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(71) Applicant: TOUCHSTONE RESEARCH LABORATORY, LTD. [US/US]; R.D. #1, Box 100B, The Millennium Centre, Triadelphia, WV 26059 (US).

(72) Inventor: JOSEPH, Brian, E.; 18 Lynwood Avenue, Wheeling, WV 26003 (US).

(74) Agent: LANE, Philip, D.; McGuireWoods, LLP, Suite 1800, 1750 Tysons Boulevard, McLean, VA 22102 (US).

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(54) Title: MICROWAVE ASSISTED TREATMENT OF CARBON FOAM

(57) Abstract: Accelerated heat-up of carbon foam materials is achieved through the use of microwave and/or induction heating devices. According to various preferred embodiments of the present invention, such microwave/induction heating acceleration is obtained through the use of microwave/induction heating devices alone or in concert with more conventional radiation or convection based heating devices. The method of the present invention permit the relatively rapid and uniform heat-up of carbon foam materials particularly in such processes as the carbonization and/or graphitization thereof.

MICROWAVE ASSISTED TREATMENT OF CARBON FOAM

Field of the Invention

The present invention relates to the treatment, i.e. carbonization and/or graphitization of carbon foam materials, and more particularly to the use of microwave and induction heating devices to expedite such heating.

Background of the Invention

The treatments of carbon foams conventionally referred to as carbonization and graphitization are well known in the art and involve the treatment of such foams at elevated temperatures, on the order of above about 1000°C, to remove all residual volatile matter therefrom. Such treatments can and generally do affect the properties of such materials by rendering them more thermally and/or electrically insulating, more abrasion resistant, etc.

While such treatments are highly desirable for controlling the aforementioned and similar properties of carbon foams, they tend to involve extended heat up periods, on the order of many hours to days depending on the particular carbon foam being treated as well as its physical shape and thickness of the sample being treated in a conventional radiation or convection based heating device. Such extended treatment times can and do significantly affect the economics of the production processes for such carbon foams both in terms of energy required and equipment utilization.

While a portion of the heat up time required is due to the need for care that the carbon foam is not subjected to excessive stress during the heat up period (and also the cool down period), much of the time is required because of the inherent thermal insulating properties of carbon foams and the fact that convection and radiant heating devices expose only the outer surfaces of the carbon foam under treatment to thermal energy that then must be conducted via the thermally insulating carbon foam to the interior of shape undergoing treatment. Hence, the innate thermal insulating properties of the carbon foam inhibit faster heating of the carbon foam to achieve carbonization and/or graphitization.

Thus, it would be highly desirable to provide a method for the heating of carbon foams that permits acceleration of the heat-up cycle and therefore reduction of the overall treatment time required to obtain carbonization and/or graphitization of carbon foams.

Objects of the Invention

It is therefore an object of the present invention to provide a method for the acceleration of the heat-up rate of carbon foams in such processes as carbonization and graphitization.

It is another object of the invention to provide such a process that does not adversely affect the physical or structural properties of the carbon foam during such accelerated heat-up.

Summary of the Invention

According to the present invention, accelerated heat-up of carbon foam materials is achieved through the use of microwave and induction heating devices while the carbon foam is under an inert atmosphere. According to various preferred embodiments of the present invention, such microwave/induction heating acceleration is obtained through the use of microwave/induction heating devices alone or in concert with more conventional radiation or convection based heating devices. The methods and apparatus of the present invention permit the relatively rapid heat-up of carbon foam materials particularly in such processes as the carbonization and/or graphitization thereof.

Detailed Description

U.S. Patent Application Serial No.09/902,828, filed July 10, 2001 entitled "Cellular Coal Products and Processes", describes the production of coal based carbon foams having a density of preferably between about 0.1 g/cm^3 and about 0.8 g/cm^3 that are produced by the controlled heating of a preferably high volatile bituminous coal particulate preferably up to ¼ inch in diameter in a "mold" and under a non-oxidizing atmosphere. According to specifically preferred embodiments, the starting material coal has a free swell index as determined by aforementioned ASTM D720 test of between about 3.5 and about 5.0 and preferably between about 3.75 and 4.5. The porous product/carbon foam thereby produced, preferably as a net shape or near net shape, can be machined, adhered and otherwise fabricated to produce a wide variety of low cost, low density products, or used in its preformed shape as a filter, heat or electrical insulator etc. Such carbon foams, without further treatment and/or the addition of strengthening additives have been shown to exhibit compressive strengths of up to about 4000 psi. Further treatment by carbonization or graphitization yields carbon foams that can be used as electrical or heat conductors.

