Original Paper

Diopside marble-like sintered glass-ceramics

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Experimental results on the synthesis of a new marble-like glass-ceramic material to be used for wall covering are given. The material is prepared by sintering and surface-induced crystallization of a precursor frit. In contrast to usual glass-ceramic materials similar to natural marbles and granites, where the major crystalline phase is β-wollastonite ($CaO \cdot SiO_2$), in the new material diopside ($CaO \cdot MgO \cdot 2SiO_2$) is formed. Due to the enhanced crystallization ability of the initial glasses, the duration of the heat treatment needed for the synthesis of the new materials can be considerably reduced.

Marmorähnliche gesinterte Diopsid-Glaskeramik

Es werden experimentelle Ergebnisse zur Synthese einer neuen Klasse von marmorähnlichen Glaskeramiken gegeben, die architektonische Verwendung als Wandverkleidungsmaterialien finden können. Diese Materialien werden durch das Sintern und die oberflächeninitiierte Kristallisation gefritteter Gläser hergestellt. Während in den bekannten marmor- oder granitähnlichen Glaskeramiken die sich bildende kristalline Phase hauptsächlich aus β-Wollastonit ($CaO \cdot SiO_2$) besteht, kristallisiert in den neuen Glaskeramiken Diopsid ($CaO \cdot MgO \cdot 2SiO_2$) aus. Wegen der höheren Kristallisationsgeschwindigkeit des Diopsids kann die thermische Behandlungsdauer für die neuen Materialien stark herabgesetzt werden.

1. Introduction

Glass-ceramic materials for wall and floor tiling are prepared in various countries. However, only two materials possess an appearance that may compete with good-quality marble and granite. These are the Japanese material "Neoparies" [1 and 2], whose production was started in 1974, and the Russian "Sigran" developed in 1985 [3]. Neoparies is prepared by sintering and crystallization of a frit, which is associated with the growth of needle-like crystals from the surface of the separate sintering grains. Sigran is obtained by casting and subsequent press-forming followed by a thermal treatment during which fibre-like crystals begin to grow in an outward direction from fluorine-containing liquation drops uniformly distributed in the bulk of the sample. Contrary to most glass-ceramics, the crystals observed in these two cases have sizes of the order of millimetres, which makes them appear similar to natural wall-covering materials. The main crystalline phase in Neoparies and Sigran is β-wollastonite ($CaO \cdot SiO_2$), which allows application of cheap and accessible raw materials.

The purpose of the present investigation is to demonstrate the possibility of obtaining building glass-ceramics similar to marbles by means of sintering and surface crystallization of a frit, in which the main crystal

phase formed is not $CaO \cdot SiO_2$ but diopside ($CaO \cdot MgO \cdot 2SiO_2$) or pyroxene solid solutions [4]. The CaO- and MgO-containing raw materials are also cheap and accessible, and the corresponding melts are more easily obtained and less aggressive with respect to the refractory materials than the initial substances used for the preparation of the wollastonite materials.

The formation of pyroxene solid solution permits the utilization of various waste materials, especially such containing a significant percentage of FeO and Fe_2O_3. This, however, will be the subject of another publication.

In fact, a number of glass-ceramic materials based on $CaO \cdot MgO \cdot 2SiO_2$ or pyroxene solid solutions and characterized by a high wear resistance have been known for a long time [5]. Catalyzed bulk crystallization is observed with all of these materials, the crystalline phase formed exceeding 50 to 60 wt%. The authors looked for compositions in which surface crystallization proceeds, forming a front of needles, the crystalline phase content being below 50%. These requirements and the size of the crystals obtained are decisive for the excellent appearance of marble-like sintered glass-ceramic material.

2. Experimental

Glasses of 1 kg each, having the compositions (in mol%): 55 to 65 SiO_2, 2 to 10 Al_2O_3, 0 to 4 B_2O_3, 0 to

