

Description

A Composition for Manufacturing Sinter-Molded Articles

Technical Field:

The present invention relates to a composition for manufacturing sinter-molded articles.

Background Art:

Accurate sinter-molded articles and sinter-molded articles that have complicated shapes are generally manufactured by the following method through use of a sinterable powder. First, a sinterable powder and a binder are kneaded with heat, cooled, and then granulated to afford a material for molding. Subsequently, the resultant material is injection-molded to thereby obtain a green molded article. The green molded article is sequentially subjected to a degreasing step and a sintering step.

Of the above-described steps, the degreasing step is performed for the purpose of removing a binder from a green molded article. The degreasing step is the most important step for obtaining sintered articles with excellent quality, i.e., sintered articles that do not have defects such as crazes, blisters, or deformation.

In the degreasing step, a green molded article may be subjected to a thermal degreasing method in which the green molded article is heated to thermally decompose a binder and

to gasify it for removal in the form of a gas. Alternatively, the green molded article may be treated with a solvent to thereby dissolve soluble binder components for removal, after which the remaining binder may be removed after being heated and gasified.

When the thermal degreasing method is performed, gases of decomposed binder are only permitted to escape from the surfaces of the green molded article, or the binder is only permitted to move to the surfaces for vaporization. Therefore, when the heating rate or temperature elevation rate is increased so as to cause thermal decomposition and gasification of the binder contained in a green molded article intensively within a short period of time, gases generated from thermal decomposition in the center portion of the molded article cannot be transferred to the surfaces smoothly. As a result, pressure is accumulated inside the article, and crazes and blisters may occur in the molded article. To avoid this, rapid heating should not be performed, and degreasing must be performed over a prolonged time with the application of heat under temperature conditions that do not cause the above-mentioned problems.

Particularly when the sinterable powder contained in a composition for manufacturing sinter molded articles is in the form of granules that have a small diameter and a great specific surface area, the proportion of a binder must be increased so as to stabilize the heating fluidity of a molding material during the manufacture of green molded articles. Therefore, in such cases where a composition for

the manufacture of sinter-molded articles is in the form of granules as described above, some measure such as repetition of the heating step is needed in the degreasing step for removing large amounts of binder.

Also, even when the composition for the manufacture of sinter-molded articles is by nature one which creates no fear of occurrence of crazes and blisters in the degreasing step in which heat is applied, if the sinterable powder contained in the composition is a metallic powder having a high specific gravity or powder of spherical particles, the resultant molded articles often deform during the thermal degreasing step. In this case, therefore, the temperature elevation rate during the degreasing step must be slowed.

In order to facilitate removal of the binder, a sublimable substance may be added to the binder. However, if a sublimable substance is added, it is sublimated during kneading or injection molding of a molding material in the manufacture of green molded articles, to thereby make it difficult to reuse the sprue runner portion during the manufacture of green molded articles.

On the other hand, according to a method in which a green molded article is treated with a solvent to thereby dissolve solvent-soluble binder components therein for removal of the components, and the remaining binder components are removed after being heated and gasified, voids are formed within the green molded article due to the treatment with the solvent. Since the voids serve as passages for the remaining binder to thermally decompose and

escape therethrough smoothly, the occurrence of crazes, blisters, deformation, etc. in green molded articles during the degreasing step can be prevented.

However, because currently employed binders contain great amounts of liquid materials such as mineral oils, fatty-acid-derived oils, and natural oils, these oils often ooze out of the green molded article. Particularly when the green molded article is stored for long periods, greater oozing of oils is observed. The oils that are transferred onto the surfaces of the green molded article may sometimes cause occurrence of crazes and blisters during the degreasing step.

According to another method, plasticizers and lubricants contained in the binder are dissolved in boiling water for removal. However, in view of the needs for maintaining the stability of the molding material for the manufacture of green molded articles, maintaining the heating fluidity of the molding material during injection molding, and maintaining the strength of the green molded article, amounts of plasticizers or lubricants that can be incorporated in the binder are limited.

According to yet another method, a binder formed of a water-soluble resin is used and the binder is extracted through treatment with water (Japanese Patent Publication (kokoku) No. Heisei2(1990)-101101). However, this method is not suitable for ceramic powders or metallic powders that react with water or corrode in the presence of moisture.