The production method described in that U.S. Patent Application comprises: 1) heating a coal particulate of preferably small i.e., less than about ¼ inch particle size in a "mold" and under a non-oxidizing atmosphere at a heat up rate of from about 1 to about 20°C to a temperature of between about 300 and about 700°C; 2) soaking at a temperature of between about 300 and 700°C for from about 10 minutes up to about 12 hours to form a preform or finished product; and 3) controllably cooling the preform or finished product to a temperature below about 100°C to yield a "green foam". The non-oxidizing atmosphere may be provided by the introduction of inert or non-oxidizing gas into the "mold" at a pressure of from about 0 psi, i.e., free flowing gas, up to about 500 psi. The inert gas used may be any of the commonly used inert or non-oxidizing gases such as nitrogen, helium, argon, $C0_2$, etc.

Subsequent to production of the "green foam" as just described; the "green foam" may be subjected to carbonization and/or graphitization according to conventional processes to obtain particular properties desirable for specific applications.

Carbonization, sometimes referred to as calcining, is conventionally performed by heating the "green foam" under an appropriate inert gas at a heat-up rate of less than about 5°C per minute to a temperature of between about 800°C and about 1200°C and soaking for from about 1 hour to about three or more hours. Appropriate inert gases are those described above that are tolerant of these high temperatures. The inert atmosphere is supplied at a pressure of from about 0 psi up to a few atmospheres. The carbonization/calcination process serves to remove substantially all of the non-carbon volatile elements present in the "green foam" such as sulfur, oxygen, hydrogen, etc.

Graphitization, commonly involves heating the "green foam" either before or after carbonization at heat-up rate of less than about 10° C per minute, preferably from about 1° C to about 5° C per minute, to a temperature of between about 1700° C and about 3000° C in an atmosphere of helium or argon and soaking for a period of less than about one hour. Again, the inert gas may be supplied at a pressure ranging from about 0 psi up to a few atmospheres.

As is apparent, carbonization and graphitization at temperatures of between about 1000° C and about 3000° C with heat up rates in the 1 to 5° C/minute can involve extremely long processing times, sometimes on the order of days. Such processing times are inherently necessary, partially due to the need to avoid cracking of the "green foam" due to over-rapid heat up, but are primarily due to the inherent thermal insulating properties of the "green carbon foam" that resists the transfer of thermal energy within the carbon foam mass from the outside of the structure to the internal portions thereof. Of course heat up rates and total heat up times will vary according to the shape, thickness etc. of the particular carbon foam structure being treated, however, as a general rule, such heat up times in conventional radiant energy or convection furnaces or ovens are overly long and consume large amounts of energy and valuable equipment usage time. Additionally, high temperature treatment of carbon foams in such devices often results in differential processing of portions near the surface of the structure that have been subjected to high temperature for much longer periods than portions of the structure at the "core" or center of the structure that may not reach the desired carbonization or graphitization temperature for many hours and are maintained at that temperature for the barest of minimum times to obtain the desired result. Such differential heating may result in "directional coking" from the outside of the carbon foam structure to the interior thereof.

Microwave heating units can be advantageous in that they are more energy efficient and heat more uniformly than conventional radiant energy or convection ovens and furnaces. Microwave ovens or furnaces generate electromagnetic waves, which cause the molecules of an object contained therein to move and rotate creating intermolecular friction. This friction between molecules results in the internal generation of heat. Such "internal" "frictional" heating while, as shown below being more rapid, is also more uniform, since the entire mass being heated tends to increase in temperature at a relatively uniform rate. Thus, relatively less disparity exists between externally and internally located portions of the mass of the structure being heated. Such relatively more uniform heating while leading to more uniform production of properties within the structure of the heated object, also produces less propensity for thermal cracking due to significantly different temperatures being achieved in different portions of the carbon structure during heat up. The air or inert gas atmosphere inside the microwave chamber does not heat due to the fact that molecules in a gas are too dispersed to create much friction or absorb much of the electromagnetic energy, hence little if any radiant or convection heating is produced.

