(54) Title: METHOD FOR PRODUCING MOULDS AND CORES FOR METAL CASTING AND MOULDS AND CORES PRODUCED ACCORDING TO THIS METHOD

(57) Abstract:
The invention relates to a method for producing casting moulds and cores, in which a foundry base material comprising at least one refractory material and a binder curable by CO₂, preferably based on water glass, is cured by gassing with CO₂ and flushing with a second gas. The invention further relates to moulds and cores produced according to this method.
Abstract

The invention relates to a method for producing casting molds and cores, in which a foundry base material comprising at least one refractory material and a binder curable by CO₂, preferably based on water glass, is cured by gassing with CO₂ and flushing with a second gas. The invention further relates to molds and cores produced according to this method.
(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

(51) Internationale Patentklassifikation:
B22C 1/18 (2006.01) B22C 9/12 (2006.01)

(21) Internationales Aktenzeichen:
PCT/DE2013/000223

(22) Internationales Anmeldedatum:

(25) EinreichungsSprache:
Deutsch

(26) Veröffentlichungssprache:
Deutsch

(30) Angaben zur Priorität:
10 2012 103 705.1

(71) Anmelder:
ASK CHEMICALS GMBH [DE/DE];
Reisholzstrasse 16-18, 40721 Hilden (DE)

(72) Erfinder:
KOCH, Dieter; Stintener Hinterstr. 37, 40822 Mettmann (DE).
SCHMIDT, Oliver; Föhrenweg 35, 40764 Langenberg (DE).

(74) Anwalt:
SCHUPFNER, Georg, U.; Müller Schupfner & Partner, Schellerdamm 19, 21079 Hamburg (DE).

(81) Bestimmungsstaaten:
(soweit nicht anders angegeben, für jede verfügbare nationale Schutzrechtsart):

(84) Bestimmungsstaaten (soweit nicht anders angegeben, für jede verfügbare regionale Schutzrechtsart):

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

(54) Titel: METHOD FOR PRODUCING MOULDS AND CORES FOR METAL CASTING AND MOULDS AND CORES PRODUCED ACCORDING TO THIS METHOD

(55) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON FORMEN UND KERNEN FÜR DEN METALLGUSS SOBIE NACH DIESEM VERFAHREN HERGESTELLTE FORMEN UND KERNE

(57) Abstract: The invention relates to a method for producing casting moulds and cores, in which a foundry base material comprising at least one refractory material and a binder curable by CO₂, preferably based on water glass, is cured by gassing with CO₂ and flushing with a second gas. The invention further relates to moulds and cores produced according to this method.

(57) Zusammenfassung: Gegenstand der Erfindung ist ein Verfahren zur Herstellung von Gießformen und Kernen, bei dem ein Formgrundstoff bestehend aus mindestens einem Feuerteststoff und einem durch CO₂ härbaren Bindemittel, vorzugsweise aus der Basis von Wasserlas, durch Begasen mit CO₂ und Spülen mit einem zweiten Gas ausgehärtert wird. Weiterhin betrifft die Erfindung die nach diesem Verfahren hergestellten Formen und Kerne.
Method for producing molds and cores for metal casting and molds and cores produced according to this method

The invention relates to a method for producing casting molds and cores, in which a molding mixture consisting of at least one refractory material and a binder curable with CO\textsubscript{2}, preferably containing or consisting of water glass, is cured by gassing with CO\textsubscript{2} or a CO\textsubscript{2}-containing gas and purging with a second gas containing no CO\textsubscript{2}, or at least a minor fraction of CO\textsubscript{2}. In addition the invention relates to the molds and cores produced according to this method.

Prior Art

Molds and cores are generally produced using a refractory molding base material, e.g., quartz sand, and a suitable binder. The refractory molding base material in such processes is preferably present in free-flowing form, so that the mixture of molding base material and binder, the so-called molding mixture, can be filled into a hollow mold, compressed there, and cured. The binder produces solid adhesion between the particles of the molding base material, so that the molds and cores attain the required mechanical stability.

During casting, molds form the outer walls for the casting; cores are used when cavities within the casting are necessary. It is not absolutely necessary for molds and cores to consist of the same material. For example, the external shape of the casting is created using permanent metal molds. A combination of molds and cores produced in various ways is also possible. As will be explained in the following based on cores, similar statements are also true for molds (casting molds) produced according to the same method and vice-versa.

For producing cores, both organic and inorganic binders curable by cold or hot methods may be used. Cold methods are methods which are essentially performed at room temperature without heating the molding tool used for core manufacture.
In this process, curing is usually performed by a chemical reaction induced, for example, by the fact that a gas is passed through the molding mixture to be cured. In hot methods, after molding, the molding mixture is heated by the heated molding tool to a sufficiently high temperature in order, for example, to expel the solvent contained in the binder and/or to initiate a chemical reaction by which the binder is cured, for example, by cross-linking.

Curing water glass-binders with CO₂ is known, for example, from GB 654817. In the 1950s and 1960s, the water glass-CO₂ method was widely used. One of the weaknesses of this method is that the cores produced from it have relatively low strengths, especially immediately after manufacturing. Longer gassing times with CO₂, to be sure, produce higher initial strengths, but at the same time the strengths after 1 or 2 days of storage are diminished. In addition to relatively low initial and final strengths, the water glass-CO₂ method permits only low to moderate manufacturing speeds.

Therefore it has been suggested that standard CO₂ curing be combined with a subsequent so-called “hot air process,” as described by Y.A. Owusu (Y.A. Owusu, Ph.D. Dissertation “Sodium Silicate Bonding in Foundry Sands,” Pennsylvania State University, May 1, 1980, p. 88, 102-103 and AFS Transactions, vol. 89, 1981, pp. 47-54). The hot air process is defined as oven curing following the CO₂ gassing. This is also confirmed by the dissertation of Y.A. Owusu. This method, at least in the case of some water glass binders, gives better strengths than in the case of pure CO₂ curing, but has the drawback that the manufacturing time for the cores is extended from a few seconds to several minutes.

DE 102011010548-A1 describes a method for curing water glass-bonded molding mixtures wherein a combination of air and carbon dioxide flow is used. It was found in this instance that the molding mixture must first be gassed with air and then with CO₂ or an air-carbon dioxide mixture. Furthermore it is of great significance for this invention that the alkali silicate solutions used have a weight ratio of SiO₂ to metal oxide in the range of 1.5:1 to 2.0:1.
An additional patent that describes a method of this type is WO 80/01254 A1. This discloses a method for curing a water glass-containing molding mixture which is heated at a temperature of 110 to 180°C while simultaneously passing through a CO₂ or a CO₂-air mixture.

PL 129359 B2 describes a binder for producing casting molds for metal casting made of water glass and urea resin. In this case the curing is performed by flushing the molding mixture with a CO₂-air mixture. In this process it is advantageous for the gases to be heated to temperatures of 60-200°C. An additional publication describing the use of a CO₂-air mixture is CN 94111187 A.

From EP 2014392 B1 the use of amorphous spherical SiO₂, which is available in more than two particle size classes, is known. EP 2014392 B1, however, does not disclose the use of a second gas stream and introduces the SiO₂ in aqueous suspension, which as a result of the increased introduction of water is disadvantageous for the (early) strengths of molds produced according to the method of the invention provided here.

Good strengths even after brief curing times are necessary to reliably manage the increasingly complex, thin-walled casting molds that are required more and more frequently today and at the same time guarantee high productivity. Therefore it is not surprising that the water glass-CO₂ method rapidly lost its significance with the arrival of processes based on organic binders, especially the so-called Ashland Polyurethane ColdBox method.

However, all organic binders have the drawback that they undergo thermal decomposition during casting and can release harmful materials such as benzene, toluene or xylenes. In addition the organic binder systems already release solvents to the environment during core manufacturing and storing, or unpleasant-smelling gases are used as curing catalysts. To be sure it has become possible as a result of various measures to avoid all these emissions, but they cannot be avoided in the case of organic binders.
For this reason, for years there have been increasing attempts to develop binders based completely on inorganic materials or containing at most a small fraction of organic compounds. To achieve high strengths within short time periods, for example, the pathway was followed of performing the curing in a hot tool and if desired additionally passing hot air through the molding mixture to remove the water present as solvent as completely as possible. One such system is described, for example, in EP 1802409 B1 (US 7770629). However, these methods have the drawback that the tools must be designed so that they can be heated and the heating causes additional energy consumption, which represents a considerable cost burden for the method.

Problem of the invention

The inventors have therefore posed the problem of developing a method that would make it possible to manufacture molds and cores using an inorganic-based, CO₂-curable binder even in unheated tools, wherein the strengths should already be substantially higher with the same binder and identical binder content and without subsequent heat treatment than in the previously known curing with CO₂, especially immediately after removal from the tool.

