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DEPOSITION OF PYROLYTIC MATERIAL

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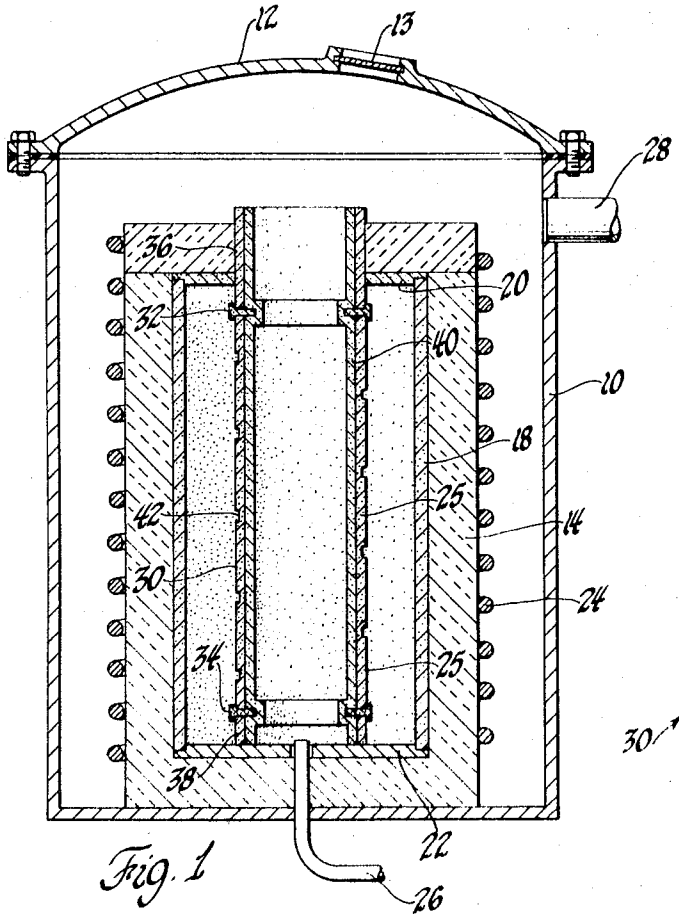


Fig. 1

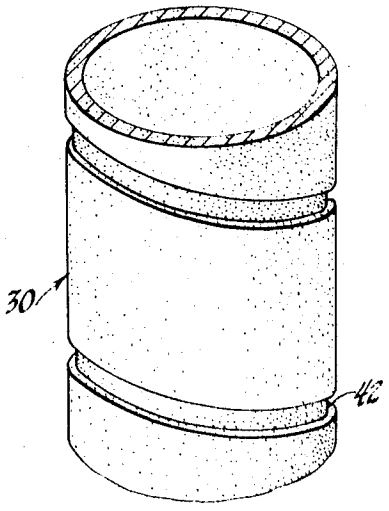


Fig. 2

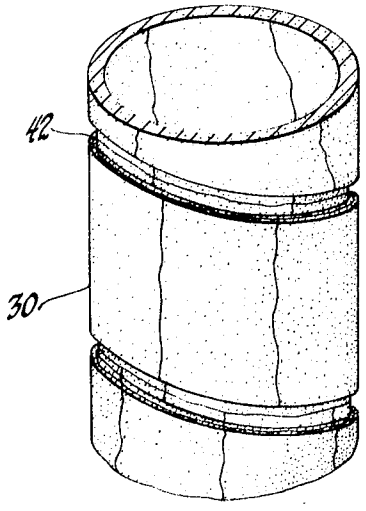


Fig. 3

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DEPOSITION OF PYROLYTIC MATERIAL

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ABSTRACT OF THE DISCLOSURE

A method for the deposition of pyrolytic material wherein the mandrel upon which deposition occurs is provided with at least one line of weakness, preferably in the form of a groove on the exterior surface of the mandrel, such that cracking is initiated and propagates at least initially along the line of weakness to assure an optimum breakage pattern.

