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HOT ISOSTATIC PRESSING OF CERAMICS

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16. Abstract

A mixt. contg. glass 70-95 and BN or B_4C powder (0.1-10 μ) 5-30 vol. % is used as a secondary pressure medium in hot isostatic pressing of ceramics. Thus, Pyrex beads were mixed with 15% vol. BN powder (av. diam. 2 μ), fused at 1400° for 2 h, cooled, crushed, and put into a graphite crucible. A Si_3N_4 sintered body was embedded in the powder, heated in vacuum at 1200° for 2 h, treated in a hot isostatic press furnace at 1700° and 1000 atm for 1 h, and cooled to give a Si_3N_4 ceramic. It was easily sepd. from the crucible.

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(54) Hot isostatic pressing method of ceramics.

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Detailed statement.

1. Name of the invention: Hot isostatic press (HIP) of ceramics.

2. Range of the patent application:

1) As a secondary pressure medium in HIP process of ceramics, a mixture of silicate glass and 5-30 vol.% of a powdered material (which does not react with the silicate glass and remains in a solid phase under HIP temperature) is used.

2) Silicate glass is selected from silica glass, Vycor glass or Pyrex glass.

3) Added material is BN powder.

4) Added material is B_4C powder.

5) Diameter of the added powder is 0.1-10μm.

6) Processed ceramics is pre-molded powder of Si_3N_4, SiC, Al_2O_3, TiC-Al_2O_3.

3. Detailed explanation:

This invention is on a HIP method of ceramics using glass as a secondary pressure medium.

In order to achieve greater heat efficiency, fuel economy, pollution reduction and weight reduction, many developments have been under way in the recent years on machines operated at high temperatures such as high temperature gas turbine, diesel engine and MHD generator. Heat resisting metals do not have satisfactory mechanical strength and natural resources of these metals are limited. Therefore, utilization of ceramics which are abundant on the earth has been expanding. Especially, Si_3N_4 and SiC are the most recognized materials because of the strength, chemical stability and heat shock resistance at high temperatures.

In order to manufacture Si_3N_4 products, Si_3N_4 is sintered by HIP process. A typical example is described in Tokkyo Koho 51-702081, where Si_3N_4 powder or its pre-molded material is enclosed in a glass capsule and processed by HIP.

However, in the HIP process using glass as a capsule or a secondary pressure medium, the glass tends to penetrate into sintered materials during the process, forming a reaction layer between Si_3N_4 and giass, and causing cracks due to difference of thermal expansion coefficients of these materials.

In order to prevent this problem, mold separation material such as BN powder is usually coated on the surface of pre-molded ceramics before enclosing into a glass capsule or glass bath. But it is difficult to obtain thick and uniform coating of BN powder, especially for complex shaped ceramics, causing distortions or density variations in the final sinters. Other methods have been also tried such as spraying the powder or coating the powder mixed in a solvent. The coating often comes off during the later process, or ceramics and glass react with each other at thinly coated areas, thus making it difficult to remove the glass capsule. Since the glass penetration depth may reach up to 0.5-1mm depending on the kinds of glass, temperature or pressure of HIP process, the coating thickness requires at least 1mm. It is difficult to achieve such thickness using the above mentioned methods.

We previously proposed a method in which presintered ceramics are dipped in BN powder, made into a simple block by pressing, covered by glass and processed by HIP. Yet the same problems have been found for coating the BN powder such as difficulties with removing glass layer, because the glass and BN powder form separate layers.

The present invention was made to improve HIP process of ceramic sinter and to further develop our previous proposal mentioned above. A mixture of BN powder and glass is used as a pressure medium. Capsule separation has become easier because of the difference in thermal expansion rates of these two materials. Material such as BN powder which does not react with glass and remains in solid phase under HIP temperature is mixed with a glass capsule material or filled in a glass bath in an amount of 5-30 wt%. HIP is applied on ceramics surrounded by this mixture.

Detailed explanations will be described as follows:

Pre-molded or pre-sintered ceramics made from Si_3N_4 or SiC powder are enclosed in a glass capsule or glass bath, and HIP is applied using this glass as a secondary pressure medium. The glass serves as a secondary pressure medium of HIP process and, therefore, it must surround the ceramic body.

Si_3N_4 powder pre-sintering is made by a conventional method such as hot press or N_2 gas sintering. When sintering aids such as Y_2O_3, Al_2O_3 or MgO is added, the amount should be less than 10 wt% relative to the Si_3N_4 powder. Relative bulk density does not have to be so high and porous material with less than 92% density is acceptable. Al_2O_3, TiC-Al_2O_3 can be also used as ceramic raw material.

Silicate glass with high melting point temperature such as silica glass, Vycor glass, Pyrex glass or their mixture can be used.

The glass can be made into a glass capsule and a work piece is enclosed as shown in Fig. 1. The glass can be also filled in a graphite crucible and serves as a secondary pressure medium for the work piece as shown in Fig. 2.

The uniqueness of the present invention is in the point that the glass is mixed with powder such as BN or B_4C which does not react with the glass and remains in solid phase at HIP temperature. SiC powder can be also used as a mixing material. Such powders do not mix with glass well and have different thermal expansion rate than glass. Therefore, after HIP process, cracks starts in the glass easily, making it easier to remove the capsule.

Mixing rate of the powder is 5-30 vol.%, desirably 5-20 vol.%. For less than 5%, glass adhesion with ceramics is unavoidable, and for more than 30%, the mixture no longer works effectively as a secondary pressure medium and satisfactory densification will not be achieved.

Since BN powder does not mix well with glass, the powder usually accumulates around the ceramics during HIP process, making it easier to remove the capsule.

