

1

2

3,553,010

CARBON OR GRAPHITE FORMED BODY

Ottmar Rubisch, Meitingen, near Augsburg, Germany, assignor to Sigrí Elektrographit Gesellschaft mit beschränkter Haftung, Meitingen, near Augsburg, Germany, a corporation of Germany
No Drawing, Filed July 24, 1968. Ser. No. 747,129
Claims priority, application Germany, July 26, 1967, 1,615,404, 1,671,065
Int. Cl. B44d 1/20

U.S. Cl. 117-217

5 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a carbon or graphite formed body, and more particularly an arc electrode having a protective layer which arrests oxidation, and which includes a primary layer, applied upon a carbon or graphite formed body, and a metallic cover layer comprised essentially of aluminum over the primary layer. The primary layer is comprised of 90 to 100%, preferably 95 to 98.9%, of silicon and 0 to 10%, preferably 1.1 to 5.0%, of sodium, magnesium, calcium, boron, aluminum, titanium, zirconium, manganese, iron, carbon, nitrogen phosphorus and oxygen, separately or in combination. The cover layer is comprised of 85 to 100%, preferably 93 to 99.5%, aluminum and 0 to 15%, preferably 0.5 to 7%, sodium, magnesium, boron, silicon, phosphorus, oxygen, copper, zinc, lead, titanium, zirconium, chromium, manganese, iron, cobalt and nickel, separately or in combination.

My invention relates to a carbon or graphite formed body, and more particularly an arc electrode having a protective layer which arrests oxidation, and which includes a primary layer, applied upon a carbon or graphite formed body, and a metallic cover layer, comprised essentially of aluminum, over the primary layer.

Carbon or graphite formed bodies are very widely used in chemical and metallurgical arts because of their excellent mechanical and thermal qualities. Frequently, however, the burning off, which occurs in these materials at temperatures above 550° C. in an oxidizing atmosphere, is disturbing.

It is known that burning off of the carbon and graphite bodies can be reduced by impregnation with phosphate. This, however, reduces the burning off only to temperatures up to approximately 1100° C.

It is further known to reduce the burning off through the utilization of cover layers on carbon or graphite bodies. It is preferred to produce said cover layers of transition metal silicides. The effect of such layers comprised of transition metal silicides is limited, though, to high temperatures within a range of 1200 to 1700° C. Furthermore, the application of said layers is possible only by means of expensive techniques. It is also known to apply double layer coatings upon carbon or graphite bodies. The base layer may be a carbide layer, e.g. a silicon carbide layer, while the cover layer may either constitute a layer of an oxide mixture or a metal or silicide layer. But even these layers do not yet afford an adequate protection, since it was not possible, heretofore, to adjust the expansion coefficients of the body to be protected and the applied layer, to each other. In the aforementioned double layers, the melting point is so high that tears which form cannot be recovered by the flow of the layer. As a result, the layer is undercut by oxidation and breaks off.

The present invention, therefore, has as an object effective protection against oxidation of the aforementioned formed body of graphite or carbon. According to the

invention, the primary layer is comprised of 90 to 100%, preferably 95 to 98.9%, of silicon and 0 to 10%, preferably 1.1 to 5%, of sodium, magnesium, calcium, boron, aluminum, titanium, zirconium, manganese, iron, carbon, nitrogen, phosphorus and oxygen, separately or in combination, and the cover layer of 85 to 100%, preferably 93 to 99.5%, of aluminum and 0 to 15%, preferably 0.5 to 7%, of sodium, magnesium, boron, silicon, phosphorus, oxygen, copper, zinc, lead, titanium, zirconium chromium manganese, iron, cobalt and nickel, separately or in combination. All percentages used in this application are by weight.

The application of such a double layer may be effected in a known manner by means of flame injection. It is particularly preferable to provide the primary layer with a layer thickness of 0.01 to 0.15 mm., preferably 0.02 to 0.1 mm., and the cover layer with a thickness of 0.05 to 0.6 mm., preferably 0.1 to 0.3 mm.

When such a protective layer is applied by flame injection, it is only mechanically bound to the carbon or graphite formed body. It was found that when the thus coated bodies are heated above approximately 550° C., the components of the double layer react with each other to form a low melting, eutectic alloy which closes the pores formed by the flame injection. Finally, I also found that silicon which is dissolved mainly in aluminum, reacts with the carbon of the fundamental body forming silicon carbide when the operational temperature of the protected parts exceeds about 550° C. which leads to a tear-free and solid bond between the protective layer to the carbon part. This bond is resistant to temperature changes.

Carbon or graphite bodies provided with such coatings have shown a long lasting excellent stability with respect to oxidation, at approximately 1700° C., due to the aforesaid alloying effect. During a particularly strong oxidation attack, the protective effect of the double layer upon the body can be increased by an additional melting of the already applied coating. This melting is carried out in a known manner by an argon arc or a direct plasma burner. The subsequent melting of the protective layers results in an elimination of the pores and in a chemical anchoring, which leads to a considerable improvement of the protection against burning off.