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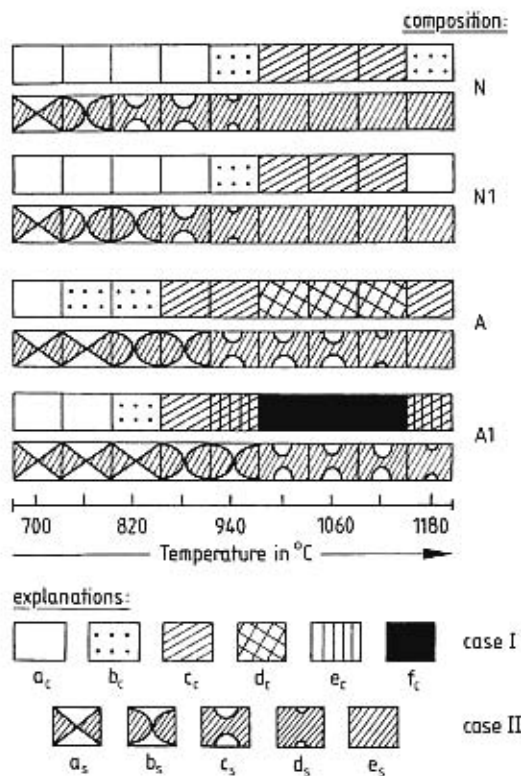Glastech. Ber. Glass Sci. Technol. 67 (1994) No. 7

Figure 1. Crystallization and sintering abilities of investigated glass frits having granulometric compositions from 1 to 10 mm as a function of temperature (schematically).
Case I: Crystallization ability. a_c: absence of crystallization, b_c: beginning of surface crystallization, c_c: surface crystallization, d_c: confluence of opposite crystallization fronts, e_c: beginning of bulk crystallization, f_c: intensive bulk crystallization.
Case II: Sintering ability. a_s: absence of sintering, b_s: edge smoothing, c_s: onset of sintering, d_s: intense sintering, e_s: complete sintering and formation of a smoothed surface.

3 BaO, 8 to 15 MgO, 8 to 15 CaO, 2 to 6 ZnO, and 2 to 10 Na_2O, were melted in corundum crucibles heated in a super kanthal furnace at 1450 to 1500 °C, maintained at this temperature for 2 h and then fritted. The raw materials used were quartz sand, dolomite, borax $CaCO_3$, $MgCO_3$, $BaCO_3$, ZnO, Al_2O_3 and Na_2CO_3. The frits were broken and sieved. The fractions thus obtained (1 to 10 mm) were placed in refractory moulds and heated with a rate of 7 K/min up to different temperatures ranging from 700 to 1180 °C at intervals of 60 K. Simultaneous experiments with isothermal heat-treating of the samples at the same temperatures for 40 min were also performed. The sintering ability of the frits and the surface crystallization of individual grains and formation of the front of needle-like crystals of $CaO \cdot MgO \cdot 2SiO_2$ were determined for each sample, using an empirically derived schedule for assessing the experimental results (figure 1).

One of the most suitable composition (denoted as composition A) consisted of (in mol%): 60 SiO_2, 4 Al_2O_3, 2 B_2O_3, 11.75 CaO, 11.75 MgO, 4 ZnO, 1.5 BaO and 5 Na_2O [4]. On its basis, a series of glasses with colouring agents of different kinds and concentrations were also melted.

A fritted glass consisting of (in mol%): 63.4 SiO_2, 4.5 Al_2O_3, 0.9 B_2O_3, 19.6 CaO, 5.2 ZnO, 1.7 BaO, 3.1 Na_2O, 1.4 K_2O and 0.1 Sb_2O_3 was also prepared. This composition, denoted as composition N, is identical with that used in production of Neoparies [2]. Coloured glasses based on this composition were also melted and fritted.

All these frits were subjected to thermal treatment as already described.

Figure 1 illustrates the crystallization and sintering abilities of samples of fritted glasses A, A1, N and N1 after isothermal heat treatment at the same temperature for 40 min. Compositions A1 and N1 are identical with A and N but contain additionally 1 wt% Cr_2O_3. A significantly higher crystallization ability of compositions A and A1, making sintering at lower temperatures difficult, was observed. It has been found that Cr_2O_3 produces no substantial change in the crystallization and sintering of composition N1 with respect to those of composition N, while in the case of A1 (in contrast to A), bulk crystallization also takes place, and complete sintering is observed only at 1180 to 1200 °C. It is known that Cr_2O_3 is a typical initiator of bulk crystallization in pyroxene glass-ceramic materials [5].

Figure 2 gives the DTA curves of N, A and A1 samples. Obviously, the diopside compositions display a considerably higher crystallization ability than the wollastonite ones. Composition A1 surpasses composition A in this respect. It is seen also that the addition of the refractory Cr_2O_3 oxide increases by 10 to 20 K the glass-transformation temperature (T_g), the temperature of crystallization peak (T_c) and the liquidus temperature (T_l).

