a) A cylindrical graphite disc, weighing 3.201 g. was placed in a suitable position in a Veeco vacuum evaporator. Gold was then deposited on it from a tungsten spiral boat containing a pure gold charge. The evaporation was done in a vacuum of 10⁻⁶ mm. mercury at 400 watts heating power for 30 minutes. The weight after evaporation was 3.215 g. indicating 14 mg. of gold deposited on approximately 5 cm.² of graphite surface which corresponds to a gold layer approximately 1.5 microns thick.

(b) The same process is repeated using another graphite disc and pure nickel charge as the source of vapor. The evaporation was done at 2×10⁻⁶ mm. mercury at 300 watts heating power for 40 minutes. The weight of the specimen was 3.528 g. before and 3.540 g. after the coating. The weight gain, 12 mg., of the very uniform Ni coating correspondings to approximately 3 micron thickness.

EXAMPLE 8

Precoat applied by brushing

A commercially obtainable gold paste, containing approximately 20% by weight of powdered gold suspended in a viscous liquid binder of an organic nature (Paste Gold UR-01-FM) was applied uniformly to the surface of a clean graphite disc by means of a stiff brush. The specimen was then oven-fired at 600° C. for 30 minutes in a carbon dioxide atmosphere to burn off the organic binder leaving a uniform gold coat behind. The weight of the graphite specimen before the application was 2.90081 g., weight after firing: 2.96195 g., giving a gold layer of 61.14 mg. in weight or approximately 7 microns thick.

EXAMPLE 9

Precoat applied by spraying

A commercial proprietary solution, "Nickel Resinate," No. 58-A, made by the Engelhard Industries, Inc., Newark, N.J., and containing dissolved nickel was sprayed by means of a conventional atomizing gun, such as manufactured by the Paasche Airbrush Co., Chicago, Ill., onto a clean graphite surface heated at 200° C. to rapidly dry and thus immobilize the sprayed liquid particles. The deposit was then heated at 600° C. in a slightly oxidizing CO₂ atmosphere to burn off the organic component and leaving behind a layer of nickel oxide, NiO, which is then reduced to nickel by heating at 300° C. in a closed, hydrogen-containing atmosphere, e.g., forming gas (90% N-10% H₂). Weight before coating: 2.760 mg., after the coating and the reduction: 2.806 mg., weight of the Ni layer: 46.1 mg. equivalent to a precoat approximately 10 microns thick.

EXAMPLE 10

Precoat applied by vapor plating

A hydrogen gas stream is saturated with nickel carbonyl, Ni(CO)₄, vapor by passage through a trap con-

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taining liquid $\text{Ni}(\text{CO})_4$ at room temperature. The saturated hydrogen gas then is passed through a chamber containing the graphite specimen heated at or about 200°C . The $\text{Ni}(\text{CO})_4$ decomposes at the hot surface leaving a bright uniform coat on the graphite. The deposition rate is approximately 4 mg. of Ni per minute per 1 cm^2 of area.

The beneficial effects of the invention on the silicon coatings applied to graphite articles can be readily appreciated from an examination of silicon-silicon carbide coated articles.

It will be readily apparent that the silicon carbide coated graphite articles which are not precoat, are marred by numbers of protrusions and an uneven surface. By way of contrast, articles which are precoat in accordance with the present invention exhibit a smooth surface on the articles.

As shown in Table 1, the silicon deposition rate is increased by using the precoat technique of the invention. Unexpectedly, the silicon deposition rate for precoat articles is higher by a factor of 6 at 1000°C . as contrasted with the rate for articles which were not precoat. While this rate difference is most striking at 1000°C ., it is likewise evident at all the deposition temperatures investigated.

What is claimed is:

1. A process for forming a silicon coating on graphite comprising the steps of precoat a graphite base with a thin layer of a material capable of forming a eutectic alloy with silicon to form a precoat graphite base, and then coating the precoat graphite base with silicon at a temperature above the melting point of said eutectic alloy, said material being substantially insoluble in graphite at the deposition temperature of the silicon.

2. The process of claim 1 wherein said material comprises a metal selected from the group consisting of gold, platinum, palladium, nickel, manganese, iron, and cobalt.

3. The process of claim 1 wherein said thin layer of material has a thickness of between about 0.1 and 100 microns.

4. The process of claim 1, wherein said precoat is applied to said substrate by electroplating.

5. The process of claim 1, wherein said precoat is applied to said substrate by evaporation under vacuum.

6. The process of claim 5 wherein said precoat material is gold.

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7. The process of claim 1, wherein said precoat is applied to said substrate by brushing.

8. The process of claim 7 wherein said precoat material comprises about 20 weight percent of gold suspended in a viscous organic binder and the precoat graphite base is heated in an oxidizing atmosphere at a temperature of about 600°C . for a time sufficient to remove said binder and leave thereon a precoat of gold.

9. The process of claim 1, wherein said precoat is applied to said substrate by spraying.

10. The process of claim 9 wherein said precoat material comprises a solution containing dissolved nickel and wherein said graphite base is preheated to about 200°C . and said solution is sprayed onto the preheated graphite base and then the article is heated in an oxidizing atmosphere at about 600°C . to form a layer of nickel oxide on said article and then said article is heated at about 300°C . in a hydrogen-containing atmosphere to reduce said nickel oxide to nickel.

11. The process of claim 1, wherein said precoat is applied to said substrate by vapor plating.

12. The process of claim 11 wherein said precoat is nickel which is applied by passing a hydrogen gas stream saturated with nickel carbonyl over a graphite article heated to about 200°C .

13. The product formed by the process of claim 1.

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U.S. Cl. X.R.

117—69, 71, 105, 106, 107, 107.2, 111, 121; 204—38.3