Summary of the invention

This task will be accomplished using a method with the features of claim 1. Advantageous further embodiments of the method according to the invention are the subject of the independent claims or will be described in the following.

Surprisingly it was found that by the combination of CO₂ curing with a first gas and flushing the molding mixture with a second gas, in the following also called flushing gas, cores with good strengths can be achieved. In this process the first gas and the second gas are not to be set up so that the first gas is applied before the second gas; on the contrary, the sequence may be as desired and in addition the first and/or the second gas can also be applied several times. However, it is preferred that the second gas be introduced last, and independently of this that the first gas be introduced into the mold first.
For the first gas, also called CO₂ gas in the following, gas temperatures during gassing of between 15°C and 120°C, preferably 15°C and 100°C, and particularly preferably between 25°C and 80°C are advantageous. The gas temperature, as used in the further description of the method according to the invention as well, means the temperature of the gas upon entry into the molding tool. The second gas preferably also has gas temperatures of 15 to 120°C, preferably between 15°C and 100°C, and particularly preferably between 25°C and 80°C, but higher temperatures frequently make it possible to shorten the flushing time. There is no upper limit to this based on the curing mechanism. In practice, depending on the shape and size of the core or the mold, the temperatures will be between 40°C and 250°C, preferably between 50°C and 200°C. First and foremost, financial considerations oppose the use of very high temperatures, since the costs of the heaters required for this purpose increase greatly with increasing power and the cost for effectively insulating the lines is very high. For example, the temperature of the first gas is approximately the same as the temperature of the second gas. Preferably, however, the temperature of the second gas is higher than the temperature of the first gas.

As a result of the above-named measures it is advantageous to control the cooling of the molding mixtures seen during gassing by controlling the temperatures of the two gas streams.

The use of available heatable tools is by no means excluded in the methods described; through the method of the invention the discloses possibility of operating the tools either cold, i.e., at ambient temperature or room temperature of 15 to 30°C or at lower than usual temperatures, i.e., less than 200°C or less than 120°C or even less than 100°C, to lower the costs. In particular, non-heatable tools may advantageously be used. Such tools are not heatable, i.e., they have no heating devices of their own such as an electrical heater, but can be heated by the gas introduced at controlled temperature. The method according to the invention also does not rule out the possibility of subsequently subjecting the cores or molds to additional heat treatment.
The method according to the invention comprises the following steps:

- producing a molding mixture from at least one refractory molding base material and a CO$_2$-curable binder, preferably based on water glass
- molding the molding mixture
- flushing the molding mixture with the CO$_2$ gas
- optionally flushing the molding mixture with CO$_2$ gas and the flushing gas alternately
- flushing the molding mixture with a second gas (flushing gas).

**Detailed description of the invention**

The procedure generally followed in producing the molding mixture is that the refractory molding base material is taken initially and the binder is added under agitation. The agitation is continued until uniform distribution of the binder on the molding base material is guaranteed.

Then the molding mixture is placed in the desired mold. In this process, the usual methods for molding are used. For example, the molding mixture can be shot into the core-molding machine using compressed air. The curing is performed subsequently, in that (especially) first the CO$_2$ gas is passed through the mold filled with the molding mixture, followed by flushing with the second gas. The expert can immediately see that a variety of designs are possible for this process.

For example, it is by no means necessary (but is frequently advantageous) to use pure CO$_2$ (for example, industrial-grade) as the CO$_2$ gas. To achieve the shortest possible curing times, however, it is advantageous for the CO$_2$ gas to contain at least 50 vol% CO$_2$, preferably at least 80 vol% CO$_2$.

On the other hand it is not necessary for the second gas to be completely CO$_2$-free, for example, synthetic air or nitrogen. Air is preferred for cost reasons. CO$_2$ can even be added to the flushing gas, but no more than 10 vol%, particularly preferably no more than 5 vol%, especially no more than 2 vol% or even no more than 1 vol%.
The transition from CO₂ gas to the second gas need not take place in a single step; stepwise or fluid transitions are likewise possible. In addition, both gases or even one of the two may be pulsed through the molding mixture.

An additional variant consists of the fact that, first, part of the water present in the molding mixture is removed by brief gassing with the gas of low CO₂ content as a flushing gas, then the binder is hardened with the CO₂ gas and optionally, for further drying, the core is treated again with the low CO₂ gas. The addition of CO₂ can take place either by establishing a certain CO₂ flow for the CO₂ gas or a certain gassing pressure. Which of the two possibilities is selected depends on many factors in practice, for example, the geometry and size of the core, the tightness of the molding tool, the ratio of gas inlet to gas outlet, the gas permeability of the molding base material, the diameter of the gas line, the binder content, the desired gassing time, etc. To optimize the properties, the gassing parameters can be adjusted depending on the requirements of the selected core or mold geometry within the framework of the present disclosure and the knowledge that is customarily possessed by a person skilled in the art. As a rule a CO₂ flow of between 0.5 L/min and 600 L/min will be selected, preferably between 0.5 L/min and 300 L/min and particularly preferably between 0.5 L/min and 100 L/min (in each case standard liters). According to another embodiment the CO₂ flow can be selected between 0.5 L/min and 30 L/min, preferably between 0.5 L/min and 25 L/min and particularly preferably between 0.5 L/min and 20 L/min. This embodiment is particularly advantageous at low gas temperatures for the CO₂ or the CO₂-containing gas of 15 to 40°C.

In the case of pressure regulation the pressures of the CO₂ gas usually vary between 0.5 bar and 10 bar, preferably between 0.5 bar and 8 bar and particularly preferably between 0.5 bar and 6 bar.
In the case of air as the flushing gas this can be taken from the pressure line usually available in foundries, so that for purely practical reasons the pressure prevailing therein represents the upper limit for gassing. The lower limit for effective gassing with air is about 0.5 bar. At a lower pressure the gassing time would be greatly prolonged, which would be associated with a loss of productivity.

All pressure statements, unless indicated otherwise, relate to gauge pressure, i.e., a pressure above ambient pressure.

It is possible for the ratio of the gassing times of the first gas (CO₂ gas) and the second gas (flushing gas) to one another to vary, for example, between 2:98 to 90:10, preferably between 2:98 to 20:80 and particularly preferably between 5:95 to 30:70. However, since it is also a goal in this application to keep the CO₂ consumption as low as possible, the gassing time with the CO₂ gas preferably should amount to no more than 60% of the total gassing time, particularly preferably no more than 50%.

By suitably selecting the gassing parameters and the layout of the tool it is possible to ensure that even for larger cores, manufacturing times that correspond to those with organic binders, e.g., less than 3 minutes, preferably less than 2.5 minutes and particularly preferably less than 2 minutes are possible. Optionally such optimization can also be performed with the aid of computer simulation.

It is easily possible to modify the curing of the molding material by known methods, for example, by applying a vacuum. In addition other known steps may follow the actual curing process, for example, treatment with microwaves or heating in an oven.

The usual materials may be employed as molding base materials for producing casting molds. Suitable materials are, for example, quartz, zirconium or chromium ore sand, olivine, vermiculite, bauxite and fireclay. It is not necessary to use exclusively new sands in such cases. For the sake of resource conservation and to avoid waste disposal costs it is even advantageous to use the highest possible fraction of regenerated old sand.
For example, a suitable sand is described in WO 2008/101668 (= US 2010/173767 A1). Also suitable are regenerates obtained by washing and subsequent drying. Usable but less preferred are regenerates obtained by purely mechanical treatment. As a rule the regenerate can replace at least about 70 wt% of the new sand, preferably at least about 80 wt% and particularly preferably at least about 90 wt%.

Also usable as refractory molding base materials are synthetic molding materials such as glass beads, glass granulate, the spherical ceramic building base materials known under the name of “Cerabeads” or “Carboaccucast” or aluminum silicate hollow microspheres (so-called microspheres). Such aluminum silicate hollow microspheres are marketed, for example, by Omega Minerals Germany GmbH, Norderstedt, in various qualities with different aluminum oxide contents under the name of “Omega-Spheres.” Corresponding products are available from PQ Corporation (USA) under the name of “Extendospheres.”

The mean diameter of the molding base material is generally between 100 µm and 600 µm, preferably between 120 µm and 550 µm and particularly preferably between 150 µm and 500 µm. The particle size can be determined, for example, by screening according to DIN ISO 3310.

In casting experiments with aluminum it was found that when synthetic molding base materials are used, for example, in the case of glass beads, glass granulates or microspheres, less molding sand remains sticking to the metal surface than when pure quartz sand is used. The use of artificial molding base materials therefore makes it possible to achieve smoother casting surfaces, so that expensive after-treatment by blasting is not necessary, or at least is necessary to a considerably lesser extent.

