Original Paper

Development of wall-covering glass-ceramics from raw materials

Salwa A. M. Abdel-Hameed

Glass Research Dept., National Research Center, Cairo (Egypt)

The possibility of producing wall-covering glass-ceramic materials from raw materials by crystallization of the glass is demonstrated. Glass-ceramics based on β-wollastonite and diopside with various ratios were designed from raw materials such as limestone and dolomite. The phases crystallized were examined by X-ray analysis. Thermal expansion and mechanical properties such as bending strength and microhardness for glasses and glass-ceramics were measured.

1. Introduction

The present paper describes an attempt to show the possibility of using raw materials such as limestone, dolomite and sand for the production of wall-covering glass-ceramic materials based on β-wollastonite and diopside which, in addition to their attractive appearance similar to that of granite, possess physico-mechanical and thermal properties surpassing those of natural wall-covering materials.

Glass-ceramics obtained from crystallization of glass compositions located in the ternary $SiO_2-CaO-MgO$ system may contain several crystalline phases such as wollastonite, forsterite, diopside, protoenstatite and akermenite. Owing to the peculiar durability and mechanical properties of the phases present in these glass-ceramics, they may be suitable for many applications [1], but initiation of internal bulk crystallization is relatively difficult in these glasses owing to nucleation problems [2].

There are two kinds of glass-ceramic wall-covering materials that are produced by sintering and crystallization of the frits [3]. These are the Japanese "Neoparies" [4 and 5] with β-wollastonite ($CaO \cdot SiO_2$) as the main phase and a similar material developed by a Bulgarian team [6], the major crystalline phase in this case being diopside ($CaO \cdot MgO \cdot 2SiO_2$). These two kinds of materials have an appearance similar to that of natural marble, and physico-mechanical and thermal properties that considerably surpass the properties of natural wall-covering materials. The absence of nucleating agents allow surface crystallization to take place, which produces the excellent appearance of these products.

The purpose of the present paper is to demonstrate the possibility of obtaining wall-covering glass-ceramics by crystallization of frits prepared from raw materials.

2. Experiments

The glass-ceramic compositions (table 1) were formulated through a modification to the CIPW chemico-mineral norm [7] to yield compositions of the β-wollastonite and diopside. This norm is a hypothetically calculated composition from the chemical composition of the rock or glass; CIPW refers to the initials of the researchers Cross, Iddings, Prisson and Washington who created the norm in 1903.

Egyptian limestone, dolomite and sand (≈ 95.8 % in total with Na_2CO_3 (≈ 4 %) were used as starting materials. The chemical compositions of the starting raw materials are listed in table 2. Well mixed 100 g of the batch materials were melted in a platinum crucible in an electrically heated Globbar furnace at 1500 °C for 3 h with occasional swirling every 30 min to ensure homogenization. The homogeneous glass obtained was cast into 2 cm diameter discs with 1 cm thickness and $(10 \times 1 \times 1)$ cm^3 rectangular rods and transferred to the electrically heated furnace at 650 °C which was then switched off.

The effect of heat treatment on crystallization was studied in glass samples isothermally cured at temperatures ranging from 900 to 1000 °C at ≈ 50 K intervals for 2 h. The nucleation effects were studied in glass samples heated for 2 h at 700 °C followed by heat treatment at 1000 °C for 2 h.

Table 1. Chemical compositions (in mol%) of the initial glasses

glass samples	CaO	MgO	SiO$_2$	Na$_2$O
G1	26.20	21.70	47.89	4.21
G2	28.47	19.42	47.87	4.24
G3	30.77	17.10	47.86	4.27
G4	33.10	14.76	47.85	4.29
G5	35.46	12.38	47.84	4.32

Table 2. Chemical compositions (in wt%) of the starting materials used

oxide	limestone (Samalout (Egypt))	dolomite (Ataqua (Egypt))
SiO$_2$	0.27	1.02
Al$_2$O$_3$	0.39	0.95
MgO	0.18	39.61
CaO	99.16	58.42

Figure 1. X-ray diffraction analysis of sample G3 heat-treated at various temperatures.

X-ray powder diffraction analyses of the heat-treated glass were carried out using a Philips PW 1390 X-ray diffractometer with nickel-filtered CuK$_\alpha$ radiation. The instrument settings were maintained for all the analyses by using an external standard silicon disc.

The linear thermal expansion coefficients were determined for glasses and their crystalline products using specimen rods of ≈1.5 to 2 cm length that were heated at a rate of 5 K/min from room to softening temperature for glass and to 700 °C for glass-ceramics.

