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METHOD OF MANUFACTURING CERAMIC SHAPED ARTICLES

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16. Abstract

A method of manufacturing ceramic shaped articles, wherein tapes of ceramic powder material in mixture with a binder material and special additives are shaped and then articles are stamped out from said tapes and sintered in a sintering furnace.

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(54) METHOD OF MANUFACTURING CERAMIC SHAPED ARTICLES

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PATENT SPECIFICATION

1. <u>Title of Invention</u>: Method of Manufacturing Ceramic Shaped Articles

2. <u>Claims:</u>

(1) A method of manufacturing ceramic shaped articles, wherein, in order to produce a sheet, tape or shaped body of at least of one type of ceramic powder, said at least one type of ceramic powder is kneaded with a binder material and formed into a plate of required shape and dimensions; a first layer is formed by rolling said plate or by adhesively attaching a predetermined amount of said ceramic powder to the surface of a rolled tape; a second layer is formed by combining the similarly shaped ceramics and binder of the same or

another type; if necessary, a third layer is formed by combining the ceramic and binder of the same or another type with an additive material serving to impart specific properties to the mixture; a tape, which is formed by superimposing said first layer onto the second layer or the first layer onto the third layer, or the first and second onto the third layer, or a tape which is formed of a plurality of tapes and which has a predetermined shape and dimensions with a predetermined distribution and density of ceramic grains is rolled under a certain pressure into an integral final tape and following this, articles are stamped out of this tape and converted into sintered articles with removal of a certain amount of the contained binder and adhesive materials due to at least one sintering operation.

(2) A method of manufacturing ceramic shaped articles according to Claim 1, wherein said additive for imparting specific properties comprises an electrically conductive and heat conductive material, magnetic and magnetizable material, wear-resistant and corrosion-resistant material, antifriction and lubricating material, coloring material or other material.

(3) A method of manufacturing ceramic shaped articles according to Claim 1, wherein articles of predetermined shape and dimensions are formed by stamping or any other method and then an antifriction powder is baked in pores formed due to evaporation of said binder,etc. or the porous article is sintered at high temperatures in a vacuum or enriched air.

(4)A method of manufacturing ceramic shaped articles according to Claims 1, 2 or 3, wherein the binder comprises an organic compound taken in the quantity of from 3 to 20% by weight in ratio to the content of the ceramic powder or a mixture of two or more adjuvants taken in the quantity of from 1 to 40% by weight.

3. Detailed Description of Invention

The present invention relates to a method of manufacturing ceramic articles by sintering ceramic powder along with a binder or adhesive material.

Ceramic materials, which are distinguished by their wear-resistant, shock-resistant, chemical-resistant, corrosion-resistant, electromagnetic properties and strength, are widely used in the industry for manufacturing various articles, pipes,parts of chemical equipment, electrotechnical materials, furnaces, thermal insulation materials or dental materials. However, it is difficult to use ~~the~~ ceramic materials for precision molding or manufacturing articles of a complicated configuration. They are not easily amenable to the formation of plate-like or tape-like products.

The present invention eliminates disadvantages mentioned above and provides for a method of manufacturing easily shaped ceramic articles such as plate-like, tape-like or fashioned articles, specially shaped porous articles, precision parts, e.g. artificial teeth, which at the same time preserve the color and shade of natural teeth.

Furthermore, the method of the present invention can also be used for preparing raw materials necessary for manufacturing ceramics of various types and applications. The present invention is also used for manufacturing shaped articles of high accuracy and efficiency. Another purpose of the invention is to provide a method for producing porous or solid articles of as complicated a configuration as possible

Further the invention is explained in detail. A binder is added and mixed with a ceramic powder material, the mixture is molded into a plate-like body of predetermined shape and dimensions, the plate is then rolled into a tape, and a first layer is formed by adhesively attaching a ceramic powder to the surface of the rolled tape whereonto it is added in a predetermined amount. A second layer is formed in a similar manner with the use of the ceramic powder and binder of the same or different types. If necessary, a third layer can be formed with the use of the ceramic powder and binder of the same or different types in combination with an additive which imparts specific properties to the mixture. According to the function and purpose of articles, the layers are selected and superimposed one onto another forming a tape of predetermined shape and dimensions with a specific distribution and density of the ceramic powder. The combined tape is again rolled under pressure and then articles are stamped out of the tape. These articles are sintered. In the course of sintering, a predetermined amount of the binder, adhesive and moisture is removed by means of evaporation. The sintered product comprises a porous body.

According to a particular application, the product can be used as it is in a porous state, or it may be rolled, compressed or compacted in any other manner.

