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METHOD OF FORMING CARBON-BONDED SILICON CARBIDE BODIES

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7 Claims

ABSTRACT OF THE DISCLOSURE

This disclosure relates to a method for fabricating silicon carbide bodies and an improved silicon carbide body particularly suitable as a silicon carbide side wall for an electrolytic reduction cell.

This invention relates to a method for fabricating silicon carbide bodies and an improved silicon carbide body.

More particularly, this invention relates to a method of fabricating silicon carbide sidewalls for electrolytic reduction cells and to improve silicon carbide refractories for electrolytic reduction cell sidewalls.

In the production of aluminum by the conventional electrolytic process, the electrolytic cell comprises in general a steel shell having disposed therein a refractory lining separated from the shell by a layer of insulating material. The bottom of the refractory lining along with a layer of electrolytically produced molten aluminum which collects thereon during operation serves as the cathode. One or more consumable carbon electrodes is disposed from the top of the cell and is immersed at its lowest extremity into a layer of molten electrolyte which is disposed in the cell. In operation, the electrolyte or bath which is a mixture of alumina and cryolite is charged to the cell, and an electric current is passed through the cell, from the anodes to the cathode via the layer of molten electrolyte while oxygen collects at the anode. A crust of solidified electrolyte and alumina forms on the surface of the bath, and this is usually covered over with additional alumina.

Traditionally the refractory lining for the reduction cell has been of carbon, either carbonaceous material rammed into place or preformed carbon blocks. Carbonaceous materials that have been used include petroleum coke, anthracite, gilsonite coke, or various mixtures thereof. It has long been thought desirable to form the sidewalls of a different material than the bottom cathode area of the cell lining. If this were done and a poor electrical conductor selected as the sidewall material, the flow of current from the anode to the cathode floor of the cell via the molten metal pad could be more easily controlled and there would be less problem with stray current flow through the sidewall. A material that was early looked at for this was silicon carbide. An additional advantage that can be realized from the use of silicon carbide refractory brick to replace thick carbon cell sidewalls is that the cell cavity capacity is increased and consequently the cell productivity is increased also. However, if the standard silicon carbide refractories that are bonded with silicon nitride or silicon oxynitride are used, the disadvantage of erosion by molten fluoride electrolyte and contamination of the cell aluminum product with silicon has resulted.

Thus, in general the properties of an ideal sidewall material for electrolytic reduction cells would be poor electrical conductivity, high density or low porosity, high strength, and good thermal conductivity, or at least a thermal conductivity appropriate to the cell design, so that frost heave isotherms are minimized in the sidewall

area. "Frost heave isotherms" refers to the penetration of the sidewall by and the fusing therein of the molten salts present in the reduction cell bath. The action is similar to the "frost heave" that may occur in the foundations of cold storage buildings or cause the lifting of the surface of the ground with certain types of soils in frosty weather, where the growth of columnar ice crystals at the freezing interface can develop large forces.

A method has now been developed for producing a silicon carbide body which body is suitable for use in electrolytic reduction cell sidewalls and meets these desired properties. Specifically, there has been developed a process and a unique carbon bonded silicon carbide body which has the high compressive strength and good electrical resistivity and thermal conductivity of conventional silicon nitride or silicon oxynitride bonded silicon carbide refractories and also has the high erosion resistance of the more conventional carbon bonded carbon refractory. More specifically, there has been developed a method of fabricating a silicon carbide body comprising preparing a mixture of silicon carbide particles, from 4%–12% of a cokable, carbonaceous bonding agent, and from 0.5%–10% added elemental sulfur. These percentages are by weight of total mixture. Any suitable cokable carbonaceous bonding agent may be used such as tar, asphalt or pitch. Applicant has found that pitch is particularly suitable. Pitches having softening points from 55° C. up to and including 170° C. have been successfully used. The softening point of the pitch materials is determined by the cube in water method which carries the American Society for Testing Materials designation D61–38. In general, this method consists of measuring the temperature at which a ½" cube of pitch when suspended at a specified distance above the bottom of a container will elongate and touch the bottom of the container.

The materials may be all mixed together initially according to this invention, but for best results they should be added incrementally. The mixture is heated to a temperature at which the bonding agent softens and flows to coat the particles and form a uniform mixture. The uniform mixture is then compressed either by ramming, tamping or pressing to form a body having a density of at least 2.5 grams/cc. It is essential that the green mixture achieve at least this density in order that a product having a satisfactory baked density may be attained. The compressed body is then baked at a controlled rate of heating to permit slow evolution of vapors whereby a dense baked product is formed.

It is desirable that the silicon carbide particles be size graded for dense packing in order that the density criterion can be satisfied. Any suitable size gradation which will achieve dense packing can be used. Applicant has found that a particularly suitable size gradation for the silicon carbide particles comprises 1¾%–10% of a –4 and +8 mesh Tyler screen fraction, 17%–10% of a –8 and +14 mesh Tyler screen fraction, 22%–10% of a –14 and +28 mesh Tyler screen fraction, 8½%–10% of a –28 and +48 mesh Tyler screen fraction, 18%–10% of a –48 and +100 mesh Tyler screen fraction, 8%–10% of a –100 and +200 mesh Tyler screen fraction, 10%–20% of a –200 and +325 mesh Tyler screen fraction, and 12¾%–20% of a –325 mesh Tyler screen fraction. These percentages are by weight of silicon carbide present.