A similar additional increase of the protective action may be obtained by sealing the metallic double layer with a coating of an aqueous solution of 10 to 30% alkali borate and/or phosphate and/or silicate.

The effect of the cover layer is also heightened through the fact that during operation of the arc furnace, the current load of the electrodes is so measured that the cover layer is heated to above its melting point or softening point. This counteracts an otherwise possible tear formation in the cover layer caused by a difference in the thermal expansion coefficients of the fundamental material and the cover layer, thus preventing increased oxidation which is feasible in and near the tears.

In this type of operation, the coating layers in the total region between the electrode holder which serves as a current supply and the arc, are in a fluid or even in a plastic state, so that no voltages whatsoever can be produced in the coating layer through the different expansions of the coating layer and the fundamental body. Previously formed tears are automatically sealed by the plastic or fluid coating layer. Therefore a breaking off of the applied protective layer is not possible.

I found it particularly advantageous to produce, using the aforementioned preferred method of operation, coatings of components which in a temperature range between 600 and 1200° C., preferably 700 to 1000° C., form melting eutectics and to measure the current load such that the melting point of the eutectic is at least obtained on the electrode surface.

Handwritten notes: Thinning above 550°C. 3039

Handwritten notes: 365 X340

Handwritten notes: LAD EPL

3

The aforedescribed invention will now be disclosed with some embodiment examples.

EXAMPLE 1

A graphite electrode with a diameter of 450 mm. and a length of 2000 mm. is left to rotate at about 50 revolutions per minute, following the customary, accurately scaled turning off, in a rotating lathe. Two flame injection electrodes, arranged in sequence at a distance of 200 mm., uniformly coat the electrode surface (injection distance 100 mm.), first with an 0.05 mm. thick primary layer of 98.5% silicon+0.8% Fe+0.5% Al+0.2% Ca and thereafter with an 0.15 mm. thick cover layer of 99% Al+0.7% Mg+0.3% Si.

When used in an arc furnace, electrodes coated in this manner result in a graphite saving of 25 to 35% compared to untreated electrodes.

EXAMPLE 2

A graphite crucible 200 mm. in diameter, 500 mm. high and with 20 mm. wall thickness is slowly rotated on a turntable, e.g. at 30 r.p.m. An approximately 0.1 mm. thick primary layer of 95% Si+3% Ti+1.5% Fe+0.5% Al is applied by means of a powder flame injection pistol. The coating which is still approximately 70° C. is injection coated with a cover layer of 0.2 mm. thickness, comprised of 98.2% Al+1.5% Mg+0.3% Mn, by using a wire flame injection pistol. The coated crucible is subsequently dipped briefly into a 20% sodium phosphate solution (pH 5) and thereafter dried at 120° C.

When employed to operate in a copper casting installation, the above-described crucibles achieve a life span which is 4 to 6 times longer than in untreated crucibles.

I claim:

1. Formed body of carbon or graphite having an oxidation arresting protective layer which encompasses a primary layer on the carbon or graphite formed body and a metallic cover layer on the primary layer, said primary layer being comprised of 90 to 100% silicon and 0 to 10% of sodium, magnesium, calcium, boron, aluminum, titanium, zirconium, manganese, iron, car-

4

bon, nitrogen, phosphorus and oxygen, separately or in combination, the cover layer being comprised of 85 to 100% aluminum and 0 to 15% sodium, magnesium, boron, silicon, phosphorus, oxygen, copper, zinc, lead, titanium, zirconium, chromium, manganese, iron, cobalt and nickel, separately or in combination.

2. The body of claim 1 wherein the primary layer comprises 95 to 98.9% silicon and 1.1 to 5.0% of a material selected from sodium, magnesium, calcium, boron, aluminum, titanium, zirconium, manganese, iron, carbon, nitrogen, phosphorus, oxygen and mixtures thereof and the cover layer comprises 93 to 99.5% aluminum and 0.5 to 7% sodium, magnesium, boron, silicon, phosphorus, oxygen, copper, zinc, lead, titanium, zirconium, chromium, manganese, iron, cobalt and nickel and mixtures thereof.

3. The body of claim 1, wherein the primary layer has a thickness of 0.01 to 0.15 mm. and the cover layer has a thickness of 0.05 to 0.6 mm.

4. The body of claim 1, wherein the primary layer has a thickness of 0.02 to 0.1 mm. and the cover layer has a thickness of 0.1 to 0.3 mm.

5. The body of claim 4, wherein a sealing layer consisting of alkali borate, phosphate, silicate or mixtures thereof is on the cover layer.

References Cited

UNITED STATES PATENTS

2,295,379	9/1942	Beck et al	117—223X
3,120,453	2/1964	Fitzer et al.	117—217
3,348,929	10/1967	Valtschev et al.	117—217X
3,390,013	6/1968	Rubisch	117—221X
3,476,586	11/1969	Valtchev et al.	117—217X

ALFRED L. LEAVITT, Primary Examiner

C. K. WEIFFENBACH, Assistant Examiner

U.S. Cl. X.R.

13—18; 117—71, 169, 219, 227, 228