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(54) Process for production of sintered body.

(57) A sintered body is produced by a process comprising suitably mixing powders with different average particle diameters and particle size distributions to prepare a starting raw powder with a tap density of 40% or more, kneading the obtained starting raw powder with less than 38% by volume of a binder, and injection molding the obtained mixture, debinding the resulting molded body in an atmosphere containing 1 to 30% of oxygen, and finally sintering the molded body in a reducing atmosphere.

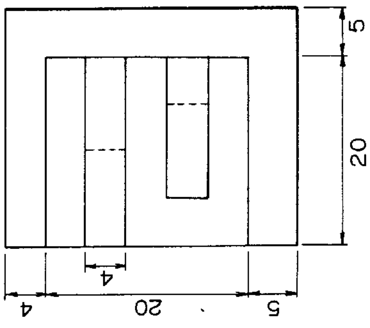
Fig. 1b

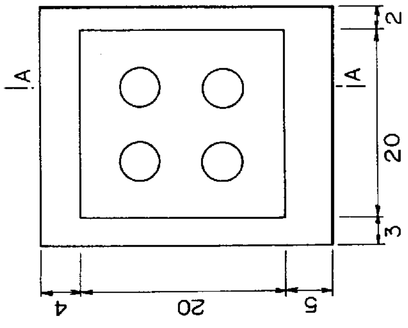
Fig. 1a

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The present invention relates to a process for the production of a sintered body. More specifically, the present invention relates to an injection molding sintering process for producing a sintered body having a complex shape, by an injection molding of a powder mixture, and sintering the thus-obtained molded body.

In an injection molding sintering process, a metal or various alloys thereof, as well as various ceramics powders containing a nitride, boride and the like as raw materials, are kneaded with an organic substance called a "binder" to form a mixture, and thereafter, the mixture is molded by an injection molding process and the binder is removed by a heat evaporation process, by which the binder is decomposed. Thereafter, the thus-debound molded body is sintered, whereby a sintered component is produced. According to this process, components having complex shapes may be obtained even when using a metal or various alloys thereof, as well as ceramics, and therefore, it becomes possible to integrally mold components that have been manufactured, without machining or welding or the like. Accordingly, a large reduction of the number of components becomes possible, and thus this process plays an important role in providing a noticeable improvement of the performance and a reduction of the cost of many devices, including office automation equipments. Conventionally, as the starting powder, carbonyl powder or atomized powder with an average particle diameter of less than 20 µm is used in the injection molding sintering process, as described in, e.g., Japanese Unexamined Patent Publication No. 61-210101. Further, the binder used for the injection molding, is a mixture of several kinds of compatible organic substances, as described in, e.g., Japanese Examined Patent Publication No. 61-48563, and the amount of binder added is between 40 and 50% by volume based on the starting powder. In particular, when a powder with a particle diameter of less than 20 µm is used as described above, the amount of binder added must be more than 45% by volume.

On the other hand, in the debinding step in which the binder contained in the molded body is removed by sintering after the injection molding, to prevent a rapid decomposition of a great amount of the binder and the occurrence of cracks or blisters due to the evaporation of the decomposed product of the binder, the binder has been subjected to pyrolysis in a non-oxidative atmosphere such as nitrogen and argon, for a long time.

The conventional processes described above have the problems indicated below.

Since the carbonyl powder as the starting raw material is limited to iron and nickel powder, the conventional processes have a defect in that the degree of freedom in selecting a material is limited. On the other hand, although the degree of freedom in selecting the material is high in the case of an atomized powder, the particle size distribution or surface conditions of the powder particles differ for each lot, and the surface oxidation conditions also differ, and thus the kind or amount of binder must be adjusted for each obtained lot. Further, the conventional processes have a drawback in that, when the properties of a powder are not suitable for injection molding, the powder cannot be used as the starting raw powder. Furthermore, since the recovery by the atomized process of fine powder with an average particle diameter of less than 20 µm is as low as less than 10% of a charge, the cost of the starting raw powder becomes very high.

With regard to the binder, since a great amount of within 40 to 50% by volume of a binder is used, when producing a complex and large-size component or a component having a large height, when debinding, inconveniences such as a softening of the binder often occur or the shape of the molded body cannot be maintained, or the like. Also, a problem arises in that the shrinkage becomes so large that the dimensional precision is lowered, and it is difficult to produce a minute component with a near net shape.

3. The debinding is accompanied by a defect that, owing to the use of a non-oxidative atmosphere in the thermal decomposition of the binder of an organic substance, the decomposition reaction is retarded and carried out at a relatively higher temperature, and the reaction requires a long time, thus lowering the productivity. A problem also arises in that, when debinding the molded body in a non-oxidative atmosphere, the deformation of the molded body becomes very noticeable and cracks or blisters in the molded body often appear.