Background of the invention

The subject matter of the present invention is a method and apparatus for froming articles by gas pyrolysis deposition within a tubular mandrel, the key feature of which is an improved method and means for assuring a good separation of the mandrel from the article after deposition without adverse effect on the article. The invention has particular utility in the manufacture of pyrolytic graphite and will be described in detail specifically with reference thereto; however, it will be understood that the invention, in its broader aspects, is applicable to the manufacture of other types of pyrolytic articles, examples of which will be given hereinafter.

Pyrolytic graphite is anisotropic, and by reason of this fact and its extremely high temperature resistance and also its nuclear properties, has a broad field of utility such, for example, as for lamp filaments, furnace linings, nuclear reactor moderators, rocket nozzles and re-entry heat shields. The latter two types of articles have become particularly important in recent years and generally require that the pyrolytic graphite article be of tubular or circular cross section. Pyrolytic graphite is manufactured by pyrolysis, or thermal decomposition, of carbonaceous gas. Any of a wide variety of carbonaceous gases may be used, though in practice methane, either alone or in combination with hydrogen, is preferred. To make a tube or annular article of pyrolytic graphite, for example, the carbonaceous gas is passed through a tubular-shaped mandrel preferably formed from ordinary electrographite having a controlled relatively smooth inner surface finish, the mandrel being heated to a sufficiently high temperature to cause pyrolysis of the carbonaceous gas with resultant deposition of the pyrolytic graphite on the interior wall of the tubular mandrel. The graphite deposits in laminae and the process is continued until the desired thickness is accomplished. The mandrel having the deposited article thereon is then cooled, whereupon the mandrel cracks due to differences in coefficients of thermal expansion between the mandrel and the deposited article. The formed article is then separated from the mandrel.

It is generally recognized that one of the important factors in the success of the pyrolytic process is the thickness of the mandrel. It must not be so thick that it imposes loads on the deposited article causing the latter to crack during cool-down. Yet, it must not be so thin as to allow an undesirable amount of creep during deposition or so thin as to subject the mandrel to premature breakage, both of which frequently lead to out-of-roundness of the deposited article. Good practice has established that when the mandrel is fabricated from conventional electrographite, its thickness should be one to one and a

half times the thickness of the article to be deposited thereon.

Unfortunately, however, regardless of how carefully the thickness of the mandrel is chosen, it frequently happens, owing to differences in the coefficients of thermal expansion of the deposited article and the mandrel, that one or more axial cracks (i.e., cracks parallel to the longitudinal axis of the mandrel) develop in the mandrel as the mandrel, with its associated deposited article, is cooled. Such axial cracks cause the deposited article to be "out-of-round" with the maximum radii corresponding to the locations adjacent to such axial failures. In addition, when a mandrel fails axially, such failure is often so violent that, regardless of the use of various pretreatment techniques, serious spalling of the deposited article occurs.

Ideally, the stresses of cooling should ultimately cause the mandrel to fail in a generally crazed breakage pattern. Such a breakage pattern does not distort the deposited article and, furthermore, it facilitates the uniform separation of the deposited article and the mandrel. Under present practice, utilizing a mandrel of uniform thickness equal to about one to one and a half times the thickness of the deposited article, the mandrel does at times break with the desired crazed pattern. Yet all too often it breaks instead in the undesirable axial pattern. Thus, the pyrolytic graphite manufacturing process, using present state of the art mandrels, continues to result in a high scrap loss in the manufacture of such articles due to damage resulting from unwanted axial mandrel failures. The art is in need of a simple and economical method for insuring that the mandrel breaks, upon cooling, in a pattern which assures against damage to the deposited article and which enables a good separation of the mandrel from the article. The present invention fulfills this need.

Summary of the invention

In accordance with the present invention, the mandrel is provided with at least one linear frangible section, i.e., a line of weakness, preferably in the form of a groove on the exterior surface of the mandrel, which extends both axially and circumferentially on the mandrel such that when the stresses occur during cool-down, cracking is initiated and propagates at least initially along the line of frangibility thereby assuring an optimum breakage pattern. In the preferred embodiment of the invention, the mandrel is made thicker than the thickness that would normally be used and is provided with at least one spiral groove from one end to the other in the exterior surface thereof, the thickness of the grooved portion being that which would normally be used for the mandrel. With such structure the mandrel has increased "hoop" strength to better assure against axial cracks during and subsequent to the deposition due to its greater than normal thickness. Yet, the stresses developed during cooling, because they are at least initially released through the failure of the grooved portion, result in a breakage pattern which is ideal, the cracks occurring ultimately not only along the spiral groove but also along lines between and intersecting the groove. Hence, by reason of the spiral groove, a breakage pattern resembling, and in fact superior to, the desired crazed pattern of conventional mandrels is attained and with assurance against an undesirable axial breakage pattern.

