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·SiO₂), in the new material diopside (CaO·MgO·2SiO₂) 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-Glasthermik

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 gefertigter Gläser hergestellt. Während in den bekannten marmor- oder granitähnlichen Glaskeramiken die sich bildende kristalline Phase hauptsächlich aus β-Wollastonit (CaO·SiO₂) besteht, kristallisiert in den neuen Glaskeramiken Diopsid (CaO·MgO·2SiO₂) aus. Wegen der höhern Kristallisationsgeschwindigkeit der Diopside kann die thermische Behandlungszeit für die neuen Materialien stark reduziert 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 liquid droplets 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·SiO₂), 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·SiO₂ but diopside (CaO·MgO·2SiO₂) 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 Fe₂O₃. This, however, will be the subject of another publication.

In fact, a number of glass-ceramic materials based on CaO·MgO·2SiO₂ or pyroxene solid solutions and characterized by a high wear resistance have been known for a long time [5]. Cationic bulk crystallization is observed with all of these materials, the crystalline phase formed exceeding 50 to 60% of the total content. In the authors' experiments, 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 SiO₂, 2 to 10 Al₂O₃, 0 to 4 B₂O₃, 0 to
A fired glass consisting of (in mol%): 63.4 SiO₂, 4.5 Al₂O₃, 0.9 B₂O₃, 19.5 CaO, 5.2 ZnO, 1.7 BaO, 3.1 Na₂O, 1.4 K₂O and 0.1 Sb₂O₃ was also prepared. This composition, denoted as composition N, is identical with that used in production of Neoparities [2]. Coloured glasses based on this composition were also melted and fired.

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 were identical with A and N but contain additionally 1 w% Cr₂O₃. A significantly higher crystallization ability of compositions A and A1, making sintering at lower temperatures difficult, was observed. It has been found that Cr₂O₃ 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 Cr₂O₃ 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 Cr₂O₃ oxide increases by 10 to 20 K the glass-transformation temperature (Tₜ), the temperature of crystallization peak (Tₜ) and the liquidus temperature (Tₗ).

To obtain glass-ceramic samples of composition A with sizes (10 × 10 × 2) mm³, 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 Neoparities 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 w% Cr₂O₃ 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 w% Cr₂O₃.
The crystalline phase for composition N is $\beta$-wollastoni-ite, 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 ($1200^\circ$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 $\beta$-wollastonite in composition N. At 850 to $1180^\circ$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 $1165^\circ$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 $1200^\circ$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 $95^\circ$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.

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.

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.

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 precedes at the end of sintering and the formation of a smooth surface becomes 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.

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

<table>
<thead>
<tr>
<th></th>
<th>diopside marble-like glass-ceramics</th>
<th>Neoporics</th>
<th>Sigran</th>
<th>marble</th>
<th>granite</th>
</tr>
</thead>
<tbody>
<tr>
<td>density in kg/m³</td>
<td>2.8 ( \times 10³ )</td>
<td>2.7 ( \times 10³ )</td>
<td>2.6 to 2.8 ( \times 10³ )</td>
<td>2.6 to 2.7 ( \times 10³ )</td>
<td>2.6 to 2.8 ( \times 10³ )</td>
</tr>
<tr>
<td>bending strength in MPa</td>
<td>40 to 50</td>
<td>50</td>
<td>30 to 70</td>
<td>10 to 18</td>
<td>12 to 20</td>
</tr>
<tr>
<td>Mohs hardness</td>
<td>6.5 to 7</td>
<td>6.5</td>
<td>6 to 7</td>
<td>3.5 to 4</td>
<td>5.5 to 6.5</td>
</tr>
<tr>
<td>coefficient of thermal expansion (at 20 to 400°C) in ( 10^{-6} ) K⁻¹</td>
<td>6.3 to 7.6</td>
<td>6.2</td>
<td>8.0 to 8.5</td>
<td>9.0 to 29</td>
<td>5.0 to 15</td>
</tr>
<tr>
<td>chemical resistance in wt%</td>
<td>0.01 mol/l HCl</td>
<td>0.3</td>
<td>0.7</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>0.01 mol/l NaOH</td>
<td>0.3</td>
<td>1.0</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

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.

4. References