The following materials can be used as a binder according to the present invention: natural and artificial rubbers such as gum arabic, tragacanth gum, EP rubber, SBR, NBR, CR, IIR, PI, PB; various resins such as vinylacetic, vinyl chloride, acrylic, cellulose, asphalt , polyesteric, poluolefin, polyurethane, phenolic, urea resins; and a mixture composed of more than one or two compounds such as alginic acid, dextrin, glycerol, gelatin, water glass, etc. If necessary, various adjuvants can be added.

The following materials or their mixtures can be used as a ceramic powder according to the present invention:........[x), metal oxides, metal carbonates, metal nitrides, various types of glass, fiber glass, clay, porcelain clay, quartz, silicate, alumina,feldspar, sand, etc.

Additives,which are added to the material of the third layer in order to impart to the material specific properties,may comprise a hardener to increase hardness, an antifriction substance,a, metal or alloy to impart heat and electric conductivity, pigment for coloring the compound, a magnetizing or magnetizable material, a lubricant or any other additive, which can impart special properties to the compound.

[x) Not legible in the original (Translator's note).

The invention will be explained further with reference to accompanying drawings. Figure 1 illustrates a flow chart showing a process of manufacturing shaped articles from a ceramic powder material. Figures 2 and 3 illustrate the manufacture of shaped articles by stamping articles from a tape of a ceramic material (side views). Figure 4 is a longitudinal cross-sectional view of a conveyor and a unit for heat treatment of sintered articles.

Practical Example 1

Composition A:

styrene	45	% by weight
toluene	25	-"-
dioctyl phthalate	20	-"-
dimethyl ketone	10	-"-

A coke was prepared by mixing 10 parts by weight of the compound A mentioned above with 90 parts of feldspar having an average grain size of about 300 mesh. Following this the material was rolled at 60^{o}C to produce a ceramic tape with the thickness of 0.2mm. As shown in Figure 1, a hopper 1A contains one ceramic component, and hopper 1B contains another ceramic component. These components are fed in required quantities onto the surface of a conveyor 2 through supply ports 11 in the bottom of the hoppers. The conveyor 2 is driven in the D direction from a driving roller 12. The ceramic powder material mentioned above is unloaded into a hopper 3 and admixed with the component A. Following this the mixture is discharged from the hopper 3 through an unloading port 13 into a kneading machine 4 wherein it is kneaded between rolls 1 and then discharged from the kneading machine through a discharge opening 14 onto the surface of a conveyor 5 driven into motion from a driving roller 15. The kneaded mass is fed into a guide passage 18 and passed between rolls 6, 7 and 17. If necessary, one end of the tape can be supported and controlled by auxiliary rollers 16. After passing between the rolls, a ceramic tape 22, which has a predetermined width and thickness, is obtained. In a similar manner the second and third tapes 21 and 23 are produced with predetermined dimensions and shape. As shown in Figure 2, all tapes 21,22 and 23 are superimposed one onto the other and then passed between rolls 27 and 24 thereby producing a three-layer tape,which is guided between guide rollers 2. After the tape has assumed the predetermined shape and dimensions, a punch 25 goes down and coacts with a die 26, whereby the surface 29 of the die 26 forms a shaped article 41. The article 41 is unloaded onto a conveyor 42 shown in Figure 4, which passes through a heat-treatment furnace 43. When current flows through a heating coil from electric source terminals 40, the temperature in the furnace is raised up to 600°C, whereby presintered articles 44 are produced. The articles are transfered by means of a driving roller 49 and guide rollers 48 of the conveyor to a cooling conveyor 46, which is also driven into motion from the driving roller 49. Following this,the articles are heat treated and sintered at 1200°C under a vacuum of 10^{-3} mmHg (this unit is not shown in the drawings). Articles produced by means of the punch 25, die 26 and surface 29 have the dimensions and shape of an artificial tooth.

These articles are compacted and their inner surfaces are densified, which make them more suitable for dental applications. If necessary, a metal pin can be inserted into an artificial tooth. As a result, strong, attractive and easily insertable teeth are obtained.

The required configuration of the shaped article can be easily obtained by combining several layers until a predetermined thickness is attained in the tape 22, which forms an inner structural element of the artificial teeth. A special coloring agent is added to the material of the tape 23, which forms the outer surface of the tooth, in order to impart to the artificial tooth the same color and shape as the natural one. As a result, the artificial teeth take the same color and attractive appearance as natural teeth. Metal components are admixed to the material of the tape 21 in order to improve adhesion to the surface. These properties are achieved by controlling the proportions of special additives fed from the hoppers 1C and 1D shown in Figure 1.

Practical Example 2

Composition B:

polystyrene	42 % by weight
dioctyl phthalate	20 -"-
toluene	25 -"-
methyl ethylketon	13 -"-

Ceramic powder composition A:

aluminum oxide	93 % by weight
magnesium oxide	7 -"-

Ceramic powder composition B:

lead oxide	44 % by weight
aluminum oxide	18 -"-
boron oxide	7 -"-
silicon oxide	21 -"-
ferric oxide	10 -"-

Composition C:

composition B	55 % by weight
tung oil	45 % by weight

The material of the first ceramic tape is obtained by mixing 10 parts by weight of composition B with 100 parts by weight of composition A.

