METHOD OF MAKING A METAL IMPIREGNATED CARBON PRODUCT

4 Claims, 4 Drawing Figs.

ABSTRACT: A seal material having an improved wear resistance under a severe rotary and vibration condition at elevated temperatures can be produced by the steps of providing a mass of coke powder with a particle size less than 40 micron, mixing the coke powder and a binder by a mixer of Banbury type, molding the mixture to shape, selecting a product having a bulk density in the range of 1.68-1.79, impregnating the product with a molten metal, and cooling it to room temperature.

Carbonaceous Material up to 40 micron

Binder, 40-50% by wt

Mixing
Kneading, 200°C
Air Cooling
Processing, up to 100 mesh, Tyler
Molding under 21/cm²
Heat Treatment, 1st
Impregnating Product with Pitch
Heat Treatment, 2nd
Classifying to 1.68-1.79, B.S.G
Impregnating with Molten Metal
Cooling and Working to Shape
Desired PRODUCT

Banbury Mixer 5 minutes

Room Temperature

In N₂ atm, 800°C 1 hr

Acheson type electric furnace 1300°C 30 minutes

Reduced Pressure, up to 5 Torr 2 hours
Carbonaceous Material up to 40micron

Binder, 40-50% by wt.

Mixing

Kneading, 200°C.

Pulverizing, up to 100mesh, Tyler

Air Cooling

Molding under 2t./cm²

Heat Treatment, 1st

Impregnating Product with pitch

Heat Treatment, 2nd

Classifying to 1.68-1.79, B.Sp.G

Impregnating with Molten Metal

Cooling and Working to Shape

Desired PRODUCT

FIG. 1
METHOD OF MAKING A METAL IMPREGNATED CARBON PRODUCT

The present invention relates to a seal material having an improved dynamic strength, and more particularly, to the seal material consisting of a novel carbon-metal composite article having a high strength as a mechanical seal, and further an enhanced dynamic strength under a severe rotary and vibration condition of a rotary machine, and to a method of making the same.

Hence, it is known that many and various materials adapted for the mechanical seal have been proposed and available in the market. However, it has been a difficult problem to provide a satisfactory seal material for use in a rotary chamber of a high temperature and high pressure, such as, a rotary compressor.

In case the seal of the conventional material is positioned in a stationary bearing housing, it is required only to have a high static strength and a pressure resistance, since it does not move. Further, in case the seal of the prior art is installed as a rotatable part under a high temperature condition, it soon loses its own strength, though the carbonaceous seal is reinforced by a binder with a synthetic resin. In spite of a considerable bending or flexural strength in the static state, in case the seal of the above kind is applied in a machine of a high vibration, a defect or destruction soon ensues therefrom. The seal available in the market hardly meets the above requirement in the service of vibration. It is also very difficult to attain a uniform quality in the production of the seal material.

With an advance of technology, a seal material to meet a more rigorous requirement than ever has been in much demand, but none of the seal of the prior art has ever satisfied the above requirement.

We, inventors, have developed the following method of making a novel seal material consisting of a carbon-metal composite product adapted to be an adequate endurance for an exceedingly rigorous operation of a machine wherein a very high vibratory motion prevails.

Accordingly, it is an essential object of the invention to provide an improved seal material having both physical and mechanical enhanced properties in flexural and dynamic strength adapted for a rotating part of a rotary machine and a method of making the same.

It is another object of the invention to provide an improved seal material having good properties under a high temperature and high pressure condition adapted for a rotary compressor.

Other objects and further advantages of the invention will appear to those skilled in the art from a reading of the following specification in connection with the accompanying drawings, in which:

Fig. 1 is a flow sheet for making a seal material in accordance with the invention.

Fig. 2 is a diagrammatic view showing a vibration test machine in which a test specimen made of the seal material is examined in point of fatigue and impact under a vibrating condition.

Fig. 3 is a front view of Fig. 2.

Fig. 4 is a view showing the test specimen.

A carbonaceous raw material for making a seal of this invention can be selected from the group of coke powder of both coal and petroleum origin, carbon black, coking coal, anthracite, and mixtures thereof. As a coke, it is preferred that it contains about 0.2 percent ash, 99 percent fixed carbon, and 0.8 percent of both volatile and moisture contents, and has a true bulk density in the range of 1.98 to 2.02. The hardness of coke is indicated by the hardness index specified by ASTM, O-409-1 which shows that the less the index the harder the coke. In this invention, the harder the coke the better. Less than 25 of the index is preferred. It is understood that the raw coke material is not limited to the above composition and property.