According to the present invention, there is provided a process for the production of a sintered body, comprising mixing a plurality of powders with different average particle diameters and particle size distributions to prepare a starting raw powder with a tap density of 40% or more, kneading the obtained starting raw powder with less than 38% by volume of a binder to obtain a mixture and injection molding the mixture to obtain a molded body, debinding the molded body in an atmosphere containing 1 to 30% of oxygen, and finally sintering the molded body in a reducing atmosphere.

The debinding may be carried out under pressure.

For a better understanding of the invention, and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings, in which:-

Figures 1a and 1b are views showing the shapes and dimensions of the molded bodies prepared in the examples, wherein Fig. 1a is a plan view and Fig. 1b is a cross-sectional view taken along the line A-A in Fig. 1a, and the unit of the numerals is mm;

Fig. 2 is a graph showing the heating and cooling curve used in the examples;

Fig. 3 is a graph showing the amount of oxygen in the debound body and the sintered body when the amount of oxygen in the debinding atmosphere was varied between 0 and 100%.

Fig. 4 illustrates graphs showing the relationships between the highest temperature and the amount of the binder remaining, where the amounts of oxygen in the debinding atmosphere were 0% and 20%, respectively;

Fig. 5 is a graph showing the relationship between the amount of the debinding atmosphere and the shortest total debinding time during which a desired debound body can be obtained;

Fig. 6 is a graph showing the relationship between the amount of oxygen in the debinding atmosphere and the height from which the debound body could be dropped onto a wooden base without being chipped or broken, on the basis of which the handling property of the debound body was evaluated.

In the process of the present invention, first, powders with different average particle diameters and particle size distributions are suitably mixed, and the thus-obtained powder mixture is used as a starting material. Further, the powder mixture is controlled on a tap density basis, and the tap density of the powder mixture is made more than 40%, preferably more than 55%.

By suitably mixing powders with different average particle diameters and particle size distributions, it is possible to change the average particle diameter and particle size distribution of the powder mixture, and therefore, it becomes possible to eliminate the differences among the characteristics of the obtained lots, and simultaneously, to obtain a powder with a particle size distribution exhibiting an excellence powder fluidity during injection, which is difficult to obtain by a normal process for the preparation of powder. The powder mixture is controlled on a tap density basis because the tap density varies in accordance with the powder characteristics, such as the average particle diameter, particle size distribution, particle shape and surface conditions, and may be considered a comprehensive value of the powder characteristics. When the tap density is more than 40%, an injection molding of the powder mixture, with a good dimensional precision and a small amount of binder, is possible, and when this value is more than 55%, the amount of the binder added can be greatly reduced.

Next, the starting raw powder mixture is kneaded with less than 38% by volume of a binder, and then injection molded. In this case, preferably two or more kinds of binders are used and at least one of the binders is formed to be incompatible with the others or having a softening point different from that of any of the other binders. Further, when kneading the starting raw powder mixture with these binders, the kneading is preferably effected at least twice. By the first kneading, the binder with the highest softening point is coated around each of the powder particles, and by effecting the second and further kneadings at a temperature and pressure such that the coating layers around each of the powder particles are not broken, the above-described coating layer acts as sliding layers when powders are brought into contact with each other by the temperature and pressure at the time of injection molding, whereby an agglomeration of the powders can be prevented and a high fluidity of the powder mixture ensured. Also, according to this process, it is sufficient that the kneaded body have a fluidity enabling injection molding, and therefore, the amount of binder added may be largely reduced to a value of less than 38% by volume of the starting raw powder mixture, whereby the dimensional precision of the obtained sintered body is greatly improved.

The obtained molded body is then debound in an atmosphere containing 1 to 30% of oxygen. When oxygen is present in the debinding atmosphere, as the binder is an organic substance the decomposition reaction of the binder, which is started owing to scission of the main chain, is accelerated in a linked state as radicals are generated. Accordingly, the decomposition-initiating temperature of the binder becomes lower, and the decomposition-terminating temperature also becomes lower by a high degree of about 100°C, whereby the debinding temperature may be set low and the decomposition reaction promoted. On the other hand, although the rapid decomposition of the binder in a non-oxidative atmosphere results in an outbreak of defects such as cracks or blisters on the debound molded body, when oxygen is present, the oxidized films formed on the metal particles strongly bind the powder particles, and thus the above-described unsatisfactory debinding may be suppressed. Also, these oxidized films enable the handling property of the debound body to be greatly improved, and accordingly, the hitherto required long debinding time may be reduced.