It is not necessary in such instances for all of the molding base material to consist of the synthetic molding base materials.
The preferred fraction of the synthetic molding base material is at least about 3 wt%, particularly preferably at least 5 wt%, especially preferably at least 10 wt%, advantageously at least about 15 wt%, particularly advantageously at least about 20 wt%, based on the total quantity of the refractory molding base material. The refractory molding base material preferably is in the free-flowing state, so that the molding mixture according to the invention can be processed in conventional core shooting machines.

As an additional component the molding mixture according to the invention contains a binder based on water glass. The water glass that may be used includes the usual water glasses such as those already in use as binders in molding mixtures.

Water glasses are aqueous solutions of alkali silicates, especially lithium, sodium and potassium silicates, and are also used as binders in other areas, for example, in construction. The water glass is manufactured, for example, on a large industrial scale by melting quartz sand and alkali carbonates at temperatures of 1350°C to 1500°C. In this process the water glass is initially obtained in the form of a blocky, solid glass, which is dissolved in water under the application of temperature and pressure. An additional method for producing water glasses is the direct dissolution of quartz sand with sodium hydroxide.

The alkali silicate solution obtained can then be adjusted to the desired SiO₂/M₂O molar ratio by adding alkali hydroxides and/or alkali oxides or the hydrates thereof. In addition the composition of the alkali silicate solution can be adjusted by dissolving alkali silicates with a different composition. In addition to alkali silicate solutions, water-containing alkali silicates in solid form, for example, the product groups of Kasolv, Britesil or Pyramid from PQ Corporation are available.

The binders can also be based on water glasses containing more than one of the alkali ions mentioned, for example, the lithium-modified water glasses known from DE 2652421 A1 (= GB 1532847). Furthermore the water glasses may also contain polyvalent ions such as boron or aluminum (corresponding compounds are described in EP 2305603 A1 (= WO2011/042132 A1).
The water glass preferably has an \( \text{SiO}_2/\text{M}_2\text{O} \) molar ratio in the range of 1.6 to 4.0, especially 2.0 to less than 3.5, wherein \( \text{M} \) represents lithium, sodium or potassium.

The water glasses preferably have a solids fraction of greater than or equal to 30 wt\%, particularly preferably greater than or equal to 33 wt\% and especially preferably greater than or equal to 36 wt\%. The upper limits for the solids content of the preferred water glass are less than or equal to 65 wt\%, particularly preferably less than or equal to 60 wt\% and especially preferably less than 55 wt\%. The solids fraction is determined on a Sartorius MA30 Moisture Analyzer, wherein about 3 - 4 g of the binder is heated on an aluminum dish (diameter = 10 cm, height = 0.7 cm) at a temperature of 140°C to constant weight.

In addition the water glasses have a solids fraction, calculated as \( \text{M}_2\text{O} \) and \( \text{SiO}_2 \), in the range of 25 to 65 wt\%, preferably 30 to 60 wt\%. The solids fraction is based on the quantity of alkali silicates, calculated as \( \text{SiO}_2 \) and \( \text{M}_2\text{O} \), contained in the water glass.

Depending on the application and desired liquid level, between 0.5 wt\% and 5 wt\% of the binder based on water glass are used, preferably between 0.75 wt\% and 4 wt\%, particularly preferably between 1 wt\% and 3.5 wt\%, in each case based on the molding base material. The information here is based on water glasses with solids contents as given above and includes the diluent, water.

Based on the amount of alkali silicates, calculated as \( \text{M}_2\text{O} \) and \( \text{SiO}_2 \), which are added to the molding base with the inorganic binder according to the invention, without considering the diluent, the quantity of the binder used is 0.2 to 2.5 wt\%, preferably 0.3 to 2 wt\% relative to the molding base material, wherein \( \text{M}_2\text{O} \) has the meaning stated above.
The molding mixture also preferably contains a quantity of a particulate metal oxide
selected from the group of silicone dioxide, aluminum dioxide, titanium dioxide and
zinc oxide and mixtures thereof or mixed oxides, especially silicone dioxide,
aluminum dioxide and/or alumosilicate. The particle size of these metal oxides
preferably amounts to less than 300 μm, preferably less than 200 μm, particularly
preferably less than 100 μm and has, for example, a mean primary particle size
between 0.05 μm and 10 μm.

The particle size can be determined by screen analysis. Particularly preferably the
screen residue on a screen with a mesh size of 63 μm amounts to less than 10 wt%,
preferably less than 8 wt%. Particularly preferably, silicone dioxide is used as the
particulate metal oxide, wherein synthetically produced amorphous silicone dioxide
is particularly preferred.

Precipitated silica and/or pyrogenic silica is preferably used as the particulate
silicone dioxide.

Optionally the molding mixture can contain amorphous SiO₂. Surprisingly it was
found that the addition of amorphous SiO₂ to the molding mixture not has only
positive effects in the hot curing described in EP 1802409 B1 (= US 7770629), but
also in the curing with CO₂ gas and flushing gas. In terms of the initial strengths, the
strength increase comes out to be much greater than that of raising the binder
content by the same amount, while in terms of the final strength the higher binder
content turns out more advantageously, so that alternatives are available according
to the desired effect.

The amorphous SiO₂ preferably used according to the present invention has a
water content of less than 15 wt%, especially less than 5 wt% and particularly
preferably less than 1 wt%. In particular, the amorphous SiO₂ is used as a powder.

Both synthetically manufactured and naturally occurring silicas can be used as the
amorphous SiO₂. However, the latter, known, for example, from DE 102007045649
are not preferred, since they generally contain appreciable crystalline fractions and
therefore are classified as carcinogenic.
Synthetic means non-naturally occurring amorphous SiO₂, i.e., the manufacturing thereof comprises a chemical reaction, e.g., the manufacturing of silica sols by ion exchange processes from alkali silicate solutions, precipitation from alkali silicate solutions, flame hydrolysis of silicone tetrachloride or the reduction of quartz sand with coke in an electric furnace during the manufacturing of ferrosilicon and silicon. The amorphous SiO₂ produced according to the two last-named methods is also called pyrogenic SiO₂.

Sometimes synthetic amorphous SiO₂ is defined exclusively as precipitated silica (CAS No. 112926-00-8) and SiO₂ produced by flame hydrolysis (pyrogenic silica, fumed silica, CAS No. 112945-52-5), whereas the product produced in ferrosilicon or silicon manufacturing is known merely as amorphous SiO₂ (Silica Fume, Microsilica, CAS No. 69012-64-12). For the purposes of the present invention the product produced in ferrosilicon or silicon manufacturing will also be defined as synthetic amorphous SiO₂.

Precipitated silicas and pyrogenic, i.e., flame-hydrolytic or electric arc-manufactured SiO₂ are preferably used. Particularly preferably used is amorphous SiO₂ produced by thermal decomposition of ZrSiO₄ (see DE 102012020509) as well as SiO₂ produced by oxidation of metallic Si with an oxygen-containing gas (see DE 102012020510). Also preferred is quartz glass powder (principally amorphous SiO₂) that was produced by melting and rapid cooling from crystalline quartz, so that the particles are spherical and not present as splinters (see DE 102012020511). The mean primary particle size of the synthetic amorphous silicon dioxide can be between 0.05 μm and 10 μm, especially between 0.1 μm and 5 μm, particularly preferably between 0.1 μm and 2 μm. The primary particle size was determined by dynamic light scattering on a Horiba LA950 and checked by scanning electron microscopy (SEM microscopy) on a Nova NanoSEM 230 from the firm of FEI. Furthermore, with the aid of the SEM images, details of the primary particle size could be made visible down to the order of magnitude of 0.01 μm. The SiO₂ samples were dispersed in distilled water for the SEM measurements and then applied to an aluminum holder bonded to a copper strip before the water was evaporated.
Furthermore the specific surface area of the synthetic amorphous silicone dioxide was determined with the aid of gas adsorption measurements (BET method) according to DIN 66131. The specific surface of the synthetic amorphous SiO₂ is between 1 and 200 m²/g, especially between 1 and 50 m²/g, particularly preferably between 1 and 30 m²/g. Optionally the products can also be mixed, for example, to systematically obtain mixtures with certain particle size distributions.

The amorphous SiO₂ types mentioned easily form larger aggregates by agglomeration. For a uniform distribution of the amorphous SiO₂ in the molding material mixture it is important that the aggregates can break up again into smaller units upon mixing or do not exceed a certain size from the beginning. Preferably the screen residue -- used to describe the extent of aggregation -- amounts to no more than about 10 wt%, particularly no more than about 5 wt% and most particularly preferably no more than about 2 wt% upon passage through a screen with a 45 μm mesh size (325 mesh).

Depending on the manufacturing method and the manufacturer, the purity of the amorphous SiO₂ can vary greatly. Types containing at least 85 wt% SiO₂ proved suitable, preferably at least 90 wt% and particularly preferably at least 95 wt%.