As a starting raw material, coke only is preferred, but when another material is added, it is preferred that about 5-15 parts by weight of carbon black, such as, channel black are added to about 100 parts by weight of coke. When coal or anthracite is added, it should be in an amount corresponding to the above of the carbon black to be added, but not limited.

A particle size of carbonaceous material is a very important matter in this invention for making a desired product. Its maximum particle size should be 40 micron. The particle size of coke powder is one of the most important requirements for attaining the desired product of this invention. Raw coke is ground or pulverized to the particle size of 40 micron. At first coke is roughly ground by a jaw crusher, then by a micron mill and it is screened by an air separator to the desired particle size of 40 micron. It is known that when a material is ground with a view to grinding to the particle size of a predetermined dimension, for example, a very small dimension, such as, 40 micron, the distribution of a predetermined particle size cannot be complete, but it tends to be so by a grinding method and apparatus. In this case, the results of sedimetry have shown a particle larger than 40 micron zero, 18.8 percent of that of 40-20 micron, 31.3 percent of 20-10 micron, 31.0 percent of 10-5 micron, and 23.5 percent of less than 5 micron.

The particle size of a raw material is very important, but we do not intend to limit all the particle size of the material to 40 micron only. We do not limit that each and every particle size of the material should be 40 micron only. A somewhat non-uniform distribution of a particle size less than 40 micron and larger than 1 micron is allowable if it contains more than 60 percent, preferably 80 percent when the material is pulverized to the particle size in view by a known manner.

It is known that a carbonaceous product is manufactured by the steps of grinding a carbonaceous material, mixing the material and a binder, molding the mixture to shape, and baking it. In grinding the carbonaceous material, a feature of the invention consists in a specified particle size, that is, less than 40 micron. In general, the particle size of carbon black is known to be less than 40 micron, and that of even the biggest one is less than 1 micron, hence the carbon black only should not be preferred to be a raw material in this invention. However, it has been found that a product made of the carbon only in accordance with this invention is much inferior in strength to the one made of coke powder ground to the particle size of 40 micron or below. Therefore, it is not desirable to select the carbon black having a particle size less than 1 micron only as a raw material for the product of this invention from a particle size point of view.

To bond the particles of a carbonaceous material together, a binder is selected from the group of pitch, tar, and a non-curing synthetic resin, and a mixture thereof. For example, pitch has a softening point, 70°C, and a composition of 52 percent volatile constituents, 48 percent free carbon, and 18 percent benzol-insoluble constituents. Tar has 70 percent volatile constituents, 30 percent free carbon, and 5 percent benzol-insoluble constituents. The synthetic resin is selected from the group of a highly carbonizable one such as, phenolic or furan when it is baked. It is known that in adding the binder to the coke powder material, an amount of the binder to be added should be sufficiently large so as to cover the surface area of each particle of the material completely, since the finer the particle the more the surface area thereof. In addition, as a matter of fact, in general, the binder is added in an amount more than the minimum required. It is because when a powdery material is to be mixed with a least required amount of binder, a stronger mixing power is required than with an excess thereof, and a suitable mixer to attain its full ability has never occurred to those skilled in the art, and further, it has been considered to be difficult in that an excess of binder is used to make a sufficient contact of each particle therewith. When mixing and kneading step is carried out with the excess of the binder, it has been found that a local deviation thereof occurs with the result that an article of uniform structure is hardly obtained. Further, it has been also found that the excess of the binder was undesirable to make a carbonaceous blank having a porous structure adapted for the manufacture of a seal
material to be impregnated with metal in accordance with this invention. We have discovered during the period of our extensive research that when we used a Banbury mixer in the kneading step of the process of this invention, it was an ideal machine for the purpose thereof. It is known that the Banbury mixer was originally designed for mixing a highly viscous rubber. It is seen that a Banbury mixer is so effective for kneading a mixture of coke powder and pitch that an amount of a binder to be added can be reduced to a minimum, for example in this invention 40-50 percent by weight of the carbonaceous material. In reference to the results of our test, a comparison in connection with mixing and kneading between the Werner-type kneading machine common in the carbon industry and the Banbury-type mixer in the rubber industry is shown as follows:

<table>
<thead>
<tr>
<th>Electric power, per</th>
<th>Amount of binder,</th>
<th>Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg. of charge, kw.</td>
<td>percent</td>
<td></td>
</tr>
<tr>
<td>Prior art</td>
<td>Werner mixer</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>This invention</td>
<td>Banbury mixer</td>
<td>1-20</td>
</tr>
</tbody>
</table>

As shown in the above table, it is seen that in treating an equal quantity of charge, 1-20 kw. of a kneading power per kg. thereof is required by the Banbury mixer while 0.1-0.5 kw. of a power per kg. is consumed by the Werner mixer. Accordingly, in comparison, the kneading power 10-200 times in the Banbury mixer as strong as that of the Werner mixer is given. In the experiments conducted by us, we have ascertained that an electric power required for mixing and kneading exhibits its effect from 1 kw. upwards. As a result, the kneading step is carried out by so strong an electric power that the material heats itself by a kneading friction so as to facilitate mixing thereof, whereby an external heating as in the Werner mixer is entirely required. Sometimes it may be necessary to cool the charge with a view to preventing it from deterioration when it is treated for a rather long period, or, for example, in case the synthetic resin is used as a binder, an exothermic reaction takes place.

By the above powerful kneading operation, the addition of a binder can be reduced as little as possible, since an excess thereof is no longer necessary. The addition of the binder in a minimum amount is one of the most important requirements for the manufacture of a carbonaceous article in order to enhance its property. It is understood that an additive agent selected from the group of machine oil, and creosote oil may be added to the charge to aid kneading, but not limited.

Next, the charge material completely kneaded by the Banbury mixer is cooled, and again pulverized to a particle size up to 100 mesh Tyler. We call it "re grind." A carbonaceous material obtained from this regrind has a more uniform structure than the previous one. Particular care is taken so that a particle size of regrid is not too fine. It should not be regrid to less than the maximum particle size of the starting material. A powdered material having the particle size up to 100 mesh Tyler is placed in a predetermined metallic mold, and molded with no binder at all to shape at room temperature. The mold employed is two dimensions, 5x9" and 3x3", respectively. A molding pressure of about 2 tons per cm.² (about 29,000 p.s.i.) was applied. It is to be understood that the regrid powder can be molded into shape by heating it a little. Subsequently, the molded shape was baked at the rate of 5° C. per hour in a nitrogen atmosphere furnace up to the maximum temperature of 800° C. wherein it was held for a period of 1 hour. This we call the first baking step. After the first baking step, the product is subjected to the second baking step at a temperature of 1,300° to 1,400° C. in an Acheson-type direct resistance electric furnace. If the requirements of baking in a furnace are permissible, then if there is any furnace wherein the first and second baking steps can be carried out in a single furnace, the carbonaceous product may be subjected directly to the first and second backing steps in the one furnace.

An object in view lies in baking the product at a temperature of 1,300° to 1,400° C. We have selected this temperature range because we have discovered that it is a most favorable baking temperature range for the carbonaceous product in order to develop an excellent property in wear resistance and strength as a seal material. A bulk density in view of the seal material of this invention is between 1.68 and 1.79. When the product obtained by the first baking is subjected to the second one, it is seen that contraction happens to it during baking so that in general the bulk density of the second baked product increases in the order of 0.1 to 0.15 percent. Further, there are instances where we cannot attain a desired bulk density even by the combination of first and second baking steps. In this case, it is preferred that either the first or second baked product is subjected to an additional baking after a pitch impregnation imparted thereto.

Whether the pitch impregnation is necessary or not depends upon the bulk density of a baked product.

If the bulk density of a first baked product is 1.58 or more, it is preferred that the first baked one is subjected to a second baking with no pitch impregnation thereto. If it is less than 1.58, it is subjected to the second baking after the pitch impregnation. If the second baked product has a bulk density of less than 1.68, it is preferable to subject it to a further baking after the pitch impregnation. The pitch impregnation is preferred because when a molded carbonaceous article is baked, the porous cavities resulting from evaporation due to carbonization of part of the binder should be filled with pitch so as to increase its bulk density.