Coating BN powder on ceramics by spraying also works well. Acceptable powder grain radius is 0.1-10μm, or practically 1-5μm.

It is usually practical to mix powder and glass when making the glass capsule or glass bath. Therefore, powder is usually added to glass beads. This powder-glass mixture is fused into a uniform glass ingot at high temperature, for example, in case of Pyrex glass at 1400°C for 2 hours, then crushed by a conventional method such as ball mill and filled in a glass capsule or a graphite crucible.

In case of a glass bath, the glass is heated up above melting point by a vacuum furnace to effectively surround the ceramics.

Once the mixture of BN powder and glass surrounds the ceramics, HIP is applied. In the HIP process, pressure and temperature are increased according to operating conditions in an inert gas atmosphere such as Ar or N_2, and uniform pressurization is made.

Although HIP temperature varies with materials, ceramics usually require higher temperature. Therefore, glass must be selected considering this temperature. In case of Si_3N_4, HIP temperature is usually more than 1400°C, desirably 1600-1900°C. Depending on the material, temperature can be increased up to 2000°C. But, of course, it must be lower than the decomposition temperature of ceramics. Since the decomposition temperature increases with the HIP pressure, temperature should be selected at least 100°C lower than the decomposition temperature of the operating HIP pressure.

HIP pressure should be higher than 500 atm. If pressure is lower than 500 atm, longer HIP process time is necessary. Furthermore, since amount of reacting Si_3N_4 increases with the process time, weight reduction of ceramics is caused and densification itself is affected. Therefore, HIP pressure must be higher than 500 atm, desirably higher than 700 atm.

Although higher HIP pressure reduces the reaction rate of Si_2N_4 and densification becomes easier, longer pressurization time is necessary and, therefore, a larger compressor and HIP equipment are required. Practically, HIP should be applied under 2500 atm. HIP process time is 20 min - 5 hours.

Fig. 3 and Fig. 4 show BN powder cohesion situation during HIP process. Although the glass melts at HIP temperature, the powder remains in solid phase and does not react with the glass. As a result, a BN powder layer (5) is formed separated from glass-BN powder mixture (1) and glass (6), and the ceramics can be separated easily.

After HIP process, the glass capsule or graphite crucible is taken out of the furnace, cooled and the glass is removed. Because of the difference of thermal expansion rates of BN powder and glass, small cracks are formed during cooling and the mold can be easily separated.

According to the present invention, mold removing process can be simplified without sacrificing the quality of the final products.

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More detailed explanations will be described using some examples as follows:

Example 1:

Pyrex beads with grain diameter 1mm (melting point 320°C) mixed with 15 vol % of BN powder with grain diameter 2μm were fused at 1400°C for 2 hours to make a uniform BN mixed glass ingot and crushed into powdered glass by a ball mill. Then, this BN mixed glass powder was filled into a graphite crucible and the Si_3N_4 pre-sintered work piece was embedded in the powder. The crucible was heated in a vacuum furnace at 1200°C for 2 hours to get a SI_3N_4 body surrounded by a continuous glass layer. HIP process was applied at 1700°C, 1000 atm. for one hour. After the process, the crucible was removed from the furnace and cooled. During the cooling, many small cracks were recognized in the glass capsule and the ceramic was easily separated. The surface of Si_3N_4 sinter was good.

Example 2-8:

Various glasses and powders have been tried and the results are shown in Table.

1)	2)	3)	4)	5)	6)	7)
実施例	ガラスの種類	粉末添加量	被処理物	HIP条件	離型性	備考
2	パイレックス 9)	BN 15 容量%	SIC	2000℃, 1hr 1000atm	●	
3	〃	BN 30 容量%	Si_3N_4	1700℃, 1hr 1000atm	●	
4	シリカ 10)	BN 7 容量%	〃	〃	○	
5	パイコール 11)	〃	〃	〃	○	
6	パイレックス 12)	B_4C 10 容量%	TiC− Al_2O_3	1400℃, 1hr 1000atm	○	
7	〃	B_4C 15 容量%	Al_2O_3	〃	○	
8	〃	Mo 5 容量%	〃	〃	○	
比較1 13)	〃	BN 3 容量%	Si_3N_4	1700℃, 1hr 1000atm	△	ガラス 付着 14)
比較2 15)	〃	BN 40 容量%	〃	〃	−	成形体 酸化 せず 16)

1) Example; 2) Glass; 3) Powder amount; 4) Ceramics; 5) HIP condition;

6) Mold separation; 7) Comment; 8) Pyrex; 9) Vol.%; 10) Silica; 11) Vycor; 12) Pyrex; 13) Comparison 1; 14) Glass adhesion; 15) Comparison 2; 16) No densification.

These examples show that the powder-glass mixture achieved satisfactory mold separation as well as HIP densification.

Fig. 1 Capsule method used to enclose work piece.

Fig. 2 Glass bath method used to embed work piece.

Fig. 3 and 4. Powder cohesion situation. Fig. 4 Enlarged view of area A.

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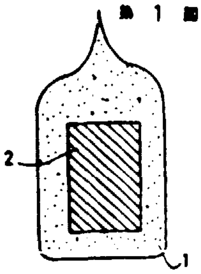

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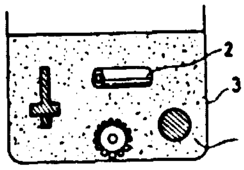

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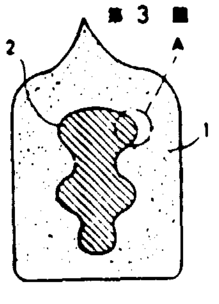

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