The amount of thermal energy imparted to a sample as a result of the microwaves can be altered varying the power settings by percentages. With the equipment used for the studies reported below, the power setting actually only set the time a microwave heats versus adjusting the actual power. For example, if the power is set on 40%, then the microwave heats for 40% of the time, instead of 40% power. Microwave ovens/furnaces are commercially available with adjustable power settings that alter the power delivered to a contained sample and these would be similarly useful and perhaps preferred as with such systems, continuous, uniform heating at a reduced power level is possible.

According to the method of the present invention, "green foam", i. e. a material produced by the controlled foaming of a coal-based particulate as described hereinabove and in greater detail in U.S. Patent Application Serial No. 09/902,828 (which is incorporated herein by reference in its entirety), is carbonized and/or graphitized using microwave energy to obtain more rapid and uniform heating thereby reducing the potential for thermal cracking of the carbon foam and significantly shortening the carbonization and/or graphitization processing cycle(s).

As will be apparent to the skilled artisan, the microwave based heating methods of the present invention can be applied alone or in concert with more conventional radiant energy or convection based heating devices. Additionally, while the microwave heating methods described herein are described primarily in connection with the carbonization/graphitization of carbon foams produced from coal particulate, it should be recognized that these methods are equally applicable to the carbonization/graphitization of carbon foams produced from other starting materials such as petroleum or synthetic pitch as well as carbon foams that are the product of the controlled foaming of blends of coal particulate and petroleum or synthetic pitch.

Thus, the method of the present invention comprises carbonizing and or graphitizing a "green foam" structure, i.e. a carbon foam mass, that has not been subjected to carbonization and/or graphitization under an inert atmosphere using microwave energy to obtain relatively more rapid and uniform heating.

The power capability of the microwave device utilized in accordance with the present invention is not particularly critical except that it should be of adequate power capability to achieve heating of the carbon foam structure in a shortened period of time.

While the microwave power applied and the duration and variation of the power application will vary from carbon foam material to carbon foam material and according to the mass, i. e. thickness, density etc. of the carbon foam, the power parameters are readily determinable by trial and error or experimentation and accordingly can vary widely depending upon the foregoing carbon foam characteristics. As shown in the Examples below, it has been found advantageous to increase the power level as heating occurs. The amount of such power increase is again readily determinable by experimentation.

The following examples will serve to better illustrate the successful practice of the present invention.

Examples

In all cases reported below, three holes are drilled into a 6-inch thick sample of "green foam" that is then placed into a 1500-watt microwave oven under an inert atmosphere and the power increased over time as reported in Tables 1, 2 and 3 below. Dwell times at specified power levels are shown in the Tables. Temperature measurements are taken by inserting a thermocouple into the pre-drilled holes while the microwave was turned off and at the noted time intervals. In example 1 (reported in Table 1), the "green foam" sample was placed directly into the microwave oven on the turntable thereof. In Example 2 (reported in Table 2) the sample was placed on a firebrick located upon the oven turntable. In Example 3 (reported in Table 3) the sample was placed on an oven brick and wrapped in an insulating material.

Example 1

Table 1

Time (min)	Temp (C)	Power (%)	Current (A)
5	66.8	10	
10	146.2	20	11
15	166.4	30	10.8
20	239.8	40	10.7
25	335.3	50	10.6
30	792	60	10.5
35	848.7	60	10.5

Example 2

Table 2

Total Time (min)	Temp (C)	Individual Time (min)	Power (%)	Current (A)
131	166.8	10	10	10.6
	120.8	10	10	10.6
	351.9	15	20	10.8
	360	10	20	10.8
	480	5	30	10.6
	445	5	30	10.7
		5	40	10.7
	353	5	40	10.7
	341	10	40	10.7
	450	10	50	10.5
	680	10	50	10.6
	783	10	50	10.6
	826	10	50	10.6
		3	60	10.8
		7	70	