Brief description of the drawing

Other objects, features and advantages of the invention will appear more clearly from the following detailed description of the preferred embodiment thereof made with reference to the drawings in which:

FIGURE 1 is a sectional view of a furnace incorporating a mandrel embodying the invention, which man-

drel has deposited thereon a pyrolytic grapihte article;

FIGURE 2 is an isometric view of a portion of the mandrel of FIGURE 1 before cooling occurs; and

FIGURE 3 shows the mandrel of FIGURES 1 and 2 after cooling has occurred.

Description of the preferred embodiment

Referring now to FIGURE 1, the apparatus shown comprises a generally cylindrical casing **10** having enclosure plate **12** which is removably secured as by bolts or a suitable hinge and latch. A viewing window **13** enables inspection of the deposition operation within the casing and also viewing with an optical pyrometer. A body of the insulating material **14**, such as carbon black, defines an inner cylindrical chamber, the walls of which are formed by a graphite cylinder **18** and top and bottom graphite plates **20** and **22** respectively. An induction heating coil **24** surrounds the insulated material **14**, the graphite cylinder **18** functioning as the susceptor whereby intense heat is generated within the cylinder **18** by reason of the passage of current through the induction coil **24**.

Extending through the heating chamber defined by the cylinder **18** and its end plates is a mandrel assembly **25**. An opening in plate **22** accommodates an inlet tube **26** for the flow of carbonaceous gas into and through the mandrel, the upper end of the mandrel assembly being open to the interior of the casing **10** whereby the non-deposited products of the pyrolysis of the carbonaceous gas can exit through the outlet tube **28**. Hence, in operation, the carbonaceous gas, such as methane or a mixture of methane and hydrogen, is admitted through tube **26** to the interior of the mandrel assembly which is intensely heated by the heat generated by the cylinder **18**. Pyrolysis of the carbonaceous gas thereby occurs with resultant deposition of pyrolytic graphite on all of the interior walls of the mandrel assembly thereby forming article **40**, the hydrogen and other gaseous pyrolysis products being withdrawn from the chamber through the outlet tube **28**. As is well known in the art, temperatures on the order of 1200° C. to 2500° C. can be used to cause the pyrolysis reaction.

In accordance with conventional practice, the mandrel assembly comprises a central tubular part **30**, which constitutes the mandrel in which the desired pyrolytic graphite article is deposited, and termination mandrel portions **36** and **38** separated from the part **30** by parts **32** and **34** which provide radially inwardly extending flanges. This enables the high quality deposit in the central portion of the assembly to be cleanly separated from the lower quality deposits in the top and bottom termination portions of the mandrel assembly.

In accordance with the present invention, the mandrel **30** is provided, as by a cutting operation, with a spiral groove **42** on the outer surface thereof. Preferably, the groove depth should be from 20% to 70% of the thickness of the mandrel. The ungrooved portion of the mandrel **30** is of a thickness greater than 1.5 times, and more specifically, about twice that of the article **40**.

Instead of using only one groove, as shown, a plurality of spiral grooves may be cut in the mandrel. Where a plurality of grooves is used, all may be of the same lead, lefthanded or righthanded, or they may be of different leads such that they intersect. I have found that the most desirable form of spiral is one having a lead angle (i.e., the angle between the spiral, at any point thereon, and the longitudinal axis of the mandrel) of from about 45° to 80°. Preferably, the groove or grooves should circumscribe the mandrel at least once, from one end to the other thereof, and it is most desirable that the distance along the longitudinal axis of the mandrel, between one groove turn and the next groove turn (where a single groove is used, such constituting the "pitch") not be greater than a third of the length of the mandrel. When these conditions cannot be satisfied by one spiral groove, two or more can be used so that such optimum conditions are satisfied.