As has been indicated, a highly satisfactory cokable carbonaceous bonding agent is pitch, particularly pitch having a cube in water softening point of about 55° C. Under these conditions, a suitable temperature at which the mixture should be heated in order for the bonding agent to soften and flow to coat the particles and form a uniform mixture is about 150° C.

The baking is desirably carried out in a reducing atmosphere. The baking must be at a controlled rate of heating to permit slow evolution of vapors. It is believed that the sulfur present in the mixture chemically strips the hydrogen content of the pitch as H_2S and promotes an early condensation or concentration of the carbon content of the pitch into a well ordered high carbon resin. Thus, the vapors that are evolved are H_2S , sulfur, and other vaporous products of the baking out stage of the process. It has been found that a controlled rate of not more than $50^\circ C.$ temperature rise per hour to a temperature from $700^\circ C.$ – $1500^\circ C.$ permits this slow evolution of vapors to occur and results in a dense baked product being formed. The most desirable temperature range to which the body should be baked is from $900^\circ C.$ – $1200^\circ C.$ Obviously, any suitable temperature and length of holding time within this range can be utilized. For example, if one desires to bake only to $900^\circ C.$, a satisfactory product can be achieved by holding the body at this temperature longer than if one desires to use a final baking temperature of $1200^\circ C.$ where a shorter holding time can be utilized.

Although as has been indicated above, all of the ma-

point of the sulfur yields an increased pitch-coke binder residue over that of normal pitch. Hence, with a pitch-sulfur binder, after compaction and baking, a significantly more dense and strong carbon bonded silicon carbide body results. As has been stated, such a bonded body lends itself to either the making of refractory-type brick or slabs of larger rammed monolithic unbaked shaped articles.

Table I shows the physical properties of various baked silicon carbide bodies including a silicon carbide body prepared in accordance with this invention. The molten fluoride spin erosion test results shown in Table I clearly indicate the superior erosion resistance of the silicon carbide bodies produced according to this invention over the commercial silicon carbide brick. The molten fluoride spin erosion test involves suspending a wafer of the material to be tested in a bath of molten ($1000^\circ C.$) cryolite containing 8% calcium fluoride and 6% Al_2O_3 . The wafers are from $\frac{1}{8}$ – $\frac{1}{4}$ inch thick, $\frac{3}{4}$ inch wide and $2\frac{1}{2}$ inches long. The wafers are agitated in the bath by rotation at approximately 200 revolutions per minute and the volume loss is periodically determined.

TABLE I.—PHYSICAL PROPERTIES OF VARIOUS BAKED SILICON CARBIDE BODIES

Composition type	Green density, g./cc.	Baked density, g./cc.	Elec. res., Ω -cm.	Comp. strength, p.s.i.	Percent bake change		Molten fluoride spin erosion test (1,000° C.)
					Ave. lineal	Wt. loss	
Commercial SiC brick silicon oxynitride bonded.		2.5–2.6	>30	6,500			From 5–10% volume erosion after 5 hours.
Carbon bonded SiC (SiC+6% 55° C. pitch +2% sulfur)	2.70	2.63	0.2	6,400	0.0	1.55	Only sl. surface erosion after 5 hrs. <5% volume. Not tested.
Carbon bonded SiC (SiC+10% 55° C. pitch +no sulfur).	2.58	2.37		2,000	+3.80	1.75	
As above (SiC+5% 150° C. pitch+no sulfur).	2.49	2.46	.41	900	— .06	1.51	Do.
Carbon bonded carbon.							Unaffected by erosion testing.

terials may be initially mixed together and a satisfactory product formed, it has been found that a particular sequence of steps in the method would produce the most satisfactory results. This method for fabricating the silicon carbide bodies comprises uniformly heating a mixture of silicon carbide particles that have been size graded for dense packing to about $100^\circ C.$ – $105^\circ C.$ From 4%–12% of pitch binder is then added to the aggregate with mixing. Mixing continues while the mixture is heated to about $140^\circ C.$ From 0.5%–10% elemental sulfur in the form of flowers of sulfur is then added to the mixture and the heating and mixing is continued until a temperature of about $150^\circ C.$ is reached so that the bonding agent flows to coat the particles whereby a uniform mixture is attained. The mixture is then compressed in any suitable manner, e.g., by tamping into place in the cell, to form a body having a density of at least 2.5 grams/cc. The body is then baked at a controlled rate of not more than $50^\circ C.$ temperature rise per hour to a temperature from $700^\circ C.$ – $1500^\circ C.$

The silicon carbide containing composition resulting from the practice of this invention may be rammed in place in the cell and baked out therein as indicated above or it may be compressed into a preformed product which is baked out before being placed into the cell. It has been found that for best results, the quantity of cokable carbonaceous bonding agent should be about 5% and the quantity of elemental sulfur about 2% when the desired size gradations of silicon carbide particles are used.