Depending on the application and the desired level of strength, between 0.1 wt% and 2 wt% of the particulate amorphous SiO₂ are used, preferably between 0.1 wt% and 1.8 wt%, particularly preferably between 0.1 wt% and 1.5 wt%, in each case based on the molding base mixture.

The ratio of water glass binder to amorphous SiO₂ can be varied within broad limits. This offers the advantage of greatly improving the initial strengths of the cores, i.e., the strength immediately after removal from the tool, without substantially affecting the final strengths. This is of particularly great interest in light metal casting. On one hand high initial strengths are desirable to transport the cores without problems after they are manufactured or to make up entire core packets, but on the other hand the final strengths should not be too high in order to prevent problems with core disintegration after casting.
Based on the weight of the binder, the amorphous SiO₂ is preferably present in a fraction of 2 to 60 wt%, preferably of 3 to 55 wt% and particularly preferably between 4 and 50 wt%, or particularly preferably based on the ratio of the solid fraction of water glass to amorphous SiO₂ of 10:1 to 1:1.2 (parts by weight).

According to EP 1802409 B1, the addition of the amorphous SiO₂ can take place both before and after the binder addition, directly to the refractory material, but it is also possible, as described in EP 1884300 A1 (= US 2008/029240 A1), to first produce a premix of the SiO₂ with at least part of the binder and then mix this in with the refractory material. The binder or binder fraction that may still be present and is not used for the premix can be added to the refractory material before or after the addition of the premix or together with it. Preferably the amorphous SiO₂ is added directly to the refractory material before the binder addition.

Without wishing to be bound to this, the inventors assume that the highly alkaline water glass can react with the silanol groups arranged on the surface of the amorphous silicone dioxide, and that when the water is evaporated an intensive bond is produced between the silicone dioxide and the water glass, which is solid at that point.

In an additional embodiment, barium sulfate may be added to the molding mixture to further improve the surface of the casting, especially in light metal casting such as aluminum casting. The barium sulfate may be synthetically produced or added as natural barium sulfate, i.e., in the form of minerals containing barium sulfate, such as heavy spar or barite. This and other features of the suitable barium sulfate as well as the solid mixture produced with it will be described in greater detail in DE 102012104934, and the disclosure content thereof is thus incorporated by reference in the disclosure of the present patent.

The barium sulfate is preferably added in a quantity of 0.02 to 5.0 wt%, particularly preferably 0.05 to 3.0 wt%, especially preferably 0.1 to 2.0 wt% or 0.3 to 0.99 wt%, in each case based on the total molding mixture.
According to an additional embodiment other substances may also be added to the molding mixture, which are characterized by a low degree of wetting by molten aluminum, for example, boron nitrite.

Such a mixture of poorly wettable substances, including among other things barium sulfate as a poorly wettable agent, can likewise lead to a smooth, casting surface free from sand adhesion. Based on the total quantity of non-wettable/poorly wettable substances the fraction of the barium sulfate should be larger than 5 wt%, preferably larger than 10 wt%, particularly preferably larger than 20 wt% or greater than 60 wt%.

The upper limit represents pure barium sulfate -- the fraction of non-wettable substances in barium sulfate in this case is 100 wt%. The mixture of non-wettable/poorly wettable substances, especially barium sulfate, is preferably added in a quantity of 0.02 to 5.0 wt%, particularly preferably 0.05 to 3.0 wt%, especially preferably 0.1 to 2.0 wt% or 0.3 to 0.99 wt%, in each case based on the molding mixture.

In an additional embodiment the additive component of the molding mixture according to the present invention can also contain at least 1 particulate or 1 particulate mixed metal oxide of aluminum or aluminum and zirconium, as described in DE 102012113073 or DE 102012113074. By means of such additives, castings, especially made of iron or steel, with very high surface quality can be obtained after metal casting, so that removal of the casting mold requires little or no surface processing of the casting afterwards.

The particulate metal oxide or particulate mixed metal oxide at room temperature exhibits little or no tendency to react with the inorganic binder, especially the alkaline water glass.
The particulate metal oxide in this can includes or consists of in particular at least 1 aluminum oxide in the alpha phase and/or at least 1 aluminum/silicone mixed oxide, with the exception of aluminum-silicone mixed oxide with phyllosilicate structure. Particulate metal oxides containing at least 1 aluminum oxide in the alpha phase and/or at least 1 aluminum/silicone mixed oxide, with the exception of aluminum/silicone mixed oxides with phyllosilicate structure, are defined as not only particulate metal oxides consisting of pure aluminum oxide or pure aluminosilicates or aluminosilicates, but also mixtures of the above metal oxides with other oxides, for example, zirconium, zirconium incorporated into the aluminum/silicone mixed oxides or heterogeneous substance mixtures, i.e., those consisting of several thicknesses, which among other things consists of at least 2 of the afore-mentioned solids or bases: alumina oxide-containing and/or aluminum/silicone oxide containing solids or phases.

Preferred is particulate metal oxide selected from the group of corundum plus zirconium dioxide, zirconium mullite, zirconium corundum and aluminum silicate (except for those with phyllosilicate structure) plus zirconium dioxide and also optionally contains other metal oxides.

Unsuitable as additives for the binders are aluminum/silicone mixed oxides with layered structure, for example, metakaolins, kaolins, and kaolinite. Also unsuitable is pyrogenic, amorphous aluminum oxide.

The particulate mixed metal oxide is at least one particulate mixed oxide or a particulate mixture of at least two oxides or is present at least as a particulate mixed oxide along with at least one additional particulate oxide, wherein the particulate mixed oxide comprises at least one oxide of aluminum and at least one oxide of zirconium.

Particulate mixed metal oxides containing in each case in addition to an oxide of aluminum, also an oxide of zirconium are defined not only to include pure zirconium oxides and zirconium oxides, but also mixed oxides, for example, aluminum silicate and zirconium oxide or heterogeneous substance mixtures, i.e., consisting of several phases, which among other things consist of one or more aluminum oxide-containing and zirconium-containing solids or phases.
Preferred is the particulate mixed metal oxide according to the invention selected from one or more members of the group of a) corundum plus zirconium dioxide, b) zirconium mullite, c) zirconium corundum and d) aluminum silicate plus zirconium dioxide and may also contain additional metal oxides.

Aluminum silicates are defined here as both aluminosilicates and aluminosilicates.

Both the aluminum/silicone mixed oxides and the aluminum silicates, insofar as they are not amorphous (i.e., crystallinity or partial crystallinity is present) are preferably island silicates. In island silicates, the SiO₄ units (tetrahedral) present in the structure are not directly linked together (no Si-O-Si bonds) but instead bonds of the tetrahedral SiO₄ units to one or more Al atoms (Si-O-Al) are present. The Al atoms are coordinated in this process with 4, 5 and/or 6 oxygen atoms.

Typical representatives of these island silicates (according to Systematik der Minerale after Strunz [Strunz' Classification of Minerals], 9th edition), for example, mullite (fused and sintered mullite are meant here as well as ZrO₂-containing mullite) and sillimanite as well as other members of the sillimanite group (for example, kyanite or andalusite), wherein kyanite is particularly preferably used from the sillimanite group. Particularly preferred is an amorphous aluminum silicate (except for those with silicate structure) with greater than 50 atom% aluminum atoms based on the total of all silicone and aluminum atoms, optionally also containing zirconium/zirconium oxide, or an aluminum oxide-containing dust which is formed as a byproduct in zirconium corundum manufacture and therefore can also contain zirconium oxide in finely divided form. This and other features of the suitable particulates metal oxides or particulate mixed metal oxides of aluminum or aluminum and zirconium are described in greater detail in DE 102012113073 or DE 102012113074) and these are thus also incorporated by reference in the disclosure of the present patent.

The particulate amorphous silicone dioxide that is added to the molding mixture to increase the strength can be added as part of the particulate mixed metal oxide or separately.
In any case the statements made here on the concentration of the particulate mixed metal oxide and the particulate amorphous silicon dioxide are in each case to be understood without the other component(s). In case of doubt the components must be calculated on this basis.

In a further embodiment the additive components of the molding mixture in accordance with the invention may comprise a phosphorus-containing compound. Such an additive is preferred in the case of very thin-walled sections of a casting mold and especially in the case of cores, since in this way the thermal stability of the cores or the thin-walled section of the casting mold can be increased. This is especially significant if the liquid metal in counters and inclined surface during casting and exerts a strong erosion effect there because of the high metallostatic pressure or can lead to deformation especially of thin-walled sections of the mold. Suitable phosphorus compounds have little or no significant effect on the processing time of the molding mixtures according to the invention. Suitable representatives of this group as well as the quantities in which they are to be added are described in detail in WO 2008/046653 A1 and this is thus also incorporated by reference in the disclosure of the present patent.

