

**(12) STANDARD PATENT
(19) AUSTRALIAN PATENT OFFICE**

(11) Application No. AU 2014261405 B2

**(54) Title
Process for producing a blank, and a blank**

(51) International Patent Classification(s)
A61K 6/027 (2006.01) **C03C 4/00** (2006.01)
A61C 13/00 (2006.01) **C03C 10/00** (2006.01)
C03B 32/02 (2006.01)

(21) Application No: 2014261405 **(22) Date of Filing: 2014.04.30**

(87) WIPO No: WO14/177659

(30) Priority Data

(31) Number **(32) Date** **(33) Country**
10 2013 104 561.8 **2013.05.03** **DE**

(43) Publication Date: **2014.11.06**
(44) Accepted Journal Date: **2018.11.15**

(71) Applicant(s)
Dentsply International Inc.

(72) Inventor(s)
Fecher, Stefan;Horhold, Heiner;Schusser, Udo;Vollmann, Markus;Kutzner, Martin

(74) Agent / Attorney
Patent Attorney Services, 26 Ellingworth Parade, BOX HILL, VIC, 3128, AU

(56) Related Art
EP 2377831 A1

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum

Internationales Büro

(43) Internationales Veröffentlichungsdatum

6. November 2014 (06.11.2014)

(10) Internationale Veröffentlichungsnummer
WO 2014/177659 A1

(51) Internationale Patentklassifikation:

A61K 6/027 (2006.01) *C03B 32/02* (2006.01)
C03C 4/00 (2006.01) *A61C 13/00* (2006.01)
C03C 10/00 (2006.01)

(21) Internationales Aktenzeichen: PCT/EP2014/058920

(22) Internationales Anmeldedatum:

30. April 2014 (30.04.2014)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
10 2013 104 561.8 3. Mai 2013 (03.05.2013) DE

(71) Anmelder: DEGUDENT GMBH [DE/DE]; Rodenbacher Chaussee 4, 63457 Hanau (DE).

(72) Erfinder: FECHER, Stefan; Sattelhecke 8, 63867 Johannesberg (DE). HÖRHOLD, Heiner; Am Molkenborn 64, 63654 Büdingen (DE). SCHUSSER, Udo; Rhönstr. 12, 63755 Alzenau (DE). VOLLMANN, Markus; Untere Röde 39, 63571 Gelnhausen (DE). KUTZNER, Martin; Wilhelmstr. 1, 63543 Neuberg (DE).

(74) Anwalt: STOFFREGEN, Hans-Herbert; Friedrich-Ebert-Anlage 11b, 63450 Hanau (DE).

(81) Bestimmungsstaaten (soweit nicht anders angegeben, für jede verfügbare nationale Schutzrechtsart): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Bestimmungsstaaten (soweit nicht anders angegeben, für jede verfügbare regionale Schutzrechtsart): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches (AM, AZ, BY, KG, KZ, RU, TJ, TM), europäisches (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Veröffentlicht:

- mit internationalem Recherchenbericht (Artikel 21 Absatz 3)
- vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eingehen (Regel 48 Absatz 2 Buchstabe h)

(54) Title: PROCESS FOR PRODUCING A BLANK, AND A BLANK

(54) Bezeichnung : VERFAHREN ZUR HERSTELLUNG EINES ROHLINGS SOWIE ROHLING

(57) Abstract: The invention relates to a blank for producing a dental moulded part such as an inlay, onlay, crown or bridge, and to a method for producing the blank. To be able to machine a dental moulded part, in particular one having thin wall thicknesses, from the blank without difficulty, the blank is designed to consist of a glass ceramic having a density of between 30 and 60% of theoretical density, and of glass-ceramic powder particles with a particle size distribution $d_{90} \leq 80 \mu\text{m}$, lithium silicate crystals being present in an amount of 10 to 90% by volume.

(57) Zusammenfassung: Die Erfindung bezieht sich auf einen Rohling zur Herstellung eines dentalen Formteils wie Inlay, Onlay, Krone oder Brücke sowie auf ein Verfahren zur Herstellung des Rohlings. Damit aus dem Rohling problemlos ein dentales Formteil herausgearbeitet werden kann, insbesondere mit dünnen Wandstärken, ist vorgesehen, dass der Rohling aus einer Glaskeramik mit einer Dichte zwischen 30 % und 60 % der theoretischen Dichte und aus Glaskeramikpulverpartikel einer Korngrößenverteilung $d_{90} \leq 80 \mu\text{m}$ besteht, wobei der Anteil an Lithiumsilikatkristallen 10 Vol.-% bis 90 Vol.-% beträgt.

Description**Process for producing a blank, and a blank**

The invention relates to a blank for producing a dental molded part, such as an inlay, an onlay, a crown, or a bridge, whereby the blank contains a lithium silicate crystal fraction of more than 10% by volume.

The invention further relates to a process for producing a dental molded part, such as an inlay, an onlay, a crown, or a bridge. The invention also relates to a monolithic dental molded part.

WO 2012/080513 A1 discloses a process for producing dental molded parts from porous glass, which does not contain a crystalline contingent. The density of the blank is in the range between 50 % and 95 % of the theoretical density of a fully sintered blank. The corresponding blanks are used to produce monolithic dental molded parts such as crowns, partial crowns, bridges, inlays or onlays by means of milling, whereby dry machining is employed.

WO 2011076422 A1 and WO 2012/059143 A1 describe lithium silicate glass ceramics that are used in the manufacture of dental molded parts. The corresponding glass ceramics reportedly have good mechanical and optical properties.

Known from WO 2013/053865 A2 is a blank composed of lithium silicate glass ceramics, from which are produced dental molded parts. The ceramic mandatorily contains a trivalent metal oxide selected from the group Y_2O_3 , La_2O_3 , Yb_2O_3 , Bi_2O_3 and mixtures thereof. Furthermore, the glass ceramic is essentially free of K_2O and Na_2O .

In the manufacture of dental prostheses based on lithium silicate glass ceramics it is also known in the art to produce cylindrical pellets and to subsequently press these in a muffle (EP 1 484 031 B1).

The objective of the present invention is to produce a blank, from which a dental molded part can be worked out without any problems. In this, it should be possible to realize thin wall thicknesses. Machining should be possible with only minimum tool wear. Furthermore, the dental molded parts produced from the blank should contain favourable mechanical characteristics.