In this case, if the amount of oxygen is less than 1%, it is so small that so effect due to the presence of oxygen is exhibited. Further, when the amount of oxygen exceeds 30%, oxidation of the starting raw powder proceeds so far that the starting raw powder cannot be sufficiently reduced in the oxidized layer formed at the subsequent sintering step effected in a reducing atmosphere, thus lowering the properties such as magnetic characteristics of the product, and since the decomposition reaction of the binder proceeds so rapidly, cracks or blisters occur in the large-sized components having a complex shape, resulting in a poor productivity.

The process of the present invention may be effected, for example, in the following way.

Three kinds of powders (A to C) with average particle diameters of 8 μm, 20 μm and 47 μm, respectively, are mixed in a volume ratio of 15 : 70 : 15 to obtain a powder mixture D. Alternatively, by using a powder E (average particle diameter: 10 μm) instead of powder A (average particle diameter: 8 μm) and mixing powders E, B and C in a volume ratio of 20 : 67 : 13, a powder with the same particle size distribution as that of the powder mixture D is obtained. In a like manner, by replacing powders B and C with other powders having different average particle diameters, and a changed mixing ratio, a powder mixture with the same particle size distribution as that of powder D can be obtained.

As described above, even if the average particle diameter or particle size distribution is varied, by changing the mixing ratio, the particle size distribution of a powder mixture before the average particle diameters or particle size distributions of the powders to be used for mixing are changed may be reproduced, and thus the difference of qualities of the obtained powders among lots may be eliminated. Further, by suitably changing the starting raw powders and the mixing ratio thereof, a powder mixture with a particle size distribution, which cannot be prepared by a normal atomizing method, may be prepared.

The powder mixture obtained as described above is kneaded with a binder consisting essentially of polymethyl methacrylate (PMMA) and polyethylene (PE), and then injection molded. With respect to the amount of the binder required for injection molding, the larger the tap density of the powder mixture, the less the required amount, and when the tap density is more than 40%, an injection molding may be conducted with a lesser amount of the binder than that of the binder to be used in a usual injection molding sintering process.

In the above description, PE has no compatibility with PMMA, and the softening points of these substances are different; that of wax is 80°C and that of PMMA is 140°C. After the powder mixture has been kneaded with PMMA at a temperature of 180°C, the temperature is lowered to 100°C, and wax is poured into the kneaded body and again kneaded. Thereafter, the finally obtained kneaded body is injection molded.

The thus obtained injection molded body is then heat-treated in a nitrogen atmosphere containing 1 to 30% of oxygen, and thus debound. The debound molded body is then sintered for one hour in a hydrogen atmosphere at a temperature of 1400°C.

The present invention will further be illustrated below with reference to working examples.

Example 1

Three kinds of Fe-6.5% Si alloy powders with average particle diameters of 8 μm, 20 μm and 47 μm, respectively, were mixed in a volume ratio of 2: 6: 2, whereby a powder mixture with a tap density of 55% was prepared. This powder mixture was kneaded with a binder (hereinafter referred to as "binder A") consisting essentially of polymethyl methacrylate, so that coating layers of binder A were formed on the circumferences of the powder particles. Further, the obtained kneaded body was kneaded with a binder (hereinafter referred to as "binder B") consisting essentially of polyethylene. The total amount of this binder was 35% by volume. The obtained kneaded body was then injection molded to prepare a molded body having the shape shown in Fig.1.

The obtained molded body was debound by changing the conditions as described below.

Atmosphere: nitrogen (admixed with 0 to 100% of oxygen), not pressurized (gauge pressure of 0 kg/cm^2)

Highest temperature: 300 to 450°C

Total debinding time: 8 to 48 hours

Heating and cooling were also conducted according to the curve shown in Fig. 2.

Where the molded body was debound in a pressurized nitrogen atmosphere (admixed with 0 to 100% of oxygen) having a gauge pressure of 4 kg/cm^2, the temperature elevation rate could be increased by 1.5 times.

Next, these debound bodies were sintered in a hydrogen atmosphere for one hour at a temperature of 1400°C. Figure 3 shows the amount of oxygen in the debound body and sintered body when the amount of oxygen in debinding atmosphere was varied between 0 and 100%. The amount of oxygen in the debound body, when the amount of oxygen in the debinding atmosphere is above 1%, is larger than the amount of oxygen when the amount of oxygen in the debinding atmosphere is 0%, which shows that the debound body is oxidized. On the contrary, the amount of oxygen in the sintered body is almost unchanged when the amount of oxygen in the debinding atmosphere is between 0 and 30%. From the above, it is clear that, when oxygen is present in the debinding atmosphere, the debound body is oxidized, and when the amount of oxygen in the debinding atmosphere is below 30%, the debound body may be reduced by a sintering thereof in a hydrogen atmosphere (reducing atmosphere).