The indentation hardness measurements were performed with a load of 100 g using a Shimadzu microhardness tester for glasses and glass-ceramics. HV in N/mm^2 was calculated from the equation:

$$HV = 2\,P\,\sin(\theta/2)/l^2$$

where P is the load in N, θ the angle between opposite faces = 136°, and l the length of the diagonal.

Bending strength of the glass-ceramics was measured using a 3-point bending tester. The bending strength, B, (in MPa) of the tested samples was calculated from the relation

$$B = 3\,P\,L/(2\,b\,D^2)$$

where P is the load of rupture, L the span, b the width and D the thickness of the sample, respectively.

3. Results

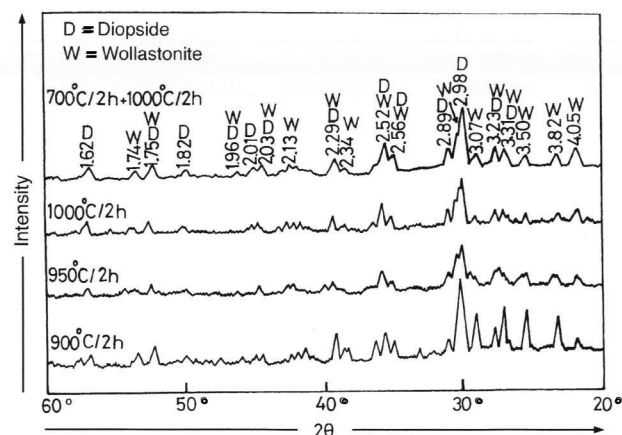The samples obtained have a smooth surface, and they are very appropriate for use as covering materials.

Figure 1 shows the results from X-ray phase analysis of glass G3 heat-treated at 900 to 1000 °C with 50 K interval and at 700 and 1000 °C for 2 h each. The crystalline phases are: β-wollastonite and diopside. It is noticed that β-wollastonite is the first phase crystallized at lower temperature (900 °C/2 h) (note the d-values in nm: 0.382, 0.350, 0.331, 0.323 and 0.307 (given in $\mathring{A}$ in figure 1)) with minor diopside. Increasing the temperature to 1000 °C for 2 h leads to an increase of the diopside over β-wollastonite. The intensity of X-ray peaks becomes sharper by using double-stage heat-treatment.

All glasses investigated are similar in their crystallization behavior but differ in the percentage of crystallized phases, where β-wollastonite is increased from 10 % in G1 to 50 % in G5 at the expense of diopside, as the compositions are designed. For all glass compositions heat-treated at the same temperature – as expected – increasing the content of MgO at the expense of CaO results in a decrease of the peak intensity of wollastonite and an increase in diopside phase.

Studying the microstructure of the crystalline glasses obtained from isothermal heat treatments at 1000 °C/2 h shows that all glass-ceramics have a coarse-grained texture due to surface crystallization but increasing the CaO:MgO ratio from G1 to G5 (i.e., by increasing the wollastonite over the diopside phase) results in much more relatively fine-grained textures. For example, G2 heat-treated at 1000 °C/2 h shows a coarse-grained microstructure of fair-sized stellate pyroxenic growths while G4 shows an interlocking fine-grained anhedral intergrowths of diopside stippled by light granules of wollastonite. G5 with 50 % wollastonite exhibits a uniform fine-grained texture of minute shapeless growths.

The measurements of thermal properties, i.e., transition (T_g) and softening (T_s) temperatures as well as the thermal expansion coefficient (α), of the studied glasses and their corresponding glass-ceramics are given in table 3 and figures 2 and 3.

Table 3. Thermal properties of β-wollastonite-diopside glasses and their corresponding glass-ceramics

| glass no.	thermal treatment at °C/2 h	expansion coefficient α in 10^{-6} K						T_g in °C	T_s in °C	identified phases
		20 to 200	20 to 300	20 to 400	20 to 500	20 to 600	20 to 700			
G1	none	8.1	8.2	8.4	8.6	–	–	611.7	636.3	amorphous
	1000	10.2	10.4	10.4	10.2	11.8	12.4	–	–	D+W
G2	none	8.8	9.0	9.2	9.4	–	–	617.7	648	amorphous
	1000	9.1	9.1	9.3	9.7	11.4	11.4	–	–	D+W
G3	none	9.0	9.0	9.2	9.2	–	–	617.9	654.8	amorphous
	1000	8.8	8.9	8.8	8.7	10.0	10.3	–	–	D+W
G4	none	8.7	8.9	9.0	9.1	–	–	607.3	635.3	amorphous
	1000	8.4	8.6	8.8	9.0	12.9	14.2	–	–	D+W
G5	none	9.0	9.1	9.2	9.3	–	–	613.4	646.4	amorphous
	1000	8.2	8.4	8.6	8.9	10.7	11.4	–	–	D+W