At least one of the problem aspects mentioned above is solved with respect to a blank for producing a dental molded part, such as inlay, onlay, crown, or bridge, by stipulating that the blank consists of a glass ceramic with a density of between 30 % and 60 % of the theoretical density of the fully sintered blank and of glass-ceramic powder particles with a grain size distribution $d_{90} \leq 80 \mu\text{m}$, in particular a grain size distribution d_{50} of between 10 μm and 60 μm , whereby the proportion of lithium silicate crystals is between 10% by volume and 90% by volume.

A blank of this type is machined by milling, whereby it has surprisingly been noted that tool wear is low so that expensive tools, e.g. diamond-tipped ones, are not required. Once dental moulded parts worked out of such a blank have been sintered to completion, one also surprisingly notices a high rigidity, whereby in comparison to a dental prosthesis worked out of a blank that has been sintered to completion, one obtains an increase in rigidity of between 10 % and 50 %. In particular this provides the option of achieving structures with thin walls that are not destroyed during sintering to completion, since the blanks possess sufficient stability on account of the crystalline phase fraction.

This also offers the advantage that no aids such as support structures or a filling of cavities are required when sintering to completion.

In particular it is intended that the crystalline content of the blank is 30 % by volume to 60 % by volume. The blank further is characterized by possessing an open porosity of between 50% by volume and 60 % by volume, more preferably between 20 % by volume and 50 % by volume.

The chosen parameter settings ensure that during the machining, which in particular is performed dry, it is possible to achieve an adequate surface smoothness, so that finishing work after the sintering is not necessarily required.

The glass-ceramic powder preferably should possess a grain size distribution $d_{50} \leq 25 \mu\text{m}$.

The grain size distribution as well as the pore size of 0.1 μm to 5 μm result in a dense packing of the powder particles in the blank, so that fine edge structures can easily be formed. No grains torn from the worked surface were visually detected.

In order to achieve the small pore size in the range between 0.1 μm to 5 μm , it is in particular intended that the fraction of fine glass particles is correspondingly high.

In particular it is intended that the blank possesses a disk-, cube-, or rod-like geometry, from which to the desired extent and in dependence on the size of the blanks one can produce one or several dental molded parts. For the purpose of clamping the blank into a milling machine it is intended that means originate from the circumferential surface, extending diametrically with respect to the centre of gravity of the blank, which may be used to fix the blank in position. One option is to lathe recesses into the blank, into which engage fixing means originating from the processing machine. Alternatively, it is possible to attach, e.g. glue, adapters to the circumferential surface, which are intended to act as holders in a processing machine. Another option is to create protrusions on the blank, which then can serve as mounts.

In particular, the invention is characterized by a blank of glass-ceramic powder particles with a composition (in % by weight) having:

SiO ₂	46.0-72.0
Li ₂ O	10.0-25.0
ZrO ₂	6.5-14.0
P ₂ O ₅	1.0-10.0
Al ₂ O ₃	0.1-8.0
K ₂ O	0.1-5.0
CeO ₂	0.1-4.0
B ₂ O ₃	0.0-4.0
Na ₂ O	0.0-4.0
Tb ₄ O ₇	0.0-2.5

as well as 0.0 to 4.0 of at least one additive.

Preferably the composition of the glass-ceramic powder particles of the blank is (in % by weight):

SiO ₂	49.0-69.0
Li ₂ O	11.5-24.0
ZrO ₂	7.0-13.5
P ₂ O ₅	1.5-9.0
Al ₂ O ₃	0.2-7.5
K ₂ O	0.2-4.5
CeO ₂	0.2-3.5
B ₂ O ₃	0.0-3.5
Na ₂ O	0.0-3.5
Tb ₄ O ₇	0.0-2.0

as well as 0.0 to 4.0 of at least one additive.

To be emphasized is a composition of the glass-ceramic powder particles for the blank of (in % by weight):

SiO ₂	52.0-66.0
Li ₂ O	12.0-22.5
ZrO ₂	7.5-13.0
P ₂ O ₅	2.0-8.5
Al ₂ O ₃	0.3-7.0
K ₂ O	0.3-4.0
CeO ₂	0.3-3.5
B ₂ O ₃	0.0-3.0
Na ₂ O	0.0-3.0
Tb ₄ O ₇	0.0-2.0

as well as 0.0 to 4.0 of at least one additive.

Also to be emphasized is a composition of the glass-ceramic powder particles of the blank (in % by weight):

SiO ₂	55.0-63.0
Li ₂ O	12.5-21.5
ZrO ₂	8.0-12.0
P ₂ O ₅	2.5-8.0
Al ₂ O ₃	0.4-6.5
K ₂ O	0.4-4.0
CeO ₂	0.5-3.0
B ₂ O ₃	0.0-3.0
Na ₂ O	0.0-3.0
Tb ₄ O ₇	0.0-2.0

as well as 0.0 to 4.0 of at least one additive.

Of particular note is a composition of the glass-ceramic powder particles for the blank of (in % by weight):

SiO ₂	58.0-60.0
Li ₂ O	13.5-20.5
ZrO ₂	8.5-11.5
P ₂ O ₅	3.0-7.5
Al ₂ O ₃	0.5-6.0
K ₂ O	0.5-3.5
CeO ₂	0.5-2.5
B ₂ O ₃	0.0-3.0
Na ₂ O	0.0-3.0
Tb ₄ O ₇	0.0-1.5

as well as 0.0 to 4.0 of at least one additive.

The at least one additive is at least one additive selected out of the group containing colour pigment, fluorescent agent. In particular it is intended that the additive is at least one oxide selected from the group of BaO, CaO, MgO, MnO, Er₂O₃, Gd₂O₃, Pr₆O₁₁, Sm₂O₃, TiO₂, V₂O₅, Y₂O₃ or contains such an oxide.

It should be noted that the total weight percentages of the components of the powder mixture in each composition add up to 100 % by weight.