Figure 4 shows the relationship between the highest temperature and the amount of binder remaining in the debound body, where the amount of oxygen in the debinding atmosphere is 0% and 20%, respectively. The amount of remaining binder was calculated on the basis of the weight loss measured when the debound body was further heated in a nitrogen atmosphere to a temperature of 600°C, and all of the components of the binder were evaporated. When the amount of the binder where the amount of oxygen in the debinding atmosphere is 0%, the amount of remaining binder becomes 10% at the highest temperature of 440°C, and the debound body can be moved to the sintering step. Further, when the amount of remaining binder becomes 0%, it becomes generally difficult to handle the debound body, and therefore, in the injection molding sintering process, the binder is allowed to remain in the debound body in an amount of from 5 to 10%. Furthermore, when the amount of remaining binder in the debound body exceeds 10%, at the time of sintering the debound body, unsatisfactory results are likely to be produced, and therefore, the maximum amount of remaining binder must be set as 10%. On the other hand, when 20% of oxygen is mixed in the debinding atmosphere, the amount of remaining binder becomes 10% at the highest temperature of 340°C, so that the highest temperature at the time of debinding may be lowered at about 100°C. In addition, with the amount of oxygen in the debinding atmosphere ranging from 1 to 100%, the same effects may be obtained as those obtained when the amount of oxygen is 20%.

Figure 5 shows the relationship between the amount of oxygen in the debinding atmosphere and the shortest total debinding time during which a good debound body can be obtained. When the amount of oxygen in the debinding atmosphere was 0%, if the total debinding the is less than 24 hours, a good debound body could not be obtained by any temperature profile. When the amount of oxygen in the debinding atmosphere was between 1 and 30%, a good debound body was obtained over the total debinding time of 12 hours (not pressurized). When the amount of oxygen in the debinding atmosphere was 50%, a good debound body was obtained over the total debinding time of 24 hours or more. When the amount of oxygen in the debinding atmosphere is 100%, a good debound body could not be obtained even by setting the total debinding time to 48 hours. It is shown by the above that the debinding time can be shortened by mixing 1 to 30% of oxygen in the debinding atmosphere. Where pressurized, similar results were obtained as shown in Fig. 5.

The handling property of the debound body was evaluated on the basis of a height from which the debound body can be dropped onto a wooden base without being chipped or broken. Figure 6 shows the relationship between the amount of oxygen in the debinding atmosphere and this height. The amount of binder remaining in the debound body is 10%. When the amount of oxygen in the debinding atmosphere was 0%, if the height from which the debound body was dropped onto the wooden base was 1 cm or more, the debound body was broken or cracked. When the amount of oxygen in the debinding atmosphere was 1% or more, the debound body was neither chipped nor cracked, even if the debound body was dropped from a height of 10 cm or more. This is considered to be because the oxidized films of the powder particles in the debound body tightly bind the powder particles to one another. In addition, when the binder was completely removed from the debound body, the debound body broke into pieces when only slightly touched. On contrary, when the amount of oxygen in the debinding atmosphere was 1% or more, the same results as where the amount of remaining binder was 10% were obtained.

Example 2

The procedure as described in Example 1 was repeated, with the exception that Fe-50% Co alloy powder was used instead of Fe-6.5% Si alloy powder in Example 1. The results were similar to those in Example 1.

The above working examples are considered applicable to almost all materials, as long as they are metals reducible in hydrogen. These examples may be applied, e.g., to materials of tools such as hard metals for a device and carbide tools, device part materials such as stainless steel, and magnetic part materials such as Fe -50% Co alloy, Fe - Si alloy and pure iron.

According to the process of the present invention, a reduction of the debinding time becomes possible, and a reduction of costs as well as an increased productivity may be expected. In addition, owing to the increase of the handling property of the debound body, transportation or the like of the debouned body can be effected, which hitherto was difficult due to the fragility of the debound body, whereby the product yield can be increased. In addition, since atmospheric air can be used as the debinding atmosphere, the running costs also may be reduced.

Claims

1. A process for the production of a sintered body, comprising mixing a plurality of powders with different average particle diameters and particle size distributions to prepare a starting raw powder with a tap density of 40% or more, kneading the obtained starting raw powder with less than 38% by volume of a binder to obtain a mixture and injection molding the mixture to obtain a molded body, debinding the molded body in an atmosphere containing 1 to 30% of oxygen, and finally sintering the molded body in a reducing atmosphere.

2. A process according to claim 1, wherein the atmosphere in which the molded body is debound is pressurized.

3. A process according to claim 1 or 2, wherein the tap density of the starting raw powder is above 55%.

4. A process according to any preceding claim, wherein the powders with different average particle diameters and particle size distributions are selected from hard metal powders, stainless steel powders, Fe-Co alloy powders, Fe-Si alloy powders and pure iron powders.

5. A process according to any preceding claim, wherein the binder is based on polymethyl methacrylate and polyethylene.

6. A process according to any preceding claim, wherein the kneading is carried out at least twice.

7. A process according to claim 6, wherein the starting raw powder is kneaded with polymethyl methacrylate and then kneaded with polyethylene.