Note: D = diopside, W = wollastonite.
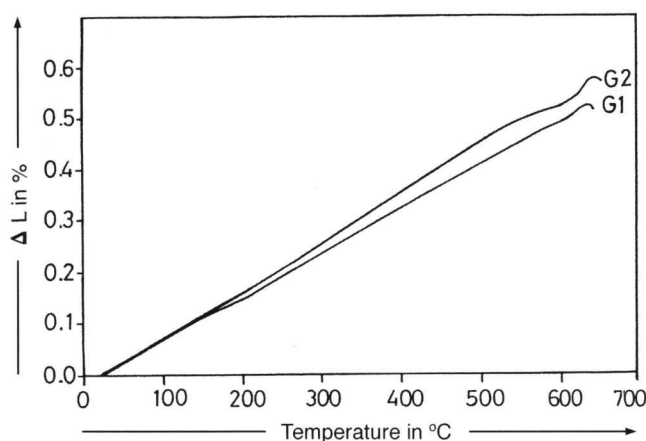
Figure 2. Thermal expansion coefficient of some selected glass samples.
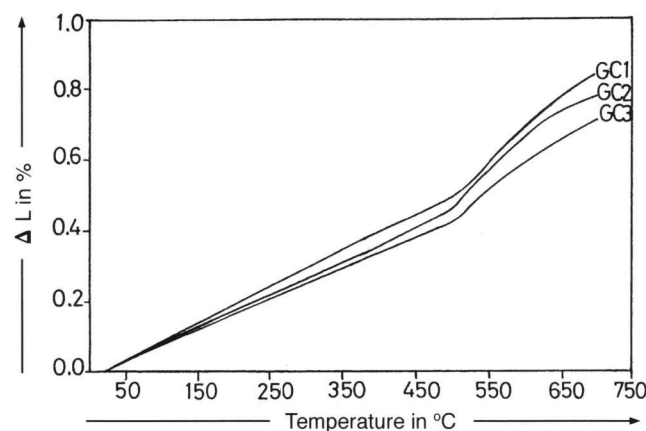

Figure 3. Thermal expansion coefficient of some selected glass-ceramic compositions heat-treated at 1000 °C/2 h.

In general, the thermal expansion coefficient of glasses increases slightly by increasing the β-wollastonite percentage. The same behavior is noticed for T_s which increases from 636.3 °C in G1 to 654.8 °C in G3 then decreases slightly to 646.4 °C in G5.

Table 4. Microhardness and bending strength measurements of some selected glass-ceramic samples heat-treated at 1000 °C/2 h

glass samples	microhardness in N/mm^2	bending strength in MPa
G1	504.8	36.412
G2	–	–
G3	588.6	–
G4	623.2	62.984
G5	–	70.029

Thermal expansion is one of the properties which are highly sensitive to structural cohesiveness. It is found that in silicate glasses, the expansion coefficient values increase with the decrease of the electrostatic bond strengths of the cations present in the glass structure [8]. The small cations (i.e. Mg^{2+}), with higher field strengths, seem to produce stronger bond structures than larger cations (i.e. Ca^{2+}), and consequently, the smaller cations-based glasses are generally characterized by lower expansion coefficients [9]. Though the thermal expansion coefficient is increased from G1 to G5 where Mg^{2+} is decreased and Ca^{2+} increased.

The opposite observation is made for glass-ceramics where the thermal expansion coefficient is decreased by increasing the β-wollastonite percentage. A transformation from $\beta \rightarrow \alpha$ wollastonite appears in the range 496 to 518 °C. Such transformations are shown in figure 3 where the thermal expansion coefficient is increased suddenly by about 2×10^{-6}/K.

The temperature for the $\beta \rightarrow \alpha$ wollastonite transformation in solid state reaction is 1125 °C [10], while in glass-ceramics the transformation is decreased to about 506 °C. Ions of high field strength such as Mg^{2+} can possibly act as surface-active agents to lower the interfacial energy (tension) between the crystal and the glass [11 and 12].