Binders, water-based binders generally have poor flow capability compared with binders based on organic solvents. This means that molding tools with narrow passages and several direction changes cannot be filled as well. As a result the cores can have sections with inadequate consolidation, which in turn can lead to casting errors in the finished castings. According to an advantageous embodiment the molding material according to the invention contains a certain fraction of a flaky lubricant, especially graphite or MoS₂. Surprisingly it was found that upon addition of such a lubricant, especially graphite, complex shapes with thin-walled sections can also be produced, wherein the casting molds always have a uniformly high density and strength, so that essentially no casting defects were observed during casting. The quantity of the flaky lubricant used, especially graphite, is preferably 0.05 wt% to 1 wt%, based on the molding base material.
Instead of the flaky lubricant, surface-active substances, especially detergents, can be used to improve the flowability of the molding mixture. Suitable representatives of these compounds are described, for example, in WO 2009/056320 (= US 2010/0326620 A1). Surfactants with sulfuric acid or sulfonic acid groups in particular may be mentioned here.

In addition to the components mentioned, the molding mixture according to the invention may also contain other additives. For example, internal release agents may be added, which facilitate removal of the casting molds from the mold tool. Suitable internal lubricants are, for example, calcium stearate, fatty acid esters, waxes, natural resins or special alkyd resins.

Surprisingly it was found that the addition of an organic additive leads to improvement of the surface quality of a casting, especially in aluminum casting. The mechanism of action of the organic additives is not clear. Without being tied to this theory, the inventors assume that at least part of the organic additive burns during the casting process and thus a thin gas cushion forms between the liquid metal and the molding material forming the wall of the casting mold, thus preventing reaction between the liquid metal and the molding material. Furthermore the inventors assume that part of the organic additive forms a thin layer of so-called glossy carbon in the reducing atmosphere that prevails during casting, and this likewise prevents reaction between the metal and the molding material. As a further advantageous effect, addition of the organic additive can cause an increase in the strengths of the casting mold after curing.

It was surprising that the improvement in the surface of the casting can be accomplished with a great variety of organic additives. Suitable organic additives are, for example, phenol-formaldehyde resins, for example, novolaks; epoxy resin, for example, bisphenol-A-epoxy resins, bisphenol-F-epoxy resins or epoxidized novolaks; polyols, for example, polyethylene glycols, polypropylene glycols; glycerol or polyglycerols; polyolefins, for example, polyethylene or polypropylene, co-polymers of olefins, such as ethylene or propylene and additional co-monomers, such as vinyl acetate or styrene and/or diene monomers;
polyamides, for example, polyamide-6, polyamide-12 or polyamide-6,6; natural resins, for example, balsam resin; fatty acid esters, for example, cetyl palmitate; fatty acid amides, for example, ethylene-diamine-bis-stearamide; carbohydrates, for example, dextrins; and metal soaps, for example, oleates or oleates of divalent or trivalent metals. The organic additives may be present either as pure materials or as a mixture of various organic compounds.

The organic additives are preferably added in a quantity of 0.01 to 1 wt%, or 0.1 - 1.0 wt%, especially preferably 0.05 to 0.5 wt%, particularly preferably 0.1 - 0.2 wt%, in each case based on the molding material.

Furthermore, silanes may also be added to the molding mixture according to the invention to increase the resistance of the molds and cores to high atmospheric humidity and/or water-based molding material coatings. According to an additional preferred embodiment the molding mixture contains a fraction of at least one silane. Suitable silanes are for example, aminosilanes, epoxysilanes, mercaptosilanes, hydroxysilanes and ureidosilanes. Examples of suitable silanes are γ-aminopropyltrimethoxysilane, γ-hydroxypropyltrimethoxysilane, 3-ureidopropyltriethoxysilane, γ-mercaptopropyltrimethoxysilane, γ-glycidoxypropyltrimethoxysilane, β-(3,4-epoxycyclohexyl)trimethoxysilane and N-β-(aminoethyl)-γ-aminopropyltrimethoxysilane. Typically 0.1 to 2 wt% silane based on the binder are used, preferably 0.1 to 1 wt%.

Additional suitable additives are alkali metal siliconates, e.g., potassium methylsiliconate, of which 0.5 to 15 wt%, preferably 1 to 10 wt% and particularly preferably 1 to 5 wt% based on the binder can be used. If the molding mixture contains an organic additive, the addition of this can be done at any time in the production of the molding mixture. The addition of the organic solvent may be made in bulk or in the form of a solution. Water-soluble organic additives can be used in the form of an aqueous solution. As long as the additives are soluble in the binder and are stable therein for several months without decomposition, they can also be dissolved in the binder and thus added together with this to the molding material. Water-insoluble additives can be used in the form of a dispersion or a paste. This dispersions or pastes preferably contain water as the liquid medium.
If the molding mixture contains silanes and/or alkali methylsiliconates, they are usually added in the form in which they are incorporated in the binder in advance. However, they can also be added to the molding material as separate components.

Organic additives can also have a positive effect on the characteristics of the cores produced according to the method of the invention. For example, the carbonates mentioned in AFS Transactions, vol. 88, pp. 601 - 608 (1980), and vol. 89, pp. 47 - 54 (1981) increase the moisture resistance of the cores during storage, while the phosphorus compounds known from WO 2008/046653 (= CA 2666760 A1) increase the thermal stability of the cores.

In manufacturing the molding mixture, the refractory molding base material is placed in a mixture, and then preferably first the liquid component is added and mixed with the refractory molding base material until a uniform layer of the binder has formed on the granules of the refractory molding base material. The mixing time is selected so that intimate mixing of refractory molding base material and liquid components take place. The mixing duration depends on the quantity of the molding mixture to be produced and the mixing device used. Preferably the mixing duration is selected between 1 and 5 minutes. Then, preferably with further agitation of the mixture, the solid component(s) is added in the form of the particulate mixed metal oxides, and optionally amorphous silicone dioxide, barium sulfate or additional powdered solids are added and then the mixture is mixed further. Here also the mixing duration depends on the quantity of the molding mixture to be produced and the mixing unit used. Preferably the mixing time is selected between 1 and 5 minutes. A liquid component may be either a mixture of various liquid components or the total of all liquid individual components, wherein the latter can be added together or successively to the molding mixture. According to another embodiment first the solid components can be added to the refractory molding material and only then the liquid components be added to the mixture.

The molding material mixture is then brought into the desired form. In this process, the usual molding methods are used. For example, the molding mixture can be shot into the molding tool using a core-shooting machine with compressed air. A further possibility con-
sists of allowing the molding mixture to flow freely from the mixture into the molding tool and compacting there by shaking, stamping or pressing.

The methods according to the invention in and of themselves are suitable for manufacturing all casting molds suitable for metal casting, for example, cores and molds.

Despite the high strengths achievable with the method according to the invention, the cores produced with the molding mixture according to the invention exhibit good disintegration after casting, especially in the case of aluminum casting. However, the use of the molded articles produced from the molding mixture according to the invention is not limited to light metal casting. The casting molds are generally suitable for casting metals. Such metals include, for example, nonferrous metals such as brass or bronzes as well as ferrous metals.

The invention will be explained in greater detail based on the following, non-limiting examples.

**Examples**

1. Production of the molding mixtures
   1.1 without addition of amorphous SiO$_2$
   In each case 5 kg of quartz sand H 32 from Quarzwerke Frechen GmbH were placed in the bowl of a Hobart mixer (model HSM 10). Then the binder was added under agitation and mixed intensively with the sand. The respective quantities added are shown in the individual experiments.
   1.2 with addition of amorphous SiO$_2$
   The procedure described under 1.1 was followed with the difference that before the binder addition, 0.5 PW amorphous SiO$_2$ calculated on the basis of sand was added and mixed with this for 1 minute. The addition form is listed in the individual experiments.
2. Production and testing of the test pieces
Part of the molding mixtures produced according to 1.1 and 1.2 were placed in the reservoir of an H 1 core shooting machine Roperwerke AG. The remainders of each of the molding mixtures were stored in a carefully closed vessel before refilling the core shooting machine to protect them from drying out and from premature reaction with CO₂ present in air. The molding mixtures were shot from the reservoir by compressed air (4 bar) into a non-temperature-controlled molding tool provided with 2 engraved grooves for round cores of 50 mm diameter and 50 mm height. Then the test cores were cured. Details of this are presented with the individual experiments. After curing the test pieces were removed from the molding tool and their compression strengths were determined immediately with a Zwick Universal Testing Machine (model Z 010) immediately, i.e., a maximum of 15 seconds after removal, and after 24 hours of storage. The values listed in the tables represent means from 8 cores in each case. To largely exclude the influence of climatic changes, all test pieces used for determining the 24-hour strengths were stored in a climate-controlled chamber at 23°C and 50% relative humidity.
In the case of examples 4.01 to 4.07 the experiments were performed on an L 1 core-shooting machine from the firm of Laempe & Mossner GmbH, which was equipped with a heating tube (model HT42-13) from Hillesheim GmbH. For testing the molding mixtures, rectangular test bars with dimensions of 150 mm x 22.36 mm x 22.36 mm were produced (so-called Georg-Fischer bars). The three-part molding tool used made it possible to produce four rectangular test bars simultaneously.
Part of the molding mixture produced according to 1.2 was transferred into the reservoir of the core-shooting machine, the molding tool of which was not electrically heated. The remainder of the respective molding material mixture was stored in a carefully closed container until it was used for refilling the core-shooting machine to protect it from drying and to avoid premature reaction with the CO₂ present in the air. The molding mixtures were introduced by compressed air (4 bar) from the storage container into the molding tool and flushed with hot CO₂ or hot air. Additional information on the flushing time with compressed air or CO₂ and the gas temperature are given in [section] 6. After curing the molding tool was opened and the test bars removed.
For determining the bending strengths, the test bars were placed in a Georg-Fischer strength testing apparatus equipped with a three-point bending device and the force leading to breakage of the test bars was measured. The bending strengths were determined both immediately, i.e., a maximum of 15 seconds after removal (initial strengths) and about 24 hours after manufacturing (final strengths).

