EXTRUDED LZS GLASS-CERAMIC MATERIALS

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ABSTRACT

A sintered glass-ceramic material belonging to the LZS (Li_2O-ZrO_2-SiO_2) system was obtained by extrusion. A 11.4wt% Li_2O - 22.6wt% ZrO_2 – 66.0wt% SiO_2 glass powder was prepared and then extruded and sintered at 750, 800 and 850°C for 10 min. The glass powder and the sintered material (glass-ceramics) were characterized and the results showed that extrusion technology is a potential candidate to obtain sintered glass-ceramics for a number of applications with optimised properties.

1. INTRODUCTION

Glass-ceramic materials are polycrystalline solids containing residual glassy phase made by controlled crystallization of particular formulated glasses [1], [2]. In the midst of these materials, the Li_2O-ZrO_2-SiO_2 (LZS) system has been widely studied [3-8]. Among several known forming processes, powder technology has recently been developed for glass-ceramic materials, in particular by uniaxial pressing. On the other hand, extrusion is a forming technology that also allows high productivity and low cost. However, the parent glass powder does not have sufficient plasticity to be extruded, even when humidified with high water contents. Consequently, the addition of a binder to the glass powder is necessary in order to perform the extrusion. This work thus shows some experimental results regarding a LZS sintered glass-ceramic material obtained by extrusion of glass powders added with an inorganic material (bentonite) as binder.

2. EXPERIMENTAL PROCEDURES

A glass with nominal composition (wt%) 11.4 Li_2O, 22.6 ZrO_2, 66.0 SiO_2 was prepared, and melted to obtain a frit. After this, the frit was ground for DTA (heating rate of 10°C.min^{-1}). The average particle size was found to be 4.79 μm by using a laser scattering particle size analyser. A commercial bentonite (5 wt%) was added to the glass powder, mixed and humidified with water up to 18 wt%. Subsequently, the mixture was stored to homogenise it and extruded. Extruded samples (G5B) were then dried and heat treated (sintered) in an electric furnace at 750, 800 and 850°C with a holding time of 10 min. Theoretical density (ρ_t), established with a pycnometer, and apparent density (ρ_{ap}), measured by the Archimedes principle, of the sintered samples were used to determine the relative density (ρ_r). After sintering, samples were prepared for X-Ray Diffractometry (XRD). Chemical analyses were performed by the atomic absorption spectroscopy technique and by wavelength dispersive X-ray fluorescence spectrometry (XRF). Samples were also used to perform measurements of the modulus of rupture, coefficient of thermal expansion and deep abrasion.

3. RESULTS AND DISCUSSION

Table 1 shows the chemical analysis related to the parent glass, bentonite and composition G5B. According to Table 1, the G5B composition has a higher Na_2O content than the parent glass due to the presence of bentonite. For this reason, since Na_2O is a fluxing agent, the G5B composition shows a melting temperature lower than that determined for the parent glass, as shown in Table 2. In addition to this, the crystallisation temperature also increases probably because crystallisation rate should have increased since bentonite addition decreases the degree of heterogeneities even if surface crystallisation in both compositions is predominant. However, the glass transition increases as a result of the addition of bentonite. Figure 1 shows the XRD patterns related to the G5B composition sintered at 750°C (Figure 1a), 800°C (Figure 1b) and 850°C (Figure 1c) for 10 min, respectively. It can be seen that crystallisation increases with rising temperature, and the main crystalline phases formed are zircon ($ZrSiO_4$), low quartz (α-SiO_2) and lithium disilicate ($Li_2Si_2O_5$). The samples were also subjected to some important measurements to better understand the sintering and crystallisation behaviour such as modulus of rupture (MOR) and deep abrasion (DA). From Table 3 it can be seen that these properties increase as a result of decreasing porosity. The coefficients of thermal expansion (CTE) of the glass-ceramics were 9.88, 9.47 and 9.05 x 10 $^{-6}$ °C $^{-1}$ according to the sintering temperatures (750, 800 and 850°C), respectively. The relatively high CTE especially at low sintering temperatures can be explained, since lithium disilicate (11 x 10 $^{-6}$ °C $^{-1}$) and quartz (9 x 10 $^{-6}$ °C $^{-1}$) have a high CTE compared to 4 x 10 $^{-6}$ °C $^{-1}$ for zircon. However, when sintering temperature increases from 750°C to 850°C the CTE decreases slightly what means that the volume fraction of zircon in the material probably increases in agreement with the XRD, which shows that zircon peak intensity increases as sintering temperature rises.