In particular, the invention also distinguishes itself by a process for producing a dental molded part, such as an inlay, onlay, crown, or bridge, comprising the procedural steps:

- Producing a molten mass with a composition (in % by weight):

SiO ₂	46.0-72.0
Li ₂ O	10.0-25.0
ZrO ₂	6.5 -14.0
P ₂ O ₅	1.0-10.0
Al ₂ O ₃	0.1-8.0
K ₂ O	0.1-5.0
CeO ₂	0.1-4.0
B ₂ O ₃	0.0-4.0
Na ₂ O	0.0-4.0
Tb ₄ O ₇	0.0 - 2.5

as well as 0.0 to 4.0 of at least one additive.

- Producing a glass frit by atomizing this molten mass and quenching in a medium,
- If applicable, producing glass-powder particles from the glass frit, with a grain size distribution $d_{90} \leq 80 \mu\text{m}$,
- Crystallization of lithium silicate crystals with a volume fraction of between 10 % and 90 % by a first thermal treatment from either the glass frit or the glass powder particles in a first temperature range at a temperature T_1 with $500 ^\circ\text{C} \leq T_1 \leq 750 ^\circ\text{C}$ for a duration t_1 with $5 \text{ min} \leq t_1 \leq 120 \text{ min}$,
- Whereby at a time when the glass frit has been subjected to a thermal treatment, one produces glass-ceramic particles with a grain size distribution $d_{90} \leq 80 \mu\text{m}$ from the heat-treated glass frit,
- Pressing the glass-ceramic powder particles to form a blank,
- Machining the blank by milling to produce a pre-form part that corresponds to the dental molded part under consideration of the shrinkage characteristics of the blank, and
- Sintering the preformed part to completion at a temperature T_2 with $800 ^\circ\text{C} \leq T_2 \leq 1050 ^\circ\text{C}$ for a time period t_2 with $5 \text{ min} \leq t_2 \leq 60 \text{ min}$.

The invention offers the choice between either subjecting the glass frit, without this having been ground to obtain glass-powder particles, to a thermal treatment for the formation of lithium silicate crystals, or at first grinding the frit, i.e. producing glass-powder particles, and carrying out the thermal treatment subsequently so that one obtains glass-ceramic particles. This means that the feature "Pressing the glass-ceramic powder particles to form a blank" consequently also comprises the glass-ceramic powder particles produced by the process alternatives.

In this, it is possible for the first thermal treatment to be implemented in two stages within the first temperature region.

In particular, the molten mass has a composition (in % by weight):

SiO ₂	49.0-69.0
Li ₂ O	11.5-24.0
ZrO ₂	7.0-13.5
P ₂ O ₅	1.5-9.0
Al ₂ O ₃	0.2-7.5
K ₂ O	0.2-4.5
CeO ₂	0.2-3.5
B ₂ O ₃	0.0-3.5
Na ₂ O	0.0-3.5
Tb ₄ O ₇	0.0-2.0

as well as 0.0 to 4.0 of at least one additive.

The molten mass preferably has the following composition (in % by weight):

SiO ₂	52.0-66.0
Li ₂ O	12.0-22.5
ZrO ₂	7.5-13.0
P ₂ O ₅	2.0-8.5
Al ₂ O ₃	0.3-7.0
K ₂ O	0.3-4.0
CeO ₂	0.3-3.5
B ₂ O ₃	0.0-3.0
Na ₂ O	0.0-3.0
Tb ₄ O ₇	0.0-2.0

as well as 0.0 to 4.0 of at least one additive.

To be particularly emphasized is a molten mass with a composition (in % by weight):

SiO ₂	55.0-63.0
Li ₂ O	12.5-21.5
ZrO ₂	8.0-12.0
P ₂ O ₅	2.5-8.0
Al ₂ O ₃	0.4-6.5
K ₂ O	0.4-4.0
CeO ₂	0.5-3.0
B ₂ O ₃	0.0-3.0
Na ₂ O	0.0-3.0
Tb ₄ O ₇	0.0-2.0

as well as 0.0 to 4.0 of at least one additive.

The molten mass preferably has a composition (in % by weight):

SiO ₂	58.0-60.0
Li ₂ O	13.5-20.5
ZrO ₂	8.5-11.5
P ₂ O ₅	3.0-7.5
Al ₂ O ₃	0.5-6.0
K ₂ O	0.5-3.5
CeO ₂	0.5-2.5
B ₂ O ₃	0.0-3.0
Na ₂ O	0.0-3.0
Tb ₄ O ₇	0.0-1.5

as well as 0.0 to 4.0 of at least one additive.

The at least one additive is at least one additive selected from the group of colour pigment, fluorescent agent. In particular it is intended that the additive is at least one oxide of the group BaO, CaO, MgO, MnO, Er₂O₃, Gd₂O₃, Pr₆O₁₁, Sm₂O₃, TiO₂, V₂O₅, Y₂O₃, or contains such an oxide.

According to a further recommendation it is intended that the blank is tempered - after the first thermal treatment and prior to the machining - at a temperature T₃ with 750 °C ≤ T₃ ≤ 900 °C for a time period t₃ with 5 min ≤ t₃ ≤ 30 min.

The corresponding thermal treatment steps serve to ensure that the glass powder crystallizes to lithium silicate crystals on the required scale, and at the same time results in a small pore size and consequently dense packing of the grains, allowing a problem-free machining, which is also necessary to achieve filigree regions.

In this, the crystalline phase of lithium silicate includes lithium metasilicate and in particular lithium disilicate.

In particular, it is intended that for producing a blank with a disk-like geometry, the glass-ceramic powder particles are at first pressed axially and subsequently, after introduction into an encompassing element, such as a pouch coated by polyethylene on the inside, are subjected to isostatic re-pressing, whereby the re-pressing in particular takes place at a pressure p_n of 250 MPa $\leq p_n \leq 350$ MPa for a time period t_4 with $5 \text{ sec} \leq t_4 \leq 30 \text{ sec}$, in particular $5 \text{ sec} \leq t_4 \leq 15 \text{ sec}$.

For producing a blank with cuboid geometry, the invention intends that the glass-ceramic powder particles are successively and in particular continuously axially pressed with rising pressure for a time period t_5 , whereby the maximum pressure p_5 is $50 \text{ MPa} \leq p_5 \leq 400 \text{ MPa}$, in particular $100 \text{ MPa} \leq p_5 \leq 200 \text{ MPa}$. The duration of the pressure increase is $10 \text{ sec} \leq t_5 \leq 20 \text{ sec}$.

