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NON-ISOTHERMAL CRYSTALLIZATION OF CORDIERITE GLASSES

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Abstract

A study is reported of the crystallization behaviour of some glass compositions which belong in the system $MgO–Al_2O_3–SiO_2$ and which lead to vitreous ceramics with α-cordierite as a main phase. DTA, X-ray diffraction and dilatometric analysis were used to investigate the influence of the type and concentration of the nucleation agents. The activation energies of crystallization were calculated and the crystalline phases were identified.

Keywords: cordierite, non-isothermal crystallization, vitreous-ceramic

Introduction

The crystallization of glasses from the system $MgO–Al_2O_3–SiO_2$ is a complex process, due to the large number of meta-steady phases which appear [1]. During recent years, many workers have investigated the synthesis of vitro-ceramics based on cordierite, in consequence of their high chemical stability and resistance to thermal shock.

The synthesis of homogeneous products through the melting of common raw materials (such as alumina, silica or magnesium carbonate) is a difficult task as it requires high melting temperatures (>1500°C). An alternative is to use talc and kaolinite, on substitution of the inert oxide raw materials the melting temperature drops to 1400–1450°C [2–4]. Addition of nucleating agents such as TiO_2, ZrO_2, CeO_2, or mixtures of them, leads to a controlled crystallization of cordierite, as primary phase, at lower temperature, and also allows control of the glass/crystal ratio and the size and shape of the crystals.

The present work involves an investigation of the effects of such additives and of various nucleating and crystallization treatments on the crystallization kinetics of these glasses.

Experimental

Preparation of vitreous-ceramic materials

The raw materials used for the synthesis of the ceramics are detailed in Table 1, whilst Table 2 lists the oxide compositions that were melted.

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Table 1 Chemical analysis of raw materials (mass%)

Compound	Kaolinite	Talc	Calcined alumina	TiO_2
SiO_2	52.63	61.49	–	0.50
Al_2O_3	28.40	0.48	99.00	traces
TiO_2	0.50	0.10	–	97.60
Fe_2O_3	1.70	0.50	–	0.15
CaO	2.24	1.85	–	0.55
MgO	6.09	30.62	–	0.45
Na_2O	1.07	0.10	0.70	0.10
K_2O	1.50	–	0.10	0.20
L.O.I.	5.87	4.86	0.20	0.10

Table 2 Oxide compositions of the glasses (mass%)

Glasscode	Components					
	SiO_2	Al_2O_3	MgO	CaO	TiO_2	CeO_2
C-3	50.4	32.9	15	1.7		
C-3.0	45.2	29.54	13.5	1.48	10.28	
C-3.1	47.7	31.1	14.3	1.6	5.3	
C 3.2	46.3	30.2	13.8	1.5	8.2	
C-3.8	44.3	29.0	13.2	1.5	7	5
C-3.9	49.4	32.3	14.7	1.6	2	

The compositions C-3.3, 3.4 and 3.5 contain 10%, 5% and 8%, respectively, of CeO_2 as nucleating agent, whilst compositions C-3.6 and 3.7 contain 5% and 8%, respectively, of ZrO_2.

The vitreous materials were obtained by melting the raw materials, weighed and homogenized in platinum crucibles, in electric furnaces at temperatures ranging from 1400 to 1450°C, depending on the composition. The homogeneous materials obtained were poured on to a metal plate and re-melted at a temperature of around 800°C for 1 h in an electric furnace.

Analysis of the vitreous-ceramics materials

The nucleating and crystallization temperatures were determined by means of DTA measurements.

The phase compositions of the crystallized glasses and the lattice constants were determined via X-ray powder diffraction analysis. The XRD curves were recorded with URD-6 equipment, by using CuK_α with a Ni filter, 2θ ranging from 5 to 60°.

The SOFT-APX software accompanying the URD-6 equipment was used to perform the calculations of the lattice constants.

DTA curves were recorded for the range 20–1200°C with a Derivatograph C. Various heating rates were used, with calcined alumina as reference.

Results

Physical properties of the glasses

All the obtained glasses were coloured. The shade strength increased as the concentration of the nucleating agent was increased. The transparency of the materials also changed during crystallization, moving from opalescence to opaque.

The glass transformation temperature (T_g), the softening temperature (M_g) and the coefficient of thermal expansion (α) were determined with a Linseis dilatometer for some of the glasses and glass-ceramics and are reported in Tables 3 and 4.