To obtain glass-ceramic samples of composition A with sizes $(10 \times 10 \times 2)$ cm^3, a frit with grain sizes of 1 to 10 mm was placed in ceramic moulds and heated with a rate of 10 to 15 K/min up to 1170 to 1180 °C. After heat treatment of the samples at this temperature for 20 min and subsequent cooling at a rate of 10 K/min, the samples were cut and polished. They showed no difference in appearance when compared with Neoparies samples. It should be noted that the preparation of a marble-like material with the composition N at these heating and cooling rates requires a two-step heat treatment for several hours to allow the same extent of crystallization. The marble-like glass-ceramics with composition A may be obtained even after isothermal heat treatment at a temperature of 1150 °C for 30 min and subsequent cooling at a rate of 10 to 15 K/min.

Under the same temperature conditions, a number of coloured samples were also obtained using composition A-based coloured frits. Compositions containing more than 0.7 to 1 wt% Cr_2O_3 are an exception. They require a sintering temperature higher by 20 to 30 K.

Figure 3 shows the X-ray patterns of a crystallized sample of composition N and of samples obtained from compositions A, A1 and A2. Composition A2 is identical with A, but it contains additionally 1.5 wt% Cr_2O_3.

The crystalline phase for composition N is β-wollastonite, whereas in the new materials of series A the crystalline phase diopside is formed. In the case of compositions A2 there also crystallizes cristobalite, which most probably is due to the higher temperature (1200 °C) and the prolonged heat treatment.

The crystal growth rates of the corresponding crystal phases in compositions A and N were measured at different temperatures and the curves illustrating the temperature dependence of the respective growth rates are plotted in figure 4. The growth rate of composition A is constant with time. The growth rate of composition N was determined for samples heat-treated for 1 h. The maximum growth rate of diopside for composition A is found to be 3 times higher than that for β-wollastonite in composition N. At 850 to 1180 °C the mean growth rate of diopside is even more than 5 times higher than the crystal growth rate in composition N.

Polished specimens were prepared from samples of composition A, obtained after isothermal heat treatment at a temperature of 1165 °C, and microphotographs were taken (figures 5a and b, 6, 7a and b). They exhibit a pronounced surface crystallization of a typical front of needles [6] oriented perpendicular to the intergrain boundary of the initial glass particles. Figures 7a and b present pictures of separate diopside crystals cut perpendicular to the growth direction (which is most probably the c-axis). This is the typical picture of skeletal crystal growth morphology.

Amounts of 200 kg of composition A and three more compositions on its basis coloured with Cr_2O_3, CoO and MnO_2, respectively, were melted and fritted under large-scale pilot plant conditions in a gas-fired pot furnace. Samples (up to $(50 \times 50 \times 2)$ cm^3) of white, light green, light blue and pink materials not differing from those obtained under laboratory conditions were prepared in a silit furnace at heating and cooling rates of 5 to 10 K/min and with constant temperature heat treatment at 1180 to 1200 °C for 30 to 40 min.

The basic physicomechanical and thermal properties of the samples thus obtained were also determined. The results are given in table 1 along with data concerning Neoparies and Sigran as well as data for natural marbles and granites.

Included are also details on the chemical resistance of the glass-ceramics with compositions A and N, as well as of granite. Grained glass samples (size from 0.4 to 0.5 mm) were used in a standard procedure in which ca. 2 g were treated 1 h at 95 °C in 65 to 70 cm^3 solution (either 0.01 mol/l HCl or 0.01 mol/l NaOH). The percentage of weight loss is given in table 1. Such low concentrations were used as they resemble in some respect real conditions of atmospheric corrosion.