To produce a blank with rod-shaped, in particular cylindrical geometry, it is intended that the glass-ceramic powder is introduced into a tubular press form, in particular of polyurethane, and subsequently is subjected to quasi-isostatic pressing. The following pressing times and parameters should be taken into consideration for this. Preferably the pressure initially rises slowly, to distribute the filled glass-ceramic powder uniformly throughout the mold. After this, the pressure may be raised to its maximum value rapidly. Once the maximum pressure has been reached, it is maintained constant for the duration of the holding time. This is followed by a phase of rapid pressure release, during which the pressure is reduced to 10% of the maximum pressure value. Complete elimination of the

excess pressure takes place slowly to prevent crack formation in the glass-ceramic blank.

With regard to the machining, which may be performed dry, it is in particular intended that an initial coarse machining is followed by precision machining.

Preferred machining parameters for the coarse machining are:

Cutter diameter:	2 to 5 mm, in particular 2 to 3 mm
Feed:	500 to 4000 mm/min, in particular 2000 to 3000 mm/min
Lateral feed ae:	0.2 to 3 mm, in particular 1 mm to 2 mm
Depth feed ap:	0.1 to 2 mm, in particular 0.5 mm to 1 mm
Cutter speed:	10,000 to 50,000 1/min, in particular 10,000 to 20,000 1/min.

The preferred cutters are carbide cutters.

With respect to the precision machining, the following machining parameters should be observed:

Cutter diameter:	0.3 to 1.5 mm, in particular 0.5 to 1.0 mm
Feed:	300 to 2000 mm/min, in particular 800 to 1500 mm/min
Lateral feed ae:	0.2 to 0.6 mm, in particular 0.1 mm to 0.2 mm
Depth feed ap:	0.05 to 0.3 mm, in particular 0.1 mm to 0.15 mm
Cutter speed:	20,000 to 60,000 1/min, in particular 25,000 to 35,000 1/min.

Here too, carbide cutters are preferable.

Particularly good machining results are achieved when the employed cutter is a radius cutter of carbide, whereby the radius cutter should be characterized by the following cutting edge angles:

Cutting angle: 0° to 13°, in particular -9° to -11°

Clearance angle: 0° to 15° , in particular 11° to 13°

Wedge angle: Results from: 90° minus clearance angle minus cutting angle.

While in principle it is not necessary to add a binding agent prior to the pressing of the glass-ceramic particles, it is still within the scope of the invention if the corresponding binding agent, such as for example cellulose ether, is added with a weight fraction of up to 5 %.

However it has been found to be particularly advantageous, if the blank, i.e. its glass-ceramic particles, after pressing are immersed in silicic acid or an alkali silicate solution (soluble glass) and after drying are subjected to the mechanical work. This causes SiO_2 bridges to form between the glass particles, which increases rigidity and consequently simplifies the subsequent mechanical processing, which includes CAD/CAM processing. When the machined molded parts are sintered to completion, the free SiO_2 diffuses into the glass ceramic, which allows one to achieve an increase in rigidity.

The invention further distinguishes itself by a monolithic dental molded part, which is produced using the blank according to the invention. In particular, the monolithic dental molded part may constitute or comprise a crown with a crown margin of a thickness D_R with $0.05 \text{ mm} \leq D_R \leq 0.4 \text{ mm}$, in particular $0.1 \text{ mm} \leq D_R \leq 0.2 \text{ mm}$. In this, the thickness of the crown margin extends starting at the front margin and at a distance of 2 to 4 mm to the latter.

The monolithic molded part is further characterized by a thermal expansion coefficient, measured in accordance with ISO6872, that is lower than $12.5 \times 10^{-6} \text{ }^\circ\text{K}$, and preferably is between $9.5 \times 10^{-6} \text{ }^\circ\text{K}$ and $11.5 \times 10^{-6} \text{ }^\circ\text{K}$.

For the pressing of the glass-ceramic particles, one in particular chooses a pressure between 50 MPa and 400 MPa, in particular between 100 MPa and 200 MPa. The temperature during the pre-sintering of the compacted glass powder, i.e. the blank in form of

of the pressed glass body, should be in the range between 500 °C and 950 °C, preferably between 600 °C and 700 °C.

The external geometry of the pressed glass-ceramic body may be disk- or plate-like or rod-shaped such as cylindrical, whereby the cross-sectional geometry can be chosen freely. The volume content of the blanks may be between 1 cm³ and 160 cm³.

After the mechanical working of the blanks consisting of the crystalline porous glass ceramic, whereby this preferably is performed by milling without cooling, the carved-out dental works are subsequently sintered to completion in a suitable sintering furnace, taking into account a suitable temperature – time cycle. The sintering to completion may be performed in a temperature range between 700 °C and 1100 °C, preferably in the range between 850 °C and 950 °C. The duration of the entire cycle is less than 2 h, preferably less than 1 h. Because of the crystalline fraction it is not necessary to provide support for the pre-form part. Rather it is possible to place the pre-formed part onto an Al₂O₃ firing pad in the sintering furnace.

Parameters of the preferred temperature – time cycle are: Standby temperature 500 °C, rate of increase 50°C/min to 90°C/min to 850 to 900 °C, hold time 1 to 5 min, then slow cooling. For the cooling one preferably chooses the slowest cooling level.

Further details, advantages, and features of the invention are not only found in the claims and the characteristic features described therein – on their own and/or in combination – but also in the following exemplary embodiments.

Figure 1 shows a graph of pressure versus time during the pressing of a blank.

In accordance with the invention, a blank consisting of pressed glass-ceramic powder is used to produce a dental molded part. To make the glass-ceramic powder, one at first melts a powder and uses the molten mass to produce a glass frit, which can possess the following preferred composition:

SiO ₂	49.0-69.0
Li ₂ O	11.5-24.0
ZrO ₂	7.0-13.5
P ₂ O ₅	1.5-9.0
Al ₂ O ₃	0.2-7.5
K ₂ O	0.2-4.5
CeO ₂	0.2-3.5
B ₂ O ₃	0.0-3.5
Na ₂ O	0.0-3.5
Tb ₄ O ₇	0.0-2.0

as well as 0.0 to 4.0 of at least one additive.

