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(54) **Title:** THREE DIMENSIONAL CARBON ARTICLES

(57) **Abstract:** A method for making a three dimensional article include depositing alternating layers of a binder and a filler to form an article. Fillers include carbon or graphite based powders. Thereafter, the article is heat treated in a non-oxidizing environment to at least about 800°C.



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THREE DIMENSIONAL CARBON ARTICLES

BACKGROUND

[001] Additive manufacturing (otherwise referred to as 3D printing) is rapidly becoming mainstream as the technology improves and the costs go down. The process involves making three-dimensional solid objects for use in any number of applications. Traditionally, 3D printing techniques were first used for rapid prototyping. However, recently with the
5 reduction in costs and advancements in equipment and related software, 3D printing may be used in distributed or discrete manufacturing applications, with uses in, for example, construction, automotive, aerospace, and biotech.

[002] As the name suggests, additive manufacturing is an additive process, where successive layers of material are laid down to form articles based on a digital design. In this
10 manner, 3D printing is distinct from traditional article machining approaches, which generally rely on the removal of material to form an article.

BRIEF DESCRIPTION

[003] According to one aspect, a method for making a three dimensional article includes depositing alternating layers of a binder and a filler to form an article. Fillers include carbon
15 and/or graphite based powders. Thereafter, the article is heat treated in a non-oxidizing environment to at least about 2000°C.

[004] According to another aspect, a method for making a three dimensional article includes forming an article by depositing alternating layers of a binder and a filler. The filler includes a carbon and/or graphite powder in combination with a milled pitch. The binder partially
20 volatilizes at a temperature greater than the softening point temperature of the milled pitch. The article is then heat treated in a non-oxidizing environment to at least about 800°C.

DETAILED DESCRIPTION OF THE INVENTION

[005] The concepts described herein relate to the formation of carbon and graphite articles using three dimensional printing techniques.

[006] According to one embodiment, a three dimensional article may be formed employing
5 a layered approach wherein alternating layers of binder, then filler (as described herein below, the filler may include an uncoated powder, coated powder or powder/pitch mixture), are deposited on a target surface. In accordance with this approach the binder should be flowable at processing temperatures but then set or become substantially solid shortly after deposition on the target surface (or on the previous filler layer). According to this method,
10 optionally the binder may be set by employing a targeted heat source such as, for example, a laser. In other embodiments, the binder sets after deposition without an additional energy or heat source. In this manner, a three-dimensional article may be formed.

[007] Exemplary binders may include coal tar pitch, petroleum pitch, or lignin based pitch. In other embodiments, the binder may be a resin, preferably having a coking value greater
15 than at least 20 percent, still more preferably greater than at least 30 percent, and still more preferably greater than 40 percent. Exemplary resins may include phenolic resins, epoxy resins, polyimides or polyacrylonitrile ("PAN") base polymers.

[008] The filler is a carbon based material and may include uncoated carbon or graphite powders. In another embodiment, the filler includes carbon or graphite powders having a
20 coating applied thereon. In still further embodiments, the filler may include a mixture of a coated or uncoated powder with a milled pitch. In still further embodiments, the filler may include two or more coated or uncoated powders. In still further embodiments, the filler may include a two or more coated or uncoated powders and a milled pitch.

[009] Exemplary uncoated powders may include calcined or uncalcined petroleum based
25 coke powder, calcined or uncalcined pitch coke powders, calcined or uncalcined lignin based

coke powder, graphitized coke powder, graphitized coal, or natural graphite. Exemplary coated powders may include a base powder including calcined or uncalcined petroleum coke, calcined or uncalcined pitch coke, calcined or uncalcined lignin based coke powder, graphitized coke, natural graphite or graphitized carbon material. The base powders are advantageously coated with a graphitizable material derived from, for example, coal tar pitch, petroleum pitch, or a resin (for example phenolic resin) at a loading level of from about 1 to about 75 percent by weight of the base powder. In other embodiments, the loading level is from between about 1 and about 50 percent by weight of the base powder. In one embodiment, after application of the coating, the coated powder is carbonized. In other
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embodiments, after application of the coating, the coated powder is graphitized. In still further embodiments, after application of the coating, the coated powder does not receive a heat treatment prior to use in the three dimensional article.

[010] In one embodiment, the coated or uncoated powders have a generally spherical shape. In this embodiment, preferably the average aspect ratio is less than about 4, still more preferably less than about 3 and still more preferably less than about 2. In other
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embodiments, the coated or uncoated powders may be other shapes, for example, plate or needle shaped. In one embodiment, the particle sizing of the coated or uncoated powders may be from about 2 micron to about 200 microns in average diameter. In other embodiments, the average diameter is less than about 200 microns. In one or more
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embodiments, a bi-modal distribution of powder is employed to increase packing density.

