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OXIDATION-RESISTANT GRAPHITE ARTICLE AND METHOD

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This invention relates to oxidation-resistant articles and it more particularly refers to such articles which are basically graphitic in nature.

Recent developments in the field of aerodynamics have revealed a need for materials which will endure under conditions of high heat flux, with consequent high surface temperatures, and high velocity oxidizing gas flow relative to the material. It has been discovered that such a material must also be resistant to thermal shock since the conditions encountered lead to very rapid temperature rise. Graphite is one of the best refractory materials known today which is adapted to fulfill the requirements above set forth. However, graphite suffers from the fault of being subject to rapid oxidation and consequent erosion under the action of high velocity oxidizing gas streams.

It is therefore the principal object of this invention to provide graphitic articles which are relatively oxidation resistant.

It is another object of this invention to provide a method of producing such articles.

Fulfilling these objects this invention broadly comprises an oxidation-resistant article comprising graphite having silicon carbide and either titanium carbide, boron carbide or mixtures thereof substantially uniformly distributed throughout said article.

An article according to this invention may be produced by mixing some form of comminuted carbon, such as petroleum coke for example, with a carbonizable binder, suitably coal tar pitch, and either boron carbide, titanium carbide or mixtures thereof. After thorough mixing, these materials are formed into the desired shape by molding, extruding or other suitable means, and then the formed article is packed in a protective covering, preferably coke, and baked to approximately 850° C. according to the usual practice in the carbon industry. This baking carbonizes the binder thus "curing" the article and making it dimensionally stable. After the article is cured, the protective covering is removed and replaced with a silicon-containing packing. The thus-packed article is placed in a suitable graphitizing furnace and heated to a graphitizing temperature, suitably higher than 2500° C., in a conventional manner. After a suitable time at the graphitizing temperature, which time depends upon the size of the article being produced, the graphitized article is cooled and removed from the furnace. The article thus produced is basically graphitic in nature having either boron carbide, titanium carbide, or mixtures thereof and silicon carbide substantially uniformly distributed throughout the article.

The article according to this invention initially should suitably contain 5 to 50 weight percent boron carbide, titanium carbide or mixtures thereof and should preferably contain 15 to 35 weight percent of such carbide after the initial baking step. A thus-constituted article, when properly graphitized according to the method described above, will pick up between 10 and 70 percent silicon from the graphitization packing. The silicon picked up reacts to form silicon carbide inside the

graphitized article. The amount of silicon pick-up and the amount of other carbide present in the article is determinative of the oxidation resistance of the finished graphitized article. The proportions of each constituent in the finally graphitized article based upon the total weight of the final article are about 30 to 80 weight percent graphite, about 15 to 60 weight percent silicon carbide, and about 10 to 30 weight percent in the aggregate of boron carbide, titanium carbide or mixtures thereof. It is preferred to have a silicon carbide concentration of from 30 to 50 weight percent.

It has been determined that the amount of silicon picked up to form silicon carbide from the silicon-containing packing during the graphitization step described above is a function of the graphitizing time and temperature and is also proportional to the amount and nature of the other carbides introduced into the mix from which the article is made. Table I below is a compilation of data comparing the silicon pick up for articles ½ inch by ½ inch by 4¾ inches containing 18 weight percent boron carbide which were graphitized at temperatures from 2500° C. to 2900° C. for 30 minutes.

Table I

Graphitizing temperature (° C.)	2,500	2,700	2,750	2,800	2,900
Silicon weight gain (percent of sample wt.—850° C. bake)	7	34	34	25	29

Table II below is a compilation of data comparing the silicon pick up, for articles ½ inch by ½ inch by 4¾ inches which have been graphitized at 2700° C. to 2800° C. for 30 minutes, to the amount of boron or titanium carbide initially added to the mix from which the article was made.

Table II

Boron carbide in original mix (percent)	7	11	17	29	0	14
Titanium carbide in original mix (percent)	0	0	0	0	29	14
Silicon weight gain (percent of sample weight—850° C. bake)	30.2	36.1	40.5	46.5	12.5	47.3

From a consideration of Table I and II, it may be seen that while silicon vapor is picked up from the packing during graphitization at any temperature up to 2900° C., an optimum graphitization temperature is 2700° C. to 2800° C. Similarly, the incorporation of amounts of boron or titanium carbide up to 50 weight percent induce silicon pick-up from the packing. However the best results are obtained when 15 to 35 weight percent boron or titanium carbide or mixtures thereof is present in the body which is baked to 850° C.

Many articles have been made according to the practice of this invention and tested to determine the amount of resistance to oxidation imparted by the method disclosed herein. This testing consisted of resistance heating a test article to a given temperature by passing an electric current therethrough and directing a stream of air, initially at room temperature, at the heated article. Table III below is a compilation of data taken from the various tests run. The measure of oxidation resistance in these tests is the time it takes for a sample article to burn through thereby interrupting the current flow. Each of the articles tested was ¼ inch in diameter and 4 inches long.