In particular it is intended that the molten glass has a composition of (in % by weight):

SiO ₂	49.0-69.0
Li ₂ O	11.5-24.0
ZrO ₂	7.0-13.5
P ₂ O ₅	1.5-9.0
Al ₂ O ₃	0.2-7.5
K ₂ O	0.2-4.5
CeO ₂	0.2-3.5
B ₂ O ₃	0.0-3.5
Na ₂ O	0.0-3.5
Tb ₄ O ₇	0.0-2.0

as well as 0.0 to 4.0 of at least one additive.

Preferably the molten glass has a composition of (in % by weight):

SiO ₂	52.0-66.0
Li ₂ O	12.0-22.5
ZrO ₂	7.5-13.0
P ₂ O ₅	2.0-8.5
Al ₂ O ₃	0.3-7.0
K ₂ O	0.3-4.0

CeO ₂	0.3- 3.5
B ₂ O ₃	0.0-3.0
Na ₂ O	0.0-3.0
Tb ₄ O ₇	0.0-2.0

as well as 0.0 to 4.0 of at least one additive.

Especially emphasized is a composition of the molten glass with a composition (in % by weight) of:

SiO ₂	55.0-63.0
Li ₂ O	12.5-21.5
ZrO ₂	8.0-12.0
P ₂ O ₅	2.5-8.0
Al ₂ O ₃	0.4-6.5
K ₂ O	0.4-4.0
CeO ₂	0.5-3.0
B ₂ O ₃	0.0-3.0
Na ₂ O	0.0 – 3.0
Tb ₄ O ₇	0.0 – 2.0

as well as 0.0 to 4.0 of at least one additive.

Preferably it is intended that the molten glass has a composition (in % by weight) of:

SiO ₂	58.0-60.0
Li ₂ O	13.5-20.5
ZrO ₂	8.5-11.5
P ₂ O ₅	3.0-7.5
Al ₂ O ₃	0.5-6.0
K ₂ O	0.5-3.5
CeO ₂	0.5-2.5
B ₂ O ₃	0.0-3.0
Na ₂ O	0.0-3.0
Tb ₄ O ₇	0.0-1.5

as well as 0.0 to 4.0 of at least one additive.

The at least one additive is at least one additive selected from the group composed of colour pigment, fluorescent agent. In particular it is intended that the additive is at least one oxide chosen from the group of BaO, CaO, MgO, MnO, Er₂O₃, Gd₂O₃, Pr₆O₁₁, Sm₂O₃, TiO₂, V₂O₅, Y₂O₃ or contains such an oxide.

The corresponding mixture of starting materials, e.g. in form of oxides and carbonates, subsequently is melted in a suitable crucible of refractory material or a noble metal alloy at a temperature between 1350 °C and 1600 °C for a time period between 1 h and 10 h, in particular for a time of 4 h to 7 h at a temperature of 1540 °C. Homogenization is achieved, e.g. by stirring, at the same time or subsequently. The liquid glass produced in this manner subsequently is fed to a nozzle, which preferably has been caused to oscillate, and which itself is set to a temperature in the region between 1250 °C and 1450°C, in particular to 1310 °C. The nozzle may possess a diameter between 1 mm and 2 mm. The oscillation frequency of the nozzle may be in the range between 40 Hz and 60 Hz, in particular in the region of 50 Hz. Subsequently the liquid glass is quenched in a suitable medium, such as water for liquids or high-temperature insulation wool. The glass frit produced and quenched in this manner is then dried. This is followed by grinding e.g. in a ball mill. A subsequent sifting stage can use a screen with a mesh width between 50 µm and 500 µm. If required, a further grinding can be performed, e.g. using a jet mill or an attrition mill.

From the glass- or glass-particle powder produced in this manner, one in particular selects those that correspond to a grain size distribution of $d_{90} \leq 80 \mu\text{m}$, in particular $10 \mu\text{m} \leq d_{50} \leq 60 \mu\text{m}$. d_{90} and d_{50} indicate that 90% or 50%, respectively, of the particles present possess a diameter that is smaller than the specified value or that is in that particular region.

In order to facilitate easy machining of the blank, without risking any instabilities during the final sintering of the molded part produced from blank, one subjects either the frit obtained after melting or the pre-ground or completely ground powder to a crystallization step. In this, one subjects the frit or the powder in a first thermal treatment step to a temperature T_1 between 500 °C and 750 °C for a duration t_1 between 5 min and 120 min. The first thermal treatment step may also be implemented as a two-stage process, i.e. first

thermal treatment step 640 °C, preferably 660 °C for 60 min and 750 °C for 40 min.

Preferably this is followed by a further thermal treatment in form of tempering, whereby the temperature T_3 to be selected should be between 750 °C and 900 °C. This tempering step is performed for a duration t_3 , in particular between 5 min and 30 min.

Subsequently the glass-ceramic particles are pressed, where in dependence on the geometry to be produced, one uses suitable pressing methods, in particular an axial or isostatic pressing or combinations of these. The compressing is carried out to such a degree that the density of the blank corresponds to 30 % to 60 % of the theoretical density of the blank material of approximately 2.64 g/cm³. In particular, the blank should possess a density corresponding to approximately 50% of the theoretical density.

During the pressing of the glass-ceramic powder, the latter preferably is subjected to a pressure between 50 MPa and 400 MPa, in particular between 100 MPa and 200 MPa.

Figure 1 shows as an example a graph of pressure versus time during the pressing of a blank. In a first phase P1 the pressure is increased from a starting value of 0 with a pressure build-up of for example 15 MPa/sec to a pressure of for example 30 MPa. In a second phase P2 the pressure is increased from 30 MPa using a pressure build-up of 100 MPa/sec to a pressure of approximately 200 MPa. In a third phase P3 the pressure is kept constant at a value of approximately 200 MPa for a hold time of approximately 10 sec. A fourth phase preferably contains a two-stage pressure reduction, whereby in a phase P4a the pressure is reduced from approximately 200 MPa to approximately 20 MPa with a pressure-reduction of 40 MPa/sec and in a phase P4b the pressure is reduced from 20 MPa to 0 MPa excess pressure with a pressure reduction rate of approximately 10 MPa/sec.

The pressing is followed by machining by means of milling, whereby it is possible to at first perform a coarse machining, to be followed by precision machining. The machining may be performed without cooling, which allows dry machining.

