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Glass-Ceramics From Filter Dusts From Waste Incinerators

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Abstract: Glass-ceramics have been produced from filter dusts of domiciliary waste incinerators without the addition of nucleating additives. A two-step heat treatment of melted filter dusts (1 h at 880°C, 10 h at 950°C) was used to obtain a fine crystalline microstructure, the principal constituents being crystals of the pyroxene group. The glass-ceramic materials have better mechanical and thermomechanical properties than those of the parent glass, being potential candidates for industrial applications. A fracture-mirror analysis was carried out to evaluate the measured fracture strength and fracture toughness of the glass and glass-ceramics produced. The data are in agreement with previous studies showing that the parameter A/K_{Ic}, where A is the fracture-mirror constant, is a dimensionless, material-independent constant.

INTRODUCTION

The incineration of household or domiciliary residues leaves large quantities of waste, such as ashes, slags and filter dusts. As regards filter dusts they are produced at a rate of 130,000 ton/year in Germany and the predicted increment of waste incineration in the next few years imposes the need for searching for new alternatives for their adequate disposal or recycling in terms of environmental safeguard. Filter dusts containing a high concentration of silica can be good candidates for glass-ceramic production. Glass-ceramics have superior properties, such as high strength, hardness and wear and thermal shock resistance, which make them widely used in the construction, mechanical and chemical industries.[1] The glass-ceramic approach has already been applied for recycling coal-fly ashes[2,3] and metallurgical slags[4–7] but, as far as the authors know, no attempt has been made using the residues of waste incineration.

This communication presents the first results of research carried out to produce glass-ceramics from filter dusts without the addition of nucleating agents, using as starting materials filter dusts from German incineration plants. The emphasis of this study is the investigation of the mechanical and thermomechanical properties of the materials produced. The fracture behaviour of the materials has been assessed using a fracture-mirror analysis. The work is part of a more general research project[8–10] having the ultimate technological objective of providing a materials science concept for the treatment, i.e. recycling and disposal, of a variety of industrial wastes under economical and ecological considerations.

EXPERIMENTAL PROCEDURE

Table 1 shows the composition of the filter dusts investigated in this study. Traces of Sn, Sb, Cd, Ba, As, Sr, Zr, Pb and Mo were also detected. Amorphous glass from the filter dusts was prepared by a pre-thermal treatment of the as-received dusts at a temperature $T = 600°C$ for 2 h followed by melting in alumina crucibles at 1300°C for 2 h. No nucleating melting agents were added. The as-quenched glass, annealed for 1 h at 600°C was cut by a diamond saw in samples suitable for

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Table 1. Composition of filter dusts from waste incinerators

Oxide	Wt%
Al_2O_3	17·5
CaO	21·1
Fe_2O_3	8·0
K_2O	1·8
MgO	2·4
MnO	0·4
Na_2O	3·5
PbO	0·3
P_2O_5	1·6
SiO_2	38·0
SO_3	0·2
TiO_2	1·7
ZnO	3·5

the experimental investigations: bars for dilatometry and mechanical bending tests, small pieces for microstructural examination and Vickers indentation tests and samples appropriated for ultrasonic Young's modulus measurements and thermal shock testing. The bars were drawn from the melts as cylinders of about 4 mm in diameter and of different lengths. A part of the glass was ground and ball-milled to produce a glass powder appropriate for sintering-ceramization experiments. The results of these experiments, which explore a powder technological route to produce glass-ceramics from filter dusts, are reported elsewhere.[11,12]

On the basis of previous results on differential thermal analysis (DTA) of powdered glass from filter dusts,[11,12] the following heat-treatment of the as-quenched glass samples was carried out to obtain the glass-ceramic: heating at a rate of 10°C/min to 880°C and holding at this temperature for 4 h and subsequently heating at 5°C/min to 950°C and holding for 1 and 10 h. The samples were cooled down in the furnace.

The amorphous nature of the as-quenched glass and the crystalline phases developed during the heat treatment were analysed by means of an X-ray (CuKα) powder diffractometer (XRD) (Philips PW 130/00) using powdered material (particle size < 63 μm). The X-ray diffraction patterns were matched to JCPDS data to identify the crystalline phases. Scanning electron microscopy (SEM) of polished and etched samples (2% HF for 1 min) was used to study the microstructure. The density of selected samples was determined by means of the Archimedes principle.