Example 3

Table 3

Total Time (min)	Individual Time (min)	Power (%)	Temp (C)
85	10	10	
	10	10	
	15	20	
	10	20	
	5	30	
	5	30	
	5	40	
	5	40	
	10	40	
	10	50	800-900

Microwaves are thus shown to be very effective in heating carbon foam — capable of bringing a sample to 1000°C in tens of minutes. The use of an insulating blanket is desirable in the experimental set up used in these tests because of the necessity for accessing the sample to obtain temperature measurements. The location of thermocouples in the sample with access thereto from outside of the microwave device would eliminate the need for the insulating blanket. In the absence of an inert atmosphere, samples (not reported) tended to oxidize and in some cases burn, thus the need for such an atmosphere.

This experimentation shows that a controlled atmosphere microwave heating unit with a programmable power/temperature controller can substantially reduce the time, energy and cost of producing calcined/graphitized carbon foam.

Samples of fully graphitized foam at 2600°C have also been shown to heat successfully using microwave heating. This shows that microwaves could be used for a range of heat treating of carbon foam from partial calcination, at 1000°C calcination temperatures, to complete graphitization to at least 2600°C.

While the foregoing examples demonstrate the effectiveness of microwave heating in reducing the processing time required to carbonize and/or graphitize a green carbon foam that has been formed and then is separately processed in a microwave device, it is equally possible that such an operation be performed by the incorporation of the microwave device into the autoclave or "mold" described in foregoing U.S. Patent Application Serial No. 09/902,828 so that carbonization and/or graphitization can be accomplished through the use of microwave heating in the same apparatus that was used to accomplish foaming.

Additionally, combinations of microwave heating and convection or radiant heating can also be used under certain circumstances to assure complete and uniform treatment of the green carbon foam.

While the invention has been described herein largely in the context of the use of microwave heating, it should be noted that induction heating may be similarly applied with similar results as induction heating that involves the introduction of magnetic energy into the green carbon foam structure for purposes of heating the same is similarly useful. As with the application of microwave devices, with induction heating devices the level of power and duration of its application will vary with the specific carbon foam undergoing treatment according to its density, thickness, composition etc., but the appropriate treatment parameters are readily determinable by experimentation.

As the invention has been described, it will be apparent to those skilled in the art that the same may be varied in many ways without departing from the spirit and scope of the invention. Any and all such modifications are intended to be included within the scope of the appended claims.

CLAIMS

What is claimed is:

1. A method for carbonizing and/or graphitizing a green carbon foam comprising heating the green carbon foam under an inert atmosphere in a microwave or induction heating device for a treatment period adequate to achieve carbonization and/or graphitization.

2. The method of claim 1 wherein a microwave heating device is utilized.

3. The method of claim 2 wherein said green carbon foam is produced by the controlled foaming of small particle size high volatile bituminous coal particulate.

4. The method of claim 2 wherein said green carbon foam is produced by the controlled foaming of a blend of small particle size high volatile bituminous coal particulate and petroleum pitch.

5. The method of claim 2 wherein said green carbon foam is produced by the foaming of a member selected from the group consisting of synthetic pitch, petroleum pitch, high volatile bituminous coal particulate and combinations and blends of the same.

6. The method of claim 2 wherein the power level or time of application of the power of said microwave device is varied over the treatment period.

7. The method of claim 5 wherein said variation of the power or time of application of the power comprises an increase in the power over the period of treatment.

8. The method of claim 2 wherein said inert gas is selected from the group consisting of helium, argon, nitrogen and CO_2.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : H05B 6/64; B29C 35/08; C01B 31/00; B01D 53/34; B32B 3/26; C08J 9/00; C08G 18/00
US CL : 219/678; 264/402, 29.7; 422/179; 428/304.4; 521/107, 165
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 219/678; 264/402, 29.7; 422/179; 428/304.4; 521/107, 165

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,344,159 B1 (KLETT) 05 February 2002 (05.02.2002), see entire document.	1-8
A	US 6,339,031 B1 (TAN) 15 January 2002 (15.01.2002), see entire document.	1-8

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
Facsimile No. (703)305-3230

Authorized officer
Quang Van
Telephone No. 703-306-9162