Use of vitrified urban incinerator waste as raw material for production of sintered glass-ceramics

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ABSTRACT

The crystallisation behaviour of vitrified industrial waste (fly ash from domiciliary solid waste incineration) was examined by differential thermal analysis, X-ray diffractometry and scanning electron microscopy. It was demonstrated that powder processing route was required to transform the vitrified industrial waste into glass-ceramics products. Time-Temperature-Transformation (TTT) diagrams were drawn for the two main crystalline phases, diopside and wollastonite. The wollastonite existed in both monoclinic and triclinic forms and an iron-rich phase was also observed at the boundaries between glass particles. The morphology of the crystalline phases and the development of microstructure were observed as a function of heat treatment time and temperature. The optimum heat treatment was 900°C for 40-50 minutes.

KEYWORDS: A. glasses, A. ceramics, C. X-ray diffraction, C. electron microscopy, D. microstructure

INTRODUCTION

Industrial development over the last decades has generated large amounts of toxic and hazardous inorganic waste, for example fly-ash, slags and muds which contain appreciable amounts of Pb, Cr, Cu, Zn, Cd and Hg. Most is buried in landfills, which is costly and environmentally unsatisfactory. Therefore, it is essential to seek new options to recycle or reuse the inorganic residues.

In developed countries each inhabitant is estimated to produce 1kg/day of domiciliary solid waste (DSW); the total for the European Union (EU) is about 13.9×10^6 ton/year. Recycling, which involves selection and classification of the waste is suitable for only 47% of DSW and hence, recycling alone cannot solve the disposal problem. The complementary and growing option in Europe, for disposal of the non-recyclable fraction (53%), is incineration with energy recovery. Unfortunately, incineration leaves large amounts of solids residues, such as fly ashes and slags, which form 10-25 wt% of the DSW incinerated. The total production for the EU is about 1.12×10^6 ton/year of

residues, most of which is buried in landfills. The increasing tendency for waste incineration, together with the disadvantages of landfill disposal, makes it essential to search for new options for reuse of the solid residues from waste incineration.

Recycling is well-established for wastes such as exemplified by glass and aluminium, but is not always feasible and it is necessary to develop alternative processes for reuse. Recent reuses proposed for fly-ash, slags and muds include fabrication of building materials [1, 2], catalysts and pigments [3], refractories [4], puzzolanic material [5], glasses and glass-ceramics [6-9].

Glass-ceramics prepared by controlled devitrification of glasses were developed in the 1950s [10, 11] and find a wide variety of applications such as microelectronic substrates and packaging [12, 13], optically transparent components [14-16], biomedical implants [17, 18], catalytic supports, membranes and sensors [19] as well as for the matrix of composite materials [20, 21].

The earliest glass-ceramics were produced by a conventional glass route and subsequently crystallised, usually by heat treatment in two stages give nucleation followed crystal growth [22]. More recently, a powder-processing route, similar to that used for “conventional” ceramics, has been developed in which the glass is reduced to a fine powder, shaped and crystallised. During heating the glass particles densify by viscous flow and then nucleate and crystallise from the original glass particle boundaries [23].

For glass-ceramic production via conventional glass processing nuclei must readily form throughout the bulk of the parent glass; surface nucleation is to be avoided as it is usually detrimental to mechanical performance. In contrast, glasses showing a strong tendency for surface crystallisation may be successfully converted into glass-ceramics by the powder processing route [24]. Consequently, microstructure of a glass-ceramic produced by the two routes is different.

It is essential that the microstructure, and hence properties, of a glass-ceramic be optimised. This is achieved by control of the thermal history of the parent glass, especially the heat treatment time and temperature. In this context, Time-Temperature-Transformation (TTT) diagrams are extremely useful; they may be used as guides for heat treatment scheduling in the processing of glasses [25] and glass-ceramics [26], to assess glass-forming ability [27], to predict critical cooling rates [28] and as an aid to the analysis of phenomena such as phase separation and the precipitation of stable and metastable crystals [27].

It has previously been shown that glasses, and conventionally processed and sintered glass-ceramics, can be produced by vitrification of DSW incinerator fly ashes [29-33]. However, to our knowledge, TTT diagrams for these materials are not available and form the basis of the present study together with microstructural and mechanical property measurements of the resulting glass-ceramics.