Furthermore, there are methods in which a polyacetal

resin, which is a depolymerizable polymer, is used singly or in combination with other polymers (Japanese Patent Application Laid-Open (kokai) Nos. Heisei4(1992)-247802, Heisei5(1993)-98306, etc.). According to these methods, the rigidity of polyacetal resins is utilized to thereby improve the shape-retaining property of a green molded article or the shape-retaining property of a molded article in the thermal degreasing step, as well as to improve the production efficiency by accelerating thermal degreasing and making use of the depolymerization properties so as not to leave residues after completion of thermal degreasing.

However, polyacetal resins are chemically stable and thus have poor compatibility with other resins, waxes, and lubricants that constitute a binder. Therefore, if polyacetal resins are incorporated in a binder, they tend to separate from other binder components to cause separation of layers, thus preventing uniform sinter-molded articles from being obtained. Specifically, in order to improve the shape-retaining property of a green molded article and the shape-retaining property of a molded article during the degreasing step, as well as to enhance the thermal degreasing efficiency, the amount of the polyacetal resins contained in the binder must be increased. However, this increase aggravates the aforementioned drawback, due to insufficient compatibility of polyacetal resins with other resins, waxes, or lubricants.

In addition, there is another method in which a polyacetal resin is used as a binder and the polyacetal resin contained in a green molded article is decomposed by use of

an acid catalyst for degreasing, to thereby greatly reduce the time required for degreasing. However, since this method employs a strong acid such as nitric acid, sinterable powder may be degraded through oxidation, etc. and the kinds of sinterable powder that can be used are greatly limited.

Disclosure of the Invention:

The present invention provides a composition for manufacturing a sinter-molded article, which composition enables a reduction in the time required for heating a green molded article for degreasing, so that during the degreasing step the molded article does not have defects such as crazes, blisters, deformation, etc. and in addition, the molded article has high dimensional accuracy and uniformity without suffering separation of layers.

Accordingly, the present invention provides a composition for manufacturing a sinter-molded article, which composition contains a sinterable powder and a binder, characterized in that the binder comprises a polyacetal resin (A), a modified polyolefin resin (B), and other binder components (C), the proportion of (A) being in the range of 5 to 60 vol%, the proportion of (B) being in the range of 5 to 85 vol%, and the total amount of the polyacetal resin (A) and modified polyolefin resin (B) being in the range of 10 to 90 vol% with respect to the total amount of the binder. There is also provided a composition for manufacturing a sinter-molded article as described above, wherein the modified polyolefin resin (B) is a copolymer of an olefin and an

unsaturated monomer having a glycidyl group.. There is also provided a composition for manufacturing a sinter-molded article as described above, wherein the modified polyolefin resin (B) is a copolymer obtained by chemically bonding a vinyl polymer, by way of branching or cross-linking, to a base polymer which is a polymerized product of olefin or a copolymer of olefin and another unsaturated monomer. There is further provided a composition for manufacturing a sinter-molded article as described above, wherein the vinyl polymer is a polymer prepared from one or more monomers selected from the group consisting of (meth)acrylic acid, alkyl esters thereof, acrylonitrile, and styrene. There is still further provided a composition for manufacturing a sinter-molded article as described above, wherein the modified polyolefin resin (B) is a copolymer of polyethylene, polypropylene or an ethylene-glycidyl methacrylate copolymer with an acrylonitrile-styrene copolymer, polymethyl methacrylate or polystyrene. There is still further provided a composition for manufacturing a sinter-molded article as described above, wherein the binder components (C) include at least a polyethylene or a paraffin wax. In addition, there is provided a composition for manufacturing a sinter-molded article as described above, wherein the proportion of the binder contained in 100 vol% of the composition is between 20 and 60 vol% inclusive. The present invention will next be described in detail.

Best Mode for Carrying Out the Invention:

The composition of the present invention for manufacturing sinter-molded articles is formed of a sinterable powder and a binder.

Examples of a sinterable powder that can be incorporated into the composition of the present invention for manufacturing sinter-molded articles include ceramics, metals, and cermets.