Evidently, all three glass-ceramic materials considerably surpass the natural materials in their properties, the diopside material obtained exhibiting no essential difference from the known wollastonite materials.
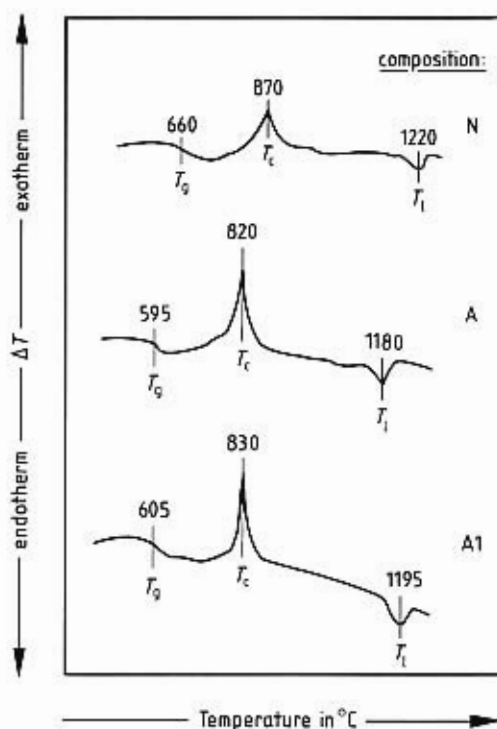

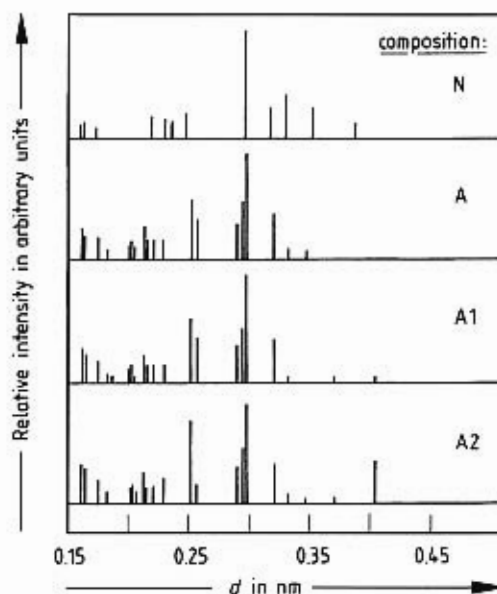Figure 2. DTA curves of powdered frits at a heating rate of 7.5 K/min.

Figure 3. X-ray patterns of samples with different compositions.

3. Conclusions

The preparation of glass-ceramic materials by a sinter-crystallization process allows the production of glass-ceramic plates having dimensions of up to $(100 \times 100 \times 2)$ cm^3, which is difficult to be achieved by other technologies. In addition, the use of various coloured frits permits the preparation of high-quality ornamental materials where diverse colours are shaded into one another.
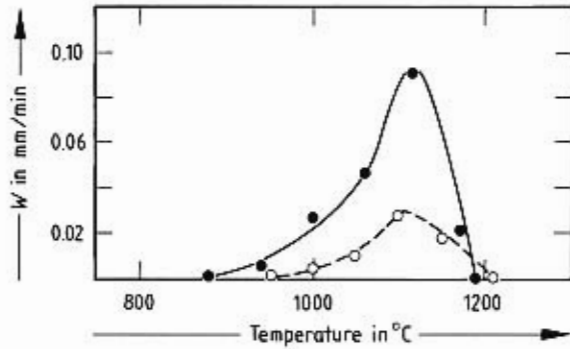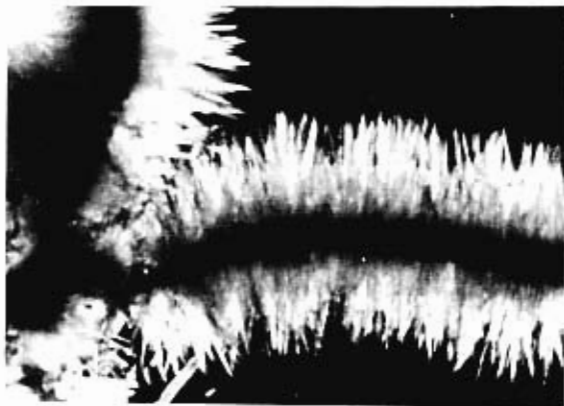
Figure 4. Crystal growth rate as a function of temperature. Solid line: composition A, broken line: composition N.

Figure 6. Optical microscope photograph of a thin section of a sintered surface-crystallized frit of composition A at 1165 °C after heat treatment of 30 min.

a) ⊢—————————————————⊣ 1 mm

a) ⊢—————⊣ 0.1 mm

b) ⊢—————⊣ 1 mm

Figures 5a and b. Optical microscope photographs (under crossed Nicols) of thin sections of a sintered surface-crystallized frit of composition A at 1165 °C after a heat treatment of a) 10 min, b) 20 min.

b) ⊢————⊣ 10 μm

Figures 7a and b. Optical microscope photographs (under crossed Nicols) of thin sections of a sintered surface-crystallized frit of composition A at 1165 °C after heat treatment of 40 min; a) needle-shaped crystals cut perpendicular to the growth direction, b) detail of figure a) at higher magnification.