Tests on the bending strength for samples heat-treated at 1000 °C/2 h have shown that for none of the samples it is below 30 MPa (table 4). This value is twice

as high as that of natural marbles and granite [3]. The bending strength values are increased from G1 ≈ 36 MPa to G5 ≈ 70 MPa by increasing the β-wollastonite percentage.

The microhardness values (table 4) are in most cases higher than those of granites, which leads to a higher wear resistance. It should be noted that the increasing microhardness is a result rather of the total amount of the crystal phases formed than of the nature of the phases separated in the materials [3]. According to Moh's scale these β-wollastonite-diopside glass-ceramics show values of ≈5.5.

It is noticed that the increase of MgO content generally results in lower hardness and bending strength values. This is related to the pore growth process owing to the difference in density between crystals (≈2.73 g/cm^3) and residual glass (≈2.66 g/cm^3) and also to the phase separation in the glass phase which increases the viscosity [13] at high content of MgO retarding the escape of gases during glass melting and casting [2]. In order to ensure zero porosity, the molten batch is held for 2 to 3 h at higher temperature (1550 °C) with occasional swirling to achieve a homogeneous and air-bubble free melt.

4. Conclusion

Wall-covering glass-ceramic materials based on crystallization of β-wollastonite and diopside were produced from raw materials such as limestone and dolomite. β-wollastonite is the first crystalline phase followed by crystallization of diopside. Increasing the crystallization of β-wollastonite over diopside, i.e. the CaO:MgO ratio, leads to more relatively fine-grained textures. This also leads to a decrease in thermal expansion coefficient and an increase in bending strength and microhardness. The bending strength of all the glass-ceramics is between 36 to 70 MPa, which is higher than twice the value of natural marble and granite. The microhardness is also higher than that of granite.

5. References

[1] Baldi, G.; Generali, E.; Leonelli, C.: Effects of nucleating agents on diopside crystallization in new glass-ceramics for tile-glaze application. J. Mat. Sci. **30** (1995) p. 3251−3255.
[2] Alizadeh, P.; Marghussian, V. K.: The effect of compositionl changes on the crystallization behavior and mechanical properties of diopside-wollastonite glass-ceramics in the SiO$_2$-CaO-MgO(Na$_2$O) system. J. Eur. Ceram. Soc. **20** (2000) p. 765−777.
[3] Karamanov, A.; Gutzow, I.; Chomakov, I. et al.: Synthesis of wall-covering glass-ceramics from waste raw materials. Glastech. Ber. Glass Sci. Technol. **67** (1994) no. 8, p. 227−230.
[4] Strand, Z.: Glass-ceramic materials. Amsterdam et al.: Elsevier, 1986.
[5] Nakamura, S.: Crystallized glass article having a surface pattern. U.S. pat. no. 3 955 989. Publ. date 11 May 1976.
[6] Karamanov, A.; Penkov, I.; Gutzow, I. et al: Diopside marble-like glass ceramics. Bulg. pat. no. 50879. Publ. date 13 July 1990.
[7] Abdel-Hameed, S. A. M.: Controlled crystallization of some Egyptian basalt-based glasses. Zagazig Univ., M. Sc. thesis 1995.
[8] Takahashi, K.: Calculating the expansion coefficient of silicate and borosilicate glasses. Bull. Foc. Eng. Yokohama Not. Univ. 2, 145.
[9] Uhlmann, D. R.: The energetics of nucleation. Ind. Eng. Chem. **57**, p. 19−31.
[10] Kotsis, I.; Balogh, A.: Kinetics of isothermal solid state reaction of β-wollastonite synthesis from natural raw materials. Ceram. Int. 20 (1971) no. 2, p. 119−125.
[11] Hillig, W. B.: A theoretical and experimental investigation of nucleation leading to uniform crystallization of glass. In: Proc. Symp on Nucleation and Crystallization in Glasses and Melts. Columbus, OH: Am. Ceram. Soc. p. 77.
[12] Doremus, R. H.: Glass science. 2nd ed. New York: Wiley, 1994.
[13] Mazurin, O. V.; Porai-Koshits, E. A.: Phase separation in glass. Amsterdam: North-Holland, 1994.

Contact:

Dr. Salwa A. M. Abdel-Hameed
Glass Research Department
National Research Center
P. Code 12622
Dokki, Cairo
Egypt
E-mail: Salwa_NRC@hotmail.com