COMPOSITION (wt%)														
Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MnO	TiO_2	MgO	P_2O_5	PbO	ZnO	ZrO_2	Li_2O
Parent Glass	66.4	0.9	0.1	0.4	0.1	0.1	< 0.1	< 0.1	0.3	0.1	0.1	0.4	22.1	8.9
Bentonite	62.8	20.3	3.8	1.2	2.4	0.5	< 0.1	0.1	2.3	0.2	-	-	-	-
G5B	65.0	1.8	0.2	0.4	0.5	0.1	< 0.1	< 0.1	0.4	0.1	0.1	0.1	20.9	8.7

Table 1. Chemical analysis of bentonite and the studied compositions

SAMPLE	**T_m (°C)**	**T_c (°C)**	**T_g (°C)**
Parent Glass	976.9	864.7	507.3
G5B	958.5	841.4	536.3

T_m: melting temperature; T_c: crystallization temperature; T_g : glass transition temperature
Table 2. DTA measurements of the studied compositions

PROPERTY	**750°C**	**800°C**	**850°C**
MOR (MPa)	52.2 (±6.6)	167.9 (±0.3)	147.3 (±0.5)
ρ_r (%)	80.4	78.8	77.0
DA (mm^3)	203.0 (±7.1)	34.0 (±1.1)	37.0 (±1.3)
CTE x 10^6 (°C^{-1}) (25-325°C)	9.88 (±0.1)	9.47 (±0.1)	9.05 (±0.1)

Table 3. Properties related to the G5B composition sintered at 750, 800 and 850°C for 10 min

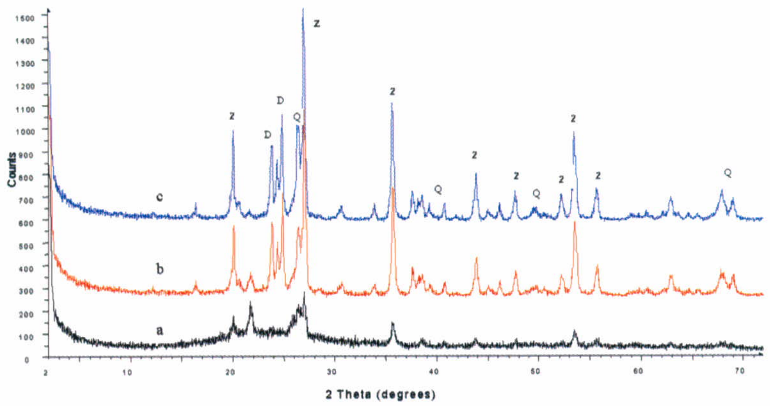

Figure 1. XRD patterns of samples: (a) powdered sample sintered at 750°C for 10 min; (b) powdered sample sintered at 800°C for 10 min; (c) powdered sample sintered at 850°C for 10 min. Z - Zircon ($ZrSiO_4$), Q - Low Quartz (α-SiO_2) and D - Lithium Disilicate ($Li_2Si_2O_5$).

4. CONCLUSIONS

A lithium disilicate zircon-based glass-ceramics was obtained by the sintering and crystallization of an extruded glass powder in the LZS (Li_2O-ZrO_2-SiO_2) system. Sintering was found to start at about 750°C and was completed in a very short temperature interval (100°C); crystallization took place just after sintering and was almost completed at about 850°C for a heating time of 10 min. On heating, the glass powder compacts first crystallize into zircon and quartz, and subsequently also to lithium disilicate. It can be concluded that the extrusion technology is a potential candidate for producing sintered glass-ceramics for a number of applications with optimised properties.

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