[011] In one embodiment, the powder mixture may include one or more of the above described coated or uncoated powders and a powdered pitch. The powdered pitch may be, for example, coal tar pitch or petroleum pitch. The pitch may be milled or otherwise processed to powder form. The average pitch powder diameter is preferably less than about
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500 microns and still more preferably less than about 400 microns. Other examples of

average pitch powder diameter include up to 350 microns, up to 300 microns, up to 250 microns, up to 200 microns and up to 150 microns. In other embodiments, the pitch powder is from between about 1 micron and about 100 microns. In one embodiment, the pitch particles are smaller than the coated or uncoated powder to ensure the shape and surface integrity of the final printed artifact. The pitch should be mixed with the coated and/or uncoated powder to a loading level of from between about 1 to about 75 percent by weight. In other embodiments, the pitch is mixed with the coated and/or uncoated powder to a loading level of from between about 10 and about 50 percent by weight. In one embodiment, the pitch material may have a softening point from between about 80°C and about 300°C. In one embodiment, the pitch material has a softening point greater than about 80°C. In other embodiments, the pitch material has a softening point greater than about 120°C. In still further embodiments the pitch material has a softening point greater than about 150°C. Preferably the coking value of the pitch is greater than about 30%, more preferably at least about 50% and still more preferably at least about 60%.

[012] A 3D article formed in accordance with the present disclosure, and prior to any further heat treatment is hereafter referred to as a green article. In one embodiment, the green article is heat treated in a non-oxidizing atmosphere to at least about 800°C, in other embodiments at least about 1000°C, still other embodiments at least about 1200°C. For purposes of the present disclosure, heat treatment above 800°C is hereinafter referred to as carbonizing the article. In one embodiment, the carbonized article may thereafter be heat treated in a non-oxidizing atmosphere to at least about 2000°C, in other embodiments at least about 2500°C, and still other embodiments least about 3000°C. For purposes of the present disclosure, heat treatment above about 2000°C is hereinafter referred to as graphitizing the article. In one embodiment, the step of carbonizing the article is separate from the step of graphitizing the article. In other words, the article is carbonized, allowed to cool, and

thereafter graphitized. In other embodiments, the article is carbonized and graphitized in the same step, in other words, the article is heated to at least 800°C, and without a subsequent cooling step, the article is heated further to at least 2000°C.

[013] In one or more embodiments, the article may receive a pitch impregnation treatment.

5 Examples of impregnation pitch include petroleum pitch, coal tar pitch or other carbonaceous resin systems. The pitch impregnation step commonly is performed using an autoclave system. Pitch impregnation treatment may be performed before or after the article is carbonized. If performed after, advantageously the pitch impregnated article is again carbonized. Pitch impregnation generally increases strength and density while reducing
10 porosity of the article.

[014] According to one embodiment, a three dimensional article may be formed employing a layered approach as described above wherein successive layers of binder, and filler (wherein the filler is a powder mixture), are deposited on a target surface. In accordance with this embodiment, the binder preferably volatilizes at temperatures greater than the melting
15 point of the pitch in the powder mixture. In accordance with this embodiment, for example, the binder may be selected such that substantially all of the binder volatilizes at temperatures above about 200°C and the pitch of the powder mixture has a melting point less than about 200°C. In other embodiments, the binder volatilizes at temperatures above 300°C and the pitch of the powder mixture has a melting point less than about 300°C. In this manner, a three
20 dimensional article may be formed wherein the binder sets the shape during three dimensional formation. During the later heat treatment step, the pitch in the powder mixture first softens, then carbonizes, which maintains the form and structural integrity of the article. Likewise, substantially all of the binder volatilizes during the heat treatment so that the final heat treated article (either carbonized or graphitized) is substantially free of the original
25 binder. Thus, the binder in accordance with this embodiment is a sacrificial binder which

may be any material that provides adequate adhesive characteristics during formation, but then substantially or completely volatilizes in later heat treatment steps. The advantage of this process is in the printing/forming of the three dimensional article, wherein the sacrificial binder can be liquid at room temperature (where pitches are in solid form), yet the final artifact would allow each carbon or graphite particle to connect to form a cohesive structure as the binder pitch particles are melted and re-crystallized during heat treatment to form the final artifact.

[015] According to one embodiment, the final carbonized or graphitized article may have a density of from between about 1.0g/cc to about 2.2 g/cc. In particular, density is increased by one or more pitch impregnation steps. In other embodiments, the carbon or graphite article may be generally porous, having a density from between about 0.10 g/cc to about 1.0 g/cc. Generally, porous relatively low density carbon or graphite articles do not receive a pitch impregnation step prior to or after heat treatment.

[016] According to another embodiment a three-dimensional article is formed by building up an article through an extrusion technique wherein a flowable binder is mixed with one or more of the fillers described herein above and the mixture is deposited on a target surface in a layered approach. In accordance with this approach the binder is flowable but then sets or becomes substantially solid shortly after being deposited on the target surface (or on the previous layer of the binder/powder mixture. According to this method, optionally the binder may be set by employing a targeted heat source such as, for example, a laser. In this manner, a three-dimensional article may be formed. The formation of the three dimensional green article may then be followed by heat treatment and/or pitch impregnation as described herein above.