The results of the strength tests are shown in table 4. The values presented here are means from multiple determinations on at least 4 cores.

3. Curing with CO₂
3.1 To manufacture the test pieces, molding mixtures consisting of quartz sand H 32 and 2.0 PW (PW = parts by weight), 2.5 PW and 3.25 PW, respectively of a sodium water glass with a molar ratio of about 2.33 and a solids content of about 40 wt% were used. For curing, CO₂ (supplier and purity in each case: Linde AG, at least 99.5 vol% CO₂) passed through the molding mixture. The temperature of the gas at the inlet into the molding tool was between 22 and 25°C. Table 1 presents the gassing times, the CO₂ flow rate and the compressive strengths determined under these conditions (see Examples 1.01 to 1.21 and 1.29 to 1.42).

3.2 Some of the experiments according to 3.1. were repeated with the difference that 0.5 PW amorphous silicone dioxide in powder form was mixed into the molding mixtures before addition of binder. The results are also presented in Table 1 (Examples 1.22 to 1.28).

The following are apparent from Table 1 (see Appendix):

Without addition of amorphous SiO₂:

The strengths depend on the quantity of CO₂ used for curing, wherein the initial strengths increase with increasing CO₂ quantity, whereas on the other hand strengths after 24 h of storage time decrease because of the known over-gassing effect (see Examples 1.01 to 1.21), wherein the over-gassing effect as expected occurs later at higher binder fractions.
At the same absolute CO₂ volume, a low CO₂ flow has a predominantly positive effect on the initial strengths, while a high CO₂ flow on the other hand has a positive effect on the final strengths (see Example 1.03/1.08, 1.04/1.09/1.15, 1.05/1.16/1.06/1.11/1.17, 1.07/1.12/1.18, 1.14/1.20).

With addition of amorphous SiO₂:
The addition of amorphous SiO₂ causes an increase in strength compared with cores cured with the same gassing parameters but containing amorphous SiO₂ (see Example 1.22-1.28 compared with 1.08-1.14).

The loss of strength after 24 hours of storage due to over-gassing is reduced by the amorphous SiO₂ (see Examples 1.22-1.28 compared with 1.08-1.14).

Other than at long gassing times the addition of amorphous SiO₂ produces a greater increase in the initial strengths than increasing the binder content by the same amount. On the other hand, the final strengths increase substantially more greatly at elevated binder contents, but also decrease again more greatly at long gassing times because of the over-gassing effect (see Examples 1.22-1.28 compared with 1.29-1.35).

Even at the same solids content the mixture of water glass binders and amorphous SiO₂, other than at long gassing times, offers advantages in terms of the initial strengths relative to the increased binder quantity without amorphous SiO₂. In the case of the final strengths, the increased binder content on the other hand has a greater effect, wherein the decrease in strengths at long gassing times is once again pronounced because of over-gassing (see Examples 1.22-1.28 compared with 1.36-1.42).

4. Curing with air
4.1 For producing the test pieces, molding mixtures consisting of quartz sand H 32 and 2.0 PW, 2.5 PW or 3.25 PW of a sodium water glass with a molar ratio of about 2.33 and a solids content of about 40 wt% were used. For curing, compressed air was conducted through the molding mixture.
The temperature of compressed air at the inlet to the molding tool was between 22 and 25°C. In Table 2 the gassing times, the gassing pressure and the compressive strengths found under these conditions are shown (see Examples 2.01-2.03 and 2.07-2.12).

4.2 Some of the experiments corresponding to 4.1 were repeated with the difference that 0.5 PW of powdered amorphous silicone dioxide was mixed into the molding mixtures before addition of binder. These results are likewise presented in Table 2 (see Examples 2.04-2.06).

From Table 2 it can be seen that:

Without addition of amorphous SiO$_2$:
The strengths depend on the volume of air passed through, wherein the initial strengths increase more greatly with increasing air volume than the final strengths (see Examples 2.01-2.03 and 2.07-2.12).

A higher binder fraction does not necessarily result in better strengths. This can presumably be explained by the poorer compaction ability and the higher water fraction in the molding mixture (see Examples 2.01-2.03 compared with 2.07-2.12).

With addition of amorphous SiO$_2$:
The addition of amorphous SiO$_2$ causes an increase in strengths relative to cores cured with the same gassing parameters but containing no amorphous SiO$_2$, wherein a greater effect is seen on the initial strengths than on the final strengths (see Examples 2.04-2.06 compared with 2.01-2.03).

The increase in strengths caused by the amorphous SiO$_2$ is greater than that of increasing the binder content by the same amount (see Examples 2.07-2.09 compared with 2.04-2.06).

The increase in strengths produced by the amorphous SiO$_2$ is greater than that of increasing the binder content to the same solids content (see Examples 2.10-2.12 compared with 2.04-2.06).
5. Curing with a combination of CO₂ and air
5.1 To produce the test pieces, mixtures of solids consisting of quartz sand H 32 and 2.0 PW, 2.5 PW and 3.25 PW of a water glass with a molar ratio of about 2.33 and a solids content of about 40 wt% were used. For curing, first CO₂ and then compressed air were passed through the molding mixture. The temperatures of both gasses upon entering the molding tool were between 22 and 25°C.

In Table 3 the gassing times of CO₂ and air, the CO₂ flow, the gassing pressure (air) and the compressive strengths found under these conditions are shown (see Examples 3.01-3.09, 3.19-3.27, 3.37-3.45).

5.2 Some of the experiments corresponding to 5.1 were repeated with the difference that 0.5 PW powdered amorphous silicone dioxide was mixed with the molding mixtures before addition of the binder. These results are also shown in Table 3 (see Examples 3.10-3.18, 3.28-3.36 and 3.46-3.48).

5.3 Some of the experiments according to 5.1 were repeated with the difference that the compressed air passed through the molding mixtures was heated to about 100°C, measured at the entrance to the molding tool. The results are also presented in Table 3 (see Examples 3.49-3.51).

5.4 Some of the experiments according to 5.2 were repeated with the difference that the compressed air passed through the molding mixtures was heated to about 100°C, measured at the entry into the molding tool. The results are also shown in Table 3 (see Examples 3.52-3.54).

The following are apparent from Table 3:

Without addition of amorphous SiO₂:
As a result of the combined CO₂/air gassing, substantially better strengths are achieved than by gassing with CO₂ or air alone (see Examples 3.01-3.09 and 3.19-3.27 compared with 1.01-1.21 and 2.01-2.03, respectively).

Increasing the pressure during gassing with air results in a further increase in strengths (see Examples 3.43-3.45 compared with 3.04-3.06).
Heating the air used for gassing increases the final strengths (see Examples 3.49-3.51 compared with 3.04-3.06). The fact that the initial strengths do not show the same effect can probably be explained by the fact that they were still hot at the time of strength testing.

Extending the time of gassing with CO₂ does not always have positive effects on the strengths because of the over-gassing effect (see Examples 3.01-3.09 and 3.19-3.27).

Increasing the CO₂ flow causes an increase in the initial strengths, although this is disadvantageous for the final strengths (see Examples 3.01-3.09 compared with 3.19-3.27).

A higher binder fraction results in higher final strengths but not necessarily higher initial strengths. The latter can presumably be explained by the increased water fraction in the molding mixture (see Examples 3.37-3.42 compared with 3.04-3.06).

With addition of amorphous SiO₂:

The addition of amorphous SiO₂ causes an increase in strengths compared with cores cured with the same parameters but containing no amorphous SiO₂, wherein the effect on the initial strengths is greater than that on the final strengths. At higher CO₂ flow rates and/or longer CO₂ gassing times, the final strengths decrease to some extent because of the over-gassing effect (see Examples 3.10-3.18 compared with 3.01-3.09 and Examples 3.28-3.36 compared with 3.19-3.27).

