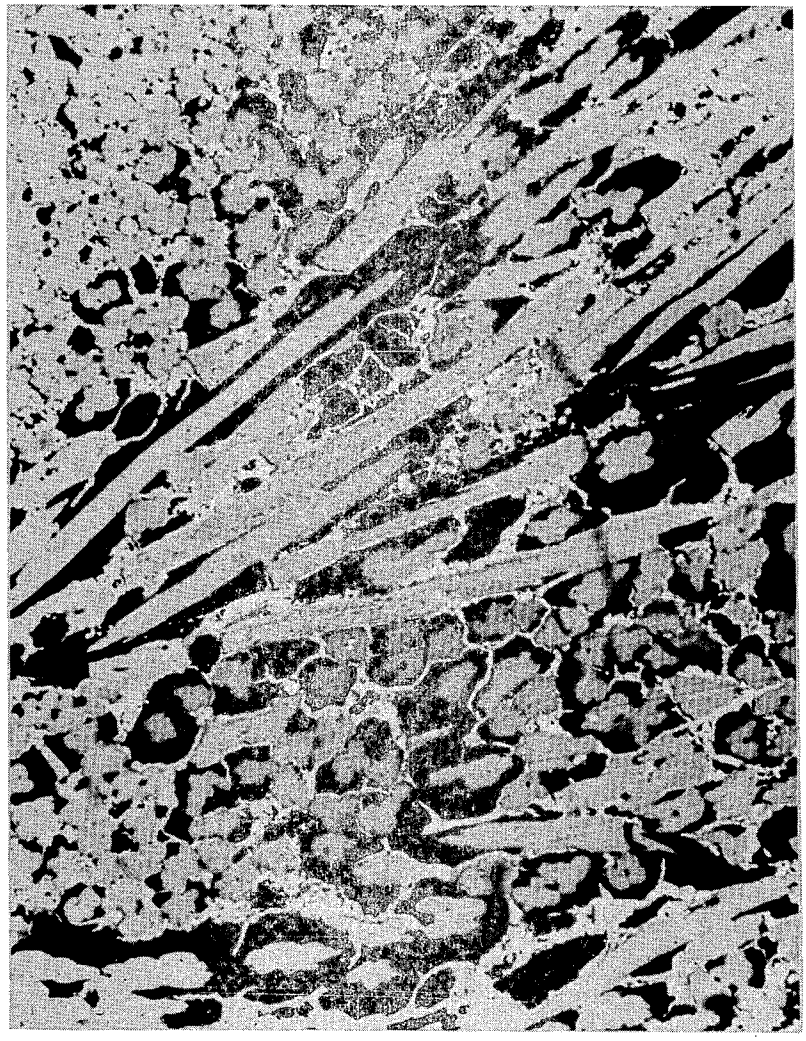
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SHREDDED CARBONACEOUS FIBER COMPACTIONS AND METHOD OF MAKING THE SAME

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SHREDDED CARBONACEOUS FIBER COMPACTIONS AND METHOD OF MAKING THE SAME

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This invention relates to new and useful forms of carbon and graphite, and more particularly, the invention relates to compactions of shredded fibers of carbonized or graphitized textile fabrics.

Manufactured carbon and graphite in a flexible textile form has recently become available.

United States Patent 3,011,981, issued Dec. 5, 1961 to W. T. Soltes discloses a method for manufacuring textile carbon from fibrous and substantially pure cellulosic materials, such as strands, skeins, ropes, fabrics and batting pads. The textile carbon product is reported to be electrically conductive while retaining the flexibility and other physical characteristics of the textile starting material.

Electrically conductive graphite in a flexible fiber and fabric form is reported in Metal Progress, May 1959, pp. 115–116, and is commercially available in any textile form such as yarns, braids, felts, and woven or knit fabrics.

As used herein and in the appended claims the term "shredded fiber" relates to material obtained by reducing a woven carbon or graphite textile fabric to a completely fibrous mass consisting of short lengths of randomly oriented fibers.