The reason why a secondary or additional baking is performed after the pitch impregnation is to impart an enhanced property as a seal material to the pitch itself by baking it at a temperature of 1,300° to 1,400° C. as similar as the base material which has been already baked in the second baking. However, everyone of the products thus baked cannot always attain a desired bulk density of 1.68 to 1.79. There are instances where the desired bulk density cannot be attained by any of the above-mentioned measures. In this case, we can sometimes pick up a product having a bulk density of less than 1.68 among the second baked ones, and subject it to the pitch impregnation so as to increase its bulk density. A number of times of pitch impregnation should be preferred to be at most twice, because the increase of bulk density cannot be expected despite of multiplying the number of times of pitch impregnation. Pitch impregnation of two times or more tends to produce a variation in the carbonaceous structure so that the construction of each pore becomes unsuitable for a subsequent metal impregnation to be treated. Hence, in this invention, the number of cycle of pitch impregnation has been determined to be at most two.

A carbonaceous product thus obtained from the second baking step has the following properties:

<table>
<thead>
<tr>
<th>Bulk density</th>
<th>Shore hardness</th>
<th>Flexural strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.70</td>
<td>98</td>
<td>Against grain</td>
</tr>
<tr>
<td>700 kg./cm.²</td>
<td>10,000 p.s.i.</td>
<td>Against grain 102</td>
</tr>
</tbody>
</table>

"With grain" refers to an orientation parallel to the direction of grain while "against grain" to an orientation vertical to that of grain.

The above carbon article of a high strength with no metal impregnation can be applied where there is a static load, but it cannot be used where there is a severe rotary and vibratory
motion at a high temperature, which is the subject matter of this invention.

In this invention, as a next step, a carbon product obtained from the second baking step is subjected to a metal impregnation in order to improve its dynamic property. This carbon product should have a bulk density of 1.68 - 1.79 prior to the metal impregnation. As described in the examples to follow, a carbon product with less than 1.68 of a bulk density is of a relatively weak strength while that of higher than 1.79 cannot exhibit a sufficient reinforcement advantage of metal impregnation on account of a scarce porosity into which metal infiltrates.

A metal for impregnating a carbonaceous product therewith is a metallic element or an alloy which has a melting point of 200°C to 1000°C. The range of the melting point of the metal and alloy has been specified in the above because if the melting point of a metal or alloy for impregnation is lower than 200°C, the metal or alloy infiltrated into the sealed material will be molten under the condition of a high temperature service to destroy it while if the melting point is higher than 1000°C, an impregnating process thereof will be difficult.

It has been found that an improved seal material having an excellent dynamic property can be obtained by impregnating the carbon product having a bulk density of 1.68 - 1.79 manufactured in accordance with this invention with a metal selected from the group consisting of tin, lead, antimony, silver, an antimony-lead alloy, an antimony-tin alloy, Y alloy (an aluminum alloy having the designation Alcoa 142, SAE 39, ASTM CN 42A and containing about 4 percent copper, about 1.5 percent magnesium, and about 2.0 percent nickel), an antimony-copper alloy, and a lead-silver alloy. These metals and alloys have the range of melting points specified above.

The impregnating process is effected in an autoclave by causing the carbon product to immerse in a molten metal bath. In accordance with a preferred embodiment of the invention, the autoclave of 100 liters is evacuated by a vacuum pump per 500-liters/min. up to the vacuum of 5 Torr., preferably up to 1 Torr., and then the carbon product is impregnated with the molten metal in a nitrogen or argon atmosphere in order to prevent the metal from oxidizing under a pressure of 20 to 150-kg/cm² for a period of 10-30 minutes. Then, the product is lifted up, cooled to room temperature, and the carbon product treated with metal is withdrawn from the autoclave. In this treatment, it is necessary to secure the carbon product to the bottom of an impregnating vessel so as to not to float up since it is much lighter than the molten metal.

In the above description we have specified a reduced pressure to be less than 5 Torr. and an applied pressure to be in the range of 20-150-kg/cm² because we have confirmed based on various experiments that this condition is a most advantageous on an industrial scale view of the fine particle of the material, its porosity obtained from the control of the bulk density, the size of the pore, and the wettablity between carbon and metal.