EXPERIMENTAL PROCEDURE

Chemical analysis of the incinerator fly ash was determined using an inductively coupled plasma method (ICP-Atomic Emission Spectroscopy). A 60 g batch of fly ash

was placed in Pt crucible in an electric furnace and heated in air at $10^{\circ}\text{C min}^{-1}$ to 1500°C , held for 30 min at 1500°C and the resulting melt poured onto a cold metal plate and allowed to cool to room temperature. The resulting glass was crushed and sieved to a particle size $< 75\text{ }\mu\text{m}$. Cylindrical compacts (10 mm x 15 mm) were fabricated by uniaxial cold-pressing the powder at 250 MPa without using binder.

Differential thermal analysis (DTA) was employed (Netzsch thermal analyser, STA 409 Series) to determine the crystallisation behaviour and the glass transition temperature (T_g) of the parent glass. Pt crucibles were used with calcined alumina as reference in flowing air at $100\text{ cm}^3\text{ min}^{-1}$ and a heating rate of $25^{\circ}\text{C min}^{-1}$. DTA was performed on both bulk monolithic ($4\times 2\times 2\text{ mm}^3$) and powder samples. The DTA curves were normalised with respect to the sample weight.

Glass-ceramics were prepared by sintering the cylindrical glass compacts in air. The compacts were heated at a rate of $10^{\circ}\text{C min}^{-1}$ to a temperature in the range 800 to 925°C , held for times in the range 4-120 min and then samples cooled in the furnace.

After heat treatment, the samples were ground and sieved to a particle size $< 70\text{ }\mu\text{m}$ and X-ray diffraction (XRD) data were obtained (Philips analytical diffractometer, PW 1710 Series, using CuK_{α} radiation). The relative crystallisation range was determined by drawing the TTT curve from the time and temperature when crystallisation became noticeable by XRD. The heat-treated glass was considered to be “amorphous” when no XRD peaks corresponding to crystalline phases were observed, “partial crystallisation” when small peaks appeared and “total crystallisation” when these peaks were intense and there was no evidence at low 2θ of a glassy phase. The boundary between “amorphous” and “partially crystallised” states represent the onset of crystallisation.

Scanning electron microscopy (SEM) was used to examine the crystalline morphology of the sintered glass-ceramics. Samples were embedded in epoxy and surfaces ground (120, 320, 600 grit abrasive paper) and polished with diamond spray ($6\text{ }\mu\text{m}$, $3\text{ }\mu\text{m}$ and $1\text{ }\mu\text{m}$). Energy dispersive X-ray (EDX) analysis was used for elemental analysis.

RESULTS AND DISCUSSION

Table 1 shows the composition of the fly ash. The major components were CaO and SiO_2 although the SiO_2 content was considerably less than reported previously for urban incinerator fly ashes [32]. There was a significant loss on ignition (LOI), which was probably due to volatiles associated with decomposition of the different calcium compounds and the presence of residual carbon. The sum of oxides plus LOI was near to 80%; the remaining 20% corresponds to elements such as Cl and S that cannot be determined by ICP.

In spite of the low SiO_2 content, the melting and casting techniques used produced a glass. DTA results are shown in Figure 1; both bulk and powder samples exhibit a glass transition at around 740°C . In contrast to previous studies [30, 32], the bulk sample does not exhibit crystallisation peaks. This is attributed to the lower amount of nucleating agents, such as Fe_2O_3 , P_2O_5 and TiO_2 , in the present glass. However, the powder sample has two exothermic peaks at 980°C and 1025°C followed by an endothermic at 1100°C , indicating either re-resolution of a crystalline phase or the formation of a liquid phase. The crystallisation of the powder sample is attributed to its large surface area facilitating

surface crystallisation. These results indicate that this particular incinerator fly-ash glass could be converted into a glass-ceramic using the processing route. Similar crystallisation behaviour was observed in glasses from the systems $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ [24, 34] and $\text{Na}_2\text{O-SiO}_2$ [35].

Table 1. Chemical analysis (wt%) of the investigated incinerator fly ash

OXIDE	PERCENTAGE (wt%)
SiO_2	11.47
Al_2O_3	5.75
Fe_2O_3	1.29
MgO	3.02
CaO	29.34
Na_2O	8.70
K_2O	7.02
P_2O_5	1.69
TiO_2	0.85
MnO	0.18
LOI	9,2
TOTAL	78.51

Figure 1. DTA curves for bulk (a) and powder (b) vitrified incinerator fly-ash glass.

Figure 2 presents the TTT diagram for the crystallisation of the incinerator fly-ash glass. The C-shaped curves, which are characteristic of nucleation and growth processes, give the combinations of time and temperature needed for the onset of crystallisation. Thus, at or above 775°C led to a least partial devitrification of the glass compacts. At 775°C and 800°C, crystallisation still has not reached completion after 60 minutes. The glass compacts are fully devitrified at or above 850°C within the times employed. The fastest rate of crystallisation is at 900°C where the onset time was only 3 minutes.