Manufactured graphite articles which conventionally are fabricated from either a lampblack or a petroleum coke base material have found a myriad of uses. Today, with the ever increasing demand for high temperature resistant materials, graphite has become a refractory workhorse in scores of industrial and military applications. The properties of any particular piece of manufactured graphite depend on the raw materials used as well as the method of manufacture. It has long been attempted in the art to control these variables so that a manufactured graphite article having desired properties may be produced at will. Unfortunately, attempts to produce a manufactured graphite article characterized by low density and a high strength modulus, that is to say, a high strength to density ratio have not been completely successful. As a result, the manufactured graphite which is available is often usuable in certain refractory applications which require an exceptionally light weight material which is resistant to thermal shock. In addition, manufactured carbon articles which have a higher strength to density ratio than is presently available, is sometimes also in demand.

With these limitations in mind, the principal object of the invention is to provide a form of manufactured carbon and manufactured graphite which has a high strength to density ratio.

Broadly stated, the object of the invention is accomplished by a carbonaceous article which comprises a molded compaction of shredded fibers of a carbonized or graphitized woven fabric; the shredded fiber being bound together by a carbonized or graphitized carbonizable binder.

In the accompanying drawing, the sole figure is a photomicrograph which has been magnified 500 times and which shows the low fiber orientation of an all graphitic compacted and shaped article which is typical of the invention.

The compacted carbonaceous article of the invention may be provided by mixing shredded pieces of carbonized or graphitized woven fabric with a suitable carbonizable

binder, molding the mixture to the desired shape under pressure and carbonizing or graphitizing the carbonizable binder as desired. If convenient, the mixture can be shaped and the binder carbonized or graphitized concurrently. It will be appreciated that if a shaped compaction of shredded pieces of textile carbon and carbonizable binder is heated to graphitizing temperatures in order to graphitize the binder, the shredded pieces of textile carbon will likewise be graphitized.

Among the many suitable binders for use in the practice of the invention are phenolics, pitches, epoxies, furfural, furfuryl alcohol and combinations of these resins. The preferred thermosetting binders for use in the practice of the invention are those which deposit the highest amount of a bond forming carbonizable coke. A specific preferred binder is a mixture comprising 50% by weight phenolic resin, 25% by weight furfuryl alcohol and 25% by weight furfural. The binder to shredded pieces of woven fabric ratio may vary from 1:3 to 1:2.

As outlined above, the articles of the subject invention are formed by molding under pressure to the desired shape a mixture of shredded pieces of carbon or graphite woven fabrics and a suitable carbonizable thermosetting binder and concurrently therewith or subsequent thereto, as desired, heating the shaped article to a carbonizing or graphitizing temperature.

A specific example of the preparation of a shaped article which comprises carbon bonded shredded pieces of carbon cloth is the following:

EXAMPLE I

A 9¾" diameter x 3" thick article was fabricated from a mixture of shredded carbon cloth and the preferred binder mixture set forth above. The shredded pieces of cloth to binder mixture was in a 2:1 ratio and was formed into an article at pressure of 750 p.s.i. and cured for 6 hours at approximately 130° C. Carbonization of the binder was carried out by packing the article in coke in a double sagger. The larger sagger was inverted over the smaller which formed an annular space between the two. This space was filled with a 3" layer of charcoal and a 2" layer of sand which formed a seal and prevented oxidation during baking. A heating rate of 10° C./hr. to 600° C., 60° C./hr. to 800° C. with a two hour hold was employed.

Typical properties at room temperature for such articles are reported in Table I below.