The binder which is incorporated into the composition of the present invention for manufacturing sinter-molded articles is constituted by a polyacetal resin (A), a modified polyolefin resin (B), and other binder components (C). The proportion of polyacetal resin (A) is in the range of 5 to 60 vol%, preferably 10 to 50 vol%, and particularly preferably 15 to 40 vol%.

When the proportion of polyacetal resin (A) present in the binder is less than 5 vol%, the temperature at which a green molded article deforms with the application of heat decreases considerably, and as a result, the molded article tends to become deformed during the degreasing step in which heat is applied. Moreover, since the amount of residual carbon after the green molded article has undergone degreasing increases, sintered articles of good quality cannot be obtained. On the other hand, when the amount of polyacetal resin (A) contained in the binder is in excess of 60 vol%, increased amounts of gases formed as a result of decomposition of the polyacetal resin emit during the thermal degreasing step of the green molded article, permitting easy occurrence of crazes, blisters, etc. in the molded article

during the degreasing step. In addition, since compatibility with other binder components (C) greatly decreases, the green molded article may lose its strength and may become brittle.

The polyacetal resin (A) that is a constituent of the binder used in the present invention may be a polymer compound containing an oxymethylene group ($-\text{CH}_2\text{O}-$) as the primary structural unit. There can be used polyoxymethylene homopolymers, as well as copolymers, terpolymers, and block copolymers which have structural units other than oxymethylene. Their molecules may be linear, branched, or cross-linked. Examples of comonomers that serve as the aforementioned other structural unit include ethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide, 1,3-dioxane, 1,3-dioxolan, and dioxepan.

The binder to be incorporated into the composition for manufacturing sinter-molded articles according to the present invention contains modified polyolefin resin (B), preferably in an amount of 5-85 vol%, more preferably 10-70 vol%, and most preferably 15-60 vol% with respect to the binder. A proportion less than 5 vol% with respect to the binder considerably decreases compatibility of polyacetal resin (A) and other binder components (C), making it difficult to obtain excellent green molded articles. Thus, crazes and blisters may result during the thermal degreasing step. On the other hand, when modified polyolefin resin (B) is in excess of 85 vol% with respect to the binder, the amount of polyacetal resin (A) is inevitably restricted, and therefore, during the degreasing step the molded article may be

deformed as a result of reduction in thermal deformation temperature of the green molded article. Moreover, the amount of remaining carbon after completion of the degreasing step may increase.

The proportion of the total amounts of polyacetal resin (A) and modified polyolefin resin (B) is 10 to 90 vol%, preferably 15 to 80 vol%, and particularly preferably 20 to 70 vol% with respect to the binder. The remaining portions are constituted by other binder components (C). When the proportion of the total amounts of (A) and (B) is less than 10 vol% with respect to the binder, the molded article is easily deformable by heat in the degreasing step, whereas when it is in excess of 90 vol%, fluidity of the composition decreases, hampering smooth injection molding for obtaining the green molded article.

Modified polyolefin resin (B) is a olefin polymer which has been modified by introduction of an aromatic group or a polar group. Illustrative examples of modified polyolefin resin (B) include a variety of polymers as described below that are obtained through copolymerization, graft copolymerization, etc.

(1) Copolymers of olefin (or monomers that can be copolymerized with olefin) and an unsaturated compound having a glycidyl group such as α,β -unsaturated acid, e.g., a glycidyl ester of glycidyl methacrylate (e.g., ethylene-glycidyl methacrylate copolymer)

(2) Copolymers obtained by chemically bonding, by way of branching or cross-linking, a vinyl polymer, e.g.,

polymethylmethacrylate, polystyrene, or a copolymer primarily containing polystyrene to an olefin polymer such as polyethylene, polypropylene, an ethylene-propylene copolymer.

(3) Copolymerized products obtained for example by performing graft copolymerization of a copolymer between α -olefin and an unsaturated compound (e.g., a glycidyl ester of α,β -unsaturated acid) and at least one of other monomers that can be polymerized with the copolymer (examples of such "other monomers" include acrylonitrile, styrene, methyl methacrylate, methyl acrylate, methacrylic acid) or a vinyl (co)polymer composed of these monomers (examples of the vinyl (co)polymer include polymethylmethacrylate, polystyrene, polyacrylonitrile, and acrylonitrile-styrene copolymers). Illustrative examples of this category include a graft polymer obtained by graft-polymerizing an acrylonitrile-styrene copolymer, polymethylmethacrylate, or polystyrene to an ethylene-glycidylmethacrylate copolymer.