The mechanical and thermomechanical properties of the glass-ceramics produced have been assessed using a range of techniques. Dilatometric measurements (Netzsch 402E) between room temperature and 700°C were conducted on bars (3 mm diameter, 24 mm length) from the as-quenched glass and from the crystallized material. Vickers indentation was used to characterize the hardness (HV) and fracture toughness K_{IC} of the materials using indentation loads of 20 N. Four-point bend test with 40 mm outer span and 20 mm inner span at crosshead speeds of 1 mm/min was used to determine the flexural strengths (modulus of rupture) of cylindrical bars of ~4 mm diameter. At least ten bars of each material, amorphous parent glass and glass-ceramic, were tested. The surfaces of the bars tested were in the as-fabricated state without grinding or polishing treatment. Standard SEM and optical microscopy were used to observe fracture surfaces. The Young's moduli and Poisson's ratios were determined from ultrasonic measurements on discs of 40 mm diameter. Furthermore, cylindrical pieces (diameter 12 mm, length 15 mm) were used for water-quench thermal shock tests. Thermal shock testing involved heating test cylinders in air to the desired temperature and equilibrating for 30 min. Then the samples were quenched in distilled water at room temperature and examined for surface cracks using a stereo light microscope. The appearance of cracks was used as the failure criterion to determine the critical temperature difference. The machinability of the materials was qualitatively investigated by turning and drilling operations using regular hardmetal (WC–Co) high-speed tools.

RESULTS AND DISCUSSION

The XRD patterns of the as-quenched glass have broad humps characteristic of the amorphous state, as shown in Fig. 1 (a). The XRD patterns of samples heated to T_2 = 950°C for 1 and 10 h are shown in Fig. 1 (b) and (c). No difference in the kind of phases formed for the two holding times is apparent. The reflections were assigned to crystalline phases of the pyroxene group (mainly diopside) although the agreement between the reflection values and the JCPDS cards was not complete. Results of the mineralogical characterisation, phase volume fractions and compositions are reported elsewhere[13] and further studies on this topic are currently being carried out. Glass-ceramic materials produced by a heat treatment of 10 h at 950°C were further considered in this study because they showed a more developed microstructure.

Figure 2 shows the microstructure of a sample, obtained by SEM. The fine crystalline structure formed after heat-treatment can be observed. Table 2 summarizes the results of the thermomechanical and mechanical properties measured. For calculating the K_{IC} values the relation of

Anstis *et al.*[13] was used, as proposed in an earlier work on glass indentation measurements.[14] During the drilling and cutting tests the glass samples behaved in a brittle manner and broke, while the glass-ceramic samples could be worked easily with the regular hard-metal (WC–Co) high-speed tools used.