It has been found that a sufficient impregnation of metal cannot be attained by a process comprising carrying out a reduced pressure to a high degree and regaining a normal pressure, and furthermore, another process comprising applying a high pressure without doing a reduced one beforehand has been attempted, but it is not advisable, since the property of a product is not satisfactory, because the gases occluded in the pores prevent the molten metal from penetration into the carbon product.

To impregnate the carbon product with metal should be carried out as completely as possible. The impregnating requirement to achieve a satisfactory result has been described above. A simple test for measuring a ratio of impregnation is to measure a bulk density of a product. For example, a carbon product impregnated with antimony has a bulk density of more than 2.32, and lead more than 2.69, when the ratio of metal impregnation is more than 80 percent.

The ratio of metal impregnation is obtained by the following formula:

\[
\text{Ratio of metal impregnation} = \frac{\text{Density of product after impregnation}}{\text{Density of second baked product}} \times (\text{Metal density}) \times (\text{Carbon porosity})
\]

The degree of rate of metal impregnation which meets the requirements of this invention should be preferred to be at least 80 percent or more. If there is a product having the rate of less than 80 percent, it should be omitted since an adequate strength thereof cannot be expected therefrom.

It has been found from a quality control point of view that the presence of a specified bulk density of the product impregnated with metal of this invention tends to be rate in the periphery and dense in the center thereof. Therefore, a uniform quality in property of the product can be improved by cutting off the peripheral portion, for example, in this case by an amount of about 5 mm., of the blank of a desired product.

A carbon product treated is withdrawn from the autoclave, and then it is subjected to a finish work, such as, described above, in a conventional manner to produce a desired seal material. Thus, a mechanical seal material of a high dynamic strength can be manufactured in accordance with the principle of this invention.

In reference to the examination of dynamic strength of the carbon product of this invention, particularly, for testing an endurance thereof under a vibratory condition, a test specimen (FIG. 4) support of our device (FIGS. 2-3) is provided on an electromagnetic vibratory testing machine in order to conduct an impact-fatigue test. The electromagnetic vibration test machine is employed to test various parts of missiles, aircrafts, and automobiles, etc. by means of resonance frequency, and the specification is as follows:

- **Exciting Force**: 180 kg.
- **Frequency**: 5, 8, 10, 12, 16 Hz
- **Table Diameter**: 150 mm.
- **Maximum Output Power**: 1.5 kW.

The test of this invention is conducted as follows: a test specimen, 6×10×60 mm., weight 8-11 g., is made from a blank of the carbon product of this invention. The specimen is freely supported at both ends in a recess, 7 mm., of two posts of a testing machine as shown in FIGS. 2-3, and further, it is secured to a weight W of 344 g. The recess is 7 mm. high and the specimen 6 mm. thick, so there is a gap 1 mm. therebetween.

A rig for holding the specimen is simple as shown in the drawing, and the rig is placed on the electromagnetic vibratory table, a drive of which is not shown. It is understood that the details of the above testing machine and the rig are omitted because they are not part of the invention.

The vibratory table can be arranged in such a manner that it vibrates at 1 G. (gravity) to 30 G., the more the number of G. the more vibration. As the test starts with the specimen fixed in the rig, G. is gradually increased upon vibration of the table when a switch thereof is on. Upon vibration of the table which is arranged to be set from 1 G. upwards, the specimen rig sets in vibration up and down. As the specimen is freely supported in the rig, it strikes up and down in the recess. When G. reaches 30 G. in a period of about 5 seconds, a time prior to destruction of specimen is measured by a stop watch. A material having a poor dynamic strength is usually destroyed before 10 G. It is understood that the specimen with the weight is arranged not to leap out of the rig by vibration.

A period of longer than 10 minutes at 30 G. is a passing mark of the above test for the seal material of this invention.

From the comparison between practical test and impact-fatigue one, we have confirmed that a good seal material should endure this test at least 30 minutes longer at 30 G. However, in accordance with the use or application of our seal, we have found that we have obtained a satisfactory result from the seal material which has passed an endurance test of longer 10 minutes in a range of 10 to 30 G.

The present invention will be described in connection with the examples hereinafter.
EXAMPLE 1.