Table I

Bulk density, g./cm.^{3}	.94
Flexural strength, p.s.i.:	
With grain	1400
Against grain	900
Young's modulus; p.s.i.$\times 10^6$:	
With grain	1.0
Against grain	.5
Resistivity, ohm-cm.:	
With grain	.022
Against grain	.031

A specific example of the preparation of a shaped article composed of carbon bonded shredded pieces of graphite cloth is the following:

EXAMPLE II

A number of articles comprising shredded pieces of graphite cloth and binder were shaped and compacted under a pressure of 750 p.s.i. The binder in each instance consisted of a mixture of 50% by weight phenolic resin, 25% by weight furfuryl acohol and 25% by weight furfural. The shaped articles were 9¾ inches in diameter and 2½ inches thick. These samples were placed vertical-

ly in a 12 inch x 12 inch x 14 inch high metal sagger, coke was packed around the individual samples and the sagger sealed as previously described. The heating schedule which was used was: 15° C./hr. to 500° C., 60° C./h. to 800° C. with a two hour hold. The articles were allowed to cool to a temperature of 300° C. prior to removal from the sagger in order to prevent oxidation.

Typical properties at room temperature for these articles are reported in Table II below.

Table II

Bulk density, g./cm.^{3}	1.1
Flexural strength, p.s.i.:	
With grain	1700
Against grain	300
Elastic modulus, p.s.i.$\times 10^6$:	
With grain	1.13
Against grain	.32
Resistivity, ohm-cm.:	
With grain	.010
Against grain	.024

Such articles are quite distinct from conventional laminates in that they have a lower degree of fiber orientation. They are also different from conventional solid carbon forms in their strength to weight ratio and elastic modulus.

A specific example of the preparation of an all graphite shaped article composed of graphite bonded shredded pieces of graphite cloth is the following:

EXAMPLE III

Compacted and shaped articles composed of carbon bonded shredded pieces of graphite cloth which were prepared according to Example II were reduced to a size suitable for packing in a graphite sagger 20 inches long and having a 9 inch inside diameter. The top and bottom of the sagger had small holes to provide for escape of the volatiles which were evolved during graphitization. The sagger was placed in the hot zone of a 10" tube furnace and was heated to a temperature of 2800° C. in four hours. During graphitiziation, the furnace was swept with nitrogen at the rate of 6 to 12 cubic feet per hour to remove the evolving volatiles. After cooling to approximately 500° C. the articles were removed.

Typical properties at room temperature for these articles are reported in Table III below.

Table III

Bulk density, g./cm.^{3}	1.0
Flexural strength, p.s.i.:	
With grain	1700
Against grain	500
Young's modulus:	
With grain	.78
Against grain	.24
Resistivity, ohm-cm.:	
With grain	.003
Against grain	.007

A specific example of the preparation of an all graphitic article obtained by the concurrent graphitization of a compacted carbon bonded shredded carbon cloth article is the following:

EXAMPLE IV

An article fabricated and processed according to the method set forth in Example I was graphitized in the manner set forth in Example III, except that the heating rate was decreased such that approximately 8 hours were required to graphitize to 2800° C. This extended heating rate prevents cracks due to increased shrinkage and allows a longer period for the escape of additional volatile matter in the carbon cloth.

Typical room temperature properties for this article is reported in Table IV.

Table IV

Bulk density, g./cm.^{3}	.96
Flexural strength, p.s.i.:	
With grain	2000
Against grain	700
Elastic modulus, p.s.i.$\times 10^6$:	
With grain	.93
Against grain	.40
Resistivity, ohm-cm.:	
With grain	.005
Against grain	.009

The all graphitic articles of the invention are distinct from conventional laminates due to the lower degree of orientation of the fibers. This highly random distribution of the fibers will be appreciated from the accompanying photomicrograph.

The all graphitic articles of the invention are useful as substrates for pyrolytic carbon, vapor deposited tungsten and other high temperature coatings as well as back-ups for free standing inserts of tungsten, pyrolytic carbon and graphite. This material should also find wide applications in low erosion areas such as entrance caps, exit cones, and blast tubes for missiles and rockets.