Fig. 1a

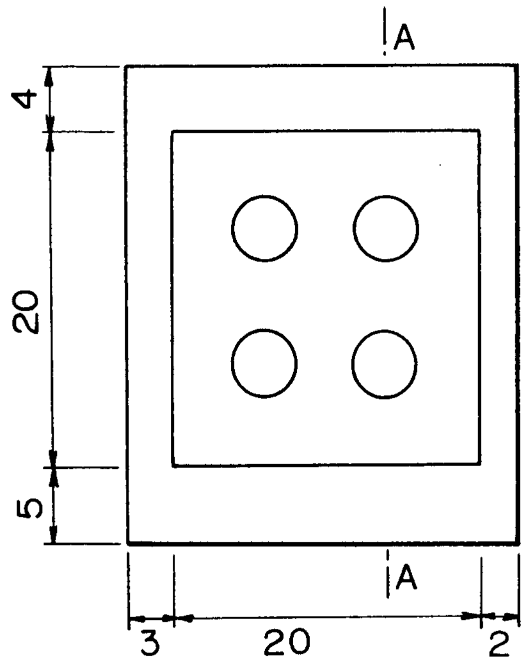


Fig. 1b

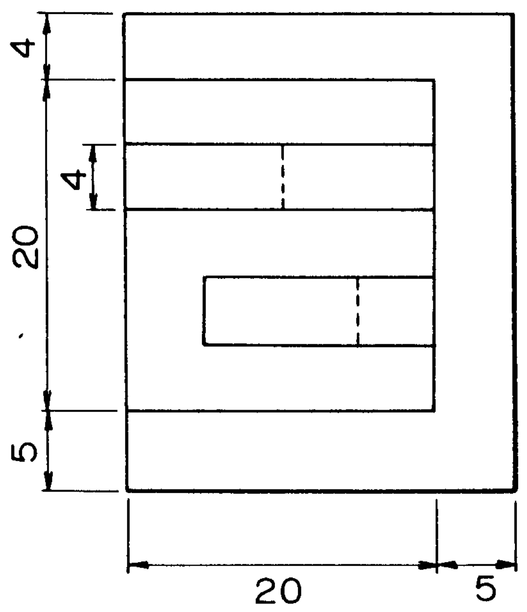


Fig. 2

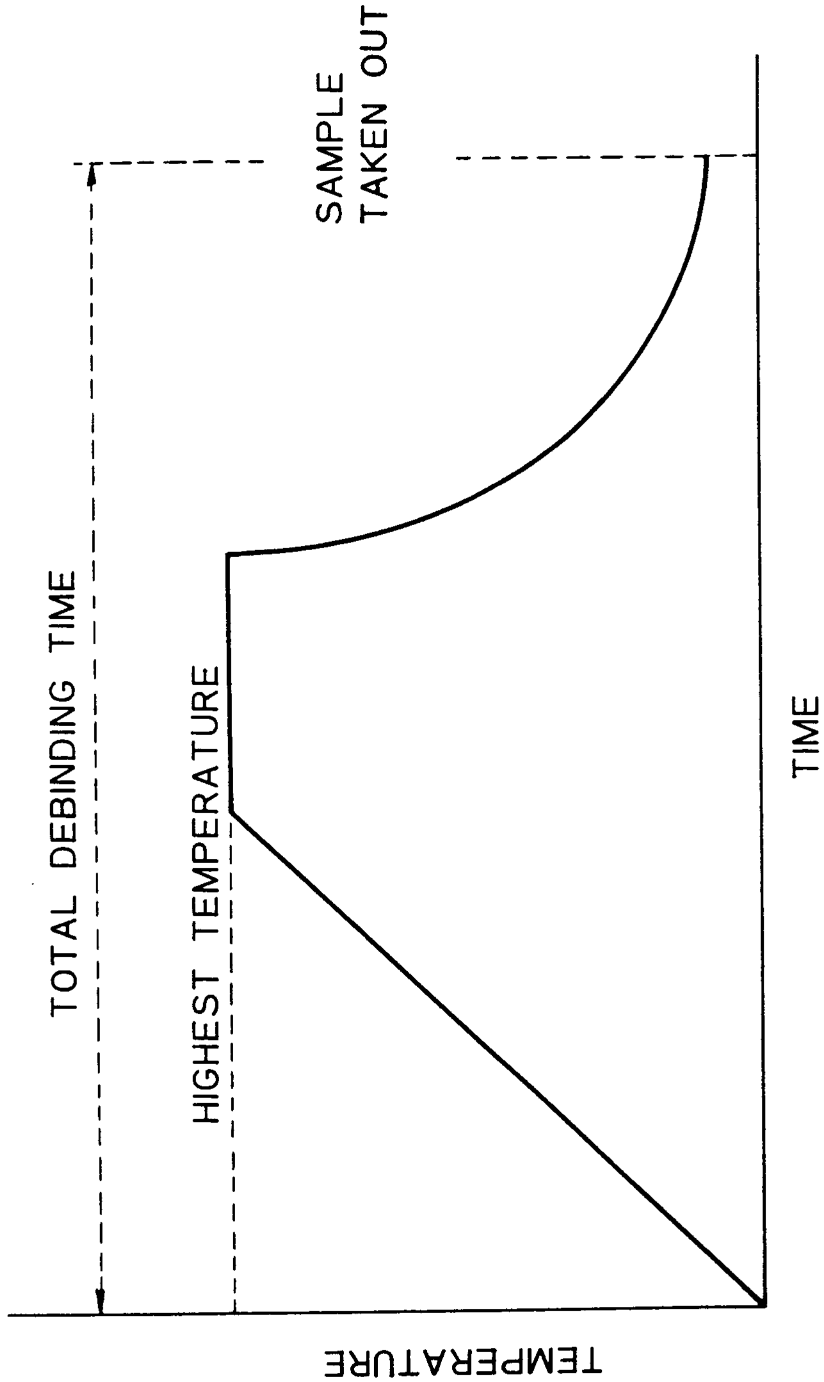

TOTAL DEBINDING TIME
HIGHEST TEMPERATURE
SAMPLE TAKEN OUT
TEMPERATURE