The sulfur additive serves several purposes in the mixture. Sulfur is thoroughly miscible with coal tar pitch and makes it much more fluid at normal mixing temperatures, that is, from $80^\circ C.$ – $150^\circ C.$ This permits superior wetting and compaction with a silicon carbide aggregate. Sulfur is well known as a dehydrogenization agent. Hence, during baking of pitch sulfur bonded silicon carbide bodies, the sulfur chemically strips the hydrogen content of the pitch as H_2S and promotes an early condensation or concentration of the carbon content of the pitch into a well ordered carbon resin. This resin despite the total loss of remaining sulfur by heating to above the boiling

As shown in Table I, commercial silicon carbide brick, that is silicon carbide brick and that is silicon oxynitride bonded, has a baked density of from 2.5–2.6 grams/cc. It has a high electrical resistivity and a high compressive strength of 6500 pounds per square inch. However, this brick suffers from a 5%–10% volume erosion after five hours of the molten fluoride spin erosion test. Carbon bonded silicon carbide brick, that is carbon bonded silicon carbide that has been prepared in accordance with this invention by mixing silicon carbide particle size graded for dense packing with 6% of 55° C. pitch and 2% sulfur, as shown in this example has a green density of 2.70 grams/cc., a baked density of 2.63 grams/cc. and a satisfactory electrical resistivity. The compressive strength was comparable to that of a commercial silicon carbide brick being about 6400 pounds per square inch. In addition thereto, and surprisingly, the body prepared according to the invention showed only slight surface erosion after five hours in the molten fluoride spin test. The amount of erosion was less than 5% by volume. Where sulfur is not used in the preparation of the carbon bonded silicon carbide, the bodies have unsatisfactory compressive strength as shown in Table I. Table I includes for purposes of comparison carbon bonded which as indicated was unaffected by the erosion testing.

Throughout an extensive series of tests, green densities of greater than 2.5 grams/cc. have been consistently achieved in silicon carbide bodies made according to this invention. All of these bodies showed the superior properties characteristic of the process of this invention. Thermal conductivity measurements were also made between the silicon carbide bodies prepared according to this invention and commercial silicon carbide brick by placing the ends of 4.5 inch thick samples in $980^\circ C.$ molten bath and observing the time required to reach several temperature levels at the other radiated shield end. Both bodies reached $60^\circ C.$ in 30 seconds. The carbon bonded silicon carbide prepared according to this invention reached $306^\circ C.$ in 4 minutes and the commercial silicon carbide brick reached $306^\circ C.$ in 3.95 minutes. The carbon bonded silicon carbide prepared in accordance with this invention

reached 523° C. in 10 minutes and the commercial silicon carbide brick reached 534° C. in 10 minutes.

It is to be understood that many changes and variations can be made to the above outlined process and product description without departing from the spirit and scope of the instant invention. As has been indicated, cokable carbonaceous bonding materials of various types may be used and specifically pitches having softening points up to 170° C. have been successfully used. The mixture can also include carbon or graphite aggregate, furfural or furfural alcohol impregnation of the baked body and variations in pitch and sulfur levels as has been indicated without departing from the spirit and scope of the instant invention.

What is claimed is:

1. A method of fabricating a silicon carbide body comprising:

- (a) preparing a mixture of silicon carbide particles, from 4% to 12% of a cokable, carbonaceous bonding agent, and from 0.5% to 10% added elemental sulfur, said percentages being by weight of total mixture;
- (b) heating the mixture to a temperature from about 80° C. to about 150° C. at which the bonding agent softens and flows to coat the particles and form a uniform mixture;
- (c) compressing the uniform mixture to densify to a density of at least 2.5 grams/cc.;
- (d) baking the compressed body at a controlled rate of heating to permit slow evolution of vapors to a temperature not greater than about 1500° C. whereby a dense baked product is formed.

2. The method of claim 1 wherein the silicon carbide particles are size graded for dense packing.

3. The method of claim 1 wherein the cokable, carbonaceous bonding agent is pitch.

4. The method of claim 1 wherein the mixture is heated to about 150° C.

5. The method of claim 1 wherein the baking is at a

controlled rate of not more than 50° C. temperature rise per hour to a temperature from 700° C. to 1500° C.

6. The method of claim 1 wherein the baking is at a controlled rate of not more than 50° C. temperature rise per hour to a temperature from 900° to 1200° C.

7. A method of fabricating a silicon carbide body comprising:

- (a) uniformly heating a mixture of silicon carbide particles size graded for dense packing to about 100° C. to 105° C.;
- (b) adding about 4% to 12% pitch binder to the aggregate with mixing;
- (c) heating, while mixing continues, the mixture to about 140° C.;
- (d) adding 0.5% to 10% elemental sulfur to the mixture;
- (e) continuing the heating and mixing to about 150° C. so that the bonding agent flows to coat the particles whereby a uniform mixture is attained;
- (f) compressing the mixture to form a body having a density of at least 2.5 grams/cc.;
- (g) baking the body at a controlled rate of not more than 50° C. temperature rise per hour to a temperature from 700° C. to 1500° C.

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