The following milling parameters should be taken into account for the coarse machining:

Cutter diameter:	1 to 5 mm, in particular 2 to 3 mm
Feed:	500 to 4000 mm/min, in particular 2000 to 3000 mm/min
Lateral feed ae:	0.2 to 3 mm, in particular 1 mm to 2 mm
Depth feed ap:	0.1 to 2 mm, in particular 0.5 mm to 1 mm
Cutter speed:	10,000 to 50,000 l/min, in particular 10,000 to 20,000 l/min.

In particular, the milling tool should be a carbide cutter.

Milling parameters to be considered for the precision machining:

Cutter diameter:	0.3 to 1.5 mm, in particular 0.5 to 1.0 mm
Feed:	300 to 2000 mm/min, in particular 800 to 1500 mm/min
Lateral feed ae:	0.2 to 0.6 mm, in particular 0.1 mm to 0.2 mm
Depth feed ap:	0.05 to 0.3 mm, in particular 0.1 mm to 0.15 mm
Cutter speed:	20,000 to 60,000 l/min, in particular 25,000 to 35,000 l/min.

In particular, the milling tool should be a carbide cutter.

Preferably one uses a radius cutter of carbide that may be coated with titanium nitride. In this, the following cutting edge angles represent preferred values:

Cutting angle:	0° to -13°, in particular -9° to -11°
Clearance angle:	0° to 15°, in particular 11° to 13°
Wedge angle:	results from: 90° minus clearance angle minus cutting angle

Because of the density of the blank and the crystalline fraction, it becomes possible to easily produce dental molded parts with filigree edges. For crowns in particular, it has been found that this results in stably extending edge thicknesses between 0.05 mm and 0.4 mm.

After the cutting work, the molded part created from the blank should be referred to as pre-form part, since it exhibits an oversize compared to the dental molded part after complete sintering in accordance with the shrinkage characteristic of the blank material. The oversize is calculated in dependence on the density of the blank, in order to provide a high-precision dental prostheses after the final sintering.

The sintering to final density takes place at a temperature T_2 between 800 °C and 1050°C for the duration of a holding time t_2 between 5 min and 60 min. Holding time in this regard means that the blank is kept at this temperature during the final sintering stage.

For the final sintering, the pre-form part is arranged on a fire-proof base, such as firing pads, or on free-of-scale metal layers. Support structures are not required, since the dimensional stability is guaranteed by the preceding crystallisation of the original powder material.

The following exemplary embodiments illustrate further characteristic features of the invention, whereby the listed parameters are of particular significance on their own but not necessarily in combination:

1. Producing a disk-shaped blank

A quantity of 230g pre-crystallized glass-ceramic powder, which also contains lithium silicate crystal, with a composition (in % by weight):

SiO ₂	58-60
Li ₂ O	13.5-20.5
ZrO ₂	8.5-11.5
P ₂ O ₅	3.0-7.5

Al ₂ O ₃	0.5-6.0
K ₂ O	0.5-3.5
CeO ₂	0.5-2.5
B ₂ O ₃	0-3
Na ₂ O	0-3
Tb ₄ O ₇	0-1.5

as well as 0 to 4 of at least one additive,

with a grain size distribution of $d_{50} = 18.7 \mu\text{m}$ are pre-compacted at a pressure of 50 MPa by means of a tool with a diameter of 105 mm using a hydraulic press. Subsequently the pellet is introduced into a PE-coated pouch, which is evacuated and sealed watertight. The pellet is subjected to an isostatic re-compression at 290 MPa for 10 sec in a water-oil emulsion. The unpacking is followed by a thermal treatment and a partial sintering at 650 °C. The blank density is 1.88 g/cm³.

The final geometry of the blank is created by lathing to an outside diameter of 98.5 mm. A recess is lathed on each of the two front ends to facilitate acceptance into a milling machine.

Into the blank surface with a circular geometry one nests dental molded parts with an appropriate sintering oversize. If crowns are the chosen molded part, they exhibit an excellent and fine crown margin and an outstanding milling surface.

Sintering takes place in a dental furnace on Al₂O₃ firing pads with a multi-step sintering program over a total duration of 60 min. A multi-stage sintering program in this context means that holding times are provided for at least two different temperatures, so that these temperatures are maintained constant for the duration of the respective holding times. The maximum sintering temperature was 950 °C, and was kept for a duration of 10 min. The subsequent evaluation of the crowns revealed an aesthetic visual appearance with a good dental fit.

2. Producing a cuboid blank

A quantity of 9.6 g of pre-crystallized glass-ceramic powder with a composition (in % by weight):

SiO ₂	58-60
Li ₂ O	13.5-20.5
ZrO ₂	8,5-11,5
P ₂ O ₅	3.0-7.5
Al ₂ O ₃	0.5 – 6.0
K ₂ O	0.5 – 3.5
CeO ₂	0.5-2.5
B ₂ O ₃	0-3
Na ₂ O	0-3
Tb ₄ O ₇	0-1.5

as well as 0 to 4 of at least one additive,

with a grain size distribution of $d_{50} \approx 21.3 \mu\text{m}$ is axially compressed under continuously rising pressure up to 120 MPa using a hydraulic press in a carbide mould and is demolded under a suitable load of preferably 5 MPa. The resulting pellet possesses dimensions of 20.2 x 19.1 x 15.9 mm and a density of 1.56 g/cm³. Subsequently the pellet is subjected to two-stage thermal treatment at 630 °C and 700 °C in an elevator furnace. The blank density after the thermal treatment rose to 1.75 g/cm³.

A mushroom-shaped adapter is glued to the narrow side of the blank to facilitate acceptance into a processing machine. The carving work on the dental crown that was oversized to compensate for sintering shrinkage took place using a special speed milling operation with significantly reduced cutting time using a cutting feed of up to 2000 mm/min. This represents a significant shortening of the cutting time in comparison to the part produced in example 1. The crown exhibited a smooth exterior and the crown margin was free from break-outs. The sintering took place on Al₂O₃ firing pads in a dental furnace with a stepped cycle with a total duration of 65 min and a maximum sintering temperature of 950 °C for 10 min. A subsequent evaluation of the crown revealed an aesthetic colour and a good dental fit.