(4) Hydroxyl-group-modified olefin polymers obtained by reacting an unsaturated compound having a hydroxyl group with an olefin polymer formed for example of an olefin homopolymer, olefin copolymer, or a copolymer which primarily contains olefin and which is obtained through copolymerization of olefin and other vinyl monomers such as diene compounds, α,β -unsaturated acids, their derivatives such as esters, or vinyl compounds.

(5) Copolymerized products obtained through graft polymerization of an olefin polymer (formed for example of an olefin homopolymer, olefin copolymer, or a copolymer which

primarily contains olefin and which is obtained through copolymerization of olefin and other vinyl monomers such as diene compounds, α,β -unsaturated acids, or their derivatives such as esters) and an unsaturated carboxylic acid or its derivatives (e.g., an unsaturated dicarboxylic acid such as maleic acid and fumaric acid, anhydrides thereof, an unsaturated carboxylic acid such as acrylic acid and methacrylic acid, and esters thereof).

(6) Copolymerized products obtained by chemically bonding, by way of branching or crosslinking, an olefin polymer and an ether polymer such as polyethylene oxide or polypropylene oxide.

(7) Epoxy-modified olefin polymers obtained by heating, in the presence of a radical initiator, an olefin polymer and an epoxy-containing monomer such as glycidylmethacrylate and glycidyl acrylate.

(8) Olefin polymers which have been modified with isocyanate-containing monomers.

In the present invention, particularly preferred modified polyolefin resins are those listed under items (1), (2), and (3) above.

The binder which is incorporated into the composition of the present invention for manufacturing sinter-molded articles may contain, as "other binder components (C)," organic substances such as thermoplastic resins, waxes, plasticizers, and lubricants, which are materials other than the above-described polyacetal resins (A) and modified polyolefin resins (B).

Examples of thermoplastic resins include acrylic resins, polyethylene, polypropylene, polystyrene, and polyvinyl butyral.

Examples of waxes include paraffin wax, polyethylene wax, carnauba wax, polyethylene glycol, beeswax, Japan wax, and synthetic waxes.

Examples of plasticizers include phthalic compounds such as dioctyl phthalate, dibutyl phthalate, and diethyl phthalate.

Examples of lubricants include fatty acid esters such as stearic acid esters and derivatives of fatty acid esters.

Preferable "other binder components (C)" are thermoplastic resins other than the above-described polyacetal resins (A) and modified polyolefin resins (B), as well as waxes such as paraffin wax, polyethylene wax, and polyethylene glycol. Particularly, polyethylene, paraffin wax, and polyethylene glycol are preferred. In the present invention, these components may be used singly or in combination of two or more species. In the latter case, it is preferred that at least one species is polyethylene or paraffin wax.

According to the present invention, the binder is preferably contained in the composition for manufacturing sinter-molded articles in an amount of 20-60 vol%, preferably 25-55 vol%, and particularly preferably 30-50 vol%, based on 100 vol% of the composition. The proportions of respective components that constitute the binder may be suitably determined in accordance with the type of the sinterable

powder to be used; i.e., ceramics, metals, cermets, etc.

When the composition of the present invention for manufacturing sinter-molded articles is prepared, no particular limitation is imposed on the order of blending the constituent components. For example, polyacetal resin (A) and modified polyolefin resin (B), which are binder components, may be mixed in advance, or may be used after being melted and kneaded. Alternatively, the binder components may be blended together with other components, without being subjected to mixing or kneading in advance.

The composition of the present invention for manufacturing sinter-molded articles serves as a molding material, which is subjected to injection molding for obtaining a premold, or a green molded article, of a sinter-molded article. The composition for manufacturing sinter-molded articles is kneaded with heat, cooled, and then granulated so as to afford a molding material for obtaining a green molded article. The molding material is used in injection molding to prepare a green molded article, and subsequently, the green molded article is subjected to a degreasing step in which the green molded article is degreased with the application of heat, etc. Finally, after undergoing degreasing the molded article is sintered, to thereby obtain the target sinter-molded article.