TIME

FIG. 3

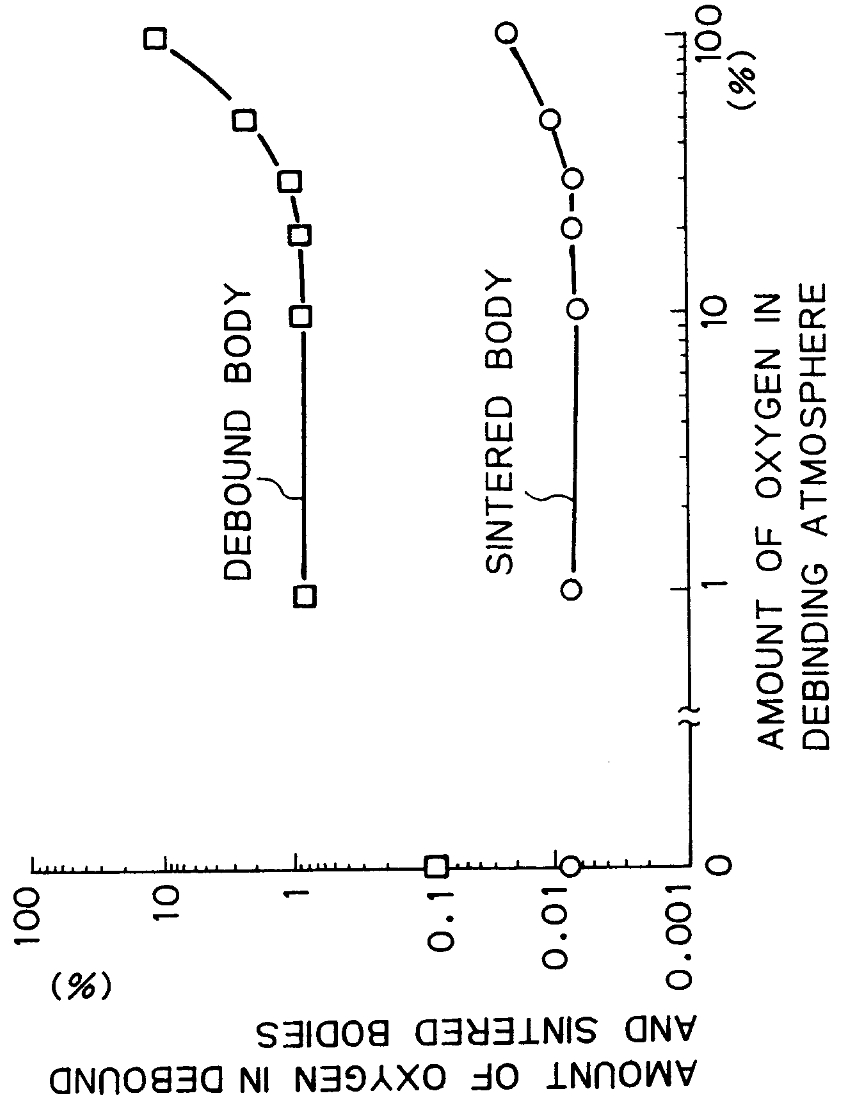

DEBOUND BODY
SINTERED BODY
AMOUNT OF OXYGEN IN DEBOUND AND SINTERED BODIES
(%)
100
10
1
0.1
0.01
0.001
0
1
10
100
(%)
AMOUNT OF OXYGEN IN DEBINDING ATMOSPHERE