Table 3 Dilatometric determination of T_g, M_g and α for glasses

Glass code	T_g/°C	M_g/°C	$\alpha \cdot 10^{-6}/K^{-1}$ at 20–300°C
C-3	710	750	4.7
C-3.0	715	750	4.2
C-3.1	714	754	3.6
C-3.2	682	707	4.7
C-3.3			5.0
C-3.4	728	766	4.8
C-3.5	688	738	4.6
C-3.8	716	736	4.9

Table 4 Dilatometric determination of α for glass-ceramics

Code	$\alpha \cdot 10^{-6}/K^{-1}$			
	20–300°C	20–400°C	20–600°C	20–800°C
C-3.0	–1.0	–0.2	0.8	
C-3.1	–0.6	0.4	1.4	2.5
C-3.2	1.9	2.4	2.9	3.6
C-3.8	–0.5	1.0	1.8	2.2

The heating rate was 5 K min^{-1} and the samples were re-baked at 800°C for 1 h before measurement. Table 3 reveals variations in T_g and M_g, but α did not change significantly for the glasses. For the glass-ceramics, negative values of α were obtained (Table 4), which confirms cordierite formation.

Differential thermal analysis

With the exception of sample C-3.2, which displays two weak exothermic effects, all the analysed samples exhibited only one exothermal effect; the maximum temperatures are given in Table 5.

The data in Table 5 demonstrate the influence of the nucleating agent on the maximum temperature of crystallization; 10.28%, TiO_2 had the greatest effect.

Table 5 Temperatures of maximum crystallization, T_M/°C from DTA curve

Sample code	T_M/°C
C-3	1028.09
C-3.0	974.84
C-3.1	1001.01
C-3.2	887; 1011.56
C-3.3	1072.46
C-3.6	1083
C-3.8	1001.64

The activation energy of the crystallization process was calculated by using the following equation [5]:

$$\frac{E_a}{R}\left(\frac{1}{T_{f1}}-\frac{1}{T_{f2}}\right)=a$$

where E_a is the activation energy (in J mol^{-1}), R=8.314 J mol^{-1} K^{-1} is the gas constant, T_{f1} and T_{f2} are the temperatures measured for the extremes in the DDTA curve (the inflection points in the DTA curve) and a is a constant which has two values: 1.59 for surface-nucleated powders and 0.64 for mass-nucleated powders.

Thermal analysis on samples of various granulation indicated that the temperature of maximum crystallization shifted with the size of the grains only for sample C-3. As a consequence, we chose a=1.59 for sample C-3 and a=0.64 for all the others.

Table 6 Activation energies of glass crystallization

Sample code	E_a/kJ mol^{-1}
C-3	587.5
C-3.0	289.9
C-3.1	170.6
C-3.3	196.2
C-3.6	262.3
C-3.8	189.5

The calculated values of the activation energy E_a for the crystallization process are given in Table 6.

It may be observed that the nucleating agents reduced the value of E_a.

Crystalline-phase analysis

Samples nucleated at 750°C for 1 h and kept at the maximum crystallization temperature for 3 h were investigated by XRD. The analyses were performed on the basis of the highest peaks recorded by XRD.

The presence of α-cordierite is shown by the peak at $2\theta=28.20^{\circ}$ (0.313 nm) (ICDD File Nos. 12-303), which occurs in all the XRD curves.

Sample C-3.2 also exhibits a peak with $2\theta=26.20^{\circ}$, which characterizes the presence of μ-cordierite.

The parameters of the elementary cell for sample C-3.0, calculated via the program SOFT-APX for the XRD equipment, were a=0.9797 nm, b=1.6919 nm and c=0.9359 nm, characterising orthorhombic α-cordierite, while the values for sample C-3.2, for orthorhombic $MgTi_2O_5$ (ICDD File Nos. 35-792), were a=0.96404 nm, b=0.98548 nm and c=0.36844 nm, demonstrating a slight shrinkage of the basic cell.

The efficiency of TiO_2, but only at certain concentrations, is probably due to the similarity of the titanate cell parameters with those of α-cordierite.

Conclusions

Homogeneous vitreous materials were obtained at the low-temperature of 1400–1450°C by using talc and kaolinite instead of inert oxides. The synthesized vitrous-ceramics contained α-cordierite as principal phase.

Some nucleating agents led to a decrease in the crystallization temperature and an increase in the rate of crystallization by decreasing the value of the activation energy, E_a. This effect was more evident when certain amounts of TiO_2 or mixtures of TiO_2/CeO_2 were used.

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