[017] According to another embodiment, a three dimensional article may be formed employing a non-carbonized pitch coated powder. According to this approach (which is

similar to a selective laser sintering approach), the article may be produced by tracing a targeted heat source over a dispersed bed of pitch coated powder. In accordance with this approach a separate flowable binder may not be required to form the three dimensional article. The formation of the three dimensional article may then be followed by heat
5 treatment and/or pitch impregnation as described herein above.

[018] A further method disclosed herein for making a three dimensional article includes depositing a plurality of binder coated filler particles to form a monolithic article, wherein said filler includes carbon or graphite. The method also includes heat treating the article in a non-oxidizing environment to at least about 800°C. The word particle used in this
10 application has the same meaning as the word powder.

[019] Another advantage of the above embodiments is that the carbon article which is formed may have a shape other than that of a traditional rectangular or cylindrical billet as known in the carbon and graphite industry. Optionally such shape is a monolithic article and not two (2) or more carbon/ graphite articles joined together by a carbonizable and optionally
15 graphitizable cement.

[020] A further advantage is that such shape may be formed without the use of pore formers or other sacrificial material that is consumed during subsequent processing.

[021] Examples of densities of articles which may be made using the above methods include anyone of the following: at least about 1.7 g/cc, at least about 1.75 g/cc, at least
20 about 1.8 g/cc, at least about 1.85 g/cc, at least about 1.9 g/cc, at least about 1.95 g/cc, at least about 2.0 g/cc and at least about 2.05 g/cc.

[022] A further advantage of the above methods is that they may be used to produce a carbon or graphite article with minimal extra material. Preferably the mass of the produced article is within twenty (20%) percent of the mass of the desired final article, more preferably
25 within fifteen (15%) percent and even more preferably within ten (10%) percent.

[023] The above description is intended to enable the person skilled in the art to practice the invention. It is not intended to detail all the possible variations and modifications that will become apparent to the skilled worker upon reading the description. It is intended, however, that all such modifications and variations be included within the scope of the invention that is defined by the following claims. Thus, although there have been described particular
5 embodiments of the present invention of a new and useful method for making carbon and/or graphite articles, it is not intended that such references be construed as limitations upon the scope of this invention except as set forth in the following claims.

CLAIMS

I claim:

1. A method for making a three dimensional article comprising:
depositing alternating layers of a binder and a filler to form an article, wherein said filler includes at least one of carbon, graphite and combinations thereof; and
heat treating said article in a non-oxidizing environment to at least about 2000°C.
2. The method according to claim 1 wherein said filler further comprises a powder blend including a carbon or graphite powder and a pitch.
3. The method according to claim 2 wherein said binder volatilizes at temperatures less than about 200°C.
4. The method according to claim 2 wherein said pitch has a softening point from between about 80°C and about 300°C.
5. The method according to claim 1 further comprising the step of infusing said article with an impregnating pitch.
6. The method according to claim 1 wherein said powder further comprises a coated powder having a carbon or graphite base powder and a pitch coating.
7. The method according to claim 6 wherein said coated powder has an average diameter from between about 2 to about 200 microns
8. The method according to claim 7 wherein said coating is from between and 1 and about 50 percent by weight of the base powder.
9. The method according to claim 1 wherein said binder comprises coal tar pitch or petroleum pitch.
10. The method according to claim 1 wherein said binder comprises a resin having a coking value greater than about 20 percent.

11. The method according to claim 1 wherein said filler further comprises carbon or graphite powder derived from amorphous carbon, green, calcined or graphitized petroleum, coal tar coke, graphitized powder from synthetic sources, or natural graphite.

12. A method for making a three dimensional article comprising:

forming an article by depositing alternating layers of a binder and a filler, wherein said filler includes a carbon or graphite powder in combination with a milled pitch, said binder volatilizing at a temperature greater than a softening point temperature of said milled pitch; and

heat treating said article in a non-oxidizing environment to at least about 800°C.

13. The method according to claim 12 wherein said binder volatilizes at temperatures greater than 300°C and said milled pitch has a softening point less than 300°C.

14. The method according to claim 12 wherein said binder volatilizes at temperatures less than about 200°C.

15. The method according to claim 12 wherein said pitch has a softening point temperature from between about 80°C and about 300°C.

16. The method according to claim 12 wherein further comprising the step of infusing said article with an impregnating pitch.

17. The method according to claim 12 wherein said powder further comprises a coated powder having a carbon or graphite base powder and a pitch coating.

18. The method according to claim 17 wherein said coated powder has an average diameter from between about 2 to about 200 microns

19. The method according to claim 17 wherein said pitch coating is from between and 1 and about 50 percent by weight of the base powder.

20. The method according to claim 12 wherein said binder comprises coal tar pitch or petroleum pitch.
21. The method according to claim 12 wherein said binder comprises a resin having a coking value greater than about 20 percent.
22. A method for making a three dimensional article comprising:
depositing a plurality of binder coated filler particles to form a monolithic article, wherein said filler includes carbon or graphite; and
heat treating said article in a non-oxidizing environment to at least about 800°C.
23. The method of claim 22 wherein a shape of the article prior to the heat treating comprises a shape other than a rectangular billet and a cylindrical billet known in the carbon and graphite industry.