3. Producing a rod-shaped blank

A quantity of 210 g of pre-crystallized glass-ceramic powder with a composition (in % by weight) of:

SiO₂ 58 - 60

Li ₂ O	13.5-20.5
ZrO ₂	8.5-11.5
P ₂ O ₅	3.0-7.5
Al ₂ O ₃	0.5 - 6.0
K ₂ O	0.5 - 3.5
CeO ₂	0.5-2.5
B ₂ O ₃	0-3
Na ₂ O	0-3
Tb ₄ O ₇	0 - 1 . 5

as well as 0 to 4 of at least one additive,

with a grain size distribution of $d_{50} = 19.1 \mu\text{m}$ is compressed using a wet-bag press at a quasi-isostatic pressure of 195 MPa in a tubular polyurethane mould. The demolding is followed by a thermal treatment for additional crystallization at 620 °C and pre-sintering at 680 °C. The final blank geometry is created by lathing to an outside diameter of 25 mm and a length of 198 mm. The blank possesses a density of 1.81 g/cm³

From the face of rod-shaped glass-ceramic blanks one cuts dental crowns with an appropriate sintering oversize. The crowns possess a narrow crown margin free of break-outs and a good cutting surface. Sintering takes place in a small batch furnace on trays with Al₂O₃ firing pads. One employs a sintering program with an overall cycle time of 45 min. The maximum temperature of the sintering treatment is 980 °C. The blank was kept at this temperature for 5 min. The completed crowns exhibit an aesthetic visual appearance and a good dental fit.

Claims:

1. A method to produce a dental moulding such as an inlay, onlay, crown, or bridge, comprising the procedural steps of:

- producing a melt with a composition (in % by weight):

SiO ₂	46.0-72.0
Li ₂ O	10.0-25.0
ZrO ₂	6.5 -14.0
P ₂ O ₅	1.0-10.0
Al ₂ O ₃	0.1 - 8.0
K ₂ O	0.1 - 5.0
CeO ₂	0.1 - 4.0
B ₂ O ₃	0.0 - 4.0
Na ₂ O	0.0 - 4.0
Tb ₄ O ₇	0.0 - 2.5

15

as well as 0.0 to 4.0 of at least one additive.

- producing a glass frit by atomizing the melt and curing it in a medium,
- if necessary, producing glass powder particles from the glass frit with a grain size
distribution $d_{90} \leq 80 \mu\text{m}$,
- crystallizing lithium silicate crystals with a volume percent between 10% and 90% by a
first heat treatment of either the glass frit or the glass powder particles in a first temperature range at a
temperature T_1 with $500^\circ\text{C} \leq T_1 \leq 750^\circ\text{C}$ for a time t_1 with $5 \text{ min} \leq t_1 \leq 120 \text{ min}$,
- wherein, then when the glass frit is subjected to a heat treatment, glass-ceramic particles
with a grain size distribution $d_{90} \leq 80 \mu\text{m}$ are produced from the heat-treated glass frit,
- pressing the glass-ceramic powder particles to a blank, having a density between 30%
and 60% of the theoretical density,
- machining the blank by milling to produce a pre-form corresponding to the dental
moulding in consideration of the shrinkage characteristics of the blank, and
- total sintering the pre-form at a temperature T_2 with $800^\circ\text{C} \leq T_2 \leq 1050^\circ\text{C}$ over a time
 t_2 with $5 \text{ min} \leq t_2 \leq 60 \text{ min}$.

2. A method to produce a dental molding, comprising the procedural steps of:

- producing a melt with a composition in wt%:

35

SiO ₂	46.0-72.0
Li ₂ O	10.0-25.0
ZrO ₂	6.5 -14.0
P ₂ O ₅	1.0-10.0

A ₁₂ O ₃	0.1 - 8.0
K ₂ O	0.1 - 5.0
CeO ₂	0.1 - 4.0
B ₂ O ₃	0.0 - 4.0
Na ₂ O	0.0 - 4.0
Tb ₄ O ₇	0.0 - 2.5

- producing a glass frit by atomizing the melt and curing it in a medium,
- producing glass powder particles from the glass frit with a grain size distribution $d_{90} \leq 80 \mu\text{m}$,
- crystallizing lithium silicate crystals with a volume percent between 10% and 90% by a first heat treatment of the powder particles in a first temperature range at a temperature T_1 with $500^\circ\text{C} \leq T_1 \leq 750^\circ\text{C}$ for a time t_1 with $5 \text{ min} \leq t_1 \leq 120 \text{ min}$,
- pressing the glass-ceramic powder particles to a blank, having a density between 30% and 60% of the theoretical density,
- machining the blank by milling to produce a pre-form corresponding to the dental moulding in consideration of the shrinkage characteristics of the blank, and
- total sintering the pre-form at a temperature T_2 with $800^\circ\text{C} \leq T_2 \leq 1050^\circ\text{C}$ over a time t_2 with $5 \text{ min} \leq t_2 \leq 60 \text{ min}$.

3. A method according to claim 1 or claim 2 wherein a melt is produced with the composition (in % by weight):

SiO ₂	49.0-69.0
Li ₂ O	11.5-24.0
ZrO ₂	7.0 -13.5
P ₂ O ₅	1.5 - 9.0
A ₁₂ O ₃	0.2 - 7.5
K ₂ O	0.2 - 4.5
CeO ₂	0.2 - 3.5
B ₂ O ₃	0.0 - 3.5
Na ₂ O	0.0 - 3.5
Tb ₄ O ₇	0.0 - 2.0

as well as 0.0 to 4.0 of at least one additive.

4. A method according to claim 1 or claim 2, wherein a melt is produced with the composition (in % by weight):

SiO ₂	52.0-66.0
Li ₂ O	12.0-22.5
ZrO ₂	7.5 -13.0

19 Oct 2018

2014261405

	P ₂ O ₅	2.0 - 8.5
	Al ₂ O ₃	0.3 - 7.0
	K ₂ O	0.3 - 4.0
	CeO ₂	0.3 - 3.5
5	B ₂ O ₃	0.0 - 3.0
	Na ₂ O	0.0 - 3.0
	Tb ₄ O ₇	0.0 - 2.0

as well as 0.0 to 4.0 of at least one additive.