Fig. 4

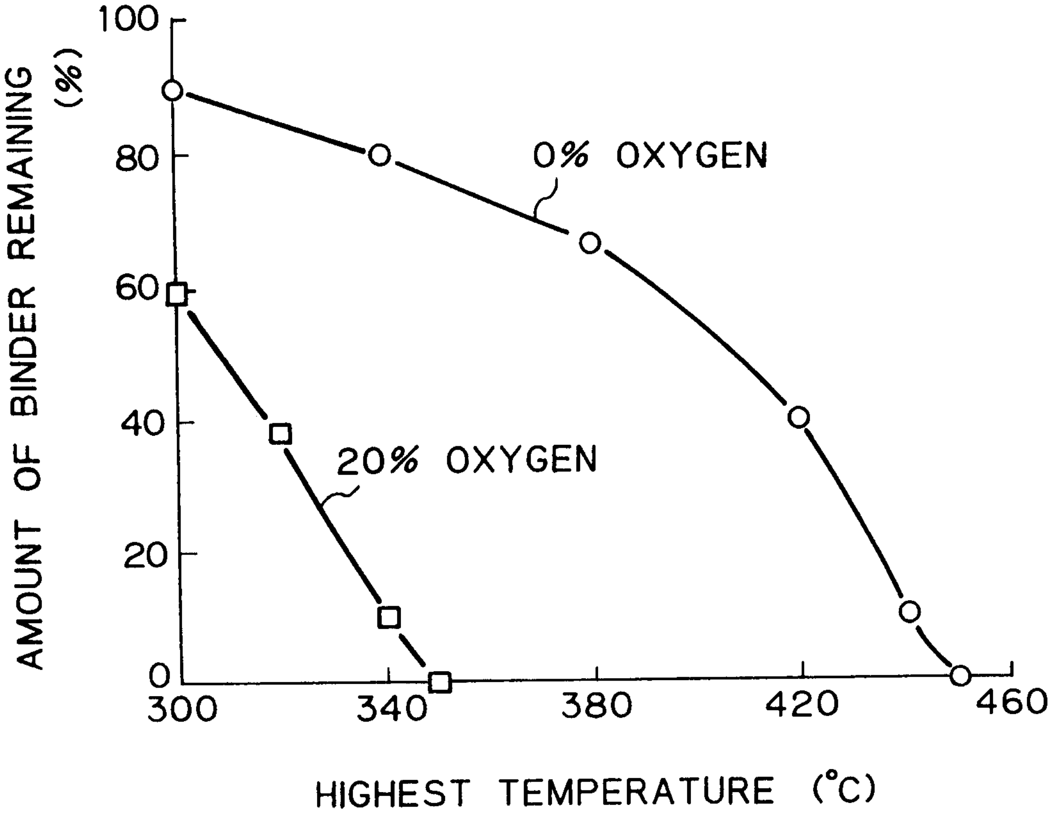

100
80
60
40
20
0
300
340
380
420
460
AMOUNT OF BINDER REMAINING (%)
HIGHEST TEMPERATURE (°C)
0% OXYGEN
20% OXYGEN

FIg. 5

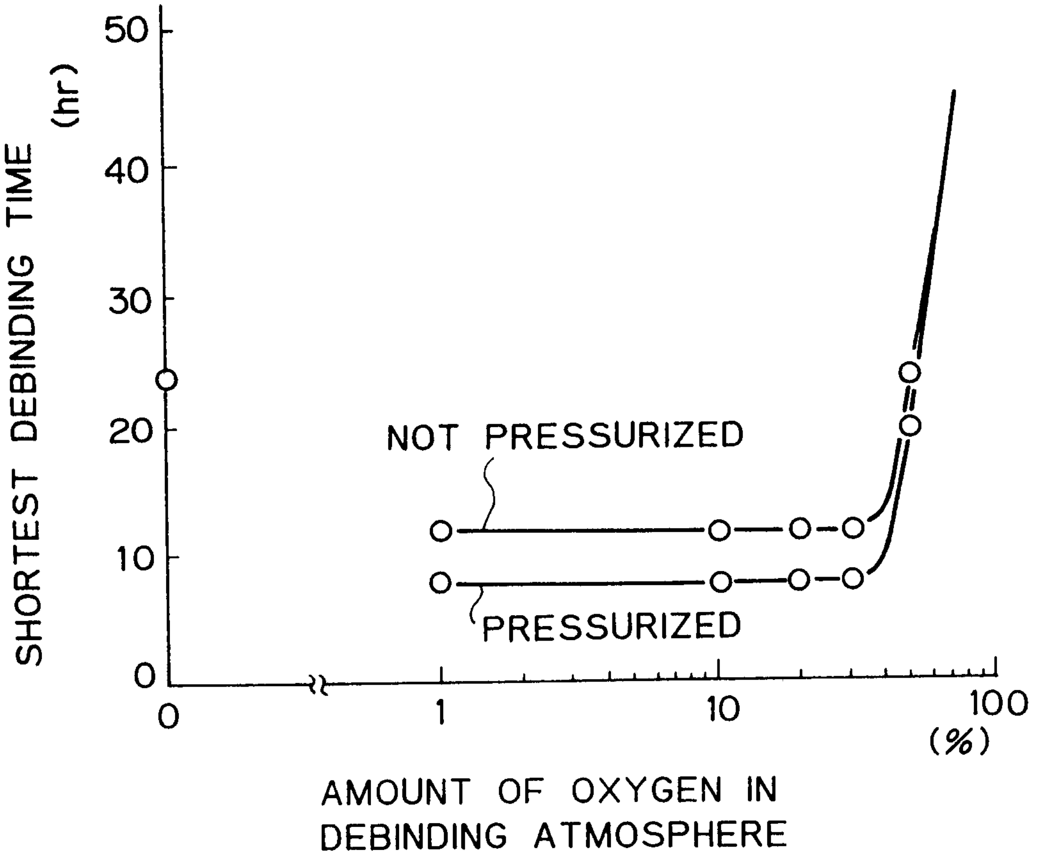