The composition of the present invention for manufacturing sinter-molded articles enables the manufacture of dimensionally accurate sintered articles such as chronometer parts, industrial machine parts, medical

instruments, and automobile parts, as well as sinter-molded articles having complicated shapes.

Examples:

The present invention will next be described by way of examples, which should not be construed as limiting the invention thereto.

(Examples 1 - 8, Comparative Examples 1 - 5)

Preparation of compositions for manufacturing sinter-molded articles:

The sinterable powder employed was SUS 316L having an average particle diameter of 10 μm . As binder components, polyacetal resin (A), modified polyolefin resins (B) shown in Table 1, and other binder components (C) were blended at proportions indicated in Tables 2 and 3 so as to prepare compositions for manufacturing sinter-molded articles.

Preparation of green molded articles:

Each of the compositions of Example 1 through 8 and Comparative Example 1 through 5 were kneaded at 160°C for 40 minutes by use of a pressure-applied kneader. Subsequently, the resultant kneaded material was cooled and crushed so as to obtain a molding material. The molding material was subjected to molding at a temperature between 140 and 180°C, to thereby obtain a dumb-bell-specimen-shaped green molded article.

Degreasing step:

Each green molded article was subjected to a degreasing step, in which heating was performed as follows: the

temperature of the green molded article was elevated to 120°C over 2 hours, then to 320°C at a heating rate of 30°C/hour, and the temperature was maintained at 320°C for 2 hours.

Sintering step:

The molded articles that have undergone degreasing were sintered at 1,320°C for 2 hours, to thereby obtain sintered articles.

Evaluation

In each of the above steps, the green molded articles were observed for the below-described properties. In each item of properties, evaluation was made on the basis of A (excellent), B (intermediate), and C (poor). Properties that can be measured were subjected to quantitative measurement. The results are shown in Tables 2 and 3.

(1) Moldability: Ease of molding when green molded articles were manufactured, and properties of the resultant green molded articles (particularly uniformity of the molded articles) were evaluated with one another.

(2) Deformation amount after degreasing: The amount of deformation of the central portion of each dumb-bell-shaped green molded article was measured after the article was heated and degreased while being retained as shown in Fig. 2.

(3) Properties of sintered articles: crazes and blisters after sintering were observed and evaluated.

(4) Residual carbon in sintered articles: Amounts of carbon remaining in sintered articles after undergoing sintering were measured.

Table 1

Code	Modified polyolefin resin	Amount of modification (wt.%)
A	Graft copolymer of polyethylene and polymethyl methacrylate	30
B	Graft copolymer of polyethylene and acrylonitrile-styrene copolymer	20
C	Ethylene-glycidyl methacrylate copolymer	10
D	Graft copolymer of ethylene-glycidyl methacrylate copolymer and acrylonitrile-styrene copolymer	30

Table 2

	Composition for manufacturing sinter-molded articles		Composition of binder (vol% in binder)					Evaluation			
	Powder (vol%)	Binder (vol%)	POM	Modified polyolefin resin		LDPE	P.Wax	Mold-ability	Deformation of degreased article	Properties of sintered article	Residual carbon in sintered article
				Code							
Ex. 1	60	40	20	A	20	10	50	A	A (0.4 mm)	A	A (150 ppm)
Ex. 2	60	40	20	B	20	10	50	A	A (0.3 mm)	A	A (130 ppm)
Ex. 3	60	40	20	C	20	10	50	A	A (0.5 mm)	A	A (160 ppm)
Ex. 4	60	40	20	D	20	10	50	A	A (0.5 mm)	A	A (150 ppm)
Ex. 5	60	40	10	A	20	20	50	A	A (0.8 mm)	A	A (450 ppm)
Ex. 6	60	40	45	A	15	10	30	B	A (0.1 mm)	A	A (35 ppm)
Ex. 7	60	40	20	A	10	20	50	A	A (0.5 mm)	A	A (170 ppm)
Ex. 8	60	40	15	A	55	-	30	A	A (0.6 mm)	A	B (420 ppm)