Although a spiral groove shape is preferred, other groove shapes may be used if desired, the essential feature being that the groove extend in a direction which is askew to the longitudinal axis of mandrel **30**, such that the line of the groove has an axial component and a circumferential component at substantially all points therealong.

Referring again to the apparatus show nin FIG. 1 and to its operation, after the pyrolytic graphite deposition is completed, mandrel **30** and article **40** are cooled. Since the mandrel has increased "hoop" strength by reason of the greater than usual thickness in the ungrooved portions, initial failure will occur in the spiral grooved portion. Cracks will then ordinarily develop between the spirals, an example of the final breakage pattern being shown in FIG. 3. Hence, the mandrel develops, upon cooling, a breakage pattern resembling, and in fact superior to, the desired crazed pattern of conventional mandrels.

As previously pointed out, whereas the invention has its greatest utility and has been described specifically with reference to the manufacture of pyrolytic graphite articles, it will also find utility in the manufacture of pyrolytic articles of other materials. Such additional materials include the refractory metals of Groups IV, V and VI of the Periodic Table and their carbides, borides, nitrides and silicides such as those of hafnium, molybdenum, niobium, silicon, tantalum, tungsten, titanium and zirconium. As is well known in the art, the gas composition used for the pyrolysis reaction to form such pyrolytic articles will vary depending upon the precise material desired. For example, the aforesaid metals may be pyrolytically deposited by using as starting materials the halogenated derivatives of the metals, whereas to form the nitrides or carbides, for example, the starting materials will consist of a mixture of the metal derivatives plus ammonia or carbonaceous gas, respectively. In its broader scope, therefore, the invention will find utility for the manufacture of any pyrolytic article wherein there exists the problem of separating the mandrel from the deposited article while yet insuring that the mandrel, upon cooling, does not crack only along axial lines.

It will be understood that while the invention has been described specifically with reference to a particular embodiment thereof, various changes and modifications may be made, all within the full and intended scope of the claims which follow. For example, instead of being a right cylinder, as shown, the mandrel **30** can be of varying radius from one end to the other, the precise shape of the tubular mandrel being determined by the shape desired for the article deposited thereon.

I claim:

1. A method for manufacturing an article of pyrolytic material comprising pyrolytically depositing said material on the interior surface of a tubular mandrel having at least one exterior groove which extends in a direction having both axial and circumferential components, cooling the mandrel having the deposited pyrolytic material thereon whereupon the mandrel cracks, and separating the pyrolytic material from the mandrel.

2. A method as set forth in claim **1** wherein said groove constitutes a spiral.

3. A method as set forth in claim **1** wherein said deposition is by pyrolysis of a carbonaceous gas forming a pyrolytic graphite article and wherein said mandrel is of electrographite.

4. A method as set forth in claim **2** wherein said spiral has a lead angle of from about 45° to 80°.

5. A method as set forth in claim **2** wherein said spiral circumscribes said mandrel at least once from one end to the other thereof.

6. A method as set forth in claim **1** wherein the depth of said groove is from 20% to 70% of the thickness of the mandrel.

7. In apparatus for the deposition of a pyrolytic article comprising a chamber, pyrolytic material feed means con-

nected to said chamber, a tubular mandrel within said chamber upon an interior surface of which the pyrolytic material is deposited, and heating means surrounding said mandrel,

the improvement in which the tubular mandrel has at least one exterior groove extending in a direction having both axial and circumferential components such that when stresses occur during cool-down, cracking is initiated and propagates at least initially along said groove.

8. Apparatus as set forth in claim **7** wherein said groove is a spiral.

9. Apparatus as set forth in claim **7** wherein said mandrel is formed from electrographite.

10. Apparatus as set forth in claim **8** wherein said spiral groove has a lead angle of from about 45° to 80°.

11. Apparatus as set forth in claim **8** wherein the spiral groove circumscribes the mandrel at least once from one end to the other thereof.

12. Apparatus as set forth in claim **8** wherein the depth of said spiral groove is from 20% to 70% of the thickness of the mandrel.

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U.S. Cl. X.R.

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