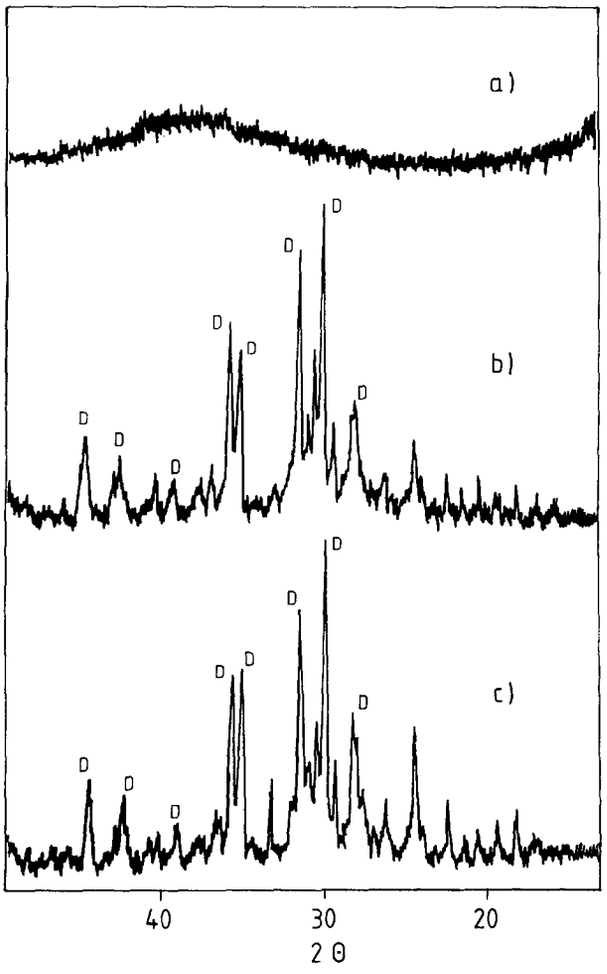

Fig. 1. XRD patterns of the materials investigated: (a) as-quenched melted filter dusts; (b) glass-ceramic, heat-treatment: 1 h, 880°C; 10 h, 950°C; (c) glass-ceramic, heat treatment: 1 h, 880°C; 10 h, 950°C/. (D: Diopside).

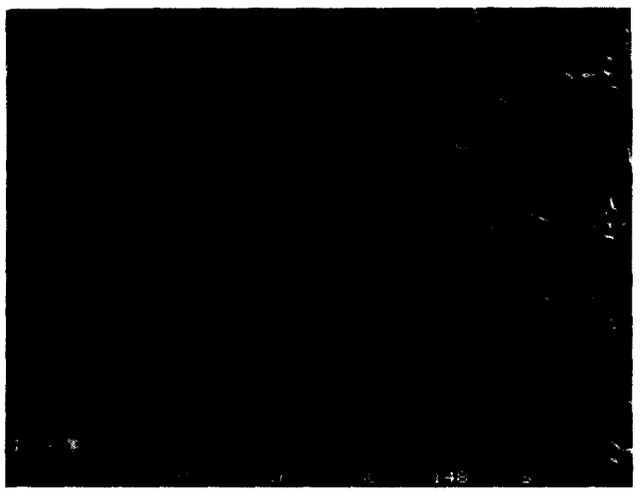

Fig. 2. SEM micrograph of a polished, etched (2% HF, 1 min) surface of a glass-ceramic sample heat treated for 1 h/880°C and 10 h/950°C.

Table 2. Physical and mechanical properties of glass and ceramics from filter dusts

Property	*Material*	
	Glass	*Glass-ceramic*
Density (g/cm^3)	2·80	2·89
Hardness (GPa)	5·5±0·2	7·9±0·3
Young's modulus (GPa)	92·6	124
Poisson's ratio	0·28	0·26
Thermal expansion coefficient (10^{-6} °C^{-1})	5·9 (20–600°C)	6·5 (20–700°C)
Indentation fracture toughness (MPa m$^{1/2}$)	0·6±0·1	1·7±0·1
Fracture strength (±10%) (MPa)	90	240
Thermal shock resistance (ΔT_c) (°C)	≈150	≈280
Machinability	Poor	Good

The mechanical and thermomechanical properties of the glass-ceramics are better overall than those of the parent glass. There is a simultaneous increment of the fracture strength, the hardness and the fracture toughness, that also indicates a more wear resistant material, although this behaviour was not quantitatively assessed. The improvement of the thermal shock resistance behaviour of the glass-ceramic over the parent glass as measured by the higher critical temperature difference is also very remarkable. The increment of the Young's modulus and (slightly) the thermal expansion coefficient, which should have a negative effect on the critical temperature difference, are compensated for by the strong increment of the fracture strength.

Fracture surfaces of glass-ceramic samples broken during the strength tests were investigated by SEM as Fig. 3 shows. The presence of elongated grains, which should contribute to the reinforcement of the material, can be detected upon examining the fracture surfaces.

The measured data for the fracture strength and toughness can be evaluated by means of a fracture-mirror analysis. It has been shown (see for example Ref. 15) that the radius r of the fracture-mirror formed on fracture surfaces of glass or glass-ceramics is related to the fracture stress σ by the following empirical relationship,

$$\sigma = \frac{A}{\sqrt{r}} \tag{1}$$

where A is the mirror constant for the particular material considered. Furthermore, working with different ceramics and glass-ceramics Bansal and Duckworth[16] demonstrated that the parameter