10 5. A method according to claim 1 or claim 2, wherein a melt is produced with the composition (in % by weight):

	SiO ₂	55.0-63.0
	Li ₂ O	12.5-21.5
	ZrO ₂	8.0 -12.0
15	P ₂ O ₅	2.5-8.0
	Al ₂ O ₃	0.4 - 6.5
	K ₂ O	0.4 – 4.0
	CeO ₂	0.5 - 3.0
	B ₂ O ₃	0.0 - 3.0
20	Na ₂ O	0.0 - 3.0
	Tb ₄ O ₇	0.0 - 2.0

as well as 0.0 to 4.0 of at least one additive.

25 6. A method according to claim 1 or claim 2, wherein a melt is produced with the composition (in % by weight):

	SiO ₂	58.0-60.0
	Li ₂ O	13.5-20.5
	ZrO ₂	8.5 -11.5
30	P ₂ O ₅	3.0 - 7.5
	Al ₂ O ₃	0.5 - 6.0
	K ₂ O	0.5 - 3.5
	CeO ₂	0.5 - 2.5
	B ₂ O ₃	0.0 - 3.0
35	Na ₂ O	0.0 - 3.0
	Tb ₄ O ₇	0.0 - 1.5

as well as 0.0 to 4.0 of at least one additive.

7. A method according to any one of the previous claims, wherein before the machining and after the first heat treatment, the blank is tempered at a temperature T_3 with $750 \text{ }^{\circ}\text{C} \leq T_3 \leq 900 \text{ }^{\circ}\text{C}$ over a time t_3 with $5 \text{ min} \leq t_3 \leq 30 \text{ min}$.

5 8. A method according to any one of the previous claims, wherein for the production of a blank having a disk geometry, the glass-ceramic powder particles are at first axially pressed and then, after being inserted into an envelope, such as a bag made of polyethylene which is coated at the inside, the particles are isostatically redensified, wherein the redensification is conducted especially at a pressure p_n with $250 \text{ MPa} \leq p_n \leq 350 \text{ MPa}$ over a time t_4 with $5 \text{ sec} \leq t_4 \leq 30 \text{ sec}$, especially $5 \text{ sec} \leq t_4 \leq 15 \text{ sec}$.

10 9. A method according to any one of claims 1 to 7, wherein for the production of a blank having a cuboid geometry, the glass-ceramic powder particles are successively, especially continuously, axially pressed with increasing pressure over a time t_5 , wherein the maximum pressure p_5 , is $50 \text{ MPa} \leq p_5 \leq 400 \text{ MPa}$, especially $100 \text{ MPa} \leq p_5 \leq 200 \text{ MPa}$.

15 10. A method according to any one of claims 1 to 7, wherein for the production of a rod-shaped blank, especially of cylindrical geometry, the glass-ceramic powder is filled into a tubular press mold, especially made of polyurethane, and then quasi-isostatically pressed.

20 11. A method according to any one of the previous claims, wherein the blank is at least roughly machined by milling and then finished, wherein for the rough machining preferred milling parameters are considered:

Milling diameter:

2 to 5 mm especially 2 to 3 mm

Forward Feed:

500 to 4000 mm/min, especially 2000 to 3000 mm/min

Lateral feed motion ae:

25 0.2 to 3 mm, especially 1 mm to 2 mm

Depth feed motion ap:

0.1 to 2 mm, especially 0.5 mm to 1 mm

Milling speed:

10,000 to 50,000 1/min, especially 10,000 to 20,000 1/min

and/or for the finished preferred the milling parameters are considered:

Milling diameter:

0.3 to 1.5 mm, especially 0.5 to 1.0 mm

Forward Feed:

300 to 2000 mm/min, especially 800 to 1500 mm/min

Lateral feed motion ae:

0.2 to 0.6 mm, especially 0.1 mm to 0.2 mm

Depth feed motion ap:

0.05 to 0.3 mm, especially 0.1 mm to 0.15 mm

Milling speed:

35 20,000 to 60,000 1/min, especially 25,000 to 35,000 1/min.

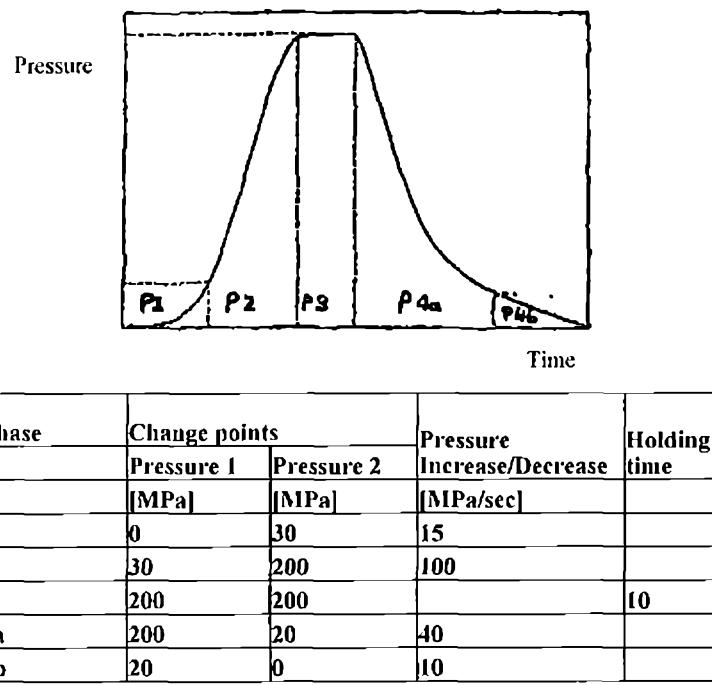
12. A method according to any one of the previous claims, wherein as a milling tool a ball cutter with the following edge angles is used:

Rake angle: 0° to -13° , especially -9° to -11°
Clearance angle: 0° to 15° , especially 11° to 13°
Wedge angle: Resulting in 90° minus tool orthogonal clearance minus tool orthogonal rake.

5 13. A method according to any one of the previous claims, wherein the blank is dipped into silica or alkali silicate solution (water glass), dried, and then dryly machined by milling, or that the blank is machined by milling and then, before it is sintered to final density, dipped into silica or alkali silicate solution (water glass) and dried.

10

15



Example of pressurization during pressing.

Fig. 1