Figure 2. TTT diagram for incinerator fly-ash glass (○ amorphous; ⊕ partial crystallisation; ● total crystallisation)

The crystalline phases identified by XRD are diopside ($\text{CaMg}(\text{SiO}_3)_2$) and both monoclinic and triclinic wollastonite (CaSiO_3). The TTT diagram for each is given in Figure 3. The two wollastonite phases crystallise in the same temperature-time interval and hence, their formation is represented by a single curve. Diopside starts to crystallise at lower temperatures and shorter times than wollastonite. Thus, the lower temperature DTA exotherm is due to the crystallisation of diopside and the higher temperature peak is associated with wollastonite. The shape of the TTT curves at 850°C and below indicates that the activation energy for crystallisation of wollastonite is much higher than for diopside with approximate values of 500kJ mol^{-1} and 270kJ mol^{-1} respectively. Furthermore, Figure 3 shows that with a suitable thermal treatment schedule, it is possible to prepare glass-ceramics comprising of one (diopside) or two (diopside and wollastonite) crystalline phases. However, the relative location of the TTT curves indicates that it is impossible to prepare glass-ceramics with wollastonite as the only crystalline phase.

Figure 3. TTT diagram for diopside and wollastonite phases devitrified from incinerator fly-ash glass compacts.

The relative proportions of the various phases were estimated by XRD from the ratio $I_{\text{relative}} = I_n / I_{\text{total}}$. The peaks used for I_n were 3.00 – 3.01 Å (diopside), 3.07 – 3.08 Å (triclinic wollastonite) and 2.17 – 2.18 Å (monoclinic wollastonite).

Plots of I_{relative} versus crystallisation temperature and time are given in Figures 4 and 5, respectively. Only diopside is present at 775°C but monoclinic and triclinic wollastonite appear by 825°C. The relative proportion of the three phases initially increases with temperature and time. Figure 4 is consistent with Figure 2 in that it demonstrates maximum crystallinity at 900°C and hence, this is the optimum temperature for glass devitrification. Both Figures 2 and 4 show crystallisation to be slower at 925°C than at 900°C. From Figure 5, it may be concluded that 20 minutes is sufficient for almost complete crystallisation of triclinic wollastonite. In contrast, 40 and 50 minutes are required for the maximum proportions of monoclinic wollastonite and diopside respectively but at longer times there is partial solution of these phases. The shape of the curves in Fig.5 suggests that devitrification occurs essentially by a steady state heterogeneous nucleation mechanism without a significant induction period [36].

Figure 4. Plot of I_n / I_{total} versus crystallisation temperature for incinerator fly-ash glass (heat treatment time is 30 min.).

Figure 5. Plot of I_n / I_{total} versus crystallisation time at 900°C for incinerator fly-ash glass.

Figures 6-8 provide SEM images, EDX analyses and XRD patterns of the heat-treated samples for the time-temperature conditions indicated by points (a)-(h) in Figure 2. In Figure 6, samples (a) to (c) were heat treated at various temperatures for 30 minutes.

Figure 6. SEM images and XRD patterns for samples heat treated for 30 minutes at various temperatures as indicated by the points labelled (a) to (c) in Figure 2.

The XRD pattern of (a) is characteristic of a glass and the accompanying SEM photograph reveals a microstructure typical of an intermediate state of densification an almost continuous channel of pores at particle boundaries [37]. This sample, and all others exhibited anomalous white contrast at the particle boundaries due to higher secondary and backscattered electron emission as a result of an increase of Fe content at the boundaries. Segregation of solutes from the interior of a grain to the vicinity of a grain boundary is commonly observed in sintered materials [38]. Also, it is well-established that Fe ions have strong tendency to diffuse to the surface during bulk glass crystallisation giving rise to an iridescent layer [39]. In the present case, each particle acts as an individual small bulk glass sample as far as diffusion and segregation of Fe is concerned thus causing the observed particle boundary contrast. For sample (b), which is partially crystallised, the formation of diopside is noticeable in the XRD pattern and the morphology corresponds to a final stage of sintering with closed and spherical pores located in both particle boundaries (intergranular) and within the particles (intragranular). When the temperature is increased to 850°C the sample is fully

crystallised and diopside, monoclinic and triclinic wollastonite are observed throughout the entire sample, Figure 6(c).