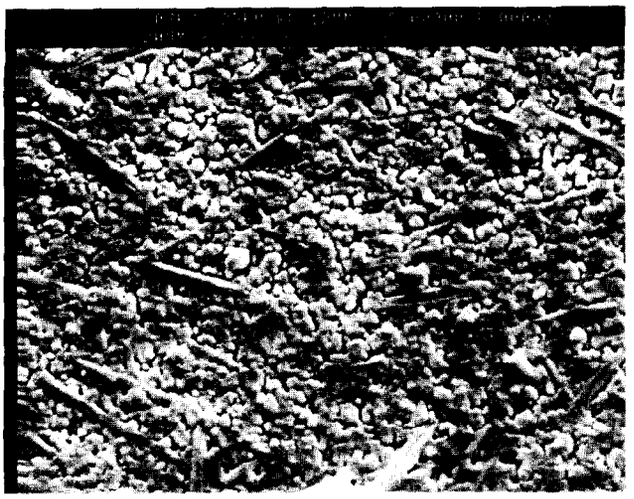

Fig. 3. SEM micrograph of a fracture surface of a glass-ceramic sample broken during the fracture strength tests.

A/K_{Ic} is a dimensionless, material-independent constant. Our data on glass and glass-ceramics confirms this behaviour. Fracture surfaces of samples broken in the strength testing were examined microscopically and fracture-mirror boundaries were identified using an optical microscope, as shown in Fig. 4 for a glass-ceramic sample. Very similar values of mirror radius, within the error of the measurements, were found for both materials. The measured mirror radius values were substituted in eqn (1), together with the data of the fracture strength, to calculate the mirror constants. With the values of A and the independently measured values of fracture toughness shown in Table 2, the parameters A/K_{Ic} for each material were determined. The data of the fracture-mirror investigation are summarized in Table 3. The data confirm that A/K_{Ic} is independent of the material, as pointed out in the previously mentioned study.[16] While the mirror constant for the parent glass is

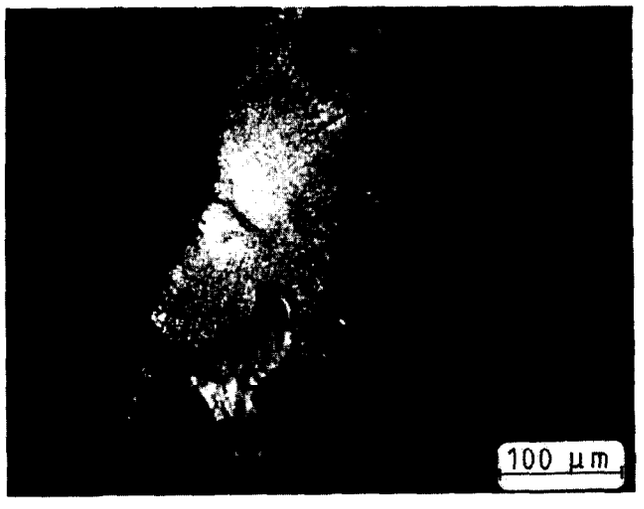

Fig. 4. Optical microscopy micrograph of a fracture surface of a glass-ceramic sample, showing the fracture mirror.

Table 3. Measured and calculated parameters for the fracture-mirror analysis

Parameter	Material	
	Glass	Glass-ceramic
Mirror radius (mm)	0·25	0·27
Mirror constant, A (MPa $m^{1/2}$)	1·41	3·94
A/K_{Ic}	2·34	2·32

lower than the value $A = 2$ MPa $m^{1/2}$, which is normally found for soda-lime glasses,[15] the mirror constant of the glass-ceramic approximates the values found for other glass-ceramic systems.[16]

CONCLUSIONS

The possibility of fabrication of glass-ceramic materials from filter dusts from waste incinerators without addition of any nucleating agent was shown. Crystals belonging to the pyroxene group were identified as the principal components. The glass-ceramic produced has better mechanical properties than the parent glass and its mechanical behaviour is similar to that of other glass-ceramics produced from wastes.[6,7] The fracture-mirror analysis carried out confirmed that the parameter A/K_{Ic} is a material-independent constant, providing an experimental verification of this fact, for which very little work in the literature can be found.

The material can be suitable for different applications in floors of industrial buildings and constructions, outside and inside facings of walls or for fabricating machine elements, although further characterisation of its behaviour, for example wear resistance and chemical durability, is necessary. This is the subject of on-going studies.

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