Table III

	Composition of Article baked to 850° C.			Graphitization Temperature, ° C.	Graphitization packing	Percent wt. gain from packing	Final Composition				Test Temp.	Failure time (minutes)
	Percent C	Percent B_4C	Percent TiC				Percent C	Percent B_4C	Percent TiC	Percent SiC		
1	100	------	------	2,800	coke	0	100	------	------	------	4,800 watts input.	0.99.
2	81.9	18.1	------	2,500	do	0	84.8	14.6	------	0.6	do	0.86.
3	81.9	18.1	------	2,500	SiC+coke	7.37	76.1	13.5	------	10.4	do	0.92.
4	81.9	18.1	------	2,800	do	38.2	49.6	10.6	------	39.8	do	15.9.
5	81.9	18.1	------	2,800	coke	0	84.8	14.6	------	0.6	3,600 watts input.	0.83.
6	81.9	18.1	------	2,700	SiC+coke	52.0	41.2	9.6	------	49.2	do	34.0.
7	81.9	18.1	------	2,800	do	45.0	45.2	10.1	------	44.7	do	60.0.
8	88.3	12.7	------	2,900	do	22.7	65.8	7.4	------	26.8	do	2.8.
9	81.9	18.1	------	2,725	do	47.1	43.9	10.0	------	46.1	1,600° C.	still good after 80.
10	69.4	30.6	------	2,700	do	46.5	36.3	18.4	------	45.3	1,600° C.	still good after 60.
11	69.4	------	30.6	2,800	coke	0	83.0	------	17.0	------	1,600° C.	1.9.
12	69.4	------	30.6	2,800	SiC+coke	26.6	58.5	------	12.5	30.0	1,600° C.	6.7.
13	69.4	------	30.6	2,700	do	14.0	67.5	------	14.9	17.6	1,600° C.	7.5.
14	69.4	15.3	15.3	2,800	coke	0	72.4	13.8	13.8	------	1,600° C.	2.4.
15	69.4	15.3	15.3	2,800	SiC+coke	58.0	30.1	8.7	8.8	52.4	1,600° C.	8.4.

An analysis of the data presented in this table reveals that the oxidation resistance of an article which is basically graphitic in composition is increased provided the proper carbide in the proper proportions is incorporated into the mix from which the article is formed and that such formed, cured article is graphitized at the proper temperature while it is protected by a silicon-containing pack. A comparison of runs 5 vs. 7, 6 vs. 7, 7 vs. 8, and 10 vs. 13 points up the value of having all the variables noted above at their optimum in order to insure oxidation resistance.

What is claimed is:

1. A formed graphite oxidation-resistant article having silicon carbide and at least one member of the group consisting of boron carbide and titanium carbide substantially uniformly distributed therethrough.

2. A formed oxidation-resistant article consisting essentially of 10 to 30 percent by weight in the aggregate of at least one member of the group consisting of boron carbide and titanium carbide and the remainder graphite which additionally contains silicon carbide in a proportion of 15 to 60 percent by weight of said graphite and said aggregate; said carbides being substantially uniformly distributed throughout said article.

3. A formed oxidation-resistant article consisting essentially of 10 to 30 percent by weight in the aggregate of at least one member of the group consisting of boron carbide and titanium carbide and the remainder graphite which additionally contains silicon carbide in a proportion of 30 to 50 percent by weight of said graphite and said aggregate; said carbides being substantially uniformly distributed throughout said article.

4. The method of making a formed oxidation-resistant article which comprises mixing at least one member of the group consisting of titanium carbide and boron carbide with carbon and a carbonizable binder; forming said mixture into at least one shaped article; baking said formed article, thereby carbonizing said binder and curing said article, in a non-oxidizing atmosphere; covering said baked article with a silicon-containing packing; and graphitizing said article at 2500° C. to 2900° C.

5. The method of making a formed oxidation-resistant article which comprises mixing at least one member of the group consisting of titanium carbide and boron carbide with comminuted petroleum coke and coal tar pitch; forming said mixture into at least one shaped article; baking said formed article to about 850° C., thereby carbonizing said pitch and curing said article, in a protective coke covering; replacing at least part of said coke covering with sand; and graphitizing said article at about 2700° C. to about 2800° C. for about 30 minutes.

References Cited in the file of this patent

UNITED STATES PATENTS

2,154,271	Higgins	Apr. 11, 1939
2,307,550	Toepfer	Jan. 5, 1943
2,358,615	Arnott	Sept. 14, 1944
2,906,632	Nickerson	Sept. 29, 1959
2,908,553	Frank	Oct. 13, 1959
2,997,744	Stoddard et al.	Aug. 29, 1961
3,003,860	Sermon et al.	Oct. 10, 1961
3,019,128	Smiley	Jan. 30, 1962