It is worth noting that samples of composition A are similar to natural wall-covering materials even without grinding and polishing, while without additional treatment samples of composition N have a poor flame-polished appearance. Most probably this difference can be attributed to the fact that in the case of compositions A crystallization preceds at the end of sintering and the formation of a smooth surface beomes possible as a result of which the surface grains are well-shaped 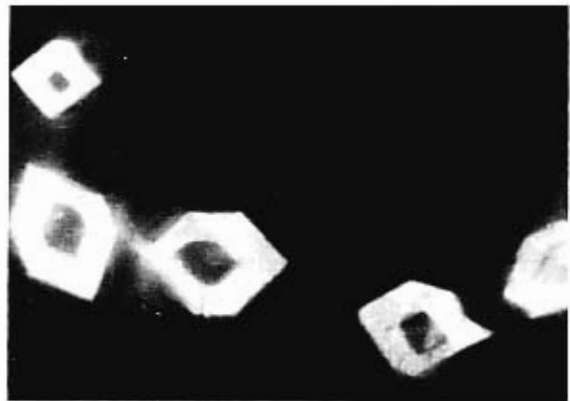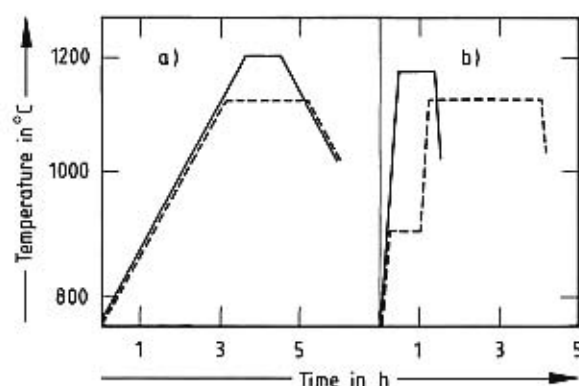and clearly seen. This as well as the high microhardness and chemical durability allows the direct use of diopside marble-like glass-ceramics for floor coverings and similar applications.

Table 1. Properties of architectural glass-ceramic and natural materials

	diopside marble-like glass-ceramics	Neoparies	Sigran	marble	granite
density in kg/m^3	$2.8 \cdot 10^3$	$2.7 \cdot 10^3$	2.6 to $2.8 \cdot 10^3$	2.6 to $2.7 \cdot 10^3$	2.6 to $2.8 \cdot 10^3$
bending strength in MPa	40 to 50	50	30 to 70	10 to 18	12 to 20
Mohs hardness	6.5 to 7	6.5	6 to 7	3.5 to 4	5.5 to 6.5
coefficient of thermal expansion (at 20 to 400 °C) in $10^{-6} K^{-1}$	6.5 to 7.0	6.2	8.0 to 8.5	9.0 to 20	5.0 to 15
chemical resistance in wt% 0.01 mol/l HCl 0.01 mol/l NaOH	0.3 0.5	0.7 1.0	– –	– –	2.2 2.5

Figures 8a and b. Heat treatment regimes used for the production of marble-like ceramics of compositions A (solid line) and N (broken line) at heating and cooling rates of a) 2 K/min, b) 20 K/min.

The two processes determining the heat treatment regime in the production of marble-like glass-ceramics are sintering and crystallization. The more intense the crystallization and the broader its temperature range, the more the sintering process is inhibited. Temperatures close to the liquidus temperature are to be attained in order to ensure that sintering comes to completion and that smooth surfaces are obtained. However, in the case of glasses with low crystallization ability, where sintering ends at lower temperatures, a much longer time is needed for completion of the crystallization process.

Figures 8a and b show the regimes of thermal treatment for compositions A and N with a maximum grain size of 10 mm and heating and cooling rates of 2 K/min (figure 8a) and 20 K/min (figure 8b), respectively. It is obvious that at high heating and cooling rates composition A permits a substantial reduction of the duration of the thermal treatment.

The present contribution is meant to give an outline of a new series of marble-like tiling glass-ceramic materials to be produced by sinter-crystallization.

4. References

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