POM: Polyacetal resin

LDPE: Low-density polyethylene

P. Wax: Paraffin wax

Table 3

	Composition for manufacturing sinter-molded articles		Composition of binder (vol% in binder)					Evaluation			
	Powder (vol%)	Binder (vol%)	POM	Modified polyolefin resin		LDPE	P.Wax	Mold-ability	Deformation of degreased article	Properties of sintered article	Residual carbon in sintered article
				Code							
Comp. Ex. 1	60	40	20	-	-	30	50	Not moldable	-	-	-
Comp. Ex. 2	60	40	-	A	20	30	50	A	C (3.8 mm)	C (Cr/Bl)	A (1200 ppm)
Comp. Ex. 3	60	40	3	A	37	10	50	A	C (3.5 mm)	C (Cr/Bl)	A (1000 ppm)
Comp. Ex. 4	60	40	37	A	3	10	50	B	A (0.1 mm)	C	A (80 ppm)
Comp. Ex. 5	60	40	70	A	5	-	25	B - C	A (0.1 mm)	C (Cr/Bl)	A (30 ppm)

POM: Polyacetal resin

LDPE: Low-density polyethylene

P. Wax: Paraffin wax

Cr/Bl: Crazes/Blisters

Brief Description of the Drawings:

Fig. 1 shows the shape of the dumb-bell-shaped test piece of a green molded article, and Fig. 2 shows the position at which the deformation amount after degreasing was measured for the dumb-bell-shaped green molded article.

Industrial Applicability:

The composition for manufacturing sinter-molded articles according to the present invention makes use of a polyacetal resin, which is a depolymerization polymer, as a binder. Green molded articles prepared from the composition of the present invention for manufacturing sinter-molded articles exhibit excellent shape-retaining property attributed to the rigidity of the polyacetal resin, as well as excellent shape-retaining property of the molded article in the degreasing step. Moreover, shorter time is required for the degreasing step because of the depolymerization characteristics of the polyacetal resin. In addition, since the composition of the present invention for manufacturing sinter-molded articles contains as a binder a modified polyolefin resin, which exhibits excellent compatibility with other binder components, uniformly sintered articles can be obtained without inviting separation of layers. Accordingly, when the composition of the present invention for manufacturing sinter-molded articles is used, the degreasing step for green molded articles can be completed within a shorter period, without causing defects such as crazes, blisters, deformation, etc. in the molded articles under

processing in the degreasing step. In addition, it is possible to obtain uniform sintered articles exhibiting high levels of dimensional accuracy which do not suffer from separation of layers.



What is Claimed is:

1. A composition for manufacturing a sinter-molded article, which composition contains a sinterable powder and a binder, characterized in that the binder comprises a polyacetal resin (A), a modified polyolefin resin (B), and other binder components (C), the proportion of (A) being in the range of 5 to 60 vol%, the proportion of (B) being in the range of 5 to 85 vol%, and the total amount of the polyacetal resin (A) and modified polyolefin resin (B) being in the range of 10 to 90 vol% with respect to the total amount of the binder.

2. The composition for manufacturing a sinter-molded article according to Claim 1, wherein the modified polyolefin resin (B) is a copolymer of an olefin and an unsaturated monomer having a glycidyl group.

3. The composition for manufacturing a sinter-molded article according to Claim 1, wherein the modified polyolefin resin (B) is a copolymer obtained by chemically bonding a vinyl polymer, by way of branching or cross-linking, to a base polymer which is a polymerized product of an olefin or a copolymer of an olefin and another unsaturated monomer.

4. The composition for manufacturing a sinter-molded article according to Claim 3, wherein the vinyl polymer is a polymer prepared from one or more monomers selected from the group consisting of (meth)acrylic acid, alkyl esters thereof, acrylonitrile, and styrene.

5. The composition for manufacturing a sinter-molded article according to Claim 3, wherein the modified polyolefin



resin (B) is a copolymer of polyethylene, polypropylene, or an ethylene-glycidyl methacrylate copolymer with an acrylonitrile-styrene copolymer, polymethyl methacrylate, or polystyrene.

6. The composition for manufacturing a sinter-molded article according to any one of Claims 1 through 5, wherein the binder components (C) include at least a polyethylene or a paraffin wax.

7. The composition for manufacturing a sinter-molded article according to any one of Claims 1 through 6, wherein the proportion of the binder contained in 100 vol% of the composition is between 20 and 60 vol% inclusive.