As a coke material, the coke of the highest grade, NPC (Hardness Index 25 or less specified by ASTM, D-409-51) of the Nittetsu Chemical Industry Co., Ltd., Japan was selected. This coke was ground to the maximum particle size 40 micron or less. A mixture of 100 parts by weight coke powder and 43 parts by weight binder consisting of 1 part of weight tar and 9 parts by weight pitch was made. This mixture was kneaded by a mixer of Banbury type with an electric power of 17 kw. per one kg. of charge. The resulting mixture was cooled, reground, and screened by 100 mesh Tyler or less. The resulting powder was placed in a metallic mold, 3x3x1 inch, and molded at a molding pressure of 2 tons per sq. cm. The molded shape was baked at the rate of 5° C. per hour in a nitrogen atmosphere furnace up to the maximum temperature of 800°C wherein it was held for a period of one hour in order to obtain a first baked product. This first baked product was subjected to pitch impregnation, and thereafter it was baked at the temperature of 1,350°C. for a period of about 30 minutes in an Acheson-type direct resistance electric furnace to produce a second baked product. A bulk density of this second baked product was found to have one between 1.68 and 1.81. All of second baked products were placed in an autoclave to be impregnated with a molten alloy of 7 parts by weight Sb (antimony) and 3 parts by weight Cu (copper). They were impregnated with a molten alloy in the autoclave under the condition of 0.1 Torr, reduced pressure, at the temperature of 660°C, and under the pressure of 60 kg. per sq. cm. Physical properties of the final product thus produced are shown as follows:

<table>
<thead>
<tr>
<th>No. of Test Specimen</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. D. of Second Baked Product</td>
<td>1.70</td>
<td>1.78</td>
<td>1.66</td>
<td>1.81</td>
</tr>
<tr>
<td>B. D. of Product Impregnated with Metal</td>
<td>2.07</td>
<td>2.10</td>
<td>2.70</td>
<td>2.44</td>
</tr>
<tr>
<td>Rate of Metal Impregnation, %</td>
<td>88</td>
<td>88</td>
<td>89</td>
<td>11</td>
</tr>
<tr>
<td>Flexural Strength, kg/cm.</td>
<td>940</td>
<td>980</td>
<td>920</td>
<td>850</td>
</tr>
<tr>
<td>Dynamic Strength, 30 G.</td>
<td>(i)</td>
<td>(i)</td>
<td>(i)</td>
<td>(i)</td>
</tr>
</tbody>
</table>

1 20 minutes longer. 2 3 minutes failure. 3 4 minutes failure.
NOTE—B. D. = bulk density.

EXAMPLE 2.

Petroleum coke (Hardness Index 30) of the Great Lakes Carbon Corp., U.S.A. was adopted as a raw material. A second baked product was obtained in the same procedure as in example 1. Antimony was used for a metal for impregnation. The second baked product was impregnated with antimony under the condition of 0.05 Torr, reduced pressure, at the temperature of 700°C., and under the pressure of 100 kg. per sq. cm. The properties of the final product are shown:

<table>
<thead>
<tr>
<th>No. of Test Specimen</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. D. of Second Baked Product</td>
<td>1.68</td>
<td>1.73</td>
<td>1.71</td>
</tr>
<tr>
<td>B. D. of Product Impregnated with Metal</td>
<td>2.62</td>
<td>2.85</td>
<td>2.44</td>
</tr>
<tr>
<td>Rate of Metal Impregnation, %</td>
<td>87</td>
<td>90</td>
<td>74</td>
</tr>
<tr>
<td>Flexural Strength, kg/cm.</td>
<td>180</td>
<td>1,200</td>
<td>870</td>
</tr>
<tr>
<td>Dynamic Strength, 30 G.</td>
<td>30 min.</td>
<td>30 min.</td>
<td>2 min. longer</td>
</tr>
<tr>
<td>longer</td>
<td>longer</td>
<td>longer</td>
<td></td>
</tr>
</tbody>
</table>

EXAMPLE 3.