The addition of amorphous SiO₂ causes a greater increase in the initial strengths than does increasing the binder content by the same amount. In the case of the final strengths, however, the effect of the increased binder strength is greater (see Examples 3.13-3.15 compared with 3.37-3.39).

Even at the same solids content the mixture of water glass binder and amorphous SiO₂ results in advantages in initial strengths versus the correspondingly increased binder quantity without amorphous SiO₂. In the case of the final strengths, on the other hand, the effect of the higher binder content is stronger (see Examples 3.13-3.15 compared with 3.40-3.42).
An increase in the pressure in the case of gassing with air brings about a further increase in strength (see Examples 3.46-3.48 compared with 3.13-3.15).

6 Curing with CO₂, air or a combination of CO₂ and air at a gassing temperature of 115 to 90°C.

6.1 For producing the test pieces, molding material mixtures consisting of quartz sand H 32 and 2.0 PW of a water glass with a molar ratio of about 2.33 and a solids content of about 40 wt% were used. Furthermore 0.5 PW powdered amorphous silicone dioxide was added to the molding mixtures before binder addition. For curing, first CO₂ and then compressed air was passed through the molding mixture. Both gases were heated to temperatures of up to 120°C using a heating tube. The temperatures of both gases on entry into the molding tool initially amounted to 115°C and declined to 90°C during the 35-second gassing. This temperature drop is attributable to the fact that the heating tube is unable to keep the gas temperature constant during gassing.

Immediately before the beginning of the experiments, experiment 4.04 was first repeated about 80 times over a period of 50 minutes, so that the molding tool had reached the necessary operating temperature of about 60°C.

In Table 4 the gassing times of CO₂ and air, the CO₂ flow, the gassing pressure (air) and the bending strengths found under these conditions are presented (see Examples 4.01-3.07).

Table 4 shows:
The values for the strengths clearly confirm that a combination of CO₂ and air gassing is distinctly superior to gassing with either air or CO₂ alone. Especially Examples 4.01-4.03, in which the curing was performed exclusively with CO₂, show distinctly lower initial values and, except for example, 4.01, also final strengths compared with Examples 4.05-4.07 of the method according to the invention.
The strengths of Example 4.04, which shows the values for gassing with air alone, are likewise significantly lower than the strengths for the combined CO\textsubscript{2}-air gassing according to the invention. Whereas the final strengths for examples 4.05-4.07 are 10-60 N/cm\textsuperscript{2} above the values for example 4.04, their initial strengths are 50-60 N/cm\textsuperscript{2} higher. Thus the distinctly higher initial strengths of Examples 4.05 to 4.07 positively demonstrate the effect according to the invention even at the elevated gas temperature of 115 to 90°C for CO\textsubscript{2} and air. Examples 4.05 to 4.07 show only slight differences from one another, but these are not significant.
Table 1 (Not according to the invention)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.01 1.02 1.03 1.04 1.05 1.06 1.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>1.08 1.09 1.10 1.11 1.12 1.13 1.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.15 1.16 1.17 1.18 1.19 1.20 1.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>1.22 1.23 1.24 1.25 1.26 1.27 1.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>2</td>
<td>0.5</td>
<td></td>
<td></td>
<td>1.29 1.30 1.31 1.32 1.33 1.34 1.35</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>1.36 1.37 1.38 1.39 1.40 1.41 1.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Sodium water glass, molar ratio approx. 2.33 (molar), Solids approx. 40%
(b) Elkem 971 U, added as dry powder
(c) Added according to the amount of binder + amorph. SiO2 in experiments 1.22 - 1.28
(d) Solids (1.3 PW = 2 PW x 40% + 0.5) corresponding to experiments 1.22 - 1.28 calculated from binder + amorph. SiO2

h = hours s= seconds
Table 2
(not according to invention)

<table>
<thead>
<tr>
<th>Exper. No.</th>
<th>Binder content [PW]</th>
<th>amorph. SiO₂ [PW]</th>
<th>Air pressure [bar]</th>
<th>Test piece storage time [h]</th>
<th>Example / Compression strengths in [N/cm²] after 30 s Air</th>
<th>45 s Air</th>
<th>60 s Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.01 2.02 2.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(a)</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>27 71 101</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.04 2.05 2.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(a)</td>
<td>0.5</td>
<td>15 s</td>
<td>24 h</td>
<td>60 126 161</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.07 2.08 2.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>(a)(c)</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>16 35 78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.10 2.11 2.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.25</td>
<td>(a)(d)</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>8 31 68</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Sodium water glass, molar ratio approx. 2.33 (molar), solids approx. 40 %
(b) Elkem 971 U, added as dry powder
(c) Addition corresponds to amount of binder + amorph. SiO₂ of experiments 2.04 -2.06
(d) Solids (1.3 PW) corresponds to that of experiments 2.4 - 2.6 calculated from binder + amorph. SiO₂

h = hours s= seconds
## Table 3

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>3.01</td>
<td>3.02</td>
<td>3.03</td>
</tr>
<tr>
<td>5.1</td>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>52</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>212</td>
<td>211</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.04</td>
<td>3.05</td>
<td>3.06</td>
</tr>
<tr>
<td>5.1</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>28</td>
<td>67</td>
<td>117</td>
</tr>
<tr>
<td>5.1</td>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>236</td>
<td>233</td>
<td>238</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.07</td>
<td>3.08</td>
<td>3.09</td>
</tr>
<tr>
<td>5.1</td>
<td>2</td>
<td>2</td>
<td>10</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>32</td>
<td>70</td>
<td>134</td>
</tr>
<tr>
<td>5.1</td>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>211</td>
<td>194</td>
<td>183</td>
</tr>
<tr>
<td>5.2</td>
<td>2</td>
<td>0.5</td>
<td>2</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>99</td>
<td>192</td>
<td>233</td>
</tr>
<tr>
<td>5.2</td>
<td>(a)</td>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>296</td>
<td>293</td>
<td>295</td>
</tr>
<tr>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.13</td>
<td>3.14</td>
<td>3.15</td>
</tr>
<tr>
<td>5.2</td>
<td>2</td>
<td>0.5</td>
<td>2</td>
<td>6</td>
<td>15 s</td>
<td>24 h</td>
<td>92</td>
<td>200</td>
<td>229</td>
</tr>
<tr>
<td>5.2</td>
<td>(a)</td>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>277</td>
<td>238</td>
<td>233</td>
</tr>
<tr>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.16</td>
<td>3.17</td>
<td>3.18</td>
</tr>
<tr>
<td>5.1</td>
<td>2</td>
<td>0.5</td>
<td>2</td>
<td>10</td>
<td>15 s</td>
<td>24 h</td>
<td>80</td>
<td>154</td>
<td>182</td>
</tr>
<tr>
<td>5.1</td>
<td>(a)</td>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>211</td>
<td>165</td>
<td>139</td>
</tr>
<tr>
<td>5.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.19</td>
<td>3.20</td>
<td>3.21</td>
</tr>
<tr>
<td>5.1</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>44</td>
<td>96</td>
<td>133</td>
</tr>
<tr>
<td>5.1</td>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>181</td>
<td>181</td>
<td>205</td>
</tr>
<tr>
<td>5.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.22</td>
<td>3.23</td>
<td>3.24</td>
</tr>
<tr>
<td>5.2</td>
<td>2</td>
<td>0.5</td>
<td>6</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>46</td>
<td>117</td>
<td>152</td>
</tr>
<tr>
<td>5.2</td>
<td>(a)</td>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>216</td>
<td>225</td>
<td>220</td>
</tr>
<tr>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.25</td>
<td>3.26</td>
<td>3.27</td>
</tr>
<tr>
<td>5.2</td>
<td>2</td>
<td>0.5</td>
<td>6</td>
<td>10</td>
<td>15 s</td>
<td>24 h</td>
<td>41</td>
<td>114</td>
<td>165</td>
</tr>
<tr>
<td>5.2</td>
<td>(a)</td>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>187</td>
<td>189</td>
<td>182</td>
</tr>
<tr>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.28</td>
<td>3.29</td>
<td>3.30</td>
</tr>
<tr>
<td>5.2</td>
<td>2</td>
<td>0.5</td>
<td>6</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>105</td>
<td>190</td>
<td>234</td>
</tr>
<tr>
<td>5.2</td>
<td>(a)</td>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>311</td>
<td>317</td>
<td>322</td>
</tr>
<tr>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.31</td>
<td>3.32</td>
<td>3.33</td>
</tr>
<tr>
<td>5.2</td>
<td>2</td>
<td>0.5</td>
<td>6</td>
<td>6</td>
<td>15 s</td>
<td>24 h</td>
<td>91</td>
<td>192</td>
<td>229</td>
</tr>
<tr>
<td>5.2</td>
<td>(a)</td>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>306</td>
<td>270</td>
<td>262</td>
</tr>
<tr>
<td>-----------</td>
<td>---------------------</td>
<td>-------------------</td>
<td>-------------------</td>
<td>--------------</td>
<td>----------------------------------------</td>
<td>-----------------------------</td>
<td>-----------------------------------------------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>5.2</td>
<td>2</td>
<td>0.5</td>
<td>6</td>
<td>10</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>3.34</td>
<td>3.35</td>
</tr>
<tr>
<td>5.1</td>
<td>2.5 (a)(c)</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>28</td>
<td>76</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>28</td>
<td>79</td>
<td>140</td>
</tr>
<tr>
<td>5.1</td>
<td>3.25 (a)(d)</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>15 s</td>
<td>24 h</td>
<td>9</td>
<td>364</td>
<td>383</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9</td>
<td>32</td>
<td>83</td>
</tr>
<tr>
<td>5.1</td>
<td>2</td>
<td></td>
<td>6</td>
<td>4</td>
<td>15 s</td>
<td>24 h</td>
<td>101</td>
<td>424</td>
<td>414</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>101</td>
<td>158</td>
<td>196</td>
</tr>
<tr>
<td>5.2</td>
<td>2</td>
<td>0.5</td>
<td>6</td>
<td>4</td>
<td>15 s</td>
<td>24 h</td>
<td>194</td>
<td>334</td>
<td>309</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>194</td>
<td>245</td>
<td>290</td>
</tr>
<tr>
<td>5.3</td>
<td>2</td>
<td></td>
<td>6</td>
<td>2 (e)</td>
<td>15 s</td>
<td>24 h</td>
<td>18</td>
<td>258</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18</td>
<td>53</td>
<td>112</td>
</tr>
<tr>
<td>5.4</td>
<td>2</td>
<td>0.5</td>
<td>6</td>
<td>2 (e)</td>
<td>15 s</td>
<td>24 h</td>
<td>31</td>
<td>294</td>
<td>276</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>31</td>
<td>78</td>
<td>151</td>
</tr>
</tbody>
</table>