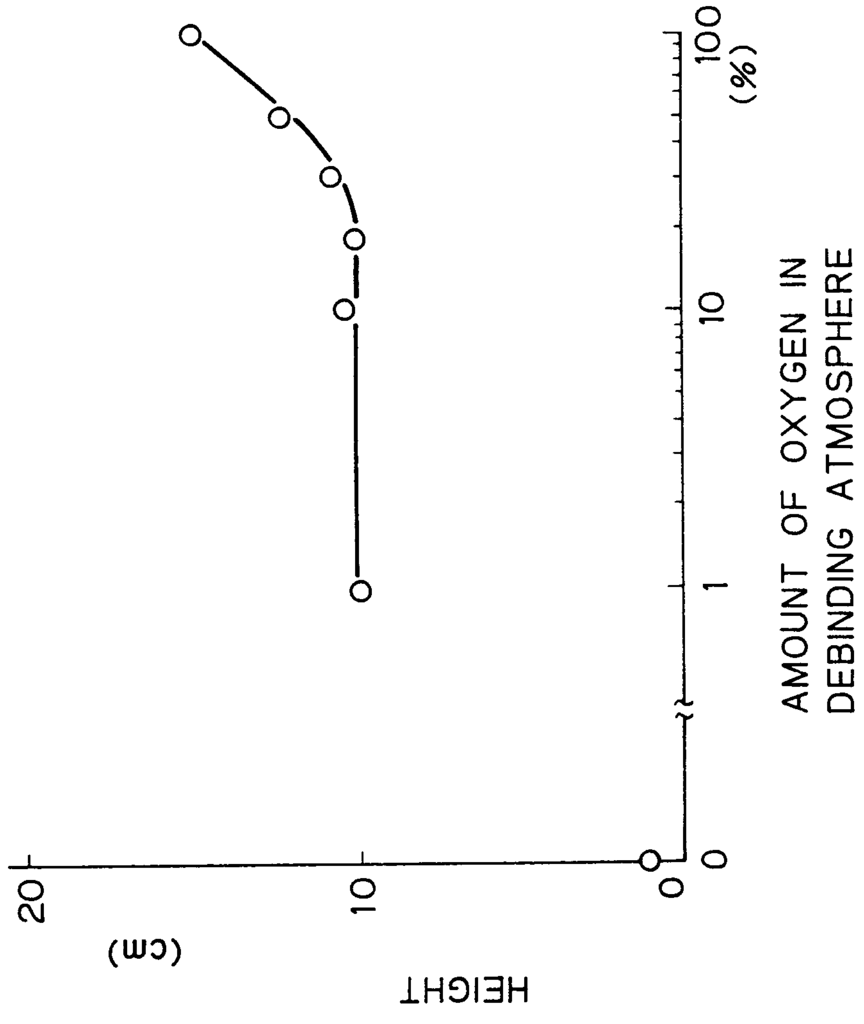

SHORTEST DEBINDING TIME
(hr)
50
40
30
20
10
0
0
1
10
100
(%)
NOT PRESSURIZED
PRESSURIZED
AMOUNT OF OXYGEN IN
DEBINDING ATMOSPHERE

Fig. 6


HEIGHT
(cm)
20
10
0
0
1
10
100
(%)
AMOUNT OF OXYGEN IN
DEBINDING ATMOSPHERE