Coal coke (Hardness Index 18) of the Yokohama Chemical Industry Co., Ltd., Japan was used as a raw material. A second baked product was produced in accordance with the same procedure as in example 1. The second baked product was impregnated with lead under the condition of 0.5 Torr, reduced pressure, at the temperature of 450°C., and under the pressure of 50 kg. per sq. cm. The properties of the final product are shown:

<table>
<thead>
<tr>
<th>No. of Test Specimen</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. D. of Second Baked Product</td>
<td>1.73</td>
</tr>
<tr>
<td>B. D. of Product Impregnated with Metal</td>
<td>3.07</td>
</tr>
<tr>
<td>Rate of Metal Impregnation</td>
<td>87</td>
</tr>
<tr>
<td>Flexural Strength, kg/cm.</td>
<td>900</td>
</tr>
<tr>
<td>Dynamic Strength, 30 G.</td>
<td>30 min. longer</td>
</tr>
</tbody>
</table>

EXAMPLE 4.

The same raw material as in example 3 was used. This raw material was pulverized to the particle size of 74 micron to which 43 parts by weight pitch binder were added. Then, this mixture was kneaded by a Werner-type mixer. The other steps than the above were the same as in example 1. A second baked product thus made was impregnated with an alloy of antimony and tin under the same conditions as in example 2. The properties of the final product are shown:

<table>
<thead>
<tr>
<th>No. of Test Specimen</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. D. of Second Baked Product</td>
<td>1.73</td>
</tr>
<tr>
<td>B. D. of Product Impregnated with Metal</td>
<td>2.32</td>
</tr>
<tr>
<td>Rate of Metal Impregnation</td>
<td>82</td>
</tr>
<tr>
<td>Flexural Strength, kg/cm.</td>
<td>920</td>
</tr>
<tr>
<td>Dynamic Strength, 30 G.</td>
<td>Destroyed at 10 G.</td>
</tr>
</tbody>
</table>

As fully described in the foregoing, we have made a success of obtaining an improved seal material consisting of a novel carbon-metal composite having a dynamic as well as static strength heretofore unable to attain under a high vibration, high rotation, and high temperature condition.

While we have described our invention in detail in its preferred embodiments, it will be obvious to those skilled in the art, after understanding our invention, that various changes and modifications may be made therein without departing from the spirit or scope thereof.

We claim:

1. In a method for the production of a carbon-metal composite article adapted for use as a seal material, the steps comprising:
a. grinding a carbonaceous raw material selected from the group consisting of coke powder of both coal and petroleum origin, carbon black, coking coal, anthracite and mixtures thereof,
b. mixing the ground carbonaceous material of step (a) with a binder selected from the group consisting of pitch, tar, a highly carbonizable synthetic resin and mixtures thereof,
c. kneading the mixture of said carbonaceous material and said binder in a Banbury-type mixer, with an electric power of at least 1 kw. or more per kg. of said mixture,
d. cooling the kneaded mixture of step (c),
e. further grinding the thus kneaded mixture to a particle size of at least as fine as minus 100 mesh Tyler,
f. molding the mass of step (e) into a mold,
g. subjecting the carbonaceous shape of step (f) to a baking procedure at a maximum temperature of 1,300°C. to 1,400°C. in an inert atmosphere,
h. selecting the carbonaceous shape of step (f) so that it has a bulk density in the range of 1.68 to 1.79,
i. impregnating the baked shape of step (h) having the specified bulk density with a metal or alloy having a melting point of 200°C. to 1,000°C. and selected from the group consisting of tin, lead, antimony, silver, an antimony-lead alloy, an antimony-tin alloy, Y alloy, an antimony-copper
alloy, and a lead-silver alloy, said impregnation step being
effected by first introducing the baked shape into an au-
toclave, evacuating the autoclave to a partial pressure,
surrounding the baked shape with molten metal and pres-
surizing the autoclave with an inert gas,
j. continuing step (i) until at least 80 percent of the voids of
the baked shape is impregnated with the molten metal, and
k. withdrawing the thus-impregnated baked shape from the
autoclave.

2. A method according to claim 1 wherein those car-
bonaceous shapes of step (h) which have bulk density of less
than 1.58 are subjected to one or more pitch impregnations
followed after each pitch impregnation by a baking step so as
to increase the bulk density to within 1.68 to 1.79.
3. A method according to claim 1 wherein those car-
bonaceous shapes of step (h) which have a bulk density of
more than 1.58, but less than 1.68 are subjected to a second
baking step with no pitch added so as to increase its bulk den-
sity to within 1.68 to 1.79.
4. A method according to claim 1 wherein the raw car-
bonaceous material used in step (a) is coke powder of both
coal and petroleum origin.

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