Table V below compares the bulk density, flexural strength, electrical resistivity, coefficient of thermal expansion and thermal conductivity values for conventionally prepared graphite, graphite cloth laminates and the shredded textile fiber compactions of the invention.

The graphite cloth laminates referred to are prepared by coating the adjacent surfaces of a plurality of sheets of graphite cloth with a carbonaceous binder, laminating the sheets together with heat and pressure and finally further heating the laminate to carbonize or graphitize the binder.

TABLE V

Property	Conventional graphite		Graphite cloth laminates		Shredded carbon fiber compactions	Shredded graphite fiber compaction		Shredded graphite fiber-graphite bonded compaction fiber and binder graphitized concurrently
	Lampblack base	Petroleum coke base	Carbon bonded	Graphite bonded		Carbon bonded	Graphite bonded	
Bulk Density, g./cm.^{3}	1.53	1.58	1.19	1.16	.94	1.15	1.10	.96
Flexural Strength lbs./in.^{2}:								
W.G.	2,400	2,600	2,200	3,200	1,400	1,700	1,700	2,000
A.G.	1,800	1,000	<50	<100	900	300	500	700
Resistivity, ohm-cm.:								
W.G.	.0063	.0008	.01	.0025	.022	.042	.003	.005
A.G.	.0063	.0013	.072	.0130	.031	.025	.007	.009
C.T.E.$\times 10^{-7}$/°C.:								
W.G.	45-50	25.0	24.8	28.3	22	28.7	29.2	26
A.G.	45-50	35.0	41.8	34.7	N.A.	36.5	34.4	N.A.
Thermal Conductivity, B.t.u./(hr.) (ft.^{2})(° F./ft.):								
W.G.	15-20	80-120	N.A.	14-21	2.5	3.8	17-21	N.A.
A.G.	15-20	50-70	N.A.	5-15	1.2	1.8	6-12	N.A.

W.G.=With grain. A.G.=Against grain. N.A.=Not available.

From a study of the table it will be appreciated that the subject shredded graphite and carbon textile fiber compactions are much stronger in the "against grain" direction than are graphite cloth laminates and thus can be used in certain load bearing applications where a force is exerted on the graphite body in both the with and against grain directions. Also, the shredded graphite fiber compactions of the invention have a thermal conductivity in the against the grain direction which is much less than conventionally produced graphite. This is an important feature in that it is desirable in certain applications for a graphite article to have an exceptionally low total thermal conductivity while its thermal conductivity is lower in one direction than in the other.

The manufactured carbon and graphite shredded fiber compactions of the invention, may of course, be molded in various shapes and geometric patterns.

I claim:

1. A unique compacted carbonaceous article which has been manufactured by shaping under pressure a mass of randomly oriented shredded fibers of a carbonaceous woven textile material and a carbonizable bonding agent selected from the group consisting of thermosetting resins, pitches and mixtures thereof, and subsequently carbonizing said bonding agent.

2. The article of claim 1 wherein said fibers are graphite.

3. The article of claim 2 wherein said fibers are graphite and said bonding agent has been graphitized.

4. A process for making a unique article of manufacture which comprises reducing a woven carbonaceous textile fabric to a completely fibrous mass consisting of short lengths of randomly oriented fibers, mixing said randomly oriented fibers with a carbonizable binder selected from the group consisting of thermosetting resins, pitches and mixtures thereof, shaping under pressure the mixture of randomly oriented fibers and binder to form a compacted article, and heating said article to a temperature sufficient to carbonize said binder.

5. The process of claim 4 wherein said shaping of said article and carbonizing of said binder is done concurrently.

6. The process of claim 4 wherein said woven carbonaceous textile fabric is graphite.

7. The process of claim 6 wherein said article is heated to a temperature sufficient to graphitize said binder.

8. The process of claim 4 wherein said article is heated to a temperature sufficient to graphitize said randomly oriented fibers of said woven carbonaceous textile fabric and graphitize said binder.

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