Following this, a corresponding quantity of composition C is added to 89 parts by weight of composition B as a binder. 45 parts by weight of the B and C mixture is added and mixed with 55 % by weight of a silver powder x), whereby the material for the second tape is produced. In this Practical Example 2 the second ceramic tape is prepared in a similar way as the first ceramic tape. This process has been explained with reference to Figure 1. Due to addition of the silver powder, the second ceramic tape acquires electric conductivity.

As shown in Figure 3, several layers can be superimposed onto the

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x) Not legible in the original (Translator's note) first ceramic layer, which is used as a substrate. For example, two electrically conductive layers 31 are applied on either side of the first layer 32. The combined structure of the layers 31,32, 31 is guided between rollers 38, and elongated between pressure rollers 37, whereby the combined structure 31,32,31 is densified. The material is then compacted by a pressure roller 37 and fed to the die 36 and punch 35. An article punched from the condensed tape is unloaded through an opening 39. The stamped out articles, similar to the example illustrated in Figure 4, is subjected to baking. For example, after treating for 12 minutes at 800°C the outer electrically conductive layers are sintered, whereby a ceramic condenser is produced.

Barium titanate can be used as a dielectric material in manufacturing the substrate tape 32. Condensers of this type can be easily reproduced.

According to another example of practical applications, wear-resistant shaped articles are produced by adding to the mixture a predetermined amount of tungsten oxide or titanium carbonate, preparing ceramic tapes similar to the process described in Pracrical Example 1 or Practical Example 3, shaping articles of the tapes by stamping them out or by any other method and then sintering them at an elevated temperature.

A series of investigations has confirmed that satisfactory results are obtained when the material of tapes for manufacturing sintered shaped articles contains from 1 to 40 % by volume or from 3 to 20 %

by weight of the binder material in proportion to the volume or weight of the ceramic powder respectively.

Furthermore, electrically conductive, wear resistant or other special additives are used in the form of powder with an average grain size within the limits of from several microns to several dozen microns. In the case of Practical Example 2, the grain size of the silver powder was equal to 5 - 50 microns.

The first sintering is performed usually at temperatures below 1000°C (according to particular circumstances, presintering may be required) and the second sintering, at which the energy applied is 10-50 times as high as the first sintering, is performed within the temperature range of from 1200 to 1400°C. Experience has shown that the best results are obtained under these conditions. Furthermore, the sintering is not necesserily performed under a vacuum , as has been described above. Good results are obtained also under atmospheric pressure. The sintering can be carried out under a vacuum of from 10^{-1} to 10^{-5} torr, or in a reducing atmosphere such as hydrogen, as well as in an atmosphere of an inert gas such as nitrogen. It is clear that conditions have to be chosen in view of materials used, purpose of articles, reactivity, etc.

Because, in the course of sintering, air is removed from the material, the latter acquires a porous structure. However, when a presintering stage is introduced, air and dissolved fractions are removed at the first sintering and the material is compacted and densified at the second sintering, or the evaporation is performed by heating at low temperature before the first sintering operation and then the first sintering is carried out under normal conditions. Treatment at a relatively low temperature is possible, when liquid sintering is performed. The material can be used as it is with a porous structure. Furthermore, hardness, color and other properties of articles can be varied by selecting additives to the surface tape material.

As follows from the description given above, the present invention makes it possible to provide ceramic shaped articles of predetermined shape and dimensions with characteristics of the surface specified according to particular requirements. By varying constitutients of the mixture and methods of treatment articles can be produced with a relatively complicated configuration which was impossible with the use of conventional methods known in the art. Thus it is possible to more efficiently utilize chemically resistant, corrosion resistant, wear resistant and electromagnetical properties of the ceramic material. It is also possible to make objects of craftwork and printing. Articles which are difficult to produce by means of conventional methods can be easily obtained with the use of the method of the present invention.

4. Brief Description of Drawings

Figure 1 illustrates a flow chart of a process according to Practical Example 1. Figures 2 and 3 comprise longitudinal cross-sectional views illustrating a process of manufacturing miltilayer tapes and stamping articles therefrom. Figure 4 is a cross-sectional view illustrating the process of sintering.

1A, 1B, 1C, 1D - raw materials

11, 13, 14 - unloading ports

2, 5, 42, 44 - conveyors

12, 15, 49 - conveyor driving rollers

3 - hopper

4 - kneading machine

8, 21, 22, 23, 31, 32- ceramic tapes

25, 35 - punch

26, 36 - die

29 - die surface

6, 7, 17, 24, 34, 27 - compression rollers

43 - heat treatment furnace

45 - heater

41 - formed ar 'cle

44 - sintered articles