Figures 7 and 8 illustrate the effects of isothermal annealing at 900°C for various times (3-50 min). At 900°C for 3 min an amorphous sintered material is obtained, Figure 7(d). After 4 min, the effect of iron segregation is more marked with heterogeneous crystallisation of a high density of small white crystals ($< 1\mu\text{m}$ size) at particle boundaries [40]. Further evidence of the effectiveness of particle boundary nucleation is the presence of diopside needle-like crystals, growing perpendicular to the boundary, which are heavily enriched in Fe_2O_3 compared with the amorphous sample (Fig.7(d)), consistent with the segregation of iron to the boundaries. EDX analysis also shows a high SiO_2 , CaO and Al_2O_3 contents in the boundary regions; this is a consequence of the small size of crystals at the particle boundaries, $< 1\mu\text{m}$, which is comparable to the analytical resolution of the SEM/EDX system. Thus, EDX analyses on particle boundary crystals are influenced by the glassy phase and diopside crystals surrounding the boundary. The SiO_2/MgO ratio of the diopside phase is about 6, which is double in $\text{CaMgSi}_2\text{O}_6$. This, together with the high Fe_2O_3 content, is attributed to the wide variety of ionic substitutions that occur in the members of the pyroxene group with, for example, complete solid solution between diopside ($\text{CaMgSi}_2\text{O}_6$), hedenbergite ($\text{CaFeSi}_2\text{O}_6$), augite and ferroaugite ($\text{CaMgFe})\text{SiO}_3$ [41]. Increasing the heat-treatment time to 5 minutes enables further development of the diopside phase into an interconnected network of feather-like crystals (Figure 7(f)).

Figure 7. SEM images and EDX analyses of samples heat treated for short times at 900°C as indicated by the points labelled (d) and (f) in Figure 2.

After 30 minutes, a fully crystallised material containing both diopside and wollastonite forms, Figure 8(g1) and (g2). One form of wollastonite crystallises as fibre-like crystals in a dendritic growth morphology (labelled as F in Fig.8(g2)). In some areas, between the dendrites blade-shaped crystals (labelled B in Fig.8(g2)) are found. Monoclinic wollastonite usually grows in lathlike aggregates whereas triclinic wollastonite crystallises in tablets or blades [42]. Thus, the two wollastonite morphologies observed by SEM at F and B, probably correspond to monoclinic and triclinic wollastonite, respectively. The wollastonite crystals also has a considerable amount of Fe replacing Ca. Longer heat-treatments at 900°C have a negligible effect on the morphology of the crystalline phases. A complementary transmission electron microscopy study of crystallisation in this glass system is underway.

Figure 8. SEM images and EDX analyses of samples heat treated for long times at 900°C as indicated by the points labelled (g) and (h) in Figure 2.

CONCLUSIONS

The possibility of fabricating sintered glass-ceramics from vitrified urban incineration waste that was not capable of bulk crystallisation has been demonstrated. DTA results suggested that crystallisation starts at external surfaces. Thus, this incinerator fly-ash glass, in contrast to some previously investigated, must be converted into a glass-ceramic by the powder processing route.

TTT diagrams showed that crystal growth started at 775°C and was most rapid at 900°C. The crystalline phases were diopside, monoclinic and triclinic wollastonite. Only diopside is present at 775°C but both monoclinic and triclinic wollastonite appear at

825°C. The relative proportion of the three devitrified phases increased with temperature and time, up to 900°C and about 50 min, respectively. Times above 20 min had negligible effect on the amount of triclinic wollastonite whereas times of 40 and 50 min led to the maximum proportions of monoclinic wollastonite and diopside, respectively. Thus the optimum heat treatment time is 40-50 minutes.

The fully crystallised products showed a morphology corresponding to a final stage of sintering with closed and spherical pores located in both particle boundaries (intergranular) and within the particles (intragranular). The heat treatment caused segregation of Fe from the interior to the vicinity of the particle boundaries and this eventually led to the formation of an iron-rich phase. Diopside initially grows normal to the boundaries as needle-like crystals, but later develops an interconnected network of crystals. Wollastonite exists in two morphologies, a fibrous dendritic morphology and blade-like crystals, which probably correspond to monoclinic and triclinic wollastonite, respectively. EDX spot analyses showed substitution of Mg by Fe in diopside (pyroxene) and Ca by Fe in wollastonite.

Overall, this work has confirmed that a powder processing route constitutes a convenient processing alternative to bulk crystallisation for the fabrication of glass-ceramics from silicate wastes.

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