(a) Sodium water glass, molar ratio approx. 2.33 (molar), solids approx. 40%

(b) Elkem 971 U, added as dry powder

(c) Addition corresponds to amount of binder + amorph. SiO₂ of experiments 1.22 - 1.28

(d) Solids (1.3 PW = 2 PW * 40% +0.5) corresponds to that of experiments 1.22 -1.28 calculated from binder + amorph. SiO₂

(e) Air preheated to 100°C (measured at inlet to molding tool) (i) no complete curing

h = hours s= seconds
Table 4

<table>
<thead>
<tr>
<th>Exper. No.</th>
<th>Binder content</th>
<th>Amorph. SiO₂</th>
<th>CO₂ time [s]</th>
<th>Air pressure bar</th>
<th>Air time [s]</th>
<th>Storage time of test pieces</th>
<th>Bending strength in [N/cm²] for a CO₂ flow of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[PW]</td>
<td>[PW]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 L/Min</td>
</tr>
<tr>
<td>6.1</td>
<td>2 (a)</td>
<td>0.5 (b)</td>
<td>35</td>
<td>4</td>
<td>0</td>
<td>15 s 24 h</td>
<td>4.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>360</td>
</tr>
<tr>
<td>6.2</td>
<td>2 (a)</td>
<td>0.5 (b)</td>
<td>0</td>
<td>4</td>
<td>35</td>
<td>15 s 24 h</td>
<td>4.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.3</td>
<td>2 (a)</td>
<td>0.5 (b)</td>
<td>1</td>
<td>4</td>
<td>35</td>
<td>15 s 24 h</td>
<td>4.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>145</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>375</td>
</tr>
</tbody>
</table>

(a) Sodium water glass, molar ratio approx. 2.33 (molar), solids approx. 40%
(b) Microsilica POS B-W 90 LD from the firm of Possehl Erzkontor GmbH, added as dry powder
Claims

1. Method for producing casting molds and cores comprising:
   Preparing a molding mixture comprising a least one refractory molding base
   material and an inorganic binder,
   Introducing the molding mixture into a mold, and
   Curing the molding mixture in the mold while flushing the molding mixture
   a) with gaseous CO₂ or a gas containing CO₂ as a first gas and
   b) a second gas, wherein the second gas contains less carbon dioxide than
      the first gas.

2. Method according to claim 1 wherein the molding material mixture is
   introduced into the air with the aid of compressed air using a core shooting
   machine and the mold is a molding tool and the molding tool is flushed with
   the first and second gas.

3. Method according to at least one of the preceding claims, wherein the mold
   either is not heatable or is heated to temperatures of less than 70°C,
   preferably less than 60°C and especially preferably less than 40°C.

4. Method according to at least one of the preceding claims, wherein the binder
   is water glass, especially water glass with a SiO₂/M₂O molar ratio of 1.6 to
   4.0, preferably 2.0 to less than 3.5 with M equal to lithium, sodium and/or
   potassium.

5. Method according to at least one of the preceding claims, wherein the
   molding material mixture contains a maximum of 1 wt%, preferably a
   maximum of 0.5 wt% and particularly preferably a maximum of 0.2 wt%
   organic compounds.

6. Method according to at least one of the preceding claims, wherein the
   second gas contains less than 10 vol% CO₂, especially less than 2 vol%
   CO₂, and especially is air or nitrogen of a mixture thereof.
7. Method according to at least one of the preceding claims, wherein the first gas contains at least 25 mol% CO₂, especially at least 50 mol% CO₂ and preferably at least 80 mol% CO₂.

8. Method according to at least one of the preceding claims, wherein the gas flow of the first and/or the second gas amounts to 0.5 to 600 L/min (standard liters), preferably to 0.5 to 300 L/min and particularly preferably 0.5 L/min to 100 L/min.

9. Method according to at least one of the preceding claims, wherein the gas flow of the first and/or the second gas amounts to 0.5 to 30 L/min (standard liters), preferably to 0.5 to 25 L/min and particularly preferably 0.5 L/min to 20 L/min, preferably when the first gas and/or the second gas is used at a temperature of 15 to 40°C.

10. Method according to at least one of the preceding claims, wherein the charging pressure of the first and/or the second gas with reference to the mold is between 0.5 bar and 10 bar, preferably between 0.5 bar and 8 bar and particularly preferably between 0.5 and 6 bar.

11. Method according to at least one of the preceding claims, wherein the ratio of the gassing time with the first gas relative to the gassing time with the second gas is 2:98 to 90:10, preferably 2:98 to 20:80 and particularly preferably 5:95 to 30:70 and especially with the first gas amounts maximally to 60% of the sum of the gassing time with the first and second gas.

12. Method according to at least one of the preceding claims, wherein the refractory molding base material is quartz-, zirconium- or chrome ore sand, olivine, vermiculite, bauxite and/or fireclay, especially with mean particle diameters of 100 to 600 μm, preferably from 150 to 500 μm.

13. Method according to at least one of the preceding claims, wherein the binder, especially water glass, up to 0.5 to 5 wt%, preferably 1 to 3.5 wt%, based on the molding base material, in the case of water glass, based on a solids fraction of 25 to 65 wt%, preferably 30 to 60 wt%.
14. Method according to at least one of the preceding claims, wherein additionally amorphous SiO₂ is used, especially synthetic amorphous SiO₂ and preferably with a mean particle size of between 0.05 μm and 10 μm, especially between 0.1 μm and 5 μm, particularly preferably between 0.1 μm and 2 μm, and independently thereof the BET surface area amounts to 1 to 200 m²/g, especially 1 to 50 m²/g and particularly preferably 1 to 30 m²/g.

15. Method according to at least one of the preceding claims, wherein the amorphous SiO₂ is used in quantities of 0.1 to 2 wt%, preferably 0.1 to 1.5 wt%, in each case based on the molding base material and independently thereof, based on the weight of the binder with 2 to 60 wt%, particularly preferably 4 to 50 wt%.

16. Method according to at least one of the preceding claims, wherein the first gas is introduced into the mold at a temperature of 15 to 120°C, preferably form 15 to 100°C and particularly preferably form 25 to 80°C, and independently thereof the second gas is introduced into the mold at a temperature within the same temperature interval or a temperature of 40 to 250°C, and preferably the temperature of the second gas upon introduction into the mold is greater than that of the first gas.

17. Method according to at least one of the preceding claims, wherein the amorphous SiO₂ used has a water content of less than 15 wt%, especially less than 5 wt% and particularly preferably less than 1 wt% and independently of this is used especially as a powder.

18. Method according to at least one of the preceding claims, wherein the first gas and the second gas are introduced into the mold in any arbitrary order and number of introduction processes, but at least temporarily separate from one another, wherein preferably the second gas is conducted through the mold last, and especially first and only once the first gas and subsequently the second gas is conducted through the mold.

19. Mold